CALPHAD XLVI

Saint-Malo, France
June 11-16, 2017

Conference Program

https://calphad2017.sciencesconf.org/
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Foreword

Dear Participants,

The Calphad meeting attracts every year more and more people. This is very positive since it means that the Calphad technique is getting more and more popular. And over this method, it shows the interest for experimental thermodynamics and its connection with ab-initio calculations.

This success makes the things more challenging for the organizers. In our case, the conference site was chosen a couple of years ago when the Calphad meeting gathered 160-170 people and we had not anticipated that more than 200 people would have liked to register.

Due to the high number of attendees, an extremely high number of abstract submissions has been received, most of them requesting an oral presentation. Even by restricting the time allowed for an oral presentation to 15 min (questions included, like it was already done at the Genova meeting), about half of the requests only could be satisfied. We hope that this format will lead to dynamic presentations and are nevertheless looking forward to numerous exchanges during the sessions and in front of the posters.

If we want to keep the idea of a single session and to preserve the special convivial atmosphere that has always prevailed at the Calphad meeting, it is perhaps time to think about the future of the conference in order to avoid causing frustration.

With this, we would like to warmly welcome you to Saint-Malo. We sincerely hope that you will have a wonderful time and fruitful exchanges here.

Annie and Jean-Marc

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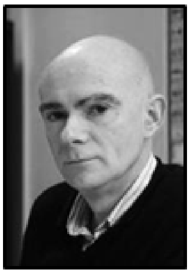

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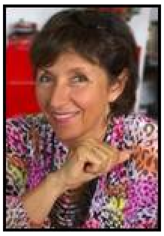
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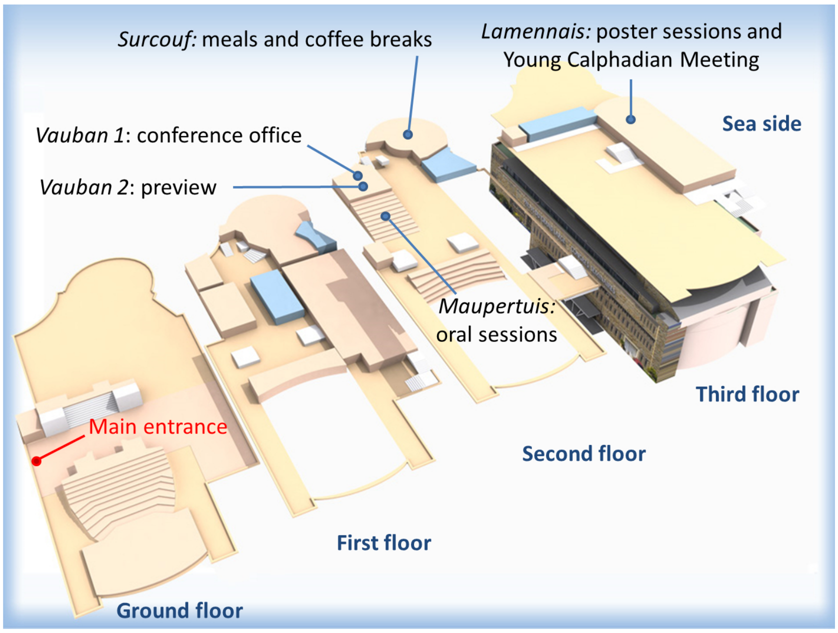

Table of contents

Conference program

Week program

	Monday 12	Tuesday 13		Wednesday 14		Thursday 15	Friday 16
08:45	Opening						
09:00	Keynote 1	Keynote 2	09:00	Keynote 3	09:00	Keynote 4	Keynote 6
09:40	Session 1 Configurational thermodynamics	Session 5 First principles and nanos	09:40	Session 9 Experimental measurements I	09:40	Session 11 Liquids and salts	Session 15 Applications
10:40	coffee break	coffee break	10:40	coffee break	10:40	coffee break	coffee break
11:10	Session 2 First principles and high-throughput	Session 6 Interface and thin films	11:10	Session 10 Experimental measurements II	11:10	Session 12 Assessment: metallic systems	Session 16 Nuclear materials, catalysts and cemented carbides
			12:10	Excursion			Closing
12:25	lunch	lunch			12:25	lunch	lunch
14:00	Session 3 Thermo-kinetics and diffusion	Session 7 Assessment: carbides and metallic systems			14:00	Keynote 5	
					14:40	Session 13 3rd generation and models	
15:30	Poster A	Poster B			16:10	coffee break	
18:00	Session 4 Phase field and molecular dynamics	Session 8 Assessment: oxides			16:45	Session 14 HEA and thermodynamic modelling	
19:00	free time	free time	19:00	free time	19:00	free time	
20:00	dinner	dinner	20:00	Conference Banquet	20:00	dinner	
21:00	Young Calphadian Meeting or free poster viewing	Computer session or free poster viewing					

Oral presentations

Monday, June 12, 2017

08:45-09:00	**Opening**	
		Keynote lecture, chair: J.-C. Crivello
09:00-09:40	**K1**	**Software tools for high-throughput CALPHAD from first-principles data** van de Walle Axel

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Session: Configurational thermodynamics
Chairs: G. Kaptay - B. Sundman

09:40-09:55	**O1**	First Principles Calculation of the WS_2-WTe_2, Phase Diagram Burton Benjamin
09:55-10:10	**O2**	Stability of $NdFe_{12}(N)$ Series Compounds: A First-principles Study Saengdeejing Arkapol, Chen Ying
10:10-10:25	**O3**	Configurational thermodynamics of C in bcc Fe: a combined computational study Yan Jiayi, Ruban Andrei
10:25-10:40	**O4**	Configurational energy of formation of alloys: Ising models vs the Cluster Expansion Sanchez Juan
10:40-11:10	**Coffee Break**	

Session: First principles and high-throughput
Chairs: A. Kroupa - B.-J. Lee

11:10-11:25	**O5**	Alloying and Phase Stability in MAX Phases: A High-throughput Cluster Expansion Approach Arróyave Raymundo, Talapatra Anjana, Duong Thien, Son Woongrak, Prehn Evan, Gao Huilio, Radovic Miladin
11:25-11:40	**O6**	Comparison of calculated and experimental values of enthalpies of formation of intermetallic compounds. Colinet Catherine, Tedenac Jean-Claude
11:40-11:55	**O7**	Nickel incorporation in Ti_2AlC ceramic Lu Chengjie, Zhang Jie, Hug Gilles
11:55-12:10	**O8**	Ground state predictions for sulfide electrolytes Iikubo Satoshi, Shimoyama Koichi, Kawano Shoya, Fujii Masafumi, Matsushita Masafumi, Shinmei Toru, Ohtani Hiroshi
12:10-12:25	**O9**	A New Methodology for High-throughput Screening of Composition-Microstructure-Micromechanical Properties Relationships Cui Yuwen, Guanglong Xu
12:25-14:00	**Lunch**	

Session: Thermo-kinetics and diffusion
Chairs: J. Ågren - A. Costa e Silva

14:00-14:15	**O10**	Impacts of thermodynamic and kinetic model parameterisation on precipitation simulations - Case study of NbC precipitation in microalloyed steel Povoden-Karadeniz Erwin, Kozeschnik E.
14:15-14:30	**O11**	Thermo-kinetic modeling for the growth/dissolution of α slabs and lamellae in Ti-55531 under continuous heating condition Chen Fuwen, Xu Guanglong, Zhang Xiaoyong, Zhou Kechao
14:30-14:45	**O12**	Overcoming the Diffusion Bottleneck: Effect of Alloying Elements on Phase Transformations and Carbide Dissolution in Martensitic Stainless Steels Miotti Bettanini Alvise, Delannay Laurent, Pardoen Thomas, Mithieux Jean-Denis, Badinier Guillaume, Pascal Jacques
14:45-15:00	**O13**	Temperature Dependence of Diffusivities from a Single Experiment - Experimental Technique and Evaluation Method Engelhardt Hannes, Rettenmayr Markus
15:00-15:15	**O14**	Diffusivities and Atomic Mobilities in fcc Cu-Ni-Sn Alloys Liu Yuling, Liu Dandan, Du Yong, Liu Shuhong
15:15-15:30	**O15**	Analytical model with interaction between species for growth and dissolution of precipitates Gandin Charles-André, Guillemot Gildas
15:30-18:00	**Poster session A, chair: M. Perrut**	

Session: Phase field and molecular dynamics
Chairs: A. Khvan - A. Gheribi

18:00-18:15	**O16**	Quantitative phase-field simulation of microstructure evolution in Ni-Al alloys during entire preparation process and its linking to mechanical property Zhang Lijun, Cao Dongjia, Lin Yan
18:15-18:30	**O17**	Microstructure evolution during melting of single crystal superalloy: A combined experimental and computational study Warnken Nils, Chen Xu, Slater Carl
18:30-18:45	**O18**	Matching time and spatial resolutions of rapid solidification: Dynamic TEM experiments coupled to CALPHAD-informed phase-field simulations Perron Aurélien, Roehling John, Turchi Patrice, Fattebert Jean-Luc, Mckeown Joseph
18:45-19:00	**O19**	Glass Transition Temperature and Phase Diagrams of Butadiene Rubber and Styrene Butadiene Rubber: Molecular Dynamics Simulation Lee Hyuck Mo, Ryu Myung Shin, Kim Hyoung Gyu, Bang K.
19:00-20:00	**Free Time**	
20:00-21:00	**Dinner**	
21:00-23:00	**Evening session: Young Calphadian Meeting, chair: S. Gossé OR free poster viewing**	
-		with the participation of C. Colinet, B. Sundman and B.-J. Lee

Tuesday, June 13, 2017

		Keynote lecture, chair: C. Guéneau
09:00-09:40	**K2**	**Ab initio based multiscale modelling in physical metallurgy** Willaime François, Lüthi B., Marinica M.C., Ventelon L., Rodney D.

Session: First principles and nanos
Chairs: P. Chartrand - S. Nishitani

09:40-09:55	**O20**	Phase stability and chemical composition of nanoprecipitates: A first principles study for the example of kappa carbides Hickel Tilmann, Dey Poulumi, Dutta Biswanath, Friák Martin, Neugebauer Jörg
09:55-10:10	**O21**	The size-dependent phase diagram form Ni-based systems by combination of CALPHAD and ab initio methods Kroupa Ales, Kana Tomas, Vykoukal Vit, Zemanova Adela, Svoboda Milan, Sob Mojmír, Pinkas Jiri
10:10-10:25	**O22**	Constructing an As-Ga-In-Sn thermodynamic database for modelling the growth of InAs, GaAs and $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}$ nanostructures Ghasemi Masoomeh, Johansson Jonas
10:25-10:40	**O23**	First-principles Calculation Assisted Thermodynamic Modeling of B-Ta and B-C-Ta System Xuemei Ouyang
10:40-11:10	**Coffee Break**	

Session: Interface and thin films
Chairs: R. Arróyave - Y. Du

11:10-11:25	**O24**	Interface energy at limit radius in metallic system Nishitani Shigeto
11:25-11:40	**O25**	Temperature and concentration dependent solid/liquid interfacial energies Lippmann Stephanie, Jung In-Ho, Paliwal Manas, Rettenmayr Markus
11:40-11:55	**O26**	Modeling of metastable phase formation diagrams for sputtered thin films Chang Keke, Music Denis, To Baben Moritz, Lange Dennis, Bolvardi Hamid, Schneider Jochen
11:55-12:10	**O27**	Calculation of phase diagrams with epitaxial orientations in Co-based binary alloy thin films Lu Yong
12:10-12:25	**O28**	Thermodynamic study on grain boundary segregation Ohtani Hiroshi, Enoki Masanori, Higashide Yusuke
12:25-14:00	**Lunch**	

