Agenda and Abstracts

CALPHAD LI

51st International Conference on Computer Coupling of Phase Diagrams and Thermochemistry

May 26 – 31, 2024, Mannheim, Germany

> “We believe that substantial progress can be made in a short period of time if we could arrange to work together for one week at one of our facilities to define problems, disband, carry out some individual activities, and meet again for a week at a second facility to compare results and chart future activities.”
>
> *Larry Kaufman and Himo Ansara, 1973*

Preface

Dear Colleagues, dear Friends,

Welcome to the 51st CALPHAD International Conference. It is our great pleasure to organize it at this year´s venue in the city centre of Mannheim, Dorint Kongresshotel. It has been a while since CALPHAD was organized in Germany, to date three times in the years 1976, 1978 and 1987, respectively. Therefore, we are very happy that this group meeting of experts is returning again with more than 200 participants from 27 countries – a true *international* event!

One year after its 50th anniversary the CALPHAD community meets again to prepare for the next 50 years of further great successful work on the Computer Coupling of Phase Diagrams and Thermochemistry. Based on this long-time experience we know that knowledge of phase equilibria plays a vital role in the successful development, processing, application, and recycling of materials.

There were many different criteria and aspects based on which we had to decide on 81 oral and 95 poster presentations, respectively. All abstracts are of high-level quality. Our poster sessions are a particularly important part of our program. Here we have the opportunity of intensive scientific discussions and also to get to know each other better. All the sessions are assembled in this spirit of reflecting on the main current topics on developing CALPHAD further, e.g. by including Data Science, more combinations with physical properties of engineering materials, and by using CALPHAD thermodynamics to quantitatively describe phase transformations and even microstructure development. As illustrated in this year´s program such aspects have growing impact on real world applications such as steels and additive manufacturing and many more. All these challenges require reliable thermodynamic CALPHAD-type databases and thus the program follows the tradition and also contains contributions on thermodynamic optimization, development of thermodynamic datasets and databases, and calculations of related phase diagrams. This type of work is inspired and enriched by ab-initio calculations and the efforts of developing third-generation databases supported by advanced experimental analytics.

Our conference site - Mannheim - is located in the Metropolitan Region Rhine-Neckar of the state of Baden-Württemberg. It is both an industrial and cultural centre. One can visit fine places of interest giving impressions of both Baroque and Jugendstil (art nouveau) architecture, respectively. The Kunsthalle Mannheim and the Technical Museum TECHNOSEUM are also quite famous institutions.

We wish everyone a great conference week with lively scientific discussions in the traditional CALPHAD spirit, to meet and make friends and to contribute to a continued growth of our community.

Hans Jürgen Seifert and Andre Schneider

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Andre Schneider, Thermo-Calc Software

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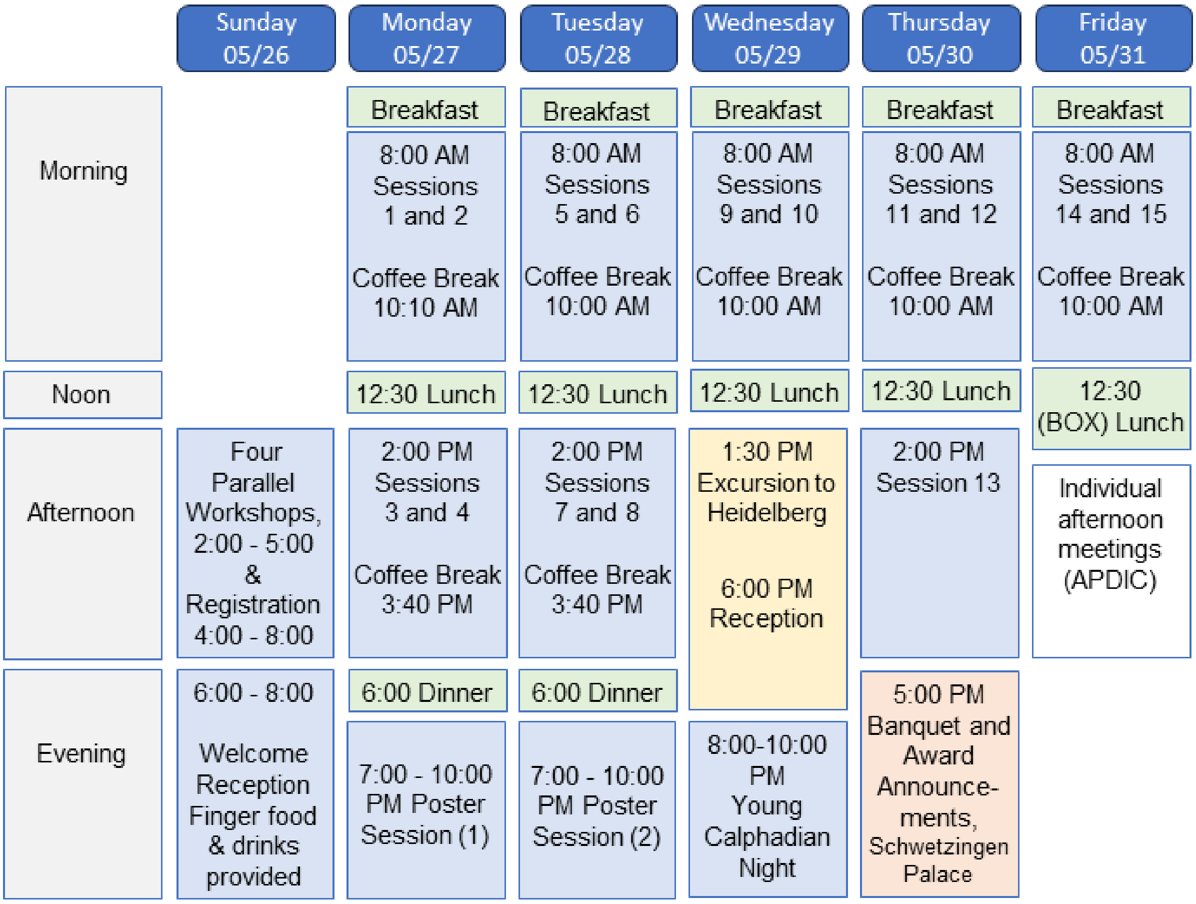
CALPHAD LI Conference Agenda Overview



	Sunday 05/26	Monday 05/27	Tuesday 05/28	Wednesday 05/29	Thursday 05/30	Friday 05/31
Morning		Breakfast 8:00 AM Sessions 1 and 2 Coffee Break 10:10 AM	Breakfast 8:00 AM Sessions 5 and 6 Coffee Break 10:00 AM	Breakfast 8:00 AM Sessions 9 and 10 Coffee Break 10:00 AM	Breakfast 8:00 AM Sessions 11 and 12 Coffee Break 10:00 AM	Breakfast 8:00 AM Sessions 14 and 15 Coffee Break 10:00 AM
Noon		12:30 Lunch	12:30 Lunch	12:30 Lunch	12:30 Lunch	12:30 (BOX) Lunch
Afternoon	Four Parallel Workshops, 2:00 - 5:00 & Registration 4:00 - 8:00	2:00 PM Sessions 3 and 4 Coffee Break 3:40 PM	2:00 PM Sessions 7 and 8 Coffee Break 3:40 PM	1:30 PM Excursion to Heidelberg 6:00 PM Reception	2:00 PM Session 13	Individual afternoon meetings (APDIC)
Evening	6:00 - 8:00 Welcome Reception Finger food & drinks provided	6:00 Dinner 7:00 - 10:00 PM Poster Session (1)	6:00 Dinner 7:00 - 10:00 PM Poster Session (2)	8:00-10:00 PM Young Calphadian Night	5:00 PM Banquet and Award Announcements, Schwetzingen Palace	

Dorint Kongresshotel Mannheim 2nd floor (Pre-Conference Workshops, Registration, Welcome Reception, Oral Presentations, Poster Sessions, Coffee breaks, Young Calphadian Night)

Dorint Kongresshotel Mannheim Restaurant Symphonie, ground floor (Breakfast, Lunch, Dinner)

Excursion to Heidelberg 1:30 PM, Wed. May 29 (Busses at main entrance of Dorint Kongresshotel, guided walking tour through Heidelberg old town)

Return from Heidelberg Castle to Mannheim 7:00 PM, Wed. May 29 (from bus parking at castle)

Conference Banquet Schwetzingen Palace 5 PM, Thu. May 30 (Busses from main entrance of Dorint Kongresshotel)

Conference Site and Floor Plan

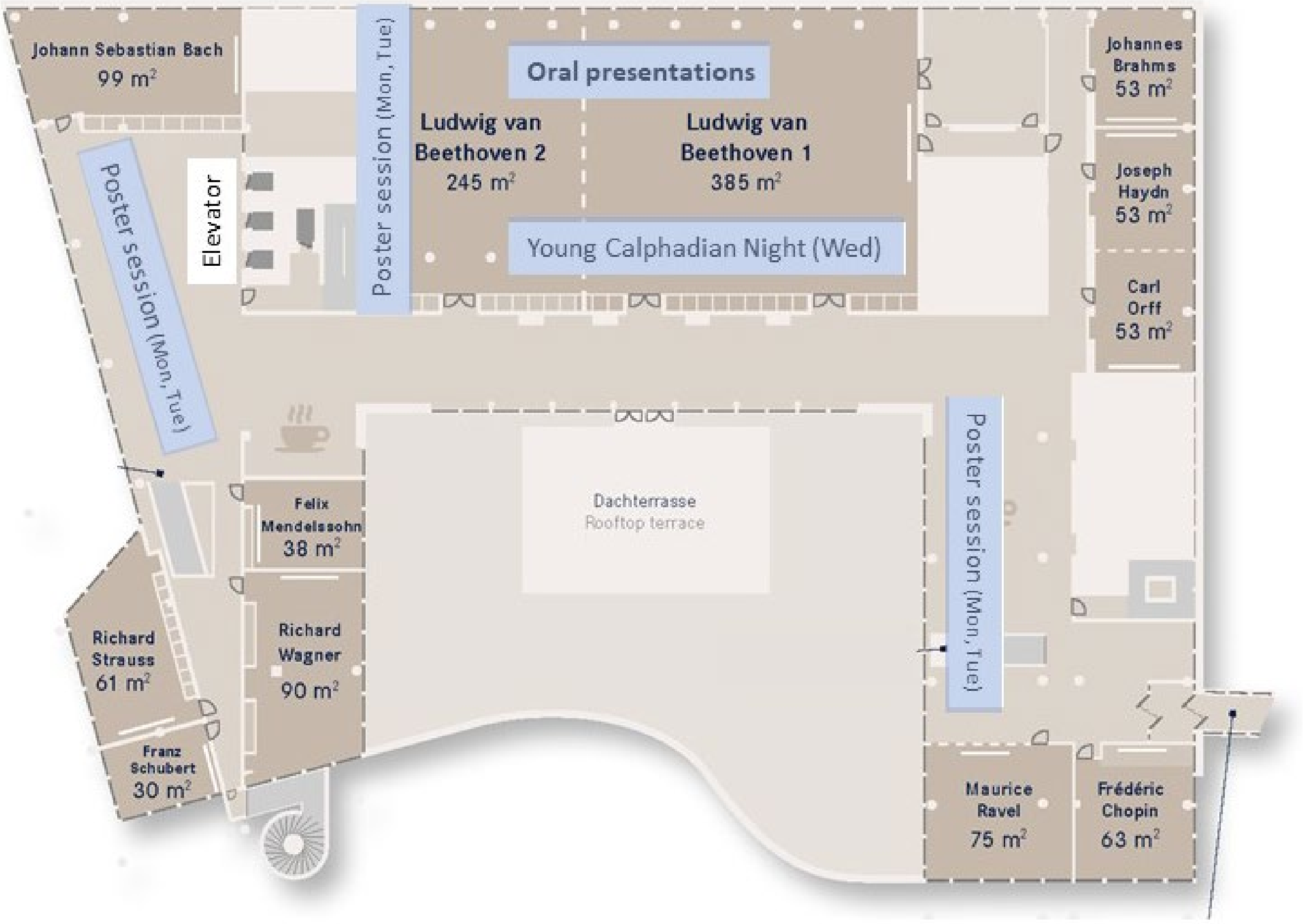
Dorint Kongresshotel Mannheim, Friedrichsring 6, 68161 Mannheim, Germany

Pre-Conference Workshops, 26 May 2024, 2 PM – 5 PM, 2nd floor
Welcome Reception, 26 May 2024, 6 PM – 8 PM, 2nd floor *Foyer*
CALPHAD board meeting, 28 May 2024, 2nd floor
APDIC committee meeting, 31 May 2024, 2nd floor

Sunday, 26 May 2024

1. Open-Source Software for Computational Thermodynamics and Phase Precipitation Modeling *(Room Bach)*
2. Augmenting CALPHAD Software and Data for Process Simulations *(Room Ravel)*
3. Software tools to ensure CALPHAD assessment quality *(Room Wagner)*
4. Demonstration of a fresh computer program for phase diagram calculations (begins at 4 pm) *(Room Chopin)*

Oral presentations, Poster sessions, Young Calphadian Night, Coffee breaks, 2nd floor



Dorint Kongresshotel, Restaurant Symphonie, Ground Floor

Breakfast, Lunch, Dinner

Social Program

Excursion to Heidelberg, Wednesday, May 29, 2024, 1:30 PM

Busses will depart at the main entrance of Dorint Kongresshotel.

Guided walking tour (about 90 minutes) through the old town.

We will split up into 8 groups. One group will do a gentle walking tour at a slower pace. Please get on the first bus, if you wish to join this group.

The Funicular Railway will take you up to Heidelberg Castle.

We will conclude the excursion with a reception on the terrace of Heidelberg Castle.

Conference Banquet at Castle Schwetzingen, Thursday, May 30, 2024, 5 PM

Busses will depart at the main entrance of Dorint Kongresshotel.

Awards will be announced during the dinner.

Young Calphadian Night

This is a traditional evening social event held during the annual CALPHAD conference. All attendees with a young mind are warmly invited to participate and have the opportunity to connect with fellow CALPHAD enthusiasts. A CALPHAD panel discussion will be organized, where attendees can gain insights into CALPHAD history, personal experiences, research anecdotes, and career development advice. Refreshments will be available, including drinks and snacks.

Time:

Wednesday, May 29th, Night event, 8:00-10:00 PM

After conference tour to Heidelberg.

Location:

Dorint Kongresshotel, 2nd floor, Room Beethoven

Organizers:

- Wei Xiong, University of Pittsburgh
- Richard Otis, NASA Jet Propulsion Laboratory
- Qijun Hong, Arizona State University

Panelists:

- Malin Selleby, KTH Royal Institute of Technology, Sweden
- Bengt Hallstedt, RWTH Aachen University, Germany
- Stephanie Lippmann, Friedrich Schiller University, Germany
- In-Ho Jung, Seoul National University, South Korea

Information about CALPHAD Young Leader Award:

- https://calphad.org/calphad-awards#CYLA
- https://calphad.org/Data/Sites/1/awards/bylaws-calphad-young-leader-award-2023.pdf

CALPHAD Pre-Conference Workshops

There will be three parallel workshops from 2 to 5 PM on Sunday, 26 May 2024.
The fourth workshop will start at 4 PM.

Refreshments are available in the workshop rooms.

Workshop 1:

Open-Source Software for Computational Thermodynamics and Phase Precipitation Modeling

Time: 2 - 5 PM, Sunday, 26 May 2024
Location: Dorint Kongresshotel, 2nd floor, room Johann Sebastian Bach

This course will give a detailed introduction to open-source computational thermodynamics and kinetics software based on the CALPHAD method. It will feature hands-on demonstrations in an interactive cloud environment and practical exercises that will enable attendees to calculate phase diagrams, simulate solid-state precipitation of alloys, and to propagate uncertainty in a given thermodynamic calculation.

PyCalphad

PyCalphad is a free and open-source Python library for calculating phase diagrams, designing thermodynamic models, and investigating phase equilibria within the CALPHAD method. It provides routines for reading thermodynamic databases and solving the multi-component, multi-phase Gibbs energy minimization problem. All Gibbs energy and property models in PyCalphad are described symbolically allowing the models to be customized or overridden by users at runtime without changing any of the PyCalphad source code. Calculation results from PyCalphad are returned as multidimensional datasets that make it easy to incorporate PyCalphad into any tool or workflow.

Kawin

Kawin is a new open-source implementation of the Kampmann–Wagner Numerical model of precipitation (concomitant nucleation, growth, and coarsening). An overview of the organization and capabilities of the program is provided, along with an outline of the constituent physics. Kawin is capable of simulating the bulk precipitation behavior of multiphase, multicomponent systems in response to complex heat treatments. The inclusion of native strain calculations enables Kawin to predict the influence of internal or external stress fields on precipitation, as well as track the evolution of precipitate geometry throughout the course of a heat treatment.

Course Goal: After following along with the provided exercises, attendees will complete the course with new tools in-hand, ready to take home.

Course Audience: Engineers and practitioners interested in learning more about open-source materials design tools.

Workshop 2:

Augmenting CALPHAD Software and Data for Process Simulations

Time: 2 - 5 PM, Sunday, 26 May 2024
Location: Dorint Kongresshotel, 2nd floor, room Maurice Ravel

Thermo-Calc Software AB & QuesTek Europe AB
The aim of the workshop is to follow data from their creation by assessments following the CALPHAD approach all the way to their use in industrial applications

Part 1: 2 - 2:45 pm: DATA (Qing Chen and Mehdi Noori, Thermo-Calc)

A team of over 10 people at Thermo-Calc are dedicated full time to the development of CALPHAD databases. Database development essentially involves combining assessments of binary and ternary systems into large multicomponent databases. The currently available models and strategies for 3rd generation databases will be outlined, specifically the Einstein model, the two-state model for liquid and amorphous phase, a new magnetic model. Further, it will be shown how the same idea of lattice stability for the Gibbs energy can be extended to other material properties, such as mobilities, density, thermal and electrical conductivity, viscosity, surface tension, ... For all these, the syntax for entering the relevant parameters into a tdb file will be explained and demonstrated.

Finally some new ideas will be presented on how CALPHAD assessments and database development can profit from machine learning ideas and methodologies.

Part 2: 3 - 4 pm: ADDITIVE MANUFACTURING (Nicholas Grundy, Thermo-Calc)

The reliability of finite element models (FEM) crucially depends on the reliability of the material properties used. It will be demonstrated how the data outlined in Part 1 is used as input for a FEM model of the Additive Manufacturing (AM) process. One of the outputs of FEM simulations are thermal gradients. It is these gradients, together with other material properties, that determine microstructure features such as columnar to equiaxed transition in the melt pool or precipitates and segregation profiles in the solid material. Examples will be shown how FEM simulations can be directly linked to kinetic simulations of nucleation and growth of precipitates and homogenization by diffusion.

This section will include a live demonstration of Thermo-Calc`s additive manufacturing module including a subsequent connection of a calculated temperature vs. time profile with the Diffusion Module DICTRA and the Precipitation Module TC-PRISMA.

Part 3: 4:15 - 5 pm: INDUSTRIAL APPLICATION (David Linder, QuesTek Europe)

This concluding section of the workshop will pull everything together and demonstrate examples of how CALPHAD data from part 1, and a collection of advanced modelling and simulation tools, including but not limited to FEM simulations of additive manufacturing from part 2, can be combined in a Integrated Computational Materials Engineering (ICME) framework to design and develop materials tailored for a specific production line and industrial application.

Workshop 3:
Software tools to ensure CALPHAD assessment quality

Time: 2 - 5 PM, Sunday, 26 May 2024
Location: Dorint Kongresshotel, 2nd floor, room Richard Wagner

Moritz to Baben and Florian Tang, GTT-Technologies, & Bengt Hallstedt, RWTH Aachen University

Reliability of assessments and databases is key for the CALPHAD community. In this workshop, software tools to ensure CALPHAD assessment quality are discussed. There will be three introductory talks:

First, Florian Tang shows how a user interface can support the assessor by providing valuable information about the CALPHAD optimization, using the FactSage Calphad Optimizer as example. Second, Moritz to Baben provides an example that shows how a data-centric approach can be used to detect probably wrong data. Finally, Bengt Hallstedt shares his experience as CALPHAD reviewer how he evaluates whether or not a CALPHAD assessment makes sense.

Together with the audience, it will be discussed what standard practices of CALPHADians should be made easy by software in order to ensure good CALPHAD assessment quality.

Agenda

2:00 PM: User interface decisions in development of Calphad Optimizer (Florian Tang)
2:45 PM: Data-based detection of unreasonable thermodynamic data (Moritz to Baben)
3:15 PM: Human-based detection of unreasonable thermodynamic data (Bengt Hallstedt)
4:00 PM: Discussion
5:00 PM: End of the workshop

Workshop 4:

Demonstration of a fresh computer program for phase diagram calculations

Time: 4 - 5 PM, Sunday, 26 May 2024
Location: Dorint Kongresshotel, 2nd floor, room Frédéric Chopin

V. B. Rajkumar, Yong Du

Our motivation in developing this indigenous software is to create a versatile tool for the calculation and optimization of phase diagrams. Beyond this, we envision seamless integration with diffusion studies [1] and phase-field simulations [2] to enhance practical applicability. While existing software packages such as Lukas, ChemSage, MatCalc, ThermoCalc, Pandat, MTDATA, CaTCalc, FactSage, PyCalphad, and OpenCalphad, have made substantial contributions to phase diagram calculations [3], our initiative uniquely addresses specific needs and challenges, providing a fresh perspective on the application of computational thermodynamics.

In the realm of computational thermodynamics, we are at the forefront of introducing a new Python software package specifically designed for calculating phase diagrams.

This workshop stands as a vital platform, offering participants a thorough grasp of computational thermodynamic software with a prime focus on the CALPHAD method. It explores the intricacies of different software functions, covering routines for reading thermodynamic databases and conducting binary phase diagram calculations. Moreover, our software produces results in a format that allows easy integration into diverse tools and workflows, ensuring flexibility for seamless incorporation into existing computational frameworks.

Our software transcends being a mere standalone tool; it represents a broader vision advancing the comprehension and application of computational thermodynamics. Its creation is in harmony with the escalating need for sophisticated and user-friendly tools in materials science and metallurgy. This initiative lays the groundwork for future advancements, including integration with diffusion studies and phase-field simulations, opening new avenues for researchers, and enriching the exploration of phase diagram intricacies.

References

[1] Yuling Liu, et al. "CALTPP: A general program to calculate thermophysical properties", *J. Mater. Sci. Technol.,* 42 (2020): 229.

[2] Rajkumar, V. B. et al. "Phase-field simulation of solidification microstructure in Ni and Cu–Ni alloy using the Wheeler, Boettinger and McFadden model coupled with the CALPHAD data", *Calphad,* 68 (2020): 101691.

[3] Taibai Fu, et al. "A new algorithm to calculate binary phase diagrams", *Comput. Mater. Sci.,* 159 (2019): 478

Biographical Note

The author is working as a technical expert to develop phase diagram calculation software at Ruirui technology Co. Ltd., R & D Headquarters, Central South University Science Park, Yingzuo Road, Yuelu District, Changsha, P.R. China.

Conference Agenda

Abstracts for each presentation can be found in the following section. To easily locate the abstract of each oral presentation, please refer to the presentation index number provided in the first column of the agenda table.

Important Notes:
To ensure a smooth session, we kindly request that **all presentation files be saved on the conference laptop prior to the start of each session**. All files will be removed from the laptop after the conference. While we discourage using personal laptops due to time constraints, if necessary, please ensure that you test the projector connection well before the session start time.

There will be **two poster sessions** scheduled as follows:

- Poster Session 1: 7:00 - 10:00 PM, Monday, 5/27.
  Please set up your poster by 2:00 PM on Monday and remove it by
  12:00 PM noon on Thursday.
- Poster Session 2: 7:00 - 10:00 PM, Tuesday, 5/28.
  Please set up your poster by 2:00 PM on Tuesday and remove it by
  12:00 PM noon on Thursday.

Should you have any inquiries or require assistance, please feel free to reach out to Hans Seifert, Andre Schneider, or any member of the organizing committee.

May 27, 2024, Monday

08:00 – 08:10 **WELCOME**

Session 1: Additive Manufacturing

Chairs: Stephanie Lippmann, Moritz to Baben *Monday, May 27, 2024*

O01	08:10 – 08:30	*Wei Xiong*: CALPHAD-based ICME Design for Additive Manufacturing of Functionally Graded Alloys
O02	08:30 – 08:50	*Silvana Tumminello:* Precipitation simulations of the O-phase inTi$_2$AlNb alloys synthesized by laser powder bed fusion
O03	08:50 – 09:10	*Bernd Böttger:* Thermodynamic Aspects of Microstructure Formation during Powder Bed Fusion of Ni-base Superalloys: A Phase-Field Simulation Approach using the Software MICRESS®
O04	09:10 – 09:30	*Wei Chen*: Phase Transformation Pathway in Additive Manufactured High-entropy Alloys
O05	09:30 – 09:50	*Manuel Sanchez-Poncela*: Triplex steel powder design to avoid hot cracking in laser-powder bed fusion using computational thermodynamics
O06	09:50 – 10:10	*Sang-Ho Oh*: Development of a novel Monte Carlo Potts model for solid-liquid phase transformations
	10:10 – 10:40	**COFFEE BREAK**

Session 2: CALPHAD Modeling and Assessments

Chairs: Malin Selleby, Bengt Hallstedt *Monday, May 27, 2024*

O07	10:40 – 11:00	*Svitlana Iljenko:* From Data to Knowledge: The Importance of Critical Evaluation in Materials Constitution
O08	11:00 – 11:20	*Andreas Czerny*: Thermodynamic assessment of the systems Mo-Si and Mo-Si-Ti
O09	11:20 – 11:40	*Jia Qi*: Experimental study and thermodynamic assessment of the metal-salt systems
O10	11:40 – 12:00	*Peter Franke*: A Thermodynamic Assessment of 5 Selected Organic Carbonates and Their Mixtures Used in Lithium-ion Batteries
O11	12:00 – 12:20	*Sinn-wen Chen*: Miscibility gaps in the Ag-Cu-Se-Te quaternary system
	12:30 – 14:00	**LUNCH**

Session 3: CALPHAD Modeling and Database Development 1

Chairs: Suzana G. Fries, Byeong-Joo Lee *Monday, May 27, 2024*

O12	14:00 – 14:20	*Rainer Schmid-Fetzer:* External magnetic field and Gibbs energy: A novel framework suitable for Calphad
O13	14:20 – 14:40	*Courtney Kunselman:* Revisiting Derivatives at Equilibrium
O14	14:40 – 15:00	*Ping Wu:* Entropy-driven synthesis of non-Van-Der-Waals crystals into nanosheets
O15	15:00 – 15:20	*Lorenzo Fenocchio:* 3rd Generation CALPHAD modelling of pure high-melting elements: case study on Mo
O16	15:20 – 15:40	*Alexander Walnsch:* Thermodynamic assessment of the Al–Ni system using revised 3rd generation unaries, thermal vacancies and 4-sublattice models
	15:40 – 16:10	**COFFEE BREAK**

Session 4: Thermodynamic Software and Model Development

Chairs: Caroline Toffolon-Masclet, Zi-Kui Liu *Monday, May 27, 2024*

O17	16:10 – 16:30	*Fan Zhang*: Pandat Software and Its Applications in Materials Design and Process Optimization
O18	16:30 – 16:50	*In-Ho Jung:* FactProSim Flowsheet Process Simulation Software
O19	16:50 – 17:10	*Byeong-Joo Lee:* A real scale Monte Carlo Potts model for simulation of microstructural evolution under thermal gradient
O20	17:10 – 17:30	*Luis Ladinos-Pizano:* Design of γ'-strengthened superalloys for additive manufacturing through CALPHAD-based ICME modeling
O21	17:30 – 17:50	*Lucas Ueberricke:* Optimization of Gibbs Energy of Deeply Undercooled Oxide Melts for Modelling of Crystallization Phenomena in Glasses
	18:00 – 19:00	**DINNER**

Poster Session 1

19:00 – 22:00 Subsessions 01 – 07 (detailed list on page 106)

May 28, 2024, Tuesday

Session 5: Steels 1

Chairs: Nathalie Dupin, Frank Stein *Tuesday, May 28, 2024*

O22	08:00 – 08:20	*Andre Schneider:* Influence of alloying elements on cementite formation on Fe-X (X = Si, Mo, V) alloys during carburization under metal dusting conditions
O23	08:20 – 08:40	*Michael Bernhard:* Experimental and thermodynamic evaluation of the Fe-Si system and application to the processing of silicon steels
O24	08:40 – 09:00	*Aurélie Jacob:* Microstructural investigation of the undercooled austenite in the Fe-C
O25	09:00 – 09:20	*Weisen Zheng:* CALPHAD-assisted design of ultrahigh-strength TRIP-aided autosteel plate
O26	09:20 – 09:40	*Caroline Toffolon-Masclet:* Modelisation of carbides precipitation sequences during tempering in model Fe-C-Mo-Mn-Ni ferritic alloys
O27	09:40 – 10:00	*Johann Möbius:* Thermal characterization of compositionally complex Fe-based alloys
	10:00 – 10:30	**COFFEE BREAK**

Session 6: CALPHAD and Data Science

Chairs: Enrica Epifano, Tilmann Hickel *Tuesday, May 28, 2024*

O28	10:30 – 10:50	*Irina Roslyakova:* Machine Learning and ChatGPT Integration for the Third Generation of 0 Kelvin CALPHAD Databases
O29	10:50 – 11:10	*Qing Chen:* AlloyNet – Predicting Alloy Properties by ANNs
O30	11:10 – 11:30	*Héléna Verbeeck:* Modeling of Particle Dissolution during Spent Automotive Catalyst Recycling: Overcoming Driving Force Limitations
O31	11:30 – 11:50	*Bruno Reis:* Calphad Optimizer: SQL Insights on Refining, ML, and Quality Metrics
O32	11:50 – 12:10	*Jaemin Wang:* Machine Learning-Driven Solutions to Evaporation Induced Variability in Chemical Composition of In-Situ Alloyed Products Fabricated by Direct Energy Deposition
	12:30 – 14:00	**LUNCH**

Session 7: Thermodynamic Modeling, Database and Design Applications

Chairs: Ursula Kattner, John Ågren *Tuesday, May 28, 2024*

O33	14:00 – 14:20	*Yong Du:* Thermodynamic, kinetic simulations and experiment on the chemically vapor deposited TiAlSiN coatings
O34	14:20 – 14:40	*Aurélien Perron:* Development and integration of CALPHAD databases and software tools for alloy design
O35	14:40 – 15:00	*Julian Rackwitz:* High-strength high-damping steels: A CALPHAD assisted alloy design
O36	15:00 – 15:20	*Wei-Lin Tan:* Multi-Objective Design of High Strength Thick-Plate Aluminum Alloy with Low Quench Sensitivity
O37	15:20 – 15:40	*Libin Liu:* Design of High-Strength Heat-Resistant Aluminum Alloys Based on Phase Diagram Calculations
	15:40 – 16:10	**COFFEE BREAK**

Session 8: Oxides

Chairs: Dimitra Spathara, Qing Chen *Tuesday, May 28, 2024*

O38	16:10 – 16:30	*Christine Guéneau:* Thermodynamic modelling of oxide fuels for nuclear applications: current status and prospects for improvement
O39	16:30 – 16:50	*Manuel Löffler:* Phase equilibrium investigations and thermodynamic study of the Y_2O_3-Ta_2O_5 system
O40	16:50 – 17:10	*Yu Zhong:* The Effect of A-site Doping Elements on the Activation Energy Barrier and Oxygen Diffusivity of $La_2NiO_{4+\delta}$
O41	17:10 – 17:30	*Elena Yazhenskikh:* Thermodynamic modelling of the P-containing systems: Alk_2O-Me_2O_3-P_2O_5 and $Alk_xPyO_{0.5x+2.5y}$-AlkCl (Alk=K,Na; Me=Al,Fe) for the oxide-salt database GTOx
O42	17:30 – 17:50	*Alexander Pisch:* Thermodynamic modeling of the Al-Ca-O ternary system with key experiments
	18:00 – 19:00	**DINNER**

Poster Session 2

19:00 – 22:00 Subsessions 08 – 11 (detailed list on page 106)

May 29, 2024, Wednesday

Session 9: CALPHAD Applications

Chairs: Aurélie Jacob, Manuel Sanchez-Poncela *Wednesday, May 29, 2024*

O43	08:00 – 08:20	*Enrica Epifano:* Pt effect on the bond-coating/superalloy interdiffusion: a thermodynamic and kinetic study
O44	08:20 – 08:40	*Yuan Yuan:* The multi-solute solid solution behaviour of magnesium alloys and their application on materials design
O45	08:40 – 09:00	*Parikshit Bajpai:* Accelerating thermochemical equilibrium calculations for nuclear reactor applications
O46	09:00 – 09:20	*Adamantia Lazou:* CALPHAD-based thermodynamic evaluation for integrating secondary Ni-containing dusts in ferrous processing
O47	09:20 – 09:40	*Florian Häslich:* Phases and Microstructure of Refractory Complex Concentrated Alloys $Al_xCr_yMoTaTi$ (x = 1…3, y = 0.5…1)
O48	09:40 – 10:00	*Jean-Philippe Harvey:* Eco-Innovative Process Design: Integrating LCA into Thermodynamic-based Process Simulations for the Development of more Sustainable Technologies
	10:00 – 10:30	**COFFEE BREAK**

Session 10: Experimental Equilibria and Phase Transformations 1

Chairs: Silvana Tumminello, Alexander Pisch *Wednesday, May 29, 2024*

O49	10:30 – 10:50	*Alexandra Navrotsky:* Incorporating High Pressure into CALPHAD
O50	10:50 – 11:10	*Dimitra Spathara:* Exploring the parameter space of compositions and strengthening mechanisms, for the development of electroformed CuCr alloys, for rare event searches
O51	11:10 – 11:30	*Lisa-Yvonn Schmitt:* Investigation of the Ni-Nb-Ta liquidus projection using the CALPHAD approach
O52	11:30 – 11:50	*Frank Stein:* About the ternary ω_o and O phase in the Ti-Al + Nb system
O53	11:50 – 12:10	*Kazushige Ioroi:* Experimental Determination of Phase Diagram and Thermodynamic Assessment in the Cr–Ta Binary System
	12:30	**LUNCH**

13:30 CONFERENCE EXCURSION
18:00 RECEPTION CASTLE HEIDELBERG
20:00 – 22:00 YOUNG CALPHADIANS NIGHT

May 30, 2024, Thursday

Session 11: Steels 2

Chairs: Héléna Verbeeck, Andreas Leineweber *Thursday, May 30, 2024*

O54	08:00 – 08:20	*Fabio Miani:* Calphad Science and the Art of Steel Making
O55	08:20 – 08:40	*Jiayi Yan:* CALPHAD-based modeling of pearlite transformation in multicomponent steels
O56	08:40 – 09:00	*Yiwa Luo:* CALPHAD Application in the Removal of $MgO \cdot Al_2O_3$ Spinel Inclusions during Vacuum Metallurgy
O57	09:00 – 09:20	*Nicholas Grundy:* Applying CALPHAD Data to an Industrial Production Process: Kinetic Simulation of a Ladle Furnace
O58	09:20 – 09:40	*Ikuo Ohnuma:* Extended calculation model of grain boundary segregation and its application to segregation engineering
O59	09:40 – 10:00	*Peter Presoly:* How DSC measurements and CALPHAD helps to avoid breakouts during the continuous casting of peritectic steels
	10:00 – 10:30	**COFFEE BREAK**

Session 12: Diffusion, Kinetics and Phase Transformations

Chairs: Christine Guéneau, Peter Franke *Thursday, May 30, 2024*

O60	10:30 – 10:50	*John Ågren:* Hillert-style irreversible thermodynamics and the entropy production
O61	10:50 – 11:10	*Zi-Kui Liu:* On Gibbs Equilibrium and Hillert Nonequilibrium Thermodynamics
O62	11:10 – 11:30	*Qiang Du:* The calculation of kinetic interface contact condition phase diagram and its applications to additive manufacturing
O63	11:30 – 11:50	*Hyo-Sun Jang:* Diffusion of methane in metal-organic frameworks: An atomistic approach
O64	11:50 – 12:10	*Tatsuya Tokunaga:* Evaluation of crystallization behavior during rapid cooling process in Al-Fe-M (M = Mg, Si, Mn) alloys by combining the CALPHAD and kinetic approach
	12:30 – 14:00	**LUNCH**

Session 13: Atomistic Modeling and Prediction

Chairs: Qijun Hong, Richard Otis *Thursday, May 30, 2024*

O65	14:00 – 14:20	*Tilmann Hickel:* Solute Induced Defect Phase Transformations in Grain Boundaries
O66	14:20 – 14:40	*Jing Yang:* Order-disorder transitions on alloy surfaces: From Monte Carlo to analytical models
O67	14:40 – 15:00	*Qijun Hong:* A generalized approach for rapid entropy calculation of liquids and solids
O68	15:00 – 15:20	*Jianchuan Wang:* First-principles study on the dehydrogenation thermodynamics and kinetics of Ti, Zr, V and Nb doped MgH_2
O69	15:20 – 15:40	*Quentin Bizot:* Atomistic simulations and active learning of the enthalpy of mixing in liquid and solid solutions
O70	15:40 – 16:00	*Masanori Enoki:* Prediction of nitride nanocluster formation in iron based on first principles calculation

17:00 DEPARTURE for CONFERENCE BANQUET at SCHWETZINGEN CASTLE

May 31, 2024, Friday

Session 14: CALPHAD Modeling and Database Development 2

Chairs: Fan Zhang, Rainer Schmid-Fetzer *Friday, May 31, 2024*

O71	08:00 – 08:20	*Ursula Kattner:* Calphad Databases for Co-base Superalloys
O72	08:20 – 08:40	*Ernst Gamsjäger:* Thermodynamic functions of low temperature data
O73	08:40 – 09:00	*Zhangting He:* Modelling allotropes for the third generation Calphad: a comprehensive exploration with focus on Fe
O74	09:00 – 09:20	*Brandon Bocklund:* Implementation of an extensible property modeling framework in ESPEI
O75	09:20 – 09:40	*Wenhao Ma:* Thermodynamic modeling of the Ni-S based bulk metallic glass-forming system
O76	09:40 – 10:00	*Bengt Hallstedt:* The SGTE Binary Collection
	10:00 – 10:30	**COFFEE BREAK**

Session 15: Experimental Equilibria and Phase Transformations 2

Chairs: Wei Xiong, Yong Du *Friday, May 31, 2024*

O77	10:30 – 10:50	*Fangfang Zeng:* Phase composition, microstructure and mechanical properties of CVD Ti-B-N coatings deposited at different temperatures guided by thermodynamic calculations
O78	10:50 – 11:10	*Andreas Leineweber:* High-pressure studies in the Fe–N system
O79	11:10 – 11:30	*Weiping Gong:* Formation kinetics and thermodynamic stability of the compounds in $Bi_4Ti_3O_{12}$-$BiFeO_3$ system
O80	11:30 – 11:50	*Ondřej Zobač:* Experimental and theoretical study of La-Ni-Sn system as a perspective hydrogen storage material
O81	11:50 – 12:10	*Weronika Gozdur:* Calorimetric measurements and thermodynamic modeling of Ag-Mg-Ti liquid alloys
	12:10 – 12:20	CLOSING
	12:30 – 13:00	(BOX) LUNCH and DEPARTURE

Collection of Abstracts for Oral Presentation

There are 81 oral presentations in total.

[O01] CALPHAD-based ICME Design for Additive Manufacturing of Functionally Graded Alloys

Wei Xiong, Luis Ladinos-Pizano, Liyi Wang
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Keywords: Functionally graded materials, Additive manufacturing, CALPHAD, ICME

Functionally graded materials (FGM) can be fabricated using directed energy deposition (DED) techniques, facilitating the incorporation of multiple functionalities into alloy components. In this presentation, I will share some experiences gained from the work on printing FGM using various DED techniques guided by ICME (Integrated Computational Materials Engineering) [1,2]. The discussion will showcase several case studies illustrating the advantages of employing the CALPHAD-based ICME approach in additive manufacturing design [1,3].

One of the case studies highlighted is related to the additive manufacturing of bimetallic structures involving Cu alloy and Inconel 625. Utilizing CALPHAD databases, it becomes possible to predict phase stability and solidification cracking susceptibility in a high-throughput manner. This approach also aided in comprehending the microstructure features observed in both printed and post-heat-treated prototypes.

It was found that some of the critical ternary systems require refinement to accurately predict phase boundaries in such a complicated multicomponent system. These ternaries require thorough evaluation and CALPHAD assessment. Nonetheless, a semi-quantitative guideline provides valuable insights for initiating the introduction of the third alloy as an interlayer, reducing cracking susceptibility.

This study also investigates the phenomenon of liquid phase separation evident in microstructural analysis and its implications on crack formation in the printing process. Furthermore, it shows the importance of comprehending the underlying phase stability when fabricating intricate interlayers with composition gradients during additive manufacturing. The printed sample in this work shows the successful printing of FGM with a crack-free sample. However, phase analysis of the undesired intermetallic phases indicates the essence of interlayer design using a third alloy.

Integration of the CALPHAD, physics-based mods, and experimental validation/calibration will be emphasized in this talk as it demonstrates the systematic application of CALPHAD methodology in additive manufacturing design. This talk highlights the importance of advancing the development of CALPHAD databases to improve our comprehension and capabilities in advanced alloy manufacturing.

Acknowledgments

The authors appreciate the constructive discussions with Michael A. Klacka at RTX Technology Research Center and Kelsay Neely at Marshall Space Flight Center, NASA. The work related to bimetallic printing of Cu alloy and Inconel 625 is supported by NASA Early Stage Innovations under Award number 80NSSC23K0230. Some cases discussed in this talk are supported by the National Science Foundation under the Faculty Early Career Development Award: CMMI 2047218.

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3. X. Wang, W. Xiong, Uncertainty quantification and composition optimization for alloy additive manufacturing through a CALPHAD-based ICME framework. *npj Computational Materials*. 6 (2020) 188.

Biographical Note

Professor Wei Xiong is the Director of the Physical Metallurgy and Materials Design Laboratory and the William Kepler Whiteford Faculty Fellow at the University of Pittsburgh. He joined the University in September 2016 as an Assistant Professor, and since then, he has established himself as an expert in materials design and process optimization using CALPHAD-based ICME techniques. Prof. Xiong's research is primarily focused on phase equilibria and microstructure engineering, with a strong emphasis on materials design and advanced manufacturing techniques. He received several academic awards related to the CALPHAD, including the Best Paper Awards of the CALPHAD journal in 2012 and 2013, the CALPHAD Young Leader Award in 2020, and the APDIC Best Paper Award from Alloy Phase Diagram International Commission in 2021.

[O02] Precipitation simulations of the O-phase in Ti_2AlNb alloys synthesized by laser powder bed fusion

S. Tumminello[1], J. Gussone[1], K. Bugelnig[1], S. G. Fries[2], M. Rackel[3], A. Stark[3], N. Schell[3], P. Barriobero-Vila[1], J. Haubrich[1] and G. Requena[1,4]
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[2] RUB, Materials Research Department, Bochum, NRW, 44801, Germany
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Key words: Precipitation simulations, Driving forces, Parametric analysis, LPBF

Ti_2AlNb alloys based on the ordered orthorhombic (O) phase are structural high temperature candidate materials for weight reduction in engines and aircraft. Their complex microstructure is strongly dependent on the processing conditions challenging their development for practical applications. Efforts in the last decades have been made to improve their mechanical properties by correlating the effect of different processing conditions and final microstructures [1].

In the last years Ti-22Al-25Nb alloy has received attention due to its processability by additive manufacturing. We investigate the precipitation of the O-phase in Ti-22Al-25Nb alloys during an annealing step of 3 h at 600 °C. Samples were printed by Laser Powder Bed Fusion (LPBF) with low baseplate pre-heating temperatures. The microstructure of the alloys was investigated before and after the annealing step using electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) for the chemical analysis. The phase fractions during precipitation were measured by high-energy synchrotron X-ray diffraction (HEXRD) at the beamline P07-HEMS of the PETRA III source (Deutsches Elektronen-Synchrotron, DESY) in Hamburg, Germany.

Precipitation simulations were done using the Thermo-Calc PRISMA module in combination with well-developed thermodynamic and mobility databases TCTI/Ti-alloys version 3 [2]. In particular the volume fraction of the O-phase precipitating in Ti-22Al-25Nb from a supersaturated β-TiAlNb matrix was quantified during the simulations and confronted with HEXRD measurements as well as with previous studies by Sadi and Servant [3] on the β→O phase transformation.

Different nucleation, growth mechanisms and precipitate morphologies were simulated and correlated with experimental observations at relative early stages of the precipitation process. We have carefully examined all input parameters needed to initiate the precipitation simulations in PRISMA and selected eleven of them to quantify their effect on the precipitation and growth curve. We use ANSYS Optislang software [4] for the parametrization and sensitivity analysis.

The figure presents the equilibrium diagram of Ti-Al-Nb calculated at 600 °C and phase fractions calculated as a function of temperature for the Ti-22Al-25Nb alloy. Equilibrium phase boundaries evidence the supersaturation of the initial β-TiAlNb matrix (♦, turquoise symbol) and qualitatively indicate the high driving force for O-Ti_2AlNb precipitation. On the right-hand side of the figure, the volume fractions during precipitation of ordered O-phase, experimental and simulated, are presented as well as the correlation matrix to show the effect of the input variables on three stages of the precipitation and growth process.

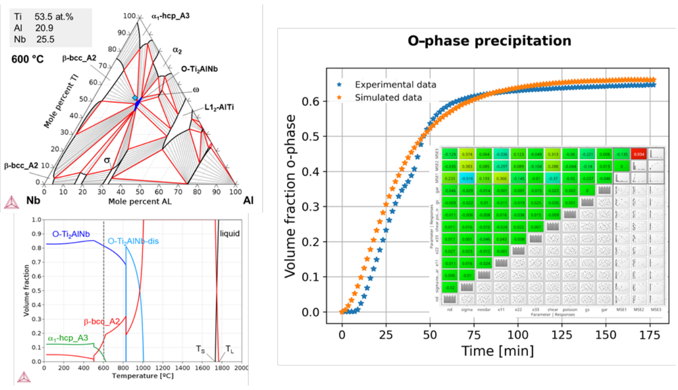

Figure. Calculated isothermal section at 600 °C of the Ti-Al-Nb equilibrium diagram, equilibrium phase fractions as function of temperature and, simulated and experimental volume fractions of O-phase as function of time with the correlation matrix for the input parameters.

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Biographical Note

Dr. Silvana Tumminello is the principal researcher of the Integrated Computational Materials Engineering (ICME) project for development of thermoelectric devices and structural materials at the German Aerospace Center (DLR), Cologne, Germany.

[O03] Thermodynamic Aspects of Microstructure Formation during Powder Bed Fusion of Ni-base Superalloys: A Phase-Field Simulation Approach using the Software MICRESS®

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Key words: Phase-field, MICRESS, Ni-base alloy, microstructure simulation

Additive processes like laser powder bed fusion (L-PBF) are gaining more and more interest, not only in research and development but also in industrial practice. Nevertheless, many aspects of this relatively new type of processes are still not sufficiently understood. The reason for this is not only its novelty and the very small time- and length-scales: What also make it so challenging is the transient nature of the process, the intertwining of fundamentally different physical phenomena like laser light absorption, melting and solidification, as well as the complexity of process parameters and hatching strategies which lead to extremely inhomogeneous local conditions and process history dependencies.

To overcome the high complexity of the additive processes there have been many efforts to apply numerical simulation in order to shed more light onto the different processes involved and to achieve a more profound understanding. In this contribution we focus on a phase-field approach for microstructure simulation of Ni-based superalloys during the laser powder bed fusion process, based on the commercial software MICRESS®[1]. When setting up suitable simulation models, there are many challenges which arise and which are directly or indirectly linked to thermodynamics. One fundamental question is whether local equilibrium assumptions, which are usually applied in phase-field models to describe solute re-distribution and the driving forces at the interface, are still valid at the typically high cooling rates up to 10^6 K/s.

A second challenge is presented by the high-alloyed (almost high-entropy) and multi-component materials, which cannot be reasonably described without direct coupling to Calphad databases [2]. It has been addressed using the quasi-equilibrium approach together with efficient extrapolation methods [3], which allow for online coupling to thermodynamic and mobility databases without unreasonably high computational costs.

Further challenges are the important role of latent heat release, requiring strong coupling, or at least iterative coupling, between the temperature solver and the phase-field model [4], as well as the interplay between melting and solidification, which represent the most important stages of the layer-wise additive production process.

During the presentation, 2D- and 3D-simulation results for different L-PBF-processes and Ni-based alloys will be shown and discussed. The importance of latent heat for the correct description of the local temperature field and solidification conditions is highlighted. Furthermore, the role of melting and fragmentation of dendrite arms for the formation of new grains and the production of multiple layers is addressed.

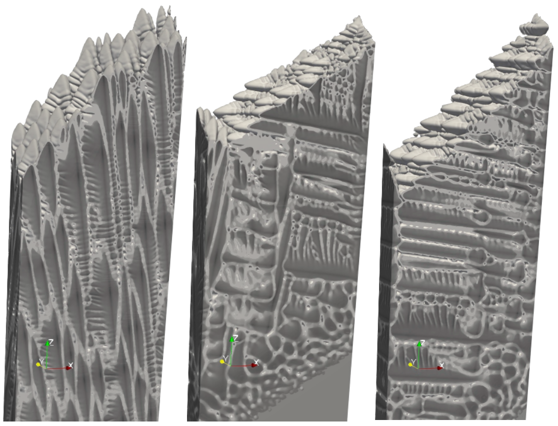

Figure 1. Simulated 3D-microstructures for different directions of the temperature gradient

References

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Biographical Note

Bernd Böttger studied chemistry at the Technical University of Karlsruhe. After his PhD in electro-chemistry he made his post-doctorate at the University of Córdoba in Spain. Since 1998 he is working for Access e.V in Aachen/Germany in phase-field modelling and the development of and support for the commercial software MICRESS®[1].

[O04] Phase Transformation Pathway in Additive Manufactured High-entropy Alloys

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Key words: phase transformation, high-entropy alloy, first-principles, mechanical properties

High-entropy alloys (HEAs) have garnered significant attention for their potential in delivering excellent mechanical performance. Additive manufacturing (AM), with its far-from-equilibrium solidification conditions, presents abundant opportunities to create materials with unique microstructures and properties. To harness the combined benefits of AM and HEAs, a fundamental understanding of the processing-structure-property relationship in additively manufactured HEAs is crucial yet challenging due to the complex phase selection and non-equilibrium solidification microstructures involved. In this study, we investigate the effect of solidification rate on the microstructure of laser additively manufactured eutectic HEAs. By varying the laser scan speed and hence the solidification rate, we reveal distinct solidification modes, including single-phase solidification, anomalous eutectic solidification, and coupled lamellar eutectic solidification. The resulting varied solidification microstructures and phase constituents lead to a wide range of mechanical properties. Thermodynamic modeling and atomistic simulations are performed to gain insights into the transition of solidification mode from coupled eutectic to anomalous eutectic and eventually to single-phase solidification as the solidification rate continuously increases. Our findings highlight that AM enables the development of multi-component alloys with tailored properties by offering a broad space for phase and microstructure design.

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Biographical Note

Dr. Chen is currently an Associate Professor in Materials Science and Engineering at University at Buffalo, State University of New York. He received his Ph.D. in Materials Science and Engineering from Northwestern University. His research interests include first-principles and data-driven methods for materials discovery and design.

[O05] Triplex steel powder design to avoid hot cracking in laser-powder bed fusion using computational thermodynamics

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Key words: Hot Cracking, L-PBF, High-Mn steel, Alloy design

High manganese steels offer exceptional combinations of high strength and ductility, resulting in weight reduction when utilized in structural applications. Nevertheless, the conventional manufacturing routes of these steels is hindered by many production problems. Additive Manufacturing (AM) has emerged as a reliable solution to fabricate thin or complex shape compounds using these steel grades. Indeed, several studies have demonstrated the success to fabricate high manganese twinning-induced plasticity (TWIP) and transformation-induced plasticity (TRIP) steels by laser-powder bed fusion (L-PBF) [1–3]. However, a recent study on a high manganese triplex steel composition has revealed the occurrence of both hot cracking and micro segregation during rapid solidification in L-PBF [4], highlighting potential processability issues of this family of high alloy steels. In this study, the hot cracking susceptibility of different triplex steels is evaluated, focusing on the impact of the composition on the solidification paths and final microstructures. A Computer Coupling of Phase Diagrams and Thermochemistry (CALPHAD) approach is employed to predict alloy-dependent hot cracking susceptibility so as to establish guidelines for preventing hot cracking and provide insights into alloy design for AM. Microstructural observations are used to determine the accuracy of CALPHAD predictions in terms of elemental segregation, phase formation and hot cracking susceptibility. To this end, scanning transmission electron microscopy is used to evaluate elemental segregation at grain boundaries, while the local distribution of phases and their relative amount is measured by electron backscattered and X-ray diffraction, respectively. Hot cracking susceptibility is experimentally evaluated by measuring the length of cracks (when present) in the cross section of printed specimens.

References:

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Biographical Note

Manuel Sanchez-Poncela holds a degree in industrial engineering from the Polytechnic University of Gijón and Grenoble INP, he is also a material scientist specializing in Large Scale Facilities from the Universities of Munich TUM and LMU, and PhD. by the Polytechnic University of Valencia (UPV). He is experienced in modeling the thermoplastic behaviour of metals (at CEA), and measuring residual stresses by neutron diffraction (at FRM II). Since 2018, he joined ArcelorMittal Global R&D as a Senior Research Engineer. In this role, he led the development of various steel families in Additive Manufacturing, utilizing CALPHAD-based calculations, resulting in multiple patents and articles.

[O06] Development of a novel Monte Carlo Potts model for solid-liquid phase transformations

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Key words: Monte Carlo Potts, solidification, melting

Solidification and melting are the most fundamental but complicated microstructure phenomena. The prediction of such reactions becomes more significant as metal additive manufacturing technology is highlighted.

During the additive manufacturing process, the melt pool forms by melting of powder particles, while the final microstructure is significantly affected by solidification. To reasonably predict and control the microstructure of final products with theoretical approaches, solidification and melting phenomena should be well considered.

Monte Carlo Potts model is a microstructure simulation model known to reasonably describe the grain growth kinetics with low computational cost and simple algorithm [1]. It has been developed for the quantitative prediction of grain growth kinetics with realistic simulation quantities [2].

Monte Carlo Potts model has already been applied to describe solidification in a casting situation by Brown and Spittle [3]. Their study showed the possibility of the Monte Carlo Potts model to describe solidification phenomena, whereas it could not deal with nucleation kinetics and only contains qualitative evaluation of simulation results rather than quantitative comparison with experimental results.

Recently, the present authors have developed a Monte Carlo Potts model for solid-state interfacial reactions accompanying phase transformations [4]. Our previous model can simultaneously consider grain growth and interfacial reactions in a single algorithm, reproducing the growth kinetics of an intermetallic compound layer as well as the microstructure evolution within the growing layer. This model may be able to describe solidification and melting reasonably.

In the present work, a novel Monte Carlo Potts model for melting and solidification was developed. It utilizes fundamental materials properties and employs realistic simulation variables to enable reasonable quantitative predictions. The novel model reproduces melting and solidification phenomena in good agreement with common knowledge and experimental results.

The newly developed Monte Carlo Potts model will be a powerful theoretical approach to predict microstructure evolution with high computational efficiency and reasonable predictive performance.

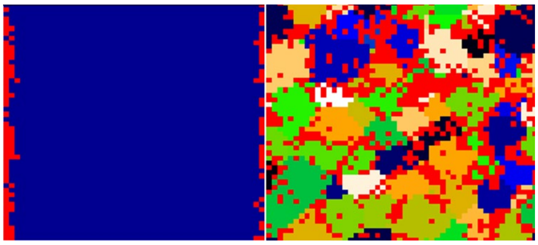

Figure 1. Simulated melting behavior of (left) single crystal and (right) polycrystalline samples

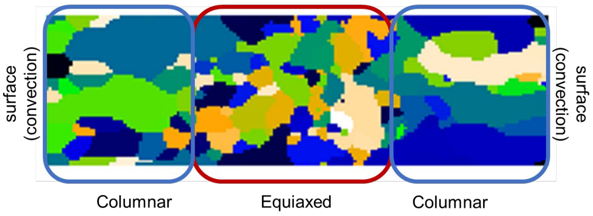

Figure 2. Simulated microstructure of a hypothetical ingot casting sample

References

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Biographical Note

Dr. Sang-Ho Oh is a postdoctoral fellow at Pohang University of Science and Technology (POSTECH), Republic of Korea. His research focuses on computational thermodynamics, solid-state diffusion and relevant phenomena, and microstructure evolution modeling. He experienced atomistic simulations, CALPHAD approach, diffusion simulation, and microstructure evolution simulations with the Monte Carlo Potts model.

[O07] From Data to Knowledge: The Importance of Critical Evaluation in Materials Constitution

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iljenko@msiport.com

Key words: phase equilibria, critical evaluation, reliability, MSI Eureka database

Understanding the stable and metastable phase equilibria in a materials system is fundamental for numerous research challenges and engineering applications. The wealth of phase diagram data accumulated over decades serves as the cornerstone for today's innovative research, validating thermodynamic simulations, guiding experiments, and facilitating alloy development. With thousands of new publications added annually, the need for a reliable evaluation strategy is paramount.

Since 1986, the Materials Science International Team (MSIT®) [1] has developed a critical evaluation procedure [2] to address this need. This approach offers an efficient and trustworthy method to reconcile often-conflicting data on phase diagrams and thermodynamics, providing a comprehensive description of entire material systems. The primary objective of critical evaluations is to present a concise and easily understandable set of self-consistent phase diagrams and thermodynamic properties that represent the current best knowledge of a given system.

The results of the MSIT global Program on critical evaluation of constitutional data of inorganic materials are published in 64 volumes of handbooks and in the materials knowledgebase MSI Eureka [3]. MSI Eureka stands as the most comprehensive source of critically evaluated data on inorganic materials, encompassing over 4700 evaluated binary and ternary systems. Additionally, it includes a number of other data categories, e.g. a vast bibliographic database "Links to Literature" with over 505,000 relevant citations related to ca.79,000 materials systems, providing unparalleled depth for researchers and R&D professionals.

This presentation will spotlight the diverse array of experimental techniques employed for phase equilibria determination. It will delve into the necessity and concept of intellectual critical evaluations, which are vital for navigating the complexities of conflicting individual data. Criteria for evaluating data reliability, correctness, coherence, and interpretation will be elucidated, illustrated through examples drawn from MSIT critical evaluations published in the MSI Eureka database.

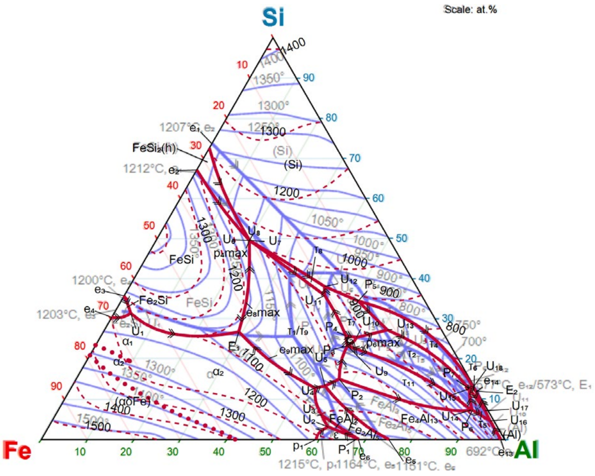

Figure 1. Comparison of evaluated phase diagram with the original literature data – liquidus surface of the Al-Fe-Si system.

References

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[3] https://www.msi-eureka.com

Biographical Note

Dr. Svitlana Iljenko, a materials scientist with over 25 years at German company MSI – Materials Science International Services, specializes in materials constitution. She has edited 27 handbooks on critical evaluations of materials-constitution-data and serves as an ex-officio member of the MSIT Editorial Board for the MSI Eureka knowledgebase.

[O08] Thermodynamic assessment of the systems Mo-Si and Mo-Si-Ti

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Key words: CALPHAD, Mo-Si-Ti system, thermodynamic assessment

Contemporary gas turbine alloys operate at temperatures 90% of their melting point. To improve efficiency, load cycle resistance and meet environmental impact requirements, new materials are needed. Alloys in the Mo-Si-Ti system exhibit excellent mechanical properties at high temperatures and resistance to corrosion and oxidation, making them a promising candidate.

In 2003, Yang et al. created a thermodynamic dataset for this system [1]. Using this dataset, key experiments were planned and conducted to refine the areas of the system most relevant to the research goal. The alloys must exhibit resistance against oxidation and corrosion, as well as sufficient ductility. Materials with a high metal content, limiting the Si content to a maximum of 37.5 at.%, are ideal for gas turbines. Beyond this composition, the (Mo,Si,Ti) solid solution is not in equilibrium, resulting in extremely brittle materials. Since most research on the Mo-Si-Ti system has focused on the disilicides, the metal area remains relatively underexplored.

The alloys analyzed in this study were prepared by vacuum arc melting from high purity raw materials and annealed at 1300 °C for 330 h. After water quenching, they were characterized by scanning electron microscopy, EDX, electron probe microanalysis and X-ray diffraction to compare experimental results with CALPHAD calculations.

Although several regions of the ternary phase diagram were confirmed, other aspects required re-evaluation. The most significant discrepancies between calculations and experiments were found in the binary system Mo-Si. For instance, the solubility of Si in the (Mo,Si,Ti) solid solution is much higher than what the dataset suggests. Furthermore, the Si deficiency of the phase Mo_3Si, which was initially reported by Rosales and Schneibel [2], was confirmed in both the binary and ternary systems. Therefore, it was decided to re-evaluate this binary system, taking into account both our own experimental data and all available literature data. Thus, the dataset could include previously disregarded data, such as the heat capacity of the Mo silicides.

The result is a new data set for the binary system Mo-Si with unprecedented agreement between experimental and calculated values for thermodynamic, thermophysical, and thermochemical data. This includes enthalpies of formation, heat capacities, invariant reactions, and enthalpy of mixing of the liquid phase [3]. The resulting phase diagram is shown in Figure 1.

Based on the new binary description, the ternary dataset for Mo-Si-Ti was updated. Literature data has been evaluated and accepted where reliable experiments exist, and the metal-rich region of the diagram has been optimized based on our own experimental results. The remaining major difference in the ternary system is the solubility of the phases Mo_3Si, Mo_5Si_3, and Ti_5Si_3 for the respective substitutional metal atom. This results in significantly different phase compositions than suggested by the Yang et al. dataset.

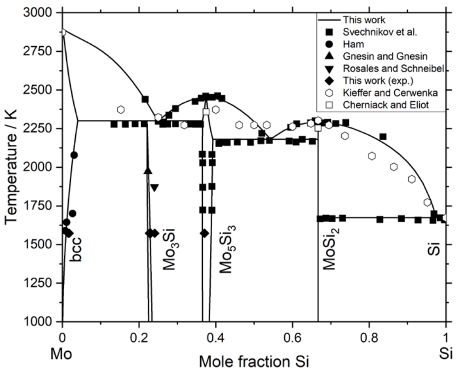

Figure 1. The re-assessed binary system Mo-Si, from [3]

Acknowledgement

We gratefully acknowledge the funding of this work by the German Research Foundation (DFG) as part of the RTG 2561: MATCOM-COMMAT.

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Biographical Note

Andreas Czerny is a Ph.D. student at the Karlsruhe Institute of Technology. He holds a Master of Science in Mechanical Engineering with a specialization in Materials Science from TU Braunschweig. His research interests include materials thermodynamics of high temperature systems.

[O09] Experimental study and thermodynamic assessment of the metal-salt systems

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Key words: metal-salt systems, thermodynamic database

Salt systems are extensively scrutinized as phase change material (PCM) within the domain of concentrated solar power (CSP). Compared with the widely-used nitrate salts, the chloride salts have relatively higher melting temperature [1]. Therefore, they emerge as promising candidates as high-temperature PCM and are supposed to enhance the energy efficiency of thermal energy storage. Nevertheless, the corrosion issue poses a significant constraint on the practical implementation of chloride salt systems as PCM [2]. The incorporation of metal into chloride salt systems is posited to mitigate the corrosion challenges associated with salt systems [3]. Furthermore, it is hypothesized to enhance the thermal conductivity of the salt systems. Unlike mechanical mixing of metals and salts, the formation of a liquid solution between the metal and salt may alter the thermodynamic properties of the salt systems. Investigating how this alteration influences the thermal conductivity of the systems is of particular interest. The development of a thermodynamic database for salt-metal systems is crucial for understanding the solubility of metals in salt systems and identifying potential phase change material (PCM) candidates. Currently, there is a notable absence of comprehensive thermodynamic databases encompassing both salts and metals. This research endeavors to fill this gap by conducting experimental investigations on the metal-salt system (Li- Na-K-Mg-Ca-KCl-NaCl-LiCl-$MgCl_2$-$CaCl_2$). The thermodynamic database for this system is established using the Calphad method with the aid of the FactSage software.

The experimental study and thermodynamic assessment of the system K-Na-KCl-NaCl was done. The systems Na-K, K-KCl and Na-NaCl were assessed based on existing literature data [4]. To study the system K-Na-KCl-NaCl, various compositions within the Na-KCl and K-NaCl systems are subjected to Differential Thermal Analysis (DTA) measurements, and the resultant samples are examined using X-ray Diffractometry (XRD). Crucial to the DTA measurements is the selection of crucibles, as metals are more prone to vaporization and oxidation compared to salt mixtures. Accordingly, closed crucibles are deemed essential to the experimental setup. Moreover, it is imperative to prevent potential reactions between the metal and the crucibles during the experimental procedures. Finally, the system K-Na-KCl-NaCl was assessed based on both the obtained experimental results and relevant literature data. The calculated phase diagram of the system Na-KCl is shown in Fig.1. The Gibbs energy of the liquid phase containing metals and chlorides was optimized using a modified associate species model in order to keep consistency with the salt database.

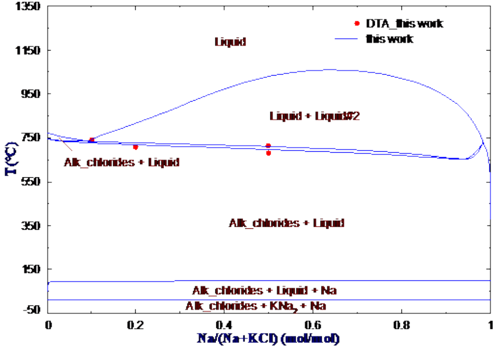

Fig. 1 Calculated phase diagram of the system Na-KCl compared with the experimental data

Acknowledgements: This work is supported by the German Research Foundation within the project "SaltMe" (DFG 497349462).

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Biographical Note

Jia Qi is now a Postdoc at the Institute of Energy and Climate Research, Structure and Function of Materials (IEK-2), Forschungszentrum Jülich, Germany. Her research focuses on the experimental study and thermodynamic assessment of the salt-metal systems (Li- Na-K-Mg-Ca-KCl-NaCl-LiCl-$MgCl_2$-$CaCl_2$).

[O10] A Thermodynamic Assessment of 5 Selected Organic Carbonates and Their Mixtures Used in Lithium Ion Batteries

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Key words: thermodynamics, Li-ion battery, electrolytic solvent, organic carbonates

Lithium-ion rechargeable batteries are widely used as power sources for many devices from portable electronics to electrical vehicles. Ideally, the electrolyte solution in these batteries is just a medium that allows the charge transport of Li-ions between the electrodes, but which itself is not involved in the electrochemical reactions. However, the solvents used here are frequently organic carbonates, the stability of which depends not only on the temperature but also on the oxidation and reduction potentials at the electrodes. In thermodynamics, the stability of these solutions is described by the Gibbs energy functions of the pure substances, as well as their mixing behavior using appropriate interaction parameters. Thermodynamic datasets for calculating the mixing behavior and phase transformations of various organic carbonates have already been published in the literature, e.g. [1, 2]. However, in these evaluations so far the reference to the standard formation reactions from the elements is missing, which is necessary to calculate combustion reactions of carbonates or their decomposition at higher temperatures. Furthermore, the datasets [1, 2] do not include a gas phase which is needed to model evaporation effects at the approach of a thermal runaway.

In the present work, a thermodynamic database for 5 organic carbonates is compiled based on data from the literature. It includes the cyclic compounds ethylene carbonate (EC) and propylene carbonate (PC) as well as the linear carbonates dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC). For all of these substances the solid, liquid and gaseous phases are assessed. The solid phases are all treated as pure substances. In the liquid state, the cyclic compounds (EC+PC) form practically an ideal mixture which is also the case for the 3 binary combinations of the linear carbonates (DMC+DEC, DMC+EMC, DEC+EMC). The 6 binary liquids consisting of a linear and a cyclic carbonate exhibit all positive deviations from Raoult's law. The gas phase is described by an ideal mixture of the 5 substances for temperatures up to 1000 K and pressures slightly above normal pressure. The Gibbs energy functions of all compounds are related to the SGTE data of pure elements (here C, H, and O) by adjusting the standard quantities of formation ($\Delta_f H°$, $\Delta_f S°$) to experimental data.

Acknowledgement

This work was funded by the German Federal Ministry of Education and Research (BMBF), Competence Cluster Battery Utilization Concepts (BattNutzung) under the grant number 03XP0311A.

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Biographical Note

P. Franke is a researcher and lecturer at KIT in the fields of materials thermodynamics and kinetics.

[O11] Miscibility gaps in the Ag-Cu-Se-Te quaternary system

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Key words: Miscibility gap, Ag-Cu-Se-Te

Ag-Cu-Se-Te is an important thermoelectric material quaternary system. Previous studies have revealed the presence of miscibility gaps with significant compositional ranges in both systems. Alloys solidify traversing these liquid miscibility gaps could exhibit distinctive two-region microstructures. These unique microstructures could give rise to distinct properties.

This study examines the miscibility gap in the Ag-Cu-Se-Te quaternary system and its constituent systems, investigating both the boundaries of the miscibility gaps and the microstructures of alloys solidified within these gaps. The evolution of these intriguing microstructures is studied under various holding temperatures and lengths of holding time within the two-liquid-field.

Furthermore, their liquidus projection and miscibility gaps are determined through Calphad-type modeling. The calculated results are then compared with those determined experimentally in this study.

Figure 1 is an optical micrograph of as quenched alloy AS#2 (Ag-20at.%Se). EMPA analysis results indicate these two phase regions are with different compositions, one is close to Ag and the other one is close to Ag_2Se. Similar results are observed for as-quenched alloy CS#2 (Cu-10at.%Se), ACS#23 (Ag-15at.%Cu-25at.%Se), ACT#29 (Ag-10at.%Cu-20at.%Te), and ACTS#20 (Ag-10at%Cu-2at%Te-8at%Se), and are shown in Figures 2-5, respectively.

Figures 6-9 show the liquid miscibility gaps superimposed on the liquidus projection of Ag-Cu-Se, Ag-Cu-Te, Ag-Se-Te and Cu-Se-Te ternary systems, respectively. The preliminary results indicate that miscibility regions exist in Ag-Cu-Se-Te and in all four constituent ternary systems. It is very interesting to explore all compositional regimes and characterize the unique microstructures.

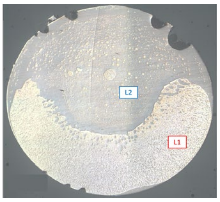

Figure 4: Optical micrograph of ACT#29 (Ag-50at.%Cu-10at.%Se)

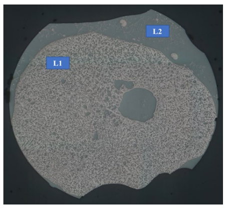

Figure 5: Optical micrograph of ACTS #20 (Ag-10at%Cu-2at%Te-8at%Se)

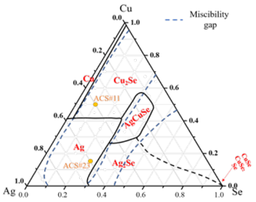

Figure 6: Miscibility gap of Ag-Cu-Se superimposed on its liquidus projection

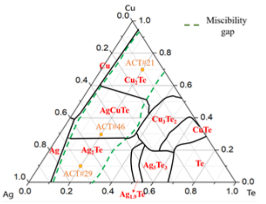

Figure 7: Miscibility gap of Ag-Cu-Te superimposed on its liquidus projection

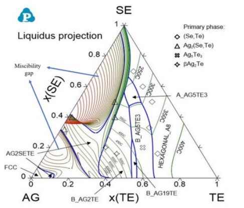

Figure 8: Miscibility gap of Ag-Se-Te superimposed on its liquidus projection

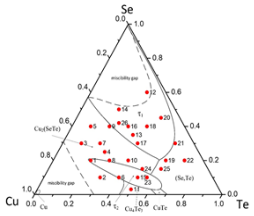

Figure 9: Miscibility gap of Cu-Se-Te superimposed on its liquidus projection

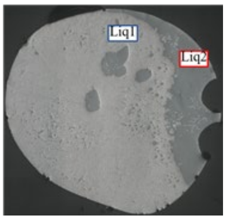

Figure 1: Optical micrograph of alloy AS#2(Ag-20at.%Se).

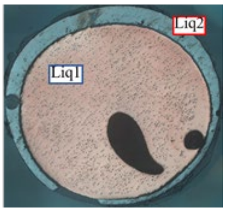

Figure 2: Optical micrograph of alloy CS#2(Cu-10at.%Se).

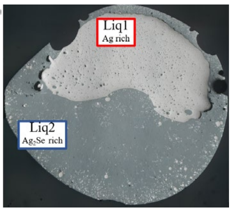

Figure 3: Optical micrograph of ACS#23(Ag-15at.%Cu-25at.%Se)

Biographical Note

Professor Sinn-wen Chen is a Chair Professor. Mr. Y.-J. Chuang and Mr. Y.-C. Tsai are master students. All are in the Department of Chemical Engineering, National Tsing Hua University in Taiwan.

