PROGRAMME

ISBN: 978-3-948023-12-6

Max-Planck-Institut
für Eisenforschung

TOFA 2020

17th DISCUSSION MEETING on Thermodynamics of Alloys

THERMODYNAMICS OF ALLOYS
AUTUMN 2020
KLOSTER BANZ

© 162172318 I Adam/56729271 I refresh(PIX) I fotolia.com · Vitold Muratov I commons.wikimedia.org I wiki I Klosterhof

2020

28 SEPT–02 OCT

Kloster Banz I Germany
Educational Center

Monday, 28.09.2020	**Tuesday, 29.09.2020**	**Wednesday, 30.09.2020**	**Thursday, 01.10.2020**	**Friday, 02.10.2020**
Seminar room 1	Seminar room 1	Seminar room 1	Seminar room 1	Seminar room 1
	09:00–10:30	09:00–10:15	09:00–10:30	09:00–10:25
	Session 1 p. 8	Session 5 p. 10	Session 7 p. 11	Session 11 p. 13
	Coffee break	*Coffee break*	*Coffee break*	*Coffee break*
	11:00–12:00	10:50–12:00	11:00–12:25	10:55–11:40
	Session 2 p. 8	Session 6 p. 10	Session 8 p. 11	Session 12 p. 13
	Lunch	*Lunch*	*Lunch*	
	14:00–15:10	13:30–22:40	14:00–15:15	
	Session 3 p. 9	Bus tour Bamberg with guided tours and conference dinner p. 7	Session 9 p. 12	
	Coffee break		*Coffee break*	
Foyer	15:40–17:05		15:45–16:55	
18:00–19:00	Session 4 p. 9		Session 10 p. 12	
Get together p. 7				
Seminar room 1				
19:00–20:15	19:00–20:30			
Conference opening p.8	Poster session p. 14			

TABLE OF CONTENTS

Scientific programme

Dear Colleagues and Friends,

A warm welcome to our 17th Discussion Meeting on Thermodynamics of Alloys (TOFA 2020). This year our meeting takes place under very special conditions. For the first time in the more than 30 years long history of TOFA conferences, we have participants and presentations not only on-site but also online owing to the worldwide Corona pandemic. Even though the number of participants expectedly is lower than usual, we have a four-days programme full of exciting presentations. Our TOFA 2020 provides an international forum for the thermodynamics community to meet, present and discuss fundamental and practical aspects of the thermodynamics of alloys.

Following the traditional scheme, TOFA 2020 is a single-session conference comprised of invited lectures, oral presentations, a high-profile poster session and sufficient time and opportunities for discussions. The conference provides a place where early stage researchers and experienced colleagues, experimentalists and theoreticians (including people from the CALPHAD community), as well as scientists focusing on fundamental questions and those working on application related topics come together.

TOFA 2020 continues the long established series of biennial discussion meetings on thermodynamics that had started already in 1988 with a first conference in Vienna. After the preceding TOFA meetings 2016 in Brazil and 2018 in South Korea, the conference now is back to Europe and TOFA 2020 takes place at the Educational Center Kloster Banz near Bad Staffelstein and Bamberg, Germany. The cloister is situated in a remote place above the valley of the river Main. As a well-known educational center, it is an ideal place for conferences with its good infrastructure and relaxing atmosphere.

We are looking forward to an exciting conference,

Welcome at TOFA 2020,

Frank Stein and Martin Palm
Meeting Chairs of the TOFA 2020

Venue

Educational Center Kloster Banz
Hanns-Seidel-Stiftung e. V.
96231 Bad Staffelstein, Germany

Date

28 September–02 October 2020

Scientific organiser

Dr. Martin Palm
Dr. Frank Stein
MPI für Eisenforschung GmbH, Düsseldorf, Germany

Local organising committee

Hans Jürgen Seifert, Karlsruher Institut für Technologie, Germany
Sergiy V. Divinski, Westfälische Wilhelms-Universität Münster, Germany
Suzana G. Fries, Ruhr-Universität Bochum, Germany
Stephanie Lippmann, Friedrich Schiller University Jena, Germany
Martin Palm, MPI für Eisenforschung GmbH, Düsseldorf, Germany
Frank Stein, MPI für Eisenforschung GmbH, Düsseldorf, Germany

International advisory board

Alan Dinsdale, United Kingdom
Aleš Kroupa, Czech Republic
André Costa e Silva, Brazil
Andy Watson, United Kingdom
Armando Fernández Guillermet, Argentinia
Boguslav Onderka, Poland
Byeong-Joo Lee, Republic of Korea
Claudio G. Schön, Brazil
Frank Stein, Germany
Gabriele Cacciamani, Italy
Gabriella Borzone, Italy
Hans-Jürgen Seifert, Germany
Herbert Ipser, Austria †
Ikuo Ohnuma, Japan
Jan Vřešťál, Czech Republic
Jean-Marc Joubert, France
Joonho Lee, Republic of Korea
Jürgen Brillo, Germany
Klaus Wolfgang Richter, Austria
Krzysztof Fitzner, Poland
Luis Filipe Malheiros, Portugal
Malin Selleby, Sweden
Mojmir Sob, Czech Republic
Nathalie Dupin, France
Olga Fabrichnaya, Germany
Philip Nash, USA
Rada Novakovic, Italy
Raymundo Arroyave, USA
Simona Delsante, Italy
Suzana G. Fries, Germany
Tetsuo Mohri, Japan
Toshihiro Tanaka, Japan
Wu Ping, Singapore
Yong Du, China

Conference organisation

Conventus Congressmanagement & Marketing GmbH
Anja Kreutzmann/Julian Unger
Carl-Pulfrich-Straße 1
07745 Jena, Germany
Phone +49 3641 31 16-357/-330
Fax +49 3641 31 16-243
anja.kreutzmann@conventus.de
julian.unger@conventus.de
www.conventus.de

Design/Layout

Layout	krea.tif-studio UG (limited liability)
Print	Junggebauer Medien GmbH
Circulation	50
Editorial Deadline	08 September 2020

Registration fees

Regular	650 EUR
Student	350 EUR
Digital participation	100 EUR
Accompanying person*	150 EUR

Social programme**

Get together, 28 September	included
Bus tour to Bamberg with conference dinner, 30 September	included

* Get together and conference dinner is included.

** Registration for the social programme is required.

General terms and conditions

Please find our General Terms and Conditions at **www.tofa2020.de**.

Opening hours Check-In

Monday	04:00 p.m.–07:00 p.m.
Tuesday	08:30 a.m.–11:30 a.m. and 03:30 p.m.–05:45 p.m.
Wednesday	08:30 a.m.–12:30 p.m.
Thursday	08:30 a.m.–11:30 a.m. and 03:30 p.m.–05:45 p.m.
Friday	08:30 a.m.–12:30 p.m.

Internet

Wireless-Lan is available for free. You do not need to enter a password/code.

Certificate of attendance

Certificates of attendance will first be made available on the last day of the conference at the check-in desk.

Poster prizes

The best poster will be awarded with 300 EUR, sponsored by our media partner Entropy.
This open access journal maintains a rigorous and a medium publication time of 42 days from submission to publication online. It is fully covered by the leading indexing and abstracting services, including SCIE (web of science), Scopus, Google Scholar and MathSciNet.

entropy
an Open Access Journal by MDPI

Poster session

All posters will be divided into recorded posters rated on Tuesday, 29 September, 07:00 p.m. and live posters rated on Tuesday, 29 September, 07:40 p.m. Authors are requested to be present at their posters during the poster session.
Pinboards will be numbered. The pinboards are only to be used with the designated pins. You will find your poster number in the programme book on page 14.
Please note that all posters should be hanging on Tuesday, 29 September, by 04:00 p.m. and be removed at the latest by Friday, 02 October, 09:00 a.m. Posters that have not been removed by that time will be considered as waste.

Catering

Foods and drinks during the breaks will be provided.
The restaurant “Klosterschänke” is directly located on the premises of Kloster Banz and is open Wednesday till Saturday from 12:00 a.m.–08:00 p.m. and Sunday from 11:00 a.m.–05.00 p.m. *(subject to change)*.
For your information: the closest city with alternative restaurants is Bad Staffelstein, which is 5.5 km away (approximately 1 hour by foot, 7 minutes by car).

Smoking

Smoking is prohibited inside the entire conference area.

GENERAL INFORMATION

Taxi

Taxi Dütsch

Phone +49 9573 52 06/+49 9571 52 06

Price from Bad Staffelstein to Kloster Banz	about 10 EUR*
Price from Lichtenfels to Kloster Banz	about 13 EUR*

* Prices are subject to change.

GENERAL HINTS FOR AUTHORS AND PRESENTERS

Submitting your presentation/technical information

Please prepare your presentation as PDF, MS Office Power-Point2007, 2010 for Windows or key for Macintosh DVD in 16:9 aspect ratio.

A presentation notebook with a PDF reader and MS Office Power-Point 2010/2007 will be provided. Notebook, presenter and laser pointer will be available at the speaker's podium in the lecture hall. The use of personal notebooks is possible upon agreement. However, it may interrupt the flow of the programme in the lecture hall. You will be assisted by a technical supervisor.

To guarantee a smooth running programme please upload your presentation on time – at least 2 hours before your presentation starts.

For submission, please use a USB flash drive, CD or DVD disc that is not protected by any software. Professional staff and equipment will be available for you to arrange and preview your presentation.
Please note: certain encodings for video and audio files could lead to technical problems.

Time Allotment

Please prepare your presentation for the allotted amount of time. Chairs and moderators may interrupt should you overrun your time limit.

Allotted time is assigned as follows (speaking + discussion time):

Plenary Talks	50 + 10 minutes discussion
Invited Talks	20 + 5 minutes discussion
Session Talks	12 + 3 minutes discussion

SOCIAL AND CULTURAL PROGRAMME

Get together* • Monday, 28 September

Come together for drinks and snacks. Enjoy the evening and allow yourself interesting conversations with colleagues, old friends and new acquaintances.

06:00 p.m.	Get together
07:00 p.m.	Conference opening

Bus tour to Bamberg with guided tours and conference dinner* ● Wednesday, 30 September 2020

Enjoy the trip to Bamberg with a guided city tour through the historic city of Bamberg as well as a culinary tour to get to know and enjoy the brewing tradition of this region. Afterwards take the chance to get in touch with colleagues and friends and have an enjoyable evening at the “Brauerei Klosterbräu”. The conference dinner includes the awarding of the poster prize. At around 10:00 p.m. the bus returns from Bamberg to Kloster Banz.

Time plan	01:30 p.m. Start at Kloster Banz (car park)
	02:00 p.m. Guided city tour Bamberg
	04:30 p.m. Culinary tour with “Bamberg Hörnla” and “Zwiebeltreter”
	06:30 p.m. Conference dinner and award ceremony at restaurant “Brauerei Klosterbräu”
	10:00 p.m. Departure to Kloster Banz
End	aprox. 10:40 p.m.
Fee	included in the conference fee (dinner & 2 drinks at the restaurant)

* A registration is necessary.

Monday, 28. September 2020

04:00 p.m.–06:00 p.m.	Registration
06:00 p.m.–07:00 p.m.	Get together
07:00 p.m.–07:15 p.m.	Conference opening Frank Stein (Düsseldorf/DE)
07:15 p.m.–08:15 p.m. O1	**Plenary talk:** High-throughput measurement of alloy phase diagrams and phase-based properties Ji-Cheng Zhao (College Park, MD/US) – virtual

Tuesday, 29. September 2020

09:00 a.m.–10:25 a.m. *Seminar room 1* Chair	Session 1 Martin Palm (Düsseldorf/DE)
09:00 a.m. O2	**Invited talk:** Thermodynamics and phase diagram based development of electrode materials for liquid metal batteries Przemyslaw Fima (Krakow/PL)
09:25 a.m. O3	Intermetallics for anodes in Li-ion batteries: The Sb-Sn-Ti phase diagram Hans Flandorfer (Vienna/AT) – virtual
09:40 a.m. O4	Experimental and theoretical study of Pb-Se-Sn system Ondrej Zobač (Brno/CZ)
09:55 a.m. O5	A thermodynamic insight into $Mg_2Si_{(1-x)}Sn_x$ solid solutions for the development of practical thermoelectric devices Silvana Tumminello (Cologne/DE)
10:10 p.m. O6	CALPHAD re-assessment of the Se-Te binary system and assessment of Pb-Se-Te ternary system Ondřej Fikar (Brno/CZ)
10:25 a.m.–11:00 a.m.	*Coffee break*
11:00 a.m.–12:00 p.m. *Seminar room 1* Chair	Session 2 Markus Rettenmayr (Jena/DE)
11:00 a.m. O7	Pressure dependent phase stabilities of binary Ti-Fe intermetallics Mario J. Kriegel (Freiberg/DE)
11:15 a.m. O8	Effect of metastable $L1_2$ Co_3Nb on microstructural evolution in Co-3.9Nb alloy Toshiaki Horiuchi (Sapporo/JP) – virtual
11:30 a.m. O9	Isothermal formation of crystalline-amorphous nano-eutectoids during nitriding Stefan Kante (Freiberg/DE)
11:45 a.m. O10	Employing processing in a temperature gradient for synthesizing pure intermetallic phases Stephanie Lippmann (Jena/DE)
12:00 p.m.–02:00 p.m.	*Lunch*

Tuesday, 29. September 2020

02:00 p.m.–03:10 p.m.	Session 3
Seminar room 1	
Chair	Martin Palm (Düsseldorf/DE)
02:00 p.m. O11	**Invited talk:** Equilibrium vs. kinetics in alloy nanoparticles Riccardo Ferrando (Genova/IT) – virtual
02:25 p.m. O12	Thermodynamic study of the binary P-Pt system Lisa-Yvonn Schmitt (Schwäbisch Gmünd/DE)
02:40 p.m. O13	Experimental study and thermodynamic modelling of the Al_2O_3-MnO system Olga Fabrichnaya (Freiberg/DE)
02:55 p.m. O14	Thermodynamic database development for the ZrO_2-MgO-MnO_x system Ivan Saenko (Freiberg/DE)
03:10 p.m.–03:40 p.m.	*Coffee break*
03:40 p.m.–05:05 p.m.	Session 4
Seminar room 1	
Chair	Frank Stein (Düsseldorf/DE)
03:40 p.m. O15	**Invited talk:** Thermodynamic properties of the Fe-N system: Influence of atomic ordering and magnetism Andreas Leineweber (Freiberg/DE)
04:05 p.m. O16	Development and application of CALPHAD databases for Ti- and TiAl-based alloys Yang Yang (Solna/SE) – virtual
04:20 p.m. O17	High temperature phase equilibria in ternary Ti-Al-Nb alloys Benedikt Distl (Düsseldorf/DE)
04:35 p.m. O18	Experimental investigation of phase equilibria in the Ti-Al-Zr system for improvement of a CALPHAD database Zahra Kahrobaee (Düsseldorf/DE)
04:50 p.m. O19	Short-range ordering of carbon in liquid alloys of 3D-block transition metals Min-Kyu Paek (Espoo/FI) – virtual
07:00 p.m.–08:30 p.m.	Poster session

Wednesday, 30 September 2020

09:00 a.m.–10:15 a.m. *Seminar room 1*	Session 5
Chair	Hans Jürgen Seifert (Eggenstein-Leopoldshafen/DE)
09:00 a.m. O20	**Plenary talk:** Exploiting temperature and concentration gradients for data mining Markus Rettenmayr (Jena/DE)
10:00 a.m. O21	Experimental setup for controlled pulse heating to investigate composition invariant phase transitions Tobias Kaaden (Jena/DE)
10:15 a.m.–10:50 a.m.	*Coffee break*
10:50 a.m.–12:00 p.m. *Seminar room 1*	Session 6
Chair	Suzana G. Fries (Bochum/DE)
10:50 a.m.	**Invited talk:** Principal concept of database creation aiming holistic views on the fundamentals of O22 materials science Pierre Villars (Vitznau/CH)
11:15 a.m. O23	Combining *ab initio*, machine learning and human learning for a CALPHAD database of chemical compound space Moritz to Baben (Herzogenrath/DE)
11:30 a.m. O24	Artifical materials intelligence (AMI) to accelerate discovery of novel superalloys Irina Roslyakova (Bochum/DE) – virtual
11:45 p.m. O25	Numerical alloy design using CALPHAD-based property models Benjamin Wahlmann (Erlangen/DE)
12:00 p.m.–01:30 p.m.	*Lunch*
01:30 p.m.–10:40 p.m.	Bus tour Bamberg with guided tour and conference dinner

Thursday, 1 October 2020

09:00 a.m.–10:30 a.m. *Seminar room 1* Chair	Session 7 Stephanie Lippmann (Jena/DE)
09:00 a.m. O26	**Plenary talk:** Fast Scanning Chip calorimetry: New measurement capabilities at high controlled rates Gerhard Wilde (Münster/DE)
10:00 a.m. O27	Thermal analysis with Gibbs inside Suzana G. Fries (Bochum/DE)
10:15 a.m. O28	Determining the Curie temperature of Ni using a temperature gradient evaluation method Sönke Wilhelmy (Jena/DE)
10:30 a.m.–11:00 a.m.	*Coffee break*
11:00 a.m.–12:25 p.m. *Seminar room 1* Chair	Session 8 Aleš Kroupa (Brno/CZ)
11:00 a.m. O29	**Invited talk:** Knudsen effusion mass spectrometry: Application to the thermodynamic study of alloys Ioana Nuta (Grenoble/FR) – virtual
11:25 a.m. O30	Thermal stability of half-Heusler (Ti,Nb)FeSb alloys Pavel Brož (Brno/CZ) – virtual
11:40 a.m. O31	2 1/2th generation CALPHAD databases: Extrapolating heat capacities of elements and compounds to 0K Abdulmonem Obaied (Bochum/DE) – virtual
11:55 a.m. O32	Pure elements: Do we know enough about them for 3rd generation of CALPHAD Alexandra V. Khvan (Moscow/RU) – virtual
12:10 p.m. O33	Application of machine learning methods to support the development of the 3rd generation CALPHAD database Irina Roslyakova (Bochum/DE) – virtual
12:25 p.m.–01:30 p.m.	*Lunch*

Thursday, 1 October 2020

02:00 p.m.–03:15 p.m. *Seminar room 1* Chair	Session 9 Jean-Marc Joubert (Thiais/FR)
02:00 p.m. O34	Precipitation in micro-alloyed steels for seamless line pipes Andre Schneider (Düsseldorf/DE)
02:15 p.m. O35	Carbide precipitation kinetic in model Fe-C-Mo and Fe-C-Mn bainitic steels during tempering: Experimental study and modelling Caroline Toffolon-Masclet (Gif-sur-Yvette/FR) – virtual
02:30 p.m. O36	Thermodynamic database and experimental studies of NiAl-Cr and NiAl-Mo composities Hans Jürgen Seifert (Eggenstein-Leopoldshafen/DE)
03:45 p.m. O37	W-Ni-Co ternary system thermodynamic description at intermediate temperatures Olivier Dezellus (Villeurbanne/FR) – virtual
03:00 p.m. O38	Phase equilibria in the Fe-N system at high-pressure/high-temperature conditions Marius Holger Wetzel (Freiberg/DE)
03:15 p.m.–03:45 p.m.	*Coffee break*
03:45 p.m.–04:55 p.m. *Seminar room 1* Chair	Session 10 Andre Schneider (Düsseldorf/DE)
03:45 p.m.	**Invited talk:** Site occupancies in α- and β-Mn solid solutions and consequences for the CALPHAD O39 modelling Jean-Marc Joubert (Thiais/FR)
04:10 p.m. O40	Thermodynamic assessment of Mn-Nb and Mn-Ta systems Jan Vřešťál (Brno/CZ) – virtual
04:25 p.m. O41	Pecularities of the α-Mn and β-Mn phases in the Mn-Ti-X (Fe, Ni) ternary systems Alexander Walnsch (Freiberg/DE)
04:40 p.m. O42	Thermodynamic assessment of the Al_2O_3-TiO_2-SiO_2 system Mariia Ilatovskaia (Freiberg/DE)