Session: Assessment: carbides and metallic systems
Chairs: B. Lindhal - P. Turchi

14:00-14:15	**O29**	A new thermodynamic database of Ti(C,N)-based cermets and its application to the control of grain growth Du Yong, Zhang Cong
14:15-14:30	**O30**	Thermodynamic assessment of the C-Zr system Davey Theresa, Mellan Thomas, Fries Suzana, Finnis Michael
14:30-14:45	**O31**	From ternary experiments back to binary modeling: Li-Si-C example Schmid-Fetzer Rainer, Liang Songmao, Drüe Martin, Kozlov Artem, Rettenmayr Markus
14:45-15:00	**O32**	Modelling the Gibbs energy of Ag-Ni, Ag-Ge and Ag-Ge-Ni by calphad approach Rajkumar V.B, Chen Sinn-Wen
15:00-15:15	**O33**	Thermodynamic modelling of Long Periodic Stacking Ordered (LPSO) phases in Mg-Gd-Al ternary system Kim Hongyeun, Ross Austin, Shang Shunli, Wang Yi, Kecskes Laszlo, Darling Kristopher, Liu Zi-Kui
15:15-15:30	**O34**	Phase equilibria of Pb-Sb-Se-Sn quaternary system Chen Sinn-Wen, Chang Jui-Shen
15:30-18:00	**Poster session B, chair: M. Perrut**	

Session: Assessment: oxides
Chairs: E. Povoden-Karadeniz - M. Selleby

18:00-18:15	**O35**	Phase relations in the ZrO_2-TiO_2-Al_2O_3 system: experimental study and thermodynamic assessment Fabrichnaya Olga, Ilatovskaya Mariia, Savinykh G.
18:15-18:30	**O36**	Thermodynamic properties of oxide compounds estimated from polyhedron method Jung In-Ho, Moosavi-Khoonsari Elmira, Wu Ting
18:30-18:45	**O37**	Integrated experimental and thermodynamic modelling research on the multicomponent Pb-Cu-Fe-Zn-Ca-Si-O system Shevchenko Maksym, Shishin Denis, Jak Evgueni
18:45-19:00	**O38**	Thermodynamic investigation of the Cr-O-U and Cr-O-Zr systems Lindahl Bonnie, Alpettaz Thierry, Bonnaillie Patrick, Brackx Emmanuelle, Chatain Sylvie, Domenger Renaud, Gossé Stéphane, Poissonnet Sylvie, Guéneau Christine
19:00-20:00	**Free Time**	
20:00-21:00	**Dinner**	
-	**Evening session: Computer session, chair: A. Pisch OR free poster viewing**	
21:00-21:30	**C1**	What is New in Thermo-Calc Chen Qing
21:30-22:00	**C2**	Demonstration of Pandat software Chen Shuanglin and Schmid-Fetzer Rainer
22:00-22:30	**C3**	Fact-Sage Jung In-Ho

Wednesday, June 14, 2017

		Keynote lecture, chair: I. Nuta
09:00-09:40	**K3**	**Experimental Thermodynamics of Nuclear Materials** Konings R.J.M., Beneš O., Capelli E., Manara D., Popa K., Pavlov T., Vlahovic L.

Session: Experimental measurements I
Chairs: S. Lippman - B. Oudot

09:40-09:55	**O39**	Standard Enthalpies of Formation of Select Cu_2YZ Compounds Nash Philip, Hasier John, Hawgood Mary, Kim George, Chen Wei
09:55-10:10	**O40**	Calorimetric determination of the formation enthalpy of ZnSb Benigni Pierre, Berche Alexandre, Pothin Romain, Adenot Aurélien, Mikaelian Georges, Ayral Rose-Marie, Jund Philippe, Rogez Jacques
10:10-10:25	**O41**	Gaseous phase thermodynamics of organometallics: a TaN-precursor study Nuta Ioana, Blanquet Elisabeth, Artaud Laurent, Collas Hervé, Chatillon Christian
10:25-10:40	**O42**	Thermodynamic Vaporization Studies of Lead Oxide and Sodium Oxide with Knudsen Effusion Mass Spectrometry Kobertz Dietmar
10:40-11:10	**Coffee Break**	

Session: Experimental measurements II
Chairs: P. Benigni - P. Nash

11:10-11:25	**O43**	A container-less electrochemical method to evaluate the thermodynamic properties of molten oxides and liquid alloys Allanore Antoine, Nakanishi Bradley
11:25-11:40	**O44**	On the Quaternary System Ce-Ni-Zn-B Rogl Peter, Failamani Fainan, Podloucky Raimund, Malik Zahida, Bursik Jiri, Grytsiv Andrij, Bauer Ernst
11:40-11:55	**O45**	Determination of phase equilibria in Fe-C-Mn-Al alloys for 3rd generation duplex steels Mestrallet Aurore, Antoni-Zdziobek Annie, Emo Jonathan, Maugis Philippe, Hallstedt Bengt
11:55-12:10	**O46**	Alloy phase stability under electric currents Lin Shih-Kang, Liu Yu-Chen
12:10-19:00	**Excursion**	
19:00-20:00	**Free Time**	
20:00-23:00	**Conference Banquet**	

Thursday, June 15, 2017

		Keynote lecture, chair: J.-M. Joubert
09:00-09:40	**K4**	**Thermodynamic and physical-property models for the production of primary aluminium** Chartrand Patrice, Gheribi Aimen Ernest, Wang K., Ouzilleau P., Robelin Christian

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Session: Liquids and salts
Chairs: C. Colinet - O. Fabrichnaya

09:40-09:55	**O47**	Uncertainty quantification in ternary interpolation methods for thermodynamic properties of liquid alloys Beyers Lesley, Van Den Bulck Amy, Wollants Patrick
09:55-10:10	**O48**	Thermodynamic modeling and experimental investigations in the H_2O - HNO_3 - $Sm(NO_3)_3$ - $Eu(NO_3)_3$ - $(C_4H_9O)_3PO$ system Kovalenko Nikita, Maksimov Aleksey, Arkhipin Anatoly, Voronin Gennady
10:10-10:25	**O49**	Phosphoric acid and sodium phosphate: Extending the limit of aqueous electrolyte modelling Wang Peiming
10:25-10:40	**O50**	DFT/CALPHAD mixed method for the prediction of the thermal transport properties within aluminium electrolysis cells Gheribi Aimen Ernest, Chartrand Patrice
10:40-11:10	**Coffee Break**	

Session: Assessment: metallic systems
Chairs: M. Kurata - A. Jacob

11:10-11:25	**O51**	Engineering applications of CALPHAD - some examples Ågren John
11:25-11:40	**O52**	The formation of magnesiowustite in steelmaking slag evaluated experimentally and via computational thermodynamics Costa e Silva Andre, Vieira Alan, Martins Antonio Augusto, Batista Rafaela, Avillez Roberto
11:40-11:55	**O53**	Thermodynamic features of the Al-Mo and Al-Mo-Ti systems Kriegel Mario, Klemm Volker, Fabrichnaya Olga, Freudenberger Jens, Leineweber Andreas
11:55-12:10	**O54**	New assessment of the Al-Fe system Zienert Tilo, Fabrichnaya Olga
12:10-12:25	**O55**	A thermodynamic database for cast iron Hallstedt Bengt
12:25-14:00	**Lunch**	

		Keynote lecture, chair: C. Toffolon Masclet
14:00-14:40	**K5**	**On the 3rd Generation of Thermodynamic Databases** Selleby Malin

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Session: 3rd generation and models
Chairs: C.-A. Gandin - B. Burton

14:40-14:55	**O56**	Experimental study and modeling of thermodynamic properties of the Ag-Cu system for the third generation of thermodynamic databases Phiri Albina, Khvan Alexandra, Dinsdale Alan
14:55-15:10	**O57**	On the temperature dependence of excess Gibbs energy of solutions Kaptay George
15:10-15:25	**O58**	Modelling thermal vacancies within the CALPHAD approach Liu Zi-Kui, Guan Pin-Wen
15:25-15:40	**O59**	Thermodynamic descriptions of pure Sn, Pb, Bi and Bi-Sn system from 0K using two state model for the liquid phase. Khvan Alexandra, Dinsdale Alan, Phiri Albina
15:40-15:55	**O60**	About the limits of applicability of the Alkemade theorem for the construction of ternary liquidus surfaces Stein Frank, He Cuiyun
15:55-16:10	**O61**	The Calphad Method - the Scientific use of Metastability Sundman Bo
16:10-16:45	**Coffee Break**	

Session: HEA and thermodynamic modelling
Chairs: N. David - R. Schmid-Fetzer

16:45-17:00	**O62**	Understanding Physical Metallurgy and Computational Design of High Entropy Alloys: Atomistic Simulation and CALPHAD Lee Byeong-Joo, Choi Won-Mi
17:00-17:15	**O63**	The fcc solid solution stability in multi-component system :towards high entropy alloys design Bracq Guillaume, Laurent-Brocq Mathilde, Perrière Loïc, Pires Rémy, Crivello Jean-Claude, Joubert Jean-Marc, Guillot Ivan
17:15-17:30	**O64**	A Constraint Satisfaction Problem Approach to High-Entropy Alloy Design Abu-Odeh Anas, Chaudhary Nayan, Gibbons Sean, Galvan Edgar, Kirk Tanner, Mao Huahai, Malak Richard, Arróyave Raymundo
17:30-17:45	**O65**	Phase stabilities of Ti materials with a focus on the thermodynamic modelling of metastable microstates Marker Cassie, Shang Shunli, Zhao Ji-Cheng, Liu Zi-Kui
17:45-18:00	**O66**	Crystal structure relations among variants of the ω phase in titanium alloys and their modeling Chen Hai-Lin
18:00-18:15	**O67**	Characterizing uncertainty of CALPHAD assessment. The Au-Pd case Kuznetsov Victor
18:15-18:30	**O68**	Thermodynamic modelling of Cr-Fe-Nb-Sn-Zr system Lafaye Paul, Crivello Jean-Claude, Toffolon-Masclet Caroline, Joubert Jean-Marc
18:30-18:45	**O69**	A New Approach of the CEF applied to the sigma phase modeling : Application to the thermodynamic re-assessment of the Nb-Al system using new experimental data. Fiorani Jean-Marc, Araújo Pinto Da Silva Antonio Augusto, Carvalho Coelho Gilberto, Nunes Carlos, David Nicolas, Vilasi Michel
18:45-19:00	**O70**	Thermodynamic study on microstructure evolution during aging process in the Al-Cu binary alloy Yabe Takahiro, Shibahara Shohei, Enoki Masanori, Ohtani Hiroshi
19:00-20:00	**Free Time**	
20:00-21:00	**Dinner**	

Friday, June 16, 2017

Keynote lecture, chair: A. Antoni Zdziobek

09:00-09:40	**K6**	**Calphad Study of Planetary Condensation** Saxena Surendra

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Session: Applications
Chairs: K. Frisk - F. Stein

09:40-09:55	**O71**	Phase diagrams of alloys under pressure Makov Guy, Emuna Moran, Yahel Eyal, Greenberg Yaron
09:55-10:10	**O72**	Thermodynamic description of the lithium manganese oxide as cathode materials for lithium-ion batteries Zhang Weibin, Cupid Damian, Seifert Hans
10:10-10:25	**O73**	Thermodynamics on Developing Earthquake Resisting Thermodynamics on Developing Earthquake Resisting Lee Joonho, Hwang Byoungchul, Shim Jae-Hyeok, Lee Myoung-Gyu, Jung Jun-Ho, Kim Bo-Sung, Won Sung-Bin
10:25-10:40	**O74**	A CALPHAD approach to modelling of slag viscosities Hack Klaus, Yakshenshikh Elena, Wu Guixuan, Mueller Michael, Jantzen Tatjana
10:40-11:10	**Coffee Break**	