[O12] External magnetic field and Gibbs energy: A novel framework suitable for Calphad

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Key words: thermodynamic modeling, external magnetic field, analytical Gibbs energy function, Bi-Mn example

Applying an external magnetic field can obtain unique microstructure and thus enhanced properties, which are unattainable without such a field. Based on the molecular field theory of Weiss in the mean field approximation using the Heisenberg model, a predictive computational framework for materials under external magnetic field is developed for the first time. Only three magnetic material parameters, atomic magnetic moment ($gJ\mu_B$), total angular momentum (J), and Curie temperature (T_C) are used to generate **explicit** and generic analytical numerical approximants for an additive contribution to functions of Gibbs energy. These developed explicit functions are implemented in **standard TDB** thermodynamic database, opening the door to the quantitative thermodynamic calculations in multicomponent systems under external magnetic field with established Calphad software such as Pandat. It is emphasized that the constructed analytical functions do **not involve any fitting to experimental** phase equilibria or other thermodynamic data.

The approach is demonstrated for the Bi–Mn system, where strong interactions of the compounds with magnetic field are known [1, 2], see Fig. 1.

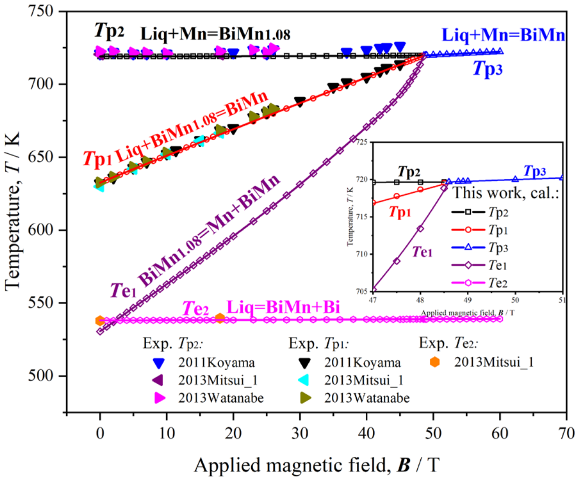

Figure 1. Calculated Bi–Mn univariant reaction temperatures compared with the measured data, $p = 1$ bar.

The four-phase equilibrium existing in this system is proven to be a true peritectic-type formation reaction, Liquid + Mn + BiMn = $BiMn_{1.08}$, at the predicted state point T_4 = 719.6 K, B_4 = 48.56 T, and $\mu_{Mn,\,4}$ = -29.288 kJ/mol-atom, as shown in Fig. 2. It is noted that the projection of the three-phase lines in the 3D space of Fig. 2 onto the T-B plane generates Fig. 1.

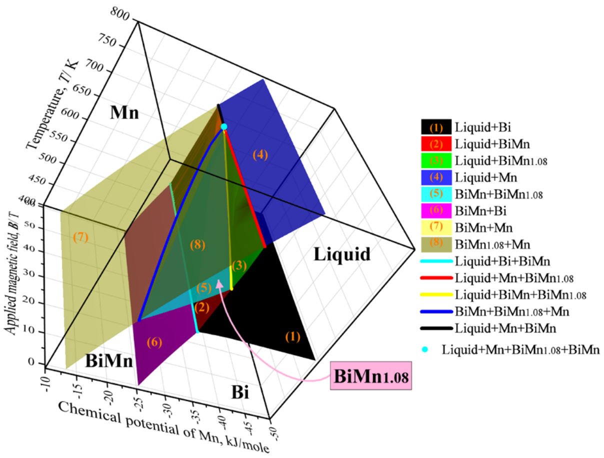

Figure 2. Bi–Mn 3D phase diagram under applied field B in the chemical potential view, state variables T-μ_{Mn}-B.

Manipulation of phase transition and microstructure under external magnetic field guided by thermodynamic considerations is also discussed. The present work provides a fundament for quantitative calculations of phase equilibria and thermodynamics in multicomponent and multiphase systems under external magnetic field.

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Biographical Note

Rainer Schmid-Fetzer is professor emeritus at Clausthal University of Technology. With background in metallurgy and physics he earned merits in thermodynamics, solidification, interface reactions and applications to designing alloys. He is Fellow of ASM International and awardee of both the Hume-Rothery Prize, IOM3, and William Hume-Rothery Award, TMS.

[O13] Revisiting Derivatives at Equilibrium

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Key words: CALPHAD, Equilibrium Calculation, Thermodynamics, Analytic Derivatives

While methods of calculating analytic derivatives of thermodynamic properties at equilibrium with respect to conditions of the equilibrium calculation have been implemented in various computational thermodynamics software packages for decades, the documentation of the mathematical underpinnings of such methods remains sparse. In this work, the mathematical formalism behind the “dot derivative” technique as implemented in Thermo-Calc, OpenCalphad, and PyCalphad is rigorously presented. This procedure is then leveraged to construct general forms of derivatives of the residual driving force, a popular metric for measuring phase stability, with respect to overall system and phase vertex compositions. Applied examples--- calculating heat capacity in the Al-Fe system, thermodynamic factors in the Nb-V-W system, and residual driving force derivatives in the Ni-Ti system--- demonstrate the versatility, accuracy, and extensibility of this method.

As the reframing of residual driving force as a differentiable quantity shows, a thorough understanding of the mathematical theory behind this decades-old technique holds the key for its future extensibility. Looking ahead, derivatives with respect to model parameters would allow for gradient-based optimization approaches, and reapplication of the mathematical arguments presented in this work could lead to the derivation of methods for calculating higher-order derivatives at equilibrium.

Biographical Note
Courtney Kunselman is currently pursuing a PhD in Materials Science and Engineering at Texas A&M University as a SECAF STEM PhD Fellow. Her previous degrees include a Bachelor's in Applied Mathematics from the United States Air Force Academy and a Master's in Materials Science and Engineering from Texas A&M University.

[O14] Entropy-driven synthesis of non-Van-Der-Waals crystals into nanosheets

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Key words: Entropy-driven synthesis, non-Van-Der-Waals crystals, 2D materials, Biaxial Straining

Our study investigates 2D materials in the wake of graphene's breakthrough, with a specific focus on converting 3D crystals of non- van der Waals bonds into 2D nanoplatelets. Recently, our team pioneered methodologies guiding the synthesis of 2D mica nanosheets from 3D mica and magnesium metal, all driven by entropy modeling. These innovative methods encompass disruptive approaches like leveraging hydrogen and liquid Gallium metal embrittlement[1] to disrupt ionic bonds, microwave-assisted liquid phase exfoliation[2], and cation substitutions[3-4] based on the entropy of resilience theory. These entropy-driven strategies effectively surmounted challenges in exfoliating robustly bonded mica. Through this exploration, we've gleaned insights into key mechanisms, notably understanding energy barriers in biaxial straining, providing crucial guidance for refining 2D nanosheet synthesis. Our methodology, integrating first-principles calculations, biaxial straining principles, and precise experimental design, not only advances 2D material synthesis but also significantly contributes to managing liquid phase exfoliation phenomena. Ultimately, these findings pave the way for pioneering approaches in fabricating 2D structures, marking a significant leap in material science applications.

Acknowledgement

This research was supported by the Agency for Science, Technology and Research (A*STAR, Singapore), under AME Individual Research Grant (Award No. A20E7c0108); the Ministry of Education (Singapore), under Tier 2 program (Award No. MOE2018-T2-1-163); the National Research Foundation, Prime Minister's Office (Singapore), under its Marine Science Research and Development program [Award No. MSRDP-P28]; and MOE-T1- program (Award No. SKI 2021_02_15).

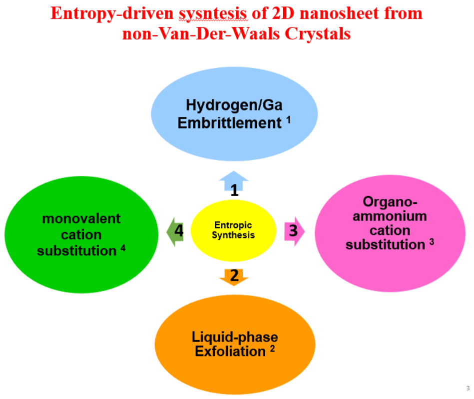

Figure 1. Entropic methods for exfoliating 3D-Mica into 2D nanosheets.

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Biographical Note

Ping Wu, a tenured faculty at Singapore University of Technology and Design, instructs courses in physical chemistry, materials, structures, applied thermodynamics, and advanced functional materials for undergraduates and graduates. His research specializes in thermodynamics theory, materials chemistry, synthesis, and characterization. He's collaborated on bio alloys, antibacterial solutions, and now explores high entropy ceramics.

[O15] 3rd Generation CALPHAD modelling of pure high-melting elements: case study on Mo

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Key words: Thermodynamic modelling, CALPHAD, 3rd Generation, Unary descriptions

Thermodynamic modelling is of abnormous importance in modern materials science, being a fundamental step in innovative materials development. Starting from the early 2000s, 3rd generation CALPHAD modelling has been developed, based on more physically sound thermodynamic descriptions. The stable phases have been described with one unique expression in the full range of temperature by using the Einstein model for the harmonic lattice vibrations, and a polynomial expression for the electronic and anharmonic contributions. Additionally, the entropy difference between stable and metastable allotropes has been used to calculate Einstein temperature of these latter. As for the liquid phase, the two-state model has been used. Despite the publication of many works on 3rd generation descriptions, how to treat solid phases after their melting is still being discussed within the CALPHAD community [1-2]. Another relevant issue consists in the re-stabilization of solid phases well above their melting point, due to the increase as a power of T of their heat capacity at high temperature [3]. One possible solution to this problem is the introduction of a second temperature range in which a polynomial contribution is added to the Gibbs energy of solid phases. Such correction is being discussed, but no fixed criteria has been established yet on how to choose its mathematical expression and the so-called changeover temperature (i.e., the temperature above which the new expression should be introduced). Anyway, it is clear that the same criteria cannot be applied for all the elements, especially if the changeover temperature is scaled to the melting temperature, given the abnormous distance between melting points of different elements. In this presentation, a strategy to develop unary descriptions of high-melting elements will be presented and proposed, using the work on Mo as a case study. After being carefully assessed, published experimental data will be compared to the calculated expressions for Cp and molar enthalpy of BCC-A2 and liquid. Criteria for initial parameters selection and fitting will be presented, also for the metastable allotropes. Moreover, several attempts to select the changeover temperature will be shown, commenting their advantages and limitations, each time calculating and considering the equal entropy temperature (EET). Finally, the overall strategy to obtain unary description of Mo, together with the achieved results will be presented, underlining upsides and disadvantages.

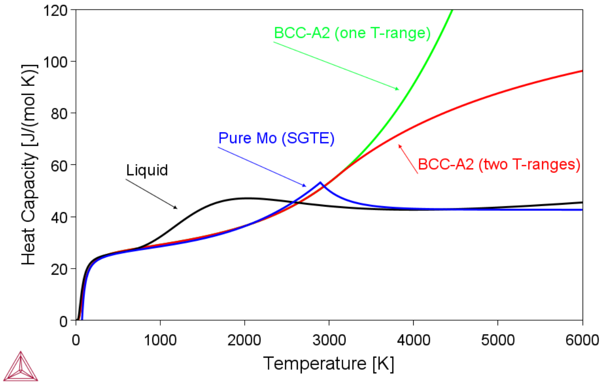

Figure 1. Heat capacity of Mo according to the present 3rd generation description compared with SGTE unary description; the "two T-ranges" trend was corrected for changeover T = Tm + 200K (=3096K), while the "one T-range" trend corresponds to the uncorrected Einstein model.

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Biographical Note

Lorenzo Fenocchio (LF) is a 3rd year PhD student at the University of Genova, Italy. His main interests are thermodynamic modelling of HEAs by CALPHAD approach, database building and alloy design. LF got a master's degree in chemistry in 2021 with a thesis about synthesis and structural/magnetic characterization of rare-earth ternary germanides.

[O16] Thermodynamic assessment of the Al–Ni system using revised 3rd generation unaries, thermal vacancies and 4-sublattice models

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Key words: Einstein Model, Thermal Vacancies, 4-sublattice model, Intermetallics

The increasing demand for materials with exceptional structural and functional properties is driving the ongoing exploration and innovation in various material systems. Hereby, alloy design is relying more and more on advanced simulation methodologies grounded in physical principles to meet these demands. Notable among these are phase-field simulations, density-functional theory, molecular dynamics simulations and CalPhaD calculations.

Hereby, a revolutionary shift is occurring in the CalPhaD approach, integrating new thermodynamic models for increased physical fidelity. These models establish connections with physical-based representations like Einstein functions for the heat capacity, replacing traditional phenomenological polynomials [1]. This ensures a consistent thermodynamic framework for solid and liquid phases in multicomponent systems across a wide temperature range (0 K – 6000 K).

Despite progress in creating new databases for advanced materials, a consensus has not been reached, hindering the 3rd generation of CalPhaD databases to be defined as the modelling approach of the upcoming decades. This study contributes to the solution of this issue by introducing an approach mitigating drawbacks in current models [2]. It reevaluates the thermodynamic description of crystalline solids within the instability range, addressing unreasonably large heat capacities in high-melting solid solutions and intermetallics. Incorporating a meaningful representation of thermal vacancies strengthens these considerations [3,4].

To validate our proposed modelling approach, the Al–Ni system was used as a model system (see Figure 1), which was selected due to its incorporation of two unary components with distinctly disparate melting temperatures and the presence of the high-melting *B*2-ordered intermetallic phase AlNi. The thermodynamic modeling is further reinforced by additional heat-capacity measurements of intermediate intermetallic compounds at both cryogenic and elevated temperatures. Furthermore, *ab initio* calculations for metastable and martensitic phases within this system were incorporated, providing a comprehensive and physically meaningful modelling. Hereby, 4-sublattice models for the BCC- and FCC-based superstructures were applied, to enhance the physical consistency of the resulting thermodynamic database. These efforts will further promote CalPhaD databases to the forefront of materials modelling, representing a significant step towards the generation of holistic and physically meaningful thermodynamic descriptions.

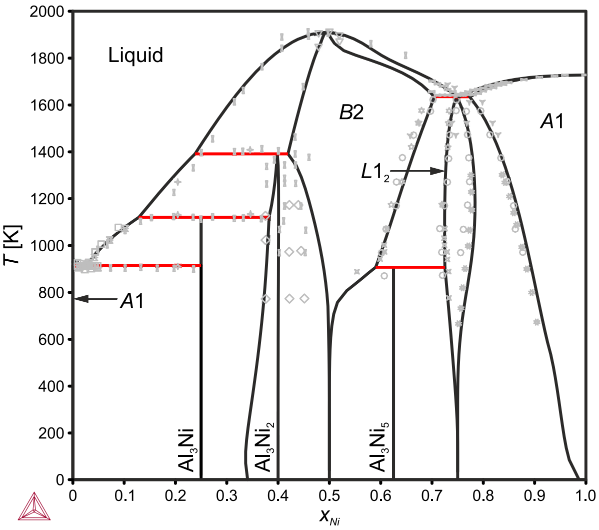

Figure 1. Assessed Al–Ni phase diagram, the gray symbols represent experimental literature data.

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Biographical Note

Alexander Walnsch completed his PhD thesis at the TU Bergakademie Freiberg on the thermodynamic analysis of Fe–Mn–Al–Ni shape-memory alloys in 2021. He is developing new CalPhaD-based modelling approaches for metallic systems, with a particular focus on the aforementioned shape-memory alloys.

[O17] Pandat Software and Its Applications in Materials Design and Process Optimization

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Key words: CALPHAD, ICME, FEM simulation, Microstructure prediction

There is no doubt that the CALPHAD method has become a key component in modern materials design and is playing an essential role in integrated computational materials engineering (ICME). The applications of the CALPHAD method have been extended from its original focus of multi-component phase equilibria to a much wider field of materials science and engineering, including industrial processes.

In this presentation, we will present new features of Pandat software. The modular design allows Pandat to extend its capability simply by adding new modules without the need to change its fundamental structure. Currently, Pandat has six modules for phase diagram and thermodynamic property calculation, parameter optimization, solidification simulation, precipitation and microstructure evolution simulation, diffusion simulation, and phase field modeling. In this presentation, we will use examples (Figures 1 & 2) to demonstrate the applications of Pandat in materials design and process optimization.

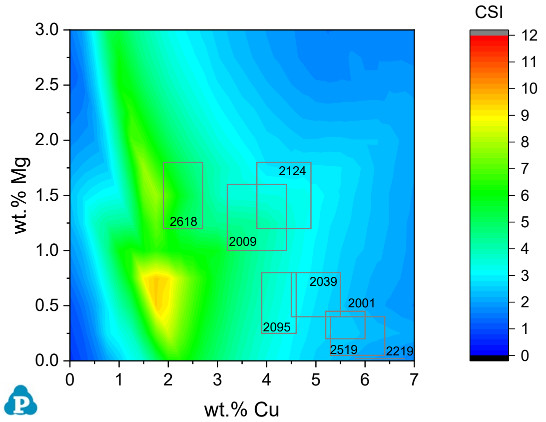

Fig. 1: Calculated cracking susceptibility index (CSI) map for AA2xxx alloys [1].

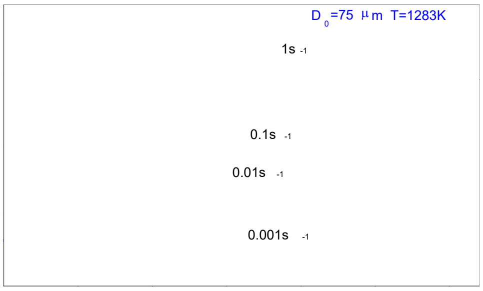

Fig. 2: Calculated strain-stress curve along with the experimental measured data [2].

Most recently, we have developed an integrated platform to couple Pandat software with finite element method (FEM) software packages. This integrated framework makes it possible for microstructure modeling to receive phase related information from thermodynamic calculation engine, while the localized state variables, such as time, temperature, strain and strain rate are obtained from FEM simulations. The platform, therefore, enables us to simulate the microstructure evolution of metallic alloys including recrystallization, grain growth and coarsening during conventional manufacturing processes, such as forging and rolling. Figure 3 shows an example simulation using this platform. In this case, the forging simulation was performed by directly coupling Pandat with FEM software ANSYS [3]. A brief description of this framework with simulated examples will be presented.

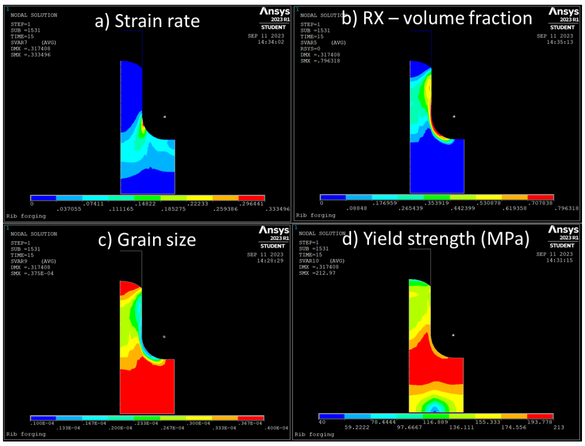

Fig. 3: Forging simulation by coupling ANSYS with Pandat. a) Strain rate, b) Recrystallized grain volume fraction, c) Grain size, d) Yield Strength.

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Biographical Note

Dr. Fan Zhang received her Ph.D. in 1997 from the Department of Materials Science and Engineering, University of Wisconsin at Madison, USA. She joined CompuTherm the same year developing simulation tools using the CALPHAD method. She has become the president of CompuTherm since 2011.

[O18] FactProSim Flowsheet Process Simulation Software

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Key words: Process simulation, Thermodynamics, Kinetics, Digital Twins

Optimization of existing metallurgical processes and development of new processes through experiments and plant trials requires a lot of time and resources, therefore modeling becomes an indispensable tool for achieving these goals. Additionally, process simulation is a powerful tool for modeling the whole life cycle of a process, from initial material insertion to final product output, making the integration of simulation tools necessary. Process Simulation is based on models, and the model should try to replicate the thermochemistry of the process as accurately as required. However, the main drawback of the existing process simulation platforms is the lack of reliable thermodynamic databases. In some cases, the need for expertise in programming make them unsuitable for general users to perform process modeling.

In order to make process calculations without any coding, we have developed a new flowsheet program "FactProSim" for process simulation applications. FactProSim software employs accurate and reliable thermodynamic databases from FactSage Thermochemical Software [1] and Gibbs Energy Minimizer (ChemSage) through ChemApp [2] to perform complex multiphase, multicomponent equilibrium calculations. FactProSim uses an intuitive flowsheet diagram approach to model the process with modules, which interact with each other through the flow of materials.

As shown in Fig. 1, the FactProSim software is designed with a complete graphical interface, allowing the user to interact with modules and the resulting flowsheet with relative ease. Based on our long experience for process simulation calculations [3] for steelmaking processes using FactSage Macro Processing and ChemApp, we found out only 5 modules are sufficient to make most process simulations. 'InputStream' is for defining the starting input materials, 'Stream' is a pack of materials at given temperature and pressure, 'Splitter' is for splitting an input stream into two separate output streams, 'Equilib' perform equilibrium calculation with selected phases at constant temperature and constant enthalpy, and 'Heat exchanger' is simply exchange the enthalpy between two streams or heat loss/gain without change of stream chemistry.

In FactProSim software, modules can be added to the flowsheet by drag-and-drop operation, and modified through their respective windows, which also auto-populates relevant phases as and when needed. FactProSim offers the possibility to enter various inputs in the flowsheet modules (such as material composition, amount and temperature, equilibrium calculation conditions, etc.) through spreadsheets by linking one or several Microsoft Excel spreadsheets to a flowsheet. Furthermore, the output of the simulation is also saved in Microsoft Excel spreadsheets to provide a convenient way to analyze and represent the output data. FactProSim is designed as process agnostic general-purpose process simulation tool.

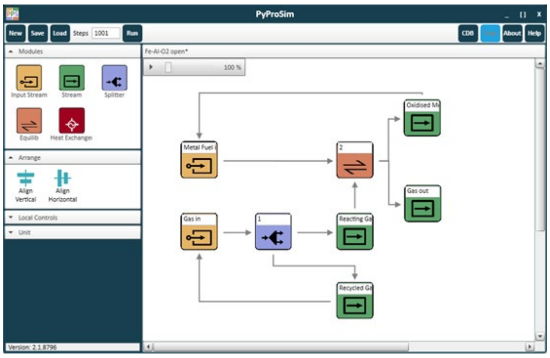

Figure 1. FactProSim software

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Biographical Note

Nishant Kumar, PhD student, Marie-Aline Van Ende, Research Professor, and In-Ho Jung, Professor, are all at the Department of Materials Science and Engineering, Seoul National University. Dr. Van Ende is also a part-time associate professor at TU Eindhoven. Mr. Kumar is working on the iron ore reduction process simulation and FactProSim software development for his PhD study. Dr. Van Ende is an expert in metallurgical process simulations, and Dr. Jung is an expert in thermodynamic database development, materials design and industrial process optimization. Drs. Jung and Van Ende are also co-developers of FactSage software.

[O19] A real scale Monte Carlo Potts model for simulation of microstructural evolution under thermal gradient

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Key words: Real Scale, Monte Carlo, Thermal Gradient, Microstructural Evolution

Prediction of microstructure evolution is important to design structural materials, and grain growth is the most fundamental but important one which determines mechanical properties. Monte Carlo Potts is a widespread simulation model for microstructural evolution with high computational efficiency, but has not been considered suitable for quantitative prediction of practical processes since the physical meaning of variables is not fully understood yet. Efforts have been made to assign realistic physical meaning to simulation variables such as time, temperature, and distance. The existing equation for converting simulation time to real time involves a strong temperature dependence, which causes a problem under non-uniform temperature distribution, as in additive manufacturing. This problem could be solved by assigning a temperature dependence to the simulation result, which was possible by using realistic temperature and energy values. We found that the simulated activation energy for grain growth could be equated to experimental value by adjusting the activation energy for grain boundary migration within a reasonable range in the simulation. The modified Monte Carlo Potts model made the time conversion equation completely temperature-independent and was free from the above-mentioned problem in time conversion. The Monte Carlo Potts simulation can now predict grain growth and microstructural evolution in various materials under various temperature conditions much more reasonably.

The grain growth can be described as follows:

$$\boldsymbol{L(t)^2 - L(0)^2 = K_e t} \qquad [1]$$

where t is the time, $L(t)$ is the grain size as a function of time, and K_e is the temperature-dependent factor for the grain growth. This equation is also valid in the MC Potts simulation.

$$\boldsymbol{L_{MC}(t_{MC})^2 - L_{MC}(0)^2 = K_{MC} t_{MC}} \qquad [2]$$

t_{MC} is the simulation time, $L_{MC}(t_{MC})$ is the grain size in the simulation length unit, and K_{MC} is the grain growth factor in the simulation. The real length and the simulation length can be linked as follows:

$$\boldsymbol{L = \lambda L_{MC}} \qquad [3]$$

where λ is the real distance between grid points in the simulation. Then, the relationship between simulation time and real time can be obtained by equating Eq. [1] and Eq. [2], ignoring the L(0) and $L_{MC}(0)$ terms for simplicity:

$$\boldsymbol{t = \lambda^2 \frac{K_{MC}}{K_e} t_{MC}} \qquad [4]$$

K_e can be determined from experimental data, and its temperature dependence is usually expressed using an Arrhenius-type function:

$$\boldsymbol{K_e = K_e^0 \exp\left(-\frac{Q_e}{RT}\right)} \qquad [5]$$

where K_e^0 is the pre-exponent factor, and Q_e is the activation energy of the grain growth. Then, Eq. [4] changes to:

$$\boldsymbol{t = \lambda^2 \frac{K_{MC}}{K_e^0} \exp\left(\frac{Q_e}{RT}\right) t_{MC}} \qquad [6]$$

K_{MC} should also be a function of temperature. Here, K_e and K_{MC} are quantities having analogy, so K_{MC} can be naturally expected to have an Arrhenius function type temperature dependence like K_e:

$$\boldsymbol{K_{MC} = K_{MC}^0 \exp\left(-\frac{Q_{MC}}{RT}\right)} \qquad [7]$$

where K^0_{MC} is the pre-exponent factor, and Q_{MC} is the activation energy of grain growth obtained from the simulation results. Taking Eq. [7] into Eq. [6] leads to:

$$t = \lambda^2 \frac{K_{MC}^0}{K_e^0} \exp\left(-\frac{Q_{MC} - Q_e}{RT}\right) t_{MC} \qquad [8]$$

With a Q (activation energy for grain boundary migration) value that makes Q_{MC} equal to Q_e, the real time conversion becomes temperature-independent, as follows:

$$t = \left[\lambda^2 \frac{K_{MC}^0}{K_e^0}\right] t_{MC} \qquad [9]$$

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Biographical Note

Byeong-Joo Lee is a professor at the department of materials science and engineering, Pohang university of science and technology (POSTECH), Korea. He developed TCFE2000, a seed version of TCFE thermodynamic database series and the 2NN MEAM (second nearest neighbor MEAM) interatomic potential formalism.

[O20] Design of γ'-strengthened superalloys for additive manufacturing through CALPHAD-based ICME modeling

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Key words: Superalloy design, Additive manufacturing, CALPHAD-based ICME modeling

The global energy demand has driven the development of more efficient and ecological power plants. An impactful way to improve thermal efficiency and reduce plant pollution is to increase the operating temperature and pressure of industrial gas turbines used for power generation. However, the turbine operating conditions are limited by the mechanical properties of key structural components, promoting the design of high-temperature materials.

Ni-based superalloys are widely used in power systems due to their excellent strength and environmental resistance at high temperatures. The operating temperature and strength of γ'-reinforced superalloys increase with the solvus temperature and fraction of γ', respectively. However, alloys with more than 40% γ', such as Inconel 738, are prone to strain-age cracking [1]. Furthermore, the amount of γ'-stabilizing alloying elements (Al, Ti, W, and Ta), and trace elements (Si, B, and Zr) could increase the risk of solidification cracking [2]. Therefore, it is imperative to optimize the chemical composition to achieve the best strength and avoid structural defects simultaneously.

In this study, an ICME (Integrated computational materials engineering) framework is developed to explore the composition space delimited by the commercial alloys: Inconel 738, Haynes 282, and SS316L, identifying potential superalloys for additive manufacturing (AM). High-throughput CALPHAD (calculation of phase diagrams) calculations and physics-based models have been combined to elucidate the effect of chemical composition on phase stability, Solidification Cracking Susceptibility (SCS), and Strain-Age Cracking (SAC). The simulation results were experimentally validated, and the optimized composition was used to print samples using Laser Powder Bed Fusion, characterizing the strength of the new PMMD alloy.

The CALPHAD-based ICME framework proposed in this work guides the computational design of superalloys with higher strength than Haynes 282 and better printability than Inconel 738 as a new high-temperature structural alloy candidate operating at temperatures above 1000°C.

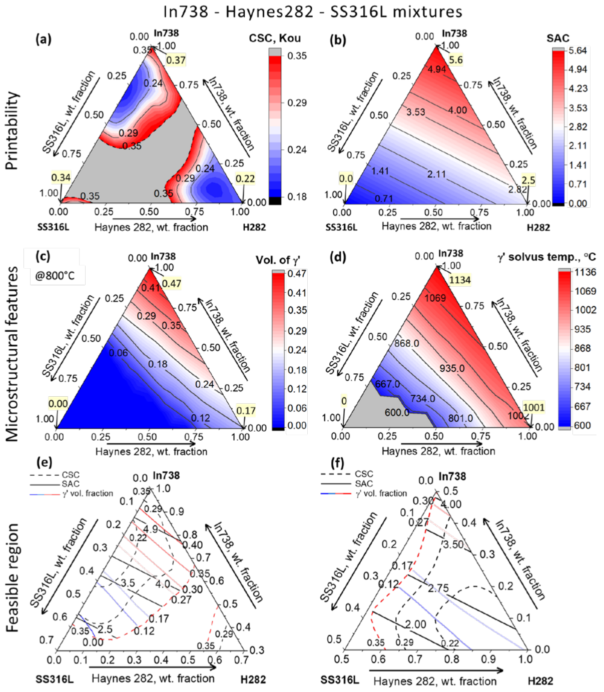

Figure 1. Design of γ'-strengthened superalloys. (a) Solidification cracking susceptibility, (b) Strain-age cracking, (c) volume fraction of γ', (d) solvus temperature of γ', and (e, f) overlaid contour plots.

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Biographical Note

Luis Ladinos-Pizano is a current Ph.D. student in the Department of Materials Science and Engineering at the University of Pittsburgh under the supervision of Prof. Wei Xiong. He specializes in the computational design of new alloys and post-heat treatment optimization, utilizing high-throughput experiments to support his research.

[O21] Optimization of Gibbs Energy of Deeply Undercooled Oxide Melts for Modelling of Crystallization Phenomena in Glasses

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Key words: crystallization, glass-forming liquids, undercooled oxide melts, associate species model

Crystallization of a glass-forming melt is a two-step transformation process, which proceeds via nucleation and subsequent crystal growth and can be controlled by heating from the glass state, especially in the production of glass ceramics, or can occur uncontrollably when cooling from the liquidus temperature, leading to glass defects. The theoretical and experimental analysis of crystallization mechanisms and thermodynamics is therefore essential for combating undesirable devitrification processes and for the development of new glasses and glass-ceramic materials [1].

In general, crystallization is a two-stage process described by nucleation and crystal growth. Both stages are driven by the increasing gain in Gibbs energy between the crystalline and liquid states with increasing undercooling from the liquidus and are thus worthwhile to be addressed by theoretical approaches such as those provided by CALPHAD (calculation of phase diagrams). Among various types of thermodynamical models of glasses, the associate species model [2, 3] can be conveniently used to derive the Gibbs energy of oxide melts. This model is rather simple due to the lower number of involved parameters as compared to e.g., the quasichemical model, and can be easily extended to multicomponent systems from corresponding binary subsystems. However, it is assumed that the specific heats of the liquid species at temperatures below the melting point, i.e., of supercooled liquids, are equal to those of the corresponding solid species [4]. Since this approximation is not strictly true, deviations of the calculated thermodynamic functions can occur in deeply undercooled liquids, i.e., well below the liquidus and shortly above the glass transition temperature. This is unfortunate, since crystallization events, especially nucleation occur at deep undercooling. Additionally, technological relevant processes, such as glass shaping processes, are performed under these conditions. Accurate expressions for the Gibbs energy of supercooled liquids covering a wide temperature range are thus essential for the correct thermodynamic description of glass melts within the technological relevant temperature range and the modeling of crystallization processes.

Here, an approach, based on optimized parameters of the supercooled liquid for the calculation of the Gibbs energy difference between liquid and crystalline state is proposed and tested for the modelling of crystallization phenomena in binary glass-forming systems. In future research, the same approach will be applied to predict crystallization behavior of multicomponent oxide melts more accurately. Thus, reducing the experimental workload required for the development of novel glasses and glass-ceramics is hoped for.

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Biographical Note

Lucas Ueberricke obtained his PhD with summa cum laude from Heidelberg University (Germany) in the field of crystal engineering in 2021. After postdoctoral research at Kyoto University (Japan) on perovskite solar cells he joined NEG (Japan) in 2022, where he is currently investigating crystallization phenomena in glasses.

[O22] Influence of alloying elements on cementite formation on Fe-X (X = Si, Mo, V) alloys during carburization under metal dusting conditions

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Key words: DICTRA, Phase Transformations, Local Equilibrium, Carburization

Metal dusting is a severe high temperature corrosion process under high carburizing atmospheres with carbon activities $a_C > 1$. Cementite (Fe_3C) formation is an important prerequisite for the initiation of the metal dusting process on iron. The question how this process can be retarded by alloying additions implicitly raises the question about the effect of alloying elements on the kinetics of cementite formation.

In this work the numerical treatment of this process is performed using the software module DICTRA (DIffusion-Controlled TRAnsformations) under the assumption of local equilibrium at the moving cementite/ferrite phase interface. The implementation of carbon mobilities in Fe_3C according to experimental results [1] has recently been performed by Xing [2].

The simulations of $(Fe,X)_3C$ layer formation on α-Fe-X are performed under conditions according to an experimental study on carburization of Fe–X (X = Si, Mo, V) diffusion couples [3]. In this study the diffusion couples were exposed to a CO-H_2-H_2O-H_2S gas mixture at 700 °C with a high carbon activity $a_C = 100$. It was found that cementite forms a well-defined surface layer up to a certain alloy composition limit. Beyond that limit the layer was found extremely thin. This observation was assumed to be attributed to a change from a fast reaction according to local equilibrium without alloying element partitioning to a slow reaction with partitioning [3].

The present study focuses on that question of the influence of the alloying elements and their concentrations on the kinetics of cementite layer formation. The respective DICTRA simulations are performed using a planar geometry with a ferrite matrix and a very thin cementite nucleus layer. Boundary conditions are set with a carbon activity $a_C = 100$, with reference to graphite and zero flux of other alloying elements. This is the driving force for carbon transfer across the surface into the cementite and the respective carbon flux through cementite. Such simulations are performed for Fe-X alloys with various X = Si, Mo, V compositions according to [3].

Cementite dissolves both elements, Mo and V. Consequently, a rapid growth of cementite without or negligible partitioning of the alloying elements according to the local-equilibrium negligible partitioning (LENP) could generally be possible. The performed DICTRA simulations show a fast growth kinetic with a certain partitioning after 10 hours of the reaction. For instance, a Fe-2.5at.%Mo alloy shows a Mo content in cementite of around 1.9 at.%, whereas a Fe-6at.%V alloy shows cementite with around 5 at.% V after 10 hours carburization.

It is generally assumed that cementite does not dissolve Si. Thus, the applied thermodynamic database TCFE13 treats cementite as a phase with almost no Si. According to this, cementite growth is expected to be strongly retarded. The respective simulations show in fact a reduced cementite growth rate. Silicon is pushed ahead in front of the moving phase interface and is thus significantly enriched in ferrite at this interface after 10 hours of carburization reaction.

The simulations are compared to the experimental findings in [3] and the growth regimes are discussed by taking into account calculated ternary isothermal sections of Fe-C-X (X = Si, Mo, V) at 700 °C.

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Biographical Note

Andre Schneider is Application Specialist at Thermo-Calc Software AB. He is a physicist and performed the studies for his Doctorate (1998) at Max-Planck-Institut für Eisenforschung (MPIE). Later he was group leader at MPIE, Academic visitor at Oxford University, and had several R&D-related positions in the steel industry. Andre is also lecturer at RWTH Aachen University.

[O23] Experimental and thermodynamic evaluation of the Fe-Si system and application to the processing of silicon steels

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Key words: silicon steel, DSC, HT-LSCM, steelmaking

Silicon steels, also known as electrical steels, are critical to the global energy transition due to their unique magnetic properties, which are enhanced by the addition of up to 6.5% by weight of Si [1] to the steel matrix. This strategic addition increases magnetic permeability and reduces core losses, making Si steels indispensable for efficient energy conversion and transmission. However, the production of Si steels presents steel manufacturers with difficult tasks. During refining treatment, Si is usually added to the melt via ferroalloys, which contain around 75 percent Si by weight. Alloying leads to a considerable increase in the steel bath temperature in the ladle due to the heat of solution of the FeSi alloys, which can only be eliminated with increased effort up to continuous casting. During casting, the exact prediction of the liquidus temperature of high-alloy Si steels is a key parameter for saving large amounts of energy by precisely adjusting the superheat. For both secondary metallurgy and the casting process, the binary Fe-Si system provides the basis for thermodynamic data for process modeling.

The aim of the present study is to obtain new experimental data on high-temperature phase equilibria using DSC and HT-LSCM. The focus is on the melting equilibrium and solid-state transformations at typical Si contents of electrical steels and higher. Based on the new findings, the thermodynamic system is re-evaluated over the entire alloy range, whereby the modeling of the individual solution phases is partly adopted from the literature [2-4]. The MQM is used to formulate the liquid's Gibbs energy and the CEF is applied to describe the significant solubility of Si in ferrite and austenite as well as of Fe in solid Si. The order contribution of the bcc_B2 structure is adopted from Ohnuma et al. [2]. The CEF is also applied to intermediate silicides (Fe_2Si, FeSi and β-$FeSi_2$) [4]. Other silicides with a specific chemical composition are treated as stoichiometric.

Finally, the thermodynamic description of the Fe-Si system is used to calculate the solidification of steels with a high Si content and to approximate a heat balance for ladle refinement of Si steels by adding ferroalloys. Therefore, the actual phase distribution in FeSi65 (Fe with 65 wt.% Si) and FeSi75 (Fe with 75 wt.% Si) is determined experimentally using the X-ray diffraction method (XRD) to calculate the ladle heating as practically as possible. The calculations are critically compared with extensive statistical analysis of the production data of Si-steels produced at voestalpine Stahl Linz GmbH. The predicted temperature increase of the ladle temperature increase is in very reasonable agreement with the results of applying statistical learning methods.

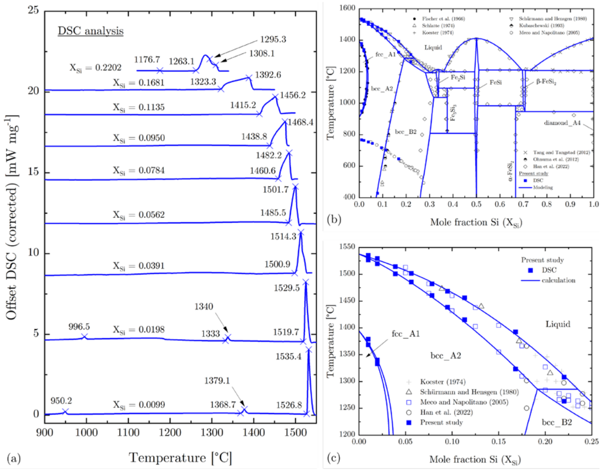

Figure 1. DSC analysis and reassessed Fe-Si phase diagram

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Biographical Note

Michael Bernhard is a senior scientist at the Chair of Ferrous Metallurgy at Montanuniversitaet Leoben. His main research interests are metallurgical thermodynamics applied to steelmaking and casting processes. His activities include thermodynamic-kinetic modeling of ladle refining, solidification simulation and high-temperature experiments for phase transformation analysis.

[O24] Microstructural investigation of the undercooled austenite in the Fe-C

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Key words: Fe-C, bainite, phase transformation, austenite

While the Fe-C system is of fundamental importance for steel, there are still some debates on the microstructure of the metastable undercooled austenite, in particular the mechanism of bainite formation. The debate arises from the fact that there are hardly any experimental results in the Fe-C system and the few present in the literature are subject to controversial interpretation. From the modeling viewpoint, extrapolations from higher-order systems to Fe-C have shown their limitation [1] in the calculation of the bainite start temperature. Recently, we have proposed to calculate it by additionally accounting for the change of crystal structure from FCC-austenite to distorted tetragonal structure [2], with excess Carbon being trapped in the interstitial site of *bcc*-ferrite, in agreement with experimental findings and previous, alternative modeling approaches [3].

In the present work, we aim to close an experimental gap of data on the bainite start temperature. We investigate Fe-C samples with four different low-C content from 0.11 to 0.4 wt.% under different thermal treatments. The samples were investigated by a combination of light-microscopy, EBSD, and XRD measurements to determine the microstructural changes with varied C-content. Additionally, phase transitions were evaluated by change of length by dilatometry and DSC measurements.

Combining theoretical calculations and experimental data, in this discussion, we will bring new justification and highlight the phase transformation of undercooled austenite to bainite in the Fe-C system.

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Biographical Note

Dr. Aurélie Jacob obtained her PhD in the development of thermodynamic database for high Cr ferritic steel in Germany after she finished her studies in chemistry in France. Since 2016 she is project assistant at TU Wien. Her research topic is focusing on the thermodynamic modeling for technological applications where Calphad is used in the kinetic simulation for the prediction of precipitation.

[O25] CALPHAD-assisted design of ultrahigh-strength TRIP-aided autosteel plate

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Key words: Retained austenite, Intercritical annealing, TRIP steel, CALPHAD

To meet the challenges of global warming, fossil fuel depletion and the surge in the number of cars, advanced high-strength steels with good combination of specific strength and ductility are required to achieve weight reduction and enhance crash safety. However, the increase of strength usually leads to the decrease of ductility. Great efforts have been made to break the strength-ductility trade-off of high-strength steels by introducing a certain amount of retained austenite (RA). TRIP-aided steels with RA have been of interest to many researchers because of their outstanding mechanical performance. The traditional TRIP steel can usually obtain tensile strength in the range of 700–900 MPa with elongation in the range of 15–35% [1].

To further enhance the mechanical properties, different strengthening strategies have been adopted for TRIP steel, such as adding Mn. The addition of 4~8 wt.% Mn increases the stability of RA and improves the TRIP effect of steel. Some Mn-TRIP steels can achieve tensile strength of 1000 MPa or more and elongation of 25–40% [2]. Unfortunately, limitations related to production cost and preparation difficulty of steel hinder the further industrial application of medium/high-Mn TRIP steels for automobile structural components. Therefore, developing low-C low-alloy TRIP steel with excellent mechanical properties and low production cost can further promote the industrial application of conventional TRIP-aided steels for automobile structural components.

In this work, a novel low-carbon (C) low-alloy transformation-induced plasticity (TRIP) steel with a nominal composition of Fe-0.3C-1.9Mn-1.0Si-0.7Al wt.% was successfully designed by combining high-throughput thermodynamic and kinetic calculations based on CALPHAD methodology. The feature parameters (i.e. AC, AF, MD, and CC) affecting the strength-plastic balance of TRIP steel were first proposed and then calculated using Thermo-Calc software and its DICTRA module with TCFE10 thermodynamic database and MOBFE5 kinetic database [3]. The design flow chart of developing low alloy TRIP steel is shown in Figure 1. According to the calculation results, the alloy components that may have excellent properties were selected for preparation, and their mechanical properties and microstructure were tested. The designed TRIP steel was subjected to a series of two-stage heat treatments according to the target intercritical annealing temperature determined by estimation in an attempt to optimize phase constituents to obtain an ideal strength-plasticity balance. After annealing at 780 °C, the ultimate tensile strength (UTS), total elongation (TEL) and the product of strength and elongation (PSE) of the experimental steel can reach ~980 MPa, ~30% and ~30 GPa·% respectively, because of the appropriate phase fraction and size of RA.

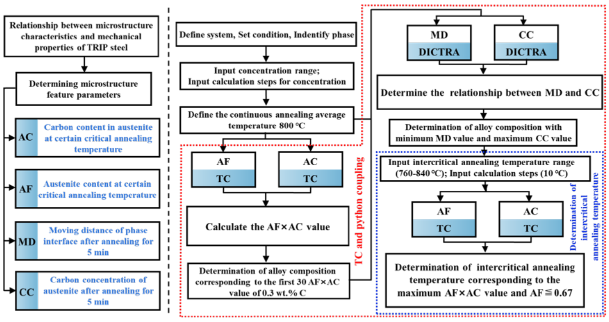

Figure 1. Design flow chart of low alloy TRIP steel.

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Biographical Note

Weisen Zheng currently works as an associated professor at Shanghai University. His research focuses on thermodynamic and kinetic modelling of metallic systems using both computational and experimental techniques, and their application in materials design.

[O26] Modelisation of carbides precipitation sequences during tempering in model Fe-C-Mo-Mn-Ni ferritic alloys

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Key words: precipitation, carbides, diffusion, Prisma

Large components of the primary circuit of nuclear reactors, made with 16MND5 low alloy bainitic steels, operate at 300°C under a pressure of 155 bars, undergoing thermal aging and irradiation, and must retain their mechanical properties throughout the plant life. A thorough understanding of the links between microstructure and mechanical properties is crucial to predict their evolution under operating conditions.

Carbides are known to play an important role in explaining the mechanical properties of the steels. Their population, size and distribution, evolve mainly during temper heat treatments performed after a step of austenitisation and quenching. However, after quenching, chemical heterogeneities can appear, locally affecting the microstructure, the carbide population, hence the mechanical properties.

A previous work has been dedicated to the understanding of the impact of alloying elements on carbide populations [1]. Within this work, the carbides precipitation sequences have been modelled using the Prisma module from the Thermocalc suite (Fig.1).

In the present work, three new model ferritic alloys are being studied: Fe-Xwt.%C-0.5wt.%Mo-1.3wt%.Mn-0.7wt.%Ni with X varying between 0.2 et 0.4wt%. Prisma modelling has been performed in order to determine the carbides precipitation sequences and the influence of carbon variation on them.

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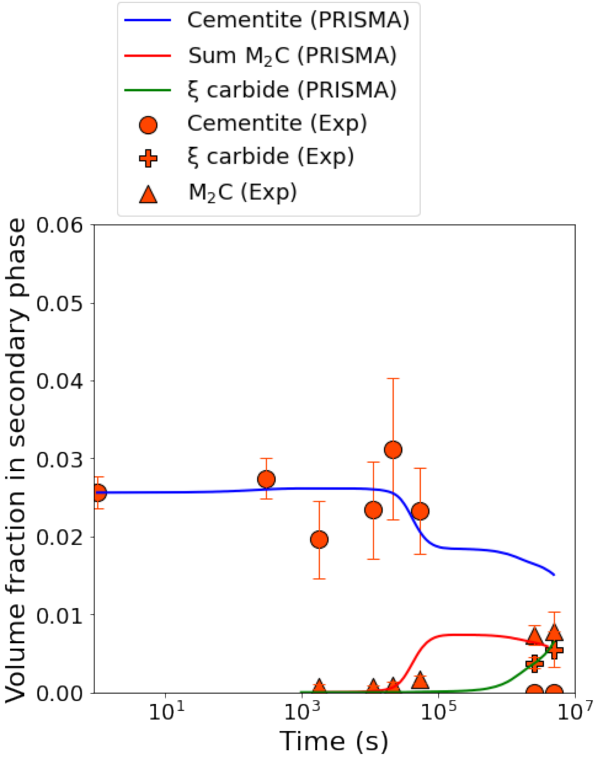

Figure 1. Variation of carbides volume fractions as a function time during tempering at 650°C: comparison between experiments and modelling from [1].

Biographical Note

C. Toffolon-Masclet is senior researcher at CEA-Paris-Saclay University, France, specialized in phase transformations, thermodynamic and kinetic studies in industrial steels and zirconium alloys used in nuclear plants

[O27] Thermal Characterization of Compositionally Complex Fe-based Alloys

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Key words: Fe-based alloys, thermal characterization, microstructure characterization

In this work the solid-state phase transformations in multicomponent and multiphase Fe-based alloys are investigated experimentally. A focus is the martensitic transformation of the fcc matrix.

Fe-based alloys with B, V, C, Cr, Mo, Mn, Ni and Si were melted in an induction levitation furnace equipped with a cold wall crucible. 5N Ar was used as protective gas. The use of a levitation furnace enables a contactless processing of the melt and continuous mixing [1]. The compositions of the produced alloys were checked using Glow Discharge Optical Emission Spectroscopy (GDOES). GDOES is sensitive to light elements and analyzing an area of several millimeters leads to a better statistical evaluation of the total composition.

Optical microscopy and scanning electron microscopy were carried out afterwards to analyze the microstructure (figure 1). The produced alloys tend to form numerous precipitations, including carbides and borides (see fig. 1). For phase identification in these complex microstructures X-ray diffraction was also used.

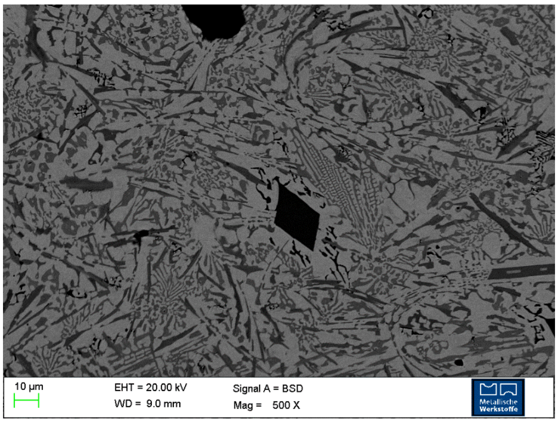

Figure 1. Microstructure of a Fe-alloy containing Cr- V-Ni-B-Si-C with precipitates e.g. VC or Cr_2B.

For investigating the transformation mechanism depending on cooling rate, quenching calorimetry is used. To set suitable conditions, equilibrium transformation temperatures were determined by Differential Scanning Calorimetry. The experimental values are found to be close to predicted values using Factsage and the FSstel database. During slow cooling the fcc lattice matrix the equilibrium transition to bcc is observed. At higher cooling rate (here 20 K/s) the austenite/ferrite-transition is suppressed, and martensite forms e.g. at 250.7 °C.

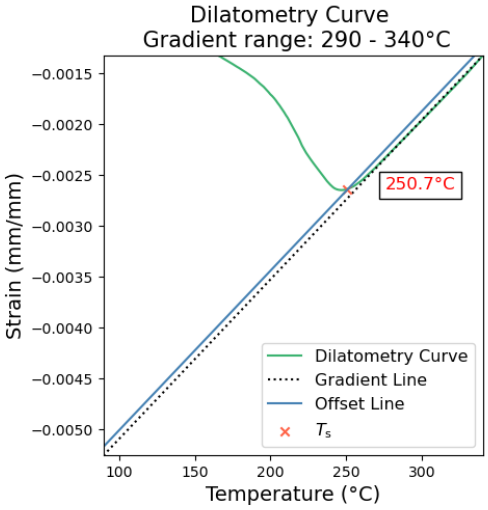

Figure 2. Measured martensite start temperature (T_s) of the alloy shown in fig. 1 after austenitization at (0,95 x solidus temperature) for 5 min. The data were analyzed based on open-source software [2].

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Biographical Note

Johann Möbius studied materials science at the Friedrich Schiller University Jena between 2016 and 2022 and is now a doctoral candidate in the working group of metallic materials. His research focusses on thermodynamics and phase transformation in high entropy alloys and diffusion couples.

[O28] Machine Learning and ChatGPT Integration for the Third Generation of 0 Kelvin CALPHAD Databases

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Key words: third generation CALPHAD databases, machine learning, ChatGPT

Recently, one of the most challenging tasks in the CALPHAD community has been the development of the third generation of CALPHAD databases and their application to the re-assessment of binary, ternary and higher order systems down to 0K [1, 2]. This development process requires a comprehensive approach that not only incorporates the latest available DFT and experimental data to construct a new database for pure elements from 0 Kelvin, but also integrates existing physical laws and recently identified relationships between critical thermodynamic properties. Classical methods for re-evaluating complex thermodynamic systems are known to be very time consuming, thus the need for a solution that synergizes machine learning (ML) techniques with traditional CALPHAD evaluations [3, 4]. This approach demonstrates the successful implementation of ML methods to accelerate the development of the third generation CALPHAD databases. In addition, the study integrates ChatGPT to automate various processes, including the re-evaluation of pure elements from 0 Kelvin, the generation of scientific reports, and analytical tasks, thereby increasing efficiency and simplifying the creation and direct integration of .TDB files for the re-evaluated pure elements into the workflow. This dual application of ML and ChatGPT is expected to significantly accelerate and streamline the database development process, providing a more effective and time-efficient approach to thermodynamic system evaluation and database expansion.

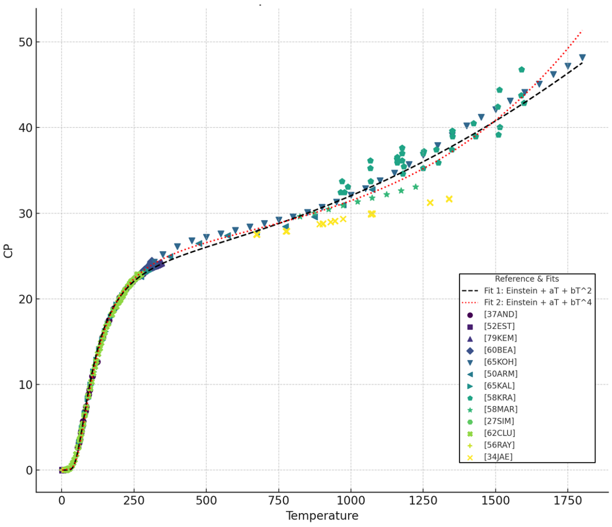

Figure 1. Experimental data of heat capacity of pure Cr in comparison to two fitted models from 0 Kelvin using ChatGPT.

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Biographical Note

Dr. Irina Roslyakova is a postdoctoral researcher at the Department of Materials Discovery and Interfaces, Ruhr-University Bochum. Her research focuses on the development and application of data-driven methods (statistics, machine learning and deep learning) for the modeling of heterogeneous material properties and the design of novel materials.

[O29] AlloyNet – Predicting Alloy Properties by ANNs

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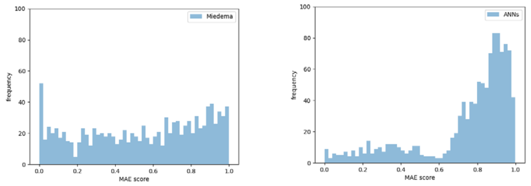
Keywords: alloy property, enthalpy of mixing, formation energy, artificial neural network

The CALPHAD (Calculation of Phase Diagrams) methodology [1] has revolutionized the calculation of multicomponent alloy properties, such as Gibbs energy, atomic mobility, molar volume, surface tension, viscosity, thermal conductivity, electric resistivity, elastic constants, etc., by employing computational thermodynamics tools and databases. This approach, grounded in both data-driven and physics-guided principles, relies on establishing properties of pure elements before modeling binary and ternary interactions through parameters fitted to all relevant experimental data. However, the accuracy of CALPHAD models and databases is contingent upon the availability and quality of these data. With the decline in experimental research funding, there is an increasing reliance on semi-empirical models and theoretical DFT calculations, which, despite their utility, face challenges in accuracy and cost.

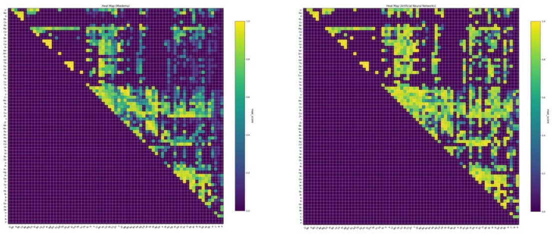
In response, Thermo-Calc Software introduced AlloyNet, a cutting-edge ensemble of artificial neural networks (ANNs) [2] designed to predict alloy mixing and formation properties with substantially enhanced accuracy for CALPHAD database development. Our present work primarily aims to improve the prediction accuracy of liquid alloy mixing enthalpy—a critical factor for Gibbs energy function modeling, phase diagram calculations, and solidification simulations. Despite the longstanding use of the semi-empirical Miedema model [3], its limitations in accuracy have necessitated the development of more reliable methods.

AlloyNet, leveraging elemental properties data from the Magpie Python module [4] with feature engineering and selection, has identified nine elemental properties and several compound features significantly impacting mixing enthalpy. Through comprehensive analysis of 1098 binary systems collected from our various thermodynamic databases and prudent assumption of data-reliability criteria, our approach distinguished "top" 220 binary systems for initial model development, eventually expanding to 875 systems (80% of the total analyzed) via iterative refinements. The culmination of this research is an ensemble of 100 ANN models, achieving an R^2 score of 0.96. Figures 1 and 2 illustrate that the performance of AlloyNet surpasses the Miedema model in predicting liquid alloy mixing enthalpy within a 71-element framework, demonstrating AlloyNet's superior generalizability and accuracy.



(a) (b)

Figure 1. Histogram of MAE scores of (a) Miedema model and (b) AlloyNet on liquid alloy mixing enthalpy.



(a) (b)

Figure 2. Heat map of MAE scores of (a) Miedema model and (b) AlloyNet on liquid alloy mixing enthalpy.

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Biographical Note

Prof. Qing Chen is the Chief Scientific Officer and Director of Research and Innovation at Thermo-Calc Software AB. His research interests include modeling phase diagrams, phase transformations, and phase properties based on CALPHAD methodology with data augmentation from DFT and ML.

[O30] Modeling of Particle Dissolution during Spent Automotive Catalyst Recycling: Overcoming Driving Force Limitations

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Key words: Phase-Field Modeling, Diffusion, Large Driving Forces, Stoichiometric Compounds, Oxide Systems

The recycling of Spent Automotive Catalysts (SACs) is essential from both ecological and economic perspectives, as they are the main source of the valuable Platinum Group Metals (PGMs). These metals, present as nanoparticles in SACs, are dispersed in a γ-Al_2O_3 washcoat layer and mounted on a cordierite substrate. They are most commonly recycled through pyrometallurgical smelting, a complex process that involves melting ground SACs (Fig. 1a) with a flux, collector metal (CM), and reducing agent. This forms a slag through which dispersed CM droplets must collect the PGMs from the Al_2O_3 carrier. One of the factors responsible for the catalytic performance loss is the encapsulation of the PGMs by the Al_2O_3 carrier, making the dissolution behaviour of both Al_2O_3 in the slag and PGMs mounted on Al_2O_3 in the CM essential to understanding PGM collection in the smelting process.

The phase-field method is the preferred numerical method for investigating diffusion and material interactions in this multi-phase multi-component system, but faces challenges when modeling stoichiometric compounds and simulating processes on experimentally relevant length scales. Stoichiometric compounds pose problems for classical phase-field models as they rely on calculating the derivative of the Gibbs energy of all phases to the composition of all elements present in the system. Since these compounds have a fixed composition, their Gibbs energy is composition independent. This problem has typically been avoided by approximating these compounds as steep parabolic functions of the composition [1], but this approach has several drawbacks. Miura [2, 3] proposed an alternative formulation of the phase-field evolution equations based on the composition independence of the Gibbs energy of stoichiometric compounds. In our current work, we extend Miura's formulation to the multi-phase phase-field framework.

The problems of upscaling the spatial resolution in phase-field simulations were first reported by Feyen et al. [4]. They presented a new multi-order parameter phase-field model for pure metals that extends the applicability range to higher length scales by stabilizing the interface through decoupling of the interfacial stability and mean curvature flow. In our work, we extend this high driving force model to diffusion controlled simulations and redefine the thermodynamic stability limit of the simulations.

By coupling the aforementioned extensions, we present a quantitative large-scale multi-phase multi-component phase-field model that can simulate diffusion-controlled dissolution in systems comprising both solution phases and stoichiometric compounds under realistic conditions. Using the presented model, the dissolution of Al_2O_3 in CaO-Al_2O_3-SiO_2 slags and of PGM particles (partially) encapsulated by an Al_2O_3-carrier in a Cu droplet is simulated on their relevant length scales (Fig. 1b). As both dissolution phenomena are crucial to our understanding of the physical principles underlying the pyrometallurgical recovery of the precious PGM metals from SACs, our model serves as a valuable advancement in computational thermodynamics and its applications in metallurgical engineering.

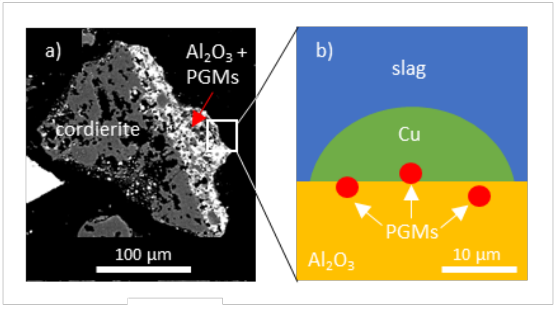

Fig. 1: a) EBSD image of a ground SAC particle. b) Simulation setup for the dissolution of (partially) encapsulated PGM particles in Cu in a slag environment.

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Biographical Note

H. Verbeeck is a third year PhD student in Materials Engineering at KU Leuven. Her key research interest is the development of a quantitative computational framework including the coupling of phase-field models with the CALPHAD method to study the interactions between slags, metallic and oxide particles in pyrometallurgical processes.

[O31] Calphad Optimizer: SQL Insights on Refining, ML, and Quality Metrics

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Key words: Calphad Optimizer, FactSage, SQL Database, Machine Learning

In computational thermodynamics, optimizing Calphad models accurately is essential for predicting phase stabilities and properties reliably. This study presents the quality gains in Calphad optimizations by taking advantage of the integrated SQL database for tracking progress in the Calphad Optimizer module of FactSage. This integration not only facilitates a detailed analysis of optimization histories but also provides a valuable level of transparency of the optimization process, a crucial advancement over simple error *versus* iteration plots that offer limited insights.

Our methodology employs the SQL database that results from every optimization with Calphad Optimizer. This structured database stores optimization data, enabling the extraction of the intricate details regarding each step of the optimization process. As example applications, we use Python packages such as matplotlib, pandas, and TensorFlow to conduct analyses of the impact of thermodynamic parameters and experiments on the error sum and optimization path. These analyses aid in refining parameter ranges and experiment weight factors, as well as identifying parameter correlations. Furthermore, we apply a machine learning model for quantifying parameter uncertainties, and we present a systematic approach for speeding up the initial stages of the optimization by identifying and dismissing experimental data points with little leverage.

These applications offer insights that can greatly improve the quality of Calphad optimizations. The findings advocate for the replication of these and similar methods within the Calphad community to enhance the quality of database assessments and deepen the understanding of the different aspects of optimizations. By ensuring the preservation of detailed optimization histories with structured databases, we even unlock the potential for evaluations that extend beyond current methodologies in future applications. This is especially relevant considering the recent democratization of machine learning tools.

Addressing the critical issue of trust in optimized thermodynamic databases, this study allows consistent and reproducible explorations into parameter uncertainty quantification and sensitivity analysis. At the same time, it shows that Calphad Optimizer serves as a robust framework for thermodynamic database optimizations.

Biographical Note
Bruno Reis is a software developer and researcher for GTT-Technologies since 2016, with his latest contributions in the co-development of the Calphad Optimizer software. He received a PhD in natural sciences from the Brandenburg University of Technology under the advisement of Klaus Hack.

[O32] Machine Learning-Driven Solutions to Evaporation-Induced Variability in Chemical Composition of In-Situ Alloyed Products Fabricated by Direct Energy Deposition

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Key words: Machine Learning, Explainable AI, Thermodynamic Properties, Additive Manufacturing

In addressing the pervasive issue of compositional change during manufacturing—a challenge that is pronounced in additive manufacturing, particularly in direct energy deposition (DED) in-situ alloying—a machine learning model capable of predicting these compositional changes is developed. This issue, critical yet historically underexplored due to its complexity, results in a scarcity of data for training machine learning models. Given the limited data from 177 experimentally produced specimens, advanced machine learning techniques, including symbolic feature engineering and a k-fold ensemble method, are employed to enhance predictive accuracy and model robustness. Furthermore, a machine learning-based process design method is developed, enabling the prediction of process conditions that align with specified compositional targets. Experimental validation of this method confirms the model's exceptional predictive accuracy and its efficacy in identifying optimal process conditions for achieving target compositions.

However, the complexity of the model escalates in tandem with its performance, leading to a significant reduction in interpretability. To mitigate this, the surrogate SHAP method is devised, enabling model analysis through a simplified surrogate model. Here, the surrogate SHAP method is a model-agnostic explainable AI method which uses Shapley additive explanations (SHAP) [1], an explainable AI technique, and is newly developed in this study. This approach facilitates the elucidation of both straightforward and complex relationships between process conditions and compositional changes during manufacturing. For instance, the increase in product composition with rising initial Mn fraction is readily analyzed, as are more intricate interactions, such as the compositional variations associated with concurrent adjustments in initial Mn fraction and laser power. The results of the SHAP analysis are explained by using thermodynamic properties such as latent heat and vapor pressure of Mn to explain the effect of DED process conditions on the evaporation of Mn. Through surrogate SHAP, the model's complexity is effectively navigated, uncovering the intricate interaction of process conditions and their impact on composition during DED in-situ alloying.

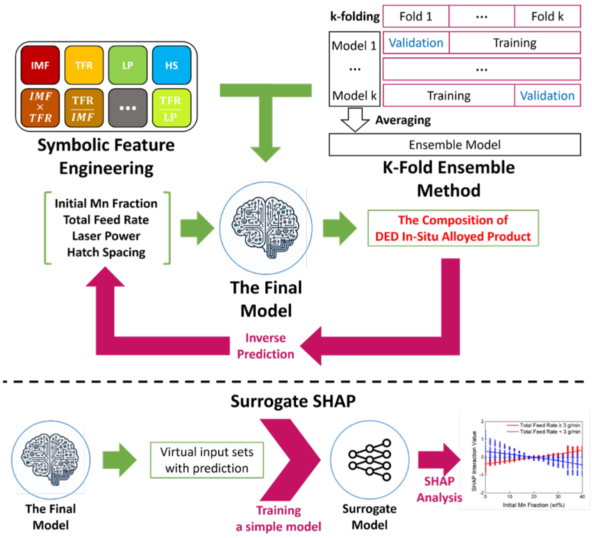

Figure 1. Graphical abstract of the machine learning model and explainable AI technique developed in this study.

References (up to four, please use following format)

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Biographical Note

Dr. Jaemin Wang is currently a postdoctoral researcher at the Computational Materials Science and Engineering Laboratory, led by Professor B.-J. Lee, at POSTECH. His research primarily focuses on advancing the application of machine learning and computational materials science techniques within the realms of materials science and additive manufacturing.

[O33] Thermodynamic, kinetic simulations and experiment on the chemically vapor deposited TiAlSiN coatings

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Key words: Ti-Al-Si-N; Chemical vapor deposition; CALPHAD method; CFD simulation

Addition of Si is known as an effective way to improve the thermal stability and oxidation resistance of TiAlN coatings. The CALPHAD (CALculation of PHAse Diagrams) and CFD (Computational Fluid Dynamics) methods are important for the optimization of process parameters and the design of compositions in the preparation of CVD (Chemical Vapor Deposition) TiAlSiN coatings. In this work, a Ti-Al-Si-N quaternary thermodynamic database was constructed, and the influence of deposition parameters on the elemental content and the deposition rate of CVD TiAlSiN coatings were predicted through thermodynamic calculations and CFD simulations. Representative thermodynamic calculation results are shown in Figure 1.

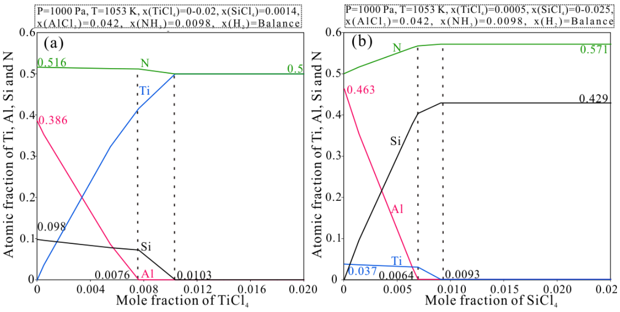

Figure 1. Calculated chemical composition of TiAlSiN coating as a function of gas mole fraction: (a) $TiCl_4$ and (b) $SiCl_4$.

Under the guidance of these calculations, three CVD TiAlSiN coatings were prepared under different $SiCl_4$ gas ratios, and the microstructures were investigated by means of X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. The results show that the calculated composition and deposition rate of the deposited coatings are in good agreement with the experimental results. The experimental results indicated that increasing the gas ratio of $SiCl_4$ was conducive to the increase of Si content in the CVD TiAlSiN coatings. When the Si content in the $Ti_{1-x-y}Al_xSi_yN$ coating reached a certain value ($y \geq 0.03$), the increase of Si content promoted the precipitation of the w-AlN phase and the formation of amorphous SiN_x phase, which resulted in grain refinement of the coatings. As a result, the coatings were composed of nano-crystalline (Ti,Al,Si)N embedded in amorphous SiN_x phase, see Figure 2. The present work provides relevant theoretical basis and data support for the selection and optimization of process parameters in industrial preparation of CVD coatings, which is of great significance for promoting the development of CVD wear-resistant coatings.

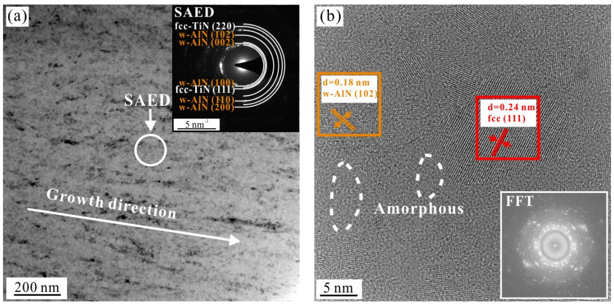

Figure 2. (a) TEM bright-field, SAED pattern, (b) HRTEM and corresponding FFT images of CVD $Ti_{0.22}Al_{0.74}Si_{0.04}N$ coating.

Biographical Note

Liying Wu received her PhD from Central South University of China in December 2023. She has published five SCI papers in the fields of thermodynamics and wear-resistance coating.

O34] Development and integration of CALPHAD databases and software tools for alloy design

A. Perron[1], **N. Ury**[1], **A. Krajewski**[1,2], **V. Lordi**[1], **B. Bocklund**[1]
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Key words: database development, automated alloy design software tool

Efforts at LLNL regarding CALPHAD database development leveraging high-throughput DFT calculations, semi-empirical thermodynamic models and dedicated experiments, and benefiting from the latest developments in the pycalphad (**https://pycalphad.org**) and ESPEI (**https://espei.org**) open-source software packages will be presented.

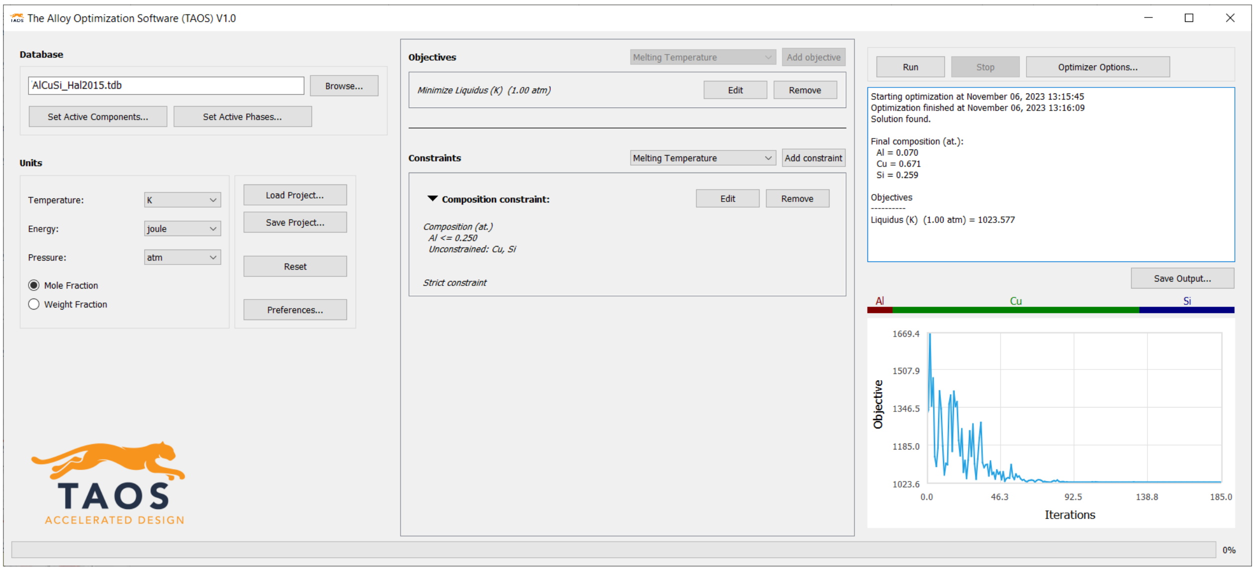
Then, the LLNL's Materials Acceleration Platform (MAP) running on high-performance computers and handling CALPHAD-based, analytical and machine-learning models will be introduced to tackle the challenging task of screening and optimizing new alloys for multiple properties in a vast composition space. Among others, we will highly the design of new refractory alloys targeting high yield strength and ductility at elevated temperatures with constraints on phase stability in a 10-element composition space.

Finally, alloy design case studies using the Alloy Optimization Software (TAOS, see Figure 1, **https://softwarelicensing.llnl.gov/product/taos**) – which is running on stand-alone computers and solving unconstrained and constrained optimization problems – will be presented with examples for structural and functional materials applications.

This work was performed under the auspices of the U.S. DOE by LLNL under contract DE-AC52-07NA27344 and supported by LLNL-LDRD program under Project No. 22-SI-007 and the Critical Materials Innovation Hub, an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing and Materials Technologies Office (AMMTO).

Biographical Note

Aurélien Perron is a materials scientist and the Actinide and Lanthanide Science deputy group leader in the Materials Science Division of the Lawrence Livermore National Laboratory (LLNL).