Friday, 2 October 2020

09:00 a.m.–10:25 a.m.	Session 11
Seminar room 1	
Chair	Andreas Leineweber (Freiberg/DE)
09:00 a.m. O43	**Invited talk:** Short-range order strengthening and its role in intermetallics and high-entropy alloys Claudio G. Schön (São Paulo/BR) – virtual
09:25 a.m. O44	Considering point defects in sub-stoichiometric ZrC_x Theresa Davey (Sendai/JP) – virtual
09:40 a.m. O45	Phase diagram evaluation and thermodynamic assessment of the chromium-hydrogen system Maxime Dottor (Thiais/FR)
09:55 a.m. O46	Thermodynamic study on diffuse interfaces in Ni-based superalloys Farsad Forghani (London/GB) – virtual
10:10 a.m. O47	First-principles study on stability of cristobalite structures in SiO_2 Ying Chen (Sendai/JP) – virtual
10:25 a.m.–10:55 a.m.	*Coffee break*
10:55 a.m.–11:40 p.m.	Session 12
Seminar room 1	
Chair	Przemyslaw Fima (Krakow/PL)
10:55 a.m. O48	Relation between excess volume, excess free energy and isothermal compressibility in liquid alloys Jürgen Brillo (Cologne/DE) – virtual
11:10 a.m. O49	Thermophysical properties of liquid Ga-Sn-Zn eutectic alloy with different metal admixtures Yuriy Plevachuk (Lviv/UA)
11:25 a.m.	Closing ceremony and handover of the TOFA triangle Frank Stein (Düsseldorf/DE)

Tuesday, 30 September 2020

07:00 p.m.–08:30 p.m. Recorded poster session
Seminar room 1

07:00 p.m. eP1	From bulk to size-dependent melting properties of Au-Ge alloys Simona Delsante (Genova/IT)
07:08 p.m. eP2	Low-temperature properties and phase transformations in pure tin Mauro Palumbo (Torino/IT)
07:16 p.m. eP3	*Ab initio* calculations of the binary and ternary subsystems of the systems V-Nb-Ta-Mo-W and V-Nb-Ta-W-Al Claudio G. Schön (São Paulo/BR)
07:24 p.m. eP4	*Ab initio* study of elastic and thermodynamic properties of uranium nitride Claudio G. Schön (São Paulo/BR)
07:32 p.m. eP5	New developments in the continuous displacement-cluster variation method: The constraint terms Claudio G. Schön (São Paulo/BR)
07:40 p.m. eP6	Thermal Barrier Coatings phase stability and in service degradation: Experimental study of CMAS corrosion on Ansaldo Energia's materials Giacomo Roncallo (Genova/IT)
07:48 p.m. eP7	3G_TDB software for automated generation of TDB files using modified segmented regression (MSR) model – pure Mn as an example Abdulmonem Obaied (Bochum/DE)
07:56 p.m. eP8	Thermodynamic modelling of the Al-Co-Mn system Mehdi Noori (Aachen/DE)
08:04 p.m. eP9	The development of the thermodynamic database for the Ag-Pb-Sn-Se-Te based thermoelectric materials Aleš Kroupa (Brno/CZ)
08:12 p.m. eP10	Fundamental investigation of high entropy alloys with focus on σ and μ phases Marlena Ostrowska (Genova/IT)
08:20 p.m. eP11	Experimental investigation and thermodynamic modelling of interfacial reactivity between liquid Ni and oxide system Saverio Sitzia (Genova/IT)

ABSTRACTS

Max-Planck-Institut
für Eisenforschung

TOFA 2020

17th DISCUSSION MEETING on Thermodynamics of Alloys

Oral abstracts

Poster abstracts

O1

High-throughput measurement of alloy phase diagrams and phase-based properties

J.-C. Zhao
Department of Materials Science and Engineering, University of Maryland, College Park, Maryland, 20742 USA

This talk will highlight some recent advances in high-throughput experimental techniques for rapid collections of materials property data. Diffusion multiples offer an efficient and reliable means to measure alloy phase diagrams. Localized property measurements on composition gradients and regions created in diffusion multiples allow effective collection of composition-dependent properties, including thermal conductivity, heat capacity, coefficient of thermal expansion, and elastic constants. A newly developed forward-simulation analysis allows accurate measurement of impurity (dilute) diffusion coefficients from regular diffusion couple profiles without using isotope tracer experiments. The impurity diffusion coefficients together with interdiffusion coefficients are essential to the establishment of reliable diffusion (mobility) databases for modeling the creep properties of materials and precipitation processes. Recently developed dual-anneal diffusion multiples (DADMs) allow rapid and systematic collection of phase precipitation kinetics and morphological evolution data across wide ranges of compositions as a function of time and temperature, thus can provide large datasets for testing and improving models. Examples will be used to illustrate the effectiveness and future essentiality of tight integration of computational and experimental approaches to rapidly establish digital materials property databases for accelerated alloy design.

O2

Thermodynamics and phase diagram based development of electrode materials for liquid metal batteries

P. Fima
Institute of Metallurgy and Materials Science PAS, Krakow, Poland

According to Eurostat [1], in 2018 renewable energy constituted 18.9 % of the total energy consumed in the European Union, with a target of 20 % in 2020. The power generated from some sources, such as wind and solar, is not necessarily generated when it is most needed, so it needs to be stored in big-scale energy storage, and later released to energy grid.

Liquid metal batteries (LMB) [2] are one of proposed solutions to energy storage problem. In simplicity, fully charged LMB is built from three liquid layers: top layer metal A (negative electrode), bottom layer metal B (positive electrode), separated by a layer of molten salts (electrolyte). Upon discharge, metal (A) goes through electrolyte layer and a binary alloy (A-B) is formed in the bottom layer. Here, strong interaction between metal A and metal B, in which activity of metal A is very low, is thermodynamic driving force for cell discharge, manifesting in the form of high cell voltage (electromotive force). A number of material designs (chemical compositions of electrodes) offering high capacity and voltage, at an acceptable operating temperature and cost, were proposed and tested in recent years [3-6]. Yet, little attention was given to understanding underlying processes in the positive electrode material upon lithiation (discharge of battery). Here, we discuss how thermodynamic measurements help create relevant phase diagrams and understand voltage changes with composition. Special attention is given to the case of Li−Pb−Sb system [6,7].

References:

[1] https://ec.europa.eu/eurostat/statistics-explained/index.php/Renewable_energy_statistics (accessed: 2020-04-02)
[2] H. Kim et al.: “Liquid metal batteries: Past, present, and future”, Chem. Rev. 113(3) (2013) 2075-2099.
[3] H. Li et al.: ”Liquid metal electrodes for energy storage batteries”, Adv. Energy Mater. 6 (2016) 1600483.
[4] H. Li et al.: “High performance liquid metal battery with environmentally friendly antimony-tin positive electrode”, ACS Appl. Mater. Interfaces 8 (2016) 12830-12835.
[5] T. Dai et al.: “Capacity extended bismuth-antimony cathode for high performance liquid metal battery”, J. Power Sources 381 (2018) 38-48.
[6] K. Wang et al.: “Lithium-antimony-lead liquid metal battery for grid-level energy storage”, Nature 514 (2014) 348-350.
[7] S. Terlicka, A. Debski, P. Fima: “Enthalpy of mixing of ternary Li−Pb−Sb alloys”, J. Phase Equilib. Diffus. 39 (2018) 412-425.

O3

Intermetallics for anodes in Li-ion batteries: The Sb−Sn−Ti phase diagram

H. Flandorfer[1], P. Berger[1], C. Schmetterer[2], H.S. Effenberger[3], D. Cupid[4]
[1]Department of Inorganic Chemistry − Functional Materials, University of Vienna, Austria
[2]Department of Physical Chemistry, University of Vienna, Austria
[3]Department of Mineralogy and Crystallography, University of Vienna, Austria
[4]Center for Low Emission Transport, AIT Austrian Institute of Technology GmbH

Li-ion batteries (LIBs) are most frequently used in various handheld devices such as notebooks, cell phones or cameras. However, for load leveling and electro-mobility applications, key performance indicator parameters such as specific capacity, energy and power density, cyclability, lifetime, and safety have to be improved. In this regard, new electrode materials have to be designed for the next generation of LIBs. Among possible candidates for anode materials are intermetallic alloys which show significantly higher theoretical capacities than the currently used graphite.

Many metals and alloys are able to form intermetallic phases with Li. For example, when $Li_{17}Sn_4$ is generated via lithiation of Sn, a theoretical charge capacity of 960 mAh/g of Sn is obtained at the maximum Li-concentration of 81 at.% Li (compare to 372 mAh/g of carbon). The main drawback of metallic active anode materials, however, is the mechanical degradation of the electrode upon cycling and the resulting short lifetime of the cell. This occurs due to the formation of brittle alloys which exhibit large volume changes on lithiation/delithiation (>180 % for Sn). To overcome this phenomenon, adding carbonaceous fillers, using partial liquid intermetallic electrodes with self-healing effects, or taking advantage of the *in-situ* precipitation of inactive matrix phases on lithiation have all been attempted. The latter can be achieved using multi-component Sb−Sn−Ti alloys instead of the pure metals Sb, Sn or binary Sb-Sn compounds. In such cases, full lithiation leads to the formation of Li_3Sb and Li_7Sn_2 islands distributed in a fine grained inactive Ti-matrix. On de-lithiation, however, nano-crystalline Sb−Ti and Sn−Ti compounds are expected to form [1,2]. The Ti-based matrix buffers the volume expansion, mechanically stabilizes the electrode material and even improves its electronic conductivity.

For the fundamental understanding of such lithiation processes, the investigation of the phase constitution, chemical thermodynamics and structural features of Li−Sb−Sn−Ti alloys is indispensable. In this regard, comprehensive experimental data on the equilibrium phase relations in the complex ternary and quaternary systems are necessary in order to assess the electrochemical behavior of the electrode active material. Therefore, as a first step, we studied the phase relations and crystal structures in the ternary Sb−Sn−Ti and Li−Sb−Sn sub-systems via XRD, thermal analysis and SEM/EDX. Isothermal sections at different temperatures are presented as well as the crystal structure of new ternary compounds. Based on this information, selected Ti−Sb−Sn alloys were processed into electrodes and tested electrochemically vs Li^+/Li via galvanostatic cycling and titration. Additionally, *ex-situ* XRD was applied to study the structural changes of the electrode active materials during the lithiation process.

References:

[1] M.T. Sougrati, J. Fullenwarth, A. Debenedetti, B. Fraisse, J.C. Jumas, L. Monconduit: “TiSnSb a new efficient negative electrode for Li-ion batteries: mechanism investigations by operando-XRD and Mössbauer techniques“, J. Mater. Chem. 21 (2011) 10069-10076.

[2] C. Marino, M.T. Sougrati, B. Gerke, R. Pöttgen, H. Huo, M. Menetrier, C.P. Grey, L. Monconduit: “Role of structure and interfaces in the performance of TiSnSb as an electrode for Li-ion batteries”, Chem. Mater. 24 (2012) 4735-4743.

O4

Experimental and theoretical study of Pb−Se−Sn system

O. Zobač[1], T.Y. Huang[2], Y.H. Hsu[2], A. Kroupa[1], S.-W. Chen[2,3]
[1]Institute of Physics of Materials, the Czech Academy of Sciences, Brno, Czech Republic
[2]Department of Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan
[3]High Entropy Materials Center, National Tsing Hua University, Hsinchu, Taiwan

Pb−Se−Sn system is studied as a potential material for thermoelectric applications. There is no phase diagram published for the entire compositional regime at any temperature up to now. Therefore ternary Pb−Se−Sn alloys were long-term annealed at 350 and 500°C respectively. Their microstructure, phase and overall composition were determined by SEM-EDX. Structural determination was carried out by XRD. The isothermal sections at 350 and 500°C of the experimental equilibrium Pb−Se−Sn phase diagram were proposed for the first time in this study. No ternary compound was found. The phase relationships are similar at 350 and 500°C. At both temperatures, the binary intermetallic phases α-PbSe and γ-SeSn have very significant ternary solubility, but the ternary solubility of Pb in the Se_2Sn phase is negligible. The experimental results and the binary subsystems data were used for the CALPHAD type theoretical assessment of this system. Thermodynamic calculation indicate the existence of liquid miscibility gap in the ternary phase diagram. Both Pb−Se and Se−Sn binary subsystems have strong tendencies to form a stable and/or metastable miscibility gaps in the Se-rich region of the phase diagrams and it is quite understandable that the miscibility gap appears in the ternary phase diagram at low temperatures.

Acknowledgement:
Authors highly appreciate financial support of the Czech Science Foundation project No. 18-25660J.

O5

A thermodynamic insight into $Mg_2Si_{(1-x)}Sn_x$ solid solutions for the development of practical thermoelectric devices

S. Tumminello[1], M. Yasseri[1,3], J. De Boor[1], S.G. Fries[2], E. Müller[1,3]
[1]Institute of Materials Research, German Aerospace Center (DLR), 51170 Cologne, Germany
[2]ICAMS, Ruhr University Bochum, 44801 Bochum, Germany
[3]Institute of Inorganic and Analytical Chemistry, Justus Liebig University Gießen, 35392 Gießen, Germany

Practical Thermoelectric Devices for power Generation (TEG) require proper design and engineering of the thermoelectric material (TE), stable contacting with the electrodes and durable assembly technology for applicable modules. We place emphasis on magnesium-silicide-stannide solid solutions as a base material for both, n- and p-type legs, simplifying the selection of electrodes for practical devices.

In a first stage, the interplay among synthesis conditions, interfacial diffusion/reaction products and the resulting microstructure of the TE material is investigated from the CALPHAD perspective. However, a subsequent step accounting for the point defect structure of the crystal lattice and its close relation with the thermoelectric properties is crucial for this type of materials. Equilibrium phase diagrams are being used to understand the observed microstructures of $Mg_2Si_{(1-x)}Sn_x$ solid solutions synthesized via mechanical milling and sintering. Experimental evidence of partial solubility and strong coherent interfaces for compositions near the Mg_2Sn–Mg_2Si isopleth motivated the re-modelling of the Gibbs energy of the C1-Mg_2X antifluorite phase accounting for the strain energy contribution to the free energy [1-3]. We investigate the stability of solid solutions that decompose via spinodal transformation under coherent strain and interfacial energy effects by carrying on long term annealing experiments and microstructural analysis.

With this model the coherent miscibility gap can be determined by calculation and confronted with experimental work. This approach is complemented with the assessment of the dependency of lattice parameters and molar volumes on composition in the isopleth of interest.

References:

[1] J.W. Cahn: “On spinodal decomposition in cubic crystals”, Acta Metall. 10 (1962) 179-183.
[2] J.W. Doak and C. Wolverton: “Coherent and incoherent phase stabilities of thermoelectric rocksalt IV-VI semiconductor alloys”, Phys. Rev. 86 (2012) 144202.
[3] G. Makov, et al.: “Effect of pressure on the interactions and phase diagrams of binary alloys”, Comp. Mater. Sci. 169 (2019) 109103.

O6

CALPHAD re-assessment of the Se-Te binary system and assessment of Pb−Se−Te ternary system

O. Fikar[1, 2], J. Vřešťál[2], A. Zemanová[2], S.-W. Chen[3], A. Kroupa[2]
[1]Brno University of Technology, Faculty of Mechanical Engineering, Technická 2, 616 69 Brno, Czech Republic
[2]Institute of Physics of Materials, ASCR, Žižkova 22, 616 00 Brno, Czech Republic
[3]Department of Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan

Phase diagrams are important tools for the design and development of new materials, selection of processing routes and assessment of reliability. Currently, great attention is paid to the development of the thermoelectric materials, which can convert heat to electricity and serve as renewable energy sources.

The Pb−Se−Te system was studied in the scope of such project. In order to assess Pb−Se−Te ternary system using the CALPHAD method, the assessments of all its binary subsystems were needed. The assessments of Pb−Se and Pb−Te systems were obtained from literature [1, 2]. In the case of Se−Te binary system, two assessments were done in the past by Ghosh [3] and Gierlotka [4], but neither of those was usable for higher order system – the description by Ghosh [3] does not agree well with available experimental data for enthalpy of mixing in liquid and the description by Gierlotka [4] contains an inverted miscibility gap at relatively low temperatures. Therefore, the Se−Te binary system was re-assessed using the substitutional model with a SeTe associate in the liquid phase. This new description of Se−Te system was then used in the assessment of Pb−Se−Te ternary system. Experimental data for this assessment were obtained in the scope of this project.

Acknowledgement: Authors highly appreciate financial support of the Czech Science Foundation project No. 18-25660J.

References:

[1] Y. Liu et al.: "Phase equilibria and thermodynamic basis for the Cd−Se and Pb−Se binary systems", J. Electronic Mater. 41 (2012) DOI: 10.1007/s11664-012-2016-7.

[2] Y. Liu, L. Zhang, D. Yu: "Thermodynamic descriptions for the Cd−Te, Pb−Te, Cd−Pb and Cd−Pb−Te systems", J. Electronic Mater. 38 (2009) DOI: 10.1007/s11664-009-0875-3.

[3] G. Ghosh, H. L. Lukas, L. Delaey: "A thermodynamic assessment of the Se−Te system", CALPHAD 12 (1988) 295-299.

[4] W. Gierlotka, W.-H. Wu: "The reoptimization of the binary Se−Te system", Int. J. Mater. Res 103 (2012) 698-701.