Session: Nuclear materials, catalysts and cemented carbides
Chairs: S. Gossé - A. Perron

11:10-11:25	**O75**	Thermodynamics of Actinide Alloys in the upcoming New Edition of the Pu Handbook Turchi Patrice, Perron Aurélien, Timofeeva Lidia, Clark David, Hanrahan Robert
11:25-11:40	**O76**	CALPHAD approach: a complementary way to determine the corrosion path way of PuAl alloys stabilized in delta-phase Oudot Benoit, Ravat Brice, Jolly Lionel, Perron Aurélien, Turchi Patrice, Guéneau Christine, Delaunay Francois
11:40-11:55	**O77**	PdZn Intermetallic compound: A pseudoelement of Cu for catalysis Tsai An Pang, Kameoka Satoshi, Shimoda Masahiko, Ishii Yasushi
11:55-12:10	**O78**	Design of grain growth inhibitors and analysis of mechanical properties in ultra-fine WC-10Co cemented carbides based on thermodynamic calculations Haixia Tian, Peng Yingbiao, Du Yong
12:10-12:25	**O79**	Thermodynamic and Kinetic Modeling Applied to Hardmetals Frisk Karin
12:25-12:40	**Closing**	
12:40-14:00	**Lunch**	

Poster presentations

Monday, June 12, 2017, 15:30-18:00
Poster session A, chair: M. Perrut

PA1	Thermodynamic modeling of long-term precipitation kinetics in heat-resistant alloys, **Shim Jae-Hyeok**
PA2	Analysis of the phase equilibria and phase transformations in the region Al-Al_3Zr during slow cooling rate solidification and long-time annealings below the solidus, **Khvan Alexandra**
PA3	Thermodynamic Optimization of Ni-Ti-V Ternary System, **Kathirvelu Santhy**
PA4	Computational Study of Atomic Mobility in HCP Mg-Al-Zn Ternary Alloys, **Wang Jingya**
PA5	High-throughput Investigation of Diffusion and creep Micro-Mechanical Properties in Mg alloys, **Li Na**
PA6	A study of the Mg-Al-C system: synthesis and thermal stability of the Al_2MgC_2 ternary carbide, **Deffrennes Guillaume**
PA7	Integration of Phase Equilibrium Calculation and Kinetic Simulation, **Chen Shuanglin**
PA8	Influence of W and Mo on the phase equilibrium and diffusion behaviour of Ni-Co-Al ternary system, **Wang Yang**
PA9	Aqueous Salt Hydrates: Unconventional Deep Eutectic Solvents, **Marcus Yizhak**
PA10	High pressure-high temperature phase diagram using electrical resistance measurements in a Paris-Edinburgh large volume press, **Emuna Moran**
PA11	Ab initio study of the phononic origin of negative thermal expansion, **Argaman Uri**
PA12	Al-B-C ternary compounds : synthesis, structure, composition and thermal stability, **Dezellus Olivier**
PA13	Comparison of various DTA methods for liquidus determination in Ag-Cd-In alloys, **Gajavalli Sai**
PA14	Thermodynamic modelling of the Al-Co-Pd system, aluminium rich corner of the phase diagram, **Homolova Viera**
PA15	Thermodynamic modelling of Fe-Cr-Ni and its implication for the calculation of multicomponent systems, **Jacob Aurélie**
PA16	Influencing factors of atomic order in binary sigma phases, **Liu Wei**
PA17	First-principles Calculation Assisted Thermodynamic Modeling of B-Ta and B-C-Ta System, **Xuemei Ouyang**
PA18	Experimental Investigation and Thermodynamic Calculation of Phase Equilibria in the Sn-Zn-Co Ternary System, **Hu Jingxian**
PA19	Phase equilibria, Thermodynamic Assessments and Microstructure Development of Mg-Alkaline Earth-Rare Earth Systems, **Xu Guanglong**
PA20	Investigation of the ternary Ag-Ga-Sn phase diagram, **Premovic Milena**

PA21	Experimental investigation and phase equilibria of Al-Zn-Cu system, **Zhang Yuhui**
PA22	Experimental investigation and thermodynamic modeling of Co-Ge system, **Zeng Yinping**
PA23	A thermodynamic study of the WC-(Fe,Co,Ni) hardmetal, **Peng Zhou**
PA24	Phase Equilibria and Thermodynamic Modelling in the System Ni-Sn-Zr, **Vrestál Jan**
PA25	Phase equilibria of Sn-Ag-In-Zn quaternary system, **Chen Sinn-Wen**
PA26	Thermodynamic and TEM investigations of Si poisoning effects on grain refinement in Al-Ti-Si and Al-Nb-Si systems, **Li Yang**
PA27	Isothermal sections of Mg-La-Zr system in Mg-rich corner at 300, 400 and 500° C, **Zhu Wenfei**
PA28	Phase Equilibria of 540° C Isothermal Section of Fe-Al-Zn-Ce System, **Zhi Li**
PA29	Phase stability of ternary compounds in Cu-Li-Sn system and path hysteresis in Cu_6Sn_5 electrode, **Jianchuan Wang**
PA30	Thermochemistry of some Bismuth-Transition metal compounds by high temperature direct synthesis calorimetry, **Meschel Susan V.**
PA31	Modelling solidification segregation in two Nb microalloyed steels, **Costa E Silva Andre**
PA32	Experimental study of Al-Cu-Zn phase diagram, **Zobac Ondrej**
PA33	Thermodynamic investigations of Fe-Mn-Al-Ni shape memory alloys, **Walnsch Alexander**
PA34	Optimization of compositions and physical properties of salt systems for latent heat storage in thermal solar energy applications, **Gheribi Aimen Ernest**
PA35	Ternary diffusivity from both the intersection of two diffusion couple and single diffusion couple: application to the Cu-Ni-Sn ternary system, **Du Changfa**
PA36	The stability investigation of $Fe_{23}Zr_6$ in the Fe-Zr system, **Zou Nan**
PA37	First principles study of hydrogen diffusion in iron, **Hirata Kenji**
PA38	Thermodynamic evaluations of the local ordering behaviors in the LPSO-forming Mg-Zn-Y system, **Egami Mariko**
PA39	Thermodynamic re-assessment of the Al-Fe-Mn system, **Zheng Weisen**
PA40	Study of thermal stability of doped CoSb based skutterudites by Knudsen effusion mass spectrometry, **Zelenka Frantisek**
PA41	Study of thermal stability of $CoSb_3$ skutterudite by Knudsen effusion mass spectrometry, **Broz Pavel**
PA42	Contribution to the experimental determination of the Ti-Al-W phase diagram, **Vaubois Thomas**
PA43	Mixing enthalpy measurements of liquid Li-Pb-Sb alloys, **Terlicka Sylwia**
PA44	Phase equilibria, thermodynamics and microstructure simulation of metastable spinodal decomposition in metastable c-TiAlN-based coatings, **Zhou Jingjing**
PA45	Cluster ordering of Mg-LPSO, **Nishitani Shigeto**
PA46	Thermodynamic descriptions of the quaternary Al-Si-Mg-RE (RE=Sc, Ce) systems and their application to design RE-containing cast aluminium alloys, **Lu Zhao**
PA47	Experimental Investigation of the Fe-Co-Ce System, **Fartushna Iuliia**

PA48	Experimental investigation and thermodynamic re-assessment of the ZrO_2-TiO_2 system, **Saenko Ivan**
PA49	Stability and defect chemistry analysis of Cu-doped Ceria by computational thermodynamic modelling, **Mcinnes Gregor**
PA50	Phase equilibria of binary Cr-Os system: experimental measurement and thermodynamic assessment, **Lin Yan**
PA51	Modeling of the Mn-Ni-Pd alloy system, **Brosh Eli**
PA52	Thermodynamic modelling of the B - Mn - V system, **Kepic Jan**
PA53	Experimental and computational study of diffusion between Fe-Cr-Al and Fe-Ni alloys at 800° C and 1000°, **Ojha Rohit**
PA54	On the configurational entropy of nano-solutions, **Kaptay George**
PA55	Thermodynamic Modelling of the Al-Mn-C System, **Tang Florian**
PA56	Phase equilibria of the Gd-Mn-Ge/Si ternary systems and magnetic properties of GdMn2(Ge,Si)$_2$ compound, **Wang Jiang**
PA57	Experimental study and thermodynamic calculation of Mn-RE (RE=Nd, Gd, Ho, Dy) binary systems, **Wang Jiang**
PA58	Development of a new thermodynamic database for slag relevant oxide systems containing P_2O_5, **Yazhenskikh Elena**
PA59	Electronic state entropy: informing thermodynamic and transport properties of the molten state., **Allanore Antoine**
PA60	Solidus surface projection of Fe-Sn-S system, **Sinyova Svetlana**
PA61	Phase Equilibria of the Fe-Al-Zr System at 600°C, **Zhao Manxiu**

Tuesday, June 13, 2017, 15:30-18:00
Poster session B, chair: M. Perrut

PB1	Experimental study on Fe-C-La system, **Mardani Masuma**
PB2	Wetting and interfacial reactivity in the Al_3Ti-SiC system, **Gambaro Sofia**
PB3	Experimental study of phase equilibria of the La/Y-Fe-B ternary systems, **Wang Jiang**
PB4	Thermodynamic optimization of Al-B-N system using ab initio calculations, **Sridar Soumya**
PB5	Prediction of heat capacity, **Zienert Tilo**
PB6	Thermodynamic study and assessment of the fluorine-iron system, **Chatain Sylvie**
PB7	Effects of Ni-doping on various properties of NbH phases: A First-principles investigation, **Wang Zhongmin**
PB8	Effects of Mo alloying on the structure and hydrogen-permeation properties of Nb metal, **Wang Zhongmin**
PB9	Evaluation of empirical rules on the phase formation of the multi-principal element alloys through Calphad approach, **Liang Song-Mao**
PB10	Ab initio calculations of the intermetallics in Ni-Zr system, **Jana Asmita**
PB11	Thermodynamic modeling of the Co-Cr-Ta system, **Yao Wang**
PB12	Experimental research on thermo-stability of the ternary compounds and related phase transformation in the Mg-Zn-Gd system, **Li Hong-Xiao**
PB13	Remodelling of Hf-V system, **Pavlu Jana**
PB14	Thermodynamic Evaluation and Optimization of the NaF - KF - ZnF_2 System, **Aubé Maxime**
PB15	Thermodynamic modelling of key metallic sub-systems for the treatment of mid-level wastes, **Soldi Luca**
PB16	Thermodynamic description of the Ga-Li-Zn system, **Dębski Adam**
PB17	The characteristic of Fe as a β-Ti stabilizer in Ti alloys, **Guo Yanhua**
PB18	Structure, elasticity and thermal decomposition of $Ti_{1-x}TM_xN$ alloys from first-principles study, **Jiong Wang**
PB19	Calculation of mixing enthalpy in Mo-Pd-Rh-Ru system, **Crivello Jean-Claude**
PB20	Experimental and computational study on surface layer microstructure evolution in single crystal superalloys during solution heat treatment, **Spathara Dimitra**
PB21	Experimental Determination of Phase Equilibria Related to Iron Silicides in the Fe-Si Binary System, **Han Kwangsik**
PB22	Theoretical study of hydrogen insertion in bcc metals, **Bourgeois Natacha**
PB23	Experimental investigation and thermodynamic calculation of the Al-Si-V system in the Al-rich corner, **Li Kang**
PB24	CALPHAD assessment of the key ternary and quaternary systems in Ti alloys, **Hu Biao**
PB25	Liquidus and solidus projections of the Fe-Co-S system, **Ilatovskaia Mariia**
PB26	Phase Equilibria of the Gd-Fe-B Ternary system at 873K and 1073 K, **Cheng Gang**