The Alloy Optimization Software (TAOS) V1.0

Database
AlCuSi_Hal2015.tdb

Units
Temperature: K
Energy: joule
Pressure: atm
● Mole Fraction
○ Weight Fraction

Objectives
Minimize Liquidus (K) (1.00 atm)

Constraints
Composition constraint:
Composition (at.)
Al <= 0.250
Unconstrained: Cu, Si
Strict constraint

```
Starting optimization at November 06, 2023 13:15:45
Optimization finished at November 06, 2023 13:16:09
Solution found.

Final composition (at.):
  Al = 0.070
  Cu = 0.671
  Si = 0.259

Objectives
----------
Liquidus (K)  (1.00 atm) = 1023.577
```

Figure 1. The Alloy Optimization Software (TAOS)

[O35] High-strength high-damping steels: A CALPHAD assisted alloy design study

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Key words: High-damping steel, CALPHAD

Various mechanisms including locally varying environments or unbalanced masses can trigger vibrations in engineering applications. It is desirable to employ self-damping materials in order to reduce noise and fatigue while improving consumer comfort and dynamic stability. These materials reduce vibrations by dissipating heat generated by internal friction related to defects moving through their microstructure. However, there exists a trade-off between damping capacity and strength in these alloys prohibiting their use in load-bearing applications. Ultimately, a new class of high-strength high-damping steels is needed.

Lately, the Fe-Mn alloy system has gained more attention as a low-cost nonmagnetic alternative to high-damping Ti-Ni and Mn-Cu alloys. The high damping capacity of Fe-Mn alloys is based on the movement of partial dislocations. Thus, to overcome the current trade-off between damping capacity and strength, the short-range motion of partial dislocations needs to be sustained while impeding the long-range movement of lattice dislocations.

Applying the Richman and Bolling technique for a thermomechanical assessment of a Fe-Mn baseline alloy (see *Figure 1*) allows monitoring the properties of single-phase and multiphase states of the system, pointing towards the need of additional strengthening mechanisms. Based on a thermodynamic evaluation, a driving-force-based damping model is developed to derive alloy design guidelines informing the subsequent design approach. Different strengthening approaches are discussed, focusing on the promising concept of precipitation strengthening. Two prototype candidates of high-strength high-damping steels are designed based on CALPHAD modeling utilizing step diagrams to determine the soluble levels of NbC and VN that can be used to strengthen the Fe-Mn system.

Experimental validation, including thermomechanical assessments, atom probe tomography, as well as tensile and damping measurements, are presented. These results can be used to improve the discussed design models for future rounds of prototype development. Further, these experimental results of a precipitation strengthened prototype alloy demonstrate the validity of this overall design approach.

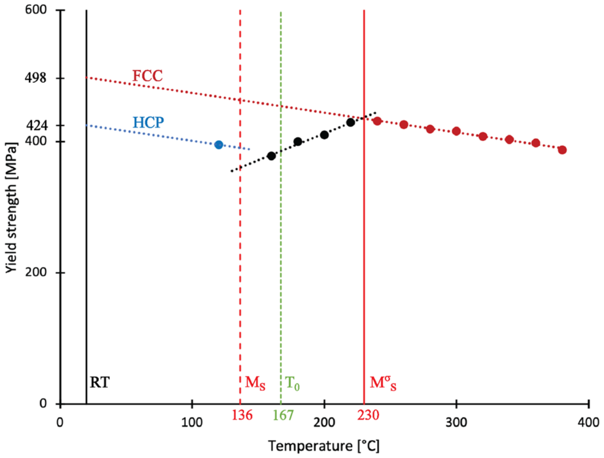

Figure 1. Yield strength versus temperature of the Fe-18.5Mn-1.7Si-0.67Ti-0.1C (wt.%) alloy indicating important transformation temperatures allowing to assess the strength properties of single-phase and multi-phase states of the system.

References

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Biographical Note

Julian Rackwitz is a fourth year Ph.D. student in DMSE at MIT. He previously graduated from TU Berlin majoring in Engineering Science. While his previous research with Lawrence Berkeley National Laboratory centered around the fatigue behavior of metals, he is currently investigating the possibilities for designing high-strength, high-damping steels.

[O36] Multi-Objective Design of High Strength Thick-Plate Aluminum Alloy with Low Quench Sensitivity

M.-I.T. Tzini[1], **W.L. Tan**[2], **H.C. Koh**[2], **J.H. Lim**[2], **A.T. Tan**[2], **G.B. Olson**[1]
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Key words: high-strength aluminum, computational design, multi-objective optimization

High-strength aluminum thick-plate alloys are widely sought after in the aerospace and defense industries due to their high specific strength and good workability. The need to fabricate thick plates at large scale and low cost presents an interesting design challenge, as superior material properties need to be achieved using only conventional ingot casting and wrought processing. Ultra-high strength aluminum thick plates are also often susceptible to stress corrosion cracking (SCC), and high quench sensitivity. High quench sensitivity is especially problematic for thick plates as slow cooling rates are unavoidable. The team had previously reported a framework for the multi-objective design of a SCC-resistant aluminum alloy with high precipitation strengthening and high grain boundary strengthening [1]. Here we build upon the previous work and incorporate an optimization for low quench sensitivity, improved parameters for grain boundary strengthening, and experimental verification of the alloy designs.

A systems approach to material design [2] was used to identify the key process-structure-property relations for the target properties of i) high strength (>750 MPa), ii) high elongation (>12%), iii) low quench sensitivity, and iv) stress corrosion cracking resistance. Pareto-optimal compositions for (i) precipitation strengthening and (iv) grain boundary cohesion were addressed in earlier work [1]. Here we perform kinetic calculations to further down-select low quench sensitivity compositions from the larger set of high strength, SCC-resistant solutions. We also optimize for compositions to promote growth of 20 nm $L1_2$ grain refining phases and calibrate a strengthening model for these phases [3] to (i) provide further precipitation strengthening, inhibit grain growth for grain boundary strengthening, and (ii) improve elongation.

From calculated solutions, 7 alloy compositions were fabricated with different degrees of thickness reduction via hot-rolling, and their stress-strain behavior characterized. Experimental results showed superior yield strength and elongation compared to commercial 7068 aluminum alloy, and demonstrates the holistic computational development of high strength aluminum alloys.

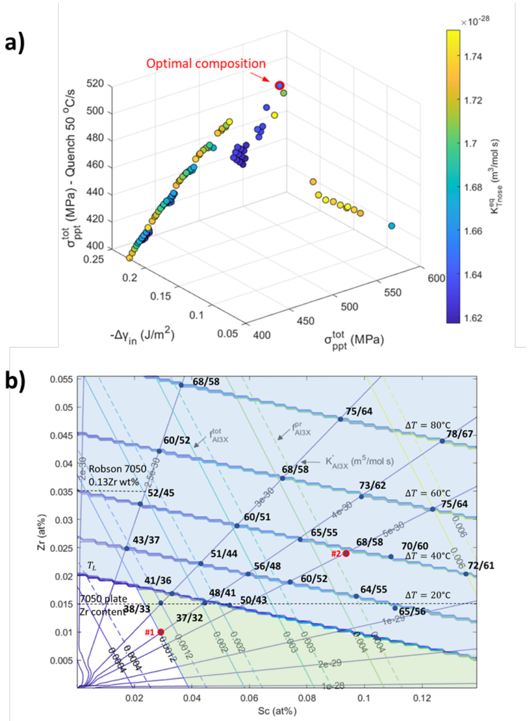

Figure 1. a) Precipitation strengthening after cooling at 50°C/s, and b) cross-plot of Sc-Zr composition for grain refining phases, where contours include Al_3X volume fraction, normalized coarsening rate, and solvus temperature. Numbers in bold represent predicted precipitation strengthening after 50h/100h at 475°C. Red circles are 'optimal' compositions chosen for fabrication.

References

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Biographical Note

Wei-Lin Tan is a Senior Member of Technical Staff at DSO National Laboratories, Singapore. Her interest is in applying ICME to the development of high-performance alloys and ceramics. This research was undertaken in collaboration with postdoctoral scholar Maria-Ioanna Tzini at MIT, under the supervision of Prof Gregory B. Olson.

[O37] Design of High-Strength Heat-Resistant Aluminum Alloys Based on Phase Diagram Calculations

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lbliu@csu.edu.cn

Key words: Heat-resistant Al alloys; Thermodynamics; CALPHAD; First-Principles calculations

Aluminum alloys are widely used in automotive, shipbuilding, and aerospace industries due to their lightweight, high strength, excellent corrosion resistance, and cost-effectiveness. However, when exposed to elevated temperatures, nanoscale precipitates within aluminum alloys tend to coarsen rapidly, resulting in strength reduction and significantly limiting their applications. Microalloying emerges as one of the most efficient methods for enhancing the overall mechanical properties of aluminum alloys. Phase diagram thermodynamics plays a fundamental role in materials design and development. The CALPHAD (CALculation of PHAse Diagram) method enables the thermodynamic assessment of multiphase materials. This study establishes a thermodynamic database for Al–Cu–Mg–Ag–Sc–Si–Zr–Mn system containing nanoscale precipitates. Using the CALPHAD approach, a high-strength heat-resistant aluminum alloy has been designed. The primary research contents are as follows:

1. Phase diagram determination and thermodynamic database construction for critical ternary systems: The phase diagrams of three critical ternary systems, Al–Ag–Si, Al–Ag–Sc, and Al–Ag–Zr, were determined through equilibrium alloy methods. The thermodynamic databases for those system have been established for the first time. These databases are essential for the development of heat-resistant aluminum alloys and serve as a significant complement to existing aluminum-based databases.
2. Development of a thermodynamic database for the Al–Cu–Mg–Ag–Sc–Si–Zr–Mn system containing nanoscale precipitates: The thermodynamic database for the Al–Cu–Mg–Ag–Sc–Si–Zr–Mn system has been successfully established. A thermodynamic model for core-shell precipitates is established. This database enables the prediction of the composition and temperature ranges for core-shell structures.
3. Design of high-strength heat-resistant aluminum alloys: Utilizing the developed thermodynamic database, we successfully designed a high-strength heat-resistant Al–Cu–Mg–Ag–Sc–Si alloy. It exhibits a Tensile Strength of 526 ± 15 MPa, Yield Strength of 487 ± 13 MPa, and Elongation of 8.2 ± 0.5%. Remarkably, even after exposure 100 hours at 200 ºC, the alloy retains a Yield Strength of 454 ± 10 MPa.

Biographical Note

Libin Liu has completed his PhD at the age of 29 years from Central South University, Changsha, China. He was a visit scholar at Swedish Institute of Metal Research from 1999 to 2002 and a Postdoctor at School of Mechanics, Chalmers University, Sweden from 2002 to 2004. His major research field is phase diagram determination and calculation thermodynamics. He has published more than 160 paper in international peer reviewed journal. Now he is a member of Chinese Academy Committee of Phase Diagram.

[O38] Thermodynamic modelling of oxide fuels for nuclear applications: current status and prospects for improvement

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[2] CEA, DES, ISEC, DMRC, Université Montpellier, Marcoule, 30207, Bagnols-sur-Cèze, France
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Key words: oxide fuels, thermodynamics, modelling, TAF-ID

Uranium dioxide UO_2 is the most widely used nuclear fuel in the current generation of nuclear power plants (PWR, BWR). Mixed uranium and plutonium dioxide $(U,Pu)O_2$ is also a reference fuel for current and future generations of nuclear reactors (SFR). These oxides have the advantage of melting at very high temperatures. Under normal operating conditions, fuel pellets are subjected to extreme conditions of temperature, irradiation, thermo-mechanical stress, leading to changes in their chemical composition and microstructure over time. To guarantee the safety of these reactors, the thermochemical behavior of the fuel and its chemical interaction with the environment (structural materials, coolant, atmosphere) must be well predicted up to very high temperatures. ATFs (Accident Tolerant Fuels), such as chromium or gadolinium doped UO_2 fuels are being studied to improve fuel behavior in the event of an accident.

Uranium dioxide $UO_{2\pm x}$ has a fluorite structure and a wide range of oxygen non-stoichiometry enabling the fuel to adapt to compositional changes due to the formation of numerous fission products [1,2]. This is linked to the existence of numerous defects in the crystal. Point defects (oxygen and uranium vacancies and interstitials) and various types of clusters are formed depending on oxygen potential and temperature. Fundamental thermodynamic and thermal properties such as heat capacity, oxygen potential, thermal conductivity and melting temperature of the fuel are essential input data for the Fuel Performance Codes which are multi-physics codes developed to simulate the thermo-mechanical behavior of a fuel pin under normal and accidental conditions. The CALPHAD method is best suited to modelling and predicting the thermodynamic properties of such a complex chemical system containing numerous fission products and surrounding structural materials. To this end, the TAF-ID (Thermodynamics Advanced Fuels-international Database) has been developed since 2013 within the OECD/NEA [2].

The current state of development of the database will be presented with a focus on modelling of the oxide fuels. In addition to the CALPHAD approach, electronic structure calculations (DFT) and molecular dynamics simulations are performed on actinide dioxides. These methods make it possible to calculate the formation energies of the various defects and to compute thermodynamic data at very high temperature where no experimental data are available.

In this context, improvements are proposed. A new method aiming at reducing the number of end-members to be described with the current version of the sublattice model $(U^{+3},U^{+4},U^{+5})(O^{-2},Va)_2(O^{-2},Va)$ ("Va" designate vacancies) will be presented [1]. And more generally, the direct incorporation of the formation energies of the various defects (calculated by DFT) into the CALPHAD models will be considered to improve the physical description of the defects and the associated thermodynamic and thermophysical properties of oxide fuels.

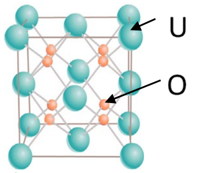

Figure 1. Crystalline structure of UO_2

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Biographical Note

Christine Guéneau is Senior Researcher at the Energy Division of the French Alternative Energies and Atomic Energy Commission (CEA) in Saclay (France). After a PhD in metallurgy, she joined CEA Saclay in 1994 for a post-doctoral fellowship and obtained a permanent research position in 1995. She is actively involved in research on the thermodynamic modelling of materials for energy applications.

[O39] Phase equilibrium investigations and thermodynamic study of the Y_2O_3 - Ta_2O_5 system

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Key words: experimental phase equilibria, differential thermal analysis (DTA), differential scanning calorimetry (DSC), heat capacity

The ZrO_2-HfO_2-Y_2O_3-Ta_2O_5 system materials have attracted attention for their potential use as innovative thermal barrier coatings [1,2]. A fundamental understanding of the thermodynamics in this system is essential for future practical applications. This work focuses on the Y_2O_3-Ta_2O_5 side system.

This study investigates phase relations in the Y_2O_3-Ta_2O_5 system using two methods: the equilibration method, which covers temperatures from 1573 K to 1973 K, and the DTA method, which extends up to 2473 K. Samples were obtained using co-precipitation method. Phase identification was carried out using X-ray diffraction (XRD). Microstructure investigation and phase composition measurements were performed using scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDX). The eutectic reaction, L→ YTa_3O_9 (P)+Ta_2O_5, occurred at 2019 K and composition of 78 mol.% Ta_2O_5. The study presents evidence that the eutectic reaction L→$YTaO_4$ (T)+YTa_3O_9 (P) shown in the evaluated phase diagram [3] does not exist. Instead, melting of YTa_3O_9 (P) occurred by a peritectic reaction L+$YTaO_4$ (T) → YTa_3O_9 (P), which was observed at 2073 K in the composition range from 51 to 76 mol% Ta_2O_5. Additionally, the heat capacity of the YTa_3O_9 phase was measured using differential scanning calorimetry (DSC) over the temperature range of 240 K to 1300 K. The experimental data were fitted to the following equation:

$$Cp\ (J\cdot mol^{-1}\cdot K^{-1}) = 306.074+0.024688\cdot T-4977661\cdot T^{-2}$$

The thermodynamic database for the Y_2O_3-Ta_2O_5 system obtained using the CALPHAD approach will be improved, accounting experimental data on the phase diagram and thermodynamic values obtained in the present study and literature [3,4].

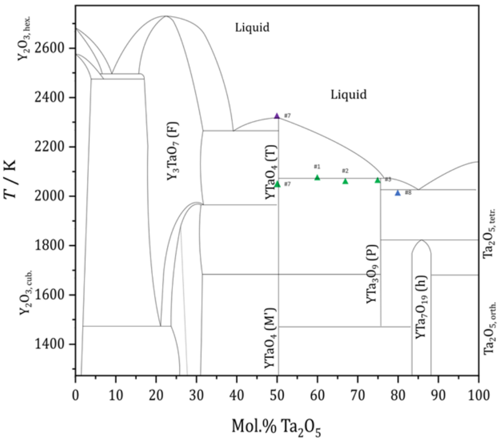

Figure 1. Y_2O_3-Ta_2O_5 phase diagram based on publication of Fernandez et al. [3] and modified according to the results of the present work i.e. peritectic melting of YTa_3O_9 (P) phase.

References

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Biographical Note

I graduated with a Diploma degree in Materials Science in 2021. For my Diploma I worked on Small-Angle-X-ray-Scattering (SAXS) both in Freiberg and Leoben. I am currently working as a PhD student on a project to investigate and model phase diagrams of oxidic high entropy materials for thermal barrier coatings.

[O40] The Effect of A-site Doping Elements on the Activation Energy Barrier and Oxygen Diffusivity of $La_2NiO_{4+\delta}$

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Key words: ab initio, SOFC, energy barrier, partition function

Solid oxide fuel cells (SOFCs) have attracted lots of attention as a promising energy conversion system, due to their high energy conversion efficiency, fuel adaptability, simplicity of system design, and low emissions and pollution. To commercialize the SOFCs, one of the strategies is to lower the operating temperature from 800 to 1000℃ to an intermediate temperature range to meet the goals of cost reduction and durability enhancement. The reduction of operating temperature, however, leads to significant degradation in electrode performances, as the activity of traditional cathode material ($La_{0.8}Sr_{0.2}MnO_{3-\delta}$ LSM) for electrochemical reduction of oxygen is low in this temperature range. To improve the reaction kinetics of cathode, the mixed ionic-electronic conducting (MIEC) materials have been considered as one of the best choices because of their extended active areas for oxygen reduction.

As a family of MIEC, the $La_2NiO_{4+\delta}$ Ruddlesden-Popper (RP) family with the K_2NiF_4-type structure has attracted significant attention as promising cathode materials due to their relatively high electronic and ionic conductivity, as well as their compatibility with commonly used electrolytes in terms of thermal expansion coefficients (TEC). The ionic conductivity of $La_2NiO_{4+\delta}$ results from the oxygen excess δ accommodated in their A_2O_2 layers involving the apical oxygen atoms (interstitialcy mechanism) [1-4]. These interstitial atoms are highly mobile, which induces a high ionic conductivity of the material.

Up to now, extensive experimental investigations have been conducted to explore the oxygen transport properties of $La_2NiO_{4+\delta}$, but the theoretic investigation is still far from enough. In the present work, we systematically investigated the equilibrium volumes, activation energy barriers, and oxygen diffusion properties of Ca, Sr, and Ba-doped $La_2NiO_{4+\delta}$ based on the *ab initio* calculations. Additionally, the diffusion coefficient of doped $La_2NiO_{4+\delta}$ will be calculated by summing the contribution from each individual diffusion pathway, which can be calculated based on the partition functions. Our investigation shows that both the ionic radii of doping elements and the equilibrium volume of the RP phase will affect the oxygen transport properties of $La_{2-x}A_xNiO_{4+\delta}$ (A=Ca, Sr, and Ba). The activation energy barrier increases as oxygen migrates toward ions with larger ionic radii, and conversely, it decreases when oxygen migrates toward ions with smaller ionic radii. When compounds possess a larger equilibrium volume, the oxygen migration barrier decreases due to the expanded travel channel, whereas it increases when the compounds have a smaller equilibrium volume, primarily because of the constricted travel channel.

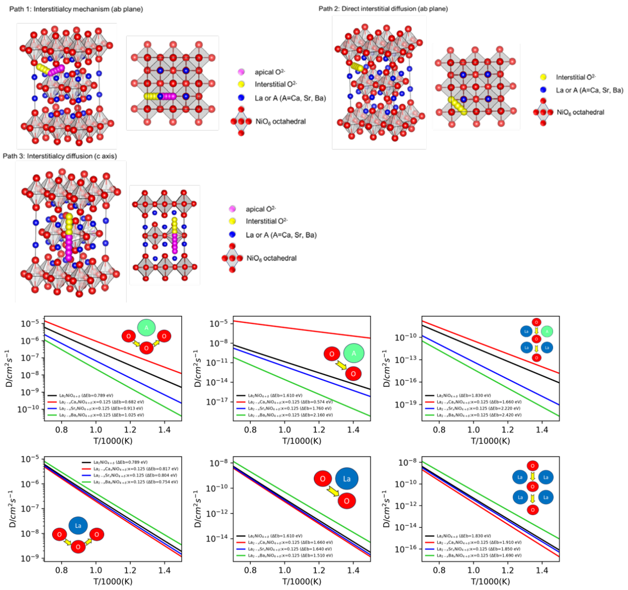

Figure 1. The migration paths and oxygen diffusivity of $La_{2-x}A_xNiO_{4+\delta}$ (A=Ca, Sr, and Ba)

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Biographical Note

Yu Zhong is an Associate Professor in the Mechanical and Materials Engineering Department at Worcester Polytechnic Institute (WPI). His research focus on CALPHAD, DFT, and machine learning on the materials design (Ceramics and alloys).

[O41] Thermodynamic modelling of the P-containing systems: Alk_2O-Me_2O_3-P_2O_5 and $Alk_xP_yO_{0.5x+2.5y}$-AlkCl (Alk=K,Na; Me=Al,Fe) for the oxide-salt database GTOx

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Key words: phase equilibria, mixed phosphates, chlorides, associate species model

For the thermodynamic description of transformations and reactions of the entire system during gasification (ashes, coatings, products of evaporation and condensation reactions of volatile compounds) under different boundary conditions, it is necessary to have a reliable thermodynamic database containing all oxide-salt phases. This database should allow the corresponding thermodynamic calculations and also the extrapolation into the unmeasured range.

The oxides-salt database GTOx [1] containing more than 17 oxides, 11 sulphides, 5 sulphates, 4 carbonates and chromates and CaF_2 covers approximately 270 binary and 220 ternary systems. GTOx is relevant for various slag applications, glass processing, coal/biomass combustion and gasification as well as for the development and production of refractory materials.

The present work describes the extension of the database with respect to further mixed phosphates and alkali chlorides. Namely the four ternary systems Alk_2O-Me_2O_3-P_2O_5 (Alk=Na, K; Me=Al, Fe) and two ternary systems Alk_2O-P_2O_5-AlkCl (Fig. 1) are considered.

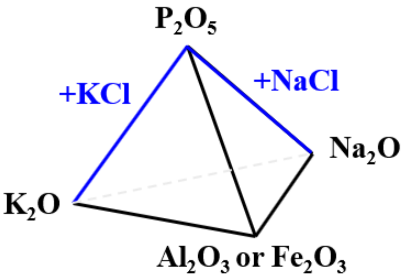

Figure 1. Schematic representation of the systems

The binary systems Alk_2O-P_2O_5 have already been added to the dataset [2]. Ternary systems Alk_2O-Me_2O_3-P_2O_5 are characterised by a large number of stoichiometric compounds. Their thermodynamic functions were generated by considering the available information including the ab-initio data from the AIMP database [3] in accordance with the phase equilibria. The solubilities between Alk_3PO_4 and the corresponding ternary compounds were treated using a simple sublattice approach according to the formula $(Alk_2O)_2(P_2O_5)(Alk_2O,Alk_2MePO_5)$ with Me=Al, Fe. The corresponding solid solution parameters were found to obtain adequate representations of the available experimental data.

Extending the database with respect to the alkali chlorides, the corresponding binary systems containing AlkCl and $Alk_xP_yO_{0.5x+2.5y}$ ($AlkPO_3$, $Alk_4P_2O_7$ and Alk_3PO_4) were considered using the phase diagram data from the literature.

The Gibbs energy of the liquid phase was modelled using a non-ideal associate solution model [4]. Alkali chlorides are introduced as constituents along with the oxide components in order to provide consistency of the database.

The phase equilibria including the sub-solidus relationships were calculated using the new data set. The pseudo-binary sections in the framework of the ternary systems are proposed in good agreement with the available experimental data.

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Biographical Note

Elena Yazhenskikh is scientist at Forschungszentrum Jülich, Germany since 2005. The research topics and scientific interests are thermodynamic modelling of oxide and salt systems, database development using CALPHAD approach, phase equilibria, thermodynamic properties.

[O42] Thermodynamic modeling of the Al-Ca-O ternary system with key experiments

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Key words: metal-oxide equilibria, Calphad modeling, Al-Ca-O

The quasi-binary Al_2O_3-CaO is one of the key systems for various research areas: cement and concrete, geoscience and planetary science. In the literature, the phase diagram has a low temperature eutectic on the lime rich side and 4 stable stoichiometric solid compounds: $Ca_3Al_2O_6$, $CaAl_2O_4$, $CaAl_4O_7$ and $CaAl_{12}O_{19}$, all of them melting peritectically [1]. In addition, there is a shortlist of other compounds, that were synthesized and reported in the literature but do not appear in the phase diagram: $Ca_2Al_2O_5$, $Ca_5Al_6O_{14}$ and $Ca_{12}Al_{14}O_{33}$. Especially the case of the last compound, $Ca_{12}Al_{14}O_{33}$ is interesting, as this compound is non-stoichiometric in oxygen with a composition range from O_{32} to $O_{33.4}$ [2]. Therefore, it is better to name this solid solution $Ca_{12}Al_{14}O_{32+x}$. The existence of a homogeneity range also indicates, that the CaO-Al_2O_3 section may not be truly quasi-binary and that the observed solid-liquid equilibria in the CaO rich region may depend on the oxygen partial pressure. As the Ca-O binary system is a eutectic system [3], this is not a big surprise. Unfortunately, only very limited experimental or theoretical data is available which could be used in a more complete thermodynamic modeling of the ternary system.

In our contribution, we are trying to improve this situation and we will report a new modeling of the Ca-Al-O ternary system from the metal to the oxides for the first time using a coupled approach of DFT calculations, Calphad modeling and key experiments. The DFT calculations are performed using the VASP software package in its most recent version and the SCAN exchange functional. This functional gives the most precise results for the energy of formation and for the ground state structural properties for the solid compounds. For the Calphad assessment, we combined the binary systems from Ozturk et al for Al-Ca [4], Deffrennes et al for Ca-O [3] and Taylor et al for Al-O [5]. New key experiments include the enthalpy of formation of $Ca_5Al_6O_{14}$ using high temperature transposed drop dissolution calorimetry in an oxide solvent and phase equilibria determinations which were performed on metal-oxide mixtures that were heat treated under neutral or reducing conditions. The oxides partly decompose under these conditions and some of the Ca dissolves in the Al metal as can be seen in Fig.1. The oxides, initially white, turned black also indicating that a reduction takes place.

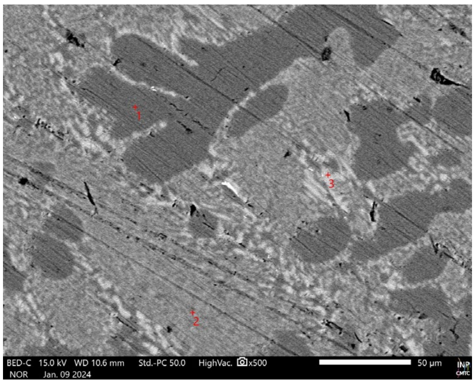

Figure 1 Microstructure of the metal component in a $Ca_3Al_2O_6$-$CaAl_2O_4$-Al(metal) ternary mixture after 2h at 1400°C and rapid cooling. The primary phase is Al(metal) with an Al_4Ca-Al eutectic.

The new experimental results together with the available literature data allowed to optimize the ternary interaction parameters of the associate liquid model used here. Based on our new experimental and theoretical results, we will discuss the quality of the modeling as well as potential future work.

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Biographical Note

Dr. Alexander Pisch is a CNRS Research Director at Laboratoire SIMaP in Grenoble, France. He holds a Master in Physics from KIT (Germany), a PhD and a Habilitation in Materials Science from Grenoble INP (France). His work focuses on DFT calculations, Calphad modeling and experimental work for building material applications.

[O43] Pt effect on the bond-coating/superalloy interdiffusion: a thermodynamic and kinetic study

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Key words: Interdiffusion, bond-coating, platinum, superalloy

A thermal barrier coating (TBC) system is a multi-layered system composed of a Ni-based superalloy, an Al-rich metallic coating (the bond-coating) and an insulating top coat (the thermal barrier). The low thermal conductivity of the ceramic used as a thermal barrier decreases the temperature of the internally cooled underlying substrate, while the high Al content of the bond-coating allows the formation of a protective Al_2O_3 layer, during the reaction with oxygen.

The formation and growth of the protective oxide layer is a key element in the degradation of a TBC system and depends on many parameters such as composition, microstructure and fabrication process of the bond-coating. Regarding the composition, Pt addition to the bond-coating is very beneficial for the oxidation resistance of TBC systems [1]. Besides, the Al uphill diffusion from the superalloy towards the surface, resulting from the decrease in Al activity due to Pt [1], allowed the development of Pt-rich $\gamma+\gamma'$ bond-coatings [2]. Also, the superalloy composition can strongly influence the oxidation resistance of the TBC system [3,4]. An element generally present in the superalloy composition and often detected in the oxide scale composition is Ti. Like Al and Ta, Ti partitions into γ' rather than γ. Therefore, during Pt diffusion in a Ti- and Ta-rich superalloy to obtain a Pt-modified $\gamma'+\gamma$ bond-coating, the γ' phase becomes enriched in Ti and Ta compared to the γ phase [5]. A noticeable Ti and Ta diffusion is not surprising when bond-coatings are obtained by Pt and/or Al enrichment of a Ti- and Ta-rich superalloy. However, a noticeable content of Ti was detected within the oxide scale formed on MCrAlY-type bond-coatings after short oxidation times [5,6]. A significant uphill diffusion of titanium was also observed during the oxidation of TBC systems composed of a Pt-modified NiCoCrAlYTa bond-coating [7-9].

This study focuses on a thermal barrier coating system based on AM3 superalloy and a Pt-modified NiCoCrAlYTa bond-coating. The TBC system was first thermally treated at 1080 °C for 6 hours (TT1), under vacuum. Then, it was thermally cycled at 1100 °C in a vertical oxidation rig under air. Characterizations were performed, before and after thermal cycling, using SEM and EDS. Based on experimental results obtained on such TBC systems, thermodynamic calculations (Figure 1) and diffusion simulations were performed in order to shed light on the Pt effect on the activity and diffusion of Al, Ti and Ta.

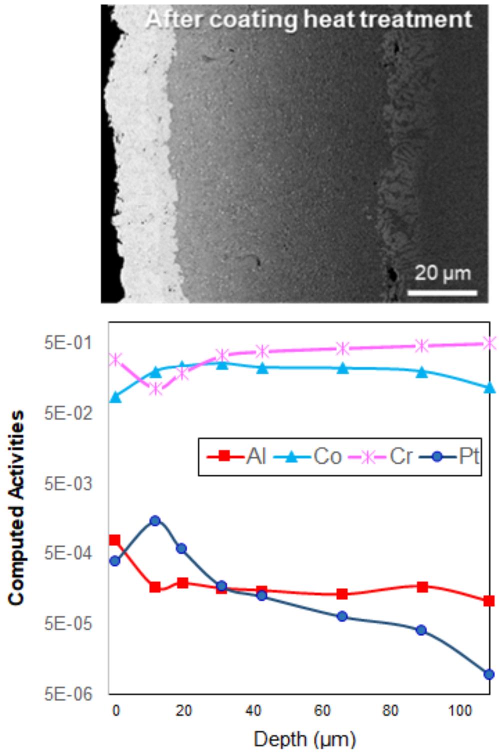

Figure 1. Micrograph of the TBC after the TT1 and computed activities for the measured compositions (Thermo-Calc, TCNI9 database).

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Biographical Note

E. Epifano obtained her PhD in chemistry in 2017 and, since October 2020, she works as a CNRS researcher at the CIRIMAT laboratory in Toulouse (France). Her domain of research focuses on the thermodynamic and kinetic modeling of Additive Manufacturing processes and oxidation behavior of metallic alloys.

[O44] The multi-solute solid solution behaviour of magnesium alloys and their application on materials design

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Key words: Magnesium alloys; Solution behavior; Materials design

The low-density magnesium (Mg) alloys are attractive for the application in aerospace, transportation and other weight-saving-required fields for their unique properties. However, the mass production and application of Mg alloys are still quite limited due to the low room-temperature ductility and anti-corrosion properties.

Alloying is always an effective method to improve the comprehensive properties of Mg alloys. It is noteworthy, as being Mg alloys, the most important phase is inevitably the primary Mg phase. Hence, the solid solution strengthening & softening, anti-oxidation, anti-corrosion mechanisms, are proposed for Mg alloys and also wildly approved and applied in various Mg alloy design. Additionally, it is also notably, the functional properties can also be tailored by controlling the alloying element solution in the matrix. To be concluded, the solution and precipitation behavior of alloying elements in Mg alloys are quite fundamental and important for the Mg alloy design. Based on extensive review, it is found the multi-alloying-element-solution in primary Mg phase may bring cocktail effects and deliver the balanced comprehensive properties [1].

In this work, the detailed effects of alloying elements on the lattice parameters, inherited chemical and physical properties of primary Mg phase have been calculated [2]. And the correlation between the alloying elements' features and solubility in primary Mg phase has been proposed. Further, the two different alloying elements solution in the primary Mg phase has been studied, including the element's interactions, the change of the properties of primary Mg phase, and etc.. Specially, the relatively substitution sites of the two different alloying elements have been considering in this calculation, where dozen pair-sites have been selected. It is observed, the similarity of the elements can significantly affect the relatively substitution sites in the lattice.

Based on the above work, the solution behavior of two alloying elements in the primary Mg phase have been thermodynamic calculated, where some of typical systems were also experimental studied [3]. With study on dozens ternary Mg-based systems, it is observed the solution behavior of two alloying elements in the primary Mg phase are with quite typical features, as shown in Figure 1. Considering the precision of the database, series alloy experiments have been performed and these solution behavior features have been validated. Combining those typical solution behaviour features and physical relation between varied properties and the matrix, the basic alloy design principles of varied targeted Mg alloys have been proposed. With the design concept, we designed the ultrahigh damping Mg alloy and the low degradation rate of Mg-Sr-Y alloy.

It is promising that by selected proper multi-alloying-elements (with optimal ratio) solid solution in the α-Mg phase, the comprehensive properties of Mg alloys with targeted performance can be synergy improved. The description of the solution behavior and the proposed material design principles can also be applied into other alloy systems.

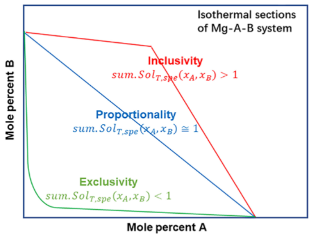

Figure 1. The classification rule of the solid solution behavior in ternary Mg alloy systems

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Biographical Note

Yuan Yuan, CCMg, College of Materials Science and Engineering, focuses on thermodynamic and kinetics of Mg alloys and alloy design, has published more than 70 papers, and was awarded of the Youth of the Year of International Magnesium Science & Technology.

[O45] Accelerating thermochemical equilibrium calculations for nuclear reactor applications

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Key words: machine learning, surrogate modeling, multiphysics simulations, MOOSE

Thermochemical properties play a key role in modeling and simulation of several key phenomena in nuclear reactors. There has been an increasing interest in incorporating CALPHAD-based formulations in multiphysics simulations including for Molten Salt Reactors where knowledge of phase evolution of the salt and the chemical potentials of various elements are of utmost importance in source term analyses and redox control. However, the size of such simulations is often limited by the high computational cost of full thermodynamic equilibrium calculations. This work discusses the current efforts aimed at accelerating thermochemical equilibrium calculations for multiphysics simulations performed using the open-source finite element / finite volume code Multiphysics Object Oriented Simulation Environment (MOOSE) [1].

While several methods have been proposed for accelerating phase equilibrium calculations [2], most focus on relatively small systems and often rely on a-priori knowledge of the state-space of the system. Nuclear materials, however, are often multi-component systems owing to the evolution of composition under irradiation and an approach based on a-priori mapping of phase diagram is often not enough. This work is aimed at demonstrating an on-the-fly surrogate modeling framework that uses active learning to reduce the number of full equilibrium calculations that must be performed. By combining with efficient coupling approaches, the surrogate framework helps in reducing the computational cost of thermodynamic equilibrium informed multiphysics simulations of nuclear materials. The performance is benchmarked against full coupling with the thermochemistry library Thermochimica [3].

This work uses a machine learning based approach for constructing surrogate models to predict the stable phases in a multicomponent system. The surrogates were constructed using neural networks and Gaussian process classification. In this work, we compare the relative performance of the two methods. We also demonstrate the use of caching previous calculations by interpolating the values from nearest neighbors.

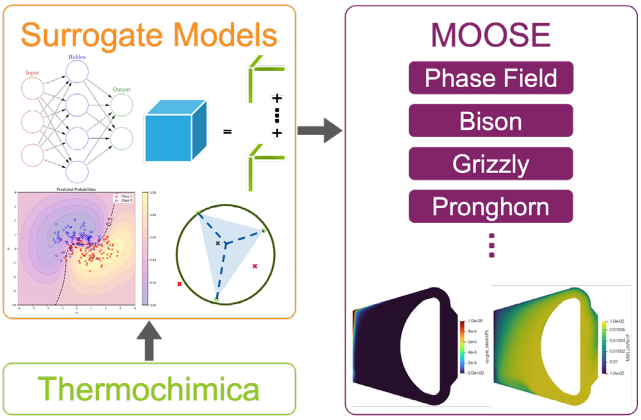

Figure 1. Thermodynamic equilibrium acceleration framework in MOOSE.

Acknowledgement

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This research made use of Idaho National Laboratory's High Performance Computing systems located at the Collaborative Computing Center and supported by the Office of Nuclear Energy of the U.S. Department of Energy and the Nuclear Science User Facilities under Contract No. DE-AC07-05ID14517.

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Biographical Note

Parikshit Bajpai is a Russell L. Heath Distinguished Postdoctoral Research Associate in the Computational Mechanics and Materials department at the Idaho National Laboratory. His research is focused on developing surrogate models and coupling approaches for CALPHAD calculations in multiphysics simulations of nuclear reactors.

[O46] CALPHAD-based thermodynamic evaluation for integrating secondary Ni-containing dusts in ferrous processing

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Key words: Ferrous alloys, Nickel, byproducts, thermodynamic simulations

Integrating alternative sources for extracting critical metals into conventional or new metallurgical processes provides significant advantages in terms of resource efficiency. Yet, it requires a comprehensive analysis of the expected behavior, an evaluation of the effect of the process parameters on the chemical equilibrium and final products, and monitoring of impure elements. The present work seeks to thermodynamically assess the integration of secondary Ni dusts sourced from a ferronickel plant into a smelting treatment to recover iron alloy and slag products. The work applies CALPHAD-based simulations (FactSage software) due to their strong ability to predict thermodynamic behavior, especially of high-temperature multicomponent systems, based on self-consistent models [1]. The main goals are to optimize feed material compositions, reinforce the understanding of process chemistry, support the experimental design considering further utilization potential of the final products. The process parameters, such as the Fe/Ni ratio in the feed mixture, temperature, and slag composition, have been optimized. It was seen that the grade of the final alloy is independent of the Fe/Ni ratio of the feed mixture. However, the feed composition influences the C and Si content of the obtained alloy, in agreement with other studies [2], [3]. The characteristics of the slag are simulated and assessed in terms of chemistry, slag/metal equilibria, and liquidus temperature. The results are discussed according to fundamental thermodynamic studies on relevant chemical systems consisting of $FeO-MgO-SiO_2$ [4]. It was seen that FeO reduces the liquidus temperature of the slag, whereas for increasing SiO_2/MgO (*wt.%/wt.%*) the liquidus decreases first and then increases. Implementing the process at high temperatures (higher than 1500^oC) can be beneficial in terms of fully liquid alloy and slag, separation of products, and thus operational requirements. According to the obtained results, the production of high-grade FeNi alloys and slag with the prospect to be utilized in the ceramic industry is thermodynamically outlined.

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Biographical Note

Dr. Lazou is a PostDoc at the National Technical University of Athens (NTUA), Greece. She holds a M.Sc. (2017) in Metallurgical Engineering (NTUA), and a Ph.D. (2021) in Materials Science and Engineering (NTNU, Norway). Her interests are in pyrometallurgy, thermodynamic and process modelling and design, and new alloy development.

[O47] Phases and Microstructure of Refractory Complex Concentrated Alloys $Al_xCr_yMoTaTi$ (x = 1…3, y = 0.5…1)

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Key words: refractory high-entropy alloys, alloy development, microstructure, powder metallurgy

The concept of so-called high-entropy alloys (HEAs) was first published in 2004 by Cantor et al. [1] and Yeh et al. [2] and describes alloys with at least five metallic elements and (near-) equiatomic compositions resulting in "simple" single- (or dual-) phased microstructures of face-centred cubic (fcc), body-centred cubic (bcc) or hexagonal closed packed (hcp) phases. Since HEAs of transition metals show outstanding combinations of structural properties, i. e. strength and ductility, a high research interest has risen for developing HEAs based on refractory metals (RHEAs) as promising high-temperature materials and alternative for nickel-based superalloys [3]. In order to broaden the multi-dimensional composition space of HEAs, their strict chemical definition was opened to non-equiatomic compositions and more complex multi-phase microstructures, called complex concentrated alloys (CCAs).

The refractory complex concentrated alloy (RCCA) AlCrMoTaTi shows a high oxidation resistance comparable to nickel-based superalloys and reasonable high-temperature compression strength [4].

In this work, the equiatomic RCCA AlCrMoTaTi is systematically altered in its Al and Cr fraction in order to improve both oxidation resistance and high-temperature strength. The non-equiatomic chemical derivatives $Al_xCr_yMoTaTi$ (with x = 1, 1.5, 2, 2.5, 3 and y = 0.5, 0.75, 1) are investigated with regards to formed phases, microstructure, oxidation resistance and hardness.

CALPHAD simulations using Thermo-Calc software predict a high phase fraction of disordered bcc/ordered B2 phase and a low phase fraction of intermetallic sigma phase at the homogenisation temperature of 1300 °C. Increasing Al concentration increases sigma phase fraction whereas decreasing Cr concentration decreases it. A very high Al concentration is predicted to result in stabilising hcp/A3 with respect to bcc/B2 and high Cr concentrations stabilise intermetallic C14 Laves phase with respect to both bcc/B2 and sigma phase.

Experimental findings confirm a significant influence of Al concentration on phase composition, i. e. increasing Al concentration results in increased phase fraction of sigma phase (see Figure 1). Thus, a transition from a microstructure with matrix and precipitates to a microstructure of interpenetrating phases is observable.

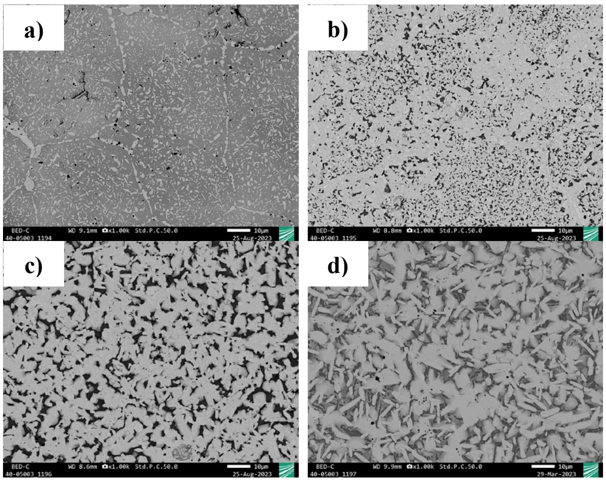

Figure 1. SEM-BSE micrographs of $Al_xCr_{y=1}MoTaTi$ at identical magnifications with x = 1.5 (a), x = 2 (b), x = 2.5 (c) and x = 3 (d)

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Biographical Note

Florian Häslich studied both Materials Engineering and Materials Science and has been working at Fraunhofer IFAM Dresden since 2015 in the scientific fields of powder metallurgy, metal additive manufacturing, high-temperature materials and CALPHAD simulations. Currently, he is a PhD student in alloy development of refractory high-entropy alloys for high-temperature applications.

[O48] Eco-Innovative Process Design: Integrating LCA into Thermodynamic-based Process Simulations for the Development of more Sustainable Technologies

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Key words: Life Cycle Assessment (LCA), Computational Thermochemistry, FactSage, Environmental Sustainability, Pyrometallurgical Process Modeling

The push towards more sustainable industrial processes is essential, driven by worldwide efforts to lessen environmental impacts and boost energy efficiency. Life Cycle Assessment (LCA) is a critical tool to quantify the environmental impacts of a process/functional unit. It is nowadays a common approach when deciding on the type of technology to be implemented for a given application. Traditional LCA approaches heavily rely on aggregated data of existing and mature processes. Such generic inventories prevent the exploration and quantification of the environmental footprint of new and disruptive technologies which are not yet commercialized and for which data are not yet available. Moreover, it is well known that traditional LCAs often lead to inconsistent mass and energy balances which prevent a precise analysis when comparing technologies.

To overcome these shortcomings, this work introduces an innovative method of incorporating LCA into computational-thermochemistry-based process simulations to virtually explore both existing and novel pyro-metallurgical operations [1-2]. A process simulation platform called *FactFlow* which is exploiting the precise thermodynamic description of a wide range of chemical systems (such as oxides, sulfides, salts, alloys and much more) via the use of FactSage databases is presented. This process simulation interface is linked to LCA inventories (such as EcoInvent [3]) and allows the complete description of direct and indirect emissions and environmental impact of pyrometallurgical processes.

In this presentation, several pyrometallurgical processes (including the direct reduction of iron using methane/H_2, the production of ferro-alloys via carbothermic and aluminothermic operations, the melting of glass culets and the recycling of scrap metals in electric arc furnaces) are simulated and analysed using this novel approach. More specifically, we showcase how our tool directly accounts for the modulation of the operating conditions on the quantification of the direct emissions and on the product quality while allowing a global assessment of the environmental footprint of these processes. Moreover, we demonstrate how this interface allows the optimization of the operating conditions of a process based on various multi-objective functions and sets of constraints linked to reactants prices, environmental impacts, and product specifications. Finally, we complete our work with an analysis on how to integrate greener technologies in the actual pyrometallurgical industry based on energy intensity and emissions.

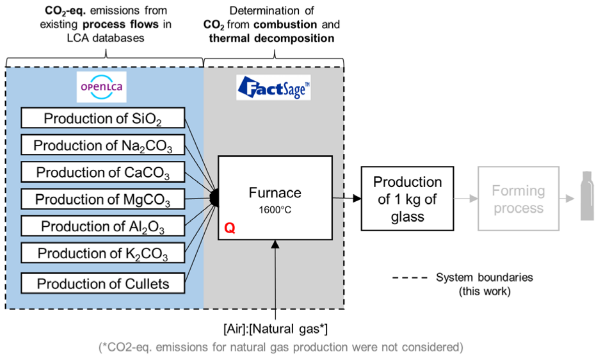

Figure 1. *Coupling of LCA and FactSage for the glass production modelling for the calculation of CO_2 emissions from raw material processing and furnace operation [1].*

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Biographical Note

Jean-Philippe Harvey is an associate professor at Polytechnique Montreal. His scientific research revolves around materials science with a focus on computational thermochemistry and the development of more sustainable pyrometallurgical processes.

[O49] Incorporating High Pressure into CALPHAD

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Although the geochemistry and planetary science communities naturally incorporate pressure as a variable in phase diagram calculations, the CALPHAD community does so to a lesser extent. The thermodynamic effects of pressure on free energies of phase equilibria can be grouped into roughly three categories. The first involves solid-fluid-gas equilibria where the major thermodynamic effects are at relatively low pressure, roughly below 1 GPa, where the gas is strongly compressed, often through a critical point. The second includes simple condensed phase (solid-solid and solid-liquid) equilibria where the volume and entropy changes are relatively constant, leading to linear P-T relations, typically at 1-20 GPa. The third is the higher pressure regime, where major changes in electronic, magnetic, and vibrational structure cause complex phase behavior. Incorporating appropriate equations of state into CALPHAD calculations in each of these regimes presents both challenges and opportunities, which I will illustrate with some examples.

[O50] Exploring the parameter space of compositions and strengthening mechanisms, for the development of electroformed CuCr alloys, for rare event searches

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Key words: electroforming, radiopurity, alloys, ICME

In the last century, immense progress has been achieved in understanding the Cosmos over more than 45 orders of magnitude in length. Alas, fundamental questions remain about the nature of; a) Dark Matter (DM); and b) neutrinos. DM's existence, corresponding to 84.5% of the Universe's matter, is established via astrophysical observations and precise measurements. Several search approaches have been employed, but "direct detection" is the most prominent: aiming to observe DM from the Milky Way halo via its coherent elastic scattering off a nucleus.

Near-future direct DM search experiments must utilize increasingly radiopure detector materials and manufacturing processes in order to achieve their physics discovery potential. Electroformed Copper (Cu) achieves extreme radiopurity, however it is limited by its mechanical properties; high ductility and low strength.

Copper is the material of choice for rare event searches: it can be procured commercially at low cost and high purity, and it has no long lifetime isotopes. Alas, it may be contaminated during manufacturing and can be activated by fast neutrons from cosmic rays. In an effort to achieve even higher radiopurity, attention is focused on electroformed copper (EFCu), which has favourable radiochemical, thermal, and electrical properties. To fulfil the unique radiopurity requirements, experiments pioneer large-scale additive-free Cu electroformation, e.g. the on-going project ECUME. This novel technique, is advanced by Pacific Northwest National Laboratory (PNNL) and the NEWS-G experiment [1], leads to extreme radiopurities with contamination below 10^{-14} grams of ^{232}Th and ^{238}U per Cu gram. However, EFCu is highly ductile and of low strength, prohibiting its use for moving mechanical, high-pressure, and load-bearing parts. This is the main challenge towards the next generation detectors, such as NEWS-G's DarkSPHERE [2], a large-scale fully electroformed underground spherical proportional counter operating under high pressure to probe uncharted territory in the search for DM.

The most promising alloying element for improved strength of EFCu is Chromium (Cr). It has been experimentally demonstrated that small additions of Cr, combined with heat treatment and aging, improve strength by 70% [3]. However, Cr additions lead to impurities, and a compromise between strength and radiopurity is required by exploring a complex parameter space of compositions and strengthening mechanisms [4].

The PureAlloys project will address this challenge by developing high radiopure CuCr and CuCrTi alloys with significantly higher strength. PureAlloys will deliver a novel approach based on the Integrated Computational Materials Engineering (ICME) framework enabling rapid design of new, application-specific alloys for fields where thermodynamic and kinetic description of the system are crucial. Thus, the CALPHAD approach is essential. PureAlloys will push the boundaries in many fields, from fundamental science to industrial applications.

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Biographical Note

Dimitra Spathara is a materials scientist with research experience in structural and functional materials. She worked on surface melting of Ni-based superalloys at high temperatures, sponsored by Rolls-Royce plc. She was awarded a UKRI EU Guarantee Fellowship to explore further her interest in interphases and their role on alloys development for a range of applications.

[O51] Investigation of the Ni-Nb-Ta liquidus projection using the CALPHAD approach

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Key words: Ni-Nb-Ta, brazing, CALPHAD,

Active brazing metals are used for the joining of metals and ceramics and find application in many different industries. The active elements, such as titanium or zirconium, form a reaction layer with the refractory ceramic with good wettability for the brazing alloy. Besides Ti and Zr, the elements niobium [1] or tantalum can be used as active elements. Most active brazing alloys are based on Ag-Cu, Ag or Au alloys, which are limited by their corrosion resistance, low melting temperatures and high cost. In order to obtain noble metal free active brazing with good oxidation and corrosion resistance and showing high operating temperatures about 1000°C, we recently developed a method to find promising Ni based Ni-Nb-Ta alloys for metal ceramic joining.

The liquidus surface, isothermal and isopleth sections of the Ni-Nb-Ta system were calculated using Thermo-Calc and the TCNI11 database. 10 alloys with compositions along the calculated monovariant lines were selected and prepared by vacuum arc melting from high purity elements. Chemical analysis of the samples was conducted in the as-cast conditions by inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis. The melting range and the microstructure were both evaluated by as-cast samples as well as samples that were annealed. The microstructure was investigated by Scanning Electron Microscopy (SEM/EDX) on metallographic samples and the phase fractions were determined by image analysis employing a machine learning script. The melting behaviour was examined by differential thermal analysis (DTA) and the experimental results were then correlated to the calculations.

Next to the eutectic reactions L=> (Ni) + Ni_3(Nb,Ta) and L => Ni_3(Nb,Ta) + μ-phase, also the quasi-peritectic ternary phase reaction L + Ni_2Ta => μ + Ni_3(Nb,Ta) could be observed. The experimentally determined composition of the quasi-peritectic reaction point was differing from the calculated composition. The composition of the phases forming the eutectic and the corresponding transition temperatures were determined.

The experimental study of the ternary system was the basis for the development of multi-component Ni-Nb-Ta based active brazing alloys. High-throughput calculations were performed using a TC-Python script to optimize their melting range and to avoid brittle intermetallic phases, such as μ-Phase, Laves-Phase or sigma phase

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Biographical Note

Lisa-Yvonn Schmitt studied Material Science at the University of Saarland. She works at fem research institute as project manager and is also a PhD student at the IAM-AWP institute of Karlsruhe Institute of Technology (KIT). Her research topics are constitution and thermodynamics and bulk metallic glasses

[O52] About the ternary ω_o and O phase in the Ti-Al + Nb system

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Key words: Ti-Al, phase stability, phase transformations, phase equilibria

TiAl-based alloys have proven to be capable to replace Ni-based superalloys at temperatures up to about 800°C in applications such as, e.g., turbine blades in aero-engines. The most important alloying element, which is present in all commercial TiAl-based alloys, is Nb. Above a critical content, Nb can stabilize the ternary intermetallic phases ω_o and O, which significantly affect the material behavior. Therefore, a detailed knowledge of the composition and stability ranges of these phases as well as of their equilibria and microstructures they form with the Ti-Al phases α-Ti, α_2 (Ti_3Al), β/β_o-Ti, and γ (TiAl) is required.

A series of ternary Ti-Al-Nb alloys containing 17.5 to 45 at.% Al and up to 25 at.% Nb as well as some solid-solid and solid-liquid diffusion couples were prepared and annealed between 700 and 1000°C for up to 1500 h. The resulting microstructures and the types and compositions of phases were analyzed by scanning electron microscopy (SEM), electron probe microanalyses (EPMA), and high-energy X-ray diffraction (HEXRD) yielding isothermal sections at 700, 800, 900, and 1000°C [1,2]. In addition, the phase transformations involving the decomposition/formation of the ω_o and O phase were studied by differential thermal analysis (DTA) and *in situ* HEXRD [3]. The slow kinetics of these solid state phase transformations was analyzed by DTA experiments with varying heating rates allowing the determination of the true equilibrium transformation temperatures. The dependence of the measured transformation temperatures on the heating rate varies systematically with the complexity of the transformations. Both, ω_o and O phase are stable to above 900°C. For the ω_o phase, a new formula $(Ti,Nb)_2Al$ is suggested based on the measured composition range and its crystal structure type. The results also indicate that the phase field of the ω_o phase is split into two parts at 900°C because of the growing phase field of the ordered β_o phase.

The research was partially carried out within the scope of the European Union Clean Sky 2 project ADVANCE, which has received funding from the Horizon 2020 research and innovation programme under grant agreement No 820647.

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Biographical Note

Frank Stein is heading the group “Intermetallic Materials” at MPIE. His research focuses on intermetallic-based materials for structural applications such as Ti-aluminides, Fe-aluminides, and Laves phase containing systems. A central role is played by investigations of phase equilibria and phase transformations using a combination of different experimental methods.

[O53] Experimental Determination of Phase Diagram and Thermodynamic Assessment in the Cr–Ta Binary System

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Key words: Experimental Phase Equilibria, Thermodynamic assessment, High temperature alloy, Cr-based alloy

The development of novel alloys capable of withstanding high temperatures is a crucial goal in the thermal power generation and aircraft industries, aiming at reducing greenhouse gas emissions. Ni-based superalloys have exhibited remarkable mechanical properties and oxidation resistance in high-temperature applications. However, their temperature capabilities are close to the melting point of Ni. Recently, refractory metal-based alloys have attracted much attention for developing novel high-temperature materials beyond Ni-base superalloys. Chromium (Cr) has a potential as high-temperature material because of its higher melting point and lower density than Ni. Cr–Ta alloys [1] strengthened by the Cr_2Ta Laves phase have been reported to exhibit excellent high-temperature strength and fracture toughness, but improvement of the oxidation resistance is required. Although an accurate phase diagram is important for alloy design, reliable experimental data of phase equilibria are limited due to difficulty of the experiments at high temperatures. Therefore, in this study, experimental determination of phase diagram and thermodynamic assessment in the Cr–Ta binary system were performed.

The experiments were performed with attention to the heat treatment conditions and temperature accuracy at high temperatures up to 2000 °C. Cr–Ta alloys were heat-treated using an electrical heating furnace below 1400 °C and a high-frequency induction heating furnace with a two-color pyrometer above 1500 °C. Equilibrium compositions in alloy samples and composition profiles obtained in diffusion couples were measured by EPMA/WDS. DTA were also used to determine the transformation temperatures. The thermodynamic parameters in the Cr–Ta system were optimized using the PARROT module implemented in the Thermo-Calc software. The Gibbs energy for Ta was taken from the SGTE database compiled by Dinsdale [2]. On the other hand, that for Cr was modified from the SGTE data so that the melting point of pure Cr is 1861 °C which was determined experimentally in our recent study [3]. The sub-regular solution approximation for substitutional solutions was used to describe the liquid and bcc solid solution phases, and the two sublattice model was applied to the C14- and C15-Cr_2Ta Laves phases.

The phase diagram was determined in the whole composition range of the Cr–Ta system. The single-phase region of the C14- and C15-Cr_2Ta phase extended from stoichiometry ($x_{Ta} = 0.333$) to both sides, as shown in Fig. 1. By composition measurements of the diffusion couples, it was indicated that the phase boundary between C14- and C15-Cr_2Ta phases exists at higher temperature than that reported by Rudy [4]. As shown in Figure 1, the phase diagram calculated using the optimized parameters showed reasonable agreement with the phase equilibrium data experimentally determined in this work.

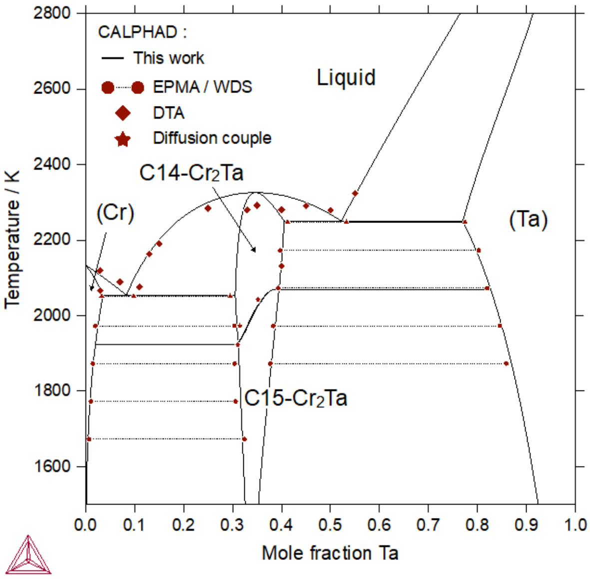

Figure 1. Calculated phase diagram of the Cr–Ta system.

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Biographical Note

Kazushige Ioroi is a Postdoctoral Researcher at Tohoku university, Japan. His research interests are experimental investigation of phase equilibria, thermodynamic assessment, and high temperature alloy.

[O54] Calphad Science and the Art of Steel Making

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Key words: Calphad Tools, Metallurgy of Solidification, Growth restriction factor, Semi-solid casting, Hot cracking, Green(er) Steel Development

This a series of simple observations, based on a discussion that has officially started with

1) a recent visit of three distinguished colleagues from Cambridge, to image a European Collaboration for the development of greener steels
2) a less recent project, XmlTDB, leaded by prof. Bo Sundman, presented elsewhere in this Calphad meeting
3) an ongoing less recent project, Calphad Tools for the Metallurgy of Solidification which has been presented in a small collection of papers in a special issue coordinated by two of the authors here, and, specifically for Fe-bases alloys, in a more recent paper by the same authors.

The collection of papers is mainly aimed at proposing a common simplified approach for different classes of materials and processes related to the solidification of metallic alloys. The whole activities have the aim of giving a common framework which could be exploited by any Calphad software and solidification model provided a relevant thermodynamic and or kinetic database would be utilized. It has also the aim of providing a quick "cookbook" approach in order to exploit the wide availability of software and databases, proposing not necessarily for a specific software the relevant steps to extract from say the Scheil solidification curve - which is normally presented in Calphad software as the relationship between the solid fraction fs with the solidification temperature T fs(T). We believe that calculating the numerical derivative is able to give a function which may depict in a simple but effective way the main features of solidification processes; while this approach has been presented in the past only for the growth restriction factor Q for solidification, some simple mathematics demonstrate that is possible to express two other important approaches customarily used in semi-solid processing and in the evaluating hot tearing.

Specifically, the derivative function of T(fs) could be exploited:

for fs-> 0 for the growth restriction factor

for 0.3<fs<0.7 for semi-solid processing (i.e. rheocasting and thixoforming)

for fs->1 for evaluating hot tearing

Implicitly, this approach has been already worked out in most of the papers presented in the special issue. Here we will propose the relevant calculations and - where available - some open thermodynamic databases in order to reproduce results with different Calphad software using just one function.

Calphad (Calculation of Phase Diagrams) approach has evolved from an empirically based approach to thermodynamics of alloys to a science of its own, which is increasingly more scientific. What about Steelmaking? Steelmaking is still considered an Art, even though there are books and academic courses. And this may be even more true considering to develop radically new steels, with compositions different from well accepted industrial standards. While the final mechanical properties and the response heat treating is the final aim of compositional improvements, variations very simple Calphad modelling could help to face different difficulties that normally are faced when casting typically large (100 t) experimental heats.

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Biographical Note

Fabio Miani is professor of Metallurgy in the University of Udine. In a Horizon project for designing a semi-solid casting machines for Copper alloys, he met Maria Balart then at Brunel University who was writing papers on Copper Alloys. And he developed simple Calphad tools to design successfully the machine. Later he had the pleasure to meet and collaborate with prof. Harry Bhadeshia for teaching activities and prof. Bo Sundman for the Calphad XMLtdb project

[O55] CALPHAD-based modeling of pearlite transformation in multicomponent steels

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Key words: pearlite, transformation, diffusion, modeling

Based on the CALPHAD thermodynamic and kinetic databases for steels, a model for austenite-to-pearlite transformation in multicomponent steels has been established[1] and implemented in the Thermo-Calc Software.

The model for growth rate considers not only classic ingredients (formation of ferrite–cementite interface, volume diffusion, boundary diffusion, and optimization of lamellar spacing) but also finite austenite-pearlite interfacial mobility which resolves some previous difficulties. A transition between orthopearlite and parapearlite is realized by optimizing the partitioning of substitutional alloying elements under constrained carbon equilibrium between ferrite and cementite. Solute drag effect is included to account for the bay in growth rate curves. The modeling approach for steady-state growth can also be extended for non-steady-state growth of the so-called divergent pearlite.

Grain boundary nucleation rate is modeled as a function of chemical composition, driving force, and temperature, with consideration of grain boundary equilibrium segregation. Overall transformation kinetics is calculated from growth rate and grain boundary nucleation rate. Further theoretical and experimental work are suggested for generalization and improvements.

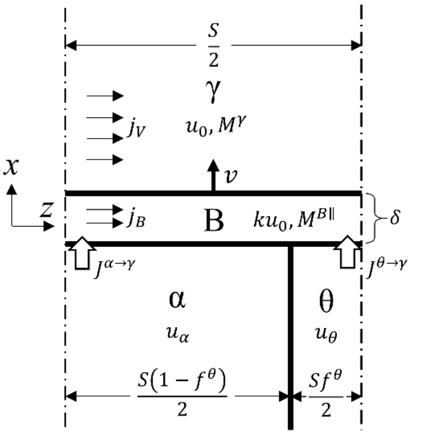

Figure 1. Schematic for the pearlite transformation front

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Biographical Note

Jiayi Yan received BEng from Tsinghua University (China) and PhD from Northwestern University (US). He worked at KTH as a postdoc and later at Thermo-Calc Software and QuesTek Europe in Sweden, before joining Tsinghua as a research assistant professor. His main research interest is CALPHAD-supported ICME materials design.

[O56] CALPHAD Application in the Removal of $MgO·Al_2O_3$ Spinel Inclusions during Vacuum Metallurgy

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Key words: $MgO·Al_2O_3$ spinel, RH vacuum, Thermodynamic calculation, Inclusion

$MgO·Al_2O_3$ spinel is a common inclusion in aluminum-killed steel, which detrimentally impact the fatigue performance of bearing steel. The effectiveness of $MgO·Al_2O_3$ inclusion removal in the Ruhrstahl-Heraeus (RH) vacuum furnace is widely acknowledged. A consensus among researchers, as noted by various studies [1-4], attributes this phenomenon to the distinct wettability exhibited by solid and liquid inclusions within molten steel.

The removal of spinel inclusions in bearing steel characterized by varying carbon content and distinct vacuum degrees was investigated by industrial experiments and thermodynamic calculations. A new removal mechanism of $MgO·Al_2O_3$ inclusions during RH process is put forward: $4[C] + MgO·Al_2O_3 = [Mg] + 2[Al] + 4CO$. Vacuum pressure and [C] content are two key factors to determine the removal efficiency of $MgO·Al_2O_3$ inclusions during RH process.

The experimental steel grades were low-carbon 20CrMnTi, medium-carbon 42CrMo, and high-carbon GCr15. Based on the calculated decomposition pressure range of spinel for 20CrMnTi, 42CrMo, and GCr15, the stability diagram of $MgO·Al_2O_3$ inclusions under different [C] contents and vacuum pressures are obtained (Figure 1). The stability of $MgO·Al_2O_3$ inclusions following the RH process is contingent upon the vacuum pressure in relation to the initial decomposition pressure. Specifically, when the vacuum pressure surpasses the initial decomposition pressure, the $MgO·Al_2O_3$ inclusions endure without removal post-RH. Conversely, in instances where the vacuum pressure falls below the threshold of complete decomposition pressure, the $MgO·Al_2O_3$ inclusions prove unstable and are entirely eradicated subsequent to RH. Within the vacuum pressure range corresponding to decomposition, a partial removal of $MgO·Al_2O_3$ inclusions transpires following RH treatment. The removal efficiency of $MgO·Al_2O_3$ inclusions for these steels at 5 kPa is 3.5%, 56.1%, and 94.6%, respectively.

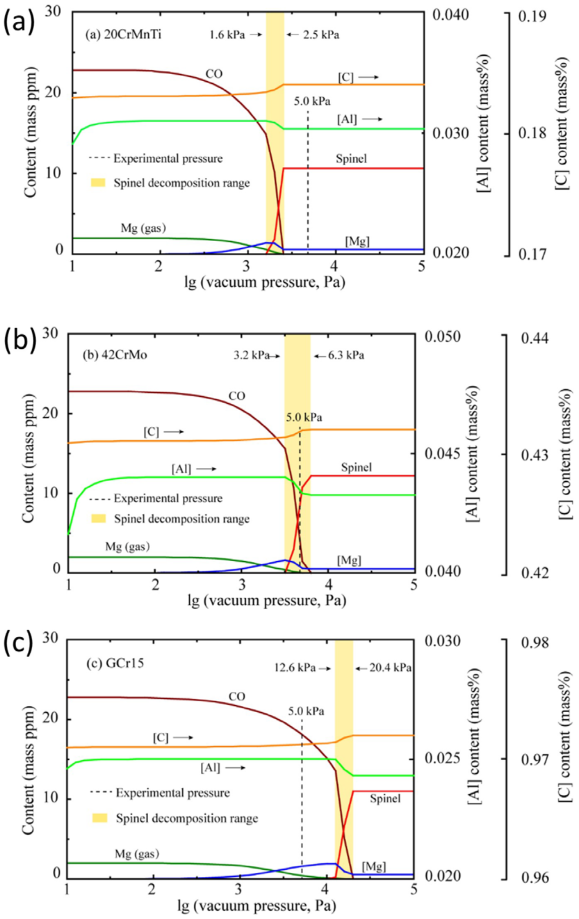

Figure 1. Effect of vacuum pressure on the stability of $MgO·Al_2O_3$ spinel inclusions for (a) 20CrMnTi, (b) 42CrMo, and (c) GCr15 at 1873 K.

Biographical Note

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[O57] Applying CALPHAD Data to an Industrial Production Process: Kinetic Simulation of a Ladle Furnace

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Key words: Process Metallurgy, Oxides, Reaction Kinetics

CALPHAD assessments and the underlying phase equilibria, thermodynamic and kinetic experiments that form the back-bone of any assessment have a high (and unfortunately sometime underrated) value, not only in pure science but also for industrial application. Published assessments however mostly cover only a few elements, typically 3 or 4, restricting their application to a few specific cases. The real power of the CALPHAD method lies in combining these assessments of lower order systems into large databases covering many elements and wide composition ranges.

Once such database is Thermo-Calc's TCOX database that is currently on release 13 and contains the elements Al, Ar, B, C, Ca, Co, Cr, Cu, F, Fe, Gd, H, Hf, K, La, Mg, Mn, Mo, N, Na, Nb, Ni, O, P, S, Si, Ti, V, W, Y, Yb, and Zr. The metallic phases are taken from the steel database, TCFE, to which a comprehensive set of oxide, sulfide and fluoride phases, as well as a gas phase are added. The liquid is modeled using the ionic 2-sublattice liquid model that allows a consistent description of the liquid from metallic to non-metallic. One main application area of the TCOX database is steelmaking and -refining where the liquid phase is of particular importance as unwanted impurities are removed from the steel by making use of partitioning of elements between the metallic- and the oxide liquid ("slag"). But other thermodynamic reactions are equally important, such as the selective oxidation of steel components by changing oxygen partial pressure or the temperature change on addition and dissolution of alloy additions, gases or heat. Apart from thermodynamic properties, the TCOX database also contains a number of thermophysical properties that are also of practical importance, such as the viscosity, surface tension and electric conductivity of the liquid phase.

Together with the TCOX database, the Process Metallurgy Module (PMM) has been developed with the purpose of making it easier to set-up thermodynamic calculations involving metallic and non-metallic materials. A very powerful feature of the PMM is the functionality of simulating time dependent processes. The kinetics of processes is accounted for by assuming that only a part of the two reacting materials (for example the liquid steel and the covering slag in the steel refining process) reach equilibrium in a given time step. This kinetic model has come to be known as the Effective Equilibrium Reaction Zone (EERZ) model and has been applied to several metallurgical processes by the group of Van Ende and Jung [1] over the last few years.

The models for kinetic simulation have been developed further at Thermo-Calc and been implemented to simulate the day-to-day operation of a real industrial ladle furnace. All the required inputs for the simulations are taken directly from the steel-plant level 2 process control system and the simulations can be run automatically on a day-to-day basis (Figure 1). The results of the simulations are made available to the plant engineers as heat reports that can be accessed through the plant intra-net. Details and first results of this project will be presented.

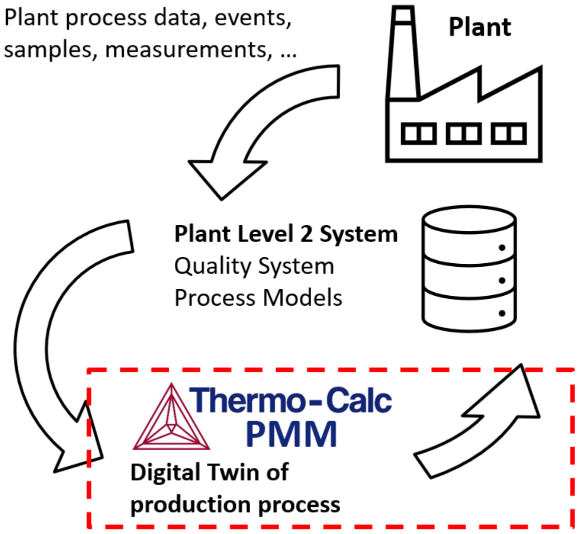

Figure 1. Process simulations using the Process Metallurgy Module (PMM) are run automatically using process data from the day-to-day production process of the steel plant.

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Biographical Note

Nicholas is an application specialist at Thermo-Calc Software. He did his PhD on CALPHAD assessments of oxide systems at ETH in Switzerland under Bengt Hallstedt using Thermo-Calc, then did a PostDoc under Arthur Pelton at CRCT in Montreal working with FactSage. Later he moved to industry, working as a metallurgist for the SMS Group before joining Thermo-Calc.

[O58] Extended calculation model of grain boundary segregation and its application to segregation engineering

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Key words: CALPHAD, grain boundary segregation, parallel tangent law, structural materials

It is a well-known that alloying elements and impurities in polycrystalline materials tend to segregate at the grain boundary (GB), which can have a significant impact on the microstructure formation and mechanical properties of structural materials. Recent experimental studies on GB segregation using atom probe tomography have yielded noteworthy results in the quantitative measurement of GB segregation. However, it is worth noting that a precise thermodynamic calculation of GB segregation in practical materials containing multiple alloying elements and impurities has not yet been carried out. In this study, we present the practical calculation method and results of GB segregation in structural materials using the CALPHAD method.

The parallel tangent law proposed by Hillert [1] has been extended to the multicomponent system up to 10 alloying or impurity elements and applied to calculate the segregated compositions using the following conditions for the chemical potential of the constituent elements:

$$\mu_M^{\mathrm{GB}} - \mu_M^{\mathrm{matrix}} = \mu_{X1}^{\mathrm{GB}} - \mu_{X1}^{\mathrm{matrix}} = \mu_{X2}^{\mathrm{GB}} - \mu_{X2}^{\mathrm{matrix}} = \cdots$$

where M is the solvent and X1, X2, ⋯ are alloying or impurity elements. The GB phase was assumed to have a random structure with the same free energy as the liquid phase. The Gibbs energy of the liquid and matrix phases were obtained from Thermo-Calc using thermodynamic databases via TQ interface and used for the calculation. The effect of (1) grain size, (2) grain boundary energy and (3) diffusion of alloying elements were also considered in this calculation, as shown in Fig. 1.

Based on experimental results of P and Mn segregation in αFe measured by STEM-EDS, calculation conditions and interpretation of the experimental results are discussed.