O7

Pressure dependent phase stabilities of binary Ti−Fe intermetallics

M.J. Kriegel, O. Fabrichnaya, M.H. Wetzel, D. Rafaja
TU Bergakademie Freiberg, Institute of Materials Science, 09599 Freiberg, Germany

Alloys based on the binary Ti−Fe system are promising materials for various applications, as they possess good corrosion resistance, high wear resistance, biocompatibility and appropriate mechanical properties. Furthermore, the binary intermetallic TiFe phase has been presented as a possible material for solid-state hydrogen storage applications. High-pressure torsion as one method of severe plastic deformation was used to reduce the surface oxidation and to activate the material in order to improve the hydrogen storage properties. The adjustment of the microstructure, e.g., through the mechanical and thermal treatments, improves further the properties of the alloys. For a better understanding of the phase formation and stabilities of the phases in the binary system, Ti-rich alloys and different initial states were produced by heat treatments at 470 and 800°C, and subjected to high-pressure torsion (HPT). The phase fractions, the distribution of individual phases and their orientation relationships in the initial and in the deformed alloys were analyzed using X-ray diffraction (XRD), electron microscopy (SEM, (HR)TEM) and electron diffraction (EBSD, SAED). The thermal stability of the high-pressure ω-Ti(Fe) phase was investigated by means of thermal analysis and high-temperature *in situ* XRD. The alloys quenched from the bcc β-(Ti,Fe) solid solution (from 800°C) show a martensitic microstructure for Fe contents below 2 wt.% and the formation of the athermal ω phase at approximately 4 wt.% Fe. Alloys annealed at 470°C exhibit a two-phase α-Ti + TiFe microstructure after quenching. During the HPT process, the phases were partially or completely transformed to ω-Ti(Fe), depending on the Fe content and the initial phase composition. Differences were also detected for the thermal stability of the HPT-induced ω-Ti(Fe) phase. The phase transformations were interpreted by means of the pressure-dependent thermodynamic calculations that were performed with the Thermo-Calc software package. The thermodynamic modelling were started from the unary titanium and iron systems. For that purpose, experimental and *ab initio* calculated heat capacities, molar volumes, thermal expansions and bulk moduli were utilized. In addition, a binary diffusion couple was heat treated in a multi-anvil press at ~800°C and at a pressure of 2.5 GPa for 6 h. The obtained data regarding the phase stabilities at 2.5 GPa were considered during the modelling procedure.

O8

Effect of metastable $L1_2$ Co_3Nb on microstructural evolution in Co−3.9Nb alloy

T. Horiuchi[1], K. Yamada[1], K. Ikeda[2], S. Miura[2], F. Stein[3]
[1]Hokkaido University of Science, Sapporo, Japan
[2]Hokkaido University, Sapporo, Japan
[3]Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany

The Nb_2Co_7 phase shows interesting features and is considered to be a promising candidate for a new crystal-structure-dependent “mille-feuille structure” material. The authors have revealed that a metastable $L1_2$ Co_3Nb ordered phase forms in this system and is considered to play the role of effective nucleation sites for precipitation of Nb_2Co_7. In the present study, microstructural evolution with or without the formation of Co_3Nb was investigated in detail in order to elucidate the effect of Co_3Nb on the precipitation behavior of Nb_2Co_7.

The Co−3.9 at%Nb alloy was prepared and was cut into small pieces. They were homogenization heat-treated in the differential thermal analyzer (DTA) at 1240˚C in order to attain a single-phase fcc-Co solid solution. Some samples were subsequently cooled to 900˚C or 1000˚C and were kept for up to 100h without formation of Co_3Nb, while others were directly cooled from 1240˚C to room temperature to preform Co_3Nb, and they were heated again to 900˚C or 1000˚C and were kept for up to 100h. Microstructure and crystal structure were observed and analyzed by SEM and EBSD. Compression tests were also conducted.

After isothermal heat treatments, equilibrium Nb_2Co_7 with plate-like morphologies was finely dispersed in the Co matrix. Microstructures are similar between samples with or without the formation of Co_3Nb. However, the microstructure is much finer in the samples with preforming Co_3Nb than those without preforming Co_3Nb. The growth direction of Nb_2Co_7 is parallel to the close-packed plane trace direction. It indicates that Nb_2Co_7 preferentially grows along a close-packed plane and hence plate-like morphology. As a result of compression tests, samples show a good deformability without breaking nor delaminating of Nb_2Co_7, while samples without formation of Nb_2Co_7, i.e. only Co_3Nb, show almost no deformability. It implies that mechanical properties will be controlled by utilizing metastable Co_3Nb in Co solid solution.

The authors would like to thank Mr. Kenji Ohkubo at Hokkaido University for his works and suggestions. This work was supported by a grant from JSPS KAKENHI for Scientific Research on Innovative Areas “MFS Materials Science (Grant Numbers JP18H05482).

O9

Isothermal formation of crystalline-amorphous nano-eutectoids during nitriding

S. Kante, A. Leineweber
Institute of Materials Science, TU Bergakademie Freiberg, 09599 Freiberg, Germany

Nitriding in NH_3/H_2 gas mixtures is employed to improve the tribological and corrosion properties of Fe base alloys. A high chemical potential of N is generated at the material's surface, which is thermodynamically related to the partial pressures of NH_3 and H_2. As a consequence, dense compound layers composed γ'-$Fe_4(C,N)$ and/or ε-$Fe_3(N,C)_{1+x}$ develop in the surface-adjacent region of pure α-Fe and low-alloy steel during nitriding. In Si-rich alloys, e.g. Si steel and cast irons, the compound layer formation is insufficiently understood. Unusual growth morphologies, complex growth kinetics and unexpected phase compositions occur, all of which originate from a negligible solubility of Si in Fe nitrides in conjunction with a low mobility of Si and slow precipitation kinetics of amorphous Si nitride in α-Fe [1].

This contribution addresses the compound layer formation in white-solidified Fe−3.5 wt.%C−1.5/3 wt.% Si alloys, which are composed of Si-rich ferritic and pearlitic regions, coarse Si-free eutectic cementite and a small volume fraction of $Fe_{23}Si_5C_4$. Nitriding conditions known to yield the formation of single-phase γ' in pure α-Fe were employed, however, a nanostructure composed of amorphous Si-rich rods/lamellae (X) embedded in a crystalline ε matrix has formed in the pearlite and ferrite. Alike, $Fe_{23}Si_5C_4$ has decomposed into a nanostructure of amorphous Si-rich rods/lamellae (X) embedded α-Fe. Both nanostructures may be considered as product of isothermal eutectoid reactions, $\alpha \rightarrow \varepsilon + X$ and $Fe_{23}Si_5C_4 \rightarrow \alpha + X$, which are driven by the gradient in the N chemical potential induced by the nitriding atmosphere, similar to the formation of δ-pearlite [2]. In the current case, however, the eutectoid transformations involve the cooperative growth of a crystalline and an amorphous phase. Besides, the reaction $\alpha \rightarrow \varepsilon + X$ implies the formation of α/ε phase boundaries, which are incompatible with available thermodynamic descriptions of the Fe−C−N(−Si) phase diagram at the process temperature. The unexpected stability of the nanostructured ε and α/ε phase boundaries is discussed.

References:

[1] S.R. Meka et al.: "Unusual iron nitride formation upon nitriding Fe−Si alloy", Metall. Mater. Trans. A 51 (2020) 3154-3166.
[2] M. Hillert and B. Uhrenius: "Eutectoid and peritectoid reactions in alloyed steel", Scand. J. Metall. 1 (1972) 223-230.

O10

Employing processing in a temperature gradient for synthesizing pure intermetallic phases

S. Lippmann[1], I. Saenko[2], O. Fabrichnaya[2], M. Rettenmayr[1]
[1]Friedrich-Schiller-University Jena, Otto Schott Institute of Materials Research, Jena, Germany
[2]Technische Universität Bergakademie Freiberg, Institut für Werkstoffwissenschaft, Freiberg, Germany

Synthesizing intermetallics as single-phase material often requires a more sophisticated technique than the simple metallurgical route of melting/solidification. For incongruently melting phases, before the target phase a primary phase will generally form that does not completely disappear upon annealing. For congruently melting stoichiometric phases, the composition of the initial materials needs to be adjusted with high precision to avoid the precipitation of secondary phases. This becomes less and less feasible with increasing number of alloying components. Densification of compressed powders by sintering does not necessarily lead to a better result, since the large surface to volume ratio of the powder particles leads to a covering oxide layer whose thickness is unknown and changes the net concentrations of the metallic part of the powders.

Synthesis of pure intermetallic phases can also be achieved, if samples of a different concentration than the target concentration are partially melted and subsequently resolidified in a temperature gradient (1). In the temperature and concentration range of the solid/liquid equilibrium, intermetallic phases form as single-phase during the resolidification of the partially melted region. The choice of the initial composition is crucial, it determines the minimum fraction of solid in the temperature gradient, the liquidus temperature and thus the processing temperature range.

Single-phase intermetallics are a prerequisite for the precise measurement of thermodynamic and thermophysical data, e.g. heat capacities that are key input data for the thermodynamic description of intermetallics. Al_3Ni, Al_3Ni_2, ε-CuSn and η/η’-CuSn serve as examples for the synthesis, analysis and subsequent thermodynamic description from 0K to the decomposition temperature.

References:

[1] S. Lippmann, R. H. Kemsies, M. Schick, B. Milkereit, O. Kessler, M. Rettenmayr, K. Hack: „Synthesis of pure intermetallic phases on the example of the ternary phase t_1 in the system Al−Fe−Ni”, Intermetallics 105 (2019) 107-112.

O11

Equilibrium vs. kinetics in alloy nanoparticles

R. Ferrando
Physics Department, University of Genoa, Via Dodecaneso 33, 16146, Genoa, Italy

The structures of the nanoparticles observed in the experiments are very often the result of a complex interplay between equlibrium and non-equilibrium (kinetic) effects. Kinetic effects are even more important in alloy nanoparticles, because in these systems both geometric shape and chemical ordering need to be equilibrated. In order to disentangle equilibrium from kinetics in the experiments, computer simulations are of great help. Here we consider a series of systems (Ag−Au [1], Pt−Pd [2], Ag−Pt [3], Au−Co [4,5]) in which different types of nanoalloy structures are produces, from core-shell, to multi-shell, to quasi-Janus, to randomly intermixed and to phase-ordered. The driving forces at the origin of these structures are discussed comparing experimental and simulation results.

References:

[1] T.-W. Liao et al: “Unravelling the nucleation mechanism of bimetallic nanoparticles with composition-tunable core-shell arrangement”, Nanoscale 10 (2018) 6684-6694.
[2] D. Nelli, A. Krishnadas, R. Ferrando, C. Minnai: “One-step growth of core-shell (PtPd)@Pt and (PtPd)@Pd nanoparticles in the gas phase”, J. Phys. Chem. C (2020) submitted.
[3] J. Pirart, A. Front, D. Rapetti, C. Andreazza-Vignolle, P. Andreazza, C. Mottet & R. Ferrando: “Reversed size-dependent stabilization of ordered nanophases”, Nature Communications 10 (2019) 1982.
[4] D. Nelli, R. Ferrando: “Core-shell vs. multi-shell formation in nanoalloy evolution from disordered configurations”, Nanoscale 11 (2019) 13040-13050.
[5] J.-P. Palomares-Baez, E. Panizon, R. Ferrando: “Nanoscale Effects on Phase Separation”, Nano Letters 17 (2017) 5394-5401.

O12

Thermodynamic study of the binary P−Pt system

L.Y. Schmitt, U.E. Klotz, M. Eisenbart
Research Institute for Precious Metals and Metal Chemistry (fem), Katharinenstrasse 17, 73525 Schwaebisch Gmuend, Germany

Since platinum phosphides gain increasing interest in technical applications e.g. as catalyst (PtP_2) or as a master alloys for amorphous Pt-based alloys, a detailed look into their thermodynamic behavior would be worthwhile. The latest version of the P−Pt phase diagram is based on studies of W. Blitz and F. Weibke from 1935 which present two stoichiometric phases and two types of non-variant phase transitions: a eutectic and a monotectic reaction. The previous work contains a thermodynamically suspicious region around the stoichiometric phase $Pt_{20}P_7$ where the number of phases is not in accordance to the Gibbs phase rule. Since the data have not been updated for a long time, a critical evatranluation as well as an experimental update appear to be necessary.

In this study a series of binary P−Pt alloys were prepared by inductive melting of red phosphorus (P) and platinum (Pt) in a ceramic crucible with subsequent centrifugal casting into a copper mold. The alloying process is challenged by the high melting temperature of platinum (ca. 1760°C) and the low vaporization temperature of phosphorus (ca. 550°C). As-cast and heat treated samples were compared to each other in order to gain more insight into their crystallization behavior and the equilibrium phases. The methods used for the investigation are X-ray scattering, chemical (ICP) and thermal (DTA) analysis. The microstructure was evaluated by metallographic sections. The evaporation of phosphorus was a significant limiting factor in DTA measurements concerning the maximum temperatures and heating rates.

The cast samples show segregation due to the miscibility gap in the liquid. The metallographic sections reveal the existence of platinum dendrites, a eutectic microstructure and two stoichiometric phases. Their quantity depends on the P-content of the alloy. With an average P-content near the suspicious phase region, where one transition is obviously missing, a further eutectic microstructure with PtP_2 is also visible. Its appearance suggests a peritectic phase transition to $Pt_{20}P_7$. By thermal analysis a third non-variant phase transition could be assumed in addition to the eutectic and monotectic reactions.

O13

Experimental study and thermodynamic modelling of the Al_2O_3–MnO system

O. Fabrichnaya, M. Ilatovskaia
TU Bergakademie Freiberg, Institute of Materials Science, 09599 Freiberg, Germany

The Al_2O_3-based materials were suggested as ceramic filter for steel and Al-alloy filtration. The aim of this study is to investigate experimentally the systems relevant to ceramic filters and derive correspondent thermodynamic descriptions. The Al_2O_3–MnO system is essential for steel industry. According to available experimental results, manganese is the main reactive alloying element in steel in combination with oxide ceramics.

The phase relations and thermodynamic properties of the Al_2O_3–MnO system were experimentally studied in several woks and several thermodynamic descriptions are also available. The advanced modelling of spinel phase taking into account different valent states of Mn and distribution of Al^{+3}, Mn^{+2}, Mn^{+3} and Mn^{+4} between tetragonal and octahedral sublattices was published [1]. However, the melting character of the $MnAl_2O_4$ spinel phase is still not established to be congruent or peritectic by reaction $L + Al_2O_3 \leftrightarrow MnAl_2O_4$. The $MnAl_2O_4$ compound has been prepared by co-precipitation routine described in Ref. [2] and then annealed at 1100°C followed by air-quenching. XRD confirmed the presence of pure $MnAl_2O_4$ spinel. Melting behaviour of the $MnAl_2O_4$ has been checked by DTA followed by microstructure investigation using SEM/EDX. Heat capacity measurements of the spinel compound have been carried out in the temperature range between −70°C and 600°C using DSC. Obtained data were fitted using Maier-Kelley equation: $C_p(J \cdot mol^{-1} \cdot K^{-1}) = 160.69 + 0.01444 \cdot T - 3.52381 \cdot 10^6 \cdot T^{-2}$ and appeared in agreement with results of Navarro et al. [2]. In the present work non-congruent melting of the $MnAl_2O_4$ at 1992 K was indicated. Temperature and composition of eutectic reaction $L \leftrightarrow MnO + MnAl_2O_4$ were determined as 1804 K and 78 mol. % MnO, accordingly. The experimental data obtained in the present study were used to derive thermodynamic description of Al_2O_3–MnO system.

References:

[1] S. Chatterjee, I.-H. Jung: ”Critical evaluation and thermodynamic modeling of the Al−Mn−O (Al_2O_3–MnO–Mn_2O_3 system”, J. Eur. Ceram. Soc. 34 (2014) 1611-1621.
[2] R.C.S. Navarro, A.M.C. Gomez, R.R. de Avillez: ”Heat capacity of stoichiometric Al_2MnO_4 spinel between 2 and 873 K”, Calphad 37 (2012) 11-17.

O14

Thermodynamic database development for the ZrO_2−MgO−MnO_x system

I. Saenko, O. Fabrichnaya
Institute of Materials Science, Freiberg University of Mining and Technology, Freiberg, Germany

Materials based on the ZrO_2−MgO−MnO_x system are of interest as directionally solidified eutectic materials [1]. Moreover, phase relations in the ZrO_2−MgO−MnO_x system play essential role for the development of TRIP-Matrix-Composite strengthened by particles of MgO partially stabilized zirconia (Mg-PSZ) [2]. Thereby, manganese provides good adhesion bonding between the steel matrix and the Mg-PSZ ceramics [3]. Therefore, knowledge of phase relations in the ZrO_2−MgO−MnO_x system is important to improve the bonding of Mg-PSZ to the steel matrix and simulate any influence of Mn to the stability of the ceramic particles.

Thermodynamic description of ZrO_2−MgO−MnO_x was derived for the first time using available experimental data on phase relations in air and protective gas atmosphere [4]. Solid solution of ZrO_2, as well as MgO−MnO-based solid solutions were modelled using compound energy formalism. The liquid phase was described by the two-sublattice model for ionic liquid. Ternary interaction parameters were optimized based on available experimental data [4]. The obtained thermodynamic description was verified by interpretation of DTA-TG. Calculated phase fraction diagrams were used to interpret observed heat effects and mass loses.

The current database can be used for further thermodynamic modelling of the high-order systems for the development of the TRIP-Matrix-Composites. Moreover, the thermodynamic description has potential for the further study of directionally solidified eutectic materials based on the ZrO_2−MgO−MnO_x system.

References:

[1] W.J. Minford et al.: “Crystallography and Microstructure of Directionally Solidified Oxide Eutectics”, J. Am. Ceram. Soc. 62 (1979) 154-157.
[2] H. Biermann et al.: “Microstructure and Compression Strength of Novel TRIP-Steel/Mg-PSZ Composites”, Adv. Eng. Mater. 43 (2009) 1000-1006.
[3] M. Kirschner et al.: “Forming Complex Graded and Homogeneous Components by Joining Simple Presintered Parts of TRIP-Matrix Composite through Powder Forging” Metals 10 (2020) 543.
[4] D. Pavlyuchkov et al.: “Phase Equilibria in the ZrO_2−MgO−MnO_x System” J. Am. Ceram. Soc. 99 (2016) 3136-3145.

O15

Thermodynamic properties of the Fe−N system: Influence of atomic ordering and magnetism

A. Leineweber
Institute of Materials Science, TU Bergakademie Freiberg, 09599 Freiberg, Germany

The binary Fe−N system shows strong similarities but also some special differences with the Fe−C system. First of all, at ambient temperature and metallurgically relevant elevated temperatures, all known intermediate phases (foremost Fe_3C in the Fe−C system; the ordered $\alpha/\gamma\delta$-Fe_4N and ε-Fe_3N_{1+x} phases) are metastable with respect to the $\alpha/\gamma/\delta$ terminal solid solutions and graphite or N_2 gas. Hence, to illustrate the phase equilibria involving intermediate carbides and nitrides, phase diagrams depicting metastable equilibria are used. Indeed, Fe−N analogues of the Fe−C/Fe−Fe_3C double diagrams can be formulated. Secondly, in both systems the interstitial element stabilizes the closed-packed cubic (ccp) based γ as compared to the body-centred cubic (bcc) based α/δ phases. The most stable intermediate phases in the Fe−N system are based on simple Fe arrangements with N in octahedral sites, whereas in the Fe−C systems, the most prominent intermediate phases, like Fe_3C, are structurally more complex. Both the Fe−C and Fe−N systems gain interest due to their relevance in metallurgy of Fe-base alloys, their magnetic properties but also due to their potential relevance for the Earth's core.

The presentation will review the current state on the thermodynamics of the Fe−N system, not only at ambient but also at elevated pressure [1]. It is shown how the structural, magnetic and vibrational properties of the known but also of hypothetical phases [2,3], in some sense, all affect their measurable thermodynamic properties and their occurrence in phase diagrams [1,4].