PB27	Next Generation CALPHAD Databases: Accurate approximation of the Debye model and its application for phase diagram calculations, **Roslyakova Irina**
PB28	The first principle calculation and experimental investigation of the $Ti_2(Al,Si)C$ solid solution, **Piven Kseniia**
PB29	Experimental and thermodynamic study of Li-O and Li_2O-P_2O_5 systems, **Jin Liling**
PB30	Thermodynamic description of spinodal decomposition in Ni-based superalloys, **Forghani Farsad**
PB31	Isothermal section of the Phase diagram of the Co-Pt-Ho ternary system at 773K, **Du Yusong**
PB32	Thermodynamic modelling of lead chalcogenide thermoelectrics for optimized ZT, **Peters Matthew**
PB33	Thermodynamic stability of substitutional- and interstitial-type of boron in fcc Fe, **Kouta Iyoda**
PB34	First-principles calculations and thermodynamic modeling of the Cu-Sn-S system relevant to CZTSSe photovoltaic materials, **Guan Pin-Wen**
PB35	Design of Ti-Alloy by Integrating High Throughput Experiments and Calculations, **Liu Libin**
PB36	,
PB37	Phase relations of the Ce_2Co_{17}-Sm_2Co_{17} system, **Du Yusong**
PB38	Experimental reinvestigation and thermodynamic description of Bi-Te binary System, **Zhang Ligang**
PB39	Application of the CALPHAD approach and First-principles calculations to electrode materials in Li ion batteries, **Chang Keke**
PB40	Experimental investigation and thermodynamic modelling of LiF-NdF_3-DyF_3 system, **Abbasalizadeh Aida**
PB41	Thermodynamic properties of liquid In-Li solutions, **Gąsior Władysław**
PB42	Ab-initio study of finite pressure-temperature phase stability for magnetic materials, **Singh Harish Kumar**
PB43	Stability study of Ni_8V phase, **Noori Seyed-mohammad-mehdi**
PB44	Progress in the development of the OECD-NEA Thermodynamics Advanced Fuels - International Database (TAF-ID): Application calculations, **Guéneau Christine**
PB45	Assessment of NiO-SiO_2 System with Kapoor-Frohberg-Gaye Model, **Farina Alexandre**
PB46	Development of cemented carbides through thermodynamic calculations, **Peng Yingbiao**
PB47	Prediction of Free Energy at Finite Temperatures by First-Principles Calculations and Statistical Mechanics, **Liu Zi-Kui**
PB48	,
PB49	Development of lightweight high entropy alloys using coupled CALPHAD-DFT modeling, **Huang Xuejun**
PB50	Thermodynamic modelling of FeO-Fe_2O_3-Ti_2O_3-TiO_2 system, **Panda Sourav Kumar**
PB51	Analysis at high lateral resolution of Mo-Ni-Re system with the CAMECA SXFIVE FE, **Robbes Anne-Sophie**

PB52	Thermodynamic properties of alloys of the binary Sb-Yb system, **Shevchenko Maksym**
PB53	Thermodynamic Assessment of Binary Subsystems of Al_2O_3-CaO-SiO_2-UO_2-ZrO_2 System Using Cell Model and Ionic Model, **Kurata Masaki**
PB54	Computational thermodynamics of solid-solid phase change materials development for thermal energy storage in ternary system: Pentaglycerine - Tris(hydroxymethyl)-aminomethane - 2-amino-2-methyl-1,3-propanediol (PG-TRIS-AMPL), **Chandra Dhanesh**
PB55	The 600°C isothermal section of the La-Zn-Si system, **Tu Hao**
PB56	Experimental investigation of the intermetallic dross phases formed in galvalume baths, **Peng Haoping**
PB57	Isothermal section of Zn-rich corner of the Zn-Al-Mg-Si system at 450° C, **Wang Jianhua**
PB58	High Temperature Experimental Contribution to the Thermodynamic Modeling of Corium Pools, **Gossé Stéphane**
PB59	Explicit calculations of vacancy profile during interdiffusion in quaternary Ni−Pt−Cr−Al system for optimization of new $\gamma -- \gamma$ bond coating, **Desgranges Clara**
PB60	Mechanical Properties of Non-Centrosymmetric $CePt_3Si$ and $CePt_3B$, **Rogl Gerda**
PB61	Kinetic simulation of alloying element partitioning in Q&P steels, **Maheswari Nandakumar**

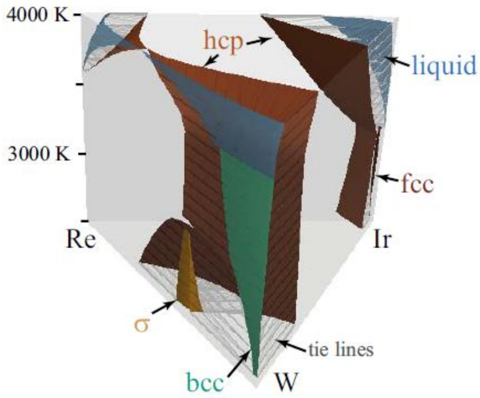
Abstracts

Software tools for high-throughput CALPHAD from first-principles data

A. van de Walle[a]

[a]School of Engineering, Brown University

An array software tools [1] facilitatingthe automated construction of thermodynamicdatabases from first-principles data is presented, with a special focus on methods based on the special quasirandom structures (SQS) formalism [2,3] and on methods designed to handle the common problem of the mechanical instability of "virtual" phases [4] (e.g. fcc W) as well as of dynamically stabilized phases [5] (e.g. bcc Ti).



The software tools rely ona pre-generated,but extensible [3],database of SQS coveringover 30 common intermetallic phases with single or multiple sublattices. Perturbative corrections for short-range order are also included. Extending recent efforts in this direction [6], these tools automate the conversion of SQS ab initio data into standard thermodynamic databases and their combination with elemental SGTE data,thus enabling rapid and effortless generation and visualization of thermodynamic data for multicomponent systems with standard CALPHAD tools.Interfaces to widely used interactive graphical visualization tools are also demonstrated.A key aspect of the process is a formal computational method to calculate the formation energies of mechanically unstable phases that is consistent with SGTE data regarding such phases.The presented tools should prove useful to extend existing high-throughput efforts in the direction of non-stoichiometric phases at finite temperatures.

[1] A. van de Walle, Calphad, 33 (2009) 266.
[2] A. Zunger, S.-H. Wei, L. G. Ferreira & J. E. Bernard, Phys. Rev. Lett., 65 (1990), 353.
[3] A. van de Walle, *et al.*, Calphad, 42 (2013) 13.
[4] A. van de Walle,Q.-J. Hong,S. Kadkhodaei,R. Sun, Nature Commun., 6 (2015) 7559.
[5] S. Kadkhodaei, Q.-J. Hong, and A. van de Walle.Phys. Rev. B, 95 (2017), 064101.
[6] J.-C. Crivello, R. Souques, A. Breidi, N. Bourgeois and J.-M. Joubert, Calphad 51 (2015) 233.

Axel van de Walle

Prof. van de Walle received his B. Eng. at the Ecole Polytechnique de Montreal in Engineering Physics, his PhD in Materials Science and Engineering at MIT, and completed a Post-Doc at Northwestern University. He has held faculty positions at Caltech and Brown University. His research interests include first-principles thermodynamic modelling, accelerated molecular dynamics and computational materials design.

Ab initio based multiscale modelling in physical metallurgy

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So called *ab initio* electronic structure methods have become increasingly important tools in modern physical metallurgy thanks to tremendous improvements during the last few decades both as regards theoretical methodology and computer power. These methods are now routinely used, often in combination with empirical potentials, kinetic models and/or phenomenological models, to make quantitative predictions, not only for bulk properties but also for point and extended defects. This will be illustrated by two recent examples in body-centred cubic (bcc) transition metals: radiation defect clusters and dislocation cores. The first example concerns the prediction of a new allotropic form of iron, namely the C15 Laves phase structure, under irradiation. According to Density Functional Theory (DFT) calculations, this morphology yields by far the lowest energy structure for small self-interstitial clusters [1]. The formation and growth of these point-defect clusters and their impact on the materials properties will be discussed. We will then address the interaction between interstitial solutes (B, C, N and O) and screw dislocations in bcc metals. First considering carbon in bcc Fe, our DFT calculations suggest a strong interaction of carbon solutes with screw dislocation cores inducing a spontaneous reconstruction of the core structure [2]. A similar behaviour for C is observed in group 6 metals (Mo, W) but not in group 5 (V, Nb, Ta). This group dependent behaviour can be linked to the group dependence of the stoichiometric carbide structure. The consequences of this interaction on the solute segregation at dislocation core and on the dislocation mobility will be discussed.

[1] Irradiation-induced formation of nano-crystallites with C15 Laves phase structure in bcc iron, M.-C. Marinica, F. Willaime, J.-P. Crocombette, Phys. Rev. Lett. 108, 025501 (2012)
[2] Dislocation core reconstruction induced by carbon segregation in bcc iron, L. Ventelon, B. Lüthi, E. Clouet, L. Proville, B. Legrand, D. Rodney, F. Willaime, Phys. Rev. B 91, 220102(R) (2015)

François WILLAIME
FW graduated from Ecole Polytechnique (France) in 1987 and got his PhD degree in Solid State Physics from the University of Paris-Sud in 1991. After a postdoc at the University of Berkeley, he started his career at CEA, where he has been recently appointed as Director of Cross-disciplinary Program on Numerical Simulation. His research activities focus on modelling and simulation of materials at the atomic scale, using ab initio electronic structure methods and empirical potentials coupled with kinetic models. Central current research topics are irradiation defects and dislocations in metals.

Experimental Thermodynamics of Nuclear Materials

R.J.M. Konings[a], O. Beneš[a], E. Capelli[a,b], D. Manara[a], K. Popa[a], T. Pavlov[a], L. Vlahovic[a]

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In experimental thermodynamics the most simple and straightforward experiments have already been done in the past by earlier generations of scientists, who developed a variety of thermodynamic and calorimetric techniques to study phase diagrams and thermodynamic properties of a wide range of compounds and phases. The nuclear materials community has played an important role in this, and UO_2 and plutonium metal are probably among the best studied substances in experimental thermodynamics, although it does not mean that there are no questions remaining. Particularly at high temperatures thermodynamic experiments are far from trivial due to reactions and or compositional changes, the main pitfalls for experimental thermodynamics.

In this presentation an overview of recent experimental studies at JRC Karlsruhe on some selected materials will be given with the goal to highlight the challenges faced and the technical solutions implemented to perform reliable high temperature measurements. We will address the following four examples:

- The high-temperature properties of solid UO_2, the most common nuclear fuel in Light Water Reactors, and other actinide oxides. In this example the use of laser flash heating for studying the heat capacity and phase transformations will be addressed.
- The melting behavior of the TaC-HfC solid solution, the highest melting material known so far, demonstrating the extreme capabilities of the laser heating technique.
- The melting behavior and thermodynamic properties of the LiF-BeF_2-ThF_4, the fuel carrier for Molten Salt Reactors systems, and the thermodynamic activities in the liquid phase. For these measurements classical calorimetric and mass spectrometric techniques are used, but had to be adapted to work with corrosive and volatile materials.
- The enthalpy of (La,Ln)PO_4 solid solutions by classical drop calorimetry, revealing lattice strain effects due to cation substitution.