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Biographical Note

I. Ohnuma is a member of the Computational Structural Materials Design Group at NIMS. His research interests focus on alloy design and microstructure control of various practical materials using the CALPHAD method.

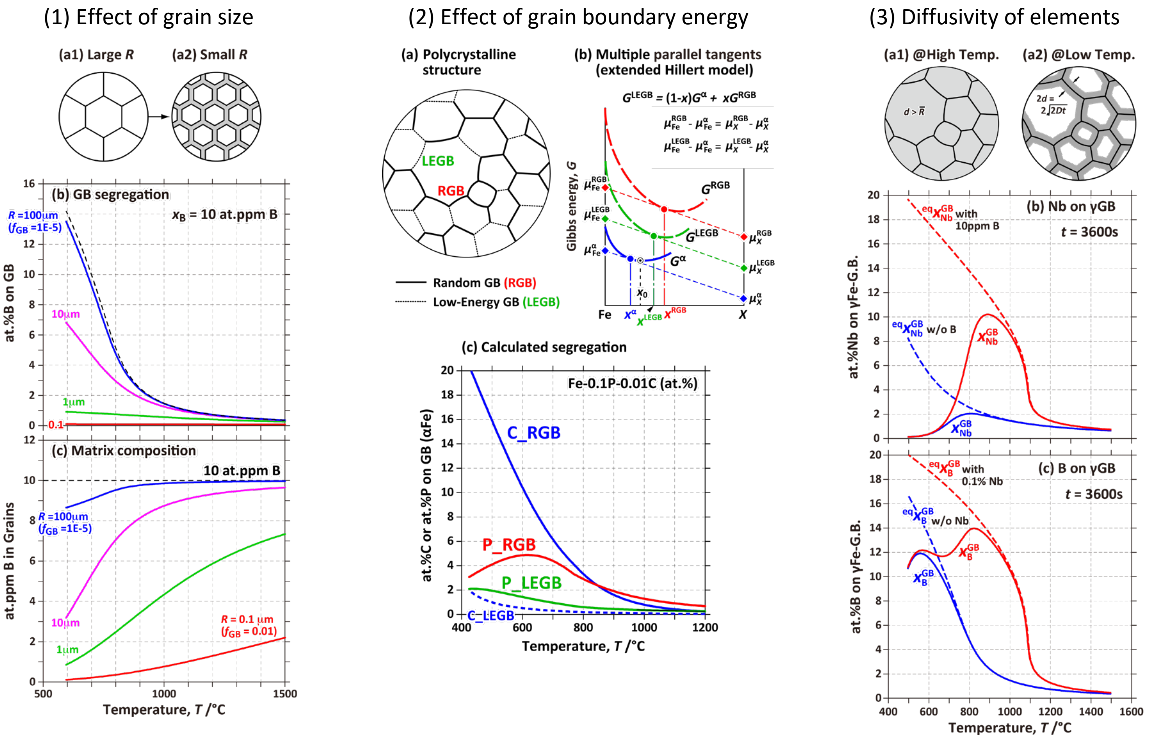

Fig.1 Extended models for calculation of grain boundary segregation using CALPHAD method.

[O59] How DSC measurements and CALPHAD helps to avoid breakouts during the continuous casting of peritectic steels

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Key words: peritectic phase transformation, continuous casting of steel, Fe-C-Si-Mn-Al-P-S, DSC

The continuous casting (CC) process for steel is the most important casting technology, whereby the initial solidification conditions in the water-cooled copper mould significantly depends on the steel composition and the associated phase transitions. In times of increasing digitalization of the CC process, the availability of high-precision thermodynamic data is of great importance. Particularly "hypo-peritectic steels", where the peritectic phase transformation (L+BCC→BCC+FCC→FCC) coincides with the final solidification and ends in the solid apply as critical, visualized in **Figure 1**. These steels exhibit unfavorable process behavior (e.g. uneven solidification, breakouts and increased temperature fluctuations (TVC) in the mold, see **Figure 2**) and show a lower product quality. If peritectic steels are pre-identified in the production program, they can be produced under controlled conditions through targeted operational requirements (e.g. selected casting powders, adjusted casting speed).

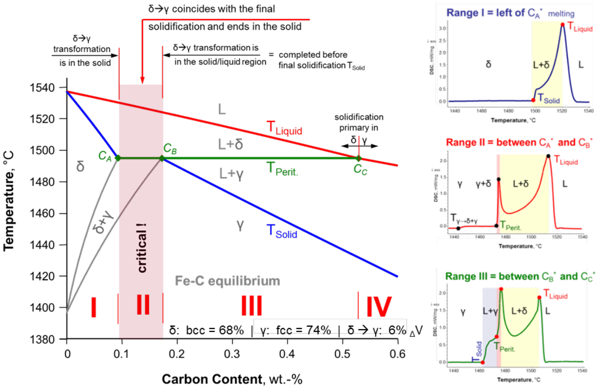

Figure 1. Fe-C equilibrium diagram with the critical peritectic range and characteristic DSC-signals.

Practical evaluation of selected laboratory tests shows that the Dynamic-Heat-Flow-Differential-Scanning-Calorimetry (DSC) enables a clear identification of peritectic steels, as the peritectic phase transformation is associated with a significant enthalpy step and its measurement is a clear proof, as shown in **Figure 1** [1]. Systematic DSC measurements of selected binary, ternary, and quaternary systems, based on model alloys, and the generation of thermodynamic data (LIQUID, FCC, BCC stabilities in the Fe-C-X-Y system) followed by the optimization of databases has been actively carried out at the Chair of Ferrous Metallurgy in Leoben.

In order to predict whether an individual alloy shows an increased risk of a peritectic casting behavior, an index (QI_{SHE} [3]) was applied. Based on the actual steel composition and the use of a thermodynamic databases the following calculation was performed $QI_{SHE} = 4/3(f^{\delta}_{SOL} - f^{\delta}_{30C})$, where f^{δ}_{SOL} is the delta ferrite fraction at the solidus temperature and f^{δ}_{30C} is the delta ferrite fraction at T_{SOL} - 30°C. A validation of the calculated QI_{SHE} data with the thermal behaviour in the CC-mould, in this case the temperature variation coefficient (TVC), shows an excellent correlation, illustrated in **Figure 2**. This comprehensive study, with more than 1400 batches and the systematic evaluation approach [2], clearly proves that thermodynamic calculation can identify peritectic steels and thus increase the process safety. Statistically prepared process data and experimentally verified thermodynamic data are the basis for the development and validation of demanding process models.

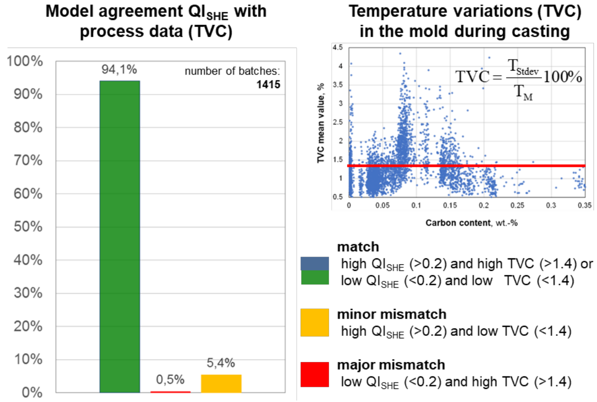

Figure 2. Comparison of thermodynamic calculations (QI_{SHE}) with process behaviour (TVC).

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Biographical Note

Peter Presoly is a senior scientist at the Chair of Ferrous Metallurgy at Montanuniversitaet Leoben. He has been working for 15 years on the field of thermal analysis, Calphad and various industrial projects.

[O60] Hillert-style irreversible thermodynamics and the entropy production

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Key words: diffusion, heat flow, chemical reactions, transport processes

The entropy production of irreversible processes such as diffusion, heat flow or molecular reactions plays a major role in the kinetics of the processes. The driving forces are derived from the entropy production and when combined with kinetic properties they allow a mathematical description of the processes.

Hillert (1) applied Gibbs' well-known equation for a multicomponent system but added the entropy-production term which he obtained by combining the first and second law for a general non-equilibrium process. This important modi-fication allows a general treatment which many researchers are not aware of. The aim of the presentation is to give an overview of Hillert's approach and some examples.

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Biographical Note

John Ågren is professor emeritus of physical metallurgy. He has a PhD from KTH with Mats Hillert as supervisor. He is an expert in thermodynamics and kinetics of phase transformations. He has published more than 200 scientific articles.

[O61] On Gibbs Equilibrium and Hillert Nonequilibrium Thermodynamics

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Key words: laws of thermodynamics, CALPHAD modeling

During his time at Royal Institute of Technology (Kungliga Tekniska högskolan, KTH) in Sweden, the present author learned nonequilibrium thermodynamics from Mats Hillert. The key concept is the separation of internal and external variables of a system. In equilibrium thermodynamics derived by Gibbs, the internal variables are not independent and can be fully evaluated from given external variables. While irreversible thermodynamics led by Onsager focused on internal variables though often mixed with external variables. Hillert integrated them together by first emphasizing their differences and then examining their connections. His philosophy was reflected by the title of his book "Phase Equilibria, Phase Diagrams and Phase Transformations" that puts equilibrium, nonequilibrium, and internal processes on equal footing[1].

In honoring Hillert, the present author reflects his experiences with Hillert in last 35 years and expresses his gratitude for all the wisdom and support from him in terms of "Hillert nonequilibrium thermodynamics" or simply "Hillert thermodynamics". The key concept in Hillert thermodynamics is the entropy production, $\boldsymbol{d_{ip}S}$, due to internal processes (*ip*) as shown in the following equation

$$dG = -SdT + VdP + \sum \mu_i dN_i - Dd\xi + D_2(d\xi)^2$$

To apply Hillert thermodynamics, it requires the accurate prediction of entropy as a function of external and internal variables. Over the last two decades, the present author's group has developed a multiscale entropy approach (recently termed as zentropy theory) that integrates DFT-based quantum mechanics and Gibbs statistical mechanics and can accurately predicting entropy and free energy of complex materials[2]. Using Hillert thermodynamics, the present author developed the theory of cross phenomena beyond the phenomenological Onsager Theorem[3,4]. The zentropy theory and theory of cross phenomena jointly provide quantitative predictive theories for experimental observables[5] and can be used as input data for CALPHAD modeling of individual phases.

Following the successful applications of the zentropy theory for magnetic materials and the theory of cross phenomena to thermoelectric materials[2,3,5], the present author's group has been working on applying the theories to predict properties of ferroelectric and superconducting materials. The key challenge is to obtain all configurations and their multiplicity. While basic theoretical understanding of ferroelectric and superconducting materials have been developed[3], the prediction of their properties remain elusive.

In this presentation, both Gibbs and Hillert thermodynamics will be discussed[6]. It will be shown that the central concept of lattice stability in CALPHAD thermodynamic modeling reflects an important internal variable in Hillert thermodynamics. With a brief discussion of zentropy theory and theory of cross phenomena, our recent progresses on prediction of free energy and phase transitions of ferroelectric and superconducting materials will be presented.

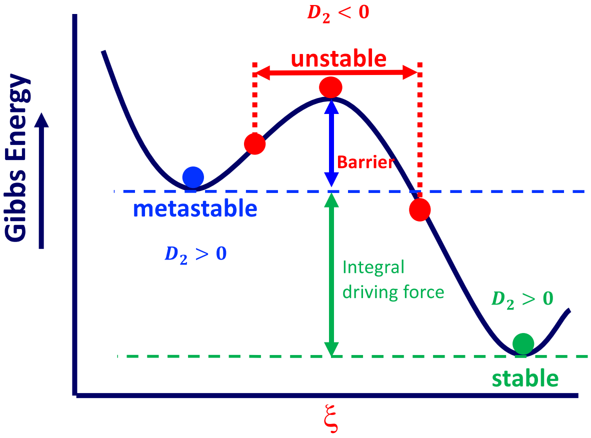

Figure 1. Schematic diagram of energy landscape as a function of one internal variable[2].

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Biographical Note

Zi-Kui Liu is the Dorothy Pate Enright Professor of Materials Science and Engineering at The Pennsylvania State University. He has been at the Pennsylvania State University since 1999, the Editor-in-Chief of CALPHAD journal since 2001, and the President of CALPHAD, Inc. since 2013.

[O62] The calculation of kinetic interface contact condition phase diagram and its applications to additive manufacturing

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Key words: kinetic phase diagram, solute drag and trapping, additive manufacturing

Due to the development of additive manufacturing (AM) technologies, there are clear needs to predict solidification microstructure formed under rapid solidification condition. It is well established that rapid solidification leads to the formation of a rich spectrum of microstructures. The core in predicting rapid solidification or additive-manufactured microstructure lies in the treatment of the deviation from thermodynamic equilibrium at the fast-migrating Solid-Liquid interface. This deviation is caused by solute drag and trapping, and a good understanding of the deviation, or kinetic interface contact condition phase diagram, would enable manipulating the alloy's microstructure during additive manufacturing and producing alloys with 'programable' properties.

In this contribution, we will present our recent activities on the calculation of kinetic phase diagram and its applications to additive manufacturing [1][2][3][4]. We will present an overview of the kinetic phase diagram calculation models including the continuous growth model, partial solute drag model and our novel solute drag and trapping model [4]. While our novel treatment is still built on irreversible thermodynamics and linear kinetic law, its novelty lies in taking into consideration of an additional interfacial kinetic process that adjusts the compositions of crystallizing liquid phase composition before they are absorbed into the interface. This novel treatment can reveal the nature of solute drag parameter. Then we move to the models' numerical algorithm and its implementation in k-Cal software. The calculated results with k-Cal software for A-B hypothetical ideal solution phases, binary and multi-component alloys will be presented. The focus is on highlighting one of the major advantages of our novel treatment. Finally, we will illustrate the practical values of the kinetic phase diagram for additive manufacturing by discussing the coupling of the kinetic phase diagram with columnar and equiaxed transition model and kinetic growth restriction factor calculation.

We conclude our presentation with the statement our novel solute drag and solute trapping model enables the calculations of kinetic phase diagram without any numerical tuning parameter. The model is expected to be useful in many scenarios to guide the optimization of AM processing parameters and alloys design. For the future work, the application of the proposed model to solid state phase transformation, i.e., austenite to ferrite transformation, is in progress.

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Biographical Note

Q. Du received his doctorate degree in materials science and engineering from Chinese Academy of Sciences. He is a Senior Research Scientist at SINTEF Norway. His research interests focus on through process modelling, meso-scale microstructure modeling, mechanical property model, computational thermodynamics, and simulation software development for metallic materials.

[O63] Diffusion of methane in metal-organic frameworks: An atomistic approach

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Key words: Methane adsorption, diffusion path, HKUST-1, Grand canonical Monte Carlo simulation, molecular dynamics simulation

Methane is a greenhouse gas with a warming potential 28 times higher than that of carbon dioxide [1], so should be removed to mitigate global warming. However, the removal or decomposition of methane using catalysts is not trivial due to its structure stability [2]. Capturing methane using adsorbents is also a possible method to remove it. Among the adsorbents, the most promising material as a methane adsorbent is a metal-organic framework (MOF) [3].

MOFs are solid structures made up of inorganic metal ions and organic linkers that are bound together through coordination bonds. The metal ions serve as nodes or centers, while the organic linkers serve as a bridge between them, creating a complex two-dimensional or three-dimensional network. Due to this network, MOFs can adsorb gas like methane, and the adsorption performance depends on the geometrical disposition of the network, the pore size, the morphology of the cavities, and the channels distribution.

To date, many types of MOFs have been developed, and among them, HKUST-1 ($[Cu_3(TMA)_2(H_2O)_3]_n$ where TMA is benzene-1,3,5-tricarboxylate) is reported to exhibit the best methane adsorption performance. In particular, this performance is further improved when activated by treatment with methanol. Despite this performance, the precise mechanism by which methane is adsorbed on HKUST-1 has not yet been elucidated.

During the activation, the labile ligand-bearing metal site is removed, creating a coordinatively unsaturated site called the open metal site. These open metal sites are thought to enhance the methane adsorption of HKUST-1. Here, this methane adsorption is fundamentally related to diffusion because methane is stable and no chemical bonds are created between HKUST-1 and methane. In this respect, the effect of this open metal site on diffusion needs to be investigated.

In this study, we investigated how methane adsorption and diffusion pathways vary with the presence or absence of open metal sites. To do so, we calculated the amount of methane adsorption using Grand canonical Monte Carlo simulations and the diffusion pathways using molecular dynamics simulations for the inactivated and activated structures. The reliability of the HKUTS-1 sample used in these simulations was confirmed by comparing the XRD patterns with the experiments in Figure 1.

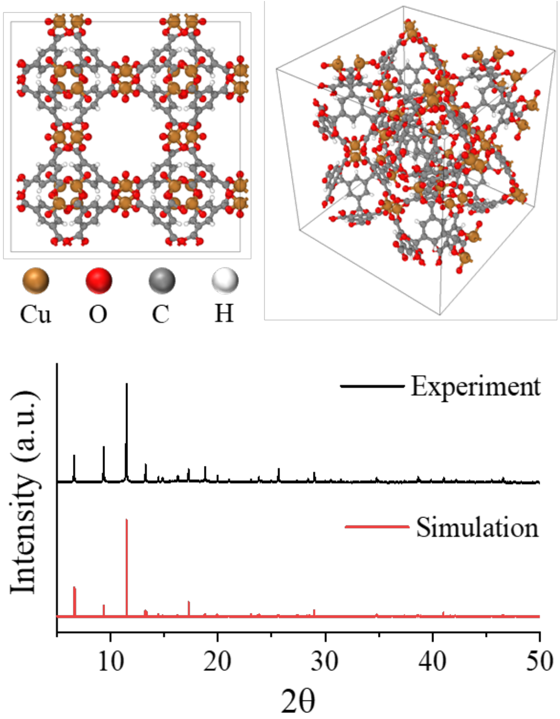

Figure 1. Structure of HKUST-1 and its simulated XRD peaks along with experimental peaks.

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Biographical Note

Hyo-Sun Jang is currently a senior researcher of the Division of Materials Digital Platform at the Korea Institute of Materials Science (KIMS). She received her Ph.D. degree at the Department of Materials Science and Engineering at POSTECH in 2021. Her research interests include molecular dynamics, first-principles calculations, computational thermodynamics, and machine learning in structural alloys and metal-organic frameworks.

[O64] Evaluation of crystallization behavior during rapid cooling process in Al-Fe-M (M = Mg, Si, Mn) alloys by combining the CALPHAD and kinetic approach

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Key words: crystallization, rapid cooling, metastable phase, entropy of fusion

In the metal additive manufacturing process, it is known that a metastable microstructure that differs from the equilibrium state may be obtained due to rapid solidification of the metal powders after melting. For example, in Al-Fe binary alloys, it has been reported that the metastable Al_6Fe phase is formed instead of the stable $Al_{13}Fe_4$ phase in alloys with Fe content below about 3 mass% [1]. Therefore, it would be useful to obtain information on the formation of the stable and metastable phases in the microstructures obtained in the additive manufacturing process for various alloy systems. In this study, the crystallization behavior of the stable $Al_{13}Fe_4$ and the metastable Al_6Fe phases in Al-Fe alloys during rapid cooling was evaluated by combining the calculation of phase diagrams (CALPHAD) method and the Davies-Uhlmann kinetic formulations [2,3].

In the computations, time-temperature-transformation (TTT) curves were obtained based on the Davies-Uhlmann kinetic formulations [2,3], which are a measure of the time necessary for the formation of detectable amounts of a crystalline phase from a supercooled liquid as a function of temperature. Among the input parameters for the calculation of the TTT curves, the driving force for crystallization of the crystalline phases was derived based on the CALPHAD method using the Gibbs energy functions of each phase reported in a previous study [4].

As an example of the calculated results, the TTT curve for crystallization from an Al-1 mass% Fe liquid alloy is shown in Fig. 1. From the calculated results, the nose of the TTT curve for the metastable Al_6Fe phase is located on the shorter time side than that for the stable $Al_{13}Fe_4$ phase, and it is predicted that the metastable Al_6Fe phase is formed by rapid cooling. This is suggested to be related to the fact that the entropy of fusion of the metastable Al_6Fe phase is smaller than that of the stable $Al_{13}Fe_4$, resulting in a smaller free energy for nucleation. On the other hand, in the Al-5 mass%Fe alloy, the nose of the TTT curve of the stable $Al_{13}Fe_4$ phase is predicted to be located on the shorter time side, indicating that the calculated crystallization behavior can reproduce the experimental results. In the presentation, the calculated results for ternary alloys will also be presented.

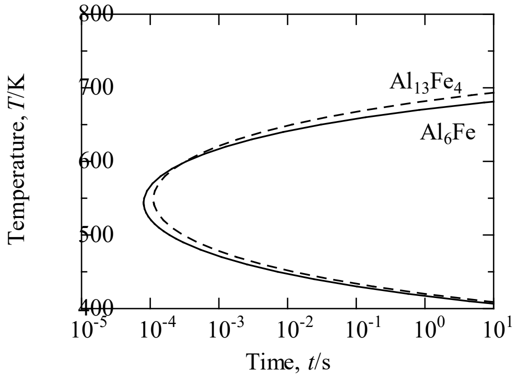

Figure 1. Calculated TTT curves for the crystallization of the stable $Al_{13}Fe_4$ and the metastable Al_6Fe phases from an Al-1 mass% Fe liquid alloy.

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Biographical Note

Tatsuya Tokunaga is professor of Materials Science and Engineering at Kyushu Institute of Technology. His main research interests are phase equilibria, phase transformation and computational thermodynamics in alloys based on the CALPHAD method and their applications to engineering materials.

[O65] Solute Induced Defect Phase Transformations in Grain Boundaries

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Key words: grain boundary, defect phase transition, defect phase diagram

The study of defect phases is important for designing nanostructured metals and alloys. Grain boundaries (GBs) form one class of defects that directly influence materials properties, such as deformability and strength. At the same time, alloying can introduce GB phase transformations and can therewith alter mechanical performance.

In this work, we will discuss the concept of GB phase diagrams for several examples. The focus will be on the defect phases of a $\Sigma7$ $(12\bar{3}0)$ [0001] 21.78° symmetric tilt GB in hcp Mg. Ab-initio simulations as a function of stress and temperature (using quasi-harmonic approximation) are performed, and different types of phase transformations are revealed. To this end, the influence of the chemical degree of freedom on the defect phases is studied for the example of Ga addition, using an efficient screening approach that combines empirical potentials and accurate ab-initio calculations. By exploiting the concept of defect phase diagrams, a phase transformation from the T to the A structural type and as well as a systematic transition of the segregation site preference is revealed. The results qualitatively agree well with experimental observations from scanning transmission electron microscopy. The underlying physical mechanisms have an impact on grain-boundary engineering in metallic alloys.

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Biographical Note

Tilmann Hickel is head of the division “Materials Informatics” at the Federal Institute for Materials Research and Testing (BAM). He studied physics at Humboldt University Berlin, where he also performed his PhD. In 2005 he joined the Max-Planck-Institut für Eisenforschung, where he became head of the group “Computational Phase Studies”.

[O66] Order-disorder transitions on alloy surfaces: From Monte Carlo to analytical models

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Key words: surface phase diagram, Monte Carlo, density functional theory, thermodynamic modeling

In this work, we propose an analytical thermodynamic model for constructing surface phase diagrams. The model is capable of accurately describing the composition-temperature dependence of order-disorder transitions on the surface. It provides a promising alternative to the sublattice model, which is commonly used in the CALPHAD framework to describe solution phases with ordering, as we demonstrate using the system of Mg surface with Ca substitutions.

First, we show the surface phase transition with grand-canonical Monte Carlo simulation coupled with cluster expansion. The system undergoes a transition from a solid solution (disordered) phase at high temperature, Ca-poor condition to an ordered phase with 1/3 Ca coverage at low temperature, Ca-rich condition. Then we show that with an analytical model that assumes Boltzmann distribution of the phase fractions, it is possible to accurately reproduce the critical transition condition. Last, we compare our method to the sublattice model. The proposed method provides a computationally highly efficient and easy-to-parametrize analytical model for describing order-disorder transition. These features make it interesting to be employed for bulk phase diagrams.

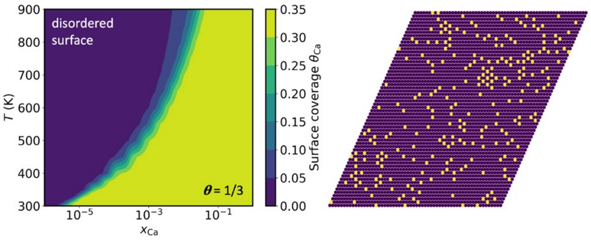

Figure 1. (Left) Surface segregation heatmap for Ca segregation to the Mg (0001) surface as a function of bulk Ca concentration. The dashed lines show the experimentally determined solubility of Ca in Mg bulk. (Right) The surface configuration of the mixed order-disorder phase obtained with grand-canonical Monte Carlo.

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Biographical Note

Jing Yang is a postdoctoral researcher at Max-Planck-Institut für Eisenforschung. She obtained her Ph.D in materials science and engineering at Massachusetts Institute of Technology in 2020. Her research focuses on thermodynamic modeling of materials defects and its applications to structural materials.

[O67] A generalized approach for rapid entropy calculation of liquids and solids

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Key words: density functional theory, thermodynamics, entropy

Entropy is a fundamental concept in thermodynamics, representing the degree of disorder or randomness in a system. While crucial, accurately computing entropy is challenging due to its non-intuitive nature and the complexity of accounting for the microstates of a system.

We aim to formulate a generalized methodology to quantify configurational entropy across a wide spectrum of phases, including defect-free solids, mechanically unstable phases, and liquids. The delineation between configurational entropy S_{conf} and vibrational entropy S_{vib} requires a careful approach to ensure the inclusion of all significant states without any overlap, or redundancy, thereby preserving the integrity of the entropy partitioning process. Specifically, the successful partitioning of S_{conf} and S_{vib} hinges upon satisfying two critical criteria:

- The inclusion of all relevant states, omitting none that could contribute meaningfully to the system's entropy, and
- The avoidance of double counting any state, ensuring no overlaps or redundancies in the accounting of states.

In this work we build a comprehensive methodology for the fast computation of entropy across both solid and liquid phases. The proposed method utilizes a single trajectory of density functional theory (DFT) molecular dynamics (MD) to facilitate the calculation of entropy. We propose a method to calculate the configurational entropy as information entropy [1, 2] of nearest neighbors, while the vibrational entropy is evaluated through phonon density of states from velocity autocorrelation [3] in MD.

We illustrate, through a variety of examples, that this method is both a versatile and valid technique for characterizing the thermodynamic states of both solids and liquids. Furthermore, this method is employed to expedite the calculation of melting temperatures, demonstrating its practical utility in computational thermodynamics. The transition temperatures of the various materials investigated are summarized in Fig. 1. The method we have developed demonstrates a high degree of accuracy, typically within a 100 K margin, for the calculation of phase transition temperatures. Such accuracy serves to corroborate the efficacy of our entropy computation approach.

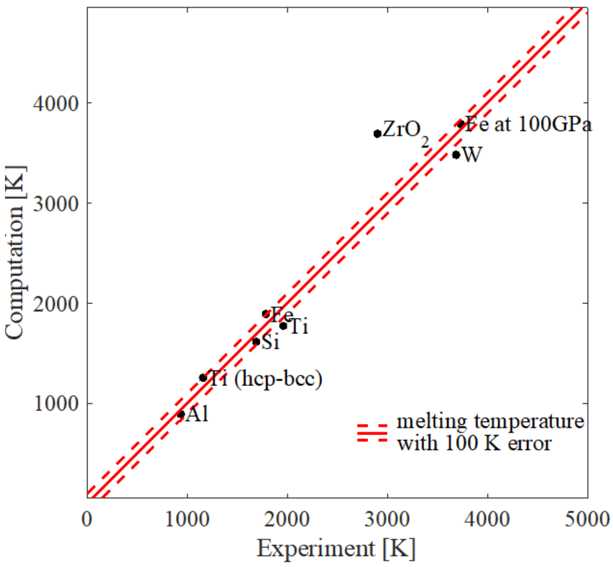

Figure 1. Computational transition temperature based on this method versus experiments. Error bars of 100 K were plotted as red dash lines. Plotted are melting temperature of materials at ambient pressure with the GGA-PBE functional employed unless elaborated in the label.

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Biographical Note

Qi-Jun Hong is an Assistant Professor of Materials Science and Engineering at Arizona State University. Hong received his Ph.D. in Chemistry from the Caltech in 2015. Before joining ASU, Hong was a Postdoc at Brown University and a Machine Learning Scientist at Amazon.com, Inc.

[O68] First-principles study on the dehydrogenation thermodynamics and kinetics of Ti, Zr, V and Nb doped MgH_2

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Key words: hydrogen storage material, magnesium hydride, first-principles calculation, doping

Understanding the desorption thermodynamics and kinetics of MgH_2 is crucial for its engineering application. Using first-principles calculations, we investigated H-related point defects in bulk MgH_2 and the role of Ti, Zr, V and Nb doping on hydrogen desorption from a defect point of view. It was found that charged, rather than neutral, H-related defects appear in the desorption process, but the four dopants prefer to substitute Mg with the neutral charge state. Electronic structure analysis reveals that covalent and ionic bonds coexist between H and the dopants. Therefore, the four dopants can weaken the ionic interaction of Mg-H. Ti, Zr, V and Nb doping not only resultes in a decrease in the microscopic removal energy for both neutral and charged nearby H atoms but also reduces the macroscopic hydrogen desorption temperature. Desorption kinetics is studied by examining the energy barriers for charged hydrogen to leave away from the dopants along several pathways. Mass transport of hydrogen in pure MgH_2 is mediated by positively charged vacancy or negatively charged interstitial. In doped MgH_2, it is very hard for charged hydrogen interstitials to escape from the doping atoms, but both positively and negatively charged H vacancies are readily to leave away from the doping atoms, implying these dopants cannot hinder mass transport of hydrogen in the desorption process. Our theoretic study on H-related defects reveals that Ti, Zr, V and Nb doping is beneficial for hydrogen desorption from MgH_2.

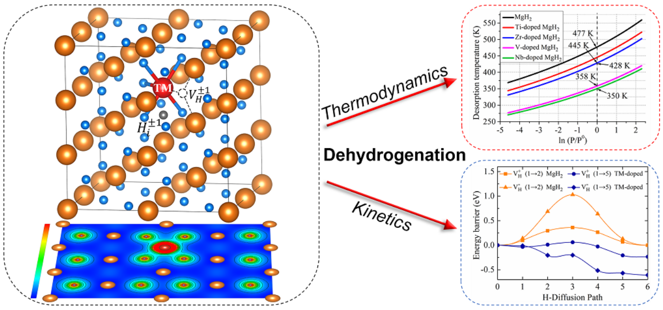

Figure 1. The aims of the current research

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Biographical Note

Jianchuan Wang received his PhD from Central South University (CSU) in 2012 and was a visiting PhD student in 2011 at Max-Planck-Institut für Eisenforschung GmbH. He is now working at CSU as an associate professor. His major research focuses on using first-principles calculation and molecular dynamics to study point defect properties, diffusion behavior, thermodynamics, and interface in condensed matter, especially in hydrogen storage materials and Li-ion batteries.

[O69] Atomistic simulations and active learning of the enthalpy of mixing in liquid and solid solutions

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Key words: enthalpy of mixing, active learning, atomistic simulations, liquid alloys

The enthalpy of mixing is an important thermodynamic property for predicting phase transformations. For the screening of new alloys, it is of great interest to be able to estimate this property in a large compositional space for different phases. This is particularly true for high entropy alloys [1]. Currently, the solutions to achieve this are to rely on Miedema's model for the liquid phase [2], or on a regular solution model based on a single density functional theory calculation at equimolar composition for solid phases [1]. An effective approach to improve the precision of enthalpy of mixing predictions is through the development of machine learning models.

To build machine learning models, we collected a large amount of experimental data from the literature. Nevertheless, many binary alloys have never been measured experimentally, notably due to technical difficulties (*i.e.* refractory components). In order to improve our models, the collection of new data is crucial. We have therefore chosen to collect new data through atomic-scale simulations. Ab-initio molecular dynamics (AIMD) is a particularly interesting simulation technique, as it enables us to simulate the liquid phase of a wide variety of binary alloys while guaranteeing high accuracy. However, the computation time required for this type of simulation is extremely high. It is therefore necessary to restrict the number of binary alloys to be simulated.

In order to optimize our models with a minimum number of simulations, we are developing active learning approaches based for instance on Gaussian processes. Their purpose is to find the binary systems and the compositions where the acquisition of new data would most improve the accuracy of our models. We will present the results obtained for the liquid phase, as well as our prospects for the solid phases for which we intend to use Special Quasi Random Structure (SQS) for data acquisition.

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Biographical Note

Quentin Bizot is currently working at the SIMAP laboratory in Grenoble, France, as a postdoctoral researcher since December 2023. His research focuses on machine learning and atomistic simulations.

[O70] Prediction of nitride nanocluster formation in iron based on first principles calculation

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Key words: first principles calculation, steel, nanocluster

In next-generation automobiles, it is highly required to develop surface hardening materials for high fatigue and wear resistant gears required for gearboxes to achieve high torque. Recently, the existence of nanoclusters consisting of substitutional solute elements and interstitial solute elements has been confirmed in steels, which exhibit remarkable surface hardening,[1] and alloy design utilizing this mechanism is being promoted. To control and design the surface hardness, it is essential to predict the clustering ability of the substitutional and interstitial solute elements. Hence, we have used first principles calculation of solute atom distribution based on atom-atom interactions to predict microstructures depending on alloy composition and heat treatment conditions., Furthermore, the thermodynamic origin of the cluster formation was discussed based on the free energy and related information obtained from the calculations.

A two-sublattice model in the crystal lattice of Fe of BCC type was used as the structural model. Specifically, N and vacancies, which are interstitial solute elements, are soluble in the octahedral interstitial sites, and Ti, which is a substitutional solute element, is soluble in the Fe atomic sites. Various ordered structures with different atomic configurations in the BCC structural model were created, and their energies were evaluated by first principles calculations. The effective cluster interactions were derived by applying the cluster expansion method to the structure–energy relationship. The equilibrium distribution of solute atoms at finite temperatures was investigated by Monte Carlo (MC) calculations using the obtained effective cluster interactions to determine the exchange of atomic positions. In the MC calculations, N concentration was controlled by changing the chemical potential (Δμ) difference between N and vacancies. On the other hand, the amount of Ti added was varied from 1% to 5% at 1% intervals. Statistical data on the distribution of solute atoms with respect to composition and temperature were obtained by changing the temperature from 400 to 1000 K at 50 K intervals.

Figure 1 shows the results of calculations for the Fe-1at.%Ti alloy performed at T = 500 K. Figure 1(a) shows the change in equilibrium N concentration for different Δμ between N and vacancies. As the Δμ is increased, the equilibrium nitrogen concentration increases monotonically. Figure 1(b) and (c) show the equilibrium atom distribution calculated for Δμ = 200 meV and Δμ = 300 meV, respectively. In this figure, Fe atoms are not shown, N atoms are shown in gray, and Ti atoms are shown in light blue. Figure 1(b) reproduces well the plate-like clusters as observed in the experiment. On the other hands, Fig 1(c) shows no plate-like clusters and a uniform distribution of Ti. The lack of plate-like clusters at higher nitrogen concentrations can be attributed to the presence of smaller clusters of Ti surrounded by N, which inhibits the formation of plate-like clusters.

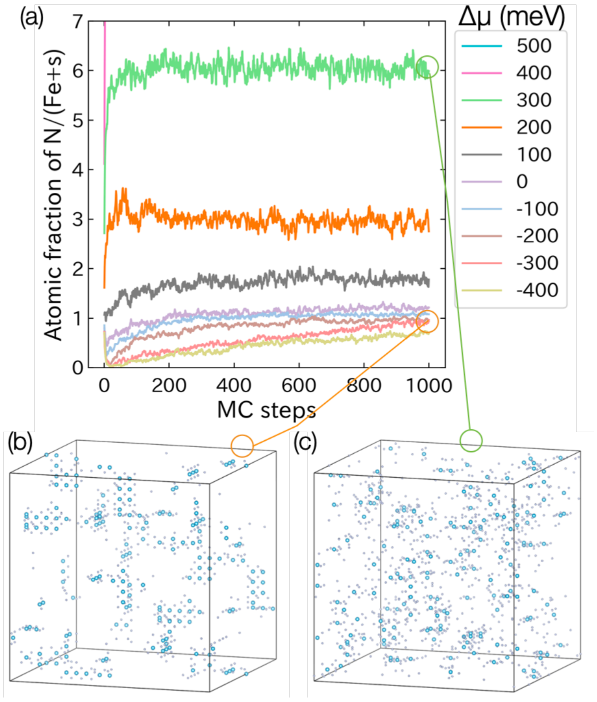

Figure 1. Results of calculations for the Fe-1at.%Ti alloy performed at *T* = 500 K.

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Biographical Note

Associate professor at Faculty of materials for energy, Shimane University, since 2023. The author studies the formation mechanism of microstructure and precipitation behavior in alloys in the atomic scale by calculating thermodynamic properties based on the DFT calculation.

[O71] Calphad Databases for Co-base Superalloys

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Key words: CALPHAD, models, EBEF, molar volume

The Calphad method is a well-established tool for obtaining phase equilibria and property information for materials design and process development. As part of the CHiMaD/NIST project on Co-base γ/γ’ superalloys thermodynamic, molar volume and diffusion mobility databases for Co-base superalloys are currently under development.

The thermodynamic database is developed for the Co-Al-Cr-Ni-Re-Ru-Ta-Ti-V-W system using the regular solution type model for the disordered solution phase and the compound energy formalism for the ordered phases. The model parameters are assessed using data from experiments and theoretical predictions, such as density functional theory (DFT). It was found that the prediction of the topologically close-packed (TCP) phases with the initial version of the database was not reliable because the descriptions were based on the formation energies of the binary endmembers of these phases. Since generation of ternary endmember data using DFT is an enormous computational effort, the effective bond energy formalism (EBEF) [1] was explored for the complex intermediate phases within the framework of existing descriptions of the binary and ternary subsystems improve reliability of predictions of higher-component systems. Initial work [2] on the σ phase in the Co-Cr-Ni-Re system has shown great promise and the approach is being explored for the description of the μ-phase in the Co-Cr-Ni-W system.

Knowledge of the misfit between the FCC_A1 matrix and the $L1_2$ precipitates is an important design variable for superalloys. Currently no models for temperature or composition dependence of the molar volume have been accepted by the community as a de facto standards. For the temperature dependence, the formalism proposed by Lu et al. [3] is used since it is based on the definition the coefficient of linear thermal expansion and the parameters for 27 elements in their stable structures have been assessed [4]. For the metastable structures of the elements their molar volume is taken from density functional theory (DFT) calculations and the thermal expansion is assumed to be the same as for the stable element. This practice is consistent with the description of the Gibbs energy functions of the stable and metastable elements. For describing the compositional dependence, the same formalisms as for the Gibbs energy are used. The initial assessment of the molar volume is focused on the FCC_A1 and $L1_2$ phases in the Co-Al-Cr-Ni-Ta-Ti-W as these are the major alloying elements being considered in the current project.

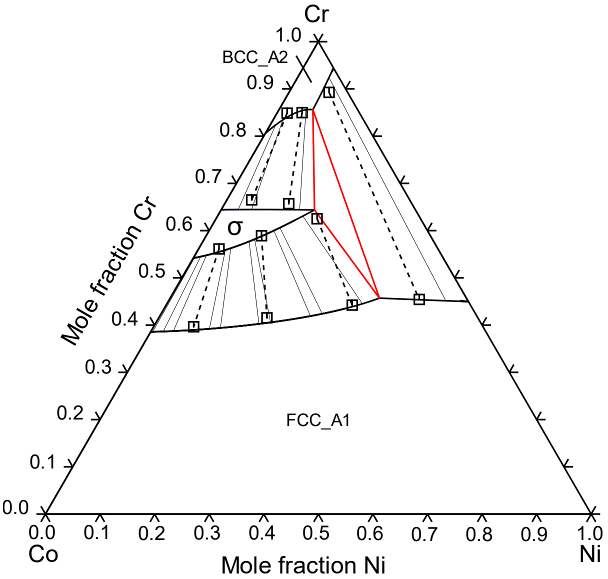

Figure 1. Extrapolation of the 1000 °C isothermal section of the Co Cr-Ni system using the EBEF to describe the σ phase.

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Biographical Note

Ursula R. Kattner is a physical scientist at NIST and her work focuses on computational thermodynamics and phase diagram evaluations. She has worked on a variety of alloy and metal-hydride systems and is currently working on the development of a thermodynamic and molar volume database for Co-base superalloys.

[O72] Thermodynamic functions of low temperature data

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Key words: Debye-Einstein functions, low temperature heat capacity data, thermodynamic data for pure elements, SGTE extension.

Temperature dependent thermodynamic functions of crystalline solids can be derived from constant pressure heat capacity data. Some sets of model parameters used to fit low temperature heat capacity measurements are purely empirical, other parameters are motivated by theory. It was suggested in the Ringberg 95' workshop that the heat capacities of elements and end members of solutions should be described by Debye integrals and / or Einstein terms [1]. In this sense, Pavlů et al. [2] extended SGTE data for pure elements to 0 K, however, their calculated heat capacities deviate considerably from experimental data in some cases. Roslyakova et al. [3] developed a very versatile, so called bent-cable model. It is possible with this model to fit heat capacities closely to experimental data from low temperatures to the melting temperature. The bent-cable model changes the fit between 0 K and 300 K, meaning that Debye's T^3 – law is superimposed by a linear term. This might result in large residuals for ultra-low temperatures. In addition, the uncertainties of the coefficients of the bent-cable model seem to be partly larger than the coefficients themselves.

Similar to the 6 parametric Debye Einstein integral applied to thermodynamic data of various crystalline solids [4], a 4 parametric Debye Einstein integral (4p-DE integral) is proposed in this work to fit molar heat capacity data of pure elements below 300 K. The Debye term and the Einstein term are weighted by a pre-factor where the sum of both pre-factors automatically approximates unity for pure elements. In case that there are no phase transformations below 300 K this fitting approach works well; low temperature molar heat capacities $C^0_{p,\mathrm{m}}$ for the elements Al, Fe, Ni and Si may serve as examples. Experimental data or recommended values for the low temperature molar heat capacities $C^0_{p,\mathrm{m}}$ of Al, Fe, Ni and Si are plotted versus temperature in Figure 1. For the sake of better visibility, the molar heat capacity $C^0_{p,\mathrm{m}}$ of Al is shifted upwards by 5 J mol^{-1}K^{-1}, $C^0_{p,\mathrm{m}}$ of Fe is shifted by 10 J mol^{-1}K^{-1} and $C^0_{p,\mathrm{m}}$ of Ni by 15 J mol^{-1}K^{-1}. The molar heat capacities $C^0_{p,\mathrm{m}}$ are approximated by 4p-DE integrals. An extension to the SGTE data valid above 300 K is possible by a switch function.

We determine the weighting factors for each measurement point by considering approximated standard deviations calculated from the residuals. This procedure allows to critically evaluate the thermodynamic model and the uncertainties of the model parameters.

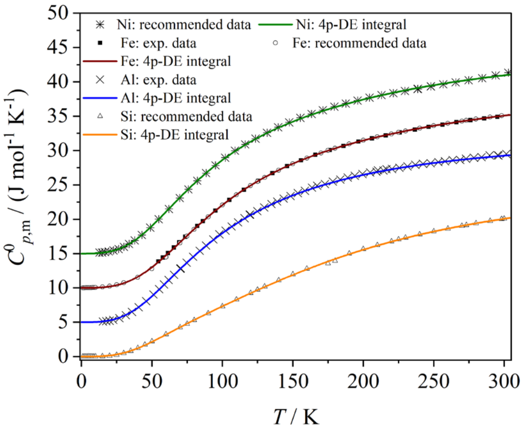

Figure 1. Low temperature molar heat capacities of Si, Al, Fe and Ni approximated by the 4p-DE integral fit.

The 4p-DE integral is suggested to be used as a standard method to describe molar heat capacities of pure elements in the range from 0 K to 300 K. Then, the resulting thermodynamic functions rely on the same theory-related semi-empirical basis.

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Biographical Notes

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[O73] Modelling allotropes for the third generation Calphad: a comprehensive exploration with focus on Fe

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Key words: 3rd gen, Calphad, metastable allotropes, Fe

Describing the metastable allotropes using lattice stability [1] has been tremendously important for the success of Calphad, which forms the foundation of the second generation of Calphad databases. In the 1995 Ringberg unary workshop, the concept of a new generation of Calphad (the third) was discussed and new models were proposed. In the past decade, these models or modified models, have been used to describe many pure elements, e.g. Al, C, Co, Cr, Fe, Ga, Mn, Ni, W, for the so-called third generation Calphad databases.

In this presentation, Fe [2] is taken as an example to demonstrate the modelling of allotropes with magnetism within the framework of the third generation Calphad. The suggestion given by Dinsdale et al. [3] is used to describe the contribution from entropy difference in lattice stability to Gibbs energy to avoid violating the third law of thermodynamics which would be the case if a bT term was added.

The third generation Calphad descriptions are valid down to 0 K. Besides, the models are more physically-based. These two features, i.e. valid down to 0 K and with more physical meaning, open the possibilities to use DFT-calculated data. Although DFT calculations often provide data at 0 K, in many cases these data are still very useful, especially for metastable allotropes where experiments are not feasible, in this case the magnetic properties of fcc and hcp Fe [4]. Instead of using the values in the SGTE compilation which were obtained from measuring the precipitates of fcc Fe in a Cu matrix, the magnetic properties obtained from DFT calculations were selected. This selection for fcc Fe enables to model the thermodynamic properties satisfactorily without using the two-state magnetic model.

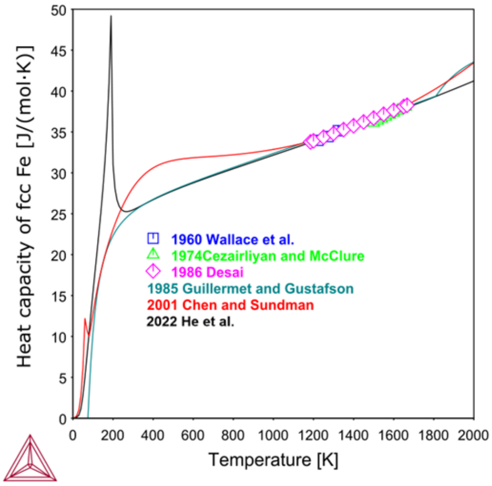

Figure 1. Comparison between the calculated and experimental data for the heat capacity of fcc Fe

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Biographical Note

Zhangting He is a researcher at Swerim AB where she works on alloy development using the ICME approach based on the Calphad method. She received her PhD degree from KTH Royal Institute of Technology and her thesis was focused on developing the third generation Calphad models and descriptions.

[O74] Implementation of an extensible property modeling framework in ESPEI

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Key words: thermophysical properties, software tools, uncertainty quantification

Property models are becoming more widely adopted by commercial Calphad databases, but they are not nearly as common in non-commercial or traditional academic Calphad databases. A primary driver is that user-friendly Calphad modeling tools that support property models are not widely available. This presentation will discuss new property modeling capabilities that have been implemented in ESPEI, the Extensible Self-Optimizing Phase Equilibria Infrastructure.

These capabilities include both generating property model parameters from data and optimizing generated or pre-existing property model parameters with uncertainty quantification. Two illustrative examples are given, one using ESPEI to generate molar volume model parameters based on the model by Lu *et al.* [1] for refractory BCC alloys. Second, the extensibility of ESPEI's new property modeling capabilities will be demonstrated by implementing a custom PyCalphad model for BCC elastic stiffness parameters, where ESPEI will be used to generate and compare parameters to the ones assessed by Marker *et al.* [2] using the same data.

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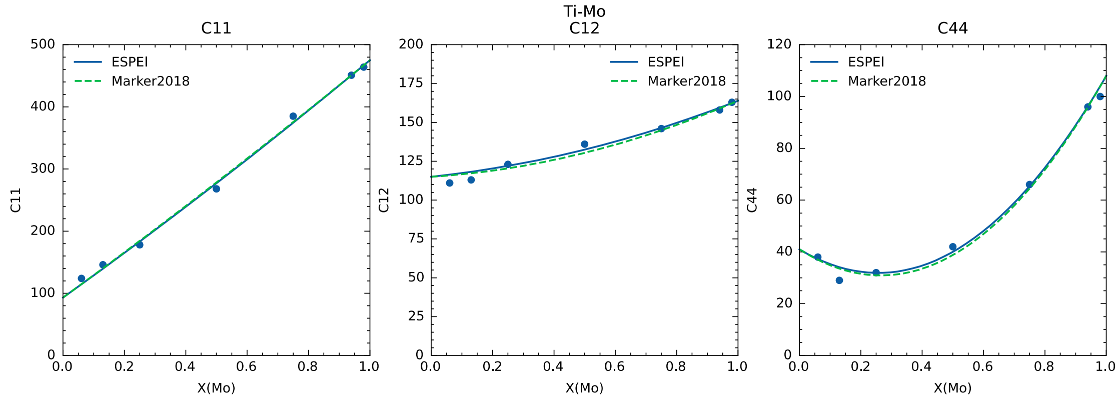

Figure 1. Ti-Mo C11, C12, and C44 interaction parameters generated by ESPEI compared to the data and assessments from Marker et al. [2].

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Biographical Note

Brandon Bocklund is a postdoctoral researcher in the Actinide and Lanthanide Science group in the Materials Science Division. His research at LLNL is focused on modeling phase transformations in metallic and ceramic systems using atomistic, mesoscale, and machine learning approaches. Brandon received his Ph.D. in Materials Science and Engineering from Penn State as a NASA Space Technology Research Fellow.

[O75] Thermodynamic modeling of the Ni-S based bulk metallic glass-forming system

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Key words: Bulk metallic glass, undercooled liquid, driving force of crystallization.

In this work, the novel Ni-S based bulk metallic glass (BMG) system[1] is studied with combined CALPHAD (Computer Coupling of Phase Diagrams and Thermochemistry) and experimental approaches. A thermodynamic dataset for the Ni-Pd-S system is first developed with the third-generation approach based on the critical literature review. In addition, key experiments are performed for the examination of the phase boundaries, and for the investigation of thermophysical properties at eutectic composition and two intermetallic compositions ($Ni_{9.54}Pd_{7.46}S_{15}$ and $Ni_{3.77}Pd_{1.20}S_4$). The calculated isothermal sections (Figure 1) and phase transition temperatures show good agreement with the experimental results from Karup-Moller and Makovicky[2].

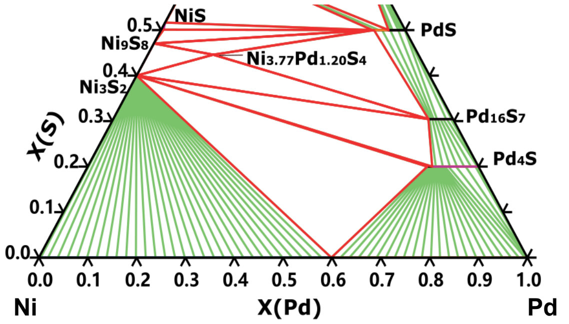

Figure 1. Calculated isothermal section of the Ni-Pd-S system at 400 ℃

The relatively stable undercooled liquid of the Ni-S based glass-forming system gives the opportunity to investigate its properties and the glass-forming mechanism. The thermophysical and thermodynamic data obtained from DSC measurements for the undercooled liquid as well as the in-situ XRD investigation for the solidification process facilitate the modelling of the undercooled liquid and its glassy state. The two-state model[3] is applied for the description of the liquid-amorphous phases of pure elements, which is then extended to the binary as well as the ternary systems. A new modification of two-state model for the undercooled liquid is proposed for the Ni-Pd-S ternary glass-forming system. The calculated results are in good agreement with the experimental data at various compositions in the glass-forming range, as shown in the example heat capacity calculation in Figure 2. The description for the liquid-amorphous phase is used for the estimation of the driving force for crystallization at different compositions, which contributes as a vital factor for the evaluation of the glass-forming ability and the Time-Temperature-Transformation (TTT) diagram.

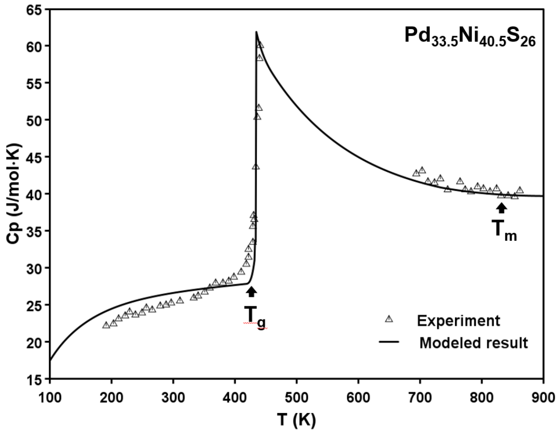

Figure 2. Calculated heat capacity of undercooled liquid – amorphous phase at the composition $Pd_{33.5}Ni_{40.5}S_{26}$

Acknowledgement

The authors gratefully acknowledge funding by the German Research Foundation (DFG) (project number: 441308809).

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Biographical Note

Wenhao Ma is a doctoral student at Karlsruhe Institute of Technology. The research focus is on the experimental investigation of thermodynamic properties and CALPHAD modelling for Ni-S based bulk metallic glass-forming system.

[O76] The SGTE Binary Collection

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Key words: binary system, thermodynamic assessment

Thermodynamic assessments of binary systems form the basic building material for any thermodynamic database. Starting with the pioneering work of Larry Kaufman, at least 1500 binary systems have been modelled through the years, many of them more than once. The actual number is not known since there is most probably a substantial number of unpublished assessments, e.g. included in commercial databases. Theoretically, there are 4005 possible binary systems if one considers 90 elements. Many of these systems are of limited practical interest, so that the actual number to consider is quite a bit smaller. SGTE has collected (published and unpublished) binary assessments since the 1980's leading to five volumes in Landolt-Börnstein (now included in Springer Materials) published from 2002 to 2007, containing about 450 binary systems. For each binary system the best assessment was selected and a binary database with all selected assessments included was created. The present collection differs from this original collection in that an attempt is made to collect as many published assessments (that use SGTE unary data) as possible. I.e. for many systems there is more than one assessment. In contrast to the original collection, there is no attempt to create a single database, but the assessments are kept as individual datasets. As previously, the crystal structures for the phases (when known) are recorded. The binary collection has proved very valuable for efficient and fast generation of ternary and higher order databases. In this context, a number of common problems with binary assessments will be discussed. Currently, the binary collection contains about 2500 datasets from about 1180 different systems.

Biographical Note

I studied physical metallurgy at KTH in Stockholm where I became fascinated by microstructures. I learned that phase diagrams are needed to understand microstructures and I spent my PhD studies and the following 30 or so years modelling phase diagrams (and trying to understand microstructures). Currently I am at a materials technology institute within the mechanical engineering faculty, dealing with a wide range of engineering materials.

[O77] Phase composition, microstructure and mechanical properties of CVD Ti-B-N coatings deposited at different temperatures guided by thermodynamic calculations

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Key words: CVD phase diagrams, TiB_xN_y coatings, Deposition temperature, Mechanical properties

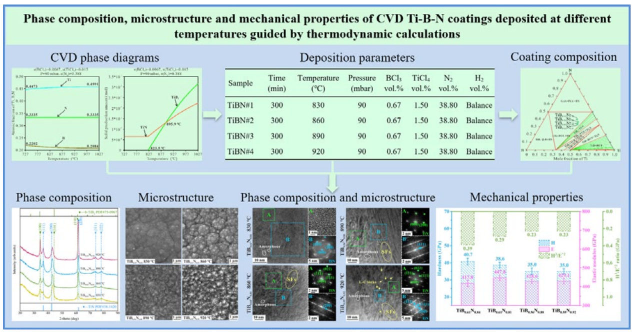
TiBN coatings, as materials with broad potential applications, have received much attention in surface engineering in recent years, but the manipulation of composition, microstructure, and mechanical properties is an extremely difficult topic. To obtain the TiB_xN_y coatings close to TiN-TiB_2 tie line, based on our thermodynamic calculations, the pressure of 90 mbar and volume fractions of 0.67, 1.50 and 38.80 vol. % for BCl_3, $TiCl_4$ and N_2 are chosen to investigate the influence of deposition temperature on the coating compositions and phases. Phase diagram calculations show that when the pressure, volume fractions of $TiCl_4$, BCl_3 and N_2 are fixed, the Ti content of TiB_xN_y coatings increases slightly, the B concentration decreases slightly, and the N concentration remains unchanged with the increase of deposition temperature at the range of 727 ~ 1027 °C. When the pressure is 90 mbar, the volume fractions of BCl_3, $TiCl_4$ and N_2 are 0.67, 1.50 and 38.80 vol. %, the TiB_2 phase does not present until the temperature is higher than 823.5 °C, and the amount of TiN and TiB_2 phases gradually increases with the elevation of temperature. Accordingly, the deposition temperatures are set to be higher than 823.5 °C for the preparation of TiB_xN_y coatings.

Under the conditions of 1.50 vol.% $TiCl_4$, 0.67 vol.% BCl_3, 38.80 vol.% N_2 and 90 mbar, four TiB_xN_y coatings are prepared on cemented carbide at different deposition temperatures (830-920°C) in an industrial CVD system. The phase composition, microstructure and mechanical properties of these TiB_xN_y coatings are investigated by EPMA, XRD, XPS, Raman spectroscopy, SEM, TEM and nanoindentation tester.

The crystallinity of the TiB_xN_y coatings rises with the increase of deposition temperature. The TiB_xN_y coatings are mainly composed of the crystalline phases TiN and TiB_2 and the amorphous phases TiB and BN. $TiB_{0.61}N_{0.84}$ coating deposited at 830 °C has a particle-like surface. The particle size on $TiB_{0.61}N_{0.81}$ coating surface increases as the deposition temperature elevates to 860 °C. The $TiB_{0.56}N_{0.88}$ and $TiB_{0.55}N_{0.92}$ coatings deposited at 890 °C and 920 °C display needle-like morphology. The deposition rate increases continuously with the deposition temperature.

As deposition temperature increases, the TiB_xN_y coatings exhibit accelerated grain growth, the grain size increases. SFs with lengths of several tens of nanometers are observed in coatings deposited at temperatures above 830 °C. Amorphous zones appear in all coatings, forming a typical nanocomposite structure of amorphous encapsulated nanocrystals. At deposition temperatures of 830, 860, 890 and 920 °C, the hardness values of $TiB_{0.61}N_{0.84}$, $TiB_{0.61}N_{0.81}$, $TiB_{0.56}N_{0.88}$ and $TiB_{0.55}N_{0.92}$ coatings are 40.7, 38.6, 35.0, and 35.0 GPa, respectively. With the increase of deposition temperature, the hardness of the coating decreases, such a decrease is associated with grain coarsening and soft phase generation.

Figure 1.



Phase composition, microstructure and mechanical properties of CVD Ti-B-N coatings deposited at different temperatures guided by thermodynamic calculations

CVD phase diagrams

Deposition parameters

Sample	Time (min)	Temperature (°C)	Pressure (mbar)	BCl_3 vol.%	$TiCl_4$ vol.%	N_2 vol.%	H_2 vol.%
TiBN#1	300	830	90	0.67	1.50	38.80	Balance
TiBN#2	300	860	90	0.67	1.50	38.80	Balance
TiBN#3	300	890	90	0.67	1.50	38.80	Balance
TiBN#4	300	920	90	0.67	1.50	38.80	Balance

Coating composition

Phase composition

Microstructure

Phase composition and microstructure

Mechanical properties

Biographical Note

F.F. Zeng (1997—), Female, Doctor, Research focus: CVD coating, thermodynamics, phase diagram.

[O78] High-pressure studies in the Fe–N system

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Key words: phase diagram, ordering, diffusion, intermetallic phases

The iron-nitrogen (Fe–N) system attracts interest due to the relevance of N in ferrous metallurgy and due to a possible N content in the earth's inner iron core. The latter aspect has led to investigation of the Fe–N system at elevated pressures. Early works focused on the volume-pressure dependence of individual phases and phase transformations, in particular, the disappearance of the γ′-phase at elevated pressures, see e.g. [1].

In our research we try to get a more comprehensive view on the phase equilibria in the Fe–N system at elevated pressure, including establishment of dual-phase equilibria requiring long-range diffusion. Experimental evidence was obtained by performing high-temperature high-pressure treatments on α-Fe+iron nitride powder compacts in a Walker-type multi-anvil module at 2…13 GPa and ≤ 1273 K (mainly 673-873 K). After quenching and relieving the pressure, the specimens were investigated by X-ray diffraction and complementary scanning electron microscopy. This revealed the phase composition and, moreover, via the lattice parameters, reliable estimations of the N contents in the individual phases [2,3]. It is in particular shown that the γ′-Fe_4N phase either decomposes at high temperatures and pressures into a mixture of N-depleted γ-solid solution and N-rich ε-iron nitride (ε′) or transforms into pure ε (ε′) phase ("ε-Fe_4N"). The temperature-dependent phase equilibria are strongly influenced by the magnetic behavior of the individual phases, causing e.g. a high molar volume for the ("high-spin") γ′-Fe_4N and a low molar volume for the low-spin γ-solid solution. Such properties of the phases strongly influence the pressure dependence of the Gibbs energy.

A pressure-dependent thermodynamic modelling was performed using the known or estimated composition-dependent ambient-pressure volumes [4], thermal expansion and compressibility data for the different phases. This modelling did not consider the observed changes in the phase equilibria encountered experimentally. It was shown, instead, that the calculated phase equilibria are reasonably well compatible with the experimental observations. Exception is the low-temperature eutectoid reaction e_3 ($\gamma' \rightleftarrows \varepsilon'+\alpha$; see e.g. Figure 1). However, it appears that the atmospheric pressure data used to predict the high-pressure thermodynamics are relatively uncertain so that the deviations appear understandable.

Experimental investigation of the low-N part of the phase diagram by the present ex-situ techniques is difficult due the non-quenchability of the corresponding high-pressure-high-temperature states. Nevertheless, ideas will be presented based on the behavior of the pure Fe (non-magnetic ε-Fe) with its small molar volume.

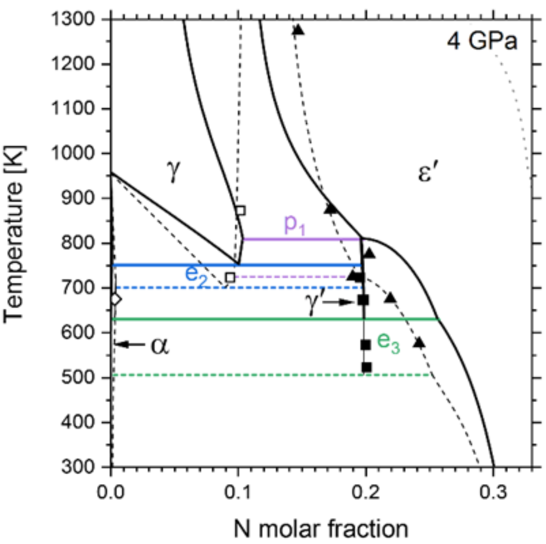

Figure 1. Fe–N phase diagram at 4 GPa with invariant reactions indicated: (full lines) CALPHAD-modelling [4]; (dashed lines and data points) evaluation of experimental observations [3].

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Biographical Note

Andreas Leineweber is Professor of Applied Materials Science at the at the TU Bergakademie Freiberg since 2014. His research focusses on the study of phase transformation processes in mainly metallic systems, like nitriding of Fe-base alloys and intermetallic formation in reactive metallic systems.

[O79] Formation kinetics and thermodynamic stability of the compounds in $Bi_4Ti_3O_{12}$-$BiFeO_3$ system

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Key words: Enthalpy of formation, Reaction kinetics, Thermodynamic stability, Thermodynamic assessment

Thermodynamics and phase diagrams are fundamental knowledge for modeling and predicting the temporal microstructure and property evolution during materials processes. This article focuses on the Bi_2O_3–Fe_2O_3-TiO_2 system with the diversity of physical properties of compounds, to clarify the phase equilibria relationship of the system and to explain the discrepancies in literature. $Bi_{12}TiO_{20}$, $Bi_4Ti_3O_{12}$, $Bi_2Ti_4O_{11}$ and $Bi_{n+1}Fe_{n-3}Ti_3O_{3n+3}$ Aurivillius compounds were prepared and their phase transformation properties,heat capacities and enthalpies of formation were studied by in situ X-ray diffraction, high temperature differential scanning calorimetry and high temperature oxide melt solution calorimetry. Thermodynamic stability of the Aurivillius compounds decreases with increasing *n*, and formation kinetics gradually slow down, demonstrating the inherent difficulty to synthesize pure Aurivillius compounds with *n* larger than 8. This difficulty was confirmed by an impurity phase coexisting with $Bi_9Fe_5Ti_3O_{27}$. Based on the experimental data obtained in the work and literature, a thermodynamic description of the Bi_2O_3–TiO_2 system was carried out, a set of thermodynamic database as well as the calculated phase diagram of the system were provided. The thermodynamic assessment work on the Bi_2O_3-Fe_2O_3 and Bi_2O_3-Fe_2O_3-TiO_2 systems is coming soon. The present work provides a good explanation for the differences in data reported in the literature and also points out their credibility.

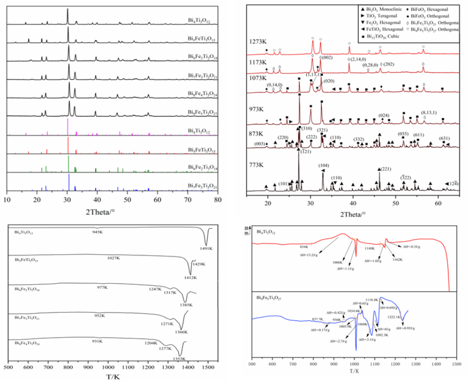

Figure 1. Formation kinetics and thermodynamic stability of the Aurivillius compounds in Bi_2O_3-Fe_2O_3-TiO_2 system

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Biographical Note

Weiping Gong works as a Professor of Huizhou University. She received Ph.D at Central South University in 2002, then worked as a postdoc at University of Marseille. She once worked as a visitor scholar at University of California Davis and Arizona State University. Her main research interests are experimental and calculated thermodynamics. She has produced over 100 international publications.

[O80] Experimental and theoretical study of La-Ni-Sn system as a perspective hydrogen storage material

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Key words: La-Ni-Sn, hydrogen-storage materials, CALPHAD, p-c-T curves

Hydrogen has a promising perspective as an energy carrier with the potential to be a clean and efficient energy source in various applications. One possible promising material for energy storage are the LaNi alloy-based systems. These materials are capable of forming hydrides at ambient temperatures and relatively low pressures with fast sorption kinetics [1]. Ternary phase diagram of the system La-Ni-Sn was studied at temperatures of 300 and 600°C in the entire concentration range. Samples were prepared from pure elements in arc-melting furnace and annealed in evacuated quartz glass ampoules. Annealed samples were quenched into the icy-cold water or liquid nitrogen. Microstructure, overall and phase chemical compositions were studied by SEM-EDX/WDX. Crystallographic structure of the phases was confirmed by XRD, temperatures of phase transitions were measured by DSC/DTA.

Ten stable ternary phases were found at 300°C (see Figure 1), where three ternary phases have unknown structure. The next planned step is a detailed study of the crystallographic structure by single-crystal XRD, TEM and ab-initio calculation of these phases. The solubility of tin in the $LaNi_5$ phase is complex at lower temperatures and a miscibility gap region is formed. Phase diagram at 400°C was studied by Zhuang [1] but although generally the phase diagram agree, some important details are different.

Based on the knowledge of experimental isothermal sections at 300, 400 and 600°C, we carried out the CALPHAD based reassessment of the system La-Ni-Sn. Due to the inconsistency of Zhuang's data [2] some simplification had to be introduced, but generally the agreement is good.

It is known, that at least two types of promising hydrides ($La_1Ni_{4.95}Sn_{1.05}H_3$ and $LaNiSnH_2$) [3,4] exist in the ternary system La-Ni-Sn. The reactivity with hydrogen and the kinetics of hydrogen sorption and desorption were studied for selected samples. The powdered alloys react with hydrogen under appropriate (p,T) conditions. Reaction temperature and pressure p_{eq} was estimated from the p-c-T curves measured at different temperatures.

The shape of the p-c-T curves will be used to determine the isothermal phase boundaries of the hydrogen containing systems.

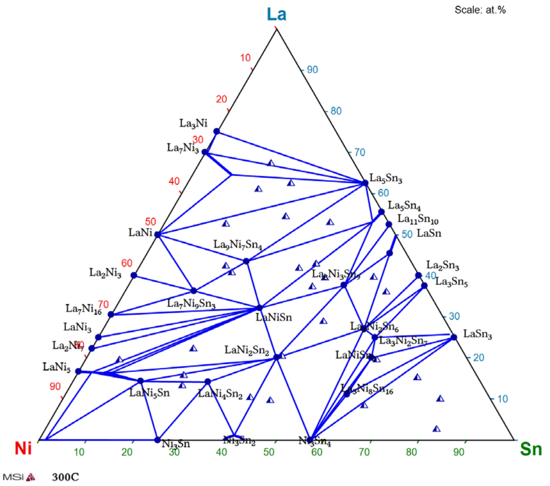

Figure 1. Isothermal section of the experimental phase diagram of the La-Ni-Sn system at 300°C. Triangles mark the overall composition of the samples

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Biographical Note

Dr. Ondrej Zobac
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The research topics: alloys, experimental description of phase diagrams, CALPHAD modelling, implementation of ab-initio data, third generation data, heat capacity measurement

[O81] Calorimetric measurements and thermodynamic modeling of Ag-Mg-Ti liquid alloys

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Keywords: thermodynamic properties, liquid alloys, enthalpy of mixing, thermodynamic modeling, calorimetry, magnesium alloys.

Magnesium and its alloys find applications across various industries. Due to their notable gravimetric capacity, they are studied as potential materials for solid-phase hydrogen storage. Moreover, these alloys exhibit attractive properties such as an excellent strength-to-weight ratio or biocompatibility [1]. Although magnesium-based alloys are widely studied for various industrial applications, they are not always thoroughly understood in terms of their thermodynamic properties. While the literature on the mentioned properties of binary alloys is readily available, the situation changes when considering materials from ternary or multicomponent systems. Due to the lack of thermodynamic data concerning the Ag-Mg-Ti system in existing literature, this work aims to fill this gap by offering the outcomes of calorimetric investigations conducted on these ternary liquid solutions. The measurements were performed using the drop calorimetry method at the temperature of 1294 K and 1297 K for liquid solutions with the following constant mole fraction ratio: $x_{\mathrm{Ag}}/x_{\mathrm{Mg}}$=9/1, 7/3, 1/1, 3/7 and $x_{\mathrm{Ag}}/x_{\mathrm{Ti}}$=19/1. Based on the thermodynamic properties of binary systems described by the Redlich-Kister [2] model and the determined experimental data from the calorimetric measurements, the ternary optimized parameters for the Ag-Mg-Ti liquid phase were calculated by the Muggianu model [3]. To optimize the achieved calorimetric data, we used homemade software (TerGexHm). The results show that negative deviations from ideal solutions characterize the liquid solutions. Also, values of integral enthalpy of mixing for all studied alloys reach negative values. The best agreement between modeled and experimental data is observed for alloys with the following mole ratio: $x_{\mathrm{Ag}}/x_{\mathrm{Ti}}$=19/1 and $x_{\mathrm{Ag}}/x_{\mathrm{Mg}}$=9/1. The results of this study are the first step in investigations and future evaluation of the thermodynamic properties of the silver-magnesium-titanium system.

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Acknowledgments

This work is supported by the National Science Centre, Poland, for funding project no. 2021/43/O/ST8/01291 entitled “Thermodynamic properties and structure of Cu-Mg-Ti and Ag-Mg-Ti alloys and their potential to interact with hydrogen” in the years 2022–2027.

Biographical Note

Weronika Gozdur is a 1St year PhD student at the Institute of Metallurgy and Materials Science, Polish Academy of Sciences. As a part of her dissertation, she is working on the thermodynamic properties of Mg-based ternary alloys that have potential use for solid-phase hydrogen storage.

Collection of Abstracts for Poster Presentation

There are 95 poster presentations in total.

[P01.01] Modeling of solidification microstructures with non-equilibrium effects at interfaces with Calphad data

P. Martin[1,2], **G. Guillemot**[1], **C.A. Hareland**[3], **P.W. Voorhees**[3], **Ch.-A. Gandin**[1]

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Keywords: Rapid solidification, Phase selection, Dendrite growth kinetics, Additive Manufacturing

A dendrite tip kinetic model for multicomponent alloys is applied to understand the microstructure formed upon rapid solidification by Laser – Powder Bed Fusion (L–PBF) [1]. On the one hand, the model considers both the diffusion in the liquid of the chemical species segregated ahead of the paraboloidal dendrite tip and the interface curvature [2]. On the other hand, non-equilibrium effects are formulated by considering energy dissipation due to interface migration and trans-interface diffusion, leading to equations known as velocity response function and composition response functions [3]. The solution of these equations gives access to non-equilibrium phase diagram boundaries such as the liquidus and solidus temperatures. The model includes a new formulation for a velocity dependent $\boldsymbol{T_0}$-line [1].

Applied to L–PBF of 316L [4], the model revisits explanations for the origin of a “fish-scale” microstructure located at the boundaries of the melt pool created by the laser. This is done by computing the temperature of $\boldsymbol{\delta}$–dendrites, $\boldsymbol{T_d^\delta}$, and $\boldsymbol{\gamma}$–dendrites, $\boldsymbol{T_d^\gamma}$, as a function of velocity and temperature gradient (Figure 1). At the bottom of the melt pool, i.e. for low solidification speed and high temperature gradient, plane front is favored. The condition $\boldsymbol{T_S^\gamma} > \boldsymbol{T_S^\delta}$ is satisfied and stabilizes the $\boldsymbol{\gamma}$–phase, hence recognized as the growing phase from the melt and identified at the origin of the “fish-scale” microstructure. This is confirmed by chemical analyses revealing accumulation of Cr and Mo in interdendritic regions, also predicted by the simulation. In other places, for higher solidification speed and lower temperature gradient, the dendritic microstructure is favored. The $\boldsymbol{\delta}$– phase is selected as $\boldsymbol{T_d^\delta} > \boldsymbol{T_d^\gamma}$ and both measurements and calculations show interdendritic segregation of Ni, as expected for $\boldsymbol{\delta}$-phase dendritic growth.