References:

[1] M.H. Wetzel, M.R. Schwarz, A. Leineweber: "High-pressure high-temperature study of the pressure induced decomposition of the iron nitride γ'-Fe_4N", J. Alloys Compd. 801 (2019) 438-448.

[2] A. Leineweber, T. Hickel, B. Azimi-Manavi, S. Maisel: "Crystal structures of Fe_4C vs. Fe_4N analysed by DFT calculations: fcc-based interstitial superstructures explored", Acta Mater. 140 (2017) 433-442.

[3] S. De Waele, K. Lejaeghere, E. Leunis, L. Duprez, S. Cottenier: "A first-principles reassessment of the Fe−N phase diagram in the low-nitrogen limit, J. Alloys Compd. 775 (2019) 758-768.

[4] H. Göhring, O. Fabrichnaya, A. Leineweber, E.J. Mittemeijer: "Thermodynamics of the Fe−N and Fe−N−C systems: the Fe−N and Fe−N−C phase diagrams revisited", Met. Mater. Trans. A 47A (2016) 6173-6186.

O16

Development and application of CALPHAD databases for Ti- and TiAl-based alloys

Y. Yang, Q. Chen, A. Engström, H.-L. Chen
Thermo-Calc Software AB, Råsundavägen 18, 169 67 Solna, Sweden

Titanium alloys are extensively used in the chemical, medical and aerospace industries attributing to their high specific strength, excellent corrosion resistance and biological compatibility. Intermetallic TiAl-based alloys offer a good balance of properties due to their high specific yield strength, good oxidation and creep resistance. To further improve the demanding high temperature properties such as creep strength and corrosion resistance, the development of the next generation of alloys is going on. CALPHAD provides a key approach to accelerate the understanding and design of multicomponent alloys with a demanding balance of different properties, since the traditional experimental approach can be onerous and expensive even for a binary system. The accuracy of CALPHAD simulations depends on the quality of the database being used.

In this talk, we are going to present our achievements on the recent development of a thermodynamic database (including data of thermo-physical properties, such as molar volume, viscosity, etc.) and a compatible atomic mobility database for Ti and TiAl based alloys in the spirit of the CALPHAD approach. The present modeling of the common phases for γ-TiAl based alloys which are known for their complexities will be highlighted. We will also demonstrate the versatility of CALPHAD simulations, which are made possible with the add-on modules in the Thermo-Calc software. The application examples include but are not limited to thermodynamics and phase equilibria within the scope of Ti- and TiAl-based alloys. Such simulations are expected to efficiently support alloy developments, as well as to promote process simulations with accurate prerequisites.

O17

High temperature phase equilibria in ternary Ti−Al−Nb alloys

B. Distl, M. Palm, F. Stein
Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany

TiAl-based alloys are in the focus of intensive research since more than three decades due to their capability to substitute Ni-based superalloys in high-temperature, high-strength applications such as turbine blades. Alloys for these applications are mainly based on a combination of the two intermetallic phases γ (TiAl) and α_2 (Ti_3Al). With the addition of elements such as Nb or Mo, so-called (βTi)-stabilizers, the phase field of cubic (βTi) is shifted to higher Al contents compared to the binary TiAl-system at temperatures above 1000°C. This is beneficial for the hot working capabilities of the otherwise very brittle alloys. Therefore, the high-temperature phase equilibria play an important role in alloy design of next generation TiAl-based alloys. Even though a lot of research has been done, the available literature data about phase equilibria above 1000°C in the ternary Ti−Al−Nb system are often contradicting each other. Therefore, the aim of the research presented here on high-temperature phase equilibria in the ternary Ti−Al−Nb system is to clarify these contradictions. The research is carried out within the scope of the CleanSky 2 EU-project ADVANCE, which uses the phase equilibria data to improve an existing CALPHAD database for TiAl-based alloys and to speed up the development of next-generation alloys based on titanium aluminides.

O18

Experimental investigation of phase equilibria in the Ti−Al−Zr system for improvement of a CALPHAD database

Z. Kahrobaee, F. Stein, M. Palm
Max-Planck-Institut für Eisenforschung GmbH (MPIE), D-40237 Düsseldorf, Germany

TiAl-based alloys are candidates for the next generation of aircraft engines components, which demands cost-efficient and light-weight materials for low fuel consumption and less CO_2 and NO_x gas emissions. However, the mechanical properties of TiAl-based alloys still can be improved by alloying elements. The addition of elements such as Zr can enhance creep and oxidation resistance significantly. Alloy developments today essentially rely on CALPHAD (CALculation of PHAse Diagram) modelling, by which phase diagrams and phase transitions can be calculated. While modelling relies on a sound database, obtaining reliable data for Ti−Al(−X…) systems is challenging, as a variety of experimental difficulties exist, e.g. small amounts of impurities such as oxygen can already lead to significant changes in phase equilibria.

Within a large-scale collaborative project, the partners Helmholtz-Zentrum Geesthacht, Germany, Montanuniversität Leoben, Austria, Thermo-Calc Software AB, Sweden and MPIE will improve thermodynamic data for a number of Ti−Al−X(−Y) systems for the next generation of advanced CALPHAD databases for TiAl alloys [1]. As a part of this ambitious project, a comprehensive assessment of the literature has been done. Accordingly, to resolve the controversies among the existing experimental results, a series of Ti−Al−Zr alloys has been prepared by crucible-free levitation melting from high-purity elements. Alloys were heat treated at different temperatures between 1000−1300 °C for 24−1000 h. Compositions of the alloys and their impurity contents in the as-cast condition and after heat treatment were established by wet chemical analysis. Phases were identified using X-ray diffraction (XRD) and compositions of the coexisting phases were determined by electron probe microanalysis (EPMA). The experimental results are compared to previous experimental and calculated data and revised isothermal sections have been established.

References:

[1] Next Generation TiAl Alloys Advanced by New European Consortium
https://news.thermocalc.com/next-generation-tial-alloys-advanced-by-new-european-consortium

O19

Short-range ordering of carbon in liquid alloys of 3D-block transition metals

M.K. Paek, J. Jeon, D. Lindberg
Department of Chemical and Metallurgical Engineering, Aalto University, Espoo, 02150, Finland

The strong interactions between C and 3d-block transition metals (e.g., Cr, Mn, Fe, Co, Ni) were thermodynamically analyzed. The liquid solution properties of binary systems containing C showed significant asymmetry due to the Short-Range Ordering (SRO) of C with the transition metals. Using the Modified Quasichemical Model (MQM) in the pair approximation [1], the C containing binary systems were re-optimized using all available experimental data in the literature. In particular, the partial enthalpy of mixing of C in binary liquid solutions has been scarcely considered by the previous optimization based on the random mixing model. On the other hand, the present model successfully reproduced the partial Gibbs energy and enthalpy of mixing data simultaneously. By considering the SRO with the asymmetric interpolation method, this model can also minimize the ternary or high-order parameters to reproduce the liquid solution properties of the C containing multicomponent systems.

References:

[1] A.D. Pelton, S.A. Degterov, G. Eriksson, C. Robelin, Y. Dessureault: “The modified quasichemical model I—binary solutions”, Metall. Mater. Trans. B 31B (2000) 651-659.

O20

Exploiting temperature and concentration gradients for data mining

M. Rettenmayr
Friedrich-Schiller-Universität Jena, Otto Schott Institute of Materials Research, Jena, Germany

Industrial R&D departments and also academic research facilities appear to be more and more pressed for time when working on improvement of existing materials or developing new materials. Computer simulations may be employed to support experimental efforts, but they heavily depend on reliable material data. Similarly, the design of components requires detailed knowledge about material properties. It is evident that the availability of comprehensive data bases accelerates material development efforts. However, for many material classes, data bases are incomplete, contain estimations or extrapolations, or are in the worst case non-existent.

One of the goals of research in materials science should thus be to provide the necessary data. However, conventional ’data mining’ is often tedious, requiring waiting times for thermal equilibrium or steady states to be achieved. The development of high-throughput methods is one of the pathways to larger data bases that contain data on pure substances and also binary and multicomponent alloys. Automated production and evaluation of a series of compositions or thermodynamic states of alloys is certainly a viable way to improve the availability of data.

Methods for efficient data mining that are at present being developed at FSU Jena are based on graded samples. Temperature gradients are used to create concentration gradients, and the changes of properties with concentration and temperature are evaluated with state-of-the-art experimental and numerical methods. The state of the research is such that the methods can be accessible for pertinent research labs. With respect to the synthesis of the appropriate graded samples, distinct development steps have been achieved recently. The potential of the evaluation of such samples is demonstrated for thermodynamic data (solidus and liquidus lines/surfaces, among others), kinetic data (frequency factors and activation energies of diffusion coefficients) and thermal data (thermal diffusivity, thermal conductivity and heat capacity).

O21

Experimental setup for controlled pulse heating to investigate composition invariant phase transitions

T. Kaaden, S. Lippmann
Friedrich-Schiller-Universität Jena, Otto Schott Institute of Materials Research, Löbdergraben 32, 07743 Jena, Germany

Concentration-invariant transformations such as martensitic or massive transformation are a common class of phase transformations. Experimental investigations on such transformations are demanding inasmuch as generally very high cooling (quenching) or heating rates are necessary to avoid alternative types of phase transformations, and especially defined holding times at intermediate or high temperatures are hard to adjust. One of the possible techniques to achieve the required heating rates is direct heating with high electric current pulses. In the experimental set-ups using pulse heating that are described in the literature, a single capacitor charged with high voltage is completely discharged into a sample of high electric resistance (e.g. a thin wire) which subsequently cools down to room temperature by convective heat transfer to the surrounding air. The resulting temperature change is generally measured by a single thermocouple that is welded to the wire, where it thermal capacity exerts an influence on the measured temperature. Such pulse heating set-ups allow for a single heating process and no subsequent isothermal holding.

For the investigation of massive transformation, a pulse heating device using low voltage and high currents has been developed. Instead of a single high voltage capacitor, multiple supercapacitors are used to provide electric energy resulting in a constant power output as they are only marginally discharged during the experiment. Temperature is measured with a high speed mid-wavelength infrared camera that provides high resolution temperature data along the length of the sample with no thermal influence on the temperature distribution by the measurement. The process is precisely controlled in terms of pulse current and pulse length, allowing to set holding times at intermediate and high temperatures, and high pressure forced convection air cooling of the sample allows a cycling operating mode with rapid rates for both heating and cooling. Samples may be significantly larger as compared to the thin wires used in earlier work. For experimental investigation Cu−Zn−Al alloys are used (1).

References:

[1] S. Lippmann, T. Kaaden, P. Wutzler and M. Rettenmayr: “The effect of adding Al on the occurrence and progress of massive transformation in Cu−Zn”, Materialia 7 (2019) 100367.

O22

Principal concept of database creation aiming holistic views on the fundamentals of materials science

P. Villars
Material Phases Data System (MPDS), 6354 Vitznau, Switzerland

Motivation for the creation of the PAULING FILE (LPF) was the following consideration. One of the most challenging tasks in material science is the design of new inorganic solids with pre-defined intrinsic physical properties. In general, two different approaches are explored:

1. The first one is to simulate the motion of the atoms of an inorganic solid as well as their electronic interactions as close to reality as possible by using simulations on the quantum-mechanical level.
2. The second approach is the use of modern computer technology to search for rules and correlations implied in experimentally determined materials data and use them in inorganic solids design.

The second approach is extremely depending on the availability of a sufficiently large number of experimentally determined data of appropriate quality. To get holistic view required to close this non-existence and was for us the motivation to create the LPF.

This was done as follows:

1. The first goal is to create and maintain a comprehensive inorganic solids database for all inorganic solids (no C–H bonds), covering crystallographic data, diffraction patterns, intrinsic physical properties and phase diagrams. An important aspect along with completeness is the quality of the data.
2. In longer term, new inorganic solid design tools will be created, which will more or less automatically search the database for correlations needed for a purposeful and rapid design of new inorganic solids with pre-defined intrinsic physical properties.

The PAULING FILE is now by far the world largest fundamental materials database and includes unary, binary, ternary and multinary inorganic solids (see https://mpds.io/). It contains about 350’000 structural data sets, 500’000 intrinsic physical property values, as well as over 45’000 phase diagrams. To reach this result, over 200’000 pre-selected scientific publications have been processed and critically analyzed. Data are exclusively taken from original publications. The linkage of the four different groups of data is considered as most important, therefore the PAULING FILE was designed as phase-oriented inorganic solids database using a relational database system. This was achieved by the creation of a distinct phases table as well as all required internal links.

Finally data-mining using the LPF resulted in the support of the 4 core principles:

First cornerstone: Infinitely many chemical element combinations; Second cornerstone: Core principle that defines compound formation; Third cornerstone: Core principle that defines ordering of chemical elements within a structure type; Fourth cornerstone: Core principle that links the position of chemical elements within a structure type ↔ in the Periodic System.

The PAULING FILE in combination with different data mining techniques give nice examples of holistic views, as its word meaning is defined: “The idea of holistic view is that the whole is greater than the sum of its parts.”

O23

Combining *ab initio*, machine learning and human learning for a CALPHAD database of chemical compound space

M. to Baben, F. Tang, C. Aras, K. Hack
GTT-Technologies, Herzogenrath, Germany

The SGTE Solutions database, one of the largest thermodynamic databases available to date, contains the description of 680 binary systems and has grown by ~20 systems per year over the last 30 years. Extrapolating these growth rates, it will take another 185 years until all 4371 binary systems among the 94 elements naturally occurring on earth will be described.

To accelerate the exploration of chemical compound space, GTT-Technologies uses human and machine learning to build CALPHAD databases based on *ab initio* calculations. Here, the major steps in aiMP (*ab initio* Materials Project [1,2]) development will be presented, which involve raw data curation and accuracy assessment, identification of correlations, machine learning of S298K, and finally quality control. Phase diagrams will be shown that resemble many features of phase diagrams calculated based on full thermodynamic assessments. A few cases will be discussed where the aiMP calculated phase diagram is in major disagreement with assessed diagrams and the source of error will be discussed.

References:

[1] Jain, A. et al.: “The Materials Project: A materials genome approach to accelerating materials innovation”, APL Materials 1.1 (2013) 011002.
[2] https://gtt-technologies.de/data/#aimp-ab-initio-materials-project

O24

Artifical materials intelligence (AMI) to accelerate discovery of novel superalloys

I. Roslyakova[1], S. Zomorodpoosh[1], M.A. Ali[1], A. Obaied[1], I. Steinbach[1]
[1]Interdisciplinary Centre for Advanced Materials Simulation (ICAMS), Ruhr-University Bochum
Universitätstr. 150, 44801, Bochum, Germany

A novel modeling strategy, which combines artificial intelligence (AI) with artificial materials (AM) will be proposed and called Artificial Materials Intelligence (AMI). Established physical laws, cross-correlations between different materials properties and well developed thermodynamic databases will be considered during the development and application of AMI. Machine learning will be used if the established physical basis is insufficient for predictive materials models. The application of such combined methodology allows keeping as much physics as possible on the one side and reducing the number of exploratory variables and required data on the other. The proposed study demonstrates the applicability of high-throughput simulations and physically-based data-driven modelling strategy combined in AMI to predict mechanical properties of complex, microstructure dominated materials, such as Ni- and Co-based super alloys, and to accelerate discovery of optimal chemical composition for these alloys.

O25

Numerical alloy design using CALPHAD-based property models

B. Wahlmann, M. Markl, C. Körner
Department of Materials Science, Friedrich-Alexander-Universität Erlangen-Nürnberg, Martensstr. 5, 91058 Erlangen, Germany

Alloy design is a challenging task due to the vast amount of possible compositions. Trial-and-error approaches that require the fabrication and testing of tens or hundreds of alloy heats are replaced more and more by thermodynamic calculations to select candidate alloys with desirable properties, as it is practiced in Integrated Computational Materials Engineering. With this, the experimental effort can be reduced significantly.

In this context, CALPHAD calculations are often used to scan composition spaces for promising alloys or a posteriori to rationalize characteristics of the material behavior. We have developed a tool, MultOpt++, that employs thermodynamic-based descriptions of alloy properties and performance as the input of an optimization algorithm, which is computationally more efficient than the conventional scanning of composition space. Optimization also allows the identification of the best possible alloys regarding the goal properties within specified composition boundaries. These optimal compositions can serve as guides for the selection of alloys for experimental characterization. The properties are either directly provided by CALPHAD calculations (phase fractions, phase transition temperatures) or derived from thermodynamic quantities (lattice parameters, creep resistance).

We used MultOpt++ for the development of a rhenium-free, low-density nickel-base superalloy with creep resistance comparable to commercial superalloys. However, the employed models only describe alloy properties in the equilibrium state. In practice, this is not adequate. Alloy solidification is better described by the Scheil model, which assumes local equilibrium at the solid-liquid interface. Through this, the presence of non-equilibrium phases, extended solidification intervals, the formation of eutectic, and the strength of elemental segregation can be predicted.

Furthermore, the calculated composition profiles allow the specification of further optimization goals based on the best or worst property values encountered in the alloy or the distribution of property values to more accurately represent the characteristics of an alloy.

These non-equilibrium calculations are significantly more computationally expensive than single equilibrium calculations. We present approaches to expedite the calculations by using metamodeling and approximate models based on the analytical Scheil equation so that these can be included efficiently in the optimization procedure.

O26

Fast Scanning Chip calorimetry: New measurement capabilities at high controlled rates

G. Wilde
University of Muenster, Institute of Materials Physics, Muenster, Germany

Calorimetric analyses involve measurements of thermodynamic properties as well as experimental analyses of phase transformations and their kinetics. The latter often requires measurements to be performed during heating or cooling, i.e. while applying a temperature change in a controlled manner. Traditionally, the range of rates that was applicable for controlled measurements was restricted to a few tens degrees per minute for either heating or cooling. Fast Scanning Chip calorimetry (FSC) now offers fascinating new opportunities for calorimetric analyses that are based on the unprecedentedly wide range of heating and cooling rates that are accessible for controlled experiments. Examples for new applications include *in-situ* vitrification of metallic glasses, statistics-based analyses of phase transition kinetics or analyses of the very early stages of precipitation reactions. A short overview of the current state in the literature will be given.

Yet, while the calibration procedures for conventional methods, such as differential scanning calorimetry (DSC), are well known, new procedures needed to be established for fast chip calorimetry. These calibration routines are more involved as compared to DSC calibrations. Moreover, special attention is required concerning the reproducibility of the signal due to the sample material as well as concerning the absolute accuracy of the determined quantities.

In addition to a detailed discussion of the calibration of FSC, case examples are discussed that include quantitative nucleation kinetics analyses. Due to the high rates that are applicable, FSC offers ideal conditions for statistics-based measurements, such as nucleation kinetics analyses, that are based on obtaining a statistically significant dataset. Thus, applying high rates, i.e. performing many measurements per given time, allows achieving high statistical accuracy for the determined parameters. In this presentation, nucleation rates of the melting/solidification transformation as obtained from FSC measurements are discussed for case examples that display the opportunities offered and the issues encountered in FSC-based nucleation kinetics analyses.