The discussion of the results will address the comparison with CALPHAD and atomistic models.

Rudy Konings is currently head of unit at the Joint Research Centre Karlsruhe of the European Commission. His research interests are nuclear reactor fuels and actinide materials, with emphasis on high temperature chemistry and thermodynamics. In addition he is professor at the Delft University of Technology (Netherlands), where he holds the chair of ‘Chemistry of the nuclear fuel cycle’.

Thermodynamic and physical-property models for the production of primary aluminium

P. Chartrand[a], A. Gheribi[a], K. Wang[a], P. Ouzilleau[a] and C. Robelin[a]

[a] CRCT - Centre for Research in Computational Thermochemistry, Department of Chemical Engineering, Polytechnique Montréal, Canada

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Aluminium is produced by reducing metallurgical alumina, obtained from the Bayer Process, by electrolysis in Hall-Héroult cells. The electrolyte in such cells is based on the Na_3AlF_6-AlF_3-CaF_2-Al_2O_3 system, but impurities and other additives are present which affect the process energy efficiency. A thermodynamic and phase equilibrium model for Al-NaF-AlF_3-CaF_2-Al_2O_3 system was developed [1] by the author's group, using the Modified Quasichemical Model in the Quadruplet Approximation for the liquid phase. Model parameters were obtained by the CALPHAD technique. Since then, in a series of projects (VLAB, *a Virtual Laboratory for the Aluminium Industry*) supported by aluminium primary producers and the National Science and Engineering Research Council of Canada, the thermodynamic and phase equilibrium model has been extended to include several crucial impurities (Al_4C_3, $CO_{2(dissolved)}$, P, S, etc), additives (LiF, MgF_2, KF) and corrosion products from cell materials (SiO_2, Fe). Recently, H_2O, HF and H_2 dissolution in the liquid electrolyte has been considered, and a new thermodynamic model has been developed for carbon anodes with sulphur [2] and hydrogen impurities [3]. In parallel, a series of models for the physical properties (density, electrical conductivity, viscosity, thermal conductivity), with a direct link to the underlying thermodynamic models, were developed for important phases in the Hall-Heroult process. The presentation will highlight the key challenges encountered during the VLAB project and the main results obtained in terms of modelling.

[1] P. Chartrand and A.D. Pelton, TMS Light Metals 2002;
[2] P. Ouzilleau *et al*., Metall. and Mater. Trans. B, 47(3), p.1817 (2016);
[3] P. Ouzilleau *et al*., CARBON, 85, p.99 (2015).

Prof. Patrice Chartrand, Ph.D.

Prof. Chartrand obtained his Ph.D. in Metallurgical Engineering from Polytechnique Montréal in 2001. He is the Canadian Research Chair (Tier 1) in Computational Thermodynamics for High Temperature Sustainable Processes. Prof. Chartrand received the *Grand Prix Alcan 2007* from the *Académie des Sciences de l'Institut de France*. He is Co-Director of the Centre for Research in Computational Thermochemistry (CRCT) of Polytechnique Montreal, and a co-developer of FactSage.

On the 3rd Generation of Thermodynamic Databases

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The 2nd generation of thermodynamic databases have been successfully used for several decades now. However, the 2nd generation uses descriptions of the pure elements based on polynomials [1] that are less accurate the lower the temperature is and give completely unphysical results below room temperature. Today many practical applications require accurate descriptions to low temperatures often far below room temperature. That is the case for the applications within the Hero-m center [2] at KTH and since its start in 2007 the CALPHAD activities at KTH have been devoted to the development of the 3rd generation of thermodynamic databases using more physically based models.

Several elements have been described using the models first presented in the paper on Fe [3] which was the first work in which the recommendations from the 1995 Ringberg Workshop were used. Binaries are described using the new unaries and applying the two-state liquid model [4] and the revised magnetic model [5]. Assessments of ternaries are ongoing.

An overview and a status report from that work will be given here presenting the models and methods used and the systems covered so far. The prevailing difficulties will be discussed.

[1] A. T. Dinsdale, CALPHAD, 15 (1991) 317.
[2] VINN Excellence Centre Hierarchic Engineering of Industrial Materials, www.hero-m.mse.kth.se
[3] Q. Chen and B. Sundman, Journal of Phase Equilibria, 22 (6) (2001) 631.
[4] J. Ågren, Journal of Physical Chemistry of Liquids 18 (1988) 123.
[5] W. Xiong, Q. Chen, P. A. Korzhavyi, M. Selleby, CALPHAD, 39 (2012) 11-20.

Malin Selleby

Malin Selleby is professor in Computational Thermodynamics at KTH Royal Institute of Technology in Stockholm. Her main research interest is thermodynamic modelling of metallic systems using the CALPHAD technique.

Calphad study of planetary condensation

Surendra Saxena,

Geocentrum, Uppsala, Sweden and Florida International University, Miami, Florida, USA.

Terrestrial planets may have formed out of planetesimals that condensed in a solar nebula. The chemical composition of the nebular gas has been determined by combining information from many sources that include the chemical composition of the primitive meteorites and the solar corona [1]. With practically all elements present in several thousand gas and solid species, the system becomes very large. The physical conditions are extreme with pressure varying from 1E-12 to 3.6 mega bar and high temperatures to 6000K. Gibbs energy minimization of such a system requires thermodynamic data at ambient pressures and equations of state that extend to planetary cores. The calphad methods of assessing data from phase equilibrium experimental and measured pressure-volume-temperature (PVT) data are required. The thermochemical data on gases and solids at 1 bar for many species has been well tested and is readily available in many compilations such as the FACTSAGE database [2]. Using such data, Saxena and Hrubiak [3] calculated the chemical composition and density of the uncompressed earth and found that the gas condensing between 600 and 700 K and at pressure between 1e-6 to 1e-3 bars had a density of 4 g/cm3 matching the uncompressed density of the planet. However, if we want to continue to study the formation process of the proto planets as they self-compress into planetary cores and mantles, we need to include the PVT data. This effort has started for the system Mg-Fe-Ca-Al-Si-C-H-O with some 90 solids and 13 fluid phase. The fluid model is based on some experimental data and some molecular dynamics extrapolations to 1 megabar.

The results of these calculations are likely to change our understanding of the chemical composition of the earth and how it would differentiate into a chemically complex core and silicate mantle.

[1] Lodders, K.,..Astrophys. J. 591,(2003) 1220–1247.

[2] http://www.crct.polymtl.ca/

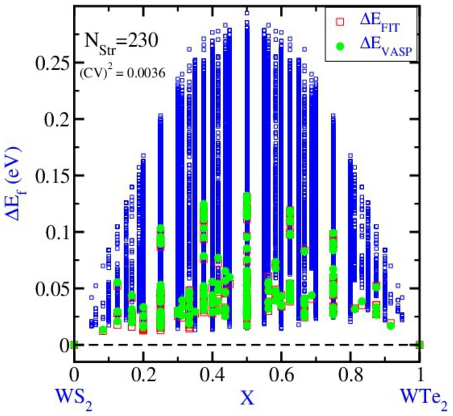
[3] Saxena, S.K. and Hrubiak R. Earth and Planetary Science Letters 393 (2014) 113–119.

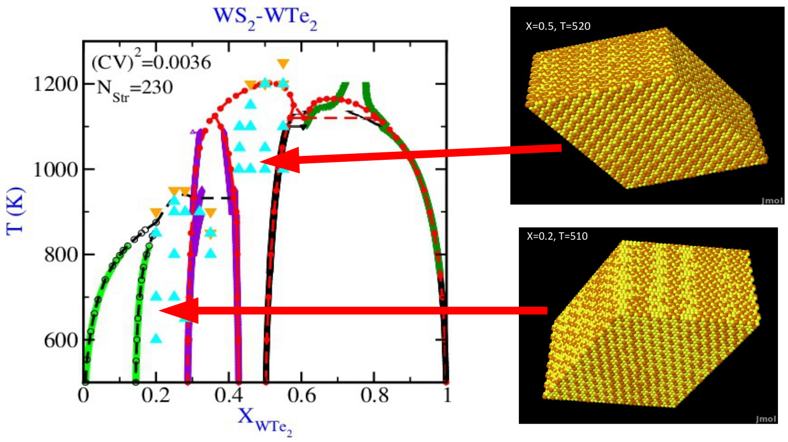
First Principles Calculation of the WS_2-WTe_2, Phase Diagram

B.P. Burton[1]
[1]NIST, 100 Bureau Dr. Gaithersburg, MD, 20899

The ATAT package, with a basis of VASP-calculated formation energies was used to calculate WS_2-WTe_2 phase diagram. This work was performed because an earlier calculation of the MoS_2-$MoTe_2$ phase diagram [1] predicted two incommensuratly ordered, entropy stabilized phases, so one might expect similar results for WS_2-WTe_2.

Incommensurare phases were predicted in WS_2-WTe_2 as well at X_{WTe2}~0.46 (upper-right panel) and X_{WTe2}~0.22 (lower-right panel).





The crystal structures of these phases are yet to be determined, but it is clear from the ground-state analysis (left panel) that neither of them is a ground-state. Note, that the order-disorder transitions and multicritical points drawn for the predicted ordered phases are conjectural; i.e. within precision of the Monte-Carlo simulations that were used to identify phase boundaries, either first- or second-order transitions are permissable.

[1] B. P. Burton and A. K. Singh, J. Appl. Phys. 120, 155101 (2016).

Benjamin Burton

Computational Materials Scientist at NIST.

Stability of $NdFe_{12}$(N) Series Compounds: A First-principles Study

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It has been theoretically predicted that $ThMn_{12}$-type compounds such as $NdFe_{12}$ and $NdFe_{12}N$ exhibit high magnetization and magnetocrystalline anisotropy energy comparable to the currently strongest $Nd_2Fe_{14}B$ permanent magnet[1–3]. However, due to the intrinsic thermodynamic instability of the both $NdFe_{12}$ and $NdFe_{12}N$ compounds, it is very difficult to synthesize the materials. By substitution of either Fe or Nd atoms with other elements, the stability of the compound is possible to be improved. In this work, we attempt to investigate the effects of substitution of several transition metal elements such as Ti, Co, Zr, V, and Sm on the thermodynamic, electronic, and dynamic instability in the $NdFe_{12}$ and $NdFe_{12}N$ compounds.

The total energy and electronic structure are calculated from first-principles that based on density functional theory (DFT) using Vienna Ab-initio Simulation Package (VASP)[4] with projector augmented-wave method (PAW) and generalized gradient approximation (GGA) that describe the exchange and correlation energies. Cluster expansion is performed using Alloy Theoretic Automated Toolkit (ATAT)[5] to investigate the mixing behavior and stable range of the 3^{rd} element substitution.

We observed that several elements can improve the thermodynamic stability of above two structures while they affect the electronic structures and atomic arrangements in the different manners.

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Arkapol Saengdeejing

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Calphad XLVI - Monday, June 12, 2017, 10:10 - 10:25 **[O3]**

Configurational thermodynamics of C in bcc Fe: a combined computational study

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It is well known that the equilibrium solubility of C in ferrite (bcc Fe) is less than 0.1 at.% while Fe-C martensite may contain up to 8 at.% C. The thermodynamic properties of C-supersaturated bcc Fe are difficult to measure experimentally, and are subject to uncertainties when extrapolated from ferrite. Computational techniques, however, can provide atomic details and quantitative thermodynamic descriptions.

The distribution of C on the octahedral interstitial sites in bcc Fe is investigated using Monte Carlo simulations in canonical (NVT) ensemble. Pairwise C–C interaction energies are taken from either density-functional-theory (DFT) calculations [1] or an empirical embedded-atom-method (EAM) potential [2]. Configurational entropy and Helmholtz free energy are obtained by integration from a reference state. In these simulations, C atoms are allowed to occupy either all the three sublattices of octahedral interstitial sites (disordered) or only one (Zener-ordered). Constant-volume phase diagrams are constructed.