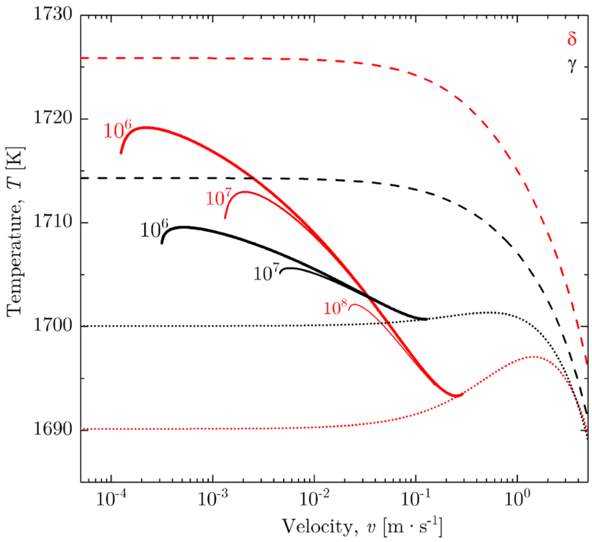

Figure 1. Tip temperature of $\boldsymbol{\delta}$-dendrites and $\boldsymbol{\gamma}$-dendrites in 316L stainless steel as a function of velocity for temperature gradient in the range $[\boldsymbol{10^6}, \boldsymbol{10^8}]$ K m^{-1}. Dashed lines and dotted lines are for velocity-dependent ($\boldsymbol{T_L}$) liquidus and ($\boldsymbol{T_S}$) solidus temperatures for the $\boldsymbol{\delta}$ and $\boldsymbol{\gamma}$ phases, respectively [1].

Additional simulations will be presented to emphasize the interest of the model to investigate

- the effect of minor chemical species on the selection of the primary phase formed from the melt in 316L,
- the prediction of solidification paths in nickel-based superalloys processed by L-PBF by combination with an incremental mass balance using the computed phase diagram.

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Biographical Note

Charles-André Gandin is with the French Centre for Scientific Research (CNRS) since 1999. His research activities focus on physical metallurgy of phase transformations, modeling of microstructures, coupling thermodynamics data with process simulations, with applications mainly oriented towards industrial metallic alloys.

[P01.02] CALPHAD-based ICME Design for Crack-free Wire-Arc Additive Manufacturing of Functionally Graded Alloy from Copper Alloy C18150 to Superalloy Inconel 625

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Key words: Functionally graded materials, Additive manufacturing, CALPHAD, ICME

The bimetallic system transitioning from Cu alloy to Inconel 625 (In625) is critical in NASA engineering applications, particularly in constructing the Channel Wall Nozzle. The nozzle features a Cu alloy hot wall on the coolant channel lands, while the cold wall comprises IN625, serving as the structural component. Although different attempts have been made to join these alloys, it has not been possible to produce crack-free components without microstructural defects, such as the formation of brittle phases and liquid phase separation [1,2]. Therefore, a better solution is introducing the third alloy between the C18150 and IN625 to form a transition layer to mitigate such a technical challenge in bimetallic printing.

This work demonstrates a comprehensive CALPHAD-based ICME (Integrated Computational Materials Engineering) modeling to facilitate such a design process. To screen the compositions of the alloy mixtures, the solidification cracking susceptibility (SCS) coefficient, liquid phase separation, and the stability of undesirable phases were estimated using high throughput modeling. Subsequently, a feasible region was defined, the simulation results were experimentally validated, and the optimized compositions were used to print graded samples using Wire Arc Additive Manufacturing (WAAM).

According to the results, Ni-rich interlayers dissolve the alloying elements of the parent alloys, preventing liquid phase separation and solidification cracking. However, due to the segregation process associated with the WAAM process, the Laves phase precipitates in the In625-rich layers, and the Cr-rich BCC phase coarsens in the C18150 side. A solution heat treatment at 1000ºC for 1 hour was applied to the graded samples to dissolve both phases. Subsequently, an aging heat treatment at 500ºC for 4 hours was carried out to reprecipitate the Cr-rich BCC phase, improving the strength of alloy C18150. This research shows that it is possible to join Cu-based alloys with Ni-based alloys using WAAM. The methodology proposed in this work will accelerate the design of functionally graded materials, contributing to the engineering applications of additive manufacturing techniques.

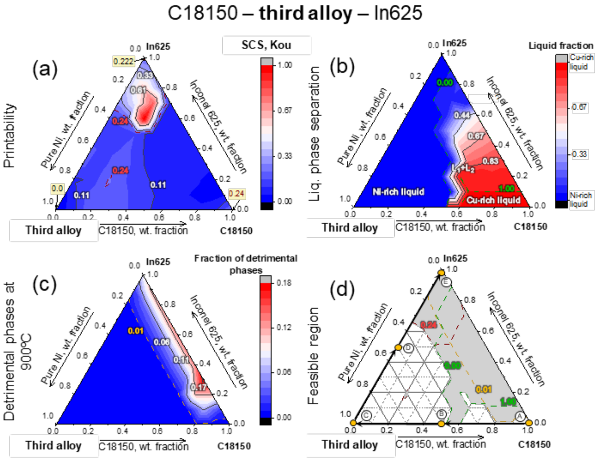

Figure 1. Compositional screening for the intermediate layers between C18150 and IN625 using Ni-rich materials as the interlayer alloy candidate. The plots of (a) Solidification cracking susceptibility, (b) liquid phase fraction at liquidus temperature, (c) total fraction of detrimental phases (σ, δ, and Laves), and (d) overlaid contour plot showing the feasible region in white color.

Acknowledgment:

The work is supported by NASA Early Stage Innovations under Award number 80NSSC23K0230.

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Biographical Note

Luis Ladinos-Pizano is a current Ph.D. student in the Department of Materials Science and Engineering at the University of Pittsburgh under the supervision of Prof. Wei Xiong. He specializes in the computational design of new alloys and post-heat treatment optimization, utilizing high-throughput experiments to support his research.

[P01.03] CALPHAD-based Prediction of Evaporation in Multi-component Melt Pool during Additive Manufacturing Process

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Key words: Additive Manufacturing, Metal Evaporation, Computational Fluid Dynamics

Additive manufacturing (AM) is a key technology which can manufacture products with complex shapes while using fewer raw materials. It involves layer-by-layer construction using laser or e-beam.

A significant challenge arises when using laser as a heat source. Laser irradiation may temporarily elevate the temperature of the melt pool over the boiling temperature, causing elemental evaporation and consequent compositional changes in the sample [1]. This phenomenon is especially significant for elements with lower boiling points (*e.g.*, Mn in high Mn steel). Such a change in composition complicates the CALPHAD-based alloy design scheme for AM processes by widening the gap between the input composition and the actual composition of the melt pool.

There have been theoretical studies to reflect evaporation during AM. Most of existing studies focus on the shape of the melt pool and defect formation rather than compositional changes [2]. Klassen and co-workers tried to consider compositional changes, but their work is limited to 2D simulation [3].

In the present work, we developed a 3D thermal fluid dynamics model that can predict compositional changes in the melt pool during the AM process. Our model utilizes both fundamental characteristics of alloys and processing conditions to predict the thermal history and area of melt pool surface. Eventually, the evaporation rate of each component and the final composition of additively manufactured product can be predicted by using the present approach.

We could confirm that our model well reproduces the compositional change in Fe-Mn alloys during a direct energy deposition (DED)-type AM process.

To sum up, the present model can predict compositional changes caused by evaporation during AM processes under various processing conditions for a large variety of alloys. This will be very beneficial to design AM alloys and determine AM process conditions.

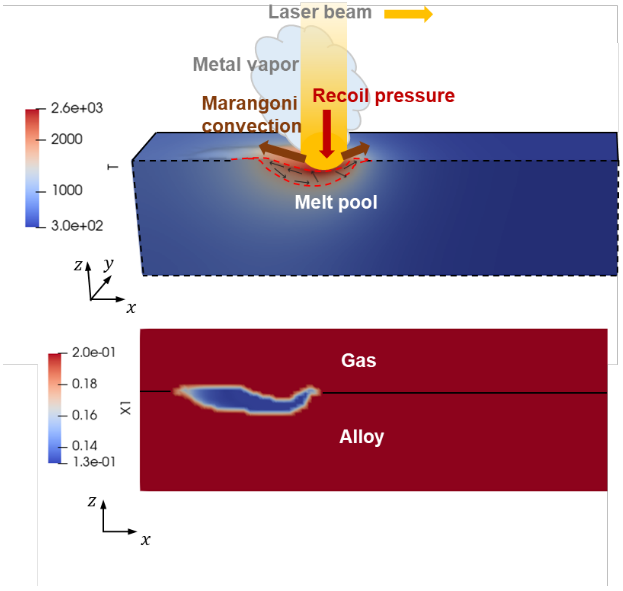

Figure 1. (a) Schematic view of the present thermal fluid dynamics model, and (b) Mole fraction of Mn during the simulation.

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Biographical Note

Matae Lee is a Ph.D. student under the guidance of Prof. B.-J. Lee at Pohang University of Science and Technology (POSTECH), Republic of Korea. His research focuses on computer-assisted applications for additive manufacturing technology.

[P01.04] Modelling the transport of hydrogen around melt-pools formed by moving heat sources.

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Key words: Hydrogen, Transport, Rosenthal, Diffusion

The source of the hydrogen in gas-pores found in welds produced under vacuum conditions was investigated by Huang, Warnken et al[1]. The authors demonstrated that *intrinsic* hydrogen in a Ti-6Al-4V workpiece under the temperature field of a moving heat source, modelled as that of an *Electron Beam Welder* (EBW), diffused *against* its hydrogen concentration gradient. The diffusion was, however, in accordance with the gradient in hydrogen's chemical potential, which, unlike concentration, is directly a function of the temperature field the metal is subject to. The result of this diffusion was that the melt-pool and *heat-affected-zone* (HAZ) generated by the EBW were enriched in hydrogen. It was conjectured that this diffusion is the source of porosity in the welds. The deleterious effects of concentrated hydrogen in metal systems, namely *hydrogen embrittlement* (HE), are well known in literature, as is the dependence of HE susceptibility on thermal history. For example, Zhou et al [2] demonstrated variation in HE resistance in 304L Steel samples and linked this to thermal history. It is obviously desirable, then, to understand the diffusion of hydrogen under moving heat sources – it would be counterproductive if an operation intended to join two materials resulted in a serious reduction in mechanical properties via porosity and HE.

The present work will model the diffusion of hydrogen through metal systems commonly subjected to joining operations, or other applications of a moving heat source (e.g. additive manufacturing). The work will employ the thermodynamic formulation of diffusion and draw on developments made in the mathematical treatment of diffusion over the last decade. In an example of the aforementioned developments; it has been independently shown by Huang, Warnken et Al [1] and by Liu[3], that the flux of a particular molar quantity, such as hydrogen, can be accurately described solely by the product of a kinetic coefficient and the molar quantity's conjugate potential, without inclusion of cross-effects arising from the gradients in the potential of other species. This is possible as the excess term in a CALPHAD assessment of Chemical Potential is already a function of the molar quantities of the other species in the system.

The present work will employ the above-mentioned thermodynamic formulation of diffusion and, coupling it to a model of a moving temperature field, investigate if the hydrogen distribution profile observed by Huang, Warnken et al[1] in their model and their comparison of it to literature can be observed in other alloy systems.

A finite difference scheme will be used to evaluate the diffusion equation - the temperature-dependent terms, mobility & chemical potential, will be determined at each step from a temperature-field described by the Rosenthal equation. The *Rosenthal equation* has been found, such as by Promoppatum et al. [4], to predict weld/melt pool geometries with broad accuracy and without intensive computation.

The authors hope that the work will improve understanding of the source of porosity and of HE in welds, and provide auxiliary validation of the cross-effects model articulated by Liu[3], which will expand understanding of the equations governing diffusion.

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Biographical Note

Jack Leeman is a 1st Year PhD student at the University of Birmingham, with research interest in computational modelling of metallurgical systems. Previously, he worked for three years in the AM industry, developing novel cemented carbide chemical compositions robust to production via blown-powder introduced to a high-power-laser.

[P02.01] Phase equilibria and solubility limits in the (Ce-Nd)-Fe-B system for new substituted permanent magnets

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Key words: thermodynamic, Rare-Earths, magnet, composition

Nd-based (Nd-Fe-B) permanent magnets are widely used in the field of new energies. However, the worldwide pressure on their supply is pushing manufacturers to develop new magnets with reduced Nd content, replaced by other less critical Rare Earths (RE), typically Ce and La [1,2]. The elaboration Nd-based magnets required a fine control of the microstructure, and more specifically of the phases present at the grain boundaries (GBP). This is also the case for Ce-substituted magnets and such complexity involves developing a numerical approach for the thermodynamic of these systems. The overall objective of this study is to better predict the manufacturing conditions of these substituted magnets of global composition $(Nd,RE)_2Fe_{14}B$.

This work focuses on the effect of the addition of Ce to the Nd-Fe-B base system. This implies a deep understanding of the thermodynamic of GBP that effectively form and not form. Presence of GBP like the Nd-rich one are needed to maintain coercivity while other like FeB will be deleterious. The presence of $REFe_2$ can be beneficial but only distributed in adjacent grains [3]. The fabrication process and heat treatments associated play a crucial role in controlling the distribution of the microstructure.

An experimental study has been carried out on the (Ce-Nd)-Fe-B system in order to improve our understanding of its thermodynamics, and results have been complied in a database according to the CALPHAD method. In addition, ab-initio and quasi-harmonic calculations have been performed to complete experimental thermodynamic results. Advantages and limitations of both experimental and computational adopted solutions will be discussed. Key systems and their thermodynamic models will be presented like the Ce-Fe-Nd system on Figure 1. The $CeFe_2$ phase solubilizes up to 54.0 at. % of Nd on the RE site at 1023 K. In a magnet, such amount of Nd in the $CeFe_2$ phase will decrease coercivity and this work helps to avoid such deleterious compositions.

Nd-based permanent magnets exhibit microstructures elaborated through successive heat treatments and largely out-of-equilibrium. Thus, magnetic performant magnet compositions cannot be directly reproduced with equilibrium CALPHAD calculation from composition. Therefore, Scheil-like solidifications have been performed and will be presented for Ce-substituted Nd-based magnet composition.

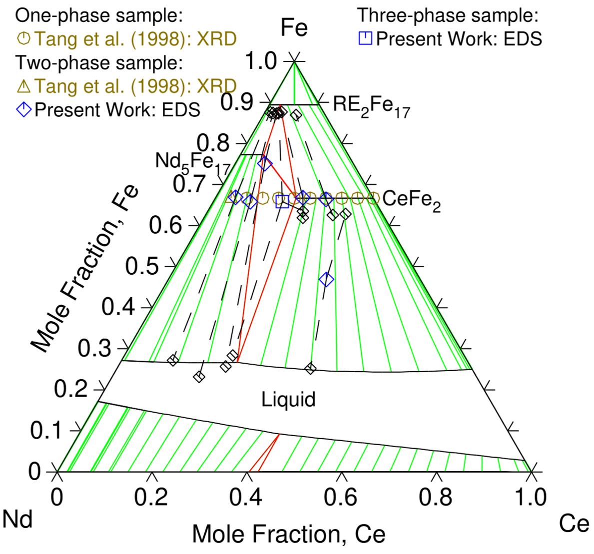

Figure 1. The Ce-Fe-Nd phase diagram at 1023 K

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Biographical Note

PhD student Eloi de Villoutreys studied Material Science at Chimie ParisTech – PSL. He is currently preparing his PhD entitled "Optimization of the manufacturing processes of Nd-Fe-B permanent magnets by an alloy design method" at CEA Paris-Saclay.

[P02.02] HP-HT modelling of Fe-Mg system: A comparison of CALPHAD-compatible models and data acquisition

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Key words: P-T modelling, Fe-Mg, LH-DAC, CALPHAD

In the realm of geology, iron and magnesium are crucial elements in the earth's internal chemistry, specifically concerning the core/mantle chemical partitioning. Recently, Dubrovinskaia et al. [1] reported that solubility of magnesium in iron reach 7.8%atMg at 89 GPa/3400°C pushing consideration of magnesium as a light element in chemical composition of the Earth's inner core. Nowadays, understanding the phase equilibria of the Fe-Mg system at high-pressure and high-temperature is crucial to enable relevant thermodynamic modelling of more complex geological systems.

In present work, we have examined this case through the lens of CALPHAD methodology. The several models existing for the modelling of Gibbs energy pressure dependence are compared in the case of unary Mg in terms of user-convenience, experimental data compatibility and physical accuracy (the model implemented in the Thermo-calc software; Brosh et al. model [2], with its own equation of state, and the Joubert et al. [3] model).

Before modelling binary Fe-Mg system, new experimental data on phase equilibria at ambient pressure and high temperature are obtained, to propose a reassessment more reliable at high temperature. Combined with pressure dependence, first Fe-Mg phase diagram at high pressure can be calculated. Finally, to improve model accuracy, new experiments under extremes pressure and temperature conditions are performed, up to in-situ measurements by X-ray diffraction in Laser-Heated Diamond-Anvil-Cells (LH-DAC) at ESRF. These measurements make it possible to follow the molar volumes of both elements during different isothermal compressions, identify melting range and potentially reveal the formation of high-pressure intermetallic phases (predicted by first-principles calculations according to Gao et al. [4])

As beam time is scheduled before the congress, initial conclusions could be drawn for the oral presentation.

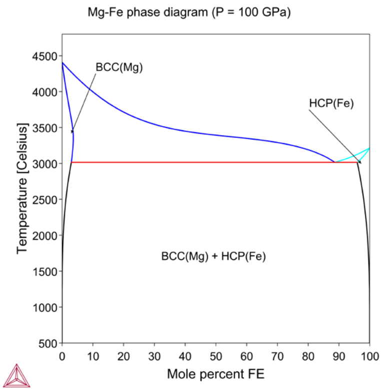

Figure 1. Fe-Mg phase diagram calculated at 100 GPa

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Biographical Note

Mathias Desseaux is a third year Ph.D student in material science at the Université Claude Bernard in Lyon. His subject of research is the high-temperature high-pressure thermodynamic study of magnesium-metal systems, especially the magnesium-iron system, which is of interest in geology. His work involves comparing various models including a pressure dependence within the CALPHAD methodology.

[P02.03] Experimental investigation and thermodynamic description of the Co–Mo–Ta system

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Key words: Isothermal sections, Liquidus surface projection, Co–Mo–Ta system, CALPHAD method

Ni-based superalloys have been widely used in aircraft engines, industrial gas turbines and other high temperature components, owing to their excellent high temperature strength and thermal stability. This is mainly attributed to the precipitation of γ′-Ni_3Al phase with $L1_2$ structure from the disordered γ matrix and the formation of a γ/γ′ coherent interface in Ni-based superalloys. Traditional Co-based superalloys are mainly strengthened by precipitation of carbide and solid solution of refractory elements. Due to a lack of precipitation strengthening from the γ′ phase, the high temperature strengths of traditional Co-based superalloys are relatively limited, which hinders further application. In 2006, Sato et al. discovered a γ′-Co_3(Al, W) phase in the Co–Al–W system and observed a γ/γ′ coherent microstructure at 1173 K in the Co–9 at.% Al–7.5 at.% W alloy. This promoted worldwide research on novel Co-based superalloys as next generation high temperature materials. However, the stability of γ′ phase was inferior at high temperature in the Co–Al–W system. To make the γ′ phase become more stable, appropriate addition of alloying elements is a common method to increase the stability and solvus temperature of the γ′ phase.

Both Mo and Ta are main constituent elements of Co-based superalloys. A small amount of Mo partitions preferentially to γ matrix and enhances the solid solution strengthening effect. In addition, Mo can improve hardness, abrasion resistance and corrosion resistance of Co-based superalloys. Ta tends to partition to the γ′ phase, which can increase γ′ solvus temperature and enhance its stability. Therefore, the Co–Mo–Ta system is one of the important subsystems of Co-based superalloys.

In order to understand the relationship between microstructure and alloy composition, accurate phase equilibria information of the Co–Mo–Ta system is required. The CALculation of PHAse Diagram (CALPHAD) method is considered to be a useful and efficient method. Therefore, the 1273 and 1473 K isothermal sections and the liquidus surface projection of the Co–Mo–Ta system were first determined using a series of equilibrated alloys and as-cast alloys in this work. Based on the obtained experimental data, thermodynamic optimization of the Co–Mo–Ta system was performed using CALPHAD method.

38 equilibrated alloys and 30 as-cast alloys were investigated using SEM/EDS and XRD methods. The isothermal sections at 1273 and 1473 K and the liquidus surface projection of the Co–Mo–Ta system were constructed. Two three-phase regions $Co_3Mo+\lambda_3+\mu$ and fcc(Co)+$Co_3Mo+\lambda_3$ at 1273 K, and one three-phase region fcc(Co)+$\lambda_3+\mu$ at 1473 K, were determined. Eight primary solidification phase regions, bcc(Mo, Ta), $CoTa_2$, σ, μ, λ_1, λ_2, λ_3 and fcc(Co), and five invariant reactions, liq.+bcc(Mo, Ta)+σ→μ, liq.+$CoTa_2$→μ+bcc(Mo, Ta), liq.+$\lambda_2\rightarrow\lambda_1+\lambda_3$, liq.→$\lambda_1+\lambda_3+\mu$ and liq.→fcc(Co)+$\lambda_3+\mu$, were obtained in the liquidus surface projection. No ternary compounds were found in the Co–Mo–Ta system. On the basis of the obtained experimental data in this work, the Co–Mo–Ta system was optimized by using CALPHAD method. A set of self-consistent thermodynamic parameters was obtained.

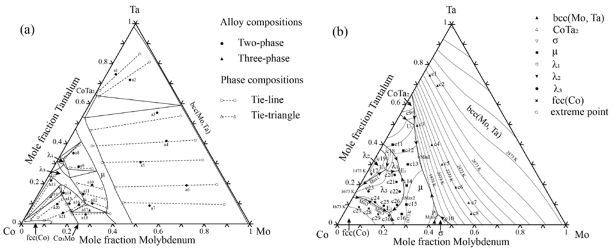

Figure 1. Calculated isothermal section at 1273 K (a) and liquidus surface projection (b) of the Co–Mo–Ta system in comparison with experimental data.

This work was supported by National Natural Science Foundation of China (NSFC) (Grant No. 52271002).

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Biographical Note

Yu Shi, a PhD student from University of Science and Technology Beijing, is mainly engaged in experimental phase diagram determination and thermodynamic calculations.

[P02.04] Study on the γ + γ′ microstructure characterization of the Co–V–Zr system based on the CALPHAD method

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Key words: Co–V–Zr system, Liquidus surface projection, Metastable phase, CALPHAD method

Some alloy elements are often added to obtain the γ + γ′ microstructure for novel Co-based superalloys. There is a metastable Co_3V phase with $L1_2$ structure in the Co–V binary system. Therefore, this paper mainly studies the evolution of γ + γ′ microstructure by adding the element Zr based on the CALculation of PHAse Diagram (CALPHAD) method. The experimental liquidus surface projection and isothermal sections at 1373 and 1273 K of the Co–V–Zr system were constructed based on solidification microstructures and phase constituents. A new ternary phase τ with $Cr_{0.5}Fe_{1.5}Zr$-type structure was confirmed using Rietveld refinement, and the heat capacity was measured using the sapphire method and enthalpy of formation at 0 K was calculated by density functional theory (DFT). The measured composition range of Zr in τ was ~ 28.6 to 57.3 at. % and 32.9 to 56.8 at. % at 1373 and 1273 K, respectively. The liquidus surface projection identified nine primary solidification areas, while an additional two primary solidification areas were inferred from binary diagrams. Moreover, eight and ten three-phase equilibria were determined at 1373 and 1273 K, respectively. The measured solubilities of V in $Co_{23}Zr_6$, λ_2 and CoZr were ~0.5, 7.6 and 4.1 at. % at 1373 K. Meanwhile, the solubilities of V in $Co_{23}Zr_6$, λ_2, CoZr and $CoZr_2$ were measured to be ~ 0.4, 7.6, 1.6 and 3.6 at. % at 1273 K. The solubility of Zr in Co_2V_3 was ~ 3.6 at. % at 1373 K, while the solubilities of Zr in Co_3V, Co_2V_3 and CoV_3 were determined ~1.3, 3.0 and 4.5 at. % at 1273 K, respectively. Based on the above experimental data, the Co-V-Zr system was optimized using CALPHAD method. Four solution phases of liquid, bcc, fcc, and hcp, were described as substitutional solution. The thermodynamic models of $Co_{11}Zr_2$, $Co_{23}Zr_6$, $CoZr_2$, Co_3V, Co_2V_3, CoV_3, λ_2 and τ were treated as $(Co)_{11}(V, Zr)_2$, $(Co)_{23}(V, Zr)_6$, $(Co, Zr)(V, Zr)_2$, $Co_3(Co, V)$, $(Co, V, Zr)_{10}(Co, V, Zr)_{20}$, $(Co)(V, Zr)_3$, $(Co, V, Zr)_2(Co, V, Zr)$ and (Co, V, Zr)(Co, V, Zr) using a two-sublattice model, respectively. $CoZr_3$ was described as $(Co, Zr)(Co, Zr)Zr_2$ by a three-sublattice model. And CoZr with a B2 structure was described as an ordered phase of bcc_A2, and the model was treated as $(Co, V, Zr, Va)_{0.5}(Co, V, Zr, Va)_{0.5}(Va)_3$. Based on the thermodynamic analyses of this work, the alloy Co80V19Zr1 (at.%) was homogenized at 1473 K for 10 h and aged at 1173 K for a different time, the γ′ phase with $L1_2$ structure coarsened and dissolved after 2 h, and transformed into needle-like $D0_{19}$-Co_3V after 67 h of aging. This shows that these γ′ phases are metastable and therefore would be stabilized via adding additional alloying elements.

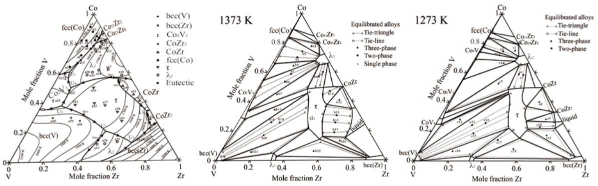

Figure 1. Calculated liquid surface projection and isothermal sections in comparison with experimental data.

This work was supported by Beijing Natural Science Foundation (Grant No. 2232077).

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Biographical Note

Jiaxing Sun, a PhD student from University of Science and Technology Beijing, is mainly engaged in experimental phase diagram determination and thermodynamic research of Co-based superalloys.

[P02.05] Thermodynamic Modeling of the Cu–Sn system: Considering the crystallography of NiAs/Ni_2In-type phases

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Key words: phase diagram, ordering, diffusion, intermetallic phases

The Sn-rich part of the Cu–Sn system is crucial for understanding the interaction of Sn-rich solder with Cu-based materials. The formation of intermetallic phases during the soldering process strongly influences the mechanical properties and, consequently, the durability of the solder joints. Although various elements beyond Cu and Sn may significantly influence the phases that develop in corresponding systems, it turns out that even the binary Cu–Sn phase diagram exhibits inconsistencies. Many published phase diagrams correspond basically to that one contained in the Hansen & Anderko's compilation [1]. This diagram contains a Cu_6Sn_5 phase with some narrow homogeneity range, as well as high and low-temperature phases designated as η and η', respectively. As reviewed in Ref. [2], both phases possess a NiAs/Ni_2In structure, where one atomic site in the hexagonal basic structure is simultaneously occupied by Cu atoms and vacancies, allowing for slight variations in composition. In the η phase this happens in a disordered fashion, whereas in the η' phase a superstructure is formed. Moreover, additional superstructures were reported (η^8, η^6, η^{4+1}), but they were not incorporated as additional phases in later versions of the phase diagram.

Recent research has made significant progress in understanding the observation of Cu_6Sn_5-related crystal structures in Cu–Sn alloys beyond the structures of η and η' (e.g. [2]). This progress was achieved by employing precise lattice parameters to assess the actual chemical composition of the intermetallic phase through the unit-cell volume. Heat-treatments at temperatures $T \geq 240°C$ were conducted in contact with Sn melt or the ε-Cu_3Sn phase to investigate characteristic compositional changes of the high-temperature η phase in equilibrium with the other phases. The heat-treatments at temperatures $T < 240°C$ were found to induce ordering, particularly towards metastable incommensurate and Cu-rich η'' phase, corresponding to what was earlier reported as η^8 and η^{4+1} (for details see [3]). At these low temperatures, Cu/Sn partitioning occurs very slowly, while partitionless ordering takes place much more rapid. Such insight is crucial to correctly interpret states as metastable or equilibrium.

The assessment was conducted based on the thermodynamic description provided in Ref. [4], together with a sublattice model introduced by Kattner in 2003 [unpublished]. Accordingly, the high-temperature η phase was modeled using three sublattices: one Sn-sublattice corresponding to the 2*c* site, one Cu-sublattice corresponding to the 2*a* site, and one Cu- and Vacancy-sublattice corresponding to the 2*d* site (see e.g. [4]). The modeling of the intermetallic phases η/η' as well as ε was based on heat capacity data and information on the enthalpies of formation for several intermetallic phases. All of these factors contribute to the phase diagram depicted in Figure 1.

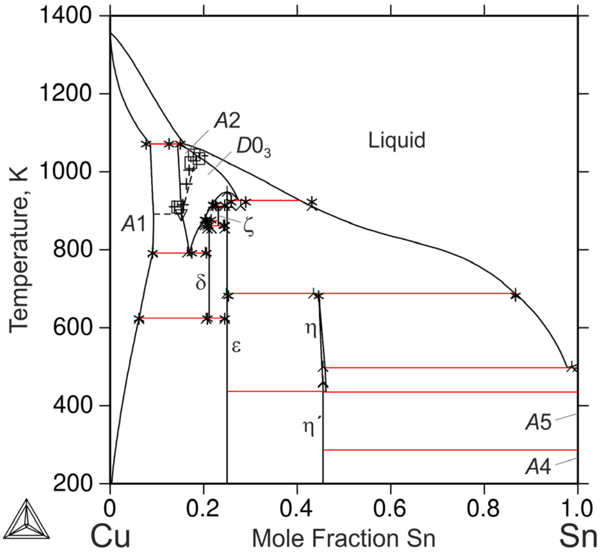

Figure 1. Assessment of the binary Cu–Sn system

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Biographical Note

Mario J. Kriegel studied Materials Science and Technology and received the doctoral degree in 2014 at the TU Bergakademie Freiberg. Since 2009, he works as research associate in the Institute of Materials Science in Freiberg. His research interests are calorimetry, experimental investigation and modeling of phase diagrams (mainly metallic systems).

[P02.06] The assessment of the Al-Ge-Mg system

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Key words: Al-Ge-Mg system, CALPHAD assessment, ab initio calculations, ternary phase

The aluminum based alloys are currently of great interest in the automotive and aerospace industry as they have a combination of favorable material properties, e.g. good castability, low density, high specific strength and stiffness, and outstanding corrosion resistance [1]. Further improvement of their material properties can be reached by addition of alloying elements. Magnesium and germanium are currently experimentally and theoretically studied for such reason [2]. The alloying elements can influence the precipitation process in Al-Si based alloys and play an essential role in controlling alloy microstructure. Nevertheless, proper exploitation of those precipitates depends on the knowledge of relevant phase diagrams.

The ternary phase diagram Al-Ge-Mg has not yet been experimentally studied in detail in the past despite of the importance of the system in above mentioned engineering application. The theoretical modelling was done by Islam *et al.* [3]. This work does not include ternary intermetallic phase with the compound formula $MgAl_2Ge_2$ experimentally identified later by Pukas [4].

The set of isothermal sections between 250 and 450 °C was studied in the scope of the experimental program and published in [2]. A consistent experimental results showed significant nonstoichiometric composition of the ternary phase. Recent ab initio calculations confirmed the theoretical possibility of such behavior. Also, several new results were obtained in the study [2], namely the nonstoichiometric composition of the $GeMg_2$ binary intermetallic phase. This phase was described as stoichiometric up to now, but the experimental Ge-Mg phase diagram is based mainly on DTA/DSC data and no information about real composition of this phase was available. Our continuing experimental program confirmed above mentioned findings and also indicates increasing solubility of Mg with increasing temperature.

These experimental results are used together with results from literature for the CALPHAD type theoretical assessment of Al-Ge-Mg system. The reassessment of the Al-Mg and Ge-Mg binary systems are necessary for correct description of the ternary system using combination of CALPHAD approach and ab initio calculations, including the theoretical modelling of heat capacities.

The main aim of this study is to obtain complete assessment of the Al-Ge-Mg ternary system, representing our new experimental data.

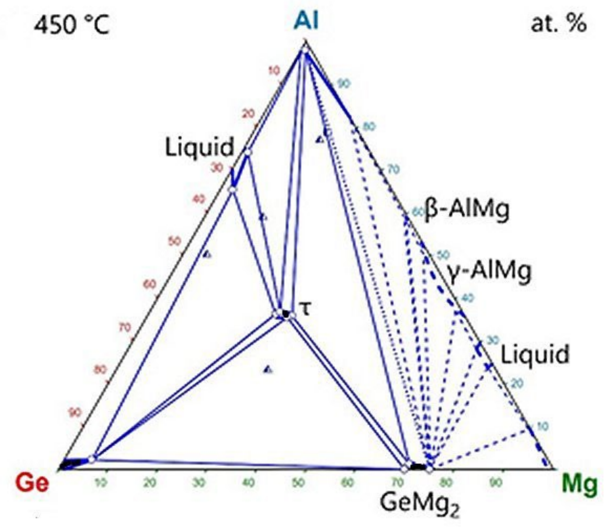

Figure 1. Isothermal section of the experimental phase diagram of Al-Ge-Mg system at 450°C

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Biographical Note

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I am specialized in the thermodynamics of alloys, theoretical and experimental assessments of complex systems, and development of thermodynamic models and databases.

[P02.07] Experimental investigation and thermodynamic description of selenium-based systems

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Key words: Co-Se, Co-Se-Sn, CALPHAD, experimental data, ab initio

A new thermodynamic description of the binary Co-Se system was introduced using the CALPHAD approach to predict and describe the phase equilibria, including the development of new models for phases CoSe[1], Co_9Se_8[1] and $CoSe_2$[1]. The models and thermodynamic description were verified by comparing the predicted phase diagram with the experimental data obtained in this study and calculated ab initio data.

Furthermore, the ternary Co-Se-Sn system has been investigated experimentally to determine the phase equilibria and the microstructure of the alloys formed at temperatures 400, 600 and 1000 °C (see **Figure 1** for an isothermal section at 600 °C).

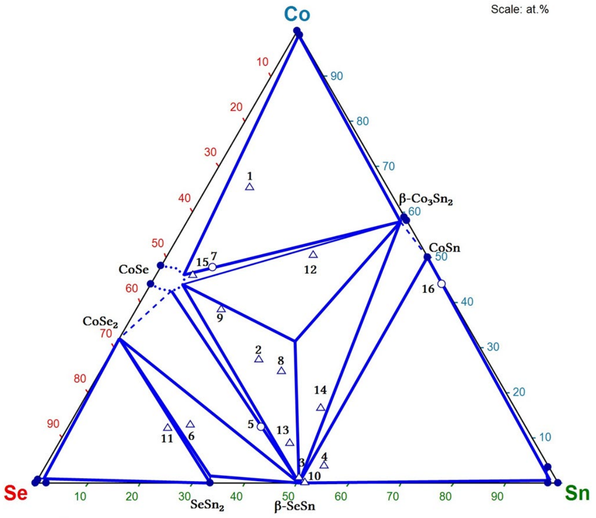

Figure 1: Isothermal section of Co-Se-Sn ternary phase diagram at 600 °C

Samples of various compositions were prepared using a preliminary ternary phase diagram based on the thermodynamic data of binary systems[1,2,3]. Samples were melted, long-term annealed, quenched and characterized using scanning electron microscopy, X-ray diffraction and thermal analysis. The combined experimental results confirmed the presence of several binary phases in this system, including Co_3Sn_2[2], $CoSn_2$[2], CoSe[1], Co_9Se_8[1], $CoSe_2$[1], SeSn[3], $SeSn_2$[3] and one skutterudite-related ternary phase $Co_2(SnSe)_3$[4].

The experimental and modelling results obtained in this study provide new insights into the behaviour of the Co-Se and Co-Se-Sn systems. They can be applied in the design and optimization of Co-based alloys for various industrial applications, such as magnetic storage media, high-temperature materials, and thermoelectric devices.

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Biographical Note

Dávid Mikšík is a PhD student at Masaryk University. His research focuses on the experimental investigation of thermodynamic properties and CALPHAD modelling of selenium-based systems.

[P02.08] Thermodynamic assessment of Si-Zr and Cu-Si-Zr systems

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Key words: CALPHAD, EPMA, Pyrometer, VASP: AIMD

Inherent challenges emerge when investigating high-temperature phase transitions and thermal measurements in 'Zr-rich' alloys, impeding precise CALPHAD modeling. This study embraces a non-contact approach, employing arc-melting with a pyrometer to accurately gauge Si-Zr and Cu-Si-Zr phase transitions.

Initially, twenty Si-Zr binary alloys are prepared using the arc-melting technique, and their compositions are determined through the ICP-OES technique. Subsequent experiments record the temperature profile of these alloys in the arc-melting device using a pyrometer. Comparing temperature-versus-time graphs with their as-cast electron micrograph reveals key features such as liquidus, primary solidifying phase, invariant temperature, and other phase transitions. The Si-Zr system encompasses seven intermetallic compounds, with their energy of formation calculated using the ab initio method. Additionally, ab initio molecular dynamics (AIMD) simulations compute the energy of mixing in the Si-Zr liquid phase. Figure 1 shows the calculated Si-Zr phase diagram.

Figure 1 portrays the calculated Si-Zr phase diagram, the comparison with the literature information and new results will form the highlight of this work and it is an input for the Cu-Si-Zr phase diagram.

The synthesis of fifty-seven Cu-Si-Zr alloys is accomplished through the arc-melting technique. As-cast EPMA analyses for forty-three alloys, encompassing thirty-six Cu-Si-Zr compositions and seven intermetallic phase compositions, elucidate the primary solidifying phase within the Cu-Si-Zr composition domain. A comparison between temperature-versus-time graphs and their as-cast electron micrograph reveals invariant points and multiple phase transitions in fifteen alloy compositions. Further, heat treatment of fourteen samples at 1073 K refines the isothermal section, with emphasis on the Zr-rich corner. The calculation of formation enthalpy ($\Delta_f H$) for stable Cu-Si-Zr ternary phases is conducted through ab initio calculations using VASP. Additionally, crystallographic, phase boundary, and thermal data about the Cu-Si-Zr system, as well as Gibbs energies of Cu-Si and Cu-Zr stable phases, are sourced from the literature.

Figure 2a displays a hand-drawn isothermal section at 1073 K from Sprenger's [1] experiments while figure 2b illustrates our experimental isothermal section results at 1073 K, consistent with the Meng et al.'s [4] findings. A comparison with the Sprenger [1] isothermal graphs at 1073 K with the present work (figure 2b) highlights discrepancies in the existence of $CuSi_2Zr$ (τ_2), and CuSi4Zr2 (τ_3) phases. CALPHAD modeling of the Cu-Si-Zr system is using the updated Si-Zr binary phase diagram.

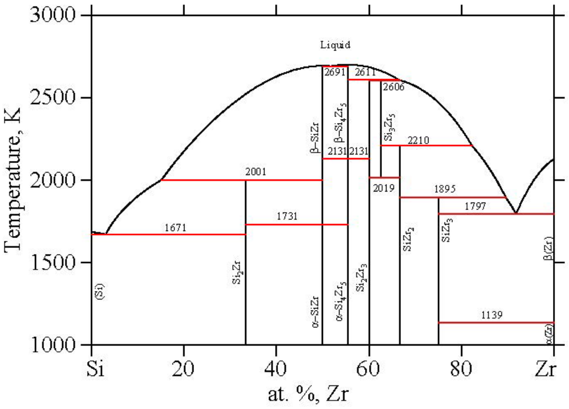
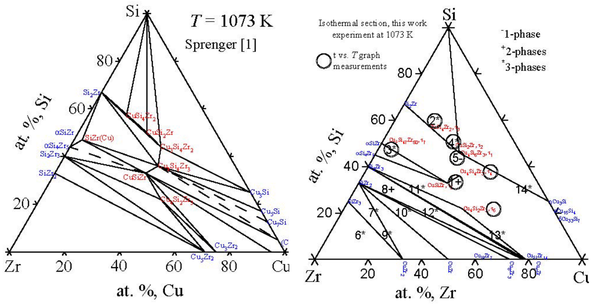


Figure 1. Calculated Si-Zr binary phase diagram



(a) (b)

Figure 2. Cu-Si-Zr isothermal sections at 1073 K.

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Biographical Note

The author is sharing insights from his post-doctoral research work at Central South University, Changsha, P.R. China.

[P02.09] Thermodynamic assessment of Cr-Mo-Si system

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Key words: Thermodynamic modelling, CALPHAD, Ternary alloys, Phase diagram

Cr rich alloys in the Cr-Mo-Si system show encouraging experimental results on oxidation resistance and mechanical performances. These materials exhibit high oxidation resistance by the formation of chromia scales with very low growth rates at both intermediate around 800 ⁰C and enhanced temperatures up to 1100 ⁰C [1]. These promising experimental results justify the need of the thermodynamic modelling of the ternary system Cr-Mo-Si using CALPHAD (Calculation of Phase Diagram) approach.

The thermodynamic modelling of the solution phases can be successfully achieved applying Compound Energy Formalism (CFE) in the framework of CALPHAD. The primary focus of the project lies in the Cr & Mo-rich regions where the Cr-Mo-Si system contains – according to experimental results – four solution phases namely liquid, (Cr,Mo)ss, $(Cr,Mo)_3Si$ (A15) & σ-phase [1]. The thermodynamic descriptions of phases in the system Cr-Mo-Si in the literature is not well established, especially for the σ-phase. Therefore, in this study thermodynamic assessment of Cr-Mo-Si will be carried out starting with binary systems. FactSage is used for thermodynamic calculations.

Czerny et al. [2] recently investigated the Mo-Si binary system considering the stoichiometry range of Mo_3Si. They successfully modelled Mo_3Si phase as a solution instead of a compound phase and updated the entire Mo-Si binary phase diagram. The results of this study were adopted for the present work (see Figure 1.) revealing good agreements between our own calculations and those from [2] and the results for calculated phase diagram and phase equilibria are well in agreement with [2].

Thermodynamic descriptions of Cr-Si binary system were taken from Chen et al. [3]. This reference described the incongruent melting behavior of Cr_5Si_3 phase by adopting two sublattice model. Our own results reveal that the calculated phase diagram is in consistent with [3]. In particular, the allotropic transformation of α-Cr_5Si_3 to β-Cr_5Si_3 is well reproduced, see Figure 1.

The phase description in the Mo-Cr descriptions were selectively adopted from Frisk et al. [4]. The calculated phase diagram (see Figure 1) shows that the binary system has a continuous body centered cubic solid solution with a miscibility gap which forms at temperatures below =1215 K that is in correspondence with [4].

Our current research activities are concentrated on the modelling of the ternary system Cr-Mo-Si including thorough experimental investigations of the selected alloys from this system.

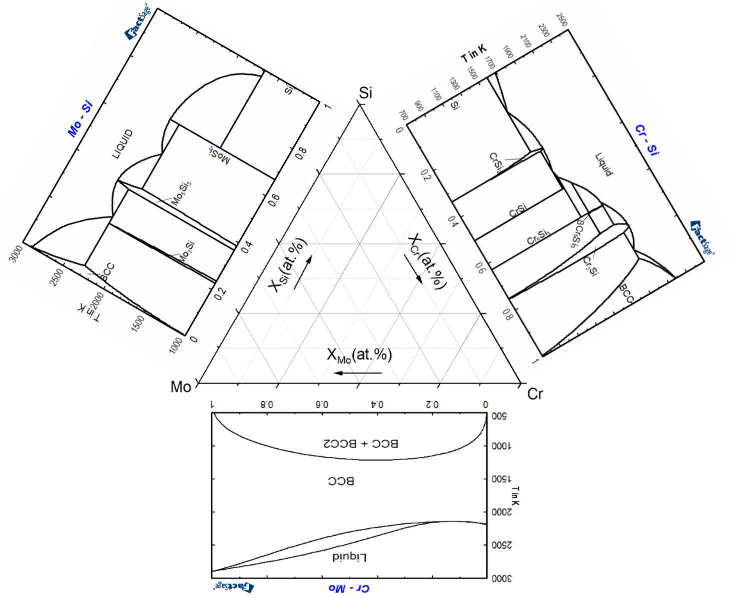

Figure 1. Calculated binary phase diagrams of the Cr-Mo-Si ternary system.

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Biographical Note

Arun Ramasamy Chitra is a 1st year doctoral candidate at Karlsruhe Institute of technology.
Bronislava Gorr is a Professor at Karlsruhe Institute of technology. She is a director of Institute for Applied Materials-Applied Material Physics (IAM-AWP).

[P02.10] Effect of strain energy on the formation of G.P. zone in the Al-Cu binary system

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Key words: Metastable phase, First-principles calculation, Monte Carlo simulation

Introduction

The Al-Cu binary alloy is known to undergo age-hardening by forming G.P. zones in the aging process. However, the thermodynamic origin of the formation of the metastable structures has not been clarified. In the previous CALPHAD meeting, [1] we presented the phase diagram including the metastable ordered phase of G.P.(II) using the CALPHAD method, but the effect of strain energy based on the large atomic radius difference peculiar to this alloy was not examined. The formation behavior of G.P. zone in the Al-Cu binary system was analyzed by the mixed-space cluster expansion method considering coherency strain energy.[2] In this study, we calculated the free energies of the FCC solid solution fixed to several equilibrium volumes, and obtained the envelope of the free energy lines for taking account of the effect of strain. The essence of this interesting phenomenon will be discussed from the viewpoint of order-disorder transformation.

Method

In some volumes that existed between the equilibrium volumes of pure Al and pure Cu, a number of super structures fixed to each volume were constructed. Each ordered structure was divided into a variety of clusters and the cluster effective interaction energies were evaluated so as to reproduce the formation energies calculated by the first-principles computational code VASP.[3] The free energy fixed to the selected equilibrium volume was calculated using the cluster variation method.[4] From the envelope of the free energy lines for these volumes, the free energy considering the effect of the lattice strain was calculated and the result was analyzed by the split 4-sublattice model to investigate the metastable equilibria in the FCC solid solution.

Result

Figure 1 shows the results of the free energy calculated at 400 K. Outline symbols represent the calculated free energy confined to each equilibrium volume. The red triangles are the strain-aware free energy derived from the envelope of those curves. Figure 2 shows the calculated metastable phase boundaries for FCC solid solution. The cross mark in the diagram represents the tie-line determined from the free energy curve. In this computation, the free energy of the disordered FCC phase as well as other phases were derived from Liang *et al.* [5] It was found that the ordered phase with G.P.(II) structure was formed in the metastable region of the FCC solid solution, however the experimentally reported G.P.(I) [6] did not appear. The Monte Carlo simulations using the analyzed interaction energetics revealed clusters of Cu atoms along the (100) plane at the early stage of aging.

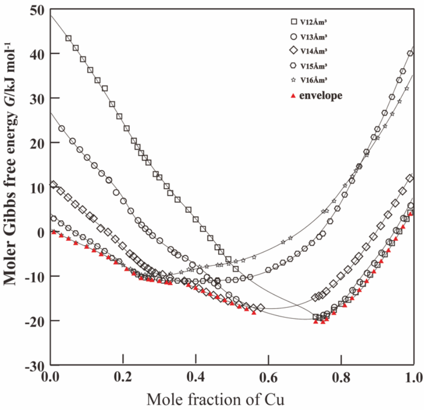

Fig.1 The result of the calculated free energies of the FCC phase at 400K.

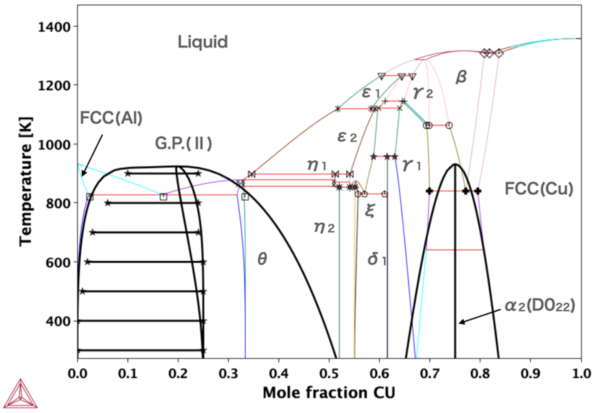

Fig.2 Metastable phase boundaries for FCC phase drawn in the equilibrium Al-Cu binary phase diagram given by the thin lines.

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Biographical Note

Takao Suzuki is a second-year doctoral student. He is working on a theoretical phase diagram method that does not use any fitting parameters.

[P03.01] High-pressure phase diagram of Bi-Ga: Polymorphism, anomalous melting curves and liquid miscibility gap

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Key words: Alloy phase diagram, High pressure, Bi-Ga, Liquid miscibility gap

The high-pressure states of the elements can significantly impact the phase diagrams of their alloys due to polymorphism in the solid state and anomalies and slope changes in the melting curve. Here, we investigate the effect of these characteristics on a model system, the monotectic Bi-Ga system, in which both Ga and Bi have anomalous melting curves and several solid phases. We constructed a CALPHAD thermodynamic model for the high-pressure phase diagrams of Bi-Ga alloys up to 10 GPa. We experimentally identified the phase lines in the phase diagram of this system by measuring the electrical resistance in a Paris-Edinburgh press under high pressure and temperature conditions. We find a strong connection between the elemental phase diagrams of Bi and Ga, the particular form of the ambient pressure alloy phase diagram, and the behavior of the high-pressure phase diagram. We also obtained very good agreement with our calculated phase diagram up to 6 GPa and the measured transitions. For example, the anomalous behavior of the monotectic temperature and the liquidus line was calculated and validated experimentally. At higher pressures, the liquid miscibility gap in this system disappears, and the phase diagram changes from a monotectic to a eutectic type at a pressure of 8 GPa.

The present contribution demonstrates the significant contribution of the high-pressure behavior of the elements in characterizing the complex behavior of alloys under pressure. It also demonstrates the necessity to consider the pressure dependence of the thermodynamic parameters in the CALPHAD method, e.g., mixing interaction parameters, for high-pressure calculations of alloy phase diagrams. This work also demonstrates the utility of the CALPHAD method in analyzing P-T experiments on such systems.

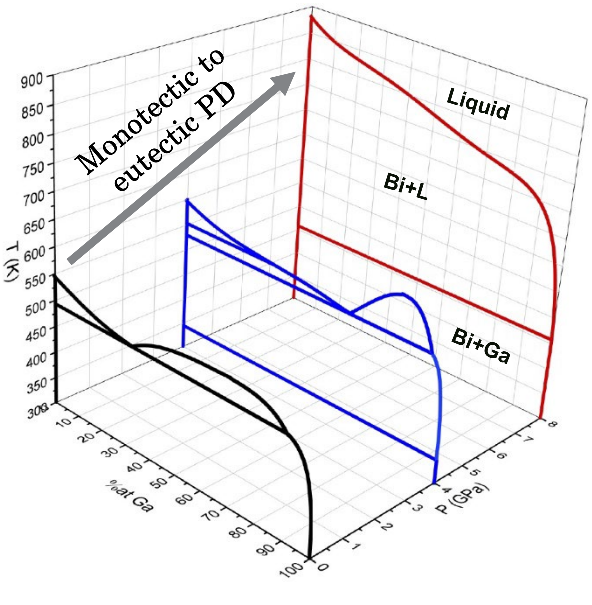

Figure 1. The phase diagram of Bi-Ga, as a function of pressure, demonstrates the transition from monotectic to eutectic phase diagram.

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Biographical Note

Shir Ben Shalom is a Ph.D. student and a teaching assistant in the Department of Materials Engineering at Ben-Gurion University of the Negev, Israel. Her research develops and applies new tools for studying pressure effects on binary phase diagrams, including thermodynamic modeling based on the CALPHAD method, which remain mostly unexplored.

[P03.02] Development of a thermodynamic database for Li recycling

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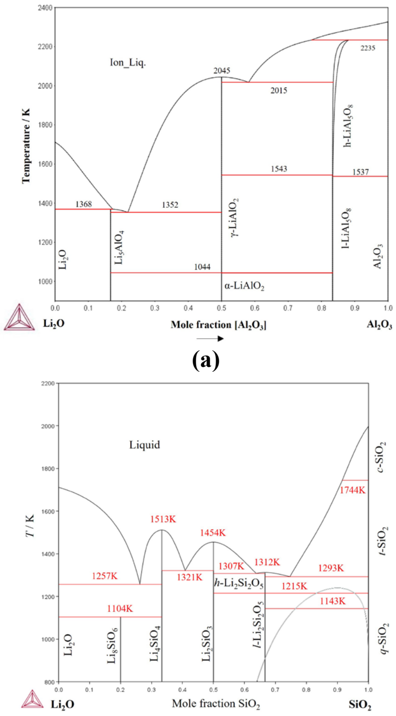
Key words: Li recycling, Phase diagram, Thermodynamic modeling, CALPHAD method

The importance to recycle and recover valuable transition metals (such Co, Ni) and Li increased in the recent years. Several metallurgical methods have been studied to obtain transition metals from their respective oxides after slag separation and crystallization processes. In this context, Li_2O reacts with slag forming $LiAlO_2$ or spinel solid solution [1-2]. Thus, the development of thermodynamic database for the Li_2O-MnO_x-SiO_2-Al_2O_3 is an important tool to optimize conditions, aiming to obtain maximal separation of Li_2O from the slag [3]. Using the CALPHAD method, investigations of pseudo-ternary and pseudo-binary systems among these oxides have been performed by our research group. The Li_2O-Al_2O_3 and Li_2O-SiO_2 systems were experimentally investigated in the present study. Crucial experiments were performed using samples produced by solid state reaction (initial chemicals were Li_2O, Li_2CO_3, SiO_2 and Al_2O_3). Microstructural investigations were carried out via microstructural characterization using Scanning Electron Microscope (SEM) and X-Ray Diffraction (XRD). Furthermore, Differential Thermal Analysis (DTA) was used to measure the temperature of invariant reactions followed by microstructure investigation to determine nature of these reactions. Heat capacities of $LiAlO_2$, $LiAl_5O_8$ and Li_8SiO_6 phases were experimentally obtained by Differential Scanning Calorimetry (DSC). Both phase diagrams were optimized using the Compound Energy Formalism (CEF) for solid phases. Two-sublattice partially model was adopted for liquid description. The spinel phase $(Al^{+3}, Li^{+1})_1^T{:}(Al^{+3}, Li^{+1}, Va)_2^O{:}O_4$ was modeled using two cationic sublattices to describe the high degree of inversion and its extension in Al_2O_3 composition region assuming presence of the vacancies in octahedral sites [4].

The derived thermodynamic databases reproduce satisfactorily the phase equilibria in Li_2O-Al_2O_3 and Li_2O-SiO_2 systems as shown in Fig.1, as well as the thermodynamic values. Preliminary thermodynamic description for the MnO_x-SiO_2 was also derived accounting the available experimental data in literature.



(a)

(b)

Figure 1.: Calculated phase diagrams of the (a) Li_2O-Al_2O_3 and (b) Li_2O-SiO_2 systems.

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Biographical Note

Danilo Alencar de Abreu is Dipl.-Ing. and M.Sc. in Materials Science and Engineering by University of Sao Paulo, where he performed experimental investigations of phase diagrams for metallic systems. Currently, he works as assistant researcher at TU Bergakademie Freiberg, studying oxide systems to provide a new thermodynamic database for lithium recycling.

[P03.03] Carbon solubility in solvent for SiC rapid solution growth: Thermodynamic evaluation of Si-Cr-Ce-C system

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Key words: SiC, Solution growth, Carbon solubility, Phase diagram

Silicon carbon is a third generation semiconductor with wide-band gap, high electrical breakdown field and high thermal conductivity, making it suitable for applications in high temperature ranges, high-frequency fields and high-power devices. The bulk SiC crystals are typically produced using the physical vapor transport (PVT) method. However, the difficulty in reducing the dislocation density in the PVT-grown crystals still affects the performance and reliability of the related devices.

During the past decade, solution growth has attracted much attention as a new method to grow SiC bulk crystals. Utilizing the solution growth route, relatively low dislocation density could be obtained because the growth interface of solution growth is more close to thermal equilibrium state compared to that in PVT process. Furthermore, the metal incorporation can also be easily realized by involving the related raw materials in the solvent. It has been reported that the p-type SiC crystals (Al doped) could be grown using the solution growth method with the Al in solvent during the SiC crystal growth. Specifically, the solution growth process of SiC crystals is carried out by employing the top-seeded solution growth (TSSG) technique, where a seed wafer is dipped in the top of the solution. Generally, the Si-based alloy solvents are used as the solution, and it is charged in a graphite crucible to dissolve the carbon as the carbon source. It has been considered that the carbon solubility in the solvent plays a key role in dominating the quality of the grown single crystals. Generally, large carbon solubility is necessary to provide enough SiC solute for the solution growth process. However, the systematic investigation of carbon solubility in multi-component solvent system is still lacking.

Here we study the thermodynamic evolution of Si-Cr-Ce-C system by CALPHAD method to investigate the carbon solubility in this multi-component alloy solvent. The carbon solubilities in Si-Cr and Si-Ce binary flux were firstly measured by the chemical component analysis. The quaternary phase $CeCr_2Si_2C$ was also synthesized, and its thermodynamic properties were determined. Based on these experimental results, phase relations of Si-Cr-Ce-C system were evaluated based on the CALPHAD technique. The carbon solubility was extracted from the different isothermal sections. It is indicated that the addition of Ce in Si-Cr binary solvent significantly enhances the carbon solubility. Our work not only presents the superiority of Si-Cr-Ce ternary solvent for the rapid solution growth of SiC, but also provides an example to detect the carbon solubility in multi-component solvent via CALPHAD method.

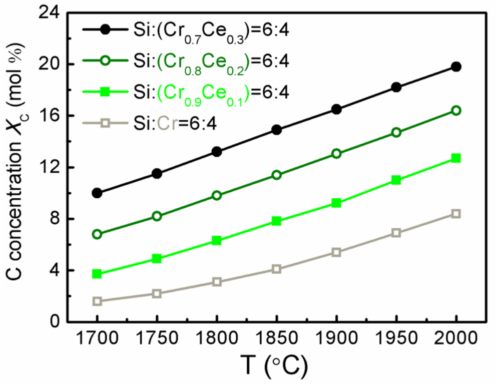

Figure 1. The carbon solubility in Si-Cr-Ce ternary alloy solvent calculated from the CALPHAD technique.

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Biographical Note

Zhongnan Guo is an associate professor of University of Science and Technology Beijing. His current research focuses on the crystal growth of inorganic functional materials, multi-component phase diagram calculation and topological electrocatalysis.

[P03.04] Experimental and computational study on phase diagram thermodynamics of the Cu-Cr-Zr-Mg-Y system

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Key words: Copper alloy, Phase equilibria, Phase diagram, CALPHAD, Thermodynamics

Copper alloys with the addition of chromium, zirconium, magnesium and yttrium are attractive high strength and high conductivity (HSHC) copper alloys which are widely used in new energy, electrical and electronic, rail transit and so on. Phase diagram and thermodynamic studies in the Cu-Cr-Zr-Mg-Y system are expected to provide new insights into designing HSHC copper alloys. In this work, the solidified and equilibrium microstructures and phase transition temperatures in the Cu–Zr–Y, Cu–Cr–Y and Cu–Cr–Mg ternary systems were studied by X-ray diffraction (XRD), electron probe microanalysis (EPMA) and differential scanning calorimeter (DSC). The isothermal sections at 973 K for the Cu–Zr–Y system and at 673 K for the Cu–Cr–Y and Cu–Cr–Mg systems were constructed experimentally. No ternary compound was found, while the Cu6Y, Cu4Y, Cu7Y2, Cu5Zr, Cu51Zr14 and CuZr phases substantially extended into the ternary system. The Cu-Zr-Y, Cu-Cr-Y and Cu-Cr-Mg systems were evaluated using the CALPHAD (CALculation of PHAse diagrams) method based on the experimental data from this work and the literature. A set of self-consistent thermodynamic parameters for the Cu-Cr-Zr-Mg-Y system was obtained by combining the thermodynamic data of all the subsystems in the literature. The isothermal sections, vertical section and liquidus projections calculated by the present thermodynamic description agree well with the experimental results. Simulations of Scheil solidification of multicomponent copper alloys were carried out and the results agree with the literature.

The thermodynamic database of the Cu-Cr-Zr-Mg-Y system constructed in this work can be used to calculate the phase diagrams and thermodynamic information of the multi-component alloys, and also as an important input parameter for microstructure simulation, which in turn can guide the composition design and process optimization of the HSHC copper alloys.

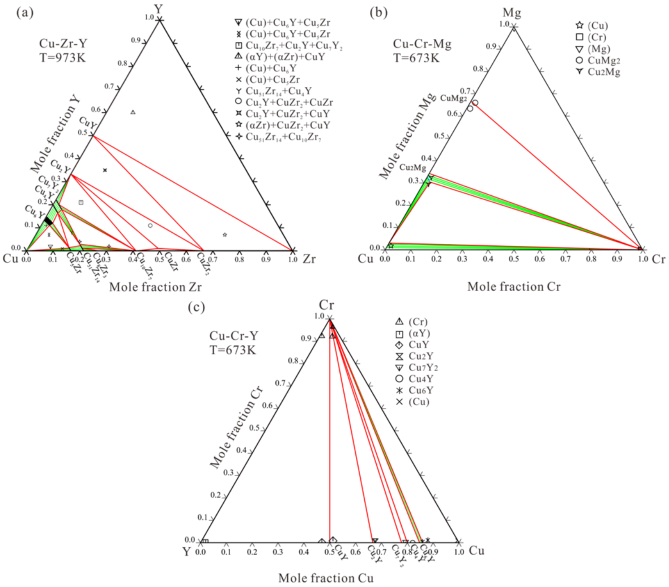

Figure 1. Calculated isothermal sections with experimental data from this work; (a) Cu-Zr-Y system at 973 K; (b) Cu-Cr-Mg system at 673 K; (c) Cu-Cr-Y system at 673 K.

Biographical Note

Fengting Jing is currently a PhD candidate at Central South University, China. She obtained her B.Sc. and M.Sc. degrees in 2020 and 2023, respectively. Her current research focuses mainly involve copper alloys, phase diagram thermodynamics, and microstructure evolution simulation.

[P03.05] A Third Generation CALPHAD Description of Pure Nb

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Keywords: Thermodynamic Database, 3rd Generation Thermodynamic descriptions, CALPHAD, Niobium

To achieve the sustainability goals, materials with improved properties need to be developed within a short time range. The CALPHAD methodology offers a great possibility to facilitate material development through thermodynamic modelling. However, current databases are based on the second generation of CALPHAD models and descriptions. It is now possible to improve the models by making them closer to physics, adding, e.g., DFT data, but still keeping the CALPHAD character. Therefore, the development of the third generation CALPHAD models has evolved [1].

In this work, a third generation thermodynamic description of pure Nb will be presented in which the heat capacity is separated into different contributions, e.g., lattice vibrations, electronic excitations, and anharmonic vibrations. The Einstein model is used to model the harmonic contribution of the lattice vibrations. The super-conducting state of Nb at low temperatures is not considered. The model parameters are fitted to experimental data and compared to ab initio calculations from the work of Jung et al. [2]. The choice of experimental data was based on Arblaster's [3] review of Nb.

Using the high value of the experimental electronic heat capacity at low temperatures (7.8 mJ/(mol·K^2)), given in the review by Stewart [4], it was not possible to fit the heat capacity data. Therefore, the electronic contribution of solid Nb was optimized instead. Based on personal communication between the authors in this work and the authors of [2], it was possible to compare the results from the optimization with ab initio calculations. The electronic heat capacity for solid Nb was optimized to 2.7 mJ/(mol·K^2), which shows good agreement with the ab initio calculations. Nevertheless, it should be noted that according to Jung et al., one should be careful in separating the different contributions of the heat capacity in DFT calculations.

In third generation databases, one Gibbs energy expression can be used to describe the solid phases in the whole temperature range as proposed by He et al. [1]. To avoid solid phases from being restabilized at high temperatures, the EEC (Equal Entropy Criterion) was used. In the present work, another method was attempted using a second expression above some high temperature above the melting point. This so-called changeover temperature will by necessity be defined differently for low- and high melting elements. In the present work, different suggestions will be put forward for this high-melting element.

The liquid phase is described using the two-state model, which assumes that the liquid atoms are either in the liquid-like state (transitional state) or the amorphous-like state (vibrational state).

In summary, a third generation CALPHAD description of pure Nb is presented.

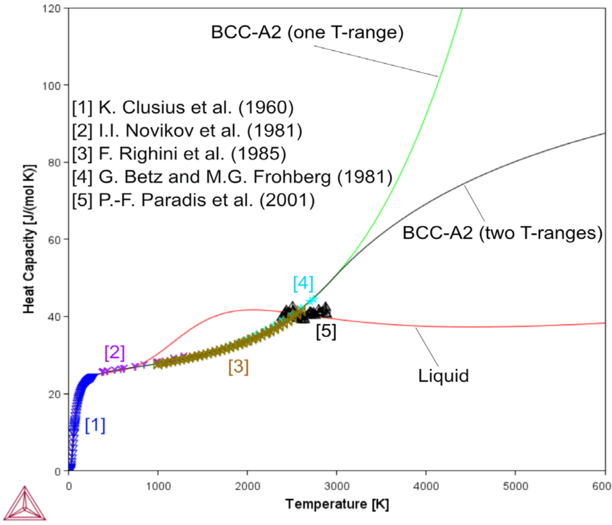

Figure 1. Calculated heat capacity of bcc and liquid Nb compared with experimental data.

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Biographical Note

Felicia Larsson is a PhD student at KTH Royal Institute of Technology, Sweden. Her work focuses on developing third generation CALPHAD models and an accurate model for stacking fault energies for TRIP/TWIP steels.

[P03.06] Thermodynamics of the Na^+, K^+, Mg^{2+}, Ca^{2+} // Cl^-, SO_4^{2-} multi-component system for the identification of potential salt-based high temperature Phase Change Materials

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Key words: salt-based PCMs, chlorides, sulphates, phase transitions

The investigation into the thermodynamic properties of the Na^+, K^+, Mg^{2+}, Ca^{2+} // Cl^-, SO_4^{2-} multi-component system holds significant importance for the identification of potential phase change materials (PCMs). In the domain of latent heat thermal energy storage (LHTES) technologies, salt systems have proven to be promising candidates as PCMs [1]. They facilitate the charging and discharging of energy at a constant temperature during the phases of melting and solidification, which is desirable for most thermal application. It is crucial to note that the specific temperature at which these processes occur is contingent upon the chosen material(s). Hence, a comprehensive understanding of the thermodynamic properties of not only pure compounds but also binary, ternary, and reciprocal systems becomes imperative in the selection and assessment of suitable systems for applications involving phase change materials.

From an initial analysis of the Mg^{2+}, Ca^{2+} // Cl^-, SO_4^{2-} reciprocal system, the alkali metal cations Na^+, K^+ are being included in the current study. In the frame of the eight-compound system, the systems marked in green in Figure 1 are being studied in this work, while those in blue have already been investigated [2].

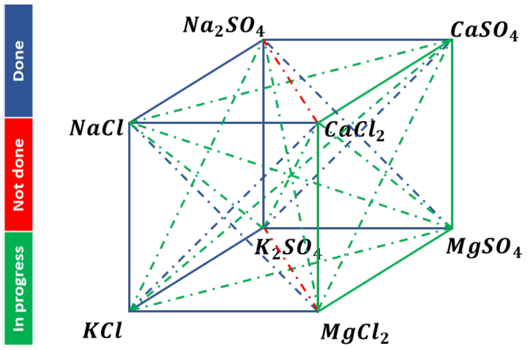

Figure 1. Graphical representation of the Na^+, K^+, Mg^{2+}, Ca^{2+} // Cl^-, SO_4^{2-} multi-component system

To determine their thermodynamic properties, the systems are studied using various methods: differential thermal analysis coupled with thermogravimetry (DTA/TG), differential scanning calorimetry (DSC) and high temperature X-ray diffractometry (HTXRD). In order to pursue our goal, the decomposition of sulphates [3], vaporization of chlorides and potential reactions with crucible materials need to be taken into consideration. The experimental results (phase equilibria, heat capacity of eutectic mixtures and intermediate compounds) are integrated in a CALPHAD-based database for prediction of thermodynamic properties of the multicomponent salt system. The liquid phase is modeled using the modified non-ideal associate species model [4], which was successfully applied for various systems, in order to provide compatibility with the general oxide-salt database GTOx [2]. Several eutectic mixtures identified in the respective phase diagrams are investigated in order to verify whether they meet the requirements for applications as potential PCMs [5].

Acknowledgements: This work was done in the framework of the PCM-Screening-2 project, which is supported by the Federal Ministry of Economic Affairs and Climate Action, Germany (FKZ 03EN6005D).

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Biographical Note

Amedeo Morsa is a third year PhD student at Forschungszentrum Jülich, Germany. His current research is on thermal investigation of salt based multicomponent systems and development of their thermodynamic database.

[P03.07] Recent developments in the TCS Mg-based alloys database

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Key words: Magnesium, TCMG, Calphad, LPSO

Magnesium-based alloys are of high interest, not only because of their lightweight properties that are advantageous in the automotive and aerospace industries, but also for their inherent biodegradability that makes them suitable for biomedical applications. In addition, Mg-based alloys can be used as hydrogen storage.

The integration of Calphad-based databases has proven instrumental in accelerating experimental investigations, facilitating the design of novel alloys through accurate predictions. Therefore, the Mg-based alloys database (TCMG) has been consistently developed by Thermo-Calc Software AB since 2012. The latest iteration, TCMG7, released at the beginning of 2024, encompasses 33 elements, 223 assessed binary systems, 124 assessed ternary systems, 5 assessed quaternary systems, and 541 phases. In addition to thermodynamic data, TCMG7 incorporates the thermophysical properties data that enables the predictions of a broad range of materials properties for multicomponent systems as a function of temperature and composition. Calculation of thermophysical properties using TCMG7 is exemplified in Fig. 1 that presents the calculated thermal conductivity compared with the experimental data from Huang [1].

One of the major features of TCMG7 is its inclusion of long-period stacking-ordered (LPSO) phases. Two variations of this phase, LPSO-14H and LPSO-18R were included in the Cu–Mg–Y, Mg–Y–Zn, and Gd–Mg–Zn ternary systems in TCMG6. In TCMG7, these two variants were remodeled for enhanced compatibility with their crystal structure. Moreover, these LPSO variants were extended to the Al–X–Mg (X=Dy, Er, Gd, Ho, Nd, Sm), Mg–X–Zn (X=Dy, Er, Ho), and Mg–Ni–Y systems, expanding the predictive capability of TCMG7. This enables users to predict the formation of the LPSO phases, for example in Gd–Mg–Y–Zn–(Zr) as shown in Fig. 2, or any other related systems whose subsystems are included in TCMG7.

Furthermore, several ternary systems such as Al–Mg–Sc, Gd–La–Mg, Mg–Mn–Sn, Mg–Mn–Sr, and Mg–Zn–Zr were assessed and included in the database. These augment the database's predictive power, providing researchers with a comprehensive tool for advancing the understanding and development of Mg-based alloys.

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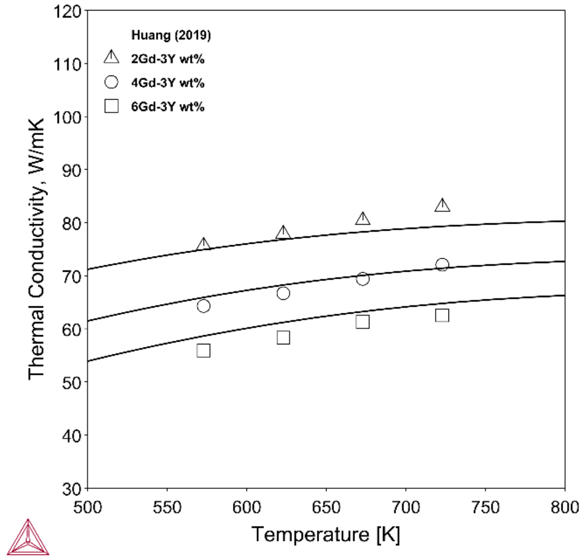

Figure 1. Calculated thermal conductivity compared with the experimental data [1].

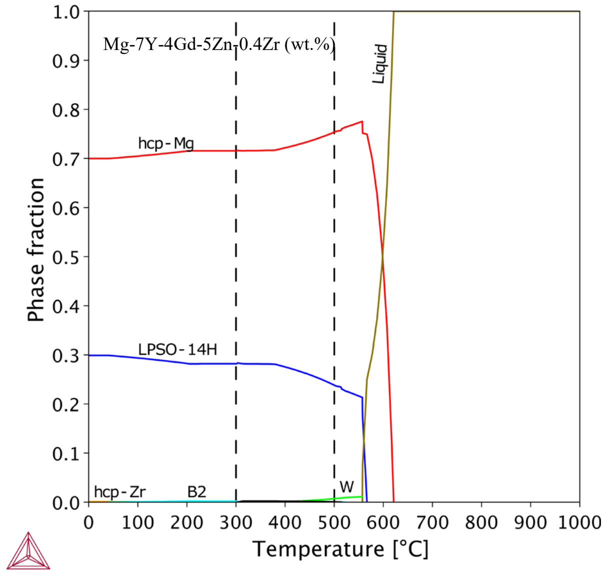

Figure 2. Calculated phase fractions for a Mg-based alloy.

Biographical Note

Mehdi Noori studied PhD in Mechanical Engineering at RWTH Aachen University. He joined Thermo-Calc Software AB as a Calphad database developer in 2022, where he focuses on the development of thermodynamic databases for Mg-based and solder alloys.

[P03.08] A proposal for an XML based format for Calphad databases

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U.R. Kattner, L. Kjellquist, F. Miani, R Otis, A. Pisch, E. Povoden-Karedeniz, N. Reza,
M. Selleby, A. van de Walle and F. Zhang

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Key words: XML databases

When the SGTE unary was presented in 1991 [1] there was also a proposal for a software independent database format, called TDB. This format has been adopted by several software and also used when publishing assessed systems.