O27

Thermal analysis with Gibbs inside

G. Fries[1], D. Ivanova[1], S. Tumminello[2], P. Presoly[3]
[1]Ruhr University Bochum, D-44801 Bochum, Germany
[2]German Aerospace Center, D-51147 Cologne, Germany
[3]Montanuniversität Leoben, A-8700 Leoben, Austria

Experimental results are extremely important to establish realistic Gibbs energies sets. They are, however, expensive to obtain: in time and in costs. Improvements to minimise these facts are therefore welcome. Boettinger and Katter [1] provide a full development about how to interpret DTA results using realistic models. Their method was used by Riani et al. [2], Tumminello [3] and Presoly [4]. In this contribution we revisited the method, creating a tool in python which prompts for the input of the equipment setups and measurement conditions. Combining this data with realistic models of melting and solidification provided by already existing Gibbs energy sets, a preliminary interpretation of the measured results can be provided.

A great potential of this method is to estimate which kind of transformations can be measured with the DTA/DSC method. Many solid-solid transformations and the formation of some precipitation show only a very small amount of heat change (data from Gibbs energy model) − in these cases the preliminary interpretation clear shows that the DTA/DSC method cannot resolve these transformations and other experimental method (dilatometry, X-ray diffractometric) will be more recommendable. This information will also save time and costs.

The authors invite equipment producers to introduce this protocol directly in their measurement devices providing what will allow the release of the measurement results with the preliminary simulation.The authors believe that this can be of great help for the equipment users and that can accelerate and low the cost of these experiments.

Note:

This work was partially presented in the Thermo-Calc users meeting 2020 in Aachen Germany.

References:

[1] W.J. Boettinger, U.R. Kattner: Metall. Mater. Trans. A 33A (2002) 1779
[2] P. Riano et al.: J. Alloys Compd. 487 (2009) 90.
[3] S. Tumminello et al.: J. Phase Equilibr. Diffus. 38 (2017) 273-287
[4] P. Presoly: PHD thesis, (2014) Leoben, Austria.

O28

Determining the Curie temperature of Ni using a temperature gradient evaluation method

S. Wilhelmy[1], A. Zimare[1], Q. Zhang[2], M. Rettenmayr[1], S. Lippmann[1]
[1]Friedrich-Schiller-Universität Jena, Otto Schott Institute of Materials Research, Jena, Germany
[2]Shagang School of Iron and Steel, Soochow University, Suzhou 215137, China

By heating one end of a rod-shaped sample, a temperature gradient forms along the sample axis. For evaluating the temperature gradient regarding thermal properties of the material, the heating process is carried out in a controlled manner, and temperature profiles along the sample axis are continuously recorded by an infrared camera. In a first step, the change of local temperatures in transient states is analyzed, and the thermal diffusivity α is calculated along the gradient employing an inverse numerical method [1], yielding the temperature dependence of α in the same step. In a second step, when heat flow through the sample and local temperature are constant, the steady state is evaluated, yielding the temperature dependent heat conductivity λ. The presented temperature gradient evaluation method allows the measurement of thermal properties as a function of temperature within a single experimental run.

In the temperature range around the Curie temperature, magnetic ordering is a major contribution to the specific heat capacity C_p, which is related to the thermal properties ($\alpha=\lambda/C_p$). High resolution characterization of the temperature profiles with an experimental set-up using state-of-the-art materials for isolation and scientific instrumentation allows for the determination of the Curie temperature based on variations in thermal conductivity and thermal diffusivity. The accuracy of the method is in the same order as that of other methods described in the literature.

References:

[1] Q. Zhang, S. Lippmann, A. Grasemann, M. Zhu, M. Rettenmayr: “Determination of temperature dependent thermophysical properties using an inverse method and an infrared line camera”, International Journal of Heat and Mass Transfer 96 (2016) 242-248.

O29

Knudsen effusion mass spectrometry: Application to the thermodynamic study of alloys

I. Nuta[1], C. Chatillon[1], S. Chatain[2], C. Guéneau[2]
[1]Univ. Grenoble Alpes, CNRS, Grenoble INP, SIMaP, F-38000 Grenoble, France 1130 rue de la piscine BP 75
38402 Saint Martin d'Hères, France
[2]Laboratoire de Modélisation, de Thermodynamique et de Thermochimie, CEA Saclay-DEN/DANS/DPC/SCP
91191 Gif-sur-Yvette Cedex, France

The high temperature mass spectrometry method is a standard method for the study of chemical equilibria at high temperature and vaporization processes. For studies involving complex mixtures, as alloys, the multiple Knudsen cell high-temperature mass spectrometry is the very usefull device to perform thermodynamic activity measurements. The present work summarizes the evolution of the efforts done in order to elucidate the real nature of the collected effusion beams by any detectors including the mass spectrometers in relation with different physico-chemical phenomena occurring at the effusion orifice or near the edges of these orifices such as spurious molecular flows.We illustrate it with the results obtained about the iron−zirconium system[1].

References:

[1] S. Chatain, C. Guéneau, and C. Chatillon: "High temperature mass spectrometry: Application to the thermodynamic study of the Fe−Zr system", Journal of Nuclear Materials 344 (2005) 281-284.

O30

Thermal stability of half-Heusler (Ti,Nb)FeSb alloys

P. Brož[1,2], F. Zelenka[1,2,3], J. Vřešťál[1,2], J. Buršík[2], A. Zemanová[2], G. Rogl[4,5], P. Rogl[4,5]
[1]Masaryk University, Faculty of Science, Department of Chemistry, Kotlářská 2, 611 37, Brno, Czech Republic
[2]Institute of Physics of Materials, Czech Academy of Sciences, Žižkova 22, 616 62, Brno, Czech Republic
[3]Thermo Fisher Scientific Brno s.r.o., Vlastimila Pecha 12, Brno 627 00, Czech Republic
[4]Institute of Materials Chemistry, University of Vienna, Währingerstraße 42, A-1090 Vienna, Austria
[5]Christian Doppler Laboratory for Thermoelectricity, Vienna, Austria

Half-Heusler (H-H) alloys with the structure formula XYZ, as a non-centrosymmetric structure variant of the Heusler alloys with the chemical formula X_2YZ, are known for their thermoelectric properties which can be optimized by doping the three individual sublattices with suitable elements. If volatile elements such as Sb or others are involved, the study of vaporization characteristics for long term thermal stability of these materials is of practical importance.

This contribution presents a study of thermal and phase stability of H-H alloys, (Ti,Nb)FeSb, prepared by hot pressing or by ball milling and hot pressing [1, 2], by means of thermal analysis and the Knudsen effusion method. The results supported by data from microstructure measurements and the measurement of the diffusion profiles are discussed in view of phase diagrams of the respective ternary systems [1, 2] and results of our previous investigation of the long term thermal stability of didymium doped p-type skutterudites [3].

Financial support by the Czech Science Foundation under the project GA 17-12844S, by the MEYS (Czech Republic) as Mobility 8J19AT011 and by the OEAD as WTZ-CZ02 is gratefully acknowledged.

References:

[1] A. Tavassoli, A. Grytsiv, G. Rogl, V.V. Romaka, H. Michor, M. Reissner, E. Bauer, M. Zehetbauer, P. Rogl: “The half Heusler system $Ti_{1+x}Fe_{1.33-x}Sb$ – TiCoSb with Sb/Sn substitution: phase relations, crystal structures and thermoelectric properties”, Dalton Trans. 47 (2018) 879-897.

[2] A. Tavassoli, F. Failamani, A. Grytsiv, G. Rogl, P. Heinrich, H. Müller, E. Bauer, M. Zehetbauer, P. Rogl: “On the half-Heusler compounds $Nb_{1-x}\{Ti,Zr,Hf\}_xFeSb$: Phase relations, thermoelectric properties at low and high temperature, and mechanical properties”, Acta Mater. 135 (2017) 263-276.

[3] F. Zelenka, P. Brož, J. Vřešťál, J. Buršík, G. Rogl, A. Grytsiv, P. Rogl: “Study of thermal stability of p-type skutterudites $DD_{0.7}Fe_3CoSb_{12}$ by Knudsen effusion mass spectrometry”, RSC Adv. 9 (2019) 21451-21459.

O31

2 1/2th generation CALPHAD databases: Extrapolating heat capacities of elements and compounds to 0K

A. Obaied[1], F. Tang[2], I. Roslyakova[1], M. to Baben[2]
[1]ICAMS, Ruhr-University Bochum, Universitätstr. 150, 44801, Bochum, Germany
[2]GTT-Technologies, Herzogenrath, Germany

With the increasing rate of newly developed materials, there is a noticeable increasing demand for accurate descriptions of thermophysical properties below the room temperature. Such demands make it essential to use modern data mining and machine learning techniques and provide a reliable description for the pure elements and compounds for low temperature ranges.

A few recent attempts were made to model the thermophysical behaviour below room temperature in the framework of the 3rd generation Calphad databases [1-4]. Nonetheless, accurate data for a large number of pure elements and the majority of known compounds are still unavailable to researchers. This is either due to the lack of data available for these models to fit, or because some of them are only valid for pure elements.

The proposed modelling work uses an automated approach to produce a robust and reliable thermophysical descriptions for a very wide range of pure elements and compounds. Cp and S at room temperature are used as only input to fit a Debye temperature plus one mathematically simple correction term. The Debye model can then again be fitted by a polynomial expression to enable the use of simple polynomials down to zero Kelvin.

This approach provides a straight-forward polynomial description for elements and compounds that can be universally utilized in different computational thermodynamic software. Moreover, they are more accurate than the solutions that rely on pure Einstein or pure Debye models.

References:
[1] Roslyakova et al.: Calphad 55 (2016) 165-180.
[2] J. Pavlů et al.: Calphad 51 (2015) 161-171.
[3] S. Bigdeli et al.: Physica status solidi (b) 252 (2015) 2199-2208.
[4] A. Khvan et al.: Calphad 60 (2018) 144-155.
[5] NIST-JANAF Thermochemical Tables, American Institute of Physics for the National Institute of Standards and Technology, 1998.

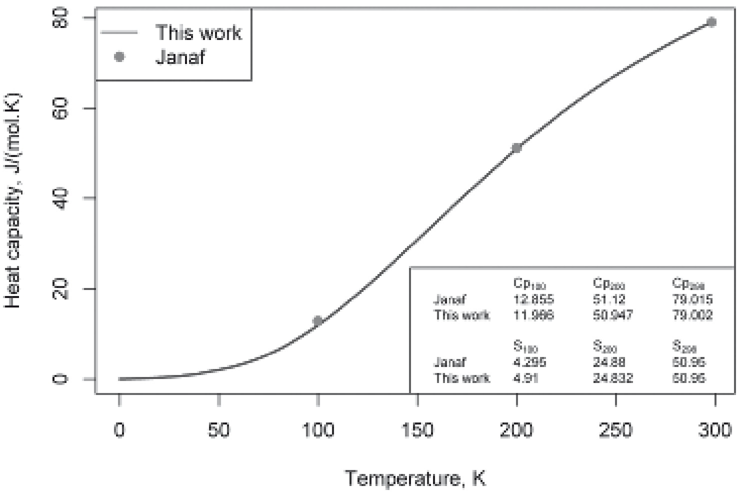


Fig.1: Specific heat curve for Al_2O_3 compared with data from JANAF [5]

O32

Pure elements: Do we know enough about them for 3rd generation of CALPHAD

A.V. Khvan[1], A.T. Dinsdale[2], I. Uspenskaya[3], N.M. Aristova[4]
[1]Thermochemistry of Materials SRC, NUST MISIS, Moscow, Russia
[2]Hampton Thermodynamics Ltd, UK
[3]Department of Chemistry, Lomonosov Moscow State University, 1-3 Leninskiye Gory, 119991 Moscow, Russia
[4]JIHT RAS, 13-2 Izhorskaya S, 125412 Moscow, Russia

A significant step in the development of CALPHAD took place between 1985 and 1991 when SGTE developed and published its database for the pure elements [1]. This database now forms the basis for almost all thermodynamic assessments for alloy systems and is the backbone of all commercial thermodynamic databases, which are widely used by materials scientists for the prediction of materials properties and also for the control of industrial plants and processes. However, now, there is growing awareness that these data and the way in which they are modelled will not be suitable for the needs of the materials science community for the next 25 years. A collaborative international research program is underway towards the development of a new set of data based on more physically realistic models to represent the variation of the thermodynamic properties of the crystalline and liquid phases with temperature and composition.

In the present talk we will discuss the new models based on the results of a series of “Ringberg” workshops [2] and highlight some of the issues the assessor faces during critical evaluation of experimental data using some recent examples where they have been applied.

Acknowledgements This work was carried out with financial support from the Ministry of Education and Science of the Russian Federation in the framework of Increase Competitiveness Program of NUST «MISiS» (№К2-2019-003), implemented by a governmental decree dated 16th of March 2013, N 211. The contribution from the co-authors from MSU was supported by by RFBR according to the research project № 20-03-00575.

References:

[1] A. Dinsdale: “SGTE data for pure elements”, Calphad 15 (1991) 317-425.
[2] M. Chase, I. Ansara, A. Dinsdale, G. Eriksson, G. Grimvall, H. Hoglund, H. Yokokawa:”Group 1: Heat capacity Models for Crystalline Phases from 0K to 6000K.” Calphad 19 (1995) 437.

O33

Application of machine learning methods to support the development of the 3rd generation CALPHAD database

I. Roslyakova, A. Obaied, S. Zomorodpoosh
Interdisciplinary Centre for Advanced Materials Simulation (ICAMS), Ruhr-University Bochum,
Universitätstr. 150, 44801 Bochum, Germany

Recently, one of the most intriguing topic in the CALPHAD community is the development of the third generation CALPHAD databases and their application to re-assessment of binary and ternary systems from 0K [1-5]. During the development of the third generation of CALPHAD databases, not only newly available DFT [4] and experimental data [5] should be considered to build a new pure elements database from 0 K, but the existing physical laws [6] and newly discovered relationships [7-9] between relevant thermodynamic properties should be established and integrated. Taking into account that the classical re-assessment procedure of high order thermodynamic systems is very time consuming, a combination of machine-learning (ML) methods with the well-established CALPHAD-type assessment will be presented as one of possible solution [10, 11]. In this work, we will show several successful partial applications of machine learning to accelerate and support the development the 3d generation CALPHAD database from 0K.

References:

[1] I. Roslyakova, et al.: CALPHAD 55 (2016) 165-180.
[2] Y. Jiang, et al.: CALPHAD 62 (2018) 109-118.
[3] Y. Jiang, et al.: Journal of Materials Research 110 (2019) 797-807.
[4] S. Bigdeli, et al.: CALPHAD 65 (2019) 79-85.
[5] A. Khvan, et al.: CALPHAD 60 (2018) 144-155.
[6] G. Grimvall: Thermodynamic properties of materials (1986).
[7] C.A. Becker: Phys. Status Solidi B 251 (2014) 33-52.
[8] A. Obaied, et al.: Calphad 69 (2020) 101762.
[9] D. Sergeev, et al.: J. Chem. Thermodynamics 134 (2019) 187-194.
[10] B. Bocklund, et al.: MRS Communications: Artificial Intelligence Research Letter 9 (2019) 618-627.
[11] N.H. Paulson, et al.: CALPHAD 68 (2020) 1-9.

O34

Precipitation in micro-alloyed steels for seamless line pipes

A. Schneider
Vallourec Deutschland GmbH, Theodorstraße 109, 40472 Düsseldorf, Germany

This presentation focuses on carbo-nitride precipitations in micro-alloyed steels for the application as seamless line pipes. It refers to a former study to investigate the precipitation reactions in low-carbon steels with different micro-alloying concepts by means of metallography, mechanical testing, and transmission electron microscopic (TEM) characterization of the respective carbo-nitride particles [1]. Three different steels are chosen for the study: one being micro-alloyed with vanadium and niobium, one with vanadium and the third one with niobium only. The TEM analyses revealed the nature and size distribution of the particles found. In the present study CALPHAD-based calculations of phase equilibria and simulations of precipitation reactions are performed and compared to the experimental results. Special efforts are put into more sophisticated simulations considering the necessity of fairly accurate interface energies as it was recently demonstrated by A. Costa e Silva in his paper on simulation of precipitation reactions in HSLA steels [2].

References:

[1] S. Harksen, Ausscheidungsverhalten in mikrolegierten vergütbaren Leitungsrohrstählen mit niedrigem Kohlenstoffgehalt, Dissertation, Shaker Verlag, Aachen, 2011.
[2] A. Costa e Silva: CALPHAD 68 (2020) 101720.

O35

Carbide precipitation kinetic in model Fe−C−Mo and Fe−C−Mn bainitic steels during tempering: Experimental study and modelling

C. Toffolon-Masclet[1], A. Benarosch[1], B. Marini[1], E. Meslin[1], R. Guillou[1], C. Mocuta[2], J.-M. Joubert[3], Z. Trzaska[3], I. Guillot[3]
[1]Paris-Saclay University, CEA-DES/ISAS/DMN, Gif-sur-Yvette, France
[2]Synchrotron SOLEIL, L'Orme des Merisiers, Saint Aubin, Gif-sur-Yvette, France
[3]Paris-Est University, ICMPE (UMR 7182), CNRS, UPEC, Thiais, France

16MND5 bainitic steels are used for French nuclear applications. The influence of carbides on the mechanical properties has for long been investigated [1]. During tempering, their distribution evolves [2]. Therefore, understanding the carbide precipitation sequences can lead to the design of steels with enhanced mechanical properties.

Given the complex composition of the 16MND5 alloy, two high-purity model ternary alloys were investigated: Fe−C−Mo and Fe−C−Mn. The construction of continuous cooling transformation diagrams has permitted the choice of starting microstructures as close as possible to the industrial one. Than, the characterization of carbide precipitation sequences in the model alloys has been performed during tempering at 650°C and 700°C, for times up to several hours.

The crystallography and chemistry of the carbides were determined by TEM on carbon extractive replicas. *Ex-situ* X-ray diffraction characterisations were performed on Diffabs beamline at Synchrotron Soleil. The analysis of these experiments by Rietveld refinements allowed the determination of the carbides weight fractions as a function of time and temperature.

At last, experimental data collected within this work enabled the modelling of the carbide precipitation kinetics using CALPHAD kinetic tools.

References:

[1] K.J. Irvine, F.B. Pickering: J. Iron Steel Inst. 194 (1960) 137-153.
[2] K. Kuo: J. Iron Steel Inst. 173 (1953) 363-375.

O36

Thermodynamic database and experimental studies of NiAl−Cr and NiAl−Mo composites

H.J. Seifert, G. Geramifard, P. Franke
Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-AWP), Eggenstein-Leopoldshafen, Germany

NiAl-based intermetallics and their composites are of interest for various high temperature engineering applications. For instance, directionally solidified metal-matrix composites of the NiAl phase reinforced with *in-situ* formed chromium and molybdenum fibers show promising mechanical properties relevant for gas turbine applications. One major prerequisite for related structural components design in the frame of ICME (Integrated Computational Materials Engineering) is the knowledge of materials thermodynamics in the quaternary Ni−Al−Cr−Mo system, taking into account all the relevant intermetallic phases and their heterogeneous reactions. Moreover, it is required to know about the oxidation behavior of the composites since in gas turbines they are exposed to high temperature oxidative environments.