Based on the Monte Carlo results using DFT and EAM inputs, some observations include: (1) there exists a two-phase region between the C-lean disordered ferrite phase and a C-rich ordered phase ($Fe_{16}C_1$ from DFT, $Fe_{16}C_2$ from EAM); (2) the excess configurational free energy of the disordered phase is of an ordering type; (3) the disordered phase has a lower free energy than the Zener-ordered one, primarily due to a higher configurational entropy. To account for the tetragonal distortion brought about by C, an approximate correction is made based on a force-dipole description of C in a linear elastic medium of bcc Fe. Such a correction reduces, but does not alter, the free-energy preference of the disordered phase.

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Jiayi Yan

Jiayi is a postdoctoral researcher at KTH. He received his B.Eng. from Tsinghua University, Beijing, China, and his Ph.D. from Northwestern University, Evanston, USA. His research involves computational materials design supported by CALPHAD and other mechanistic models, as well as the underlying physical processes. He has been working on design projects for titanium alloys, steels, and cemented carbides.

Configurational energy of formation of alloys: Ising models vs the Cluster Expansion

J.M. Sanchez

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In this presentation we establish a clear distinction between phenomenological approaches that express the energy of an alloy in the form of a generalized Ising model, i.e. with constant pair and many body interactions, and cluster expansions that use a set of complete basis functions in configurational space and define the interactions as projections of the energy onto the basis functions. For the latter case, the interactions are functions of concentration and depend, furthermore, on the full state of order of the system. Such dependence is expected since the configurational energy is shown to be a homogeneous function of degree one in the complete set of configurational variables, or correlation functions, with the interactions being the Euler derivatives of the energy with respect to the correlation functions. It is shown that, by including the concentration dependence of the interactions either explicitly or through their dependence on volume, the cluster expansion converges significantly faster than the phenomenological Ising-like models commonly used to represent the energies of disordered alloys.

J.M. Sanchez

Dr. Juan M. Sanchez is Professor in the Department of Mechanical Engineering at the University of Texas in Austin. He obtained his B.S. in Physics at the University of Cordoba, Argentina, and his M.S. and Ph.D. in Material Scienceat the University of California, Los Angeles. His primary research interest is the development and application of first principles computational methods for the construction of phase diagrams.

Alloying and Phase Stability in MAX Phases: A High-throughput Cluster Expansion Approach

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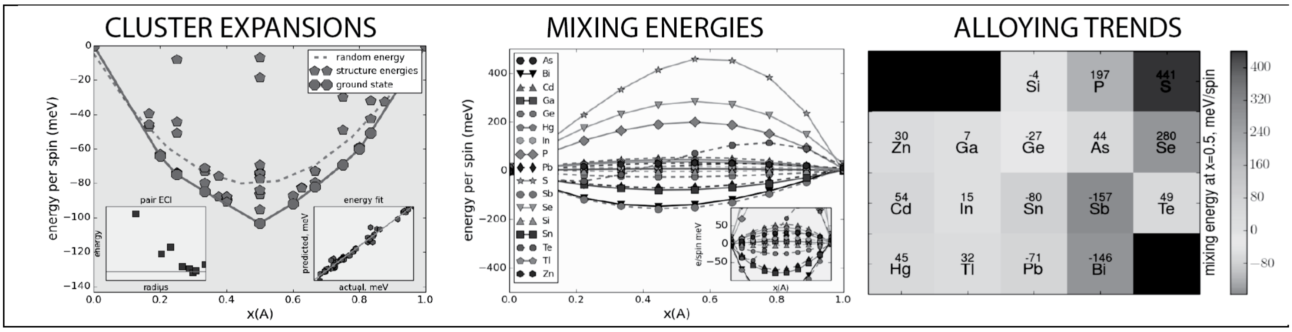

MAX phases (M=Metal, A=Group A, X=C/N) are a class of nano-layered carbides and nitrides with stacking sequences (and stoichiometry) $M_{n+1}A_nX_n$ and that have intermediate properties to those of metals and ceramics that make them promising high-temperature structural materials and coatings. Recently, it has been found that allowing in the M, A and X sublattices may result in notable improvements in properties, provided such alloying is thermodynamically favourable. In this talk, I will present recent work on the alloying trends and phase stability in the M, A and X sublattices of 211 and 312 MAX carbides. Specifically, the energetics of the configurational space in over 150 quaternary systems was explored through a so-called high-throughput cluster expansion approach in which the energy of arbitrary configurations is parameterized in terms of their constituent pairs, triples, tetrahedra, etc. Observed trends are rationalized in terms of the underlying changes in the electronic structure of the compounds. The observed mixing trends are also discussed in terms of their relevance for yet undiscovered MAX solid solutions. I will also discuss (and will provide some examples) the types of analyzes—at the DFT level--that are necessary in order to provide synthesis pathways for promising MAX solid solutions. Finally, some preliminary experimental verification of the predictions produced will be presented.

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Raymundo Arróyave

R. Arróyave is an Associate Professor in the Department of Materials Science and Engineering (and by courtesy in Mechanical Engineering) at Texas A&M University, USA. His interests are in computational thermodynamics and kinetics of materials, computer-aided materials design and accelerated materials discovery.

Comparison of calculated and experimental values of enthalpies of formation of intermetallic compounds.

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Over the past decades, *ab-initio* methods have proven accurate and useful tools for the prediction of ground states and formation energies in binary and ternary systems. For example:

- In alloy systems where significant disagreements or uncertainties in the experimental data exist, *ab-initio* calculations can offer valuable information.
- In a given binary alloy, the experimental determinations of the enthalpies of formation are the more often been performed for one or two compositions and not for all existing compounds in the system. The *ab-initio* methods allow to calculate the enthalpies of formation of all the compounds which have been listed in the system.
- The *ab-initio* methods give the possibility to calculate the enthalpies of formation of metastable (or unstable) compounds. The calculation of binary or ternary phase diagrams needs often the knowledge of such data (lattice stabilities, end-members enthalpies of formation). In the Calphad calculations, these data are the more often estimated.
- The experimental determinations of enthalpies of formation of ternary compounds are very scarce. Indeed, it is often very difficult to obtain such data with a good precision. Again the ab-initio methods can bring valuable information.

In the presented work, the enthalpies of formation as well as the lattice parameters of intermetallic compounds of two transition metals or of a transition metal and a rare earth element have calculated. A particular attention has been turned to the alloys of Ti, Zr or Hf with Ni, Pd, Pt, Co; Rh, Ir, Fe elements and to the systems of Y, La, Gd, Lu with Ni, Co, and Fe.

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Scientific interest: Thermodynamics, phase transformations, thermodynamic simulations, phase equilibria in multicomponent systems
Research topics: ab-initio calculation of enthalpies of formation and lattice parameters of intermetallic compounds of transition metals with p elements, other transition metals and rare-earth elements.

Nickel incorporation in Ti_2AlC ceramic

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In order to extend the high temperature applications of the Ti_2AlC ceramic, the brazing of the Ti_2AlC ceramic to nickel has been successfully performed using a BNi-2 filler alloy [1]. In the study, it was observed that the Ni would diffuse into the Ti_2AlC substrate during the brazing process, and then induce the decomposition of Ti_2AlC into TiC_x and $Ni_3(Al, Ti)$ compounds at high content. Recently, we have undertaken first principle calculation in the framework of the density functional theory (DFT), in order to unveil the decomposition mechanisms of the Ti_2AlC compound by Ni incorporations. The calculations reveal that in Ti_2AlC the formation energy of the Al vacancy is only half that of the Ti vacancy, and very close to that of the C vacancy, suggesting that the formation of Al and C vacancies are much easier than that of Ti vacancies. However, a large formation energy is required to insert Ni atoms at the C site. In addition, the final structure turns to be mechanically unstable since some negative bands appear in the phonon bandstructure. A significant less formation energy is required to insert Ni atoms at the Al site, and the vibrational spectrum shows that the structure is stable. However, a weak interaction between Ni and Al atoms could be observed in the phonon bandstructure. Indeed some low frequency bands can be ascribed to localized modes due to Ni solute atoms. Finally, when the concentration of Ni atoms is increased, those bands tend to distort and to become negative. This behavior could be attributed to the formation of Ni_3Al and TiC_x compounds after decomposition of the MAX compound consistently with the experimental characterization of the brazed joints.

[1] C. Lu, et al, Microstructure evolution and brazing mechanisms of the Ti_2AlC/Ni joints using nickel based filler alloy, Journal of the European Ceramic Society 36 (14) (2016) 3319-3327.

Chengjie Lu

A joint Ph.D. student from China, the Harbin Institute of Technology, now study in France, the ONERA-CNRS, LEM. The research work mainly focuses on the brazing mechanisms of the Ti_2AlC ceramic using nickel based filler alloy, using various characterization techniques and DFT methods.

Ground state predictions for sulfide electrolytes

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Solid electrolytes composed oflithium superionic conductor materials exhibit good safety and stability characteristics, and high Li-ion conductivity.Hence, they are expected to perform well in lithium-ion batteries. The last few decades have seen an ongoing search for new solid electrolyte materials. For example, the lithium superionic conductor, $Li_{10}GeP_2S_{12}$, shows an extremely high lithium ionic conductivity of 12 mS/cm at 27 °C [1], which is comparable to or higher than the conductivities of the organic liquid electrolytes used currently in lithium-ion batteries. In this study, in order to identify the ground-state structures of the sulfide system, an evolutionary algorithm was used to determine their total energies and optimized lattice structures.

The evolutionary algorithm was implemented in the USPEX code [2] and was coupled with first-principles calculations made within the framework of the density functional theory (the Vienna ab initio simulation package, VASP)[3,4]. By combining the theoretical predictions and high-pressure experiments with a multi-anvil cell, we found that a novel stable crystal structure of $Li_3PS_4$was formed under high pressures. At the ambient pressure, Li_3PS_4 shows successive structural transitions from γ- to β-, and β- to α-type with increasing temperature, which is well established. An evolutionary algorithm successfully predicted the formation ofa γ-type crystal structure at the ambient pressure and two possible stable crystal structures of theδ- and ε-type under high pressures. The stability of the obtained structures was examined in terms of both static and dynamic stability by first-principles calculation. Insitu synchrotron X-ray experiments revealed that the high-pressure phase is the predicted δ-Li_3PS_4 phase.

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Research topics: First-principles calculations, Evolutionary algorithm, Structure analysis by X-Ray and Neutron Scattering

A New Methodology for High-throughput Screening of Composition-Microstructure-Micromechanical/Properties Relationships

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We introduced a strategic high throughput Diffusion Multiple that undergoes interdiffusion annealing followed by realistic thermal treatment. The blended spectra of phases and microstructures subjected to treatment in deeply grooved composition gradients enables the microstructure and micromechanical properties (inc. modulus, nanohardness, yield strength, CRSS and creep etc for Mg-Zn, Co-Al-V, Ti-Al-Mo, Ti-Al-Cr-Mo, Ti-Al-Cr-Mo-V alloys) of structural materials to be surveyed by high-spatially resolved micro-analysis along the composition arrays. The new methodology was demonstrated as a robust high-throughput methodology that enables rapid screening of the full composition-microstructure-micromechanical/properties relationships for different metallic materials. It has also proven great success at elucidating the lasting effects of alloying elements and diffusion flux on microstructure, micromechanical properties, phase transformation, and their interrelationships as a whole.