The TDB format thus preceded the so called Markup Languages such as XML, Json etc. but it has many similar features. As the number of software tools for XML and similar ML are growing and there has been a number of software specific extensions to the TDB format
it is time to define a new software extendable format for Calphad databases.
This poster will present a collaborative effort by SGTE together with several software
and database developers to define such a format.

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[P03.09] Towards the improvement of liquid Gibbs energy assessment by the assimilation of surface tension data

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Key words: Liquid-gas interfaces, Bayesian method, Liquid Gibbs energy, CALPHAD assessment

In the event of a severe nuclear accident such as the TMI2 or Fukushima disasters, the incapacity to cool off the reactor core has led to its meltdown (temperatures exceeding 2700K). The resulting liquid mixture, known as corium, is mainly composed of molten UO_2 fuel pellets, partially oxidized Zircaloy clads and other structural material (primarily, made of steel grades). The behaviour of this internally heated (because of the decay heat) liquid is made complex because of the multicomponent nature of the mixture. For instance, in a large composition range, it displays a miscibility gap with an oxide phase and a metallic phase that can be lighter or heavier depending on the conditions (e.g. Zirconium oxidation degree). To ensure the safety of reactors and prevent environmental contamination, it is essential to predict its propagation during the accident through numerical simulations (e.g. multiphase thermohydraulics). In this context, Calphad modelling of the underlying multicomponent systems is crucial in providing thermochemical data to provide closures for both thermochemical and thermalhydraulic models. However, due to the high temperatures involved, thermodynamic knowledge of the corium liquid phase is limited because of the lack of experimental data, such as calorimetry measurements.

Consequently, thermodynamic quantities (e.g. enthalpies, chemical potentials) evaluated from a Calphad Gibbs energy model outside of global equilibrium conditions are subject to large (albeit unquantified) uncertainties and the predictive capability of corium numerical models is reduced. This trend was clearly highlighted in recent work [1] where liquid-liquid interfacial energies for U-O and U-O-Zr-Fe systems were evaluated using a Butler model approach [2] and a Calphad Gibbs energy model of the liquid phase. The comparison between calculations considering, for the liquid phase, either a non-ideal associate model (NUCLEA database [3]) or a ionic liquid model (TAF-ID database [4]), has shown that the important differences in extrapolation of the chemical potentials out of global equilibrium conditions have a large impact on the calculated interfacial energies (up to a factor of six between the two databases).

In our current research, we aim to capitalize on the remarkable sensitivity of liquid interfacial energies to enhance the liquid model itself. More precisely, confronting the results of a Butler model with surface tension measurements should provide valuable feedback on the parameters of the Gibbs energy model of the liquid phase, given its sensitivity.

This work presents advancements made to establish a proof of concept to integrate liquid-gas surface tension data into the assimilation process of Calphad database. The chosen system of reference is the binary copper magnesium used at the School for Advanced Thermodynamic Assessments (SATA). It is a well-known system with multiple experimental data including activities, mixing and formation enthalpies or equilibrium measurements. This system is also simplier with no miscibility gap in the liquid phase. In an effort to take into account uncertainties, this work is done in a rigorous Bayesian framework to assimilate those data [5].

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Biographical Note

Arthur Tourneix is a second-year Ph.D. student attached to the Grenoble-Alpes University and doing its thesis at the severe nuclear accident modelling laboratory of the the French Alternative Energies and Atomic Energy Commission (CEA). He holds a master's degree in Numerical Physics from the Montpellier University.

[P03.10] Suitability of slag solution models as the basis for thermophysical properties - A review

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Key words: Thermophysical properties , Solution models, Slags, Pyrometallurgy

Computational modelling can help us in the pyrometallurgical industry to understand our materials and processes better, improve our existing operations, and to develop new production technologies. These activities are critical, given the growing challenges of energy availability, ore quality, and environmental pressure. Importantly, modelling can enable us to do these things faster, with less uncertainty, and with much less risk. Our ability to accurately calculate slag thermophysical properties such as density, viscosity, thermal conductivity, and electrical conductivity is, however, limiting how well we can describe high-temperature processes with computational models.

Themochemical databases and software such as FactSage and Thermo-Calc have developed over decades to describe the thermochemistry of high-temperature systems well. These systems contain solution models to describe a multitude of condensed mixture phases, such as solid and liquid alloys, slags, and mattes. These models are based on principles of statistical mechanics and are therefore well-suited to describe solution thermochemical properties. These solution models have been used as the basis of thermophysical property models in some cases, such as the viscosity model by Decterov [1], the electrical conductivity model by Thibodeau [2], the Molar volume model by Thibodeau [3], and the viscosity model by Wu [4]. Due to the nature of existing solution models, they are unable to serve as a strong basis to describe certain thermophysical properties, such as electronic thermal conductivity, and electronic electrical conductivity.

In the work to be presented, we review solution models that are used to describe liquid slags, and consider their suitability to be used as a basis for calculating thermophysical properties including density, viscosity, thermal conductivity, electrical conductivity, and surface tension. We specifically consider the degree to which existing models incorporate, or are able to incorporate, slag structure and geometrical data such as ionic radii, and inter-ionic distances.

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Biographical Note

Stéfan Zaaiman is a Ph.D. student at the University of Pretoria at the department of Chemistry with a scholarship from Ex Mente Technologies. His field of study is in solution models with a focus on the thermophysical properties calculated from solution models. His interests include computational modelling, theoretical chemistry, thermochemistry.

[P04.01] Thermodynamic modelling of chlorides systems for Molten Salt Reactor Application

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Key words: Calphad, Molten salt reactor,

In Molten Salt Reactors (MSR), the nuclear fuel is dissolved in a molten salt to form a mixture that serves as both fuel and coolant for the primary circuit. In the design under study, the reference fuel is a molten chloride salt of ($NaCl+MgCl_2$) and ($PuCl_3+AmCl_3$). The liquid mixture circulates from the reactor core to intermediate heat exchanger units, where an intermediate coolant salt extracts the energy generated by the fuel. This means that the fission products formed by nuclear reactions also circulate in the primary circuit. These fission products can exist in different physical states in the reactor core, and can interact corrosively with the internal structural materials.

The knowledge of irradiated fuel salt chemistry and corrosion resistance of internal structural materials is essential to ensure safe reactor operation. In this context, phase diagrams and thermodynamics must be predicted for understanding the effect of changes of chemical composition, pressure and temperature.

This work presents ongoing studies to contribute to the development of a thermodynamic database for predicting molten salt fuel chemistry. The Modified Quasichemical Model (MQM) is used to describe the Gibbs energy of the liquid phase. After the assessment of subsystems to predict the corrosion products that may form between molten salt and steel [1], we focus our studies on modelling salt containing volatile fission products such as $ZrCl_4$ and $TeCl_4$. Depending on progress, experimental results on thermodynamic activity measurements in liquid will also be presented.

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Biographical Note

Sylvie Chatain is currently Expert Research Scientist in the Division of Energies of the French Alternatives Energies and Atomic Energy Commission (CEA) in Saclay (France). She is involved in thermodynamic experiments and Calphad modelling of materials for nuclear and new energy technologies.

[P04.02] Ordering regimes in zirconium carbide

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Key words: first-principles, UHTC, long-range ordering, short-range ordering

Zirconium carbide is an ultra-high temperature ceramic (UHTC) material with a melting point around 3700 K and the ability to retain many of its mechanical and electrical properties almost to the melting point. In addition to these remarkable high-temperature properties, zirconium carbide is also fascinating at very low temperatures, where its rocksalt structure can accommodate up to 50% structural vacancies on the carbon lattice, far below room temperature.

Historically, the full composition range of zirconium carbide has been treated as a continuous B1 phase[1], however first-principles calculations have revealed the extent of the degree of carbon vacancy ordering as a function of vacancy concentration and temperature[2]. Although the tendency for vacancies to order is, in fact, a short-range effect, it has been proven to lead to the self-assembly of a homologous series of long-range ordered phases at low temperatures. This tendency for short-range ordering persists at higher temperatures into the continuous solution phase, with the carbon vacancy arrangement approaching disorder only above 2000 K[3]. Due to the complexity of the ordering regimes, this necessitates a multi-phase description of zirconium carbide, where the long-range ordered phases are modelled separately to the continuous solution phase.

In this assessment of the carbon-zirconium phase diagram, long-range ordered phases are modelled as line compounds based on first-principles calculations, and the continuous solution phase describes both short-range ordered and disordered regimes explicitly. A model to estimate the energetic contribution attributable to short-range ordering as a function of carbon vacancy concentration and temperature was constructed based on carbon vacancy cluster energies, where parameters of the Gibbs energy model were eventually optimised considering both experimental and first-principles data. The liquid phase is also re-optimised for consistency with experimental data produced in the years since the last assessment.

Experimental observations validate the presence of long-range ordered phases at low temperature, however these observations are extremely limited[3]. Only the Zr_2C phase has been consistently observed, likely mostly due to the high temperatures used in synthesis of zirconium carbides. However, near-inevitable oxygen impurities have been shown to significantly affect the ordering tendency[4], the extent of which is also explored in defining necessary fabrication routes for ordered zirconium carbide phases.

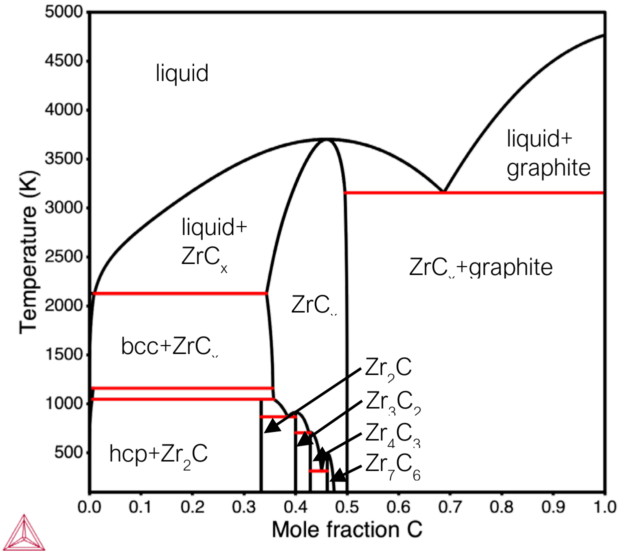

Figure 1. Assessed carbon-zirconium phase diagram incorporating low temperature ordered phases.

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Biographical Note

Tessa Davey is the UKAEA Reader in Nuclear Materials at the Nuclear Futures Institute at Bangor University in Wales, UK. Before taking up this post in September 2023, she was an Assistant Professor at Tohoku University, Japan following her PhD at Imperial College London, UK. Her research focus is understanding and improving the thermodynamic descriptions of point defects and ordering in alloys and ceramic materials using insights from first-principles and other theoretical calculations.

[P04.03] Automated Calphad Optimization Workflow

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Key words: Calphad Optimizer, Materials Project, FactSage, aiMP

In this work, we show how our aiMP database, available in FactSage (**www.gtt-technologies.de**), is optimized in an automated way to introduce liquid interaction parameters and ensure stability of the stable intermetallics. aiMP is a database available in FactSage that is developed from the 0 K repository the Materials Project. This is achieved through our third generation ML models that are trained based on high-quality Calphad data. The models predict entropies and heat capacities. While aiMP covers a larger area than possible through traditional calphad optimization, the liquid phase is not included. 20 binary systems were studied and an automated workflow was introduced using python coding and the Calphad Optimizer in FactSage. The Calphad Optimizer is run off opt files which include experimental groups, parameters for optimization and hyperparameters for the optimization. The optimization parameters were the entropy and enthalpy of formation at 298 K of all aiMP intermetallics, as well as, the liquid L0 a+bT and L1 a+bT terms. Experimental groups such as liquidus and solidus temperature were included. Along with enthalpy of mixing and experimental groups to ensure no inverse miscibility gap up to 4000 K. With the accuracy of the machine learning model of the enthalpy of formation at 298 K within 10 kJ and the accuracy of the entropy at 298 K within 3 J, experiments were included to ensure the optimization adjusted the entropy and enthalpy interaction parameters within the accuracy range. The hyperparameters used allowed for each optimization run to have 2000 evaluations. The optimizations were run in 12 steps. The first three optimization runs focused on the enthalpy-related parameters, enthalpy of formation at 298 K of any intermetallics and the L0 and L1 a terms. The next three optimization runs focused on the enthalpy and entropy at 298 K parameters of any intermetallics. The next three optimization runs focused on the liquid L0 and L1 a+bT parameters. In the final three optimizations all the parameters were optimized together. The error contribution to each experimental group was checked after the optimization runs with a threshold value. The minimum and maximum boundaries of the parameters being optimized were adjusted based on the percentage the parameter had moved from last optimization run. In this work, we show that this single automated workflow can optimize all 20 binary systems, ranging from systems with miscibility gaps in the liquid to systems containing several pure intermetallics.

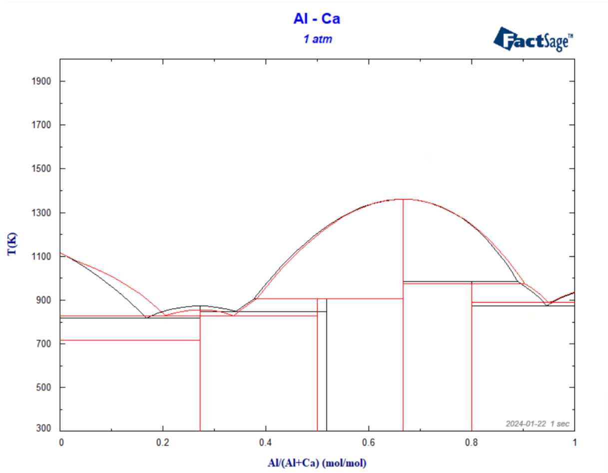

Figure 1. The Al-Ca phase diagram in black run optimized with our automated optimization compared to the SGTE optimized phase diagram in red.

Biographical Note

Cassie Frueh began working as a researcher for GTT-Technologies in September 2022. She previously worked as the Innovation Process & Computational Analysis manager at Almatis GmbH for four years. She received a PhD in materials science and engineering from the Pennsylvania State University under the advisement of Zi-Kui Liu.

[P04.04] Using the Calphad Optimizer (CO) for the assessment of the Gibbs energies of non-stoichiometric Perovskites in the system Ca-Mn-Sr-O

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Key words: perovskite, phase equilibria, sublattice model, associate species model

Metal oxides with multivalent species are very valuable for applications as redox materials. The occurrence of an oxygen non-stoichiometry δ ($\delta = 0\text{-}0.5$) in $AMO_{3-\delta}$ perovskites and the close structural relationship between perovskites and their reduced form $A_2M_2O_5$ (brownmillerite) in a defect arrangement reveals fast redox kinetics, which depend on partial pressure of oxygen and temperature:

$$AMO_3 \rightarrow AMO_{3-\delta} + \delta * O_2/2$$

The Perovskites $CaMnO_{3-\delta}$ and $(Ca,Sr)MnO_{3-\delta}$ show continuous non-stoichiometry over a wide range of temperatures and oxygen partial pressures. These Perovskites are therefore of particular interest to industry, as they can be used in a variety of applications. Despite their importance, the phase equilibria in these systems have not yet been well investigated. The experimental investigation of the entire system is complicated by the strong dependence of the equilibria on the oxygen partial pressure and the high melting temperature of the solid phases. Therefore, a critical evaluation of the data is required to better understand and model these systems.

The thermodynamic database Ca-Mn-Sr-O created for the project SESAM contains 46 compounds, the oxide melt, and the following 5 solid solution phases: bcc-A2, fcc-A1, MeO, spinel and Perovskite. All sub-systems including elemental combinations were considered in order to generate a self-consistent Gibbs energy dataset for further calculation and prediction of thermodynamic properties of the system. The liquid phase covering metallic and oxide compositions has been described using the non-ideal associate solution approach [1]. Particular attention was given to the Perovskite phase $Ca_{1-x}Sr_xMnO_{3-\delta}$ which extends significantly to higher amounts of oxygen with increasing amounts of strontium. Thermodynamic description of phase Perovskite is carried out using the Calphad Optimizer (CO) [2] for experimentally determined non stoichiometry of Perovskite [3] depending on partial pressure and temperature. The phase Perovskite is described using the sublattice model $(\underline{Ca^{2+}},Sr^{2+})(Mn^{3+},Mn^{4+})(\underline{O^{2-}},Va)_3$.

Experimental investigations [3] on the equilibrium non-stoichiometry of the materials $Ca_{0.9}Sr_{0.1}MnO_3$, $Ca_{0.85}Sr_{0.15}MnO_3$, $Ca_{0.8}Sr_{0.2}MnO_3$, $Ca_{0.7}Sr_{0.3}MnO_3$, and $Ca_{0.6}Sr_{0.4}MnO_3$ in the temperature range from 600 to 1200°C and at oxygen partial pressures of 1 to 10^{-5} bar were carried out using a thermobalance and oxygen pump. These experimental results were used to extend the thermodynamic data of the Perovskite so that meaningful process simulations could also be carried out for higher strontium concentrations.

The use of this database enables calculations in the quaternary system Ca-Mn-Sr-O and predictions of oxygen partial pressures at different temperatures and composition ranges. The general agreement between the calculated phase equilibria as well as the thermodynamic properties and the respective experimental data is good.

Acknowledgements: This work was done in the framework of project SESAM (EFRE 0801803). The funding of the European Regional Development Fund and the NRW-Ministry of Economic Affairs, Innovation, Digitalisation and Energy is gratefully acknowledged.

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Biographical Note

Tatjana Jantzen is a scientist with GTT-Technologies, Germany, since 2002. Her research topics and scientific interests are thermodynamic modelling of metal, oxide, and salt systems, database development using the CALPHAD approach, phase equilibria, and thermodynamic properties.

[P04.05] XMLTDB in FactSage Calphad Optimizer and ChemApp: Lessons learned and opportunities generated

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Key words: Calphad Optimizer, ChemApp, FactSage, XMLTDB, TDB

XMLTDB[1] as a somewhat unifying 'successor' to the TDB format is greatly appreciated as the shortcomings of all previous thermodynamic database concepts are evident by now. Crucially, finding adequately flexible and reasonable ways to integrate metadata and future proofing by using extensible concepts are key to establishing a widely supported format for thermodynamic databases.

The integration of XMLTDB within FactSage Calphad Optimizer and ChemApp has yielded some insights and promising prospects. This presentation details the pivotal lessons learned and outlines opportunities generated through this integration. Special care has been taken to carefully evaluate the format description, and expand on the previous definitions where needed, without breaking the common subset of essential functionality.

Some specific case studies and applications are presented where the integration of XMLTDB within FactSage Calphad Optimizer and ChemApp necessitated carefully expanding the format, with special respect to phase model amendments and pulling implicit assumptions into explicit definitions.

The incorporation of XMLTDB into our computational tools marks a significant advancement in establishing a common format for exchange and development of thermodynamic databases. It streamlines data accessibility and fosters enhanced collaboration and interoperability among researchers and institutions within the Calphad community and across previously tedious `format moats`. Some unique possibilities enabled by the grown feature-set of the XMLTDB format are highlighted, such as verification of dataset due to metadata validation, and e.g. semi-automatic updates of certain data fields.

Additionally, this work is seen as a contribution to the community, as FAIR data concepts are a crucial pillar of scientific advancement in modern research environments. There have been multiple efforts to build repositories and 'resource gathering' for which all somewhat fall short with respect to store complete datasets and metadata sets, such as the Thermodynamics Research Center[2] and TDBDB[3]. Suggestions for robust and reliable (meta) data authenticity and validation are presented and discussed, employing concepts like hash signatures and unique identifiers.

References

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[2] https://trc.nist.gov/MetalsAlloyUI/
[3] https://avdwgroup.engin.brown.edu/

Biographical Note

Florian Tang learned the process of Calphad optimizations from Bengt Hallstedt at RWTH Aachen University during his PhD on High-Manganese-Steels. He is with GTT in Germany since 2018, with his latest contributions the co-development of the Calphad Optimizer, and maintaining the development of the Python packages by GTT.

[P04.06] CALTPP: an intelligent software to evaluate thermophysical properties

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Key words: CALTPP, Thermophysical properties, Diffusion, Thermal conductivity, Viscosity

The software CALTPP, an acronym for CALculation of ThermoPhysical Properties, has been meticulously crafted to provide a comprehensive evaluation of diverse thermophysical properties. These properties encompass diffusion coefficient, interfacial energy, thermal conductivity, viscosity, and molar volume [1,2]. Figure 1 shows the framework of CALTPP.

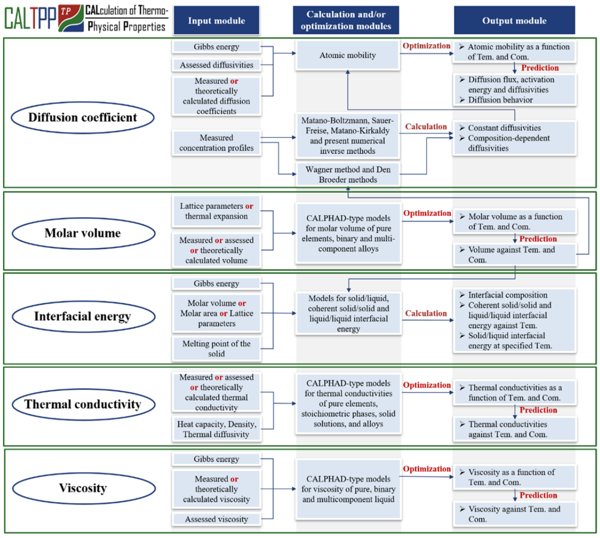

Figure 1. The framework of CALTPP software

The diffusion module in CALTPP employs a novel numerical inverse method developed within the CALPHAD framework. This numerical approach allows for the simultaneous assessment of atomic mobility and diffusivity, conducted with remarkable efficiency and reliability, as corroborated by extensive comparisons with measured data. Enhancing user experience, a user-friendly graphical user interface (GUI) for the numerical inverse method has been implemented to streamline interaction with the software. The case studies showcased using this developed GUI underscore its accessibility, making it a tool of choice for users seeking both computational efficiency and accuracy. Within the thermal conductivity module of CALTPP, we incorporated self-developed CALPHAD-type and microstructure-based methods. These methods are adept at providing precise determinations of thermal conductivity for both single-phase alloys [3] and complex multi-phase composites [4]. Furthermore, CALTPP includes robust models designed to describe interfacial energy, viscosity, and molar volume. The synergy of these models ensures a holistic and versatile tool for the comprehensive analysis of thermophysical properties.

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Biographical Note

Shiyi Wen is a lecturer from Central South University, China. He received his Ph.D in July, 2021 and was major in the investigations of thermophysical properties.

[P04.07] CALPHAD Simulations for Optimizing Composition and Processing Conditions of AA6005 Aluminum Alloys

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Key words: Aluminum Alloys, CALPHAD, Processing, Strengthening

AA6XXX alloys are known for their superior strength-to-weight ratio and enhanced mechanical properties and are highly demanded across diverse applications including military vehicles, rockets, aircraft, and automotive sectors [1]. The properties of these alloys principally depend on their microstructure features, such as average grain size, grain size distribution, precipitate volume fraction and number density, and the crystallographic orientation aspects like the texture [2]. While the microstructure of a cast aluminum alloy strongly depends on the alloy composition, it can be tailored by the subsequent processing techniques, such as homogenization, work hardening, and age hardening. Therefore, these post solidification processes are usually used to enhance the mechanical properties of AA6XXX alloys.

In this study, we used Pandat^{TM} software and PanAl database [3] to perform a series of simulations for AA6005 alloys to first understand the effect of composition variations and then explore the tailored microstructure due to the processing routes including casting, homogenization, hot-working, and aging stages as shown in Figure 1.

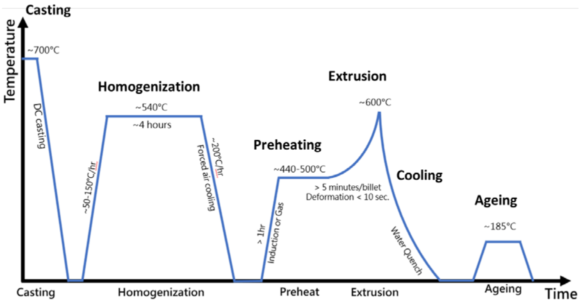

Figure 1. Schematic multi-stage processing for Al Alloy

The principal alloying elements of AA6005 are Mg (0.8~1.5wt.%) and Si (0.35~1.0wt.%), with Mg/Si ratio close to 1.73 for the formation of age hardened Mg_2Si precipitates. Typically, AA6XXX alloys contain excess Si or Mg. Surplus of Si can enhance strength and formability but can also lead to higher intergranular corrosion susceptibility. Excess Mg, on the other hand, can augment corrosion resistance, yet at the expense of formability and strength. The effects of compositional variations on the formation of inter-dendritic phases and the solidus and liquidus temperatures were investigated via high-throughput calculations using Pandat^{TM} software.

Moreover, we performed simulations for an AA6005 alloy with the composition of Al-0.55Mg-0.63Si-0.1Cu-0.15Mn-0.25Fe (wt.%) to study the effects of processing parameters, such as casting cooling rate, homogenization temperature, hot-working temperature, and aging temperature, as well as strain rate, on its final mechanical properties. Figure 2a illustrates simulated strain-stress flow curves under various temperatures (350 to 500°C) with a fixed strain rate of 0.1/s, while Figure 2b depicts artificial aging simulations at different temperatures. These simulations agree well with the experimental data, demonstrating the extended capability of CALPHAD simulation tools.

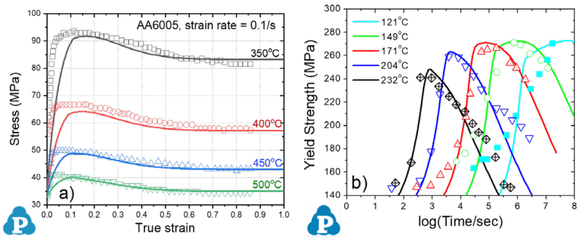

Figure 2. Simulated results with experimental data for processing of AA6005: a) hot working; b) ageing

This work demonstrates that we can now use the CALPHAD method to perform virtual experiments to unlock the insights of the effects of composition and post solidification processes on the microstructure and properties of aluminium alloys, therefore facilitate alloy design and processing optimization.

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Biographical Note

Dr. Chuan Zhang, the technical program manager at CompuTherm, specializes in thermodynamic and kinetic simulations for practical applications in alloy design and processing optimization. He obtained his Ph.D. in Materials Science and Engineering from the University of Wisconsin at Madison in 2010.

[P05.01] Thermodynamic database for the FeCrMoNiN system

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Key words: Calphad, Sigma-Phase, Stainless Steel, Thermodynamic Database

Computational thermodynamics enable accelerated alloy design and new alloy compositions for specific applications. New types of applications, for example additive manufacturing, where completely new compositions are possible, drive the need for new databases. New methods to handle data are today available and accelerated development of databases is possible providing that there is open access to previous work.

A thermodynamic description of the intermetallic phases in the FeCrMoNi system is presented based on previously unpublished experimental data in the CrMoNi system. A review of experimental information from literature together with the new data provides a reliable base for the assessment. Together with previously published alloy systems[1], an open database for the FeCrMoNiN system is presented[2]. Calculations of the stability of the σ phase in the quaternary FeCrMoNi system are compared with experiments showing good agreement. This supports the predicted phase equilibria in super-duplex stainless steel that are presented.

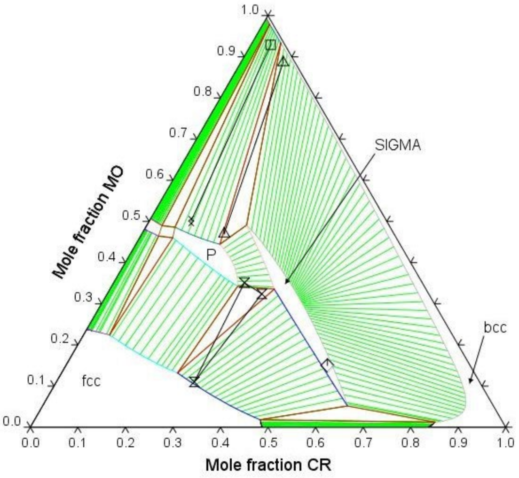

Figure 1. The calculated isothermal section of the Cr-Mo-Ni system at 1373K together with experimental data from the present work.

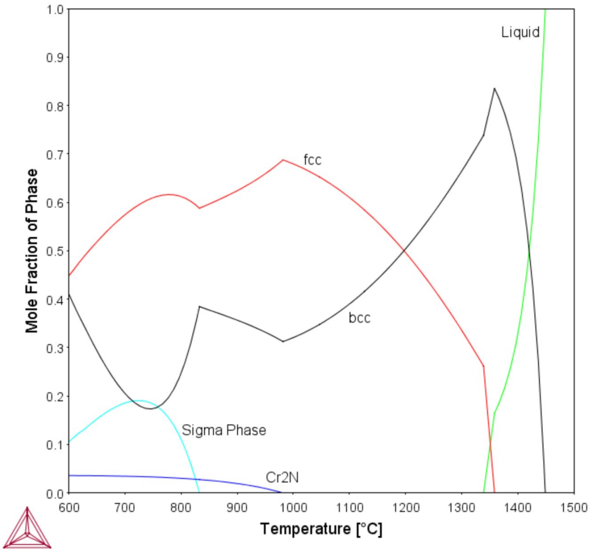

Figure 2. Phase relations in a 25%Cr, 4%Mo, 7%Ni and 0.3%N (X2CrNiMoN25-7-4), super-duplex stainless steel using the database that is presented.

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Biographical Note

Karin Frisk is PhD and Docent in Materials Science from KTH. She has worked in an industrial research institute, Chalmers University of Technology and Höganäs AB, with alloy development, powder materials, and application oriented thermodynamic databases. She is currently developing solutions for computational alloy development in Innomat AB.

[P05.02] Hybrid data-driven thermodynamically-based temperature modeling of secondary steelmaking

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Key words: temperature model, steelmaking, statistical learning, EERZ modeling

The urgent challenges facing the steel industry in terms of decarbonization demand the necessity to develop innovative solutions. The transition to new production routes poses a significant challenge, particularly for the secondary metallurgical (SecMet) process. Optimized secondary SecMet production routes and the associated process treatments (e.g. heating at the ladle furnace or vacuum treatment at the degassing plants) play an essential role in achieving the global decarbonization targets due to their high energy requirements. Being the final step before continuous casting, SecMet treatment also significantly influences the castability and, thus, the product quality of the steel. Process control systems (PCS), primarily based on thermodynamic and mass balance models, can be used to meet the desired high requirements regarding material properties and production monitoring. To precisely set the target temperature required for casting, the molten steel is heated in the ladle furnace by an electric arc. However, continuous ladle heat losses due to radiation, convection, alloying, etc., must be considered.

With the rise of Industry 4.0 and the ever-increasing amounts of data collected at SecMet plants in recent years, new techniques for handling and evaluating large quantities of process information provide new opportunities to extract new knowledge. Therefore, the present work comprehensively analyzes and acquires new insights from the SecMet process data of an entire production year of voestalpine Stahl Linz GmbH. The research can be divided into two work packages. The first part was dedicated to a detailed analysis of the production and associated temperature data. Comprehensive descriptive statistics were used to provide an overview of the data quality. Subsequently, explorative statistical methods (e.g. multiple linear regression) were used to numerically define correlations between target variables and influencing parameters. This step provided insights into the process-related influences on the alloy composition and steel melt temperature. As part of the second work package, a Python desktop application (i-clean) based on the effective equilibrium reaction zone (EERZ) [1-3] concept was developed using ChemApp Python.

The developed software product offers the possibility of coupling data-driven methods with fundamental computational thermodynamics in the CALPHAD framework. The approach enables a precise prediction of the temperature over the entire SecMet, representing a valuable tool for future optimization of metallurgical processes with respect to the transformation to green steel production.

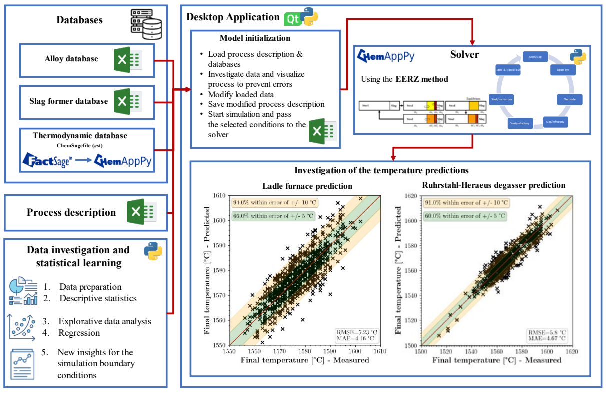

Figure 1. Concept of the hybrid temperature model for the secondary metallurgical steelmaking

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Biographical Note

Daniel Kavić is a PhD researcher working at the K1-MET GmbH and Montanuniversitaet Leoben (Austria). He deals with statistical learning and thermodynamic modeling of the secondary metallurgical steelmaking.

[P05.03] Experimental investigation and computational thermodynamics of the quaternary system Fe-C-Mn-S

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Key words: CALPHAD, Fe-C-Mn-S, DSC, Computational Thermodynamics

During the reduction of iron ores, substantial amounts of S, originating from the coke, dissolve in the molten iron. S poses several problems during the casting and processing of steels, such as hot tearing or surface defects, respectively. Residual amounts of S are typically bound by adding Mn to the steel to avoid the formation of low-melting phases. Mn is also an important alloying element for large variety of steel grades. To track the steel quality during the casting process, online quality prediction systems are currently under development in numerous steel plants. Thermodynamic data of the steel grade are combined with solidification calculations and kinetic models to describe the casting process as a function of the casting parameters, whereby the thermodynamic information is obtained from the CALPHAD approach.

In the present work, experiments in the systems Fe-Mn and Fe-Mn-S with very low amount of C (~ 150 ppm) were performed using Differential Scanning Calorimetry (DSC) and Differential Thermal Analysis (DTA). The Fe-Mn-C^{low} phase diagram at high temperatures was experimentally reconstructed up to 40 mass pct. Mn. [1] Previous thermodynamic assessments [2,3] showed noticeable deviation from the measured peritectic phase equilibria, which required further investigation and re-optimization of the thermodynamic database. Hence, a CALPHAD-type thermodynamic modeling of the Fe-Mn and Fe-Mn-C system using FactSage thermochemical software [4] was performed to improve the prediction of solid/liquid phase equilibrium temperatures. For the liquid phase, the Modified Quasichemical Model (MQM) was used, solid solutions were described by the Compound Energy Formalism (CEF) and several compounds with constant composition were treated as stoichiometric. In the second part, the experimental and computational approach is combined and applied to the ternary Fe-Mn-S system, as shown exemplary in Figure 1 (a). Two isopleth sections of 0.5 and 2.0 mass pct. Mn with up to 0.3 mass pct. S were studied.

The DSC technique enabled also to analyze the dissolution of manganese sulfides (Mn,Fe)S, as can be seen in Figure 1 (b), which was additionally *in situ* by high temperature laser scanning confocal microscopy (HT-LSCM). Hence, the proper evaluation of the DSC signals could be confirmed. Though a significant improvement was obtained for calculating the Fe-C-Mn system, the previous evaluation of the Fe-Mn-S system, which in this case was selected from the studies of Kang and coworkers [2,3], already led to excellent results.

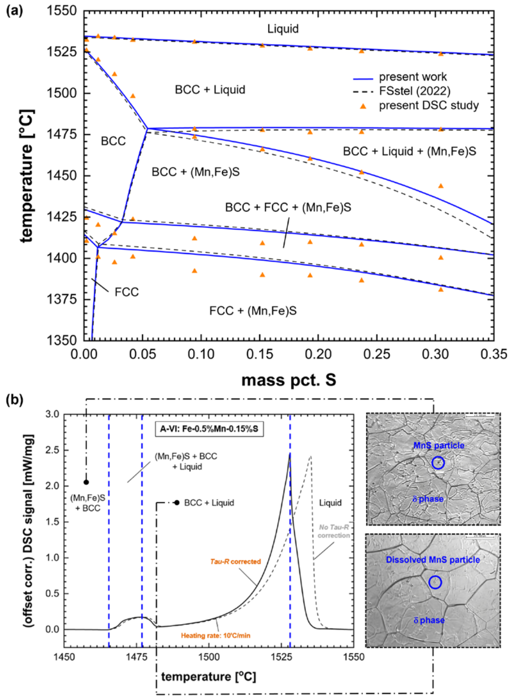

Figure 1. Experimental investigation and thermodynamic assessment of the Fe-0.5%Mn-var.%S-0.017%C alloy with emphasis on (Mn,Fe)S behavior during solidification using DSC and HT-LSCM.

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Biographical Note

Robert Littringer is a a graduate student ferrous metallurgy at Montanuniversitaet Leoben (Austria) and spent five months at GIFT (POSTECH, Rep. of Korea) working on computational thermodynamics of the system Fe-C-Mn-S.

[P05.04] Triplex steels in-situ grain refinement in Laser-Powder Bed Fusion

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Key words: Grain refinement, L-PBF, High-Mn steel, Alloy design

High manganese steels offer exceptional combinations of high strength and ductility, resulting in weight reduction when utilized in structural applications. Indeed, several studies have demonstrated the success to fabricate high manganese twinning-induced plasticity (TWIP) and transformation-induced plasticity (TRIP) steels by laser-powder bed fusion (L-PBF) [1–3]. On the other hand, because typical microstructures in laser powder bed fusion (L-PBF) are formed by elongated grains aligned with the building direction, the goal of this study is to investigate the formation of in-situ inoculation in these high Mn steels in L-PBF by modifying the solidification path based on thermodynamics and phase transformation study of the system. The efficiency of in-situ produced inoculants in grain refining is investigated using microstructural investigations.

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Biographical Note

Manuel Sanchez-Poncela holds a degree in industrial engineering from the Polytechnic University of Gijón and Grenoble INP, he is also a material scientist specializing in Large Scale Facilities from the Universities of Munich TUM and LMU, and PhD. by the Polytechnic University of Valencia (UPV). He is experienced in modeling the thermoplastic behaviour of metals (at CEA) and measuring residual stresses by neutron diffraction (at FRM II). Since 2018, he joined ArcelorMittal Global R&D as a Senior Research Engineer. In this role, he led the development of various steel families in Additive Manufacturing, utilizing CALPHAD-based calculations, resulting in multiple patents and articles.

[P06.01] Ocean of Data: Tools for Data Generation of Single Phases

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Key words: ML, First-principles calculations, Zentropy, CALPHAD modeling

Development of CALPHAD databases has been largely relied on experimental and estimated data, and predictions from density functional theory (DFT) have significantly enhanced the robustness and efficiency of CALPHAD modeling[1,2]. In the last 25 years, we have developed theories and open-source tools to generate energetic data for CALPHAD modeling, reaching a stage of accurate prediction of free energy of individual phases based on DFT calculations, statistical mechanics, and ML models as schematically shown in Figure 1 for the flow of data from MPDD, DFTTK, and Zentropy.

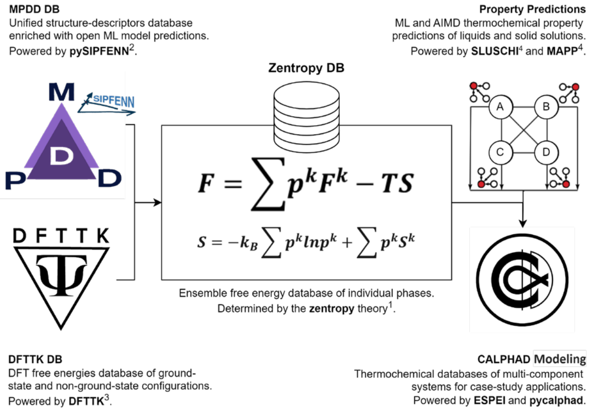

Figure 1: Schematic flow diagram of ML, DFT, and Zentropy for data generation for CALPHAD modeling.

MPDD[3] is a unified structure-descriptor database powered by pySIPFENN[4] that programmatically calculates feature vectors of structures from both DFT and experimental datasets. In addition, pySIPFENN and open ML algorithms are employed to predict properties and to aggregate and normalize data across different datasets. Currently, MPDD has almost 4.5 million structures, with over 3,532 binary and 85,141 ternary systems, which are publicly available through the OPTIMADE API. It also allows for the re-training of ML models on different subsets of data, and the discovery of novel material structures through elemental substitution using the Python toolset crystALL[5].

DFTTK[6] is a high-throughput DFT-based calculations tool and database for free energy of ground-state and non-ground-state configurations. For a given structure, DFTTK automatically runs a set of DFT calculations using the quasiharmonic approximation, predicting not only the thermodynamic properties at finite temperature, but also properties such as Seebeck coefficient, Lorenz number, and effective charge carrier concentration.

The properties from ML models and DFTTK are for individual configurations. The zentropy theory was developed to combine all conceivable configurations through statistical mechanics using their free energies in their respective partition functions, showing remarkable agreements with experiments for magnetic materials[7,8] and liquid[9,10]. Currently, an open-source tool is under development, integrated with MPDD and DFTTK for prediction of free energy of individual phases for predictive CALPHAD modelling.

The tools and databases as well as contributions from individuals to the data ecosystem can be accessed at https://mat-x.org (Figure 2).

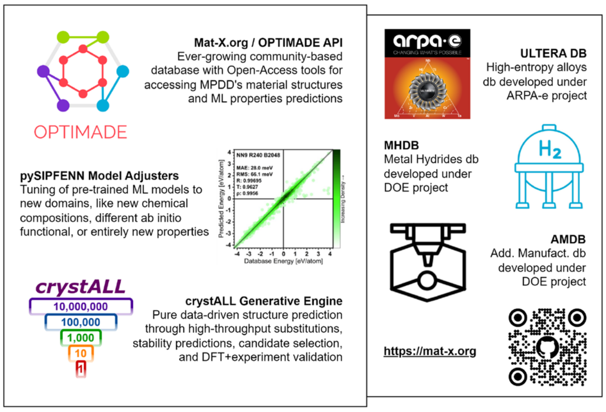

Figure 2: Integrating features, tools, and databases of https://mat-x.org.

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Biographical Note

Ricardo Amaral is a Ph.D. Candidate in the Phases Research Lab at The Pennsylvania State University. His research interests involve using first-principles calculations, statistical mechanics, and ML techniques for the computational design of energy storage materials.

[P06.02] Ocean of Data: AI-driven High-throughput CALPHAD Modeling

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Keywords: CALPHAD modeling, AI, Open-source tools, PyCalphad, and ESPEI

CALPHAD databases and tools are key components in ICME and MGI and are broadly used in education, research, and manufacturing. Their development has been primarily performed through manual operation of computer programs and largely relied on experimental data and educated estimations. In last 25 years, we have developed fundamental theories and tools to generate input data and perform high throughput CALPHAD modeling to enhance the robustness and efficiency of CALPHAD modeling[1,2] as shown in Figure 2.

Open-source CALPHAD modeling tools, PyCalphad[3] and ESPEI[4], have been integrated into an AI-driven workflow for automated high-throughput CALPHAD modeling. This integration allows for connectivity with the data generation system (mat-x.org) in Ocean of Data (OOD), including machine learning (ML), density functional theory (DFT) calculations, zentropy theory, and experimental results to establish robust modeling and data curation in MongoDB databases. Utilizing PyCalphad and ESPEI as computational engines, this workflow maximizes the robustness of data collection through AI and enables smooth conversion of data from MongoDB to JSON input files. Moreover, it minimizes manual processes during parameterization and refinement, thus significantly enhancing the efficiency and reliability of the CALPHAD modeling process. This automated workflow has been applied to model the 9-element refractory high entropy alloys (RHEA) system.

PyCalphad[3] is an open-source Python library for computational thermodynamics using the CALPHAD method. It provides researchers with the flexibility to modify and customize it for various purposes. A template generator feature has been developed to empower researchers to effortlessly implement and integrate their own custom thermodynamic models into PyCalphad. By generating model class templates and XML database formats, researchers can tailor their models to specific research needs.

ESPEI (Extensible Self-optimizing Phase Equilibria Infrastructure)[4], is an open-source tool for creating CALPHAD databases, evaluating the uncertainty of CALPHAD models and model parameters, and performing uncertainty propagation. The model selection feature in ESPEI has been applied to differentiate models for 3rd generation pure element modeling. Within ESPEI, researchers can explore multiple physically based models to describe the heat capacity of pure elements down to 0 K. These models, along with fitting tools for experimental data, are implemented into ESPEI. Additionally, Markov Chain Monte Carlo utilized in ESPEI allows for uncertainty quantification of the parameters. This enables model selection by comparing AICc[5] across different models, identifying optimal models while penalizing overly complex ones based on the input. Covariance analysis of model parameters is facilitated through corner plots, while the uncertainty and distribution of parameters can be propagated to thermodynamic properties, providing a comprehensive evaluation of the modeling process.

In summary, open-source tools PyCalphad and ESPEI provide researchers with advanced capabilities and streamlined AI-driven workflows, facilitating high-throughput CALPHAD modeling, accelerating progress in materials design and discovery.

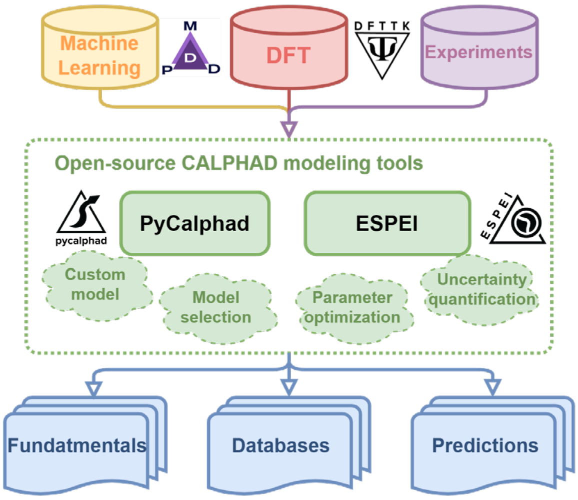

Figure 2: Features in open-source tools PyCalphad and ESPEI for AI-driven high-throughput CALPHAD modeling.

References

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Biographical Note

Rushi Gong is a Ph.D. student in Materials Science and Engineering at Pennsylvania State University. Her research focuses on investigating atomic environments in alloy and molten salts using first-principles calculations and CALPHAD modeling.

[P06.03] Ocean of Data: Efficient Data Infrastructure for Materials

A. M. Krajewski[1], **A. Debnath**[1], **R. Amaral**[2], **S. Lin**[1], **A. Richter**[1], **S.L. Shang**[1], **A. Beese**[1], **W. Reinhart**[1], **Z.-K. Liu**[1-2]
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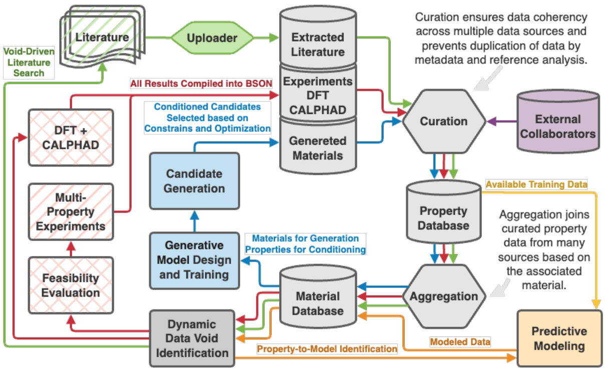
Key words: HEA, refractory, machine learning, database, data curation

Humanity has spent the last 5000 years advancing alloys, first through empirical breakthroughs and then through scientific understanding, which requires expert knowledge and support of high-quality datasets, which can then be used to harvest advances in data analysis and machine learning (ML).

As our community moves towards large-scale multi-source data collection, new challenges appear, including (1) high presence of erroneous data, sometimes over 5% caused by non-standard notations or general human errors, (2) complex structure (schema) of the data making it hard to homogenize, and (3) bottlenecks in data passing between experiment and modeling teams.

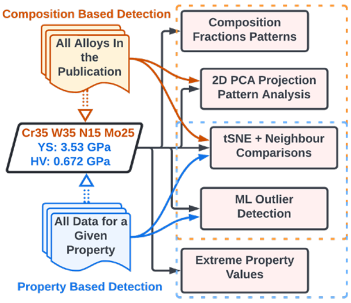
In this poster, we present a set of open-source tools for alloy datasets that efficiently solve these challenges. We first developed a robust, custom alloy data infrastructure (ULTERA) [1] targeting experimental observations of refractory high entropy alloys [2].



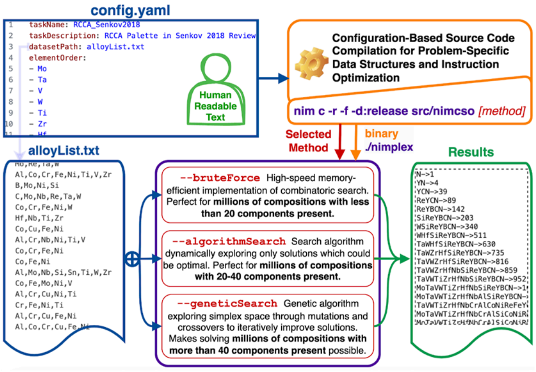
Curation ensures data coherency across multiple data sources and prevents duplication of data by metadata and reference analysis.

Aggregation joins curated property data from many sources based on the associated material.

Next, a novel data abnormality code specific to compositional data was developed (PyQAlloy) and used to screens across many contexts and data types.



With high-quality data ensured the design space has been optimized, enabling the densest available datasets for machine learning efforts using a novel extremely high-performance tool (nimCSO) capable of handling millions of compositions in tens of dimensions [3].



config.yaml

```
taskName: RCCA_Senkov2018
taskDescription: RCCA Palette in Senkov 2018 Review
datasetPath: alloyList.txt
elementOrder:
- Mo
- Ta
- V
- W
- Ti
- Zr
- Hf
```

Configuration-Based Source Code Compilation for Problem-Specific Data Structures and Instruction Optimization

```
nim c -r -f -d:release src/nimcso [method]
```

alloyList.txt

```
Mo,Re,Ta,W
Al,Co,Cr,Fe,Ni,Ti,V,Zr
B,Mo,Ni,Si
C,Mo,Nb,Re,Ta,W
Co,Cr,Fe,Ni,W
Hf,Nb,Ti,Zr
Co,Cu,Fe,Ni
Al,Cr,Nb,Ni,Ti,V
Co,Cr,Fe,Ni
Co,Fe,Ni
Al,Mo,Nb,Si,Sn,Ti,W,Zr
Co,Fe,Mo,Ni,V
Al,Cr,Cu,Ni,Ti
Cr,Fe,Ni,Ti
Al,Cr,Cu,Fe,Ni
Al,Co,Cr,Cu,Fe,Ni
```

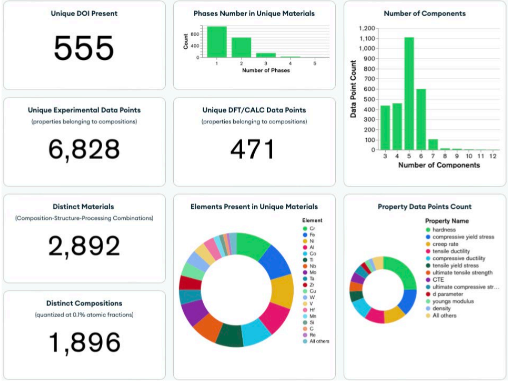
--bruteForce High-speed memory-efficient implementation of combinatoric search. Perfect for **millions of compositions with less than 20 components present.**

--algorithmSearch Search algorithm dynamically exploring only solutions which could be optimal. Perfect for **millions of compositions with 20-40 components present.**

--geneticSearch Genetic algorithm exploring simplex space through mutations and crossovers to iteratively improve solutions. Makes solving **millions of compositions with more than 40 components present** possible.

```
N->1
YN->4
YCN->39
ReYCN->89
ReYBCN->142
SiReYBCN->203
WSiReYBCN->340
WHfSiReYBCN->511
TaWHfSiReYBCN->630
TaWZrHfSiReYBCN->735
TaVWZrHfSiReYBCN->816
TaVWZrHfNbSiReYBCN->859
TaVWTiZrHfNbSiReYBCN->952
MoTaVWTiZrHfNbSiReYBCN->1
MoTaVWTiZrHfNbAlSiReYBCN-
TaVWTiZrHfNbCrAlCoNiReFeY
MoTaVWTiZrHfNbCrAlSiCoNiR
```

Using the above tools, our ULTERA database has efficiently processed thousands of experimental points from hundreds of publications with automated integration of the literature, experiments, generative modeling, predictive modeling, and validations.


Unique DOI Present
555

Unique Experimental Data Points
(properties belonging to compositions)
6,828

Unique DFT/CALC Data Points
(properties belonging to compositions)
471

Distinct Materials
(Composition-Structure-Processing Combinations)
2,892

Distinct Compositions
(quantized at 0.1% atomic fractions)
1,896

Lastly, a novel combinatorics-based algorithm for constructing graph representations of compositional spaces has been developed, offering promise to dramatically speed up the exploration of novel alloys [4].

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Biographical Note

Adam M. Krajewski is 5th year PhD Student in the Liu Group at The Pennsylvania State University. His research focuses on Machine Learning, AI, and data curation techniques in Materials Science, as well as high-entropy materials, including RHEAs.

[P06.04] From raster data to insights: Statistical microstructure characterization through composition and local property fields

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Key words: microstructure, spatial statistics, phase stability, composition field

State-of-the-art material design strategies are based on deep knowledge of the relationships between process, structure, and resulting macroscopic properties. The process-structure link describes how a material's chemical composition and manufacturing process give rise to its microstructure. On the other hand, the structure-properties connection studies the causal relation between the microconstituents' intrinsic properties, morphological features and their interaction, and the material's emergent macroscopic properties. The microstructure is at the heart of the task and mediates the step between the atomic and macroscopic worlds. As a result, microstructure characterization is a fundamental field of research within Materials Science and Engineering.

The definition of the microstructure—and its associated data—depends on the studied material family and the targeted properties. Uncovering underlying process-structure-property relationships is, thus, a profoundly multidisciplinary task that draws techniques, methods, and algorithms from diverse fields to process, explore, and interpret the often heterogeneous pools of information obtained. Most data generated for characterizing the microstructures of technological material are images from different microscopy technologies and their complementary detectors. The micrographs extracted from the imaging campaigns are then processed using techniques ranging in complexity from basic image processing to intricate segmentation using computer vision algorithms. This step generally aims to obtain representative information on the phase spatial distributions, morphology, and mean chemical composition. Finally, tools derived from spatial statistics and population survey help interpret the data.

This contribution presents an approach to statistically characterize segregation-driven spatial chemical inhomogeneities and derived properties in metallic materials. Understanding and controlling these inhomogeneities is essential as they might compromise the part's functional or structural integrity. For instance, Egels et al. have shown that, when unchecked, local chemical variations in the stainless steel AISI 304L might lead to failure through hydrogen embrittlement in loading under a hydrogen atmosphere [1]. The cause is that these inhomogeneities lead to differences in the austenite stability, leading to the local formation of martensite, which is inherently more susceptible to hydrogen

As a foundation, we use the so-called composition fields. These are matrices describing the locally resolved chemical composition of the material across the studied field of view. They are obtained through energy-dispersive X-ray spectroscopy (EDS), transmission electron microscopy EDS, or electron probe microanalysis. Using batch processing and parallelization, we can use this information to compute local properties at each position through computational thermodynamics efficiently. Examples are phase stabilities, element solubilities, or transformation temperatures in equilibrium and para-equilibrium conditions. Additional electron backscatter diffraction data can provide phase distribution information that we can use to extend the calculations further.

We propose and discuss employing variograms to extract insights from the data created. The variogram is a tool from spatial statistics that describes the spatial correlation of a property. In particular, we suggest employing first-order variograms and the newly developed [2] Gini variogram, which allow for direct physical interpretation of the measured and calculated spatial variations [3].

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Biographical Note

Santiago Benito works as a Research Group Leader at the Chair of Materials of the Ruhr-University Bochum. His research activities revolve around Materials Design and Characterization with the focus set on the microstructure of multi-phase engineering materials.

[P06.05] First-principles and machine learning prediction of stability and structural properties of transition metal HEAs

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Key words: High entropy alloy, Stability, First-principles, Machine learning

This research was started from two high entropy alloys (HEAs), Cantor alloy FeCoNiCrMn, and FeNiCoCrPd which is synthesized by intentionally substituting Mn in Cantor alloy by Pd, and was reported to achieve 2.5 times higher strength than that of FeNiCoCrMn. In order to understand the mechanism of Pd in enhancing the mechanical property, we investigated the stability and structural properties of these two HEAs based on first-principles calculation combining density functional theory (DFT) and finite temperature effects with taking special quasi-random structures (SQS) as model of solid solution. It has been revealed that the inhomogeneous feature of Pd increases the average atomic local displacement, consequently enhances the mechanical properties1). Along this work we have accumulated more than 1,300 DFT SQS data of all binary, ternary and quaternary sub-systems in all equiatomic compositions and typical non-equiatomic compositions of FeCoNiCrMn/ Pd, for fcc. bcc and hcp structures. Using this data set, systematic predictions are conducted by machine learning (ML). The elemental convolution graph neural networks (ECNet)2) in cooperating with transfer learning are attempted to predict the stability and properties of the higher compositional systems mainly based on the data of binaries and ternaries, then three new compositions of (FeCoNiCrMn)$_{1\text{-}x}$Pd$_x$ with superior values of RMSD then known quinary HEAs have been explored2-3) (Fig.1). Furthermore, the mesh searching4) for virtual systems of FeCoNiCrMnPd+x (x=all 3d-, 4d-elements, Mg, Al, Si, etc.) gave a general picture of solid solution stability of fcc, bcc and hcp lattice of the transition metal ternaries at zero K and finite temperature (Fig.2), the phase diagrams of solid solution have been derived. These results enriched the physics of those high-entropy alloys.

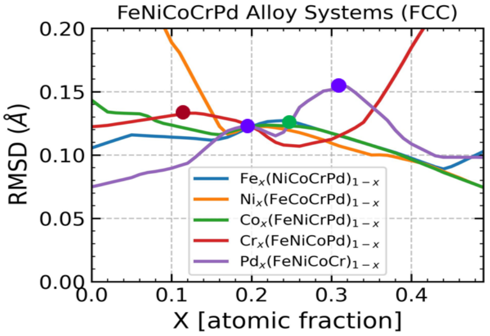

Fig.1 DFT+ML prediction of compositions with high RMSD (Root of mean square displacement) in FeCoNiCrMnPd alloys.

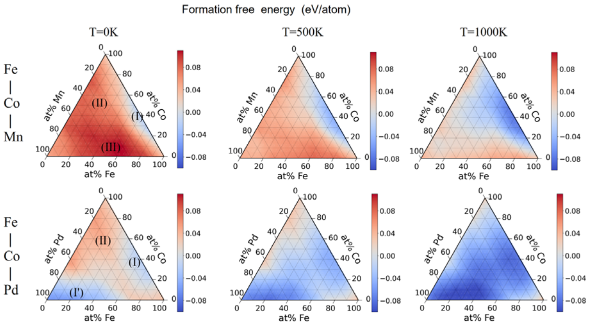

Fig.2 Two examples of DFT+ML prediction of solid solution stability of ternary systems, Fe-Co-Mn and Fe-Co-Pd at 0K, 500K and 1000K. The spectrum is formation energies.

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Biographical Note

Ying Chen has been a professor at School of Engineering, Tohoku University, Japan. Expertise in computational materials science, apply the first-principles based approaches combing electronic structures, phonon and machine learning to various materials such as high entropy alloys, nuclear materials, magnetic materials.

[P06.06] A data-driven study of the enthalpy of mixing in the liquid phase

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Key words: Enthalpy of mixing, Excess heat capacity, Liquid alloys, Machine learning

The enthalpy of mixing in the liquid phase is a key thermodynamic property for predicting phase equilibria not only using the Calphad method, but also machine learning approaches [1]. Means to reasonably estimate this property are invaluable for two reasons: first, so far, it has only been measured in at most a third of the binary systems, and second, it is not easily available from *ab initio* calculations. To estimate this property in binaries, the model developed by Miedema *et al.* in the 1980s [2] is still to this day considered the best. However, since it has never been systematically evaluated, the accuracy that can be expected from it is not well known. Combined with Muggianu's model [3], it can provide estimates in multicomponent liquids. Again, the accuracy of this extrapolation has never been systematically studied.

To address this, we collect a large amount of enthalpy of mixing data in binary liquids from a review of about 1000 thermodynamic evaluations. On this basis, we will clarify the prediction accuracy of Miedema's model, and show that more accurate predictions can be obtained from a machine learning model we developed. The data we collect also allows us to further evaluate Witusiewicz and Sommer's empirical model [4] to predict the excess heat capacity, and we will discuss the prediction results obtained in 2016 binary systems using our machine learning model as input. We then extend the data collection to ternary metallic liquids, and we will show that, when mixing is exothermic, extrapolations from the binaries by Muggianu's model systematically lead to slight overestimations close to the equimolar composition. Finally, we will present prospects of using these results to improve the machine learning models to predict binary liquidus we're developing [1].

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Biographical Note

Guillaume Deffrennes is a research fellow at the French National Centre for Scientific Research (CNRS) since 2022. His main research focus is on machine learning of thermodynamic properties and phase equilibria for alloys.

[P06.07] High Throughput Calculation at Steel Phase Diagram with Calphad and Bayesian Artificial Neural Network

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Keywords: Phase diagram, Calphad, Bayesian Artificial Neural Network, High throughput calculation

This study offers a novel approach by integrating the Bayesian Artificial Neural Networks (BANN) into the CALPHAD method to accelerate High Throughput Calculations (HTC) in multicomponent systems. The CALPHAD approach provides a strong tool for the microstructure and properties calculation of materials, which has proven to be useful in the design of new materials. The combination of the CALPHAD method with HTC allows us to explore a large composition and processing range. This is typically done by a "grid" calculation in which the composition of each/some constituents and processing conditions (heat treatment temperature etc.) are varied on a linear grid including all the possible combinations. Then, the results are filtered for the conditions which satisfy the design criteria.

Even for a not-so-sophisticated engineering alloy with 5 components and 10 variations per element, this results in 10^5 computations just to explore the composition space. Considering more sophisticated alloys such as superalloys with 8-10 components and including processing parameters will result in a very demanding computational task.

This study aims to develop an algorithm to accelerate this process using an intelligent exploration technique, that combines BANN and the HTC-Calphad method. The algorithm starts with a coarse grid and trains a BANN based on this grid. As BANN allows to study local uncertainty of the calculation**[1]**, the grid is iteratively refined using the same procedure only in the points at which it is certainly necessary to add more data in the NN, which will effectively reduce the CALPHAD calls. On the other hand, training a BANN costs a certain time which is an overhead of the calculation. However, thanks to recent hardware and software, NN training is accelerated significantly. Thus, it is expected that this approach will be faster than classical grid-HTC calculations for systems with a larger number of composition and processing variables.

In this article, we present our preliminary results about this approach. An isopleth and isotherm are calculated using "classical" grid calculation, and BANN is suggested as a novel grid approach. This example is chosen for its simplicity in visualization and tracking the algorithm's grid evolution and solution improvement. Thus, it is considered as a first development step before using in larger systems for which it will be worth using. **Figure** *3* indicates a hypothetical A-B binary diagram, which is started to be constructed using a coarse-grid calculation followed by BANN training. The pale blue lines (around the phase boundaries) indicate the regions that must be refined in the next iteration. Although the total number of calculations for a grid-based isopleth calculation is decreased, the computation time is not faster than a pure grid calculation because of the overhead of training BANNs. However, it is expected that this cost will be significantly lower than a full-grid calculation of multi-component systems also with large processing variable ranges. In the future, the system will be improved and tested on higher-order systems to calculate several material properties that can be used for material and process design on real engineering alloy systems.

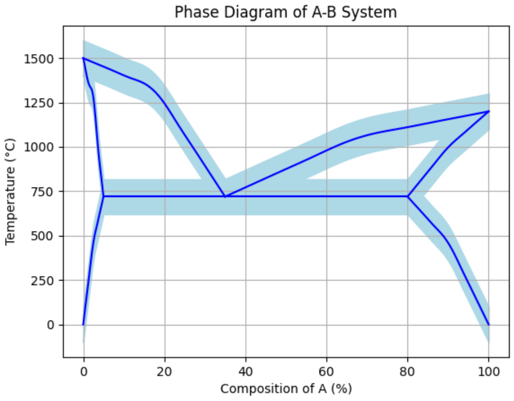

Figure 3. Phase Diagram of the A-B System: The dark blue line represents the calculated boundaries, while the shaded blue area indicates the BANN prediction with an error margin exceeding 10%.

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Biographical Note

I am Mehmet Şamil Dinçer, pursuing a master's degree in metallurgical and materials engineering at METU. Additionally, I work as an analysis and test engineer at Repkon. My goal is to become an ICME engineer, to comprehend materials from start to finish, and even to create new ones when necessary.

[P06.08] Building high-dimensional phase diagram with machine learning (ML) accelerating and the cost lowing by phase space analysis

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Key words: high-dimensional phase diagram, machine learning, phase space

Entering an alloy system that contains more than three elements makes visualizing the entire phase space through a phase diagram impossible, as it extends beyond three dimensions. Our initial study suggests a novel approach to organize phase space data into a high-dimensional array, while the Depth-First Search (DFS) algorithm is implemented to segment each continuous phase space. As the data increase rapidly with the dimensionality of phase space, we propose a machine learning approach [1]. Trained with 1,200,000 random data points in the Fe-Ni-Cr-Mn system, the model achieved high accuracy in classification and phase volume prediction tasks. Using this model, approximately 17,000,000 data points representing the Fe-Ni-Cr-Mn phase space were calculated in 8 minutes. After calculating the entire phase space, the data is organized into a high-dimensional phase diagram, and three foundational reactions in the Fe-Ni-Cr-Mn system are designed. This study demonstrates the robustness and efficiency of an ML-calculated high-dimensional phase diagram-based alloy design method by designing all eutectic reaction compositions in the Fe-Ni-Cr-Mn system, with 11 composition step figures calculated by Thermo-Calc confirming its reliability.

While the machine learning model shows its reliability and efficiency in the Fe-Ni-Cr-Mn system, the training cost remains unexamined, especially in alloy systems containing complex intermetallics. Our second study addresses this issue systematically, using the Fe-Co-Ni-Ti system as an example [2]. It proposes a method to qualitatively analyze phase space complexity using concepts such as phase density and composition space volume. The entire composition space is divided according to different phase densities. The training cost for the phase classification and volume prediction model is quantitatively analyzed by the relationship between the Mean Square Error of the model and data density. Then, regions with different phase densities are trained independently. For each region, a highly accurate model is obtained. To reduce complexity, models for different phase space predictions are combined by implementing the Mixture of Experts (MoE). A total of 1,050,000 data points are used to train the model instead of the unified training requirement of 4,740,000 data points.

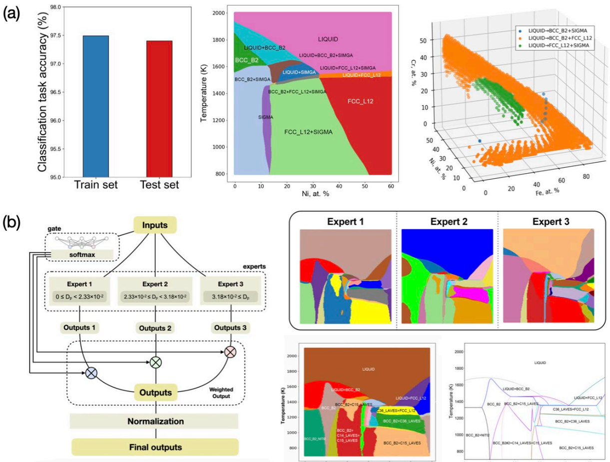

Figure 1. (a) Classification accuracy of model and its application on drawing of phase diagram. Using high-dimensional phase diagram design eutectic alloys. (b) Application of the Mixture of Experts (MoE) and a demonstration of its accuracy.

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Biographical Note

Zhengdi Liu is a bachelor student graduated from Southeast University, China, and will start his PhD program at Monash University, supervised by Prof. Christopher Hutchinson. He is interested in combining CALPHAD method and machine learning to accelerate alloy design.

[P06.09] Extending universal interatomic potential for grain boundary segregation in steel

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Key words: Machine learned inter atomic potentials, interatomic, grain boundaries, iron

Increasing the use of recycled steel is of paramount importance to reduce the carbon footprint of the steel industry. However, impurities such as copper, tin, nickel etc. in scrap iron are difficult to remove during steel refining, limiting its application. Some of these impurities such as copper and tin segregate to grain boundaries (GBs) leading to hot shortness and quality issues during subsequent processing [1]. Although GB segregation has interested researchers for decades [2], the understanding of GB segregation in relation to GB type, texture, and thermo-mechanical processing is limited. Computational studies have been much used for understanding mechanisms at the atomistic scale. However, due to the large numbers of atoms involved, geometric complexity, and the subtlety of GB segregation, computational studies have relied on empirical interatomic potentials [3] with limited accuracy.

In recent years, machine learned interatomic potentials (MLIP) have been designed that more easily fit to DFT data and at a more reasonable computational cost. Several MLIPs such as Moment Tensor Potential (MTP), Atomic Cluster Expansion (ACE), and Gaussian Approximation Potential have achieved near DFT accuracy [4]. Some MLIPs have been developed as universal interatomic potentials, meaning that they apply to any combination of elements across the periodic table [5]. Crystal Hamiltonian Graph neural Network (CHGNet) is one such universal machine-learned potential trained on 1.5 million structures from the Materials Project database [5]. Unlike other MLIPs, CHGnet predicts magnetic moments and was shown to be capable of distinguishing different ionic charge states of Mn in Li_xMnO_2 and in other transition metal oxides. In this study, the CHGNet universal potential is fine-tuned to bulk Fe using 18000 configurations [7] consisting of BCC-based structures. It is found that with hyperparameter refinement, it is possible to retain the information of the pretrained MLIP while at the same time improving the prediction accuracy for Fe-systems. The mean average error in the energy for training and for testing was found to be 4 meV/atom and 7 meV/atom respectively. After fine tuning a coefficient of determination of 0.99 was achieved for the model. In addition, even without having trained our MLIP on grain boundaries, it predicts GB energies for Σ3 and Σ5 symmetric twist grain boundaries with an average error of 8.2 %.

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Biographical Note

Naveen Mohandas, a PhD candidate at Delft University of Technology, investigates physics-based modelling of grain boundary segregation in recycled steel. Previously, he earned his Master's in Material Science and Engineering with a Cum Laude in 2022, specializing in metal science and technology, from the same institution.

[P06.10] Integrating *Ab-Initio* Calculations into Physics-Informed Neural Networks for Free Energy Predictions

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Key words: Phase stability, Gibbs Free Energies, Phase Diagrams, First-Principles Calculations, Physics-Informed Neural Networks

Accurate prediction of phase stability in materials science is essential for the advancement of contemporary technologies such as those underpinning sustainable energy. Gibbs free energies and phase diagrams are fundamental materials engineering parameters, especially in multicomponent alloy systems like high-entropy alloys (HEAs).[1] Following the establishment of the CALPHAD (CALculation of PHase Diagrams) approach as a foundational tool for predicting phase diagrams, the integration of high-quality theoretical calculations, machine learning methodologies, and experimental measurements has emerged as a pivotal strategy for refining these models.[2]

For this purpose, advanced first-principles techniques extending beyond standard density functional theory (DFT) methodologies have recently gained significant scientific attention. One such technique is lattice dynamics, which models the thermal motion (phonons) in solids and is amenable to high-throughput computing. Basic lattice dynamics calculations employ the harmonic approximation (HA) to calculate thermodynamic quantities at constant volume, including the vibrational entropy, Helmholtz free energy, and volumetric heat capacity. The quasi-harmonic approximation (QHA) extends the HA to account for the volume dependence of the lattice energy and phonon frequencies and to predict a wider range of properties, including the constant-pressure heat capacity and Gibbs free energy, as a function of temperature and pressure.[3] However, these modelling approaches are computationally intractable for complex systems like multicomponent alloys, which underscores the need for innovative methodologies to augment calculations. Among these, prediction of free energies is a crucial, yet underexplored, application of machine learning (ML) in materials science.

In this talk we will discuss work towards the development of a state-of-the-art, physics-informed neural network ML model for predicting Gibbs free energy. Our model is trained from a comprehensive dataset generated using high-throughput lattice-dynamics calculations on stoichiometric unary and binary materials. We utilise advanced feature engineering with atomistic-level descriptors and incorporate physical insights through custom loss functions that enforce physical constraints.

We first assess the reliability of our model by predicting thermodynamic properties for compounds in the binary Mg-Si and ternary Mg-Sn-Sr systems and rigorously evaluate its performance through a comprehensive approach including comparison to experimental data, cross-validation techniques, and error analysis. We then test the predictive capability of the model on data outside the training set to assess its robustness and reliability for future applications. Comparison of predicted enthalpies of formation, constant-pressure heat capacities and Gibbs free energies of compositions in the Mg-Si and Mg-Sn-Sr systems to available experimental and theoretical data allows us to determine whether our model can capture the essential thermodynamic behaviour of these systems. Attempting similar predictions for systems outside the training set then allows us to determine whether the model is capable of usefully-accurate extrapolation.

Overall, this approach addresses some problems in predicting phase behaviour and facilitates the rapid identification of stable compositions. We plan to integrate our model into a web app to make it more widely available. We also anticipate that further enhancements to the robustness and applicability of our model will be possible in the future by augmenting it with experimental data.

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Biographical Note

Ioanna completed her MChem (Hons) in Chemistry at the University of Manchester. She earned her PhD in 2023, focusing on lattice-dynamics calculations. She then joined the University of Leeds as a PDRA investigating the stability and spectroscopy of pharmaceuticals. Ioanna's current project involves constructing ML models for free energy predictions.

[06.11] Application of Machine Learning models for estimating the Glass Forming Ability of Bulk Metallic Glasses

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Key words: Bulk Metallic Glasses, Glass-Forming Ability (GFA), CALPHAD, Machine-learning.

Bulk Metallic Glasses (BMGs) have generated interest in recent years as materials with a unique set of properties (high elastic strain limit, high hardness, corrosion resistance, etc.) making them very attractive for some industrial applications [1]. One of the main challenges is to identify compositions where glass formation is easier, i.e. developing suitable approaches to predict the glass-forming-ability (GFA) *a priori*. There are several ways to express the GFA, such as the maximum attainable section thickness of a fully amorphous rod obtained after quenching from the liquid state (D_{max}), the critical amorphization cooling rate, the time to reach the nose of the TTT diagram or the reduced glass transition temperature, defined as the ratio between the glass transition and the melting temperatures ($T_{rg}=T_g/T_m$) [2].