In this work a thermodynamic database for the five component Ni−Al−Cr−Mo−O system was developed with focus on NiAl−(Cr,Mo) composites. The CALPHAD approach with sublattice models expressed in the compound energy formalism was used. The corresponding ten binary and ten ternary subsystems were taken into account and combined for computed multicomponent extensions. The database can be used to determine stability ranges of the formed intermetallic phases and oxides of the engineering alloys. The phase diagrams, such as isothermal sections, isopleths and potential diagrams, as well as property diagrams and thermodynamic properties can be calculated. The phase reactions of NiAl alloys with embedded Cr and Mo and the isothermal oxidation behavior were also studied experimentally. Samples produced from (a) arc melting and subsequent casting and (b) from directional solidification were investigated by electron microscopy, chemical analysis (EDX, WDX), electron backscatter diffraction (EBSD), X-ray diffraction and thermal analyses (TGA). For TGA a thermobalance was used for investigations at temperatures of 800 °C, 1200 °C and 1300 °C and argon gas containing 13 vol.% O_2. The interface reactions and oxide formations were studied in detail.

O37

W−Ni−Co ternary system thermodynamic description at intermediate temperatures

O. Dezellus[1], N. Bouliez[1,2], J. Andrieux[1], B. Gardiola[1], R. Cury[2]
[1]LMI, Université Lyon 1, CNR, 43, Bd du 11 novembre 1918, 69622 Villeurbanne Cedex, France
[2]Plansee Tungsten Alloys, 446 avenue des Digues, 74807 Saint Pierre en Faucigny, France

Plansee Tungsten Alloys manufactures innovative Tungsten Heavy Alloys for applications requiring optimized resistance to extreme conditions such as high impact energy and ductility. In other to be improved, these alloys require essentially an accurate phase equilibria knowledge in the W−Ni−Co−Fe quaternary system for a wide range of temperatures. Fernandez Guillermet published the first assessment of the quaternary system in 1989 [1], related with cemented carbide production. Since then, new thermodynamic binary descriptions have been published [2-4] as well as few experimental data but limited to temperatures higher than 1100°C. Hence, the data currently available do not describe properly the stable intermetallic phases at intermediate temperatures which are of utmost importance for industrial processes improvement.

In the present study, the W−Ni−Co and W−Ni−Fe samples of different compositions were manufactured by powder metallurgy (solid liquid sintering under hydrogen), heat treated at different temperatures and subsequently analysed. Isothermal sections under 1000°C are considerably more complex than expected since a new intermetallic phase appears to be stable ($D0_a$ structure − Cu_3Ti prototype). Formation enthalpies associated with the new phase were obtained through *ab initio* calculations. Both data are currently used to propose a new Co−Ni−W system Calphad type modelling.

References:

[1] A. Fernandez Guillermet: “The Co−Fe−Ni−W−C phase diagram: a thermodynamic description and calculated sections for (Co−Fe−Ni) bonded cemented carbide”, Z. Metallkunde 80 (1980) 83-94.
[2] P. Wang et al.: “Thermodynamic analysis of the Co−W system”, Journal of Materials Science 54 (2019) 10261-10269.
[3] A. Jacob et al.: “Modeling of Fe−W phase diagram using first principles and phonons calculations”, Calphad 50 (2015) 92-104.
[4] L. Isomaki et al.: “First principles, thermal stability and thermodynamic assessment of the binary Ni−W system”, IJMR 108 (2017) 1025-1035.

O38

Phase equilibria in the Fe−N system at high-pressure/high-temperature conditions

M.H. Wetzel, T.T. Rabending, A. Leineweber
Institute of Materials Science, TU Bergakademie Freiberg, Gustav-Zeuner-Straße 5, 09599 Freiberg, Germany

The potential N abundance in the Earth's core and magnetic properties of Fe−N phases triggered a large variety of high-pressure studies of the nitride γ'-Fe_4N. More recent works involving room temperature compression of γ'-Fe_4N samples showed that it is metastably retained to pressures up to 99 GPa [1], which is occasionally misinterpreted as γ'-Fe_4N being thermodynamically stable at pressures far above 10 GPa [2]. In contrast, studies of actual phase equilibria involving moderate heating to allow for N diffusion in combination with a thermodynamic analysis are scarce.

In this study, samples of γ'-Fe_4N powder as well as mixtures of α-Fe and γ' nitride have been exposed to pressures (P) between 4-13 GPa and a temperature (T) of 400 °C in a Walker-type multi-anvil press. Phase constitution and microstructures have been studied *ex-situ* (after quenching) by means of X-ray diffraction and electron backscatter diffraction. An isothermal section of the P-T-x phase diagram has been constructed from the acquired data, indicating that the γ'-Fe_4N vanishes above 5 GPa at 400°C involving a peritectoid reaction (p_1) $\gamma + \varepsilon' \rightarrow \gamma'\gamma + \varepsilon' \rightarrow \gamma'$ which is only observed at high-pressure conditions. Further, a P-T projection of the univariant reactions of the Fe−N system has been constructed which is complemented by a (preliminary) CALPHAD model that qualitatively explains the reaction path for the disappearance of γ'-Fe_4N.

The phase constitution data acquired in this study provide insight into the pressure dependent evolution of the phase equilibria in the Fe−N system and elucidate the potential transition reactions related with the pressure induced instability of γ'-Fe_4N.

References:

[1] S. Minobe, Y. Nakajima, K. Hirose, Y. Ohishi: "Stability and compressibility of a new iron-nitride β-Fe_7N_3 to core pressures", Geophys. Res. Lett. 42 (2015) 5206-5211.

[2] Y. Zhuang, X. Su, N.P. Salke, Z. Cui, Q. Hu, D. Zhang, J. Liu: "The effect of nitrogen on the compressibility and conductivity of iron at high pressure", Geosci. Front. (2020), in press, doi: j.gsf.2020.04.012.

O39

Site occupancies in α- and β-Mn solid solutions and consequences for the CALPHAD modelling

J.-M. Joubert, J.-C. Crivello
Univ Paris Est, ICMPE UMR 7182, CNRS, UPEC, F-94320 Thiais, France

The structures of α- and β-Mn are typical prototypes of pure metals having several distinct crystallographic sites. In substitutional solid solutions based on pure Mn in these structures, the question is raised about the site preference for the solute. In comparison with a first-principles calculation approach, a systematic study has been undertaken in both phases using Rietveld refinement of X-ray or neutron powder diffraction data in many different systems in which the solubility is large enough. The results previously published on α-Mn [1] are presented together with new results obtained for the β phase, allowing a comparison between the two structures. Consequences on the Calphad modelling of these solid solutions are examined [2].

References:

[1] J.-M. Joubert, M. Phejar: “The crystal chemistry of the χ phase”, Prog. Mater. Sci. 54 (7) (2009) 945-980.
[2] M. Joubert, J.-C. Crivello: “Description of terminal substitutional solid solutions using the sublattice model”, Calphad Comput. Coupling Phase Diagrams Thermochem. 67 (2019) 101685.

O40

Thermodynamic assessment of Mn−Nb and Mn−Ta systems

J. Vřešťál[1], P. Brož[1], J. Vlach[1], F. Zelenka[1], J. Pavlů[1], M. Mazalová[1], A. Zemanová[2], B. Smetana[3], X. Yan[4,5], P. Rogl[4,5]
[1]Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, Brno, 611 37, Czech Republic
[2]Institute of Physics of Materials, AS CR, Žižkova 22, Brno, 616 62, Czech Republic
[3]Faculty of Met.and Mat. Eng., VŠB-Technical University of Ostrava, 17.listopadu 15/2172, Ostrava, 708 33, Czech Republic
[4]Institute of Material Chemistry and Research, University of Vienna, Währingerstr. 42, Wien, Austria
[5]Christian Doppler Laboratory for Thermoelectricity, Wien, Austria

In diverse technological applications Nb, Ta and Mn are playing an important role such a (i) thermoelectric coolers at temperatures below 150 K and (ii) additions of Mn, able to increase the yield strength of Ti−Nb−Ta−Mn alloy foams for biomedical implants. Therefore, research of phase equilibria in both systems has been conducted in last two decades in many laboratories. In our study, a stable Laves phase was confirmed in both systems, but no other phase was detected experimentally. Melting and transformation temperatures of alloys in both systems were determined by DTA experiments, and this information was supported by phase analysis via scanning electron microscope (SEM) with wavelength dispersive X-ray (WDX) and energy-dispersive X-ray (EDX) analyses [1]. Results of these experiments supported by *ab initio* calculations [2] and calorimetric measurements of the energy of formation of Laves phases [3] enable us to determine the phase diagrams of both systems by the CALPHAD method. Significant effort was devoted to remove all inconsistencies using our new experimental data on melting of Laves phase, phase transformation temperatures and solubility of Mn and Ta in Mn-structures. Thermodynamic calculations were performed with the PANDAT software and resulted in a reasonably good agreement with experiments. This work was financially supported by the Czech Science Foundation (Project No. GA 17-12844S), and by the Ministry of Education, Youth and Sports of the Czech Republic (Project CEITEC 2020 (LQ1601), Project No. DMS CZ.02.1.01/0.0/ 0.0/17_049/0008399) and by the Austrian-Czech WTZ CZ01.

References:

[1] S. Liu, et al.: “*Ab initio* calculations and thermodynamic modeling for Fe−Mn−Nb system”, Calphad 38 (2012) 43-58.
[2] X. Yan, et al.: “Structural, thermodynamic, and electronic properties of Laves phase $NbMn_2$ from first principles, x-ray diffraction, and calorimetric experiments”, Phys. Rev. B97 (2018) 125110.
[3] S.V. Meschel et al.: “The standard enthalpies of formation of binary intermetallic compounds of some late 4d and 5d transition metals by high temperature direct synthesis calorimetry”, J. Alloys Compd. 498 (2010) 105-115.

O41

Pecularities of the α-Mn and β-Mn phases in the Mn−Ti−X (Fe, Ni) ternary systems

A. Walnsch, M.J. Kriegel, O. Fabrichnaya, A. Leineweber
TU Bergakademie Freiberg, Institute of Materials Science, Freiberg, Germany

The ternary Mn−Ti−Fe and Mn−Ti−Ni systems play a remarkable role in the development of a wide variety of materials ranging from precipitation- or transformation strengthened alloys and steels to shape memory alloys (SMAs). Especially for the SMAs based on the Al−Fe−Mn−Ni system, Ti additions were found to improve several technologically relevant properties and effects like the quenching sensitivity and the initiation of abnormal grain growth. To fully understand these phenomena, as well as to further enhance the properties of Fe-based SMAs, reliable constitutional phase-equilibria data of the corresponding multi-component systems is crucial.

In the course of the expansion of an assessed quaternary Al−Fe−Mn−Ni Calphad database [1] by the element Ti, the phase diagrams of the Mn−Ti−Fe and Mn−Ti−Ni systems were investigated at temperatures above 1000°C. The phase diagrams were investigated by means of SEM analyses of the microstructures of heat treated and quenched, as well as as-cast samples, in combination with EPMA, EBSD and XRD measurements to determine the chemical composition of the phases and their crystal structure, respectively. Special emphasis was placed on the exact determination of phase equilibria to build a solid and profound basis of the thermodynamic assessments for the Mn−Ti−X (Fe, Ni) ternary systems.

Key features of the respective ternary systems were the wide homogeneity ranges for the α-Mn and β-Mn phases even at temperatures, where no connections to the adjacent binary subsystems were present. In the case of α-Mn this can be explained taking into account its structural similarity with the χ-type Frank-Kasper phase [2]. For this type of phase, the d-electron concentration was found to be one of the limiting factors for possible homogeneity ranges. Due to the combined effect of Ti, which tends to reduce the number of d-electrons, and Fe, which increases the number of d-electrons, compared to Mn as the base element of this phase, these large homogeneity ranges can be explained.

References:

[1] A. Walnsch: “Thermodynamic assessment and experimental investigation of the systems Al−Fe−Mn and Al−Fe−Mn−Ni”, Calphad 66 (2019) 101621.
[2] J.-M. Joubert: “Crystal chemistry and Calphad modelling of the χ phase”, Prog. Mater. Sci. 54 (2009) 945-980.

O42

Thermodynamic assessment of the Al_2O_3–TiO_2–SiO_2 system

M. Ilatovskaia, F. Bärthel, O. Fabrichnaya
TU Bergakademie Freiberg, Institute of Materials Science, Freiberg, Germany

Rutile (TiO_2) coatings deposited on corundum (Al_2O_3) are supposed to actively filter the $MgAl_2O_4$-spinel phase from Al-based molten alloy. Al melt can then react with TiO_2, reducing it into sub-oxides and metallic titanium. In Si-containing Al alloy, $Ti_5(Si,Al)_3$, $Ti(Al,Si)_3$, and ternary phases can form. Therefore, to model chemical reactions at the interface between ceramic filter and Al melt, thermodynamic database of the Al–Mg–Ti–Si–O system is necessary. As a part, the thermodynamic description of the Al_2O_3–TiO_2–SiO_2 system is needed to model oxide melts.

The binary Al_2O_3–TiO_2, TiO_2–SiO_2, and Al_2O_3–SiO_2 systems were repeatedly studied experimentally, and their thermodynamic databases are available. The experimental data on phase equilibria in the Al_2O_3–TiO_2–SiO_2 system are limited [1,2]. For the vertical Al_2TiO_5–SiO_2 section [1], the high-temperature area was suggested. The system was also assessed thermodynamically, including the modeling of liquid miscibility along the TiO_2–SiO_2 side [3,4]. Thus, the present work is aimed at an experimental study of the phase relations in the Al_2O_3–TiO_2–SiO_2 and Al_2TiO_5–SiO_2 systems to verify the inconsistencies, and their thermodynamic modeling.

The samples prepared by a co-hydrolysis method followed by annealing experiments were investigated using XRD, SEM/EDX, and DTA. Isothermal sections of the Al_2O_3–TiO_2–SiO_2 system at 1213, 1449, 1474, and 1517°C and its Al_2TiO_5–SiO_2 section (Fig. 1) were constructed based on the obtained results. On liquidus of the ternary system, the temperatures of invariant reactions were detected. To model the system using the CALPHAD approach, CEF was used to describe the solid solutions and a two-sublattice partially ionic model was used for liquid.

References:

[1] Z.M. Agamawi, J. White: Trans. Brit. Ceram. Soc. 51/5 (1952) 293-325.

[2] F.Y. Galakhov: Izv. AN SSSR, OKhN 5 (1958) 529-534.

[3] L. Kaufman: Physica B 150 (1988) 99-114.

[4] M. Kirschen et al.: Eur. J. Miner. 11 (1999) 427-440.

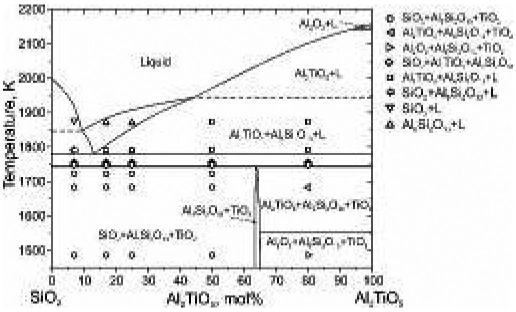


Fig. 1: Vertical section SiO_2-Al_2TiO_5 based on experimental data

O43

Short-range order strengthening and its role in intermatallics and high-entropy alloys

C.G. Schön
Department of Metallurgical and Materials Engineering, Escola Politécnica da Universidade de São Paulo
São Paulo-SP, Brazil

Short-range order (SRO) strengthening is considered one of the major strengthening mechanisms in alloys. Its role in metal physics remains, however, unclear. Early views of SRO strengthening attributed it the the increased resistance to dislocation slip caused by breaking favorable (ordered) bonds. This view is questioned because this contribution may be strong for the first dislocation slipping in a slip plane, but it is certainly less for the next dislocations slipping in the same plane. Although this explains the wavy to planar slip transition with increased alloy contents [1], it makes difficult to understand it would be relevant for determining the macroscopic strength of an alloys.

Present work discusses SRO strengthening with a different optic: instead of considering the resistance to slip initiation, we focus on the dissipated energy due to the formation of an antiphase boundary (APB), true or diffuse, and the diffusional recovery of the correlations across the APB plane. In this sense, SRO strengthening becomes similar to coherent particle strengthening. Cluster Variation Method (CVM) calculations of APB energies (both mechanical [2,3] and thermal [4]) are used to estimate the strengthening effect in BCC alloys.

The results are illustrated using ternary iron aluminides and VNbTaWAl high-entropy alloys. In all cases, *ab-initio* derived parameters are used to define the energetics of the systems. The results show that the strengthening not only is intense in the range of concentrated solid solutions, but also that this effect is strongly composition-dependent, particularly inside long-range ordered domains.

References:

[1] D. Han et al.: “Impact of short-range clustering on the multi-stage work-hardening behavior in Cu−Ni alloys”, Metals 9 (2019) 151, doi:10.3390/met9020151.

[2] C.G. Schön, R. Kikuchi: “Antiphase boundary energy determination in superlattices based on the BCC lattice using the cluster variation method”, Z. Metallk. 89 (1998) 868-878.

[3] C.G. Schön, R. Kikuchi: “Cluster variation method for determining the energy of slip-induced antiphase boundaries in BCC alloys”, Theor. Appl. Frac. Mech 35 (2001) 243-254.

[4] C.G. Schön, R. Kikuchi: “Scalar-product cluster variation method layer formulation for the irregular tetrahedron cluster approximation for bcc lattices”, Phys. Rev. B 72 (2005) 094101.

O44

Considering point defects in sub-stoichiometric ZrC_x

T. Davey, Y. Chen
School of Engineering, Tohoku University, Sendai, Japan

Zirconium (mono)carbide is a rocksalt structure compound of interest in nuclear and aerospace industries due to its extremely high melting point at around 3700 K and wide range of stable compositions (vacancies on up to ~30% of the C sites). The thermodynamic and mechanical properties of ZrC_x are strongly affected by significant structural vacancies. Recent investigations suggest that there may be a series of vacancy-ordered zirconium carbide phases at relatively low temperature (<1200 K) that are very difficult to observe experimentally [1]. Conventional CALPHAD-type phase diagram models do not directly consider such defects or defect-ordered phases, and the widely-used C–Zr phase diagram [2] has been shown to be intrinsically incompatible with our physical understanding of structural point defects [3].

Defect-related properties such as formation energies and defect-defect interaction energies are challenging to obtain experimentally with the required accuracy. In this work, state-of-the-art first-principles calculations of vacancy, substitutional, and interstitial defect-related properties are used to inform development of Gibbs energy models for cases where many structural point defects are present. Incorporating such information directly into the thermodynamic database produces a more physically consistent description and may allow further predictive ability. Elucidating the defect-ordering and stability behaviour via first-principles calculation has the potential to aid experimentalists in identifying ordered phases which may have specific low temperature applications.

References:

[1] C. Weinberger and G. Thompson: Journal of the American Ceramic Society 101 (2018) 4401-4424.
[2] A. Fernández Guillermet: Journal of Alloys and Compounds 217 (1995) 69-89.
[3] T. Davey: PhD thesis (Imperial College London) (2017).