Prof. Yuwen Cui

Prof. Yuwen Cui is a senior research at Instituto de Ciencia de Materiales de Aragón (ICMA, Zaragoza, Spain) and a full professor at Nanjing Tech University (Nanjing, China). He received his MSc and PhD in Materials Science from Central South University (Changsha, China) in 1995 and 1999, respectively. His current research focuses on CALPHAD, high throughput diffusion research, Landau model of phase transformation and many other areas of Integrated Computational Materials Engineering.

Impacts of thermodynamic and kinetic model parameterisation on precipitation simulations – Case study of NbC precipitation in microalloyed steel

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Computational simulation of precipitation in microalloyed steel is a powerful tool for improved steel processing. Since the kinetic formulations for nucleation, growth and coarsening contain thermodynamic state variables, predictive precipitation simulation requires a proper thermodynamic modelling base, or more general, thermodynamic model parameterisation affects the kinetic simulation results [1]. For face-centered cubic NbC precipitates in microalloyed Fe-Nb-C steel, these interrelations were pointed out by Radis & Kozeschnik [2]. Meanwhile, the Fe-Nb system has been re-assessed three times [3-5], associated with particular changes of alloy phase descriptions. However, none of these assessments considered available enthalpies of mixing from first-principles analysis [6].

We present and discuss the consequences of differences of suggested mixing thermodynamics in Fe-Nb alloy phases on the kinetics of NbC precipitation and propose a revised thermodynamic parameter set for the reproduction of experimental phase equilibria, first-principles enthalpies of mixing and kinetics of NbC precipitation during aging of microalloyed steels.

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Erwin Povoden-Karadeniz

obtained his doctoral degree at ETH Zurich in the field of thermodynamic oxide modeling for solid oxide fuel cell applications. He holds a position as assistant professor in computational materials engineering at TU Wien. Hisresearch topicsfocus on applied CALPHAD to physically-based simulations of phase transformations in multi-component alloy systems, including steel, Ni-base superalloys, and light metals.

Thermo-kinetic modeling for the growth/dissolution of α slabs and lamellae in Ti–55531 under continuous heating condition

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The remarkable mechanical performance of Ti–55531 alloy strongly depends on the formation or dissolution of α precipitates with complicated microstructural features, including distinct content, size, morphology, distribution, etc [1]. An updated thermodynamic model, which incorporated Gibbs-Thomson effect into the conventional Ivanstov [2-3] and Aaron's dissolution equations [4-5], was developed to describe the growth and/or dissolution behaviors of two types of α phase (α slab and α lamellae) under continuous heating condition in Ti–55531 alloy. The control of partitioned composition was implemented by real-time communication with thermodynamic database of Ti alloys released by ThermoCalc AB®. With the calculations compared with the experiments, the growth and dissolution of slab α phase are demonstrated to follow the kinetics of planar interface without the Gibbs-Thomson effect. In contrast, the Gibbs-Thomson effect are proven to do contributions to lamellar α phase. The lengthening of lamellar α tips follow a kinetics controlled by a mixture of bulk and boundary diffusion, in comparison with the pure bulk diffusion of fastest Al governs the re-dissolution of both tips and broad faces. The diffusion of Mo plays an important role in the negligible growth of broad face in α slab at lower temperature, while the diffusion of Al controls the dissolution of broad face in α slab at the elevated temperature. [6]

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Fuwen Chen

Ms. Fuwen Chen is currently a Ph.D. candidate at Central South University. She got her bachelor's and master's degree of materials science at the same university. Ms. Chen has expertise in the investigation of phase transformation kinetics of titanium alloys by combining experiments and computational thermodynamics and diffusion kinetics. She has published research papers in *Metall. Mater. Trans. A*, *J. Alloys Compd.*, *Corr. Sci.* etc.

Overcoming the Diffusion Bottleneck: Effect of Alloying Elements on Phase Transformations and Carbides Dissolution in Martensitic Stainless Steels

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Martensitic Stainless Steels (MSS) become an attractive choice for automotive industry in view of their good combination of properties such strength, formability and corrosion resistance. MSS are Fe-Cr-C alloys, which are heat treated in the austenitisation range and then quenched to room temperature to form martensite. However, depending on the chemical composition and the processing route, residual ferrite and chromium carbides can also be found in the final structure. These sub-products are detrimental for both mechanical and functional properties and therefore should be minimised. An in-depth understanding of the kinetics of sub-products formation is thus needed to optimise industrial practices. To fulfil this task, thermodynamic and kinetic models can be used to calculate carbon diffusion, elements distribution and phase transformation during heat treatments. A one-dimension moving phase boundary simulation was performed with DICTRA 26, in which the dissolution of chromium-rich carbides, diffusion of carbon and subsequent ferrite to austenite transformation reactions are treated simultaneously in a one-cell simulation. This extra complexity is needed to capture the relationship between the carbide dissolution and the ferrite to austenite transformation. Results show that the diffusion kinetics of interstitial carbon atoms is controlled by the substitutional diffusion of carbide formers elements (Cr and Mo), which decrease carbide dissolution rate and consequently inhibit the phase transformation kinetics. Numerical predictions are compared to experimental results for a newly developed AISI 410 martensitic stainless steel, confirming the trend highlighted by DICTRA calculations. Optimised steel composition and processing practices are finally suggested.

Alvise Miotti Bettanini

I hold a Master of Science degree in Material Science and Engineering from KTH, Royal Institute of Technology of Stockholm. I'm pursuing a PhD degree in Metallurgy at Université catholique de Louvain (UCL) with a project aimed at improving the mechanical properties of a Nb-modified AISI 410 martensitic stainless steel in collaboration with Aperam Stainless Steel Europe.

Temperature Dependence of Diffusivities from a Single Experiment – Experimental Technique and Evaluation Method

H. Engelhardt, M. Rettenmayr

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The temperature dependence of diffusivities istypically determined by numerous diffusion heat treatments at a series of discrete temperatures. With the aim of shortening this procedure and improving the accuracy, anew method consisting of an experimental routineand the corresponding evaluation procedure for interdiffusionsamplesis suggested. The methodutilizes diffusion in a temperature gradient. Information on the diffusion process over anextended temperature range is obtained from a single diffusion sample [1].
A sequence of pronounced concentration gradients along a rod shaped sampleisused as initial state for the diffusion experiments. Directional solidification and annealing techniques offer the opportunity to generatetunable varying concentration gradients. By applying directional solidification,the diffusion samples are created starting exclusively from solid/liquid interfaces, external interfaces with the associated oxide layers are completely avoided. This novel type of diffusion samplesexhibits significantly reduced defect density in the diffusion zone as compared to diffusion couples joined by existing techniques such as friction welding or diffusion welding under pressure, both with accompanying mechanical deformation.
When annealing directionally solidified diffusion samplesin a temperature gradient, appropriate concentration gradients over an extended sample lengthand at the same time a narrow concentration interval are guaranteed.
The method has been verified for binary interdiffusion coefficients and is currently extended to the determination of temperature dependentindividual mobilitesduringinterdiffusion in ternary alloys.

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Hannes Engelhardt

Studied materials science and engineering at FriedrichSchillerUniversity Jena (Germany). He worked on the development of novel methods for the determination of thermodynamic and kinetic data of alloys during his PhDtime and is currently working in the field of multicomponent diffusion and solidification phenomena.

Diffusivities and Atomic Mobilities in fcc Cu-Ni-Sn Alloys

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An accurate diffusion database is the key to realize the description of microstructure evolution of Cu alloy. The atomic mobility database for fcc phase in multicomponent Cu alloy including 30 key elements was established via the DICTRA (DIffusion Controlled TRAnsformation) software package [1]. By means of the solid-solid diffusion couples together with the electron probe microanalysis technique and Matano-Kirkaldy method [2], the composition dependence of ternary interdiffusion coefficients in Cu-rich fcc Cu-Ni-Sn alloy at 1073, 1023 and 973 K were measured. Based on the experimentally determined interdiffusion coefficients as well as thermodynamic description of fcc phase, atomic mobilities of fcc phase in Cu-Ni-Sn system were assessed by means of DICTRA[1]. The newly obtained parameters were incorporated in our diffusivity database. All the kinetic description was further verified by comprehensive comparisons between various model-predicted diffusion properties and the experimental data. The general agreement validates the potential application of the present atomic mobility database to simulate the diffusion in higher orders.

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Yuling Liu

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Research field:
- Phase diagram determination, thermodynamic modeling and thermodynamic database of copper alloys and its applications
- Diffusivities modeling and atomic mobility of copper alloys

Analytical model with interaction between species for growth and dissolution of precipitates

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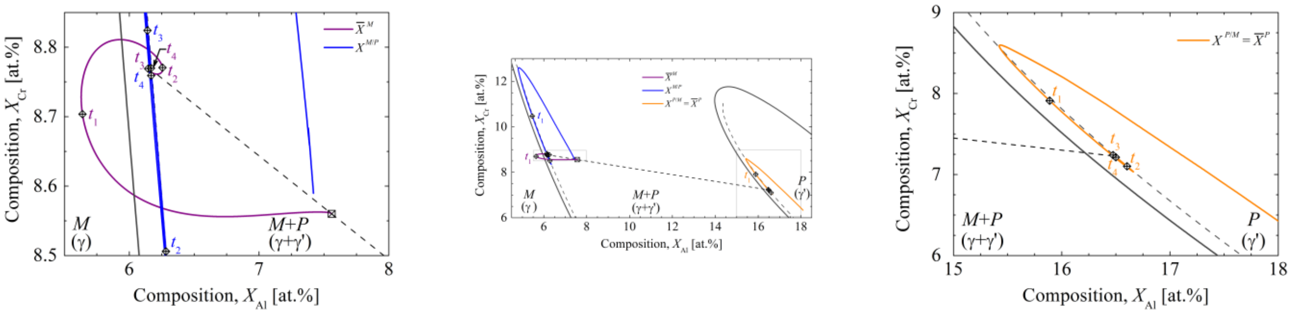
An analytical model for growth in a semi-infinite matrix with cross-diffusion between species is presented. Application is given for precipitation of the γ'-phase in the γ-matrix during isothermal holding at 600 °C in the Ni – 7.56 at.% Al – 8.56 at.% Cr alloy. The exact time dependent solutions for the solute profiles and the growth kinetics are validated with a numerical front-tracking simulation. The simulation of cross diffusion terms in a multicomponent alloy being demonstrated, extension of the analytical solution is given for growth in a matrix of finite size. The driving force is based on a mathematical estimation of the far-field composition. The Gibbs-Thomson effect is also accounted for to consider the effect of curvature on the equilibrium tie-lines. Comparison of analytical solution with the numerical front-tracking simulation shows excellent agreement. Results point out the detrimental approximation of using the average composition of the matrix for computing the driving force as well as the limitation of the solution found in the literature [1, 2]. A detailed discussion is given on the origin of oscillations observed for the time evolution of the precipitate radius which alternates between growth and dissolution regimes, pointing out the combined role of solute fluxes and tie-lines compositions at the precipitate/matrix interface illustrated hereafter by drawing the transformation paths in the phase diagram.



Evolution of interfacial and average compositionsduring growth of a γ'-precipitate in a γ-matrix at 600°C

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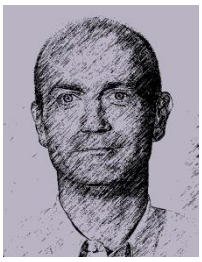

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Engineer from the InstitutPolytechnique de Grenoble, FR (1990), PhD from the EcolePolytechniqueFédérale de Lausanne, CH (1994), Habilitation from the InstitutNational Polytechnique de Lorraine, FR (2007), researcher with the Centre National de la RechercheScientifique since 1999, expert in microstructure formation during solidification processing and related phase transformations, co-author of 200 articles in journals and proceedings.