In the past, the discovery of new BMGs was based on a trial-and-error iterative approach guided by empirical rules, but this traditional approach is time-consuming, ineffective, and costly. Different CALPHAD-based approaches have also been proposed to determine the GFA [3]. Recently, data-driven approaches based on Machine Learning (ML) have become increasingly popular for alloys design, allowing to understand and identify the relationships among different types of physical quantities related to GFA [4].

In this work, ML models have been trained to estimate the D_{max}. Two datasets of 495 Fe-based alloys consisting of two different types of features (or predictors) have been created. In the first one, molar compositions are used as features and the ML model must effectively “learn” the complex correlations between composition and D_{max}. In the second dataset, the features are thermophysical quantities such as the solidus and liquidus temperature, the T_0 temperature, etc. Most of these quantities have been calculated using the CALPHAD approach, the ThermoCalc software and the HEA database, whereas others have been computed using empirical equations.

Several ML models such as Multiple Linear Regression (MLR), XGBoost (XGB), Support Vector Machine (SVM) have been tested on both datasets. Furthermore, a data augmentation approach PADRE [5] and ensemble methods have also been tested. The performance of each model was evaluated using the coefficient of determination (R^2) as cost function for training. A 10-fold cross validation was adopted to obtain a better statistics. The feature importance was evaluated with Shapley values to provide some interpretability on the predictions obtained from various ML models.

Most of the tested models showed a satisfactory performance, but with significant differences among them. The MLR model has the lowest performance, evidencing the inability of a linear model to capture the complex patterns among the alloy features and the D_{max}. ML models trained on the thermophysical features appear to perform better than the same models trained on the compositions. Data augmentation showed little or no improvement on results. An ensemble of models provided the best performance, with an obtained R^2 value of 0.68 when using a combination of four different ML models based on both compositional and thermophysical features.

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Biographical Note

Renato Dario Bashualdo Bobadilla graduated in “Industrial Chemistry” in 2023 at University of Turin, Italy and has now a scholarship at the Chemistry Department at the same university.

[P06.12] Data-centric detection of compounds containing wrong data in large Calphad databases

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Key words: data quality, ab initio, Machine Learning, large databases

Reliability is one of the core properties of Calphad databases. In the past, reliability has been mainly ensured by careful human assessment and simply the fact that the data is used successfully in application calculations. In this project conducted for the Scientific Group Thermodata Europe (SGTE), the reliability of compound data in the SGTE Pure Substance database was assessed. Given the fact that there are 3927 different compounds in the SGTE Pure Substance database, a human assessment of each compound is not viable. Therefore, a data-centric approach was used as explained here.

First, compounds which show a deviation of enthalpy of formation larger than 10 kJ/mol atom compared to the aiMP database developed by GTT-Technologies [1] are detected. For these 300 compounds, a manual assessment was used to filter out 17 compounds which contain probably wrong data.

Secondly, S and Cp at room temperature was compared to the predictions by the underlying ML models of the aiMP database, again followed by a manual assessment. Here, another 12 compounds which contain probably wrong data have been identified.

For some deviations, it is clear that errors had been introduced while copying data from the original sources while in other cases there was simply a missing update to newer data sources.

The 29 compounds with probably wrong data are (besides the elements Gd and Tb) from all material classes contained in the SGTE Pure Substance database, i.e. intermetallics, nitrides, salts, oxides, borides. They make up 0.7% of all compounds in the SGTE Pure Substance database.

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Biographical Note

Moritz to Baben is Managing Director at GTT-Technologies since 2017. He obtained his PhD at RWTH Aachen University in 2013 and joined GTT in 2016. He is fascinated by the complexity in navigating chemical space.

[P06.13] NIST data resource for curated thermophysical property data of metal systems

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Key words: thermophysical properties, database

For almost a decade, NIST's Thermodynamics Research Center (TRC) has been proactively tackling the issues related to the provision of electronic, machine-readable thermophysical property data for metallic systems. Data likes this is a key element of every robust Integrated Computational Materials Engineering (ICME) framework, which aims to expedite the development and deployment of advanced materials at a fraction of the current cost. The collection of curated experimental thermophysical property data as presented in the original literature, complete with data provenance and clear quality statements expressed in terms of uncertainty, is presented.

Having thermophysical property data of pure elements and alloys electronically available is vital in a variety of areas, including most engineering applications around heat transfer, material processing, thermal management, and the development of new materials. Dependable and comprehensive databases are indispensable for accessing this knowledge, facilitating new scientific breakthroughs, supporting ongoing metrology development, and satisfying the increasing data demands for advanced modeling and computational tools.

This presentation will delve into the continuous development of the NIST/TRC online resource for metals and alloy data, which focuses on unary, binary, and ternary systems and is freely accessible to the public. It will discuss the process of structuring pertinent information from the open literature into curated datasets, provide an update on the data coverage and a short walk through the web search for some property data. It will also feature the RESTful API that has been made available for programmatic data access for large-scale applications.

A specific use case will be highlighting how the database can assist in querying essential data for other scientific work, with a focus on the availability of data regarding the speed of sound as it pertains to temperature and pressure.

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[2] https://trc.nist.gov/metals_data

Boris Wilthan

Is a physicist at the National Institute of Standards and Technology (NIST) with an experimental background in thermophysical property measurements. His focus is to build a free online resource for thermophysical property data of unary, binary, and ternary metals and alloy systems.

[P07.01] Towards modelling the PBF-LB process of a MgZnCa alloy

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Key words: Mg-based alloys, ThermoCalc, CNGT

Magnesium is the lightest structural material and its alloys have attracted attention in research for aerospace and biomedical applications. As orthopedic implants one can benefit from their biodegradability, which could avoid secondary surgical interventions [1].

However, challenges still remain, e. g. in terms of their relatively low corrosion resistance and mechanical properties. Historically, this has been addressed by alloying with rare-earth elements (REEs). However, their production is not sustainable, mainly due to the environmental and health hazards generated in the extraction process. The end goal of this project is to decrease the corrosion rate of a REE-free composition based on Mg, Zn and Ca, by tuning its microstructure during additive manufacturing by powder bed fusion with laser beam (PBF-LB). To reduce the resource- heavy trial-and-error printing process, we aim to assist this development by numerical modelling of the composition of interest. A first step towards is the CALPHAD assessment of stable phases and the use of classical nucleation and growth theory (CNGT) to predict their precipitation in the undercooled liquid.

First system assessments using ThermoCalc TCMG7 database have showed HCP_A3, CA2MG6ZN3 and MGZN phases present at equilibrium. Here, a first approach without oxygen is undertaken due to the lack of information about magnesium oxides in TCMG7 and subsequent problems of databases compatibility. The composition shows a high glass-forming ability compared to various factors in literature [2], such as the deep eutectic point.

The melting temperature and enthalpy of melting were calculated and experimentally validated with DSC analysis. XRD results on PBF-LB samples showed peaks of crystalline Mg, but also some other intermetallic and oxides are in presence. WAXS was done to confirm the phases in presence in the final samples.

Due to limits in the ThermoCalc mobility databases and the results showing primarily HCP, only this phase and the liquid were used in the CNGT model using TC-Python. This code extracts Gibbs energy information from HCP and LIQUID phases (Figure 1) to calculate growth parameters at different temperatures for a future TTT diagram simulation. Driving forces are calculated and used to get the nucleation barrier of the precipitating phase.

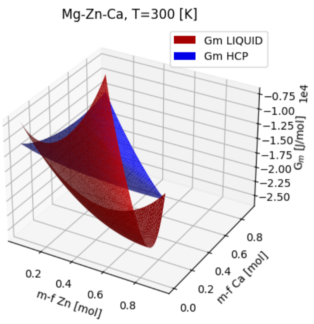

Figure 4. Gibbs energy of the LIQUID and HCP phases in the MgZnCa domain, in function of mole fractions.

Interfacial energies were obtained using enthalpies of melting to use the Turnbull expression [3] and were compared with calculations using extracted information from ThermoCalc (Becker’s energy approach). The viscosity of the liquid was simulated with ThermoCalc databases to obtain the high temperature viscosity constant and obtain growth parameters, but needs to be validated experimentally in future work.

This work was partially supported by the Wallenberg Initiative Materials Science for Sustainability (WISE) funded by the Knut and Alice Wallenberg Foundation, as well as by Sweden’s Innovation Agency through the AM4Life Competence Centre (grant number 2019-00029).

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Biographical Note

Belen Alonso Rancurel studied a Science Bachelor MPCI in Marseille, France, and a double diploma Master in Material Science at EEIGM (Nancy, France) and LTU (Luleå, Sweden). They started PhD studies in modelling Mg-based alloys manufactured by LB-PBF in August 2023.

[P07.02] Estimating the Yield Strength of Ni-based Superalloys with CALPHAD and KWN for Varying Aging Conditions

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Key words: CALPHAD, Heat treatment, Phase transformations, Thermomechanical Properties

This study proposes a generic approach for the determination of high temperature material properties such as yield strength by modelling the microstructure with the use of the CALPHAD method and the Langer-Schwarz-Kampmann-Wagner numerical model. Alloys especially used in land-based and aerospace turbine engines such as Ni-based superalloys are chosen to design the heat treatment parameters which affect mechanical properties directly for the construction and validation of this approach to scale down the trial-errors for the material design processes.

In this study, five different ɣ' strengthened Ni-based superalloys were modelled starting with solidification followed by precipitation and concluded with the determination of corresponding yield strength, which was compared with the data found in literature. The studied alloys are Waspaloy, Nimonic 263, MarM 200, IN740H, IN713LC.

Ni-based superalloys can be produced by many methods with varying cooling rates during solidification depending on the methods used. In order to determine the homogenization temperature adequately, the phases transformed during solidification and their amounts in the microstructure is a crucial subject to be known. Thus, thermodynamic modelling studies by using the CALPHAD method were used for the formation of equilibrium and non-equilibrium solidification modelling. The homogenization temperature range determined with respect to the analysis outputs by using ICME was optimized regarding the manufacturing method of each alloy. The obtained results were compared with the literature. Thereafter, modelling the aging of these alloys with the patent and/or literature parameters were completed by using related ICME software in regard to KWN model. The outputs of these models were used for the determination of yield strength of these alloys both at room temperature and elevated temperatures.

It has been noticed that the strength of these alloys mainly arises from the precipitation hardening, Orowan strengthening and coherency strengthening followed by solid solution strengthening. The effect of grain boundary strengthening, and lattice strength of nickel was also incorporated into the model that is constructed for the prediction of yield strength. Modelling results have been compared with the literature data, related patents and the yield strength assumptions that were performed with the software.

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Biographical Note

I’m a Metallurgical and Materials Engineer and I’ve recently completed my MSc. degree at METU. I’m also working at Simultura as alloy development and design engineer. The main field I am planning to get expertise on is aerospace materials where ICME methods are crucial for the material and process design.

[P07.03] Thermal stress analysis of WC-Co-Ni hard alloys based on thermodynamic calculations

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Key words: thermodynamic calculations, thermal stress, WC-Co-Ni, finite element simulation

During the working process, hard alloy materials will continuously withstand alternating bending stress, frequent mechanical impacts, and thermal shock stress caused by periodic temperature changes due to frictional heat generation, resulting in the generation and propagation of surface cracks in the alloy material, ultimately leading to premature failure of hard alloy products[1,2]. The reason for the occurrence of surface thermal shock cracks is due to the different thermal expansion and contraction rates of each phase in the material, resulting in a temperature difference between the inside and outside of the material. The difference in thermal expansion coefficient between the hard phase and the binder phase in hard alloys is an order of magnitude, making it highly susceptible to thermal shock cracks. Moreover, surface micro cracks caused by periodic temperature changes are easily propagated, reducing the wear resistance of the alloy material surface and accelerating alloy failure[3]. Therefore, it is imperative to study the thermal stress distribution and its impact on the performance of hard alloy materials under thermal shock conditions.

In order to obtain more accurate predictions, it is necessary to first obtain the corresponding material parameters. The CALPHAD method is established as a tool for processing thermodynamic functions and phase equilibria related to composition and temperature from experimentally measured phase diagrams and thermochemical data. The advantage of this method is that it can extrapolate from binary and ternary systems to multi-component systems, thereby achieving thermodynamic prediction of multi-component phase diagrams and thermochemical properties for material computational design. Based on the CALPHAD method, the thermophysical parameters of the hard phase and binder phase in hard alloys are calculated, and the target alloy is prepared to test its elastic-plastic properties according to the sintering temperature calculated from the thermodynamic phase diagram (as shown in Figure 1).

We establish a three-dimensional finite element hard alloy model, input corresponding material thermal and mechanical properties, simulate the thermal stress distribution and magnitude of hard alloys under different thermal shock temperatures, and compare the results with the thermal stress test results of alloys under different thermal shock temperatures. The results show a good agreement within the error range.

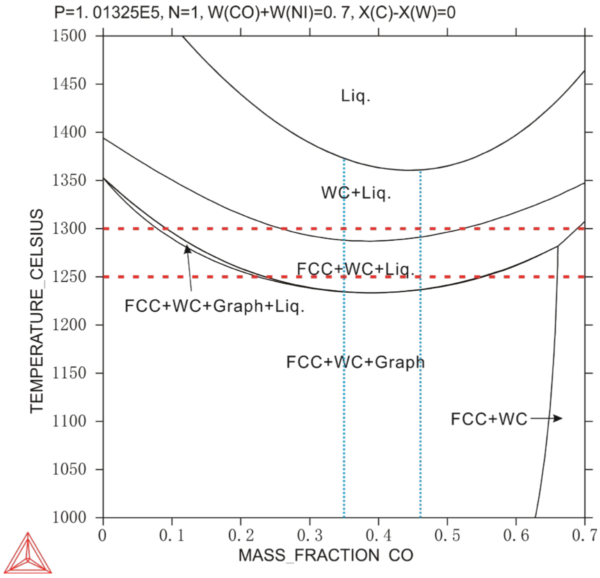

Figure 1. Vertical cross section phase diagram of WC-Co-Ni alloys.

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Biographical Note

Meiling He, from Huanggang, Hubei, China, graduated from Hefei University of Technology with a bachelor's degree in 2019. She is currently pursuing a doctoral degree at the Institute of Powder Metallurgy, Central South University. The research focuses on the thermal failure and performance prediction of hard alloys.

[P07.04] Using automated thermodynamic simulations for the development of new Cu alloys with high strength and good electric conductivity

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[2] fem Research Institute, Schwäbisch Gmünd, Germany

Key words: copper, nickel, aluminium, hardness, conductivity, high throughput experiments

By using high throughput experiments, various copper-based diffusion couples were produced and analyzed with the aim to link chemical compositions with mechanical properties in the CuAlNiX (X=Co,Fe,Sn,Mn) alloy system. The target alloys show the ability of age hardening via Ni and Al rich intermetallic phases. To enrich the received data with information of the phase fractions and further thermodynamic data, thermodynamic simulations were performed. In a first stage of development, an automated input script reads the measured chemical compositions from EDX analysis and calculates phase fractions of potential hardening phases and the residual matrix compositions. The phase fraction of the hardening phase is then compared to the measured hardness of the experimental alloys. The amount of alloying elements in the matrix phase is believed to deteriorate the electrical conductivity of the produced alloys.

In a second stage the range of alloy compositions was extended and the influence of further elements on the mechanical and electrical properties was studied. Simulations were performed on Cu-rich quaternary alloys CuAlNiX (X=Cr,Ge,Nb,Si). Target alloys can be identified, which fulfill the requirements best. This approach reduces the time for the development cycle of alloys dramatically in this specific case. More than 100.000 chemical compositions were calculated and compared with experimental data. After the experimental analyses via diffusion couples and supporting thermodynamic calculations, alloys were cast and produced in an industry-oriented processing route.

Biographical note:

Johannes Preußner is manager of the group Microstructure and Residual Stresses at Fraunhofer IWM in Freiburg, Germany. He studied Materials Science at the University of Bayreuth, Germany and made his PhD in analyzing and thermodynamic modelling of PtAlCrNi alloys. After learning new techniques in analyzing material structures including the evaluation of residual stresses and hydrogen embrittlement, he now enjoys working in the field of thermodynamic alloy development again.

[P08.01] Experimental phase equilibria study and thermodynamic modelling of the $CaO-MgO-FeO-Fe_2O_3-SiO_2$ system

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Key words: thermodynamic modelling, molten oxides, phase diagram, $CaO-MgO-FeO-Fe_2O_3-SiO_2$

The Ca-Mg-Fe-Si-O system finds applications in a variety of high-temperature metallurgical processes, the most important of which are ironmaking and steelmaking, nickel and ferronickel production, and refractory materials. High-temperature equilibration in vertical tube furnace followed by quenching and direct measurement of Ca, Mg, Fe, and Si concentrations in the phases with the electron probe X-ray microanalysis (EPMA) has been used to accurately characterize phase assemblage of samples. Four-point testing [1] was used to ensure achievement of equilibria. Quaternary $MgO-FeO-Fe_2O_3-SiO_2$ system is studied in the wide range of conditions from oxidizing (in air) to most reducing (in equilibrium with metallic iron). Influence of oxygen partial pressure on phase equilibria is analyzed. Solid solutions of orthosilicates and metasilicates in the Ca-Mg-Si-O system are characterized with the implementation of the data obtained in phase equilibria experiments in higher-order Ca-Mg-Fe-Si-O system. Solubility of magnesium in different forms of dicalcium silicate is measured. In the Ca-Mg-Fe-O system, tie lines have been determined for the first time. The experimental results are used for development of an accurate thermodynamic model together with existing thermochemical data. The present work is a part of the integrated experimental and thermodynamic modelling research program on the phase equilibria of the Cu-Pb-Fe-Zn-Ca-Si-Al-Mg-O-S-Cr-As-Sn-Sb-Bi-Ag-Au-Ni-Co-Na gas/slag/matte/speiss/metal/solids system [2].

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Biographical Note

Igor Babaian is a 3rd year PhD student focusing on high-temperature phase equilibria, thermodynamic modelling and leaching of metallurgical slags.

[P08.02] Thermodynamic modeling of the CaO-CaF_2-B_2O_3-BF_3 reciprocal system

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Key words: CaO-CaF_2-B_2O_3-BF_3, Calphad modeling, single crystal growth, non-linear optics

The generation of UV light in single crystals by means of the use of their nonlinear optical (NLO) properties is the desired path to design all solid-state UV coherent light sources. Such devices aim to replace the current excimer lasers and to find large number of applications (micro-via drilling in microelectronics, plastic marking, LED's substrate dicing, etc.).

In the field of materials and optics to develop NLO fluoroborate crystals for an efficient UV conversion, $Ca_5(BO_3)_3F$ (CBF) is one of the most promising potential candidates [1]. An example of a single crystal is reproduced in Fig.1.

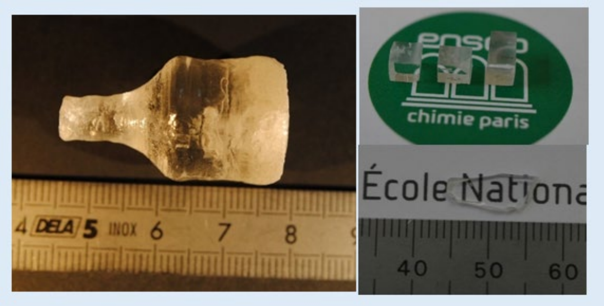

Figure 1 $Ca_5(BO_3)_3F$ boule (as grown) on the left and shaped single crystals on the right

$Ca_5(BO_3)_3F$ has a non congruent melting point which makes the single crystal growth more complicated. In addition, boron oxide is highly volatile which limits the maximum temperature and the growth duration.

In order to optimize the growth conditions, thermodynamic equilibrium calculations are mandatory. Unfortunately, no coherent Gibbs energy dataset is available for the reciprocal CaO-CaF_2-B_2O_3-BF_3 system. In addition, the heat of formation and heat capacity as a function of temperature for $Ca_5(BO_3)_3F$ are unknown.

In our contribution, we will report a first attempt to generate a coherent Gibbs energy dataset for the full reciprocal system based on literature information (CaO-CaF_2, CaO-B_2O_3 binaries), estimations (CaF_2-BF_3, B_2O_3-BF_3), DFT calculations ($Ca_5(BO_3)_3F$) and key experiments. Based on this data, the most pertinent phase diagrams for the crystal growth will be calculated and discussed.

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Biographical Note

Dr. Soukaina ED-DAHRI is a CNRS Postdoc at Laboratoire SIMaP in Grenoble, France. She holds a Master in Materials Physics from FST Béni Mellal (Morocco), a PhD in Materials Physics from FST Béni Mellal (Morocco). Her work focuses on DFT calculations, Calphad modeling for material applications.

[P08.03] Thermodynamic modelling of the ZrO_2-Ta_2O_5 and Y_2O_3-Ta_2O_5 systems

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Key words: ZrO_2, Y_2O_3, Ta_2O_5, CEF

The phase relations in the ZrO_2-Y_2O_3-Ta_2O_5 system are of interest for the development of new materials for thermal barrier coating (TBC) applications. Currently used 8 mass% yttria stabilized ZrO_2 consists of metastable t' phase which partition to a stable phase assemblage of cubic and tetragonal phase at temperatures above 1473 K. Experimental studies [1] showed that at substitution of ZrO_2 with equal amount of Y_2O_3 and Ta_2O_5 (in total 22 mol%) the tetragonal phase became stable at 1773 K.

Thermodynamic database development for the ZrO_2-Y_2O_3-Ta_2O_5 system makes it possible to calculate stable phase assemblages at conditions which were not investigated, to evaluate thermal stability of TBC materials and to calculate T^0-lines for diffusion-less transformations.

It is essential to use physically reasonable thermodynamic models for solid phases; that is why the compound energy formalism (CEF) is used in combination with available crystallographic data. Two-sublattice partially ionic liquid is applied to describe liquid phase.

Phase diagram data for the ZrO_2-Ta_2O_5 system were limited. Phase equilibria were studied using the equilibration technique and thermal analysis. The heat capacity of $Ta_2Zr_6O_{17}$ was measured using differential scanning calorimetry (DSC). The homogeneity range of $Ta_2Zr_6O_{17}$ was described by the formula $(Zr^{+4},Ta^{+5},Va)_8(O^{-2},Va)_{17}$ based on crystallographic data. Using own experimental results and data available in literature, the thermodynamic parameters of the ZrO_2-Ta_2O_5 system were assessed [2].

The phase diagram of the Y_2O_3-Ta_2O_5 system was constructed based on critical evaluation of literature data and own results by Fernandes et al. [3]. Experimental thermodynamic data are also available [4]. In the present study, it was shown that YTa_3O_9 melts by a peritectic reaction forming liquid and $YTaO_4$ at 2073 K. The temperature and composition of eutectic were determined to be 2019 K and 78 mol% Ta_2O_5. Literature data as well as our own experimental results were used for optimization of thermodynamic parameters.

Homogeneity range of the Y_3TaO_7 phase with fluorite structure was modelled according to the crystallographic data $(Y^{+3},Ta^{+5})_1(O^{-2},Va)_2$. The model for orthorhombic phase o was also based on crystal structure data $(Y^{+3})_1(Ta^{+5},Y^{+3})_2(Ta^{+5})_1(O^{-2},Va)_2(O^{-2})_6$. The preliminary thermodynamic description was derived and calculated phase diagram is presented in Figure 1.

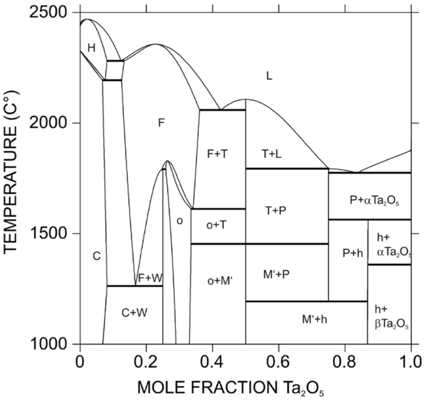

Figure 1. The **calculated phase diagram of the Y_2O_3-Ta_2O_5 system**

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Biographical Note

Olga Fabrichnaya (Ph. D., habil.) is a leader of Materials Thermodynamics group in the Institute of Materials science at TU Bergakademie Freiberg, Freiberg Germany. Research interests are thermodynamic modelling of oxide systems, experimental investigations of phase diagrams and calorimetry.

[P08.04] Experimental investigation and thermodynamic evaluation of the ZrO_2-TiO_2-SrO system

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Key words: ZrO_2-TiO_2-SrO, CALPHAD, Thermodynamic model, Phase diagram

In the present work, a series of ZrO_2-TiO_2-SrO ceramic samples were prepared through solid-state reaction, and the phase relationships at 1473 K were systematically characterized. For the TiO_2-SrO binary system, the presence of $Sr_4Ti_3O_{10}$ was considered and its binary system was reassessed through the CALPHAD method by using both the latest experimental data and first-principle calculations. The thermodynamic parameters of TiO_2-SrO system were combined with those of ZrO_2-TiO_2 and ZrO_2-SrO system, and a set of self-consistent thermodynamic parameters of the ZrO_2-TiO_2-SrO system were optimized according to our measurements and literature data. Finally, the isothermal sections at 1473 K and 1733 K, the vertical section of SrTiO3-SrZrO3 and the liquidus surface projection were calculated. The calculated results agree well with the available experimental data, which proves the self-consistency and reliability of the existing thermodynamic database.

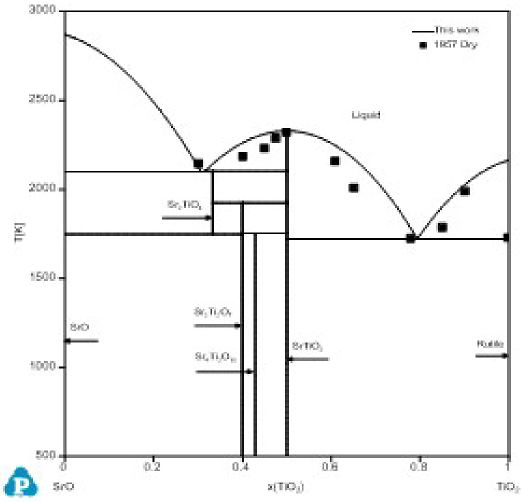

Figure 1. The calculated phase diagram of the TiO_2-SrO system in the present work with the experimental data by Dry et al. [1].

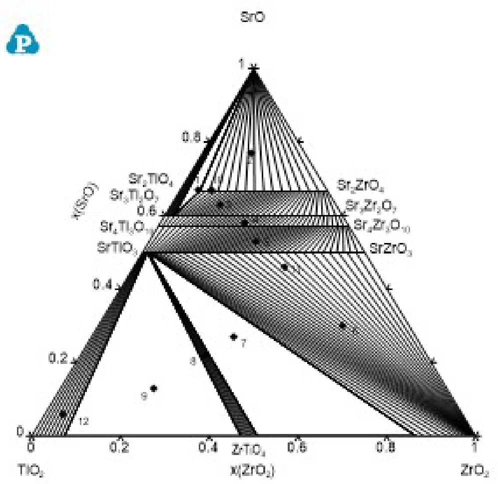

Figure 2. The calculated isothermal section at 1473 K of the ZrO_2-TiO_2-SrO system with the present experimental data.

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Biographical Note

My name is Qisheng Feng, a doctoral student at Shanghai University, China. My research direction is the establishment of thermodynamic database of Ti-based multi-element system. My tutor is Prof. Chonghe Li.

[P08.05] Thermodynamic assessment of the Al_2O_3-Fe_2O_3-FeO system by introducing the AlO_2^{-1} species into the thermodynamic model for liquid phase

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Key words: Solid wastes, Al_2O_3-Fe_2O_3-FeO system, thermodynamic modeling

The Al_2O_3-Fe_2O_3-FeO system is an important subsystem in the solid wastes and knowledge of its phase equilibria is of great significance for the phase transformation and reconstruction of mineral phases in the process of solid waste resource utilization [1]. Motivated by developing a thermodynamic database of the multicomponent system with compatible ionic two-sublattice liquid model, a reassessment of the Al_2O_3-Fe_2O_3-FeO system was conducted through the CALPHAD method. All relevant experimental data in the literature were critically reviewed. The sublattice model based on the compound energy formalism was applied for the solid solution phases to describe the homogeneity range and the distribution of cations in different lattice sites. The liquid phase was described by the ionic two-sublattice liquid model as $(Al^{+3}, Fe^{+2})_P(AlO_2^{-1}, FeO_{1.5}, O^{-2}, VA)_Q$. The species AlO_2^{-1} was introduced to model pure liquid Al_2O_3, ensuring compatibility with the latest thermodynamic optimizations of the Al_2O_3-CaO-SiO_2 [2] and the Al_2O_3-MgO-SiO_2 [3] systems. A new self-consistent set of thermodynamic parameters for the Al_2O_3-Fe_2O_3-FeO system was obtained, and comprehensive comparisons between the calculations and experimental data indicate that the present thermodynamic description is capable of reproducing the experimental data reasonably. The present thermodynamic calculations demonstrate several noticeable improvements in comparison with previous calculations. This research holds significant implications for the recycling and utilization of industrial solid wastes.

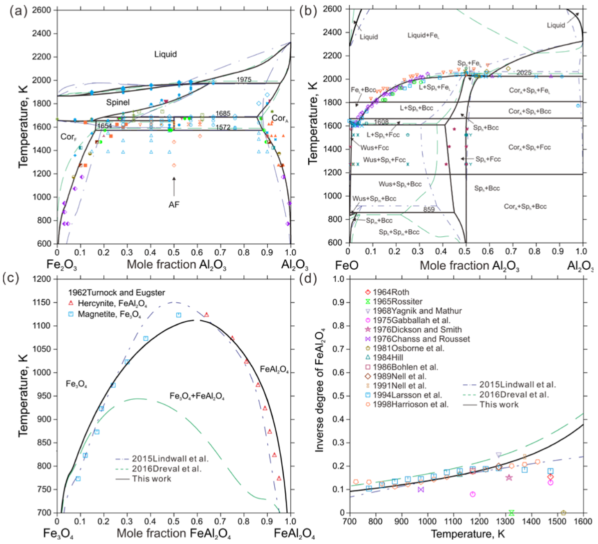

Figure 1. Calculated phase diagrams: (a) Al_2O_3-Fe_2O_3 section at $p(O_2) = 0.21$ atm; (b) Al_2O_3-FeO section; (c) Fe_3O_4-$FeAl_2O_4$ section; (d) inverse degree of the spinel phase.

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Biographical Note

Fengyang Gao is a doctoral student of Powder Metallurgy Research Institute in Central South University, China. The research focuses on the investigation of phase diagrams and thermodynamic modelling of the oxide system.

[08.06] High-temperature refractory Al-M-Si-O (M= Nb, Ta) systems

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Key words: refractories, modeling, niobates, tantalates

Refractory metal-alumina composites are investigated for a new generation of coarse-grained composites. [1] The knowledge about phase transformations and reactions during the sintering process and the long-term heat treatments are a fundamental basis in developing new materials. The quaternary systems Al-Nb-Si-O and Al-Ta-Si-O are not yet thermodynamically assessed in the literature. For the CALPHAD-type assessment key experiments such as X-ray powder diffraction (XRD) and thermal analysis (e.g. differential thermal analysis (DTA) and differential scanning calorimetry (DSC)) are used to determine phase compositions, homogeneity ranges, thermochemical and thermophysical properties.

The samples are prepared by dry-mixing powders, which are then cold isostatically pressed, heat treated (only solid-state reactions) and annealed. If thermodynamic equilibrium is not reached, samples are regrinded and the previous steps are repeated. The experiments are used to create an experimental dataset as input for the CALPHAD optimization.

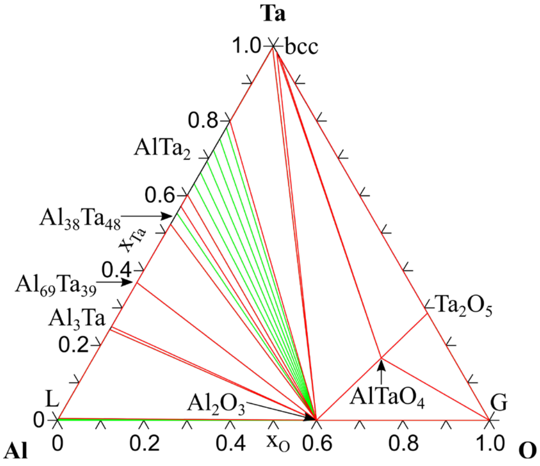

Figure 1. Calculated isothermal section of the ternary Al-Ta-O system at 1100 °C [2].

According to the planned conditions of use of the composites, the samples were placed in the composition ranges M-Al_2O_3-SiO_2-M_2O_5 (M=Nb, Ta) for the key experiments. XRD experiments show that $AlTaO_4$ is practically a stoichiometric phase and the only ternary oxide in the quasi-binary section Al_2O_3-Ta_2O_5. XRD patterns of quenched samples are used to determine the solubility of Al_2O_3 in α-Ta_2O_5 and β-Ta_2O_5. The same procedure is applied to determine the dissolution of SiO_2 in Nb_2O_5 and Ta_2O_5. No ternary oxide is formed in the quasibinary sections SiO_2-M_2O_5 (M=Nb, Ta). Within the Al_2O_3-Nb_2O_5 section three stoichiometric ternary oxides can be identified: $AlNbO_4$, $AlNb_{11}O_{29}$ and $AlNb_{49}O_{124}$. All four ternary compounds show no solid-solid phase transition. Based on the present experimental results and evaluations of binary systems from the literature, thermodynamic datasets will be evaluated which describe both quaternary systems, Al-M-Si-O (M=Nb, Ta), from the melt down to room temperature. For Al-M-O (M=Nb, Ta) datasets have already been published. [2, 3] The thermodynamic parameters and coefficients of the Gibbs energy functions of ternary $Al_xM_yO_z$ (M = Nb, Ta) oxides are assessed for the first time. [2]

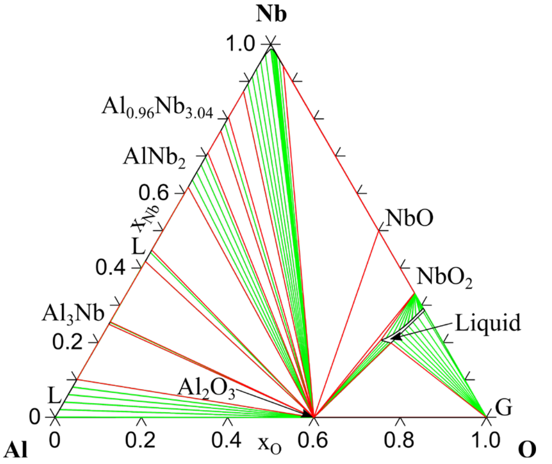

Figure 2. Calculated isothermal section of the ternary Al-Nb-O system at 1600 °C [3].

Acknowledgement

The authors gratefully acknowledge funding by the German Research Foundation (DFG) within the Research Unit FOR3010 (project number: 416817512), reference numbers FR1108/3-1 and SE647/23-1.

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[3] M. Eusterholz et al.; *Adv. Eng. Mater.*, **2022**, *24*, 2200161.

Biographical Note

Julian Gebauer is a research associate at the KIT IAM-AWP. He has a Master of Science degree in materials science from KIT. His research area includes experimental work and CALPHAD assessments of oxide systems.

[P08.07] Phase Equilibrium Investigations of the HfO_2-Y_2O_3-Ta_2O_5 System

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Key words: phase equilibria, thermal barrier coatings, thermodynamic modelling, heat capacity

The ZrO_2-HfO_2-Y_2O_3-Ta_2O_5 system is of interest for the application as thermal barrier coating (TBC) on metallic substrates to protect the components from harsh conditions for stationary energy conversion in gas turbines or for propulsion of airplanes. Therefore, TBCs must meet the following properties: phase stability at high temperatures, low thermal conductivity, compatibility with Al_2O_3, high fracture toughness and corrosion resistance. Furthermore, phase transitions in the temperature range of the application should be avoided.

Yttria-stabilized zirconia presents the state-of-the-art material in relation to TBCs. The tetragonal high temperature polymorph can be stabilized by the substitution of Zr^{4+} by Y^{3+} due to the formation of oxygen vacancies for charge compensation.[1] To further stabilize the tetragonality of the ZrO_2 lattice doping with smaller cations or cations with higher oxidation state than Zr^{4+} (e.g. Ti^{4+}, Nb^{5+}, Ta^{5+}) are used due to the beneficial ferroelastic toughening mechanism, which is strengthening the material at elevated temperatures.[1] The fracture toughness and phase and structural stability of the ZrO_2 lattice and a reduction in thermal conductivity can be achieved by adding Hf^{4+}.[2]

While the ZrO_2-Y_2O_3-Ta_2O_5 phase diagram has been well investigated in literature[3], there is lack of information in the HfO_2-Y_2O_3-Ta_2O_5 system. Due to the similarity of hafnia and zirconia no major differences are expected in the respective systems, except that the transformation temperatures of the different polymorphs of hafnia are significantly higher than that of zirconia. Additionally, the solubilities of the compounds in the different phases are expected to deviate in the HfO_2-based system from the ZrO_2-based system.

In this work, the HfO_2-Y_2O_3-Ta_2O_5 materials system is investigated. Key compositions are synthesized using reverse co-precipitation and are heat treated at selected temperatures ($\geq$ 1500 °C). Phase and chemical compositions are determined using X-ray diffraction and scanning electron microscopy/energy dispersive spectroscopy. Phase stabilities and heat capacities are measured using differential thermal analysis and differential scanning calorimetry. Thermal conductivities are measured using laser flash analysis. The key composition $YTaO_4$ is of special interest with respect to TBC applications, due to its phase stability up to 1450 °C and a low thermal conductivity. The high-temperature phase equilibria, phase transformations (shown in Figure 1) and thermochemistry of this compound were additionally investigated using high-temperature thermal analysis and drop-and-catch calorimetry.[4]

The experimental data will be used as an input for the thermodynamic modelling to build a self-consistent database of the material system.

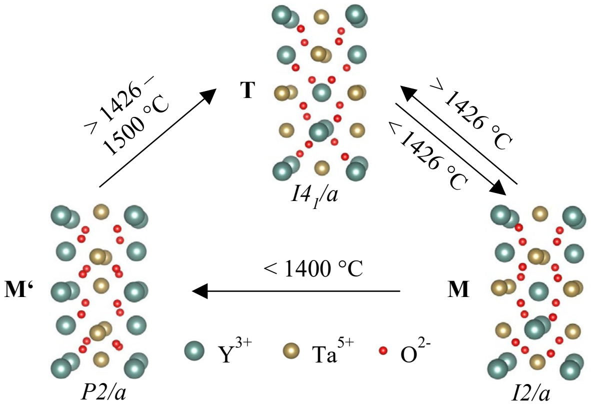

Figure 1. Conversion temperatures of $YTaO_4$.

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Biographical Note

Alina Habermann studied chemistry at the Justus Liebig University Giessen and is now a PhD student in the group of Prof. Dr.-Ing. Maren Lepple. Her research is about the thermodynamic investigation of the ZrO_2-HfO_2-Y_2O_3-Ta_2O_5 system in a DFG joint project with PD Dr. Dr. rer. nat. habil. Olga Fabrichnaya from TU Bergakademie Freiberg.

[P08.08] CALPHAD-informed phase-field modeling of incipient melting in oxidized fuel: U-Pu-O, a new step toward multicomponent systems

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Key words: Phase-field, CALPHAD, melting, two-phase, thermal diffusion, multi-component

Modeling the behavior of the fuel when subjected to high temperatures and large temperature gradients is of interest for the nuclear industry. At high temperature, fuel melting might occur. The associated phase change is complex due to the Fission Products generated in the fuel material and the transport mechanisms involved therein such as, in particular, oxygen thermal diffusion in the solid phase. In [1], we have developed a CALPHAD-informed phase-field model for a uranium-oxygen binary system within a solid/liquid mixture in order to simulate incipient melting and oxygen transport in nuclear fuel during power transients.

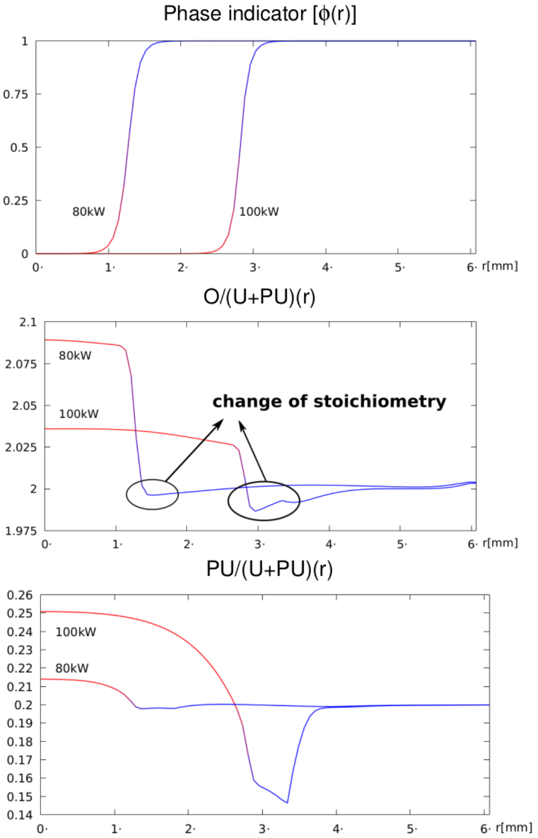

Figure 1. Incipient melting and inter-diffusion in oxidized fuel $U_{0.8}Pu_{0.2}O_{2.005}$ (results after 1000s)

Extending the simulations towards the multi-component case is a challenging task because of the direct coupling between the phase-field model and a Gibbs Energy Minimizer [2]. The most important computational issue is related to the solution of the nonlinear system associated with the interfacial description based on the Kim-Kim-Suzuki (KKS) model [3].

In this work, following [4], the phase-field model is modified by considering a non-isothermal linearization of the KKS model in order to be able to simulate systems with a much larger number of components.

As illustrated in Fig.1, this approach is first assessed on the basis of one dimensional simulations of incipient melting and inter-diffusion in oxidized fuel $U_y Pu_{1-y}O_{2+x}$.

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Biographical Note

Clément INTROÏNI is research engineer at the Fuel Studies Department at the CEA where he works on the development of Fuel Performance Codes. His current research interests include thermodynamic calculations for nuclear applications and phase-field modeling of species transport in multiphase non-stoichiometric oxide systems.

[P08.09] Thermodynamic investigation of the Li-Mo-O system

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Key words: Li_2MoO_4, Calphad modeling, vaporization, lithium molybdates

Lithium molybdates are promising materials for applications in the development of Lithium-Ion batteries, low-temperature superconductors, and heat-scintillation cryogenic bolometer detectors (HSCBs), etc. Bulk single crystal of Li_2MoO_4 (LMO) have a primary role in building HSCBs thanks to their excellent energy resolution and radio-purity.

Understanding the ternary Li-Mo-O phase diagram is mandatory for all applications of lithium molybdates; Our thermodynamic investigation began when the partition coefficients of LMO crystals were characterized and found to be greater than 1 for all its impurities [1], which is contrary to what is reported in some phase diagrams (e.g. Li_2MoO_4-K_2MoO_4 [2]). In addition, the most recent phase diagram of Li_2O-MoO_3 reported [3] is not updated, the debate on the congruence and stability of certain ternary molybdates has been rediscussed and crucial clarifications have been provided. The Li_2O-MoO_2 phase diagram is unclear due to non-stoichiometry of phases [4]. Most published sections of the system are experimentally determined by calorimetry and structural characterizations. But a thermodynamic assessment has never been conducted before.

In this study, we carried out Calphad modeling of the Li_2O-MoO_3 pseudo-binary section, based on critically assessed data. The need for thermodynamic information on certain solid phases and vapor species led us to perform additional calculations. Firstly, a determination of the free energy function (Fef) from Li_2MoO_4(g) structural and vibration data, in order to describe the Li_2MoO_4(g) in our thermodynamic database, was carried out. Secondly, DFT calculations were conducted to explore the unknown thermodynamic properties of the condensed phases.

A thermodynamic description of the Li_2O-MoO_3 section will be presented, and DFT calculations of the Li_4MoO_5, Li_2MoO_4, $Li_4Mo_5O_{17}$, $Li_2Mo_4O_{13}$ and Li_2MoO_3 condensed phases will be compared with available experimental data when available.

Thermodynamic calculations of vaporization have been performed to prove the congruent nature of Li_2MoO_4 vaporization and compared to the reported data from mass spectrometry measurements in order to critically discuss the reported phase diagrams.

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Biographical Note

Kaoutar Naciri is a 2nd Ph.D. student in Materials Science at Grenoble Alpes University, affiliated with the SIMaP laboratory. Her research focuses on mastering thermodynamic tools encompassing both modeling and experimental work. She is actively involved in building databases and simulating processes for materials applications.

[P08.10] Phase equilibria in the $FeO-Fe_2O_3-X$ ($X = SiO_2$, MgO) systems: Experimental measurement and thermodynamic modeling

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Key words: CALPHAD, phase diagram, ionic two-sublattice model, oxides

Phase diagram thermodynamic study of the $FeO-Fe_2O_3-X$ ($X = SiO_2$, MgO) systems are crucial in the fields of pyrometallurgy, ceramics, and solid waste resource utilization. Meanwhile, FeO, Fe_2O_3, SiO_2, and MgO are important oxides in the bulk aluminosilicate solid waste system, and the $FeO-Fe_2O_3-X$ ($X = SiO_2$, MgO) systems play an important role in the construction of a perfect $Al_2O_3-SiO_2-MgO-CaO-Fe_2O_3-Na_2O$ system. In this study, the phase equilibrium and thermodynamic property data of the $FeO-Fe_2O_3-X$ ($X = SiO_2$, MgO) systems were critically evaluated in conjunction with new phase equilibrium experimental data.

For the $SiO_2-FeO-Fe_2O_3$ system, in order to solve the controversy over the calculated isothermal section at 1723 K in the literature, key experiments were carried out using equilibrium/quenching, X-ray diffraction (XRD) and electron probe microanalysis (EPMA). According to the present experiments, the existence of the three-phase region liquid + spinel (Fe_3O_4) + tridymite (SiO_2) at 1723 K was confirmed. The ionic two-sublattice model $(Fe^{+2}, Si^{+4})_P(O^{-2}, Va, SiO_4^{-4}, SiO_2, FeO_{1.5})_Q$ was used to describe the liquid phase. The $FeO-Fe_2O_3-SiO_2$ system was then critically evaluated by means of the CALPHAD (CALculation of PHAse Diagram) method in view of phase diagram and thermodynamic data.

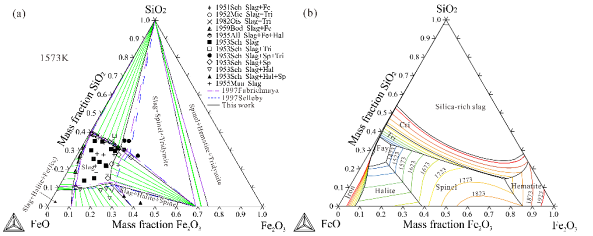

Figure 1. Calculated results of the $FeO-Fe_2O_3-SiO_2$ system: (a) isothermal section at 1573 K (b) liquidus surface.

For the $MgO-FeO-Fe_2O_3$ system, the phase equilibria and thermodynamic data of this system have been critically evaluated and re-optimized using the CALPHAD method. The ionic two-sublattice model $(Fe^{+2}, Mg^{+2})_P(O^{-2}, Va, FeO_{1.5})_Q$ was used to describe the liquid phase.

A new and improved self-consistent set of thermodynamic parameters for the $FeO-Fe_2O_3-X$ ($X = SiO_2$, MgO) systems were obtained. The calculated phase diagrams and thermodynamic properties, employing the optimized model parameters, exhibit excellent agreement with the experimental data. The established thermodynamic descriptions are of guiding significance for solid waste resourcing.

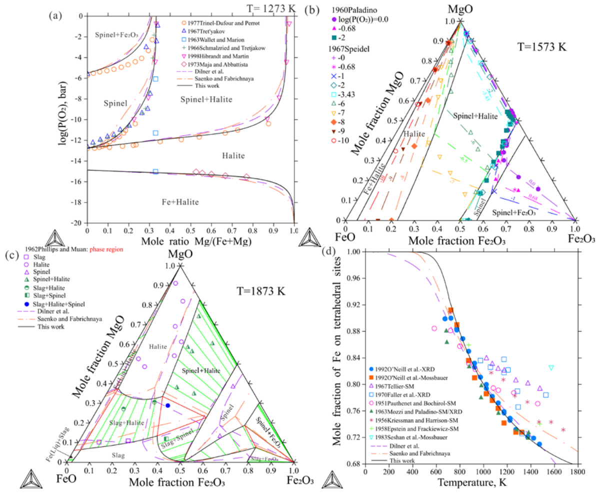

Figure 2. Calculated results of the $FeO-Fe_2O_3-MgO$ system: (a) phase diagram of oxygen partial pressure (b) isobars at 1573 K (c) isothermal section at 1873 K (d) cation distribution in the $MgFe_2O_4$ spinel.

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Biographical Note

Liang Zhang is a PhD student at Central South University. He is supervised by Prof. Yong Du and Yuling Liu. His current research is on experimental determination of oxide phase diagrams and CALPHAD assessments of oxide systems.

[P09.01] Phase equilibria, microsegregations and mechanical properties of Inconel 718 alloy samples processed in electromagnetic levitation facility

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Key words: Inconel 718, electromagnetic levitation, sharp interface model, phase distribution

The CALPHAD method facilitates the prediction of metastable equilibria. However, as the phase description itself relies on experimental data for thermodynamic equilibrium, the predictive capability of metastable phase equilibrium is constrained. In certain cases, observed phase equilibria from experiments may diverge from predicted metastable phase equilibria [1]. The exploration of the solidification process in nickel-based superalloys, achieved through a combination of experimental studies and simulations utilizing calculated phase equilibria, enables an understanding of the solidification path and phase formation in the metastable temperature range.

In this study, the properties of the Ni-fcc phase in the Inconel 718 (IN718) system have been studied based on experimental results using electromagnetic levitation (EML) and modelling results describing a freely growing dendrite. Experimentally, the velocity of the solidification front was measured with high-speed VIS and IR cameras for different degrees of undercooling. The change in velocities could be attributed to the transition from the diffusion-controlled to thermally controlled growth regime using a sharp interface model. Experimentally determined and calculated growth velocities are shown in Fig.1.

To describe the formation of microsegregations of IN718, a phase field model is employed in a quasi-binary approximation [2]. The modeling results are then compared with experimental data on phase fraction, morphology and hardness. Despite the simplifications of quasi-binary approximation, the predicted microstructure, solute concentration profiles and interface velocities exhibit good agreement with the experimental findings.

The combination of experiment and simulation presented can serve as inputs for simulating the precipitation of secondary phases. In order to further elucidate the solidification sequence and validate the accuracy of simulated results, the next step involves studying the solidification behavior of IN718 at high undercooling using a combination of mobile EML equipment and in-situ X-ray techniques.

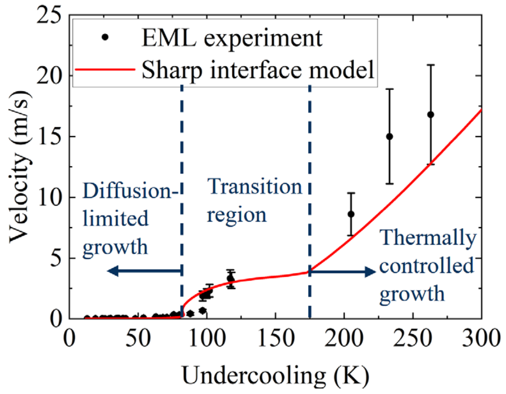

Figure 1. Dendrite growth velocity V as a function of undercooling ΔT for IN718 alloy. The experimental data are represented by the symbols and the lines give the predictions of sharp interface model.

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Biographical Note

Yindong Fang is now a PhD student at the Friedrich-Schiller-University Jena. His research focuses on rapid solidification of Inconel 718 alloy systems processed with the containerless EML method. The presented results were gained based on his PhD work under the supervision of Stephanie Lippmann and Peter Galenko.

[P09.02] The K_2O-SiO_2-CO_2 system

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Key words: carbonates, silicates, DTA, thermodynamic database, K_2O-SiO_2, K_2O-SiO_2-CO_2

Knowledge of the thermodynamics of salt-and-oxide systems is critical for selecting materials and understanding and improving their behavior during energy storage [1], heat transfer, or processing [2]. A complete, reliable thermodynamic database is required for the thermodynamic descriptions of the transformations and reactions of the entire system (ashes, deposits, products of the evaporation and condensation reactions of volatile compounds) under different boundary conditions.

Therefore, experimental validation of these systems is necessary as existing databases contain missing or incomplete information. There is no data available about the phase relations within the K_2O-SiO_2-CO_2 system (or its partial K_2O-K_2CO_3-SiO_2 section), and even the K_2O-SiO_2 system has been hardly investigated in the K_2O-rich area [3].

To better understand and provide reliable predictions of thermochemical properties and material compatibility, an experimental study was conducted to develop and refine a thermodynamic database of a complex oxide-and-salt system.

Experimental work was carried out using DTA (Netzsch STA 449F3), DSC (Netzsch 404C Pegasus, Setaram MHTC96 HFDSC), and XRD (Diffractometer EMPYREAN (PANalytical), and TOPAS v.6, Bruker AXS, for data analysis), and the database was refined in FactSage 8.3.

Samples of the K_2O-SiO_2 system were prepared using either SiO_2 (99.995%, quartz, Thermo Scientific) and K_2O made by heating KNO_3 (99.999%, Thermo Scientific) with excess K metal (99.95%, Merck) in a Ni crucible or SiO_2 and K_2CO_3 (99.997%, Thermo Scientific). Samples of the K_2O-SiO_2-CO_2 system were prepared using K_2CO_3 and SiO_2 or K_2CO_3 and intermediate compounds of K_2O-SiO_2 (prefabricated). For the latter system, DTA measurements were carried out in open Pt or hBN crucibles under a dynamic CO_2 atmosphere (total pressure 1 atm).

Certain compositions of the K_2O-SiO_2 and K_2O-SiO_2-CO_2 systems were investigated, and this work presents some results of the experimental study. These are at least melting points of K_4SiO_4 and $K_6Si_2O_7$ in the K_2O-SiO_2 and K_2O-SiO_2-CO_2 system and some vertical sections of the K_2O-SiO_2-CO_2 system (Fig. 1). Therefore, the obtained data are used to refine and improve the existing thermodynamic databases in order to increase the accuracy and reliability of the thermodynamic calculations and predictions.

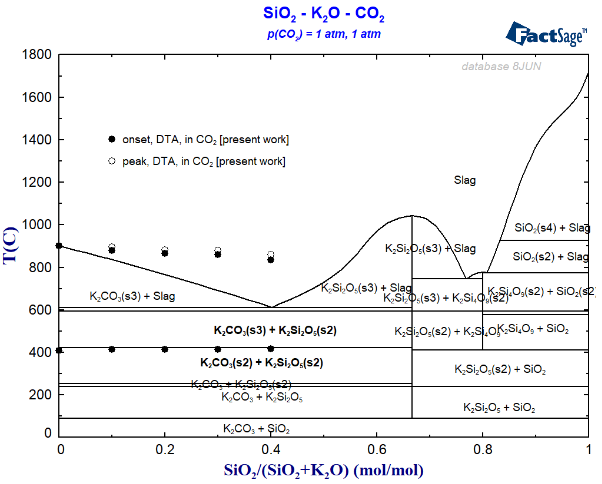

Figure 1. Calculated vertical section of K_2CO_3-SiO_2 at 1 atm CO_2 along with obtained experimental data

Acknowledgments

This work was done in the framework of the VERENA and VeRa projects, which are financially supported by the Federal Ministry for Economic Affairs and Climate Action of Germany (FKZ 03EE5044D and FKZ 03EE5064B).

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Biographical Note

Dr. Mariia Ilatovskaia received her PhD in 2023 from the Institute of Materials Science at the TU Bergakademie Freiberg, Germany. Since then, she has been working as a postdoctoral fellow at Forschungszentrum Jülich (IEK-2), Germany. Her research focuses on the development of thermodynamic databases for salt/oxide systems from both experimental and modeling perspectives.

[P09.03] Phase equilibrium of the Fe_2O_3-TiO_2 system

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Key words: Fe_2O_3-TiO_2 system; Phase equilibrium; Air atmosphere; Solid solubility

The calcination of prepared vanadium-titanium green pellets in an air atmosphere led to a complex phase transformation within the Fe_2O_3-TiO_2-Fe_3O_4-V_2O_5-CaO-MgO system. This study focused on the Fe_2O_3-TiO_2 system within the multi-component setup, employing the classic phase equilibrium and quenching method. X-ray diffraction (XRD) and Electron probe microanalysis (EPMA) were then employed to characterize the phase composition of the as-prepared samples. The valence distribution of elements was first verified by performing X-ray photoelectron spectroscopy (XPS). It was determined that the samples could reach an equilibrium state after holding at 1100°C and above for 24 h in an air atmosphere. At Fe_2O_3:TiO_2 (mol %) = 70:30, the Hematite phase (Fe_2O_3) and Pseudobrookite phase (Fe_2TiO_5) existed in the sample, while at Fe_2O_3:TiO_2 (mol %) = 25:75, Pseudobrookite phase (Fe_2TiO_5) and Rutile phase (TiO_2) were observed in the sample. All samples showed Fe with a +3 valence and Ti with a +4 valence. Furthermore, the solubility of Fe_2O_3 in the TiO_2 phase at 1100°C was 0.78 mol pct, while the solubility of TiO_2 in the Fe_2O_3 phase was 10.83 mol pct. Additionally, the Fe_2TiO_5 solid solution was expressed as $Fe_2Ti_{1+x}O_5$ ($0.07 \leq x \leq 0.21$). These new phase equilibrium data are expected to provide reliable input for future thermodynamic reassessments of the Fe_2O_3-TiO_2 system within the CALPHAD framework.

Biographical Note

Mengjiao Jiao received the B.S. degree in Metallurgical Engineering from Chongqing University, Chongqing, China in 2022. She is currently working toward the Ph.D. degree in Metallurgical Engineering with the Department of Chongqing University, Chongqing, China.

[P09.04] Preliminary results on the experimental investigation of the *liquidus* projection of the Al-Ti-Hf ternary system

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Key words: Al-Hf-Ti system, experimental phase diagrams, refractory metals, high-entropy alloys

A new class of metallic alloys has been investigated by the scientific community in recent years, these are multi-principal element alloys, also known as High Entropy Alloys (HEAs) [1]. These alloys combine five or more elements in equiatomic or semi-equiatomic proportions. HEAs with refractory metals and aluminum as constituents, are possible alloys for structural applications at high temperatures, such as in the aerospace industry. Metals with a high melting point and relatively low density are important constituents of these alloys [2] making the investigation of equilibrium relations of systems containing such metals and aluminum necessary. The study of the Al-Hf-Ti system is important as only two complete isothermal sections are available in the literature: at 1100 °C proposed by Hayes [3] and by Ezekiel et al. at 1000 ºC [4]. In the present work, a preliminary *liquidus* projection for the Al-Hf-Ti system is proposed based on the investigation of the solidification paths of 24 samples, which were produced by arc-melting mixtures of pure elements under Ti-gettered argon atmosphere. The microstructural characterization was carried out by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and X-ray diffractometry (XRD). The preliminary results identified nine primary solidification regions: β-BCC, γ-TiAl, ζ-$Ti_{2+x}Al_{5+x}$, ε(ht)-$TiAl_3$, $HfAl_3$, $HfAl_2$, Hf_2Al_3, HfAl, Hf_3Al_2. These results led to the preliminary proposal for the *liquidus* projection of the Al-Hf-Ti system.

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Biographical Note

Jéssica V. Luiz is a Ph.D. student in materials science in the Department of Materials Engineering at University of São Paulo (EEL-USP) under supervision of Dr. G.C. Coelho. She holds a Master's Degree in materials science at same institution. Her research interests are experimental phase equilibria, CALPHAD modeling and thermodynamics.

[P09.05] Gas phase from K_2TaF_7

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Key words: K_2TaF_7, fluoride, Knudsen effusion, gas phase

The compound K_2TaF_7 is dipotassium heptafluorotantalate, often used as a material in the chemical industry and in research. It is used in X-ray crystallography and spectrometry for its crystalline properties. It is often used to make crystals that are used to analyze and scatter X-ray light to study the crystalline structures of various substances. K_2TaF_7 doped with rare earth ions (such as neodymium or praseodymium) is used in the manufacture of luminescent materials. These materials have applications in lasers, display devices and other optical technologies. In chemical research, K_2TaF_7 is sometimes used as a reagent or starting material for the synthesis of complex chemical compounds and can also be used in catalysis, although this is less common. It is important to note that K_2TaF_7 is a specific chemical compound whose uses vary according to its particular properties and the way in which it is manipulated or modified. Knowledge of this compound has increased since the description of the phase diagram of the KF-K_2TaF_7 [1] and K_2TaF_7-TaF_5[2] systems, as well as its structural [3] and thermal [4] properties. Despite the large number of studies devoted to K_2TaF_7, no experimental data on its gas phase is available. We used the Knudsen effusion method to measure the vapor pressure of this compound and to find the proportions of gaseous species predicted by the literature.

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Biographical Note

Ioana NUTA, a chemical engineer, is a researcher at the SIMAP laboratory in Grenoble (France). She works in the field of materials science and researches gas phase thermodynamics using the Knudsen effusion method coupled with mass spectrometry. Her research focuses on the thermochemical properties of compounds mainly used in energy production and storage.

[P09.06] Optimized Synthesis of Reactive MgO from Rejected Brine via Integrated Thermodynamic Solution Modelling and Experimental Parameter Study

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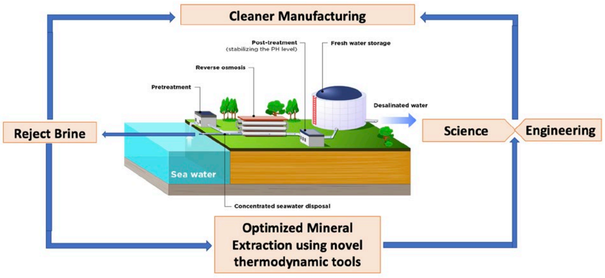
Key words: Reject brine, reactivity, MgO, solution model.

The surge in infrastructure development worldwide has brought about a significant rise in cement output and a consequently considerable CO_2 emissions from the energy-intensive procedures in the traditional cement production [1]. It is reported that about 7% of the global anthropogenic CO_2 is released during calcination of limestone ($CaCO_3$) for the clinker creation in the cement production process. An effective replacement for $CaCO_3$ has been shown to be reactive magnesium oxide (MgO). The conventional process for making reactive magnesium oxide cement (RMC) is calcining magnesia ($MgCO_3$) at a high temperature, where the emitted CO_2 can be converted into carbonate phases through hydration and mineralization/carbonation [2]. It is more advantageous to recover MgO from reject brine, a by-product of desalination. Although efforts have been put on precipitation/recovery of $Mg(OH)_2$ from reject brine, a comprehensive investigation of the parameters of pH, alkali concentration, and calcination temperature on MgO structure has not been conducted [3]. In this work, the ideal pH range for precipitating $Mg(OH)_2$ from reject brine is determined by using the advanced commercial software package FactSage. A non-ideal solution database based on the Pitzer model for concentrated aqueous solutions is developed. Chemical equilibria calculations was performed at 25 °C and 1 atm to identify the pH window at which $Mg(OH)_2$ precipitates from reject brine. This accurate calculation guarantees higher purity in the extracted $Mg(OH)_2$ to establish a guide for the recovery procedure. Subtle trends of $Mg(OH)_2$ precipitation from reject brine can be looked into from series of calculations. The precipitation begins at pH 8.7 for both NaOH and KOH solutions, climbs steeply within a narrow pH range, and reaches plateaus at about pH 10.1. A further increase in pH causes a slight variation in the precipitation of $Mg(OH)_2$.

The recovered $Mg(OH)_2$ is calcined under different circumstances to synthesize reactive MgO. The study emphasizes the accomplishment of extracting 99% of Mg^{2+} with an alkali level of 18 M from reject brine with higher reactivity and surface area. This thorough study integrates experimental parameter investigation with thermodynamic modelling using FactSage to clarify the intrinsic relationships between calcination temperature, alkali content, and MgO properties. This methodology also offers valuable insights into the optimal ways to optimize the MgO recovery from reject brine with higher purity and initiates innovative approaches to mitigate environmental issues in the construction industry.

Figure 1. Summary of the production process [4].



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Biographical Note

Hasanthi L. Senevirathna is a Ph.D. candidate at the Singapore University of Technology and Design, studying on sustainable mineral extraction from desalination waste products. Prior to her PhD, she completed a master's degree in engineering from the same university, post graduate diploma in nanoscience and nanotechnology and bachelor's degree (special) in material science and technology from Sri Lanka. Her goal is to be an innovator in her industry, creating sustainable solutions.

[P09.07] Experimental Investigation of the Mg-Sn-Gd Alloy System Assisted by First-Principles Calculations

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Key words: Mg-Sn-Gd, Phase equilibria, Diffusion couple, DFT calculations

Magnesium alloys have been at the forefront of alloy development for automotive powertrain components. Traditional Mg-Al-Zn alloys suffer from poor creep response, restricting their applications to temperatures below 120 ºC. To overcome these limitations, there has been a strong focus on the development of creep-resistant Mg alloys, with an emphasis on enhancing the thermal stability of the secondary phases. Aligning with this perspective is the Mg-Sn-Gd alloy system, where the Mg-rich corner comprises high melting point eutectics and stable secondary phases. Apart from twelve binary phases, two ternary phases namely MgSnGd and $MgSn_2Gd$ have also been identified in this system. However, relevant thermochemical information is limited. Being a relatively new alloy system, knowledge of the phase equilibria and thermochemical data is of great value for a reliable thermodynamic assessment.

In this work, the phase equilibria of the Mg-Sn-Gd system at 500 ºC has been explored using equilibrated alloys and a diffusion couple. Key samples were prepared in an induction melting furnace followed by equilibration in vacuum-sealed quartz tubes for 500 hours. Thermal analysis was carried out during alloy preparation, where the cooling curve and the corresponding first derivative curves were recorded to gain insights into the phase transformations during solidification. The alloy samples were characterized using a combination of SEM/EDS, XRD, and EPMA. DFT calculations were performed to evaluate the enthalpy of formation and thermochemical properties such as heat capacity for key phases (refer Figure 1). This will serve as a valuable input to be included in the thermodynamic optimization of the Mg-Sn-Gd system.

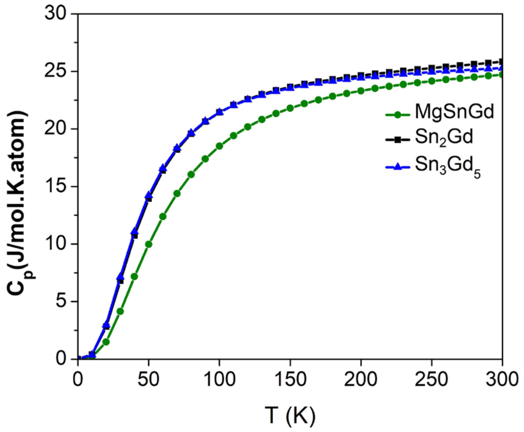

Figure 1. Heat capacities of the MgSnGd, Sn_2Gd and the Sn_3Gd_5 phases calculated from DFT, using first-principles calculations.

Biographical Note

Rohit Shandley is a Ph.D. candidate at the Dept. of Metallurgical and Materials Engineering at IIT Jodhpur, India. His research focuses on the development of thermodynamic databases for key Mg alloys using a combination of experiments and first-principles calculations.

[P09.08] Thermodynamic Modeling of Sodium Salt Solubility in Black Liquor

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Key words: Sodium double salt, Burkeite, Dicarbonate, Solubility, Themodynamic modeling

In kraft pulping, an alkaline solution containing sodium sulfide and sodium hydroxide is utilized to dissolve lignin from wood, freeing the fibers that make pulp. The pulping process yields a by-product known as black liquor (BL), which is an aqueous solution of dissolved organics and spent pulping chemicals washed from the pulp. The initial stage of chemical recovery involves evaporating water from the black liquor in a multiple effect evaporator plant. As water is evaporated, sodium salts can precipitate when the solubility limit is exceeded, necessitating subsequent washing [1]. Traditionally, the understanding of scaling has been framed by our understanding of solubility and crystallization behavior of sodium salts [2]. Recent work at UofT by Ahmed Khafhafera has filled in gaps in the solubility data for the sodium salt systems [3].

This paper investigates developing a thermodynamic modeling approach for black liquor that can be widely applied as mills look at extracting more value from black liquor through extraction of lignin or hemicelluloses. The modeling is done using OLI where there is a challenge of appropriately accounting for the anionic organic fraction of black liquor because there is no single lignin molecule in the database. This paper proposes a new working approach to model black liquor efficiently by using phenolate ions as a surrogate for lignin molecules. Besides phenolate, this study also considers the use of other anions such as hydroxide, chloride, acetate, and formate to address the charge imbalance and the results are compared. When modeling sodium salt solubility in black liquor, the choice of inorganic does seem to matter. This work offers some clarity an earlier conclusion by Grace [4], that the organics do not significantly affect solubility. These results also look like there are insights to be gained by this modeling and experimental work when considering new processes to extract hemicelluloses or lignin.

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Biographical Note

Sina Talebi, a Ph.D. researcher at the University of Toronto, specializes in solubility and thermodynamics. He focuses on thermodynamic modeling to address scaling in industrial processes, particularly in pulp and paper. His research develops predictive models for managing scaling phenomena, aiming to improve industrial efficiency.

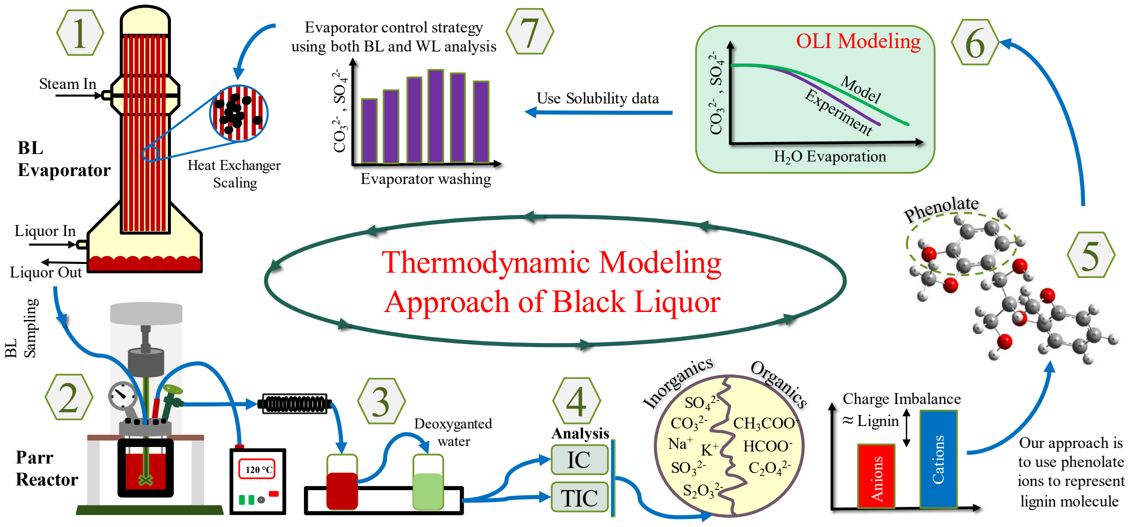

Figure 1. The proposed modeling approach to measure the sodium salt solubility in black liquor systems.

[P09.09] High-throughput determination of interdiffusivities for quaternary system: a case study on Ni-Co-Al-Ta system adopting triple and quadruple techniques

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Key words: Quaternary system, Interdiffusivity, Two-dimensional inverse scheme, Diffusion triple, Diffusion quadruple

To develop multi-component diffusion/atomic mobility databases, the widely-accepted common method adopts a hierarchical optimization scheme coupled with sequential experiment procedure (i.e. first binary then ternary sub-systems, finally extrapolation to quaternary or higher-order systems). Dedicated to accelerate the procedure, the present work explores a transformation to a compact approach to simultaneously deal with the binary and ternary sub-systems for a quaternary system, by means of the two-dimensional inverse scheme supported by high-throughput diffusion triple and quadruple experiments as a designed ensemble. The present approach largely improves the experimental and optimization efficiency. Equally important, it enables mutual verifications for binary and related ternary systems within each sample, as well as trans-sample authentications for binaries in the ensemble. The present approach applies to determine the composition-dependent interdiffusivities/mobilities in an fcc Ni-Co-Al-Ta system at 1473 K, further validated by comparing with the common experiments using diffusion couples.

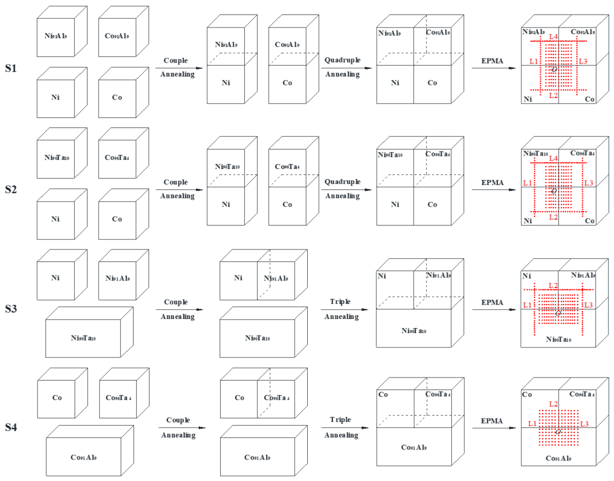

Figure 1. Broad outline of the experimental processes for the designed quadruples (S1 and S2) and triples (S3 and S4) in the present work.