O45

Phase diagram evaluation and thermodynamic assessment of the chromium−hydrogen system

M. Dottor, J.-C. Crivello, J.-M. Joubert
[1]Univ Paris Est, ICMPE UMR 7182, CNRS, UPEC, F-94320 Thiais, France

Metal−hydrogen systems offer many applications among which hydrogen storage is one of the most important. The Cr−H phase diagram is important due to its technical importance, for the chromium plating or some alloying process (nuclear industry or hydrogen storage for example). Few researchers have studied this system by doing low- and high-pressure experiment [1-5], few experimental data are available, and a complete phase diagram is not yet accessible. Having this in mind, a complete literature review and thermodynamic modelling to predict the properties of this system appear to be essential. We intend to show how the critical evaluation of the data led us to propose a complete description of the Cr−H phase diagram in the full composition and pressure ranges. Moreover, we propose to describe this phase diagram using the CALPHAD (CALculation of PHAse Diagrams) method. To our knowledge, no thermodynamic modelling has yet been done on this system. Experimental and DFT coupled with phonon calculated data have been considered to assess this system.

References:

[1] M. Tkacz: “High pressure studies of the FCC chromium hydride”, Rev. High Pressure Sci. Technol 7 (1998) 1735-1741.
[2] Y. Fukai, M. Mizutani: “Phase Diagram and Superabundant Vacancy Formation in Cr−H Alloys”, Mat. Trans. 43 (2002) 1079-1084.
[3] V.E. Antonov et al.: “Crystal structure and lattice dynamics of chromium hydrides”, J. Alloys Compd. 430 (2007) 22-28.
[4] S. Yu et al.: “Pressure-driven formation and stabilization of superconductive chromium hydrides”, Sci. Rep. 5 (2015) 17764.
[5] A. Marizy et al.: “Synthesis of bulk chromium hydrides under pressure of up to 120 GPa”, Phys. Rev. B 97 (2018) 18103.

O46

Thermodynamic study on diffuse interfaces in Ni-based superalloys

F. Forghani[1], M. Nili-Ahmadabadi[2], R. Abbaschian[3]
[1]BCAST, Brunel University London, Uxbridge, Middlesex UB8 3PH, UK
[2]School of Metallurgy and Materials Engineering, University of Tehran, Tehran, Iran
[3]Department of Mechanical Engineering, University of California Riverside, Riverside, USA

Solid-solid interfaces play a crucial role in the determination of microstructure and mechanical properties of solid materials. Nevertheless, integrated computational materials design (ICMD) techniques mostly attempt to estimate interfacial properties by applying an exhaustive process of atomistic modelling or experimentation [1]. Therefore, it could be very desirable to be able to determine the properties of the interface between individual phases via CALPHAD genomic databases. Moreover, recent advances in high-resolution scanning transmission electron microscopy (HRSTEM) and 3D atom probe tomography (APT) techniques have introduced new aspects of solid-solid interfaces, raising fundamental questions regarding the thermodynamic behaviour of interfacial region. In line with this demand, we have employed phenomenological sublattice thermodynamic modelling to describe and predict some characteristics of diffuse order-disorder interfaces in Ni-based superalloys. In this presentation, the dual nature of diffuse order-disorder interfaces, characterized by HRSTEM and 3D APT [2], is explained in detail. It is shown that the structural interface width (δ') of order-disorder interfaces can be successfully predicted based on the proposed thermodynamic modelling framework and sigmoid description of composition profile. More importantly, the thickening behaviour of diffuse γ/γ› interfaces during heat treatments and/or service exposures of Ni-based superalloys is elucidated and attributed to the changes in the total excess interfacial free energy as a result of Gibbs-Thomson pressure, which in turn alter the compositional width (δ) of the interface [3]. The presentation will highlight the potential of CALPHAD based calculations in developing understanding of different interface characteristics and their variations during heat treatment processes. The main challenges of employing current CALPHAD databases for the extrapolation of thermodynamic parameters to the non-equilibrium interfacial region will also be discussed.

References:

[1] W. Xiong et al.: Npj Computational Materials 2 (2016) 15009.
[2] F. Forghani et al.: Materials Characterization 153 (2019) 284-293.
[3] F. Forghani et al.: Journal of Alloys and Compounds 777 (2019) 1222-1233.

O47

First-principles study on stability of cristobalite structures in SiO_2

Y. Chen[1], N.-D. Tran[1], S. Kitaoka[2], T. Mohri[3]
[1]School of Engineering, Tohoku University, Sendai, 980-8579, Japan
[2]Japan Fine ceramics Center (JFCC), Nagoya, 456-8587, Japan
[3]Institute for Materials Research, Tohoku University, Sendai, 980-8577, Japan

SO_2 has many polymorphs with plentiful phase transformations. It has attracted a wide variaty of resetches for a long time due to the rich physics and the importanc as an inustry materials. The present work focus on the cristobalite phases of SiO_2 which is taken as a promising oxidation protective film in environmental barrier coating. β-cristobalite is stable at high temperature, while the phase transition to α-cristobalite happens accompanying a large volume shrinkage at 270°C, which leads to the SiO_2 film broken or peeled off. First-principles calculation has been conducted in order to get a guideline to suppress such α-β cristobalite phase transition. Taking α-cristobalite, β-cristobalite (ideal *Fd3m, P213, I42d*) and α-quartz phases as targets, the electronic structures, as well as the free energies combing with phonon vibration for each phase are calculated to investigate the stability and the tendency of phase transformation. The effect of nitrogen-doping on SiO_2 has been further investigated. Main results are summarized as following.

1) The calculation shows that α-quartz is most stable at zero K, α-cristobalite has slightly lower energy but lager volume than β-cristobalite, being consistent to experimental observation. The calculation revealed that the energy differences among these several phases are as small as 0.003eV/atom, suggesting appearance of certain phase to be subtle.

2) Free energy calculations found two phase transformations: β-cristobalite → α-quartz at 943K and β-cristobalite → α-cristobalite at 321K, which is not fully agreed with experiments, and needs investigating further the details with taking experiments condition carefully.

3) Nitrigen-doping is attampted to explore its effect on stabalizing β-cristobalite. Several configulations with single N and pair N_2 being introduced into the supercell of β-cristobalite (*I*42*d*) have been tested. It is found that the structrue with Si−N−N−Si−O ring formed from the pair N_2 substituting two oxygens at the vertexes of neighboring O−O−O−Si tetrahedron gives obviously lower energy than other configurations. This mechanism can be explained by analysis of the electronic structures.

O48

Relation between excess volume, excess free energy and isothermal compressibility in liquid alloys

J. Brillo[1], M. Watanabe[2], H. Fukuyama[2]
[1]Institut für Materialphysik im Weltraum, Deutsches Zentrum für Luft- und Raumfahrt (DLR), 51170 Köln, Germany
[2]Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku Universtity, 2-1-1 Katahira, Aoba-ku
980-8577 Sendai, Japan

The present work reviews experimental data on the excess volume ${}^EV$ of various binary and multicomponent liquid alloys and relates them to available data for the corresponding excess free energy ${}^EG$. It is found that the systems investigated can be distinguished into two different classes. For one class, the signs of ${}^EV$ and ${}^EG$ are equal, either both positive or both negative, and ${}^EV$ as function of ${}^EG$ exhibits a convex shape. In the case of the other class, the signs of ${}^EV$ and ${}^EG$ are opposite and the ${}^EV$ vs ${}^EG$ curve exhibits a concave shape. The first class mainly consists of alloys containing Al, while the second class has many alloys containing Pt. For both classes, the curves run through the origin and appear to be mirrored on the horizontal ${}^EG$-axis.

It is now the goal of the present work to develop a thermodynamic model which can describe this behaviour and which is able to quantitatively predict it correctly. It turns out that the isothermal compressibility κ_T is hereby a key parameter which linking the dependence of the excess volume on an effective internal pressure to the dependence of ${}^EG$ on this pressure as well − apart from a sign factor s. This sign factor remains undetermined but can be either +1 or −1. This way, the model decides between the two different curves observed experimentally: In the case of $s = +1$, the signs of ${}^EV$ and ${}^EG$ are equal while they are opposite for $s = -1$.

Using an average value for κ_T, calculated from the isothermal compressibility coefficients of all elements of which the considered alloys are composed of yields excellent agreement with the experimentally observed results from both, a qualitative and quantitative point of view.

O49

Thermophysical properties of liquid Ga−Sn−Zn eutectic alloy with different metal admixtures

Y. Plevachuk[1], A. Dobosz[2], V. Sklyarchuk[1], B. Sokoliuk[1], O. Tkach[1], T. Gancarz[2]
[1]Department of Metal Physics, Ivan Franko National University of Lviv, 79005 Lviv, Ukraine
[2]Institute of Metallurgy and Materials Science, Polish Academy of Sciences, Krakow, Poland

A new approach to cooling systems proposes the use of the metal alloys characterised by high heat capacity and thermal conductivity compared to water. The application of liquid metal as a coolant in the nuclear power industry and in renewable energy sources, electronics devices, new cooling management system using electromagnetic pumps and Li-ion batteries, increases the efficiency and performance of such devices.

The biggest disadvantages of using liquid metal as a cooling system are cost and weight (the density of liquid metal is more than six times higher than that of water). However, liquid metals have the advantage of excellent heat extraction and spreading capability, which leads to more effective work and a reduction in the coolant charge.

This work is on the development of heat transfer fluids to extend the working temperature range and reduce the melting point (to reduce heat tracing requirements) simultaneously with a high boiling temperature to allow efficient thermodynamic cycles. The coolant should also be characterised by high thermal conductivity, which is desired for efficient heat transfer, low viscosity, which is beneficial for pressure drop and pumping power, and a high heat capacity, which would allow for direct thermal storage and improve safety (toxicity) and corrosion behaviour. The Ga−Sn−Zn based alloys meet the best of the above requirements.

However, a lack of understanding of their thermophysical properties limits potential applications of these alloys. This study presents the results of the basic thermophysical structure-sensitive properties (density, surface tension, viscosity, electrical conductivity, thermoelectric power and thermal conductivity) for the ternary Ga−Sn−Zn alloy with different admixtures (Al, Bi, In, Li, Na, Pb) that have a significant effect on the properties of this basic eutectic.

O50

Influence of the correction to the Wills-Harrison approach on the thermodynamics of liquid binary alloys of noble metals

N.E. Dubinin
Institute of Metallurgy of the Ural Branch of the Russian Academy of Sciences, Ekaterinburg, Russia
Ural Federal University, Ekaterinburg, Russia

Some years ago, we applied the Wills-Harrison (WH) [1] approach in conjunction with the variational method of the thermodynamic perturbation theory to calculate thermodynamic properties of Fe−Co and Fe−Ni liquid alloys [2, 3].

Later, we introduce the correction to the WH model due to the non-diagonal coupling between d electrons on different atoms and applied this correction to investigate the WH effective pair interactions in liquid Fe, Co and Ni [4].

Here, the influence of this correction on the partial pair WH potentials and thermodynamics of Cu−Ag, Cu−Au and Ag−Au liquid alloy near their melting temperatures is studied.

References:

[1] J.M. Wills, W.A. Harrison, Phys. Rev. B 28 (1983) 363.
[2] N.E. Dubinin, L.D. Son, N.A. Vatolin, J. Phys.: Condens. Matter 20 (2008) 114111.
[3] N.E. Dubinin, J. Phys.: Conf. Ser. 144 (2009) 012115.
[4] N.E. Dubinin, J. Phys.: Conf. Ser. 338 (2012) 012004.

eP1

From bulk to size-dependent melting properties of Au−Ge alloys

S. Delsante[1,2], D. Giuranno[2], G. Borzone[1,2], R. Novakovic[2]
[1]Department of Chemistry and Industrial Chemistry, Genoa University and Genoa Research Unit of INSTM, Via Dodecaneso 31
I-16146 Genoa Italy
[2]Institute of Condensed Matter Chemistry and Energy Technologies, National Research Council (ICMATE-CNR), Via De Marini 6
I-16149 Genoa, Italy

The Au−Ge eutectic alloy was investigated by Differential Scanning Calorimetry (DSC) measuring the melting temperature and the heat of melting, and its surface tension was determined using the sessile drop method. Starting from bulk thermodynamics and our experimental data, solid-liquid phase equilibria in Au−Ge nanosized system has been studied analysing the melting phenomena of Au and Ge pure components and Au−Ge eutectic alloy. It is well known that the melting points of pure metallic materials decrease with decreasing the size of their particles [1,2]. The large surface/volume ratio in nanosized particle systems has significant effects on their thermodynamic properties and phase relations. In the present work the phase diagram of Au−Ge nanoalloys is evaluated qualitatively from the macroscopic thermodynamic point of view and it is calculated as a function of temperature (T), composition (c), size (d) and taking into account that the phase relations are dependent on the size of particle and its surface property [3].

References:

[1] L. Pavan, F. Baletto, R. Novakovic: “Multiscale approach for studying melting transitions in CuPt nanoparticles”, Phys. Chem. Chem. Phys. 17 (2015) 28364-28371.

[2] S. Delsante, R. Novakovic, G. Borzone: “Synthesis, characterization and thermal stability of SnAg and SnAgCu nanoparticles”, J. Alloys Compds. 747 (2018) 385-393.

[3] R. Novakovic, D. Giuranno, M. Caccia, S. Amore, R. Nowak, N. Sobczak, J. Narciso, E. Ricci: ”Thermodynamic, surface and structural properties of liquid Co−Si alloys”, J. Mol. Liq. 221 (2016) 346-353.

eP2

Low-temperature properties and phase transformations in pure tin

M. Palumbo[1,2], A. Dal Corso[2,3]
[1]Dipartimento di Chimica, Università di Torino, Torino, Italy
[2]International School for Advanced Studies (SISSA), Trieste, Italy
[3]CNR-IOM, Trieste, Italy

We present first-principles phonon frequencies and anharmonic thermodynamic properties of both tetragonal β and cubic diamond-like α allotropes of Sn, calculated within the quasi-harmonic approximation, including temperature-dependent lattice parameters, thermal expansion and isobaric heat capacity. We also report the calculated pressure-temperature phase diagram of the $\beta - \alpha$ phase transition and discuss the dependence of the theoretical predictions on the choice of the exchange-correlation functional and of the pseudopotential. The calculations are carried out using the Quantum Espresso software.

The results are systematically compared with the available experimental data and an overall satisfactory agreement is obtained. Differences with experiments are critically discussed.

eP3

Ab initio calculations of the binary and ternary subsystems of the systems V−Nb−Ta−Mo−W and V−Nb−Ta−W−Al

C.G. Schön, G.C. Gomes
Department of Metallurgical and Materials Engineering, Escola Politécnica da Universidade de São Paulo
São Paulo-SP, Brazil

The concept of High Entropy Alloys (HEA) comes as an innovative way to design alloys with properties which are not possible to obtain using the traditional alloy model. Many HEAs, often elaborated in equiatomic compositions, show promising properties, which are attributed to the high value of configurational entropy. A relevant feature of these alloys is the stabilization of disordered solid solutions, which allows an unusual combination of toughness and mechanical strength to be obtained. Recent works (C. G. Schön et al, Acta Mater. 148, 2018, p. 263-279 and J. Alloys Comp. 781, 2019, p. 595-605) using the V−Nb−Ta−Mo−W and V−Nb−Ta−W−Al system as prototypes of HEAs with a parameter obtained by first principles calculations, however, question this role of entropy in the stabilization of disordered solid solutions, arguing that this stabilizing effect is actually the result of conflicting interactions in the solid state. In order to understand this stabilizing effect, therefore, it is necessary to know the equilibrium of the subsystems which compose them. The aim of this work is to calculate binary and ternary metastable BCC phase diagrams of the V−Nb−Ta−Mo−W and V−Nb−Ta−W−Al systems using the parameters obtained in the calculations of the first principles of the previous works. To obtain these results, a new code for calculating phase diagrams by CVM was developed using a C++ library developed by C.G.Schön.

References:

[1] C.G. Schön, T. Duong, Y. Wang, R. Arróyave: “Probing the entropy hypothesis in highly concentrated alloys”; Acta Mater. 148 (2018) 263-279.

[2] C.G. Schön, T. Duong, Y. Wang, R. Arróyave: “A proof of concept: Thermodynamics of aluminum−transition metal highly concentrated alloys”; J Alloys Comp. 781 (2019) 595-605.

ePP4

Ab initio study of elastic and thermodynamic properties of uranium nitride

C.G. Schön, R.C. Andrades
Department of Metallurgical and Materials Engineering, Escola Politécnica da Universidade de São Paulo
São Paulo-SP, Brazil

One of the requirements for increasing safety and energetic efficiency of Generation IV nuclear power plants is the use of alternative accident tolerant nuclear fuels to substitute uranium oxide[1]. Candidates for such substitution are uranium nitrides, given their higher thermal conductivity, higher density of fissile atoms (which allow using lower enrichment levels) and better retention of fission products[2]. Uranium mononitride (UN), in this context, becomes an important candidate for the design of future reactors, especially in fast reactors designed for burning plutonium and long half-life actinide residues. In this work, thermal, transport, and elastic properties of uranium mononitride (UN) are investigated by density functional theory within generalized gradient approximation (GGA). Elastic constants C_{11} = 374.1, C_{12} = 116.5 and C_{44} = 46.4 GPa are calculated and used to estimate the melting temperature by using a simple empirical model (T_m = 2764 K). Specific heat capacity is derived within the quasiharmonic approximation (QHA) and used to obtain the compound's Gibbs free energy, entropy, and enthalpy. Good agreement of the elastic and thermodynamic properties with experiments even at high temperatures is observed. Using these elastic and thermodynamic properties, the thermal conductivity as a function of temperature is estimated up to the predicted melting point.

References:

[1] G. Locatelli, M. Mancini, N. Todeschini: Energy Policy 61 (2013) 1503-1520.
[2] G. Brillant, F. Gupta, A. Pasturel: J. Nucl. Mater. 412 (2011) 170-176.

ePP5

New developments in the continuous displacement-cluster variation method: The constraint terms

C.G. Schön, M.B.S. Dias
Department of Metallurgical and Materials Engineering, Escola Politécnica da Universidade de São Paulo
São Paulo-SP, Brazil

The Continuous Displacement-Cluster Variation Method (CD-CVM) was the last contribution of Prof. Kikuchi to Materials Science [1,2]. With this method it is possible to overcome explicitly the limitations of the rigid lattice approximation, allowing to numerically solve the Ising model in a constant pressure ensemble. This is achieved by discretizing the space close to the expected position of the centers of the atoms in a reference lattice and treating these atoms as a probability distribution. The method is successful in predicting a depression in critical temperature of ordering and phase separation phase transitions [2], which is probably the key to correct the temperature scale in *ab initio* phase diagrams.