Quantitative phase-field simulation of microstructure evolution in Ni-Al alloys during entire preparation process and its linking to mechanical property

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As is well known, the core task in the field of materials science and engineering is to establish the quantitative composition-process-structure-property relation in materials. The prevailing trial-and-error experimental approach for the past century is of low efficiency, and thus the underlying computation modeling/simulation may serve as an alternative way to achieve this goal. However, an extensive literature review reveals that the current status is still not satisfactory. Most of the computational modelling focuses i.e., either the microstructure simulation or the property modelling, during one materials stage. The major difficulty lies in the large scale difference, not only between different microstructure scales during various preparation processes, but also between the nano-/meso-scale microstructure simulation and macro-scale property modelling.

By coupling the multi-phase-field model with the CALPHAD databases, we have realized two-dimensional continuous quantitative phase-field simulations of the microstructure evolution in single-crystal Ni-Al alloys during the entire preparation process, ranging from solidification, solution to aging. During the phase-field simulation, a reasonable simulation domain should be chosen and the numerical grid spacing may vary in order to resolve the characteristic microstructures correctly. After that, the phase-field simulated microstructural information was linked with the strengthening models, from which the evolution of yield strength in the target single-crystal Ni-Al alloys during the entire preparation process can be predicted. The good agreement between the predicted yield strength and the experiment data indicates that the quantitative composition-process-structure-property relation in the target alloys can be established.

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Microstructure evolution during melting of single crystal superalloy: A combined experimental and computational study

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Single crystal superalloys inherit severe micro-segregation of the directional solidification process. Secondary phases -such as the γ´ phase- form towards at the end of solidification, being stabilised by the presence of chemical inhomogeneity. Solution heat treatments are commonly used to reverse this process. Optimal heat treatments aim at raising the heat treatment temperature as quickly as possible, while avoiding partial melting of the material, and ideally the heat treatment temperature closely follows the homogenisation kinetics of the material [1]. However, while the kinetics of solidification has been studied in great detail, knowledge of the kinetics of melting of alloy microstructures is currently scarce.

In this work polished samples of CMSX-4 superalloy have been heated rapidly above liquidus temperature, in Argon atmosphere, using the hot stage of a Confocal Scanning Laser Microscope (CSLM). This allows observing the appearance and spread of the liquid phase at surface of the sample during heating. The temperature was measured using a thermocouple placed directly under the 3mm thick sample. Observed onset of melting and evolution of the melt pool was then correlated with results obtained from thermodynamic calculations using lever-rule and Scheil conditions. Finally phase-field simulations, using the MICRESS package, were used to simulate the melting of a CMSX-4 as-cast microstructure.

It is found that melting starts well above the end-of-solidification temperature obtained from the Scheil model. Up 30% fraction liquid, CSLM and phase-field results are in good agreement, while above CSLM shows better agreement with the Scheil results.

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Matching time and spatial resolutions of rapid solidification: Dynamic TEM experiments coupled to CALPHAD-informed phase-field simulations

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A fundamental understanding of the impact of rapid solidification on materials microstructure and performance is critical in advanced manufacturing processes. Towards addressing this scientific challenge, a combination of dynamic transmission electron microscopy experiments (DTEM) and CALPHAD-informed phase-field modeling studies is presented to characterize the microstructure evolution in Cu-44Ni (at.%) thin-film alloys during rapid solidification [1]. Experiments – conducted in the DTEM [2,3] – consist of *in situ* laser melting and determination of the solidification kinetics by monitoring the solid-liquid interface and the overall microstructure evolution (time-resolved measurements) during the solidification process. Modeling of the Cu-Ni alloy microstructure evolution is based on a phase-field model including realistic Gibbs energies and diffusion coefficients from the CALPHAD framework (thermodynamic and mobility databases) [4,5]. DTEM experiments highlighted the formation of microsegregation-free columnar grains with interface velocities varying from ~.2 to ~.5 m/s. After an “incubation” time, the interface accelerated, and additional experiments revealed that a decrease of the temperature gradient induces a decrease in the interface velocity. The modeling strategy permitted the simulation (in 1D and 2D) of the solidification process from the initially diffusion-controlled to the partitionless regimes. Modeling successes and challenges will be discussed and compared with experimental data at the same time and spatial resolutions. Finally, future challenges and work to be done in this field of research will be discussed.

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Glass Transition Temperature and Phase Diagrams of Butadiene Rubber and Styrene Butadiene Rubber: Molecular Dynamics Simulation

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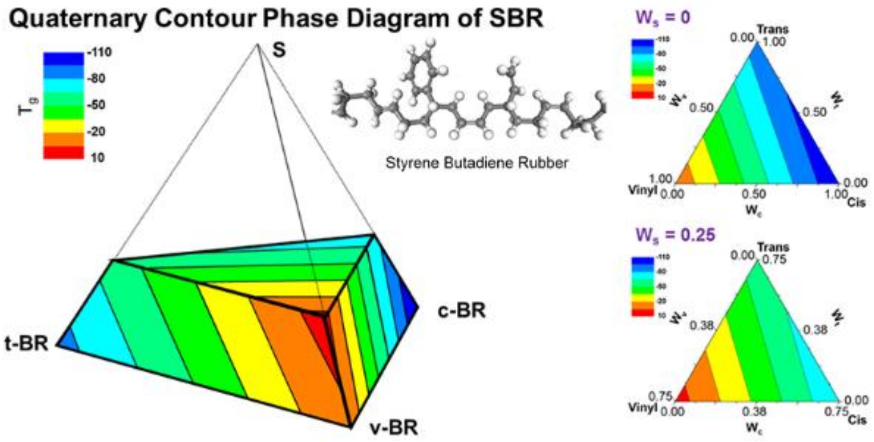
To prevent car accidents, it is important to evaluate the thermal stability of tire rubbers, such as natural rubber (NR), butadiene rubber (BR), and styrene butadiene rubber (SBR). Controlling the glass transition temperature (Tg) is the main factor of obtaining the desirable thermal stability. Here, we developed an optimized equation for the prediction of Tg of the various rubber systems using molecular dynamics (MD) simulations. We modeled a random copolymer system, blended monomers, and calculated the Tg of butadiene isomers in each composition. From these results, we designed the Tg contour of ternary cis-trans-vinyl butadiene and derived an equation of Tg for the ternary system. Moreover, we developed an equation to evaluate the pseudo-ternary Tg of quaternary SBR and plotted it. Our results present a novel way of prediction of Tg of ternary BR and quaternary SBR, which is critical for rational tire design with optimized thermal and mechanical stability.



Hyuck Mo Lee

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Phase stability and chemical composition of nanoprecipitates: A first principles study for the example of κ carbides

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Precipitates play a central role for the strength and ductility in many materials. Simulating theirimpact on the mechanical performance of the host material requires the knowledge of thethermodynamicstability and atomic configuration of the precipitates. The carbon content ofcoherent carbide nanoparticles in steels, for example, often substantially deviates fromthe ideal stoichiometric composition. This influences the interaction with dislocations and other solutes andhence the hardening and embrittlement. Calphad based evaluations determine the Gibbs energy and composition of precipitate phases from bulk phase diagrams, largely neglecting the impact of elastic energy and chemical interaction due to the presence of coherent interfaces. First principles investigations, on the other hand, typically determine the phase stability of particles taking the pure elements as reference structures and therewith disregarding the relevance of competing phases and solid solutions.

In the present work, we combinedensity functional theory with the concept of chemical potentials to simulate the interplay between precipitate and matrix phase. This combination provides a physically intuitive tool that allows one to describe continuous changes of the composition and resulting configurational entropy,though the actual calculations are limited to finite-size supercells and discrete concentrations. For the equalization of the chemical potentials of the C atoms between carbides and the matrix a constrained paraequilibrium is assumed. In addition to the chemistry, the minimization of the total Gibbs energy also takes the optimumcoherent lattice parameter of matrix and precipitates into account. This new concept is applied tonano-sized κ carbides $(Fe,Mn)_3AlC$, one of the most important precipitate phases in Fe-Mn-Al-C steels [1]. The resulting chemical composition and lattice constants compare well with accurate experimental data from atom probetomography (APT) and X-ray diffraction [2], showing the predictive power that can be achieved by combining ab initio techniques with Calphad based approaches.

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He studied physics and mathematics at Humboldt University Berlin (Germany), received a master degree at Loughborough (UK), and performed his PhD on “Theory of Magnetism” again in Berlin. In 2005 he joined the Max-Planck-InstitutfürEisenforschung Düsseldorf (Germany), where he became head of the group “Computational Phase Studies” in 2006. His research is focussed on the ab initio based prediction of phase diagrams, structural and functional properties of metallic phases, and the physics of phase transitions.

The size-dependent phase diagram form Ni-based systems by combination of CALPHAD and ab initio methods

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The method for the CALPHAD modelling of size-dependent phases diagram for simple systems was published by Tanaka et al. and Park et al. [1,2]. Recently, new approach to the modelling of size-dependent phase diagrams was developed by the present authors [3]. The combination of CALPHAD approach with the ab initio calculations of surface stresses for stoichiometric and non-stoichiometric intermetallic phases allows to calculate the phase diagrams in dependence of the nanoparticles size also for complex systems with intermetallic phases.

In this study binary Ni-based systems were studied theoretically and experimentally with the aim to describe the influence of the phase boundaries on the size of the particles. The synthesized nanoparticles were studied by DLS, SAXS, TEM, and DSC methods. The modelling of Sb-Sn system predicted the disappearing of Sb_2Sn_3 phase for particle radius below 40 nm, which was preliminary confirmed by DTA measurements.

Further, the binary systems were used to model the behaviour of ternary Ni-Sb-Sn system and compared with the results published by Mishra et al. [4]. Agreement between the experiments and modelling confirms the possibility to extend the method to higher order systems. Furthermore, as shown above, the qualitative changes in the phase diagram depending on the particle size can be predicted.

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Constructing an As-Ga-In-Sn thermodynamic database for modelling the growth of InAs, GaAs and $In_xGa_{1-x}As$ nanostructures

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The growth of metal-seeded semiconductor nanostructures involves phase formations and phase transformations. Thermodynamic modeling of the growth mechanism is useful for predicting the growth trends and to find the optimum growth conditions. We have modeled the phase equilibria of As-Ga-In-Sn quaternary system using the CALPHAD method. The thermodynamic description of this system is specifically useful for modeling the growth of Sn-seeded InAs, GaAs and $In_xGa_{1-x}As$ nanostructures, e.g. nanowires and thin films [1].
The thermodynamic description of the As-Sn system [2] was missing in the literature; hence the first step was to assess this system based on the available thermochemical and phase diagram experimental data. Furthermore, we have calculated the enthalpy of formation of the compounds via DFT. This system exhibits two intermetallic phases, AsSn and As_3Sn_4. The crystal structure and the composition of As_3Sn_4 have been under debate for a long time. The assessment was based on the very recent experimental and first-principles data for this compound [3]. Next, the two unassessed sub-ternaries, As-Ga-Sn and As-In-Sn were studied. There is no ternary phase in these ternary systems. The relevant vertical cuts were extrapolated and compared to the experimental data. The agreement was good without adding any ternary parameter.
Finally, we extracted the realistic chemical potentials from the As-Ga-In-Sn database to model the nucleation of the ternary $In_xGa_{1-x}As$ nanowires from Sn liquid particle. We used the binary nucleation modeling that we recently and for the first time used for Au-seeded ternary nanowires [4]. By linking the composition of the liquid phase to that of the nanowire phase, we found the optimum growth conditions for $In_xGa_{1-x}As$ heterostructures.

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Masoomeh Ghasemi