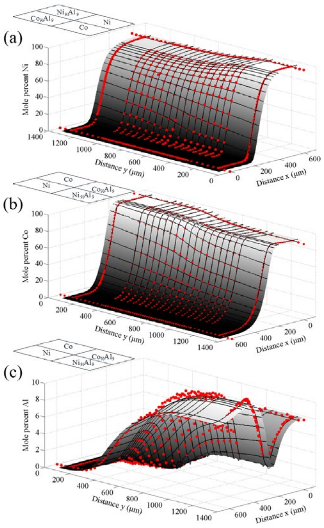

Figure 2. Calculated composition surface (grey) and lines in x/y directions (black) for (a) Ni, (b) Co and (c) Al of quadruple S1 (Ni-Co-Al) at 1473 K, along with the corresponding experimental points in the present work.

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Biographical Note

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Research fields: Two-dimensional (2D) diffusion kinetic study on multi-principal element alloys; Thermodynamic database development; Material design

[P09.10] Measurement of Thermal Conductivity and Thermal Diffusivity Through Spatial and Temporal Temperature Gradients in a Single Device

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Key words: thermal conductivity, thermal diffusivity, ill-posed problem, inverse problem, high resolution infrared camera

The measurement of thermal properties, including thermal conductivity, thermal diffusivity, and specific heat capacity, plays a crucial role in thermodynamics, particularly in the fabrication, processing, and application of metals. Presently, steady-state methods, like the guarded hot plate method, dominate thermal conductivity measurement. However, challenges like thermal resistance hinder accuracy and temperature range. Consequently, indirect measurement of thermal conductivity via thermal diffusivity and specific heat capacity is common. Transient methods, particularly the laser flash method, offer high accuracy and wide temperature range for measuring thermal diffusivity, yet they're costly with lengthy measurement times. Differential Scanning Calorimetry (DSC) for specific heat capacity is also time-intensive. With advancements in powder additive manufacturing and simulations, traditional methods fall short in meeting evolving demands.

In this respect, a device has been designed and developing to achieve high throughput, time-saving, low requirements, and measure both thermal conductivity and thermal diffusivity in a single device. Methodologically, sample is directly heated by an electromagnetic induction furnace, with no issue of thermal resistance associated with indirect heating. High-resolution infrared cameras are employed to measure temperature distribution, providing continuous temperature distribution with ultra-short time and space intervals, thus obtaining temperature-dependent thermal conductivity and thermal diffusivity. Another highlight is the use of mineral oil as a heat transfer fluid and cooling system, enabling rapid cooling and high-precision measurement of heat flow through the sample.

This device directly calculates temperature-dependent thermal conductivity by measuring spatial temperature gradients in steady state and heat flow through the sample, based on Fourier's law of heat conduction [1]. Temperature-dependent thermal diffusivity is derived using the inverse method of the one-dimensional heat diffusion equation, based on real-time measurements of transient spatial and temporal temperature gradients [2,3]. Specific heat capacity can thus be calculated by above two values.

Results obtained from measurements on 100Cr6 powder, Ti, AlTi-TNM, 100Cr6, and Ni demonstrate that this method enables rapid and accurate measurement of temperature-dependent thermal properties for both poor and good conductors.

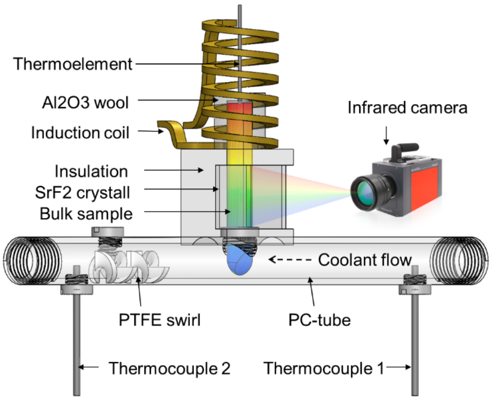

Figure 1. Set-up of device [1].

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Biographical Note

Junsheng Zhuo is a PhD student in the field of thermodynamics research. His activity is specific in the development of high throughput and high temperature thermal measurement techniques.

[P10.01] Mean-field model for hydride evolution within Zircaloys

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The evolution of Zirconium based cladding in reactor conditions controls how long fuel rods can safely remain within the reactor and thus is a limiting factor for higher burn-up use of fuel. A key part of cladding evolution is the ingress of hydrogen originating from coolant dissociation as the formation of brittle hydrides and their dispersion throughout cladding control the cladding fracture resistance.

This work considers hydrides based on a chemical thermodynamics approach utilizing the thermodynamic database TCZR1 to predict the solvus and driving force for formation. The kinetics of the transformation have been accounted for by assuming elemental rearrangement around the hydride as the limiting term and with elemental diffusivities predicted by the companion mobility database MOBZR1. These two components have been combined in a mean-field model to capture the nucleation, growth and dissolution of the hydrides.

The accuracy of both databases has been assessed against near-equilibrium literature data. TCZR1 recreates solubility limits within the zirconium matrix with accuracy and MOBZR1 presents an accurate description of zirconium and hydrogen in the alpha phase. The work highlights the importance of understanding and predicting the stoichiometry and stability of hydride phases.

The mean-field model has been validated against the behavior during a heating and cooling cycle, with dissolution and formation captured via Differential Scanning Calorimetry (DSC) measurements and isothermal holds, where measurements of matrix hydrogen content are used to infer hydride fraction. Assuming a scenario where alloy addition rearrangement is a key factor in evolution, terminal solubility and total hydrogen segregation can be reproduced within a reasonable margin of error.

Biographical Note

Connor Cladingboel is a PhD student investigating the formation of hydrides in fuel cladding in collaboration with the National Nuclear Laboratory (NNL). His project involves CALPHAD descriptions of the Zircaloy system, modelling of precipitate evolution primarily via a mean-field statistical approach and the factors affecting in reactor material evolution

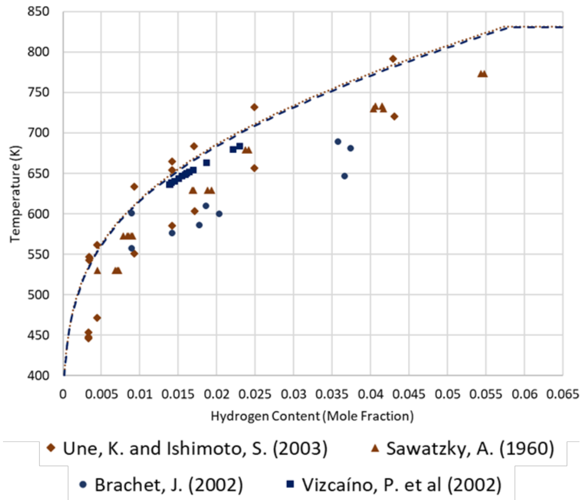

Figure 1. Comparison of TCZR1 predicted and experimental hydrogen solubility in alpha zirconium

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[P10.02] Diffusion and Thermodynamic Modeling of the Effects of Substrate Aluminum Content on Coating-Substrate Interactions During Resistance Spot Welding of Galvanized 3rd Generation Advanced High Strength Steels

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Key words: liquid metal embrittlement, 3rd Gen AHSS, resistance spot welding, thermodynamic modeling

The desire to further lightweight vehicles by implementing Third Generation Advanced High Strength Steels (3rd Gen AHSS) in automotive bodies has been hindered by the phenomenon of liquid metal embrittlement (LME) during resistance spot welding (RSW) of these zinc-coated steels. LME occurs during RSW by rapid penetration of Zn into the steel substrate under the presence of tensile stresses and a liquid coating [1-2]. This work seeks to understand the effects that Al substrate content has on LME susceptibility of 3rd Gen AHSS by analyzing and modeling the effects of Al on the coating-substrate interactions under simplified spot welding conditions. Two quench and partitioned (Q&P) alloys are considered in this study and were hot-tension tested at 800 °C: 0.05Al-0.5Si-2.67Mn-0.25C and 1.38Al-0.5Si-2.67Mn-0.25C.

Isothermal diffusion simulations were performed using the Thermo-Calc© DICTRA software package. At 800 C, the liquid Zn region in contact with a Fe-XAl-0.5Si substrate region led to enrichment of Al in the substrate region. This region of Al enrichment widened with time and was largely due to the low solubility of Al in liquid Zn as compared to the much higher solubility of Zn in the Fe substrate. Thermo-Calc© single axis equilibrium simulations of phase fractions versus Al content at 800 °C showed that intermediate Al concentrations (~1.5-3.5 wt pct Al) reduced the stability of the liquid phase in favor of the Fe-Zn intermetallic phase, Γ-Fe_3Zn_{10}. Equilibrium solubility calculations indicated a general trend of decreasing Zn solubility in the interfacial and substrate matrix phases with increasing Al content, leading to a potential decrease in the Zn flux into the substrate from the coating in the higher Al alloy.

As LME is potentially mitigated by the reduction in the amount of liquid Zn present, the flux of Zn ahead of the crack tip, and the formation of Fe-Zn intermetallics that can form as a layer that acts as a physical barrier to Zn diffusion into the substrate [3-4], diffusion and thermodynamic simulations suggest that the 1.38Al alloy should have a lower LME susceptibility than the 0.05Al alloy. This expectation was corroborated by hot-tension test results that showed a lower average percent ductility loss and lower average percent post-ultimate tensile strength energy loss for the 1.38Al alloy.

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Biographical Note

Jake Colburn is a third-year PhD student in the Advanced Steel Processing and Products Research Center at the Colorado School of Mines and is advised by Dr. Jonah Klemm-Toole and Dr. John G. Speer.

[P10.03] Approaches to model the growth of nickel oxide on nickel

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Key words: Diffusion, Oxidation, NiO, Nickel, Modelling

Alloys that operate at high temperatures in corrosive environments are designed to form protective, slowly growing, coherent oxide scales on their surface. Such surface oxides act as a barrier between the gaseous environment and the alloy, potentially providing oxidation protection. For Ni superalloys, the compositions are generally tailored so that either Cr_2O_3 or Al_2O_3 form on the surface. The layer grows by the diffusion of the gaseous or metallic ions through the oxide. Understanding the processes of ion transport through the oxide layer are important in determining growth mechanisms and in predicting kinetics. The transport of either metal cations or oxygen anions is the rate-limiting step in oxide growth [1-3].

The diffusion flux, J_i, of element i, in a phase can be determined using [1,4]:

$$J_i = -\frac{M_i x_i}{V_m} \nabla \mu_i$$

where M_i is the mobility of element i, x_i is the molar fraction of element i, V_m is the molar volume of the system, and $\nabla \mu_i$ is the chemical potential gradient of element i, determined from:

$$(\nabla \mu_i = {}^{\Delta \mu_i}/_{\Delta z})$$

where $\Delta \mu_i$ is the difference in chemical potential of element i between the two sides of the oxide, Δz is the thickness of the oxide.

The driving force for diffusion (and oxide growth) is the $\nabla \mu_i$ term. As the thickness of the oxide increases over time, and the chemical potentials at each interface remain constant, the gradient $\nabla \mu_i \rightarrow 0$. When modelled computationally, the numerical representation becomes a challenge, leading to values of $J_i \approx 0$, even though ion transport will still be taking place in the oxide. This is applicable for longer term exposures at high temperatures, where thick oxide layers are formed.

In this study, the system of external oxide scale growing on pure Ni has been chosen to validate the model. The single oxide that forms is NiO, which is well characterized [2,3] and thermodynamic and kinetic data is readily available in the literature [1-3].

NiO follows the sublattice formalism, Fig. 1:

$$(Ni^{2+}, Ni^{3+}, Va)_1(O^{2-})_1$$

The main defects in NiO are located on the cation sublattice, these are Ni^{3+} cations / electron holes and cation vacancies [1–3]. Recent work modelling the oxidation of pure Ni [1] focused on the diffusion paths for Ni cations through the oxide layer and the atomic mobility of Ni was calculated using a CALPHAD-style formalism.

The main aim of this study is to modify an existing in-house oxide growth model, capable of overcoming the numerical problem associated with thick oxides. This is inspired by atomic random-walk-style diffusion models. When the oxide is very thick, the driving force for diffusion would be the random-walk process instead of the gradient in chemical potential. By modelling long-term oxidation informed by shorter timescale experimental datasets, the aim is to save extensive experimental time while maintaining thermodynamic and kinetic accuracy in the system.

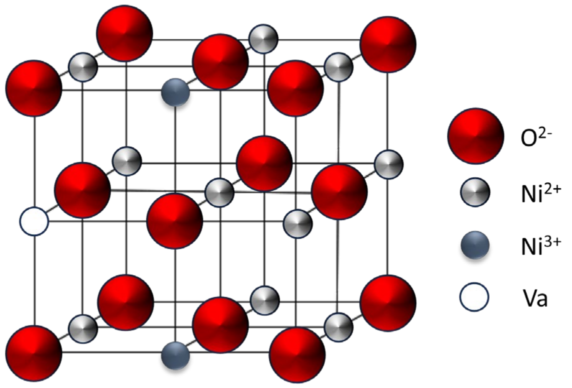

Figure 1. Schematic of a halite structured NiO lattice, including a vacancy defect on the Ni sublattice and two charge balancing Ni^{3+} cations.

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Biographical note

Harry Craven is a first year PhD researcher in Materials Science at the University of Birmingham, studying under Dr Nils Warnken. Research interests include general oxidation of metals and nickel-based superalloys, supported by Dr Mary Taylor, computer simulations and thermodynamic and kinetic modelling.

[P10.04] Phase-field simulation of core-rim structure at the early sintering stage in TiC-WC-Ni cermet

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Key words: Cermet, Core-rim structure, Phase-field simulation, CALPHAD

Understanding the formation mechanism of core-rim structure in TiC-based cermets is essential for optimizing their mechanical properties, such as strength and toughness. In this work, the formation process of core-rim structure in TiC-WC-Ni cermet at the early sintering stage was investigated by means of the multiphase and phase-concentration modeling framework [1] coupled with CALPHAD (CALculation of PHAse Diagrams) databases. The effect of W content in the Ni binder phase on the rim thickness was examined. The results reveal that W in the Ni binder phase diffuses into the undissolved TiC particles at the early sintering stage, leading to the formation of (Ti,W)C solid solution phase on the particle surface. This solid solution phase serves as the rim which constitutes the core-rim structure together with TiC particles. Furthermore, there is a positive correlation between the rim thickness and the W content in the Ni binder phase. Phase-field simulation exhibits a good agreement with the scanning electron microscopy (SEM) observations of the annealed WC-Ni/TiC-Ni cermet diffusion couple. This study offers a novel approach for exploring the formation mechanism of core-rim structure in TiC-based cermets

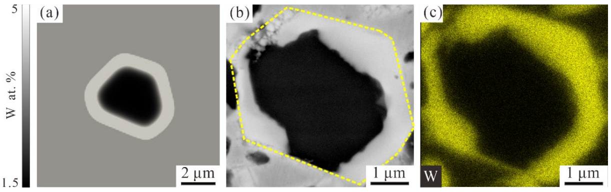

Figure 1. Morphology of core-rim structure in TiC-WC-Ni cermet, the yellow dashed line marks the outer contour of the inner rim, (a) simulated overall W concentration distribution by phase-field simulation at 900 s, (b) SEM-BSE image of core-rim structure in Region 1, (c) SEM-EDS mapping result of W.

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Biographical Note

Mr. Yiqi Guan is a PhD Student of Prof. Yong Du at the State Key Laboratory of powder metallurgy, Central South University, China. His research interest in simulation and experimental research on the mechanical behavior of cemented carbide.

[P10.05] Modeling Multi-Phase Precipitation Kinetics in Al-Mg-Si alloys including Metastable-Stable Phase Transitions

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Key words: Precipitation, Kinetic Modeling, KWN model, Computational Simulation, Metastable Phase Transition

The process of precipitation in Al-Mg-Si alloys include number of intermediate metastable phases. Although considerable amount of aging enables the formation of the final stable phase ß, main hardening effect is done by prior metastable phase ß". This phenomenon is due to different efficiencies phases have in hardening. Therefore, it is important to quantitatively track the evolution of precipitate phases.

Kampmann-Wagner Numerical (KWN) model coupled with database has been widely used to determine precipitate growth kinetics due to its mathematical simplicity and compatibility with multi-phase scenario. This paper aims to build a model, capable of predicting aging kinetics in Al-Mg-Si alloys considering coexistence of multi-phases and metastable/stable phase transitions. Phase transition equations based on total Gibbs energy of particles, including the effect of interface with the matrix, were added. The model is simultaneously linked with FTLite light alloy database to acquire needed thermodynamic values.

TEM analysis of aged 0.8Mg-0.4Si-Al alloy with various time points up to 48 hours has been performed to verify the model's consistency. This study enables the prediction of quantitative microstructure data such as mean length, number density and volume fraction of each phase and ratio between them throughout aging time. We expect these results can effectively utilize the prediction of mechanical strength after aging treatment and further, the performance of newly designed Al alloys with micro-alloying elements.

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Biographical Note

Da Weon Hwang is a Ph. D student in the department of materials science and engineering at Seoul National University, South Korea. His Ph. D study mainly focuses on the development of advanced kinetic precipitation model for Al alloys including metastable/stable precipitate phase transitions and experimental validation of the kinetic precipitation model. His recent study is also related to building an interfacial energy model for ordered phases based on thermodynamic bond energies.

[P10.06] Thermo-Kinetics of Impurities in Uranium Alloys

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Key words: kinetics, actinides, diffusion, impurities

An inherent need exists to understand the degradation mechanism presented by impurities in uranium alloys. Insight into the underlying thermodynamics and kinetics of deleterious precipitate phases within the U-Ti-Nb-C-X system is key to inform materials properties. Uranium metal is known to be very malleable and ductile, with improved ductility by alloying with elements such as Ti, Mo, Nb, etc. [1]. However, non-metallic impurities such as oxides, carbides, and nitrides in the form of inclusions, severely impact and degrade materials properties including toughness and ductility. Impurity inclusions also have the propensity to accelerate harmful effects such as corrosion and cause defect accumulation resulting in cracking [2]. The inability to mitigate impurity formation and migration is a crucial barrier to alloy processing. A comprehensive understanding of the driving forces for carbide formation, distribution and migration is still lacking, but necessary to better tailor processing efforts for metal alloy manufacturing. We present an integrated framework to provide insight into the physics and chemistry to predict impurity and alloying effects in γ-stabilized (BCC) uranium using a tailored experimental and multiscale CALPHAD-based modeling approach. Predictive models that go beyond equilibrium thermodynamics guide this work toward more productive routes that allow for the exploration between thermodynamic and kinetic driving forces that are responsible for impurity formation.

First, to compute the relative phase stability of impurity components, we employ ab-initio informed CALPHAD models for uranium alloys, where ab-initio methods provide insight into information not always available from experiment including the energetics of formation, mixing energies and interfacial energies. To extend our computational capabilities to non-equilibrium conditions and model materials properties over time, we employ diffusion modeling. DFT informed thermodynamic and CALPHAD-type mobility databases are incorporated in an open-source thermo-kinetic precipitation model [3] based Kampmann-Wagner [4] numerical models to simulate impurity formation conditions, distribution, and their evolution as a function of time and temperature. A dedicated experimental component will consist of synthesis and characterization of uranium alloys to elucidate both thermodynamic and kinetic information of impurity phases, which will also be presented in this work.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 and was supported by the LLNL-LDRD program under Project No. 24-ERD-028. (LLNL-ABS-861076)

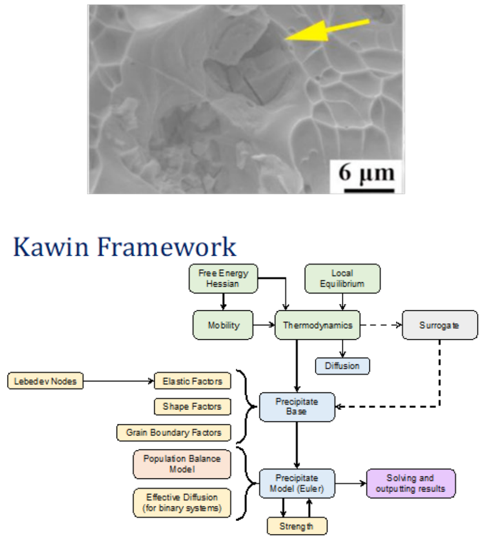

Figure 1. Microstructure of non-metallic defect (cracking) in Uranium alloy and Thermo-kinetic simulation framework for precipitate evolution using KAWIN.

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Biographical Note

Emily Moore is a material scientist at Lawrence Livermore National Laboratory. She earned her PhD at Ecole Polytechnique in Saclay, France. Her expertise and research focus is in computational thermodynamics and kinetics of actinide and lanthanide materials.

[P10.07] Parameterization of a CALPHAD-informed phase-field model to simulate incipient melting in oxidized fuel

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Key words: Phase-field, multi-component, Liquid/Solid phase transition, CALPHAD

In extreme condition, the nuclear fuel experiences high temperatures and high temperature gradients. The associated phase change is complex due to the Fission Products generated in the fuel material and the transport mechanisms involved therein such as, in particular, oxygen thermal diffusion. The dependence of the fuel solidus/liquidus temperature with the local oxygen-to-metal ratio suggests a strong coupling between the heat flux, the oxygen redistribution process and the local chemical equilibria in the fuel.

As a first step towards complex numerical simulations in these harsh conditions, Introïni et al have developed a CALPHAD-informed phase-field model for a uranium-oxygen binary system within a solid/liquid mixture in order to simulate incipient melting and oxygen transport in nuclear fuel in extreme condition of temperature and composition [1].

As usually done in phase-field modeling, the liquid/solid interface is “artificially” enlarged in order to perform quantitative numerical simulations with a limited mesh resolution. Consequently, the parametrization of the model is crucial to ensure its consistency. More specifically, this involves establishing a closure relationship between the two-phase mobility (kinetic parameter of the Allen-Cahn equation) and the interface thickness in order to be able to do simulations that are independent of the numerical parameters and that respect the modeling assumptions, such as the separation of scales and diffusion-controlled melting. This means also checking the asymptotic limit of the phase-field model (“sharp/thin” description of the interface).

This work presents the parametrization of the aforementioned phase-field model carried out on the basis of the work proposed in [2] and [3]. The main results of the theoretical analysis are presented as well as the results of 1D simulations of U-O inter-diffusion in a liquid/solid mixture validating the consistency of the closure relationships between the mobility and the interface thickness.

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Biographical Note

Clément Plumecocq is a first-year PhD student at the Fuel Studies Department of the French Alternative Energies and Atomic Energy Commission. His research focuses on CALPHAD-informed phase field modelling of species diffusion in two-phase mixtures under high-temperature gradients.

[P10.08] Thermodynamic assessment of the fcc/hcp transformation in Fe-Mn alloys

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Key words: Fe-Mn, fcc/hcp transformation, CALPHAD

The thermodynamic phase description of single elements builds the base for any thermodynamic assessment within the CALPHAD framework. As most of the kinetically relevant phase transformations are diffusion-limited and happen at considerably higher temperatures, these thermodynamic descriptions usually focus on temperature regimes well above room temperature. While working reasonably well for predicting phase diagrams at those elevated temperatures, some currently implemented descriptions violate the third law of thermodynamics at the low-temperature end.

If phase transformations in alloys are diffusion-controlled, they can be suppressed by high cooling rates, i.e., quenching to temperatures sufficiently low to slow down diffusion. The undercooled preserved phases are unstable at lower temperatures, increasing the driving force for transformation. If this driving force becomes sufficiently large, it can trigger a spontaneous diffusionless transformation of a metastable face-centered-cubic (fcc) to a hexagonal-close-packed (hcp), body-centered-tetragonal (bct), or body-centered-cubic (bcc) microstructure known as martensitic transformation. Martensitic transformation is a diffusionless first-order phase transformation associated with volumetric variation and the release of latent heat that can significantly alter the mechanical behavior of materials, i.e., through transformation-induced plasticity (TRIP). Ultimately, a thermodynamic description of the alloy system accurate down to low temperatures is needed.

Here, we focus on assessing the binary Fe-Mn system in the spirit of former CALPHAD assessments by Larry Kaufman that comply with the third law of thermodynamics [1]. Improved models for the antiferromagnetic description of the involved phases are used [2]. The resulting chemical driving force and experimental data on transformation temperatures are utilized to fit the binary interaction parameters [3]. Based on this newly implemented thermodynamic assessment, the composition-dependent austenite stability parameter is calculated and discussed in the example of high-damping Fe-Mn alloys, pointing to its promising potential for designing high-strength high-damping steels [4].

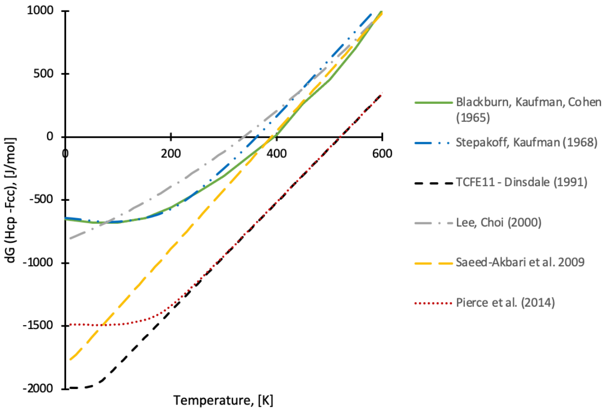

Figure 1. Comparison of different thermodynamic descriptions of the Gibbs energy difference between the fcc and hcp phase of pure iron.

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Biographical Note

Julian Rackwitz is a fourth year Ph.D. student in DMSE at MIT. He previously graduated from TU Berlin majoring in Engineering Science. While his previous research with Lawrence Berkeley National Laboratory centered around the fatigue behavior of metals, he is currently investigating the possibilities for designing high-strength, high-damping steels.

[P10.09] Modeling of kinetics of phase/pore formations in compositionally graded Ni-based superalloys under isothermal conditions: A CALPHAD-Phase field study

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Key words: CALPHAD data, Phase field method, Kirkendall voids, diffusion, Ni-based superalloy

Kinetics of the phase transformation and the interdiffusion phenomena including Kirkdendall voids in Ni-based superalloy, under isothermal annealing conditions, are investigated through the phase-field and continuum method coupled with CALPHAD data. A multi-phase-field model, taking into account the elasticity, utilizes fundamental properties of thermodynamics and kinetics, based on the CALPHAD approach, to predict γ'/γ evolution in CMSX-10/Ni diffusion couple, analogous to compositionally graded alloy. The 3D morphology of γ' precipitates as well composition distribution is simulated along this diffusion couple.

On the other hand, a new phase-field formulation is introduced for modeling Kirkendall voids formation, due to vacancy fluxes. This model compacts a comprehensive computational framework for multicomponent diffusion, non-equilibrium vacancy diffusion, void nucleation, and voids growth considering surface anisotropy and morphological instability. The generalized nature of the method enables us to include both non-equilibrium and equilibrium vacancies, covering all cases of non-ideal/ideal sinks and sources for vacancies, whether on dislocations or void surfaces. The interdiffusion behavior of elements, voids fraction/location and their morphology for CMSX-10/Ni diffusion couple at different temperatures are calculated through these models and compared to the available experimental data and a very good agreement is observed.

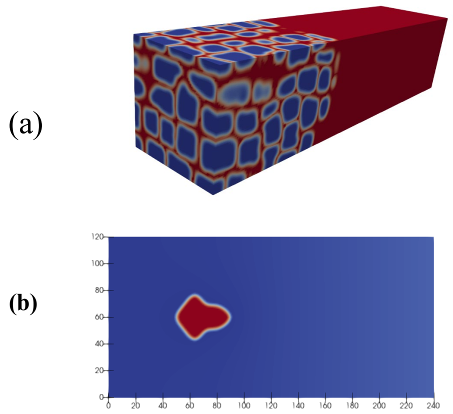

Figure 1. (a) γ'/γ**evolution simulation (3D) in a diffusion couple. (b) Kirkndeall void morphology (2D) simulation in a diffusion couple.**

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Biographical Note

I am a last-year Ph.D. candidate in Ruhr-University Bochum, Germany, supervised by professor Ingo Steinbach and Dr. Julia Kundin.

My main activities consist modeling interdiffusion and phase transformations/ Kirkendall voids in Ni-based superalloys and HEAs based on the phase field and continuum methods coupled with CALPHAD data.

[P10.10] Current results on the investigation of kinetic parameters of VAl_3, V_5Al_8 and (V)

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Key words: Multilayer systems, Pack cementation, Interdiffusion coefficient, Al-V system.

Vanadium alloys are being explored as cladding materials for nuclear fusion reactors, due to their good mechanical properties and favorable resistance to irradiation over a wide range of temperatures. Nevertheless, they suffer from low resistance to oxidation at elevated temperatures, even in oxygen rarefied environments [1]. For this reason, protective layers such as aluminide coatings are necessary for the usage of vanadium alloys in these applications. Additionally, understanding the kinetic data of phases within the Al-V system is crucial for assessing the thermal stability of substrate/coating systems when exposed to high temperatures. Thus, this study aims to calculate growth rates and interdiffusion coefficients in Al-V diffusion couples by an unconventional approach, the pack cementation technique. Parallelepiped samples were extracted from arc-melted 56V-44Al (at. %) ingots and a pure vanadium plate. The halide-activated pack cementation (HAPC) technique, as a chemical vapor deposition process, was employed in order to produce aluminide coatings at 800, 850, 900, 950 and 1000 °C, for durations of 4, 9, 16, and 25 hours. The coating formation can be understood as a classical semi-infinite diffusion couple since the gas-phase diffusion is not a rate-limiting step. The resulting coated substrates were characterized by scanning electron microscopy, energy-dispersive spectroscopy and X-ray diffractometry. The growth of the different phases that are part of the coating is governed by solid state diffusion, evidenced by the thickness variations that conform to a parabolic law. Growth constants, obtained by linearizing the kinetic curves for each phase, were used to calculate the interdiffusion coefficients. Given the multilayer nature of the obtained coatings, the Wagner's approach [2], which incorporates Boltzmann-Matano's [3] and Sauer and Freise's [4] analyses, was used to determine the interdiffusion coefficients ($\boldsymbol{\widetilde{D}_{int}}$). The calculated $\boldsymbol{\widetilde{D}_{int}}$ of the phases present in the diffusion couples lie within the range 44.10^{-12} to 94.10^{-12} for VAl_3, $0.7.10^{-12}$ to 29.10^{-12} for V_5Al_8 and 3.10^{-12} to 169.10^{-12} for (V) for temperatures between 800 and 1000 °C, respectively. The average activation energy for the interdiffusional growth of the VAl_3 phase is estimated as 39 $kJ.mol^{-1}$ for temperatures in the same range, while for the V_5Al_8 and (V) phases these values are approximately 235 $kJ.mol^{-1}$ for both phases.

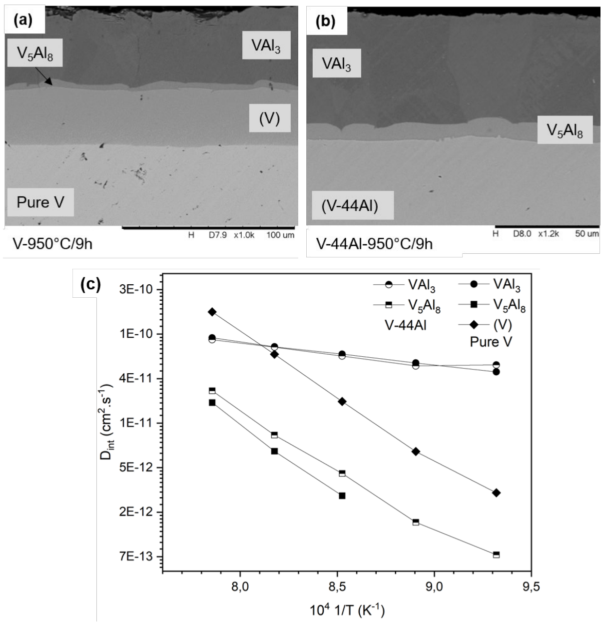

Figure 1. (a) and (b) Diffusion coatings produced by HAPC in the substrates of pure V and V-44Al, respectively. (c) Arrhenius plot of the $\widetilde{D}_{int}$ for the aluminides deposited on both substrates.

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Biographical Note

Vitória de Melo Silveira is a Master's student in Materials Engineering at University of São Paulo (USP), Brazil, under supervision of professors G.C. Coelho and N. Chaia. The author has experience with experimental determination of phase diagram and interdiffusion coefficients.

[P10.11] Thermodynamic description of concentration and diffusion of point defects in metals and compounds

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Key words: vacancy, diffusion, metals

Bulk atomic diffusion is governed by the migration of point defects. Thus, the equilibrium concentration of point defects is a key knowledge for estimating diffusion coefficients [1]. This work is devoted to the thermodynamic description of the concentration and diffusion of point defects in metals and compounds based on the results of atomistic modeling. Namely, the defects concentration and atomic diffusion in refractory metals/alloys and binary compounds (AlLi and Nb7Ni6) were calculated with use of recently developed interatomic potentials. The used approach allows to take into account anharmonicity of atomic vibrations and other entropy-temperature effects.

Among other things, this work discusses the correlation between the melting temperature T_m and the concentration of point defects in this state (figure 1). For refractory metals, the proposed model predicts that the vacancy concentration at $T = T_m$ varies from 10^{-4} to 10^{-3}, which is generally consistent with the positron annihilation spectroscopy or resistivity measurements. For binary compounds, the model makes it possible to take into account changes in both thermodynamic variables (temperature and composition) [2] and explain/reproduce the measured dependency of the diffusion coefficients on the deviation of stoichiometry.

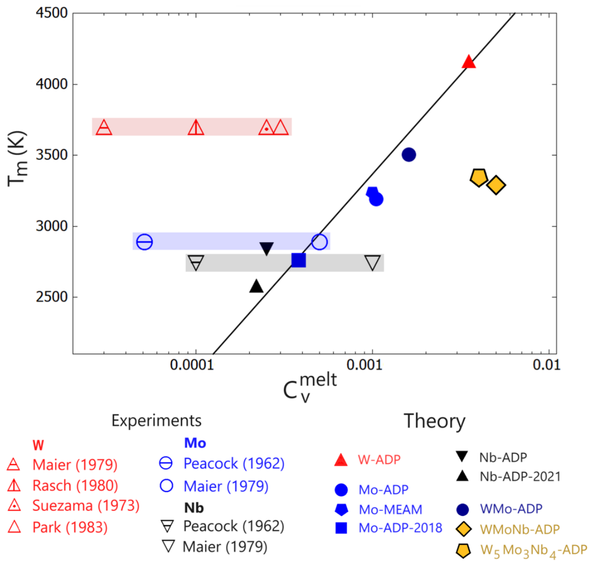

Figure 1. Correlation plot between the simulated melting temperature and the vacancy concentration in this state. The figure contains the simulation results obtained with different interatomic potentials and the vacancy concentrations obtained from the experimental data.

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Biographical Note

Dr. Sergei Starikov is project leader at the Interdisciplinary Centre for Advanced Materials Simulation, Ruhr University Bochum. His research interests focus on materials science, interatomic potentials development, atomic diffusion and plastic deformation. Author of more than 80 peer-reviewed journal publications.

[P10.12] Integrated Computational Materials Engineering (ICME) to Develop Electrical Contacts for Thermoelectric Devices

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Key words: phase transformations, interfaces, thermoelectric materials, mechanical modeling

Energy technology development is guided by international goals for sustainable energy supply to overcome the environmental crisis. Thermoelectric (TE) energy conversion is one among various approaches to feed global energy needs. It is a versatile option for harvesting and recovering waste heat by direct conversion of thermal into electrical energy, having important advantages such as absence of any harmful emission and moving parts. However, there are still challenges in the TE device technology. A crucial one is the contact between the TE material and the metallic bridge to build up a functional module for energy conversion, namely a Thermoelectric Generator (TEG) [1].

With the aim of bringing together the gained experimental knowledge and a robust computational approach, we apply Integrated Computational Materials Engineering (ICME) [2] to accelerate and transform the development of contact solutions as a critical step of the module making. ICME enables integration of material knowledge encoded in databases and materials processing to overcome the current status based on mainly empirical trial. The challenge lies in the intrinsic interdisciplinarity necessary for designing the contacts, a region that develops multiple intermetallic layers as well as new mobile interfaces and has to satisfy mechanical constraints without hindering the conversion performance and functional stability of the TE material.

In this work we investigate the phase transformations occurring at the contacting region between TE/metal, in particular for Mg-Si-based TE materials and Cu as metal electrode. We investigate the diffusion and reaction phenomena in the interconnection zone (IZ), the thickness of the IZ, the phases distribution, fraction and precipitates morphology to classify the type of bonding process and identify different joining conditions. We then run thermodynamic and diffusion calculations, using Thermo-Calc and TC-DICTRA module [3], to obtain diffusion profiles, interfaces velocities and elucidate possible diffusion paths by combining phase equilibria and diffusion. We evaluate new possible contact processing conditions and if necessary new contacting schemes, for example, by adding contacting layers. To analyze possible joining process conditions, a vertical section of the Cu-Mg-Si-Sn phase diagram like the one presented in the Figure is extremely useful, temperature vs. Cu global composition may represent all phases to be expected at the IZ at a given contacting temperature. The blue shadowed area indicates the conditions where the Liquid phase is stable and the blue line the Liquid zero phase fraction. Similarly, the red area and line shows where the TE phase is present. The presence/absence of the Liquid phase plays a crucial role on diffusion, segregation phenomena and final microstructure of the IZ.

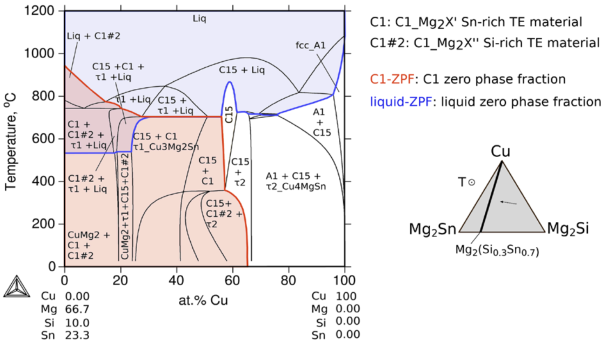

Figure. Calculated vertical section from $Mg_2(Si_{0.3}Sn_{0.7})$ to pure Cu versus temperature to indicate the curves of zero phase fraction for two phases of interest, the Liquid (blue) and C1#1 and C1#2 (red), adapted from [3].

These results are a significant complement to the investigation of the structural integrity of the assembled TE devices by mechanical modelling of the IZ with and without intermetallic layers to understand the stress distribution in the IZ due to thermal and mechanical constraints. And, a critical step towards stablishing an integrated computational modelling approach for TE devices technology.

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Biographical Note

Dr. Silvana Tumminello is the principal researcher of the Integrated Computational Materials Engineering (ICME) project for development of thermoelectric devices and structural materials at the German Aerospace Center (DLR), Cologne, Germany.

[P10.13] Kawin: An open source tool for Calphad-based kinetics

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Key words: kinetics, precipitate, diffusion, software development

Precipitation of second-phase particles can significantly change material properties. The characteristics of these particles (size, shape, number density) depend on both thermodynamic and kinetic behavior, where proper heat treatment of alloys allows for the selective tuning of precipitation behavior, which can in turn refine material properties. These properties may include tensile strength, ductility and even magnetic performance. Precipitation kinetics can be modeled through the Kampmann-Wagner numerical (KWN) model, combining classical nucleation theory and diffusion-controlled growth behavior while also modeling the precipitate size distribution [1]. This model can be coupled with Calphad to obtain the necessary driving force and mobility terms. In addition, extensions to the KWN model can be made to account for non-spherical precipitate shapes, grain boundary nucleation and internal stress fields.

Given the large variability in how the KWN model can be adapted to a given alloy system, an open-source implementation (Kawin), that couples with pycalphad as the thermodynamic backend, was developed [2,3]. Kawin aims to provide the base KWN model along with the different non-ideal assumptions exposed to the user. Given the open-source nature, Kawin also provides transparency in the implementation which can facilitate further development of precipitation models.

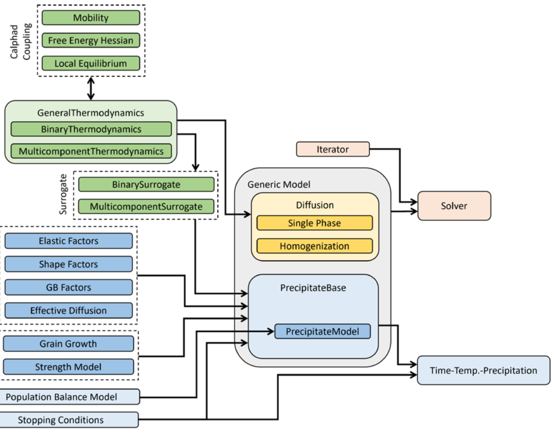

Figure 1. Kawin framework and features

Recently, Kawin has been further developed to include implementations of different diffusion models such as the single-phase diffusion model and the homogenization model. In addition, Kawin has been redesigned to allow for model coupling (such as modeling strength or grain growth) with minimal user-intervention.

A brief summary of the theory and implementation behind Kawin will be discussed along with validation with commercial-based softwares. Case-studies will also be shown to showcase the ease and flexibility of the available models. Finally, recent work will be shown on the use of the thermodynamic and mobility framework in Kawin to assess mobility parameters through ESPEI with case studies to show capabilities using both substitutional and interstitial species [4].

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 and was supported by the LLNL-LDRD program under Project No. 24-ERD-028.

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Biographical Note

Nicholas Ury is a staff scientist at the Lawrence Livermore National Laboratory. He earned his Master’s degree at Cal Poly Pomona. His research focuses on database development, software development and thermodynamic modeling.

[P10.14] Simulation of solidification paths and phase formation in the Mg-rich corner of Mg-Ca-Zn alloys

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Key words: Solidification, Multicomponent alloy, Microstructure, Casting

The alloying of magnesium is fundamental to promoting age-hardening and modulate the mechanical properties by controlling the precipitate phases. In particular, this study focuses on the influence of zinc (Zn) and calcium (Ca) on the solid-state phase transitions. In the Mg-Ca system, cuboidal-like C14_laves (Mg_2Ca) precipitates formed, while the Mg-Ca-Zn system converted these 2nd phases into GP zones on the basal plane that evolve into fine plate-like ternary $Ca_2Mg_6Zn_3$ phase [1]. However, excessive addition of Zn will promote formation of MgZn phase, thus limiting the amount of $Ca_2Mg_6Zn_3$ phase [2]. Inhibiting C14_laves and promoting GP zone generation in the Mg-Ca-Zn system has improves the age-hardening response efficiently.

Non-equilibrium solidification at the solid-liquid interface during casting can induce 2nd phase segregation at grain boundaries (GBs). SEM-EDX characterization of Cast Mg-0.8Zn-0.2Ca wt% (ZX10) and Mg-6.8Zn-0.2Ca wt% (ZX70) was conducted. Measurements presented in Figure 1 show that Ca segregated to the GBs of ZX10. In contrast, ZX70 exhibited both Ca and Zn GBs segregation. These results suggest that with different ratios of Ca and Zn, the solidification paths that produce grain boundary segregation may be different.

The classical Scheil models provide a framework for predicting the solidification paths in multi-component systems. This model assumes instantaneous diffusion in the liquid and no diffusion in the solid phase. Newly formed solid phases vary with composition during solidification, causing segregation. Boettinger [3] showed that the solidification path forms segregation along a gradient of compositional gradients along the gradient of temperature drop in the solid-liquid interface. Meanwhile, Chen et al. [4] showed that the solidification path in a ternary system will continue along the monovariant line after reaching it with the decreasing temperature gradient until it ends at the local minimum of the solid-liquid surface temperature.

In this study, it is shown that predictions based on the classical Scheil model give different solidification path ways for 2nd phase formation routes of ZX10 and ZX70 This was done by collecting the liquidus projection temperatures of Mg-rich corners in Mg-Ca-Zn alloys from the TCMG6 database (Figure 2). The results show that in Mg-Ca-Zn alloys, different alloying composition ratios result in different solidification paths for the intermetallic compounds (IMCs). As shown in Figure 1, at low Zn/Ca ratios (ZX10), Ca segregation dominates, and as the Zn/Ca ratio increases (ZX70), it changes to Zn segregation dominance. The simulated results of the secondary phase formation path in Figure 2 are in general consistent with the experimental results in Figure 1. The mole fraction of each second phase particles can be further confirmed by Classic Scheil model.

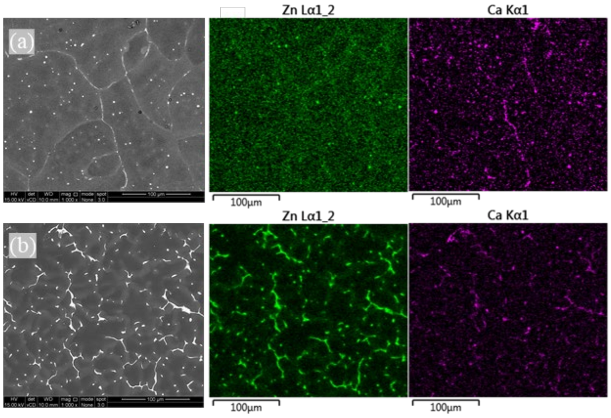

Figure 1. Zn and Ca segregation SEM-EDX results of (a)ZX10 alloy and (b) ZX70 alloy.

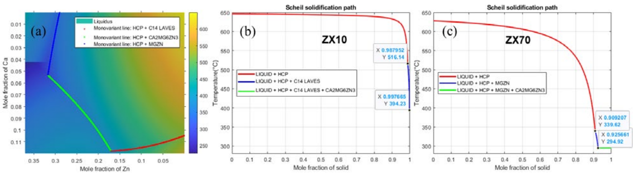

Figure 2. (a) Liquidus of Mg-Ca-Zn system Mg-rich corner and solidification path of (b)ZX10 alloy and (c) ZX70 alloy

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Biographical Note: Yanheng Xie is a PhD candidate at the University of Sheffield, M2i2 group. His research on thermodynamic modelling of solidification, diffusion and precipitation in Magnesium alloys.

[P10.15] High-throughput determination of the interdiffusion coefficients and atomic mobilities in bcc Ti-Fe-V alloys

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Key words: Interdiffusivity, Atomic mobility, Ti-Fe-V alloys, Numerical inverse method

Ti-10V-2Fe-3Al is one of the most common high-strength and high-toughness near-beta titanium alloys. It is extensively utilized in the aerospace industry and benefits from high specific strength, good fracture toughness, strong corrosion resistance, and high resistance to fatigue crack expansion [1]. However, the issue of β-flecks during the melting process of Ti-10V-2Fe-3Al alloy has posed a significant challenge to the titanium alloy industry for an extended period. For the past forty years, the CALPHAD [2] (CALculation of PHAse Diagram) technique has been implemented to provide highly accurate predictions of thermodynamic and diffusion/kinetic information for many commercially important alloy systems including the titanium alloys. By now, the diffusion coefficients and the atomic mobility parameters for bcc/hcp Ti-Al-V and bcc Ti-Al-Fe alloys have been studied in the context of CALPHAD technique, but those for Ti-Fe-V are missing. Thus, a comprehensive understanding of diffusion kinetics of the Ti-Fe-V system is crucial for elucidating the solidification process in Ti-10V-2Fe-3Al alloy.

In this paper, ten sets of diffusion couples within bcc Ti-Fe-V alloys that underwent annealing at temperatures of 1273K, 1323K, and 1373K were prepared. Composition-distance curves were determined using the electron probe microstructure analysis technique. Atomic mobility parameters and interdiffusion coefficients were obtained using the numerical inverse method with the assistance of HitDIC software. It should be noted that the atomic mobility parameters for Ti-Fe and Ti-V were reoptimized using the most up-to-date thermodynamic descriptions. This approach enables the acquisition of comprehensive data regarding the temperature-composition relationship in diffusion.

$\tilde{\boldsymbol{D}}^{Ti}_{FeFe}$ exhibits a markedly greater value compared to $\tilde{\boldsymbol{D}}^{Ti}_{VV}$. It is evident that $\tilde{\boldsymbol{D}}^{Ti}_{FeFe}$ attains its maximum value in the vicinity of the Ti-corner, registering values of 3.13×10^{-12} m^2/s, 5.06×10^{-12} m^2/s, and 7.89×10^{-12} m^2/s at 1273 K, 1323 K, and 1373 K, respectively. In contrast, $\tilde{\boldsymbol{D}}^{Ti}_{VV}$ exhibits a gradual increase with rising Fe content, reaching its peak values of 1.93×10^{-13} m^2/s, 3.61×10^{-13} m^2/s, and 6.66×10^{-13} m^2/s at 1273 K, 1323 K, and 1373 K, respectively. Both $\tilde{\boldsymbol{D}}^{Ti}_{FeFe}$ and $\tilde{\boldsymbol{D}}^{Ti}_{VV}$ demonstrate an increase with the increase of temperature. Furthermore, the Arrhenius equation can be applied to solve for the variation in frequency factors and activation energies concerning temperature and composition.

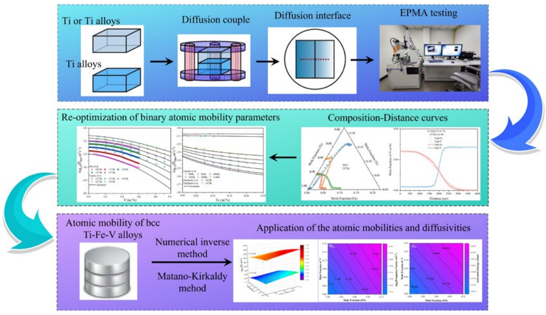

Figure 1. Graphical abstract

References (up to four, please use following format)

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Biographical Note

Hongyu Zhang

Position: Ph.D. candidate
Supervisor: Professor Dr. Ligang Zhang
Research field:

- Establishment of Atomic Mobility Database.
- Metastable β titanium

[P10.16] Simple Yet Robust Models of Diffusion Coefficients for CALPHAD Mobility Databases

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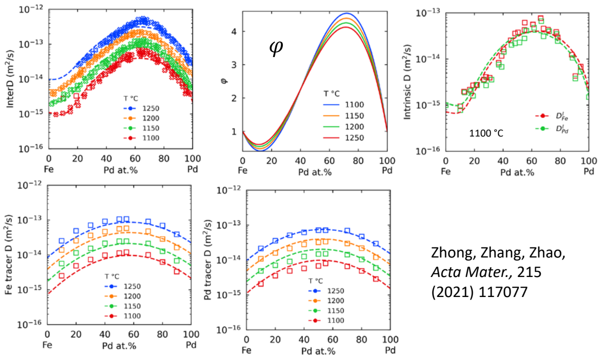
Key words: diffusion coefficient, atomic mobility, mobility assessment, diffusion multiple

A comprehensive test was performed aiming at defining the optimal number of fitting parameters for assessments of atomic mobilities of a binary solid solution based upon the Andersson-Ågren framework [1]. Our systematic test of 18 diverse binary systems has yielded a surprisingly simple model with only one fitting parameter/constant which can be evaluated from experimental diffusion data. The rest of the quantities in the model are the self-diffusion and impurity (dilute) diffusion coefficients of the pure elements and the thermodynamic factor which can be computed from a CALPHAD assessment of the pertinent binary system. The 1-parameter ***Z-Z-Z*** model [2] has been demonstrated to be very reliable and robust since the 18 binary systems tested in this study include very asymmetrical systems such as Co-Pd and Fe-Pd as well as Nb-Ti whose experimental diffusion coefficient data cover ~9 orders of magnitude and over a temperature range spanning ~1200 °C (from ~800 °C to ~2000 °C). The Z-Z-Z model is simple enough to allow both tracer and intrinsic diffusion coefficients to be reliably computed for any composition at any temperature after the sole constant is evaluated from the interdiffusion data even for those not familiar with CALPHAD. More than ***50*** binary solid solutions have been assessed using the Z-Z-Z model now and all show good model performance.

The Z-Z-Z binary diffusion model was extended to ternary and multicomponent systems [3]. The cross-binary and ternary interaction parameters in atomic mobility (diffusion coefficient) assessments were systematically tested on 4 ternary solid solutions: fcc Ag-Au-Cu, fcc Co-Fe-Ni, fcc Cu-Fe-Ni, and bcc Nb-Ti-V. A simple combination of the Z-Z-Z binary model parameters without any additional fitting parameters already provides impressive predictions of the ternary diffusion coefficients when the 3 cross-binary parameters are set to be the 3 corresponding binary Z-Z-Z model interaction parameters, leading to a robust ***Z-Z-ternary*** diffusion model [3]. Employment of 3 independent cross-binary fitting parameters leads to an even better binary and cross-binary parameters only (***BCBPO***) model [3]. Recommendations are rendered based upon the amount of available experimental ternary diffusion coefficients. These recommendations will substantially reduce the number of fitting parameters and improve the robustness of the resultant atomic mobility and diffusion coefficient databases for computational materials design.

Z-Z-Z binary **model for diffusion in an A-B solid solution**



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$$\ln D_A^* = x_A \ln D_A^A + x_B \ln D_A^B + x_A x_B \Phi^{A,B} / RT$$
$$\ln D_B^* = x_A \ln D_B^A + x_B \ln D_B^B + x_A x_B \Phi^{A,B} / RT$$
$$\widetilde{D} = (x_B D_A^* + x_A D_B^*)\varphi \qquad \Phi^{A,B} = a\ constant$$

Z-Z-ternary **model for diffusion in an A-B-C solid solution**

$$\ln D_A^* = x_A \ln D_A^A + x_B \ln D_A^B + x_C \ln D_A^C + \left(x_A x_B \Phi^{A,B} + x_A x_C \Phi^{A,C} + x_B x_C \Phi^{B,C}\right)/RT$$
$$\ln D_B^* = x_A \ln D_B^A + x_B \ln D_B^B + x_C \ln D_B^C + \left(x_A x_B \Phi^{A,B} + x_B x_C \Phi^{B,C} + x_A x_C \Phi^{A,C}\right)/RT$$
$$\ln D_C^* = \underbrace{x_A \ln D_C^A + x_B \ln D_C^B + x_C \ln D_C^C}_{\text{Self-diffusion \& impurity diffusion coefficients}} + \left(\underbrace{x_A x_C \Phi^{A,C} + x_B x_C \Phi^{B,C} + x_A x_B \Phi^{A,B}}_{\text{3 binary parameters}}\right)/RT$$

Zhong, Zhao, *Scripta Mater.*, 207 (2022) 114227

Figure 1. Simple yet robust *Z-Z-Z binary* and *Z-Z-ternary* models of diffusion coefficients for solid solutions.

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Biographical Note

Dr. JC Zhao is Clark Distinguished Chair Professor at University of Maryland where he joined in 2019 after 10 years at The Ohio State University (OSU, 2008-2019) and 12 years at GE Research Center (1995-2007). He took a leave (2014-2017) from OSU to serve as a Program Manager at ARPA-E.

[P11.01] Sampling-free thermodynamics in bulk crystalline metals from the mean-field anharmonic bond model

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Key words: thermodynamics, mean-field theory, anharmonic lattice dynamics

The mean-field anharmonic bond model (MAB) has shown remarkable accuracy in predicting finite temperature free energies for certain potential models of fcc crystals without thermodynamic sampling [1]. We extend this model to treat modern machine learning potentials in both isochoric and isobaric ensembles for bulk fcc metals. Testing against molecular dynamics (MD) simulations of Al and Cu using a moment tensor potential (MTP) and an atomic cluster expansion (ACE) potential respectively, we find free energies with an accuracy of a few meV/atom up to the melting temperature (Fig. 1). The model also predicts an accurate lattice expansion. We show that this sampling-free estimation is universally superior to the quasiharmonic approximation (QHA) for a computational cost that is nearly two orders of magnitude lower and many orders of magnitude more efficient than thermodynamic integration [2].

We further summarize recent extensions to generalize the model to all Bravais lattices. We discuss the application of the model in modern computational materials science workflows for the accurate prediction of temperature dependent Gibbs free energies and the construction of bulk phase diagrams.

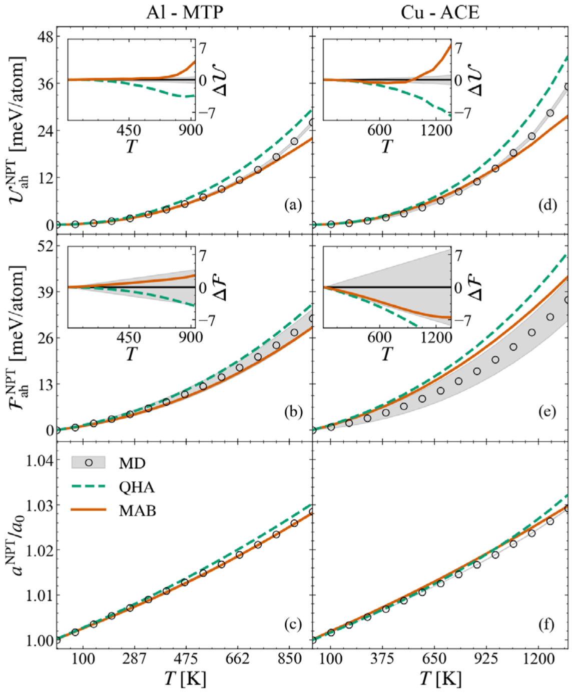

Figure 1. Per atom anharmonic internal energy, free energy, and lattice expansion for the Al-MTP (a, b, c) and Cu-ACE (d, e, f) potential models respectively. The difference between the MD-predicted and MAB-model-predicted properties are shown in the insets.

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Biographical Note

R. Dsouza is a doctoral candidate at the Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, in the Computational Materials Design group led by Prof. J. Neugebauer. His current research activities involve the development of physically-motivated surrogate models for predicting quantum-accurate material properties in crystalline solids.

[P11.02] The structural, energetic and dehydrogenation properties of pure and Ti-doped Mg(0001)/MgH_2(110) interfaces

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Key words: MgH_2, interface, doping, dehydrogenation, first-principle calculations

Due to its clean, recyclable, and high combustion efficiency, hydrogen energy has received wide attention with the dawn of the twenty-first century and has great promise as an excellent energy carrier and a sustainable energy source. However, hydrogen's practical applicability is hampered by its storage and transportation. One potential option is to chemically store hydrogen in solid materials with atomic state. Solid hydrogen storage materials not only have the merits of high safety but also high volumetric energy density. Among them, MgH_2, as a light metal hydride, has been extensively investigated due to its low cost and high hydrogen storage capacity (the gravimetric density is 7.6 wt%, and the volumetric density is 55 kg/m^3)[1]. However, its high dehydrogenation enthalpy (~76 kJ/mol H_2) and sluggish absorption/desorption kinetics have been hindering its industrial application[2].

Hydrogen desorption from MgH_2 is accompanied by the formation of Mg/MgH_2 interfaces, which may play a key role in the further dehydrogenation process. In this work, first principles methods were used to understand the structural, electronic, energetic as well as hydrogen diffusion kinetic properties of pure and Ti-doped Mg(0001)/MgH_2(110) interfaces. It is found that Ti interface doping can slightly increase the interfacial stability as revealed by the work of adhesion, interface energy and electronic structure. Additionally, for both the pure and Ti-doped Mg(0001)/MgH_2(110) interfaces, the removal energies for the H atoms in the interface zone are significantly low compared with that of bulk MgH_2. In terms of H mobility, Ti dopant is beneficial for H atoms migrating from the inner layers to the interface to aggregation. Furthermore, hydrogen desorption from the two interfaces mainly takes place by hydrogen diffusion within the interface rather than hydrogen across into the Mg matrix, and Ti doping can enhance this process significantly. These theoretical observations for hydrogen diffusion behavior at the interface are further validated by fitting the isothermal dehydrogenation curves of MgH_2-Ti with a series of kinetic models.

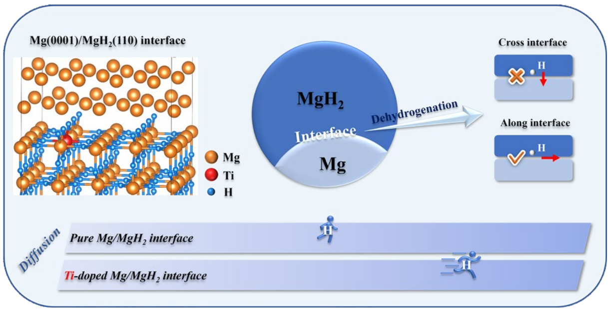

Figure 1. The schematic diagram of dehydrogenation of pure (Ti-doped) Mg(0001)/MgH_2(110) interface.

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Biographical Note

Bo Han is a PhD student in Materials Science and Engineering at Central South University. He is supervised by Prof. Yong Du and Jianchuan Wang. He mainly engages in the first-principles calculation research of Mg-based hydrogen storage materials.

[P11.03] From ab initio calculations to alloy phase diagrams: automated workflows with pyiron

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Key words: ab-initio, machine-learning potential, thermodynamic integration

An automated workflow to calculate phase diagrams purely from ab-initio calculations, i.e. without using any experimental reference data, is demonstrated for the example of the aluminum lithium phase diagram[1]. This workflow connects and combines various atomistic simulation tools, ranging from the generation of atomistic reference structures, over the evaluation of these structures with density functional theory (DFT), the fitting of machine learning interatomic potentials and calculation of free energies with the quasi-harmonic approximation or directly via molecular dynamics using thermodynamic integration [2].

The primary challenge addressed by this automated workflow, which has been developed within our pyiron framework [3], is coupling the different simulation codes developed in different communities, with different units, different input and output formats and different resource requirements. In addition, to providing a unified interface to couple the different simulation codes pyiron[3] also handles the job management and data storage of the individual calculation. This allows the users to construct the simulation protocol for calculating the phase diagram in a Jupyter Notebook to systematically document the workflow from the structure generation to the construction of the phase diagram.

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Biographical Note

Dr. Jan Janssen is the group leader for materials informatics at the Max-Planck-Institut für Eisenforschung in Düsseldorf, Germany. In addition, he leads the development of the open-source pyiron software package, is a maintainer of over 650 open-source software packages for the conda-forge community and an active contributor to open-source projects on Github.

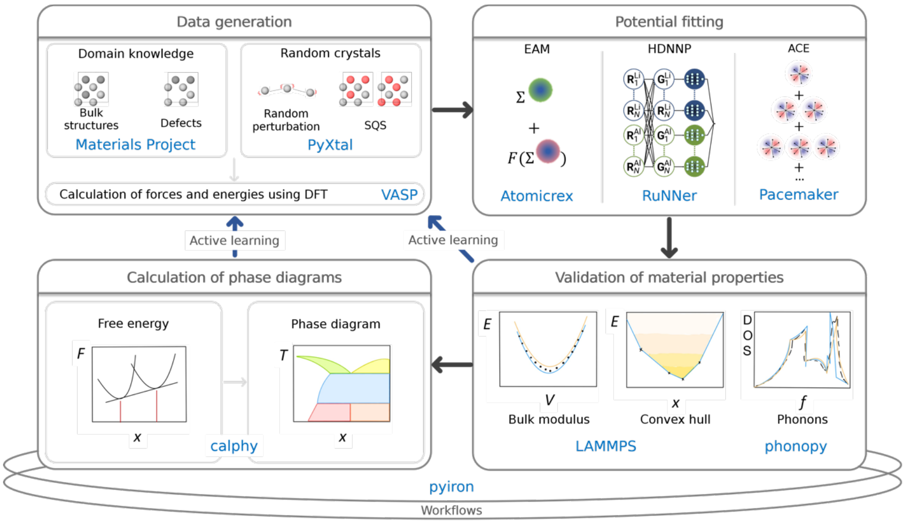

Figure 1. A schematic illustration of the automated construction of the phase diagram using the pyiron workflow framework. Starting with the generation of the training set, followed by the fitting of the machine learning interatomic potential, the validation of the material properties and finally the calculation of the phase diagram.

[P11.04] Defect Phase Diagrams at Ab-Initio Accuracy with Machine Learning Potentials

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Key words: machine learning, atomistics, defect phases, Mg/Al/Ca

Understanding the thermodynamics of segregation at crystal defects is an important part of successful materials engineering. [1] Compared to bulk thermodynamics, defect phase diagrams are additionally complicated by the additional degrees of freedom afforded by defect geometries and its interplay with chemical complexity. This makes searching for candidates for (meta-)stable configurations and reconstructions challenging.

We developed a workflow that searches the possible segregation structures with the aid of a fast proxy model and relaxes suitable candidates with an accurate and transferable Moment Tensor Potential (MTP).[2] The proxy model is physically inspired, but built on machine learning descriptors. On the other hand, using the MTP allows us to incorporate structural relaxations and move away from on-lattice models. From this we are able to approximate the density of states of segregation and thereby the free energy at a given temperature and coverage, giving access to the defect phase diagrams.

We present surface phase diagrams in the hcp Mg system segregated with Al or Ca calculated from molecular statics and verify some of them with full hybrid molecular dynamics and Monte Carlo simulations. We compare our results with a recent DFT study. [3]

As a result, we obtain accurate segregation isotherms that combine both ordered defect phases and the random solution and can predict thermodynamically stable surface states which can be further investigated for their impact on materials properties.

The workflow is implemented in the pyiron[4] framework and opens the way to routine and comprehensive studies of defect thermodynamics.

Biographical Note

Marvin is a final year Ph.D. student at the Max-Planck-Institute für Eisenforschung. He works on transferable machine learning potentials and their application to defect thermodynamics.

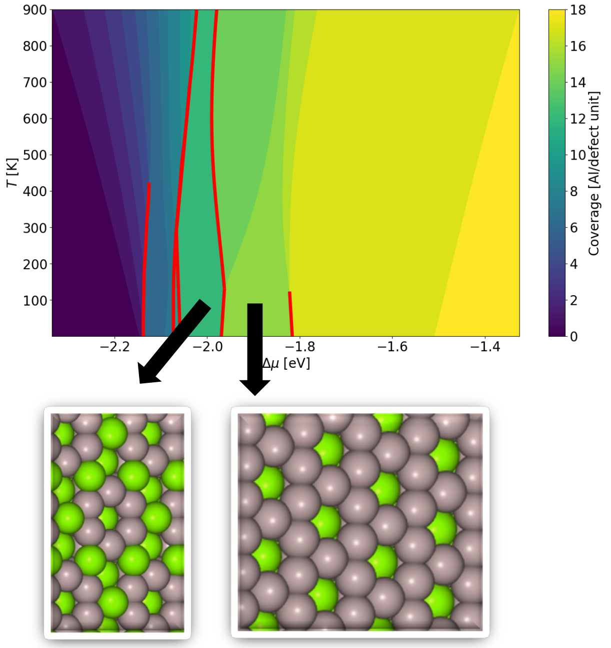

Figure 1. Defect Phase Diagram of Al (grey) on 3x3 basal hcp Mg (green) surface. Shown is the coverage of Al atoms per surface super cell (see color bar) as a function of temperature T and chemical potential difference $\Delta\mu = \mu_{\mathrm{Al}} - \mu_{\mathrm{Mg}}$. Insets show two low temperature reconstructions.

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[P11.05] Metastable defect phase diagrams as roadmap to tailor chemically driven defect formation

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Key words: Defect phase diagrams, metastability, chemical potential, alloy design

Thermodynamic bulk phase diagrams have become the roadmap used by researchers to identify alloy compositions and process conditions that result in novel materials with tailored properties. Recent experimental studies [1] show that changes in the alloy composition can drive not only transitions in the bulk phases present in a material, but also in the concentration and type of defects they contain. Defect phase diagrams [2] in combination with density functional theory provide a natural route to study these chemically driven defects. Our work reveals, however, that direct application of equilibrium bulk thermodynamics can fail to reproduce experimentally observed defect formation. Therefore, we extend the concept to metastable defect phase diagrams to account for kinetic limitations that prevent the system from reaching equilibrium (See black solid line in Fig. 1a). In this regard the exothermic formation of defect phases can be explained as depicted in Fig. 1b. We apply this concept to successfully (1) design suitable conditions for synthesis, which we subsequently realized experimentally, successfully validating the formation of the predicted defects in Mg-Al-Ca alloys. Finally, we (2) resolve the discrepancy between bulk phase diagrams and experimental observations regarding the formation of Mg-rich C14 and Al-rich C15 Laves phases in MgAlCa alloys at moderate temperatures and (3) clarify, the effect of the thermodynamic state of alloys on the competition between solute-rich hcp-like planar defects and stoichiometric basal stacking faults.

The concept of metastable defect phase diagram offers new avenues for the design of materials performance by tailoring defect structures.

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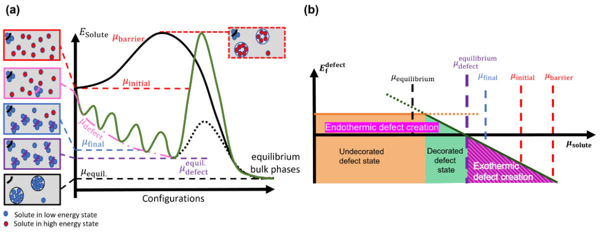

Figure 1. Schematic representation of the equilibration process (a) and the metastable defect phase diagram (b) Non-equilibrium (excess) solutes are marked by red dots. Energetically favorable solute configurations, e.g., in the bulk-like precipitates or at defects are shown as blue dots. The chemical potentials related to the various configurations sketched in the gray boxes are given by the dashed horizontal lines in (a) and vertical lines in (b).

Biographical Note:

Ali Tehranchi is currently a post-doctoral researcher at Max-Planck-Institut für Eisenforschung (MPIE) working on hydrogen embrittlement and storage as well as alloy design. He got his PhD from Laboratory for multiscale mechanics modelling at Ecole Polytechnique Fédérale de Lausanne (EPFL) where he worked on atomistic simulation of hydrogen embrittlement processes.

[P11.06] Screening of alloying elements and their combinations to improve the corrosion resistance of Mg alloys through high throughput calculations

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Key words: Mg alloys, Corrosion resistance, Solid solution, High-throughput calculations

The poor corrosion resistance of Mg alloys, as the result of the high activity and the special chemical properties like the low standard electrode potential of Mg, significantly hinders their wide applications. Many methods have been proposed to improve the corrosion resistance. Among them, alloying is one of the most commonly used methods due to the simultaneously improved mechanical properties and corrosion resistance after alloying. Our recent work also revealed that the solid solution of specific alloying elements and their combinations can effectively improve the corrosion resistance of Mg alloys [1]. Especially, the solid solution of the specific third alloying element can decrease the critical value of the reaction activity of key components, which can promote the formation of corresponding inert oxides. The formed inert oxides can be incorporated into the corrosion product layer, and thus effectively improving the corrosion resistance of Mg alloys [2, 3]. Hence, the proper selection of alloying elements and their combinations for solid solution in α-Mg to improve the corrosion resistance of Mg alloys is of importance [4]. Theoretical calculations can provide a theoretical basis to guide the design of high-performance Mg alloys. Therefore, the high-throughput first-principles calculations and thermodynamic calculations were systematically performed to study the change of properties (surface stability, hydrogen adsorption, activity of specific solute, etc.) of Mg alloys induced by the solid solution of different solutes. The derived results could provide a theoretical basis for guiding the selection of alloying elements to design Mg alloys with good corrosion resistance.

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Biographical Note

Jun Wang, a doctoral student in College of Materials Science and Engineering, Chongqing University, China. He mainly focuses on the material calculations and the design of high-performance Mg alloys. He has published 5 SCI papers and 1 conference paper.

[P11.07] A computationally highly efficient *ab initio* approach for melting property calculations and practical applications

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Key words: *ab initio*, melting, machine learning potential, liquid heat capacity

Melting properties of materials, such as melting temperature, entropy and enthalpy of fusion, are key parameters for materials design. They are essential to determine the lattice stability, a quantity that provides the basis for all multi-component phase diagrams, in particular within the CALPHAD method. However, experimental measurements on these properties, even for some unary materials, face tremendous challenges resulting in very scattered experimental data. Therefore, a highly efficient and accurate computer simulation method for computing these properties is desirable.

We have successfully developed an *ab initio* based method[1-3], significantly accelerating its computational efficiency through the integration of machine learning potentials. This method has been extended from stable to metastable phases, from unary to binary, and even to multi-component materials. The crucial aspect of our approach is accurately calculating the solid and liquid free energy surfaces from *ab initio*, where the full vibrational entropy, including anharmonic contributions, and electronic contributions, including electron-vibration coupling, need to be carefully considered. These free energy surfaces enable accurate determination of the thermodynamic properties of solid and liquid at finite temperatures.

Our method extends beyond calculating T^{m}/T_0, entropy and enthalpy of fusion, and solid-to-liquid volume change at T^{m}/T_0. It efficiently accesses *ab initio* solidus and liquidus lines for binary systems. Crucially, the longstanding challenge of experimentally measuring and theoretically computing liquid heat capacity in materials science can be addressed with our method, providing data of *ab initio* accuracy vital for constructing phase diagrams. Furthermore, our method offers profound insights into how the physical contributions influence predicted properties. Our studies on W and W-containing alloys highlight the significant impact of electronic contributions including electron-vibration coupling on melting properties and the heat capacity of both solid and liquid phases. Additionally, applying the standard exchange-correlation functional LDA and PBE yields a reliable *ab initio* confidence interval for experimental data, essential for predicting properties in materials lacking experimental validation.

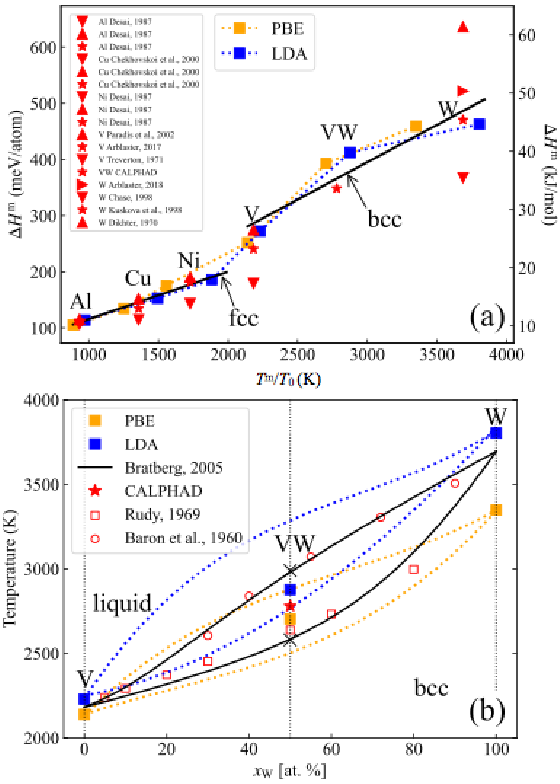

Figure 1. Comparisons between our *ab initio* results and the experimental data (a) Enthalpy of fusion, (b) V-W phase diagram.

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Biographical Note

Dr. Zhu works as DFG project leader in University of Stuttgart and as guest scientist at Max-Planck-Institut für Eisenforschung. She focuses on *ab initio*-based thermodynamics and develops new approaches to investigate melting properties of materials.