In spite of its power, the derivation of the basic equations is difficult, mainly because the probability distributions must obey the symmetries of the lattices which are described by the reference cluster. This requires deriving constraint Lagrange terms for the free energy, which have to be solved simultaneously with its minimization. In the initial formulation Kikuchi used the reason to determine the needed constraints. The present work postulates a simpler way of doing this, by combining the symmetry elements of the cluster (referred to a “inner symmetries”) and the symmetry elements of the lattice. This allows to derive the set of symmetry elements which are not already reproduced in the cluster, which are refferred to as “outer symmetries”. This procedure is exemplified by rederiving the symmetry constraint terms for the pair cluster approximation in the BCC lattice, and for the equilateral triangle approximation in the hexagonal (2D) lattice in unary systems. The results are illustrated by calculations in BCC Nb and in an hexagonal layer composed of Zr, to validate the equations.

The procedure is much simpler than the original method of derivation and shows, in particular, that the constrints for the pair approximation can be simplified.

References:

[1] R. Kikuchi: “Continuous diplacement formulation of alloys”, J. Stat. Phys. 95 (1998) 1323-1336.
[2] R. Kikuchi, K. Masuda-Jindo: “Calculation of alloy phase diagrams by continuous cluster variation method”, Comp. Mater. Sci. 14 (1999) 295-310.

eP6

Thermal Barrier Coatings phase stability and in service degradation: Experimental study of CMAS corrosion on Ansaldo Energia's materials

G. Roncallo[1,2], E. Vacchieri[1], E. Barbareschi[1], A. Bonadei[1], G. Cacciamani[2]
[1]Ansaldo Energia S.p.A., Via N. Lorenzi 8, 16152, Genoa, Italy
[2]Dipartimento di Chimica e Chimica Industriale, University of Genoa, Via Dodecaneso 31, 16146, Genoa, Italy

Thermal barrier coatings (TBC) are materials used in gas turbines to protect metal substrates from high temperatures. For this reason, the materials used must have: high melting point, low thermal conductivity, high thermal expansion coefficient, microstructural stability, chemical compatibility with substrate and high oxidation and corrosion resistance. Normally, the material used is zirconia partially stabilized with yttria (6-8 wt.%). This material has excellent characteristics, but it cannot be used at high temperatures: in fact, if it works above 1200°C it can develop the brittle monoclinic phase during cooling. For this reason materials with higher yittria content (around 14 wt.%) are studied for application at high temperature.

Another cause of thermal barrier degradation during service is CMAS (Calcium−Magnesium−Aluminum−Silicates) corrosion. Indeed, the powders of these salts, contained in the air, can enter in the turbine and form deposits on TBCs. At high temperature, they penetrate and interact with the thermal barrier, thereby compromising its properties. They can produce physical interaction, solidifying and cracking the material during engine shut down, as well as chemical, by reacting with the oxides of the barrier.

In this work, the second and most important interaction is studied: several samples were prepared to evaluate the interaction of TBCs used by Ansaldo Energia (different types according to the manufacturer) with two different compositions of CMAS.

The specimens were exposed at high temperatures ranging between 1100 and 1400°C for different times (500, 1000, 3000 and 5000h) to evaluate kinetic and thermodynamic effects during processes.

Phase transformations were studied by XRD and it was possible to evaluate the variation of the lattice parameters of the phases.

Furthermore, the samples were analyzed by FEG-SEM microscopy with EDS and EBSD detector to confirm XRD results and to study phase distributions: these results allowed us to evaluate the interaction thickness and the microstructural modifications occurring in TBC after reaction with CMAS.

ePP7

3G_TDB software for automated generation of TDB files using modified segmented regression (MSR) model: Pure Mn as an example

A. Obaied, S. Zomorodpoosh, I. Roslyakova
ICAMS, Ruhr-University Bochum, Universitätstr. 150, 44801, Bochum, Germany

There has been a rising interest in novel modelling approaches that can describe thermo-physical properties more accurately and for wider temperature ranges. New applications such as thermoelectric materials [1] require the re-assessment of related thermodynamic systems down to temperatures lower than the room temperature. With the introduction of the so-called 3rd generation CALPHAD databases, it became possible use the newly proposed physically based models to get more accurate and reliable descriptions. A novel and robust modelling approach proposed by Roslyakova et al. [2] used a combination of Debye and a segmented function to achieve a better agreement with experimental data for temperatures down to 0 K. This model was later modified [3] to expand the temperature range above the melting point without the addition of any new fitting parameters. The results for pure Mn compared with other available thermodynamic models [4-6] can be seen in Figure1. Be that as it may, there is an increasing supply-demand gap for such re-assessments that require a more robust and genuine solution to make these models more available to the CALPHAD community members.

The 3G_TDB software has been developed to systematically analyse different types of available experimental or DFT data and fit them accordingly using the MSR model, enabling the user to compare the validity of the obtained results using statistical goodness of fit criteria, and to compare the results obtained by one set of data versus another. It would also allow the user to the TDB file that can be further used in available computational thermodynamic software. This presentation will show the progress of the 3G_TDB when used to re-assess the pure Mn unary system.

References:

[1] D.-Y. Chung et al.: Science 287(2000) 1024-1027.
[2] I. Roslyakova et al.: Calphad 55 (2016): 165-180.
[3] A. Obaied et al.: Calphad, accepted (2020).
[4] Q. Chen et al.: Journal of Phase Equilibria 22 (2001) 631–644.
[5] K. Thurnay, Thermal properties of transition metals, KIT (1998) DOI: 10.5445/IR/270043419.
[6] J. Pavlů et al.: Calphad 51 (2015) 161-171.

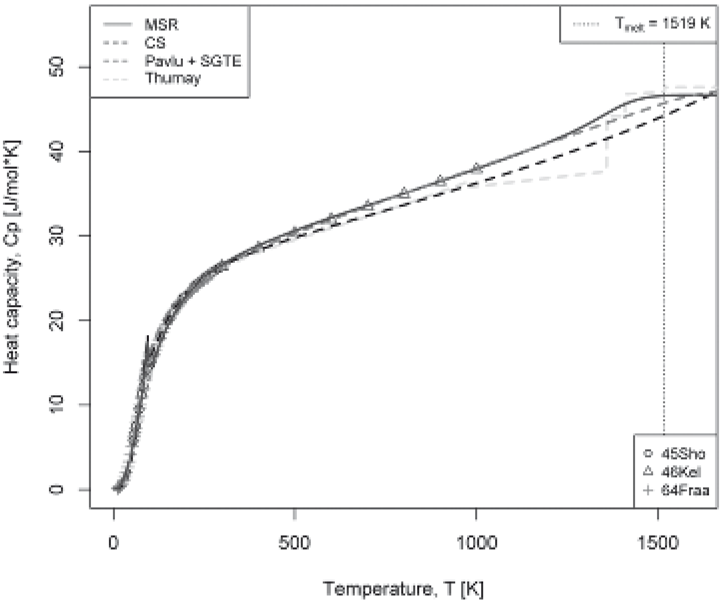


Fig. 1: Comparison of the heat capacity of the modified SR model and other assessments for pure Mn

ePP8

Thermodynamic modelling of the Al−Co−Mn system

M. Noori, B. Hallstedt
Institute for Materials Applications in Mechanical Engineering, RWTH Aachen University, Aachen, Germany

Al−Co−Mn is one of the ternary systems necessary to describe high entropy alloys and Co-based superalloys. The Al poor part is dominated by the solution phases fcc, bcc, β-Mn, and in particular, the ordered B2 phase. The transition between the bcc and B2 phase is partly second-order. The Al rich part of the system is very complex with several intermetallic phases, including the ternary $Al_{79.4}Co_2Mn_{18.6}$ phase.

The system has been experimentally investigated by means of differential thermal analysis, microstructure, crystal structure [1,2], and diffusion couple [3] methods. However, it has not yet been thermodynamically modelled. In this work, all the necessary experimental data from literature were collected. Based on this information, thermodynamic models for the included phases were selected and their parameters optimised using the PARROT module of Thermo-Calc.

References:

[1] T. Gödecke, W. Köster: Z. Metallkd. 63 (1972) 442-431.
[2] B. Grushko et al.: J. Alloys Compd. 677 (2016) 148-162.
[3] R. Kainuma et al.: J. Alloys Compd. 269 (1998) 173-180.

ePP9

The development of the thermodynamic database for the Ag−Pb−Sn−Se−Te based thermoelectric materials

A. Kroupa[1], O. Fikar[1,2], A. Zemanová[1], O. Zobač[1], Jan Vřešťál[1,3], S.-W. Chen[4,5]
[1]Institute of Physics of Materials, ASCR, Žižkova 22, 616 00 Brno, Czech Republic
[2]Brno University of Technology, Faculty of Mechanical Engineering, Technická 2, 616 69 Brno, Czech Republic
[3]Masaryk University, Instute of Chemistry, Faculty of Scince, Kamenice 5, 62500, Brno, Czech Republic
[4]Department of Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan
[5]High Entropy Materials Center, National Tsing Hua University

The existence of reliable thermodynamic database is crucial for the improvement of properties of existing materials and development of new advanced ones. Currently, great attention is paid to the development of the thermoelectric materials, which can convert heat to electricity and serve as renewable energy sources. Selection of proper composition or addition of new components to basic systems may influence their phase stability and improve their thermoelectric properties.

The subsystems in the five component Ag−Pb−Se−Sn−Te system were proposed to be perspective for the development of possible thermoelectric materials and therefore attention was given to the development of such database. It was found that the thermodynamic assessments of all binary phase diagrams currently exist, but some of them are not reliable enough or more versions existed (e.g. the Se−Te system). Several ternary assessments do not exist up to now and these assessments must be made consistent with the assessment already published in the literature.

The extensive experimental and theoretical studies were carried out in the scope of the collaboration between the teams at the National Tsing-Hua University and IPM Brno. The Pb−Se−Sn, Ag−Sn−Te and Ag−Se−Sn are among those ternaries studied, and preliminary results will be presented here. The Thermocalc software was used for the database development.

Acknowledgement:

Authors highly appreciate financial support of the Czech Science Foundation project No. 18-25660J.

 eP10

Fundamental investigation of high entropy alloys with focus on σ and μ phases

M. Ostrowska, G. Cacciamani
University of Genoa, Department of Chemistry and Industrial Chemistry, Genoa, Italy

High Entropy Alloys (HEAs) have gained an extensive popularity in the past years. In order to accelerate the research, a multicomponent database for thermodynamic calculations is being developped following the CALPHAD method. At the moment, the database contains Al, Co, Cr, Fe, Ni, Mo, Ta and W. It will be used to design novel HEAs in order to meet targeted industrial needs, for instance the request for new high-temperature alloys.

The quinary system containing Al, Co, Cr, Fe and Ni has been validated with the available literature data. Furthermore, the selection of compositions have been synthesized and annealed for 2200h at 1323K. The obtained structural information was further used for optimization of metastable parameters and overall improvement of the database quality.

The multicomponent database was then extended by addition of refractory metals: Mo, Ta and W. A special attention was paid to the TCP phases, such as σ and μ. Taking into account the crystallographic relevance, homogeneity ranges and simplification of calculations in multicomponent systems, the $(A,B)_4(A,B)_{16}(A,B)_{10}$ and $(A,B)_3(A,B)_{18}(A)_{12}(A,B)_6$ models were selected for σ and μ phases, respectively. Consequently, they had to be remodelled in several ternary systems, due to incompatibility with the published assessments. Parrot module of Thermo-Calc software and ESPEI infrastructure together with PyCalphad were used for the optimisation process (paper in preparation). In the fig. 1 the sigma solubility range is presented as a function of VEC in various ternary systems selected from the multicomponent database.

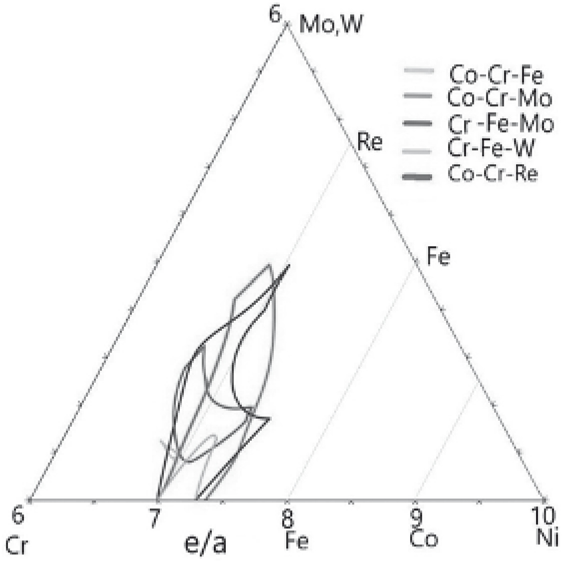


Fig 1. Homogeneity range of the σ phase as a function of e/a in selected ternary systems.

ePP11

Experimental investigation and thermodynamic modelling of interfacial reactivity between liquid Ni and oxide system

S. Sitzia[1], F. Valenza[2], M.L. Muolo[2], A. Passerone[2], N. Sobczak[3], G. Cacciamani[1,2]
[1]University of Genoa, Department of Chemistry and Industrial Chemistry, Genoa, Italy
[2]CNR, Inst. Of Condensed Matter Chemistry and Technologies for Energy, Genoa, Italy
[3]Foundry Research Institute, Krakow, Poland

Information about the high temperature interactions between liquid alloys and refractory oxide materials is of practical importance in view of the investment casting processes of Ni-based superalloys where the contact between molten alloys and the ceramic materials used as cores or shells occurs.

Such information may be obtained experimentally from specific wetting tests with improved procedures followed by microstructural and microchemical characterization. At the same time, the thermodynamic modelling by CALPHAD of the reactivity in alloys-oxides systems allows to interpret the experimental findings, to foresee the interfacial reactivity and to perform extrapolations toward non-studies domains of temperature or composition.

These are topics of the project INSURFCAST (INnovative SURFaces for superalloys CASTing processes). The wetting of Ni−Hf and Ni−Cr−Hf alloys on sapphire has been studied in this work. Wettability tests were performed by means of the sessile drop method at 1500 °C, moreover, after a certain time of liquid/solid contact, the liquid drop was pushed out from the substrate in order to open the interface and investigate and by means of *ad-hoc* calculated phase diagrams. Hf present in Ni-based melts strongly reacted with sapphire forming HfO_2 layers and inclusions; on the other hand, Cr decreased the contact angles of Ni melts without forming interfacial layers during liquid/solid contact.

Results were also interpreted by the determination of the relevant thermodynamic data (phase diagrams, activities, energy quantities) obtained by CALPHAD. These results can have an importance that goes beyond the casting industry, as they can be helpful in the design of advanced metal-ceramic brazing process, production of Metal-Matrix-Composites as well as of coating for high temperature applications.

Acknowledgments:
This work is part of the M-ERA.NET project INSURFCAST, Joint Call 2016, Project 4164.

References:

[1] F. Valenza, N. Sobczak, J. Sobczak, R. Nowak, M.L. Muolo, A. Passerone, S. Sitzia, G. Cacciamani: “Wetting and interfacial phenomena in Ni-Cr-Hf/sapphire systems”, Journal of the European Ceramic Society 40 (2) (2020) 521-528.

TOFA 2022

18th Discussion Meeting on Thermodynamics of Alloys

The 18th Discussion Meeting on Thermodynamics of Alloys will be held in Krakow, Poland in September of 2022. Krakow is a city in the southern part of Poland, second largest in terms of area and population, and well communicated with other parts of Europe.

One of the oldest cities and former capital of Poland, Krakow boasts hundreds of historical buildings, and hosts big part of Poland’s museum collections. Because of its historic riches Krakow’s Old Town is on the UNESCO World Heritage List.

Modern Krakow is also one of Poland’s leading centres of science and education with more than 20 universities and research institutes.

Like Krakow connects its past and present, TOFA 2022 will be an opportunity for all generations to meet. Researchers, scientists and students in the field of thermodynamics of alloys are welcome to join this international conference.

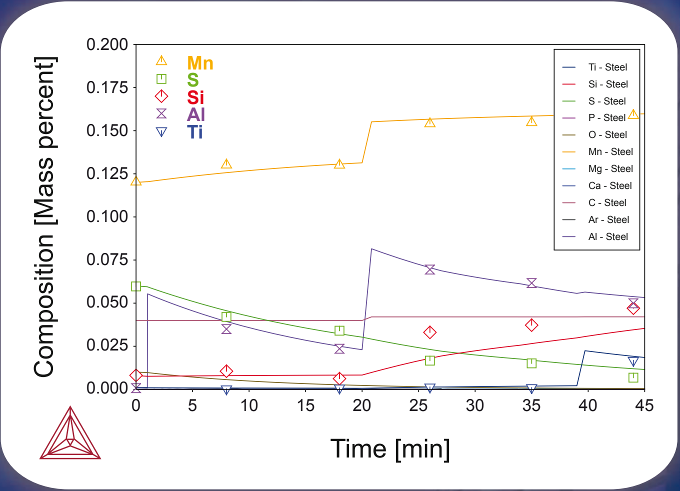
Przemyslaw Fima
Chair of TOFA 2022

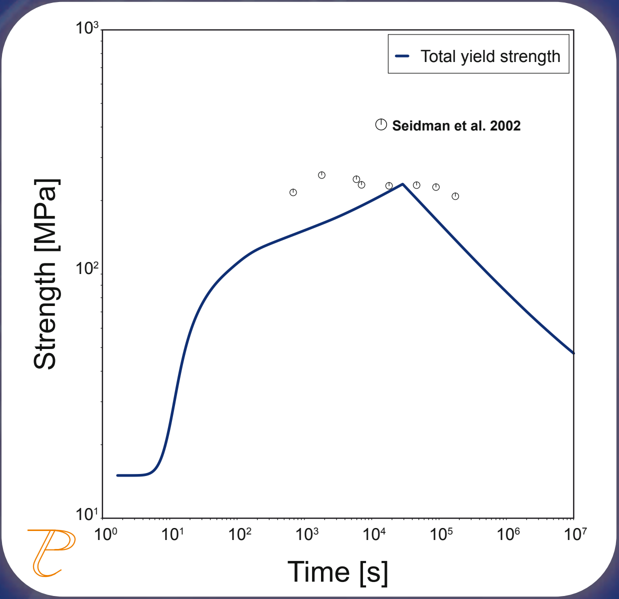
Conference topics include, but are not limited to:
- Experimental and theoretical thermodynamics – new results and techniques
- Computational thermodynamics
- Thermodynamic properties derived from *ab initio* calculations
- Phase diagrams
- Phase transformations and kinetics, solid state diffusion
- Thermodynamics of low-dimensional systems (surfaces and interfaces, nanomaterials)
- Thermochemistry of metallurgical processes
- Process simulation using thermodynamics
- Industrial applications of thermodynamics

Organized by:
Institute of Metallurgy and Materials Science of the Polish Academy of Sciences

© greens87 I 282122445 I AdobeStock

KRAKOW


Composition [Mass percent]
0.200
0.175
0.150
0.125
0.100
0.075
0.050
0.025
0.000
0
5
10
15
20
25
30
35
40
45
Time [min]
Mn
S
Si
Al
Ti
Ti - Steel
Si - Steel
S - Steel
P - Steel
O - Steel
Mn - Steel
Mg - Steel
Ca - Steel
C - Steel
Ar - Steel
Al - Steel


Total yield strength
Seidman et al. 2002
Strength [MPa]
10^3
10^2
10^1
10^0
10^1
10^2
10^3
10^4
10^5
10^6
10^7
Time [s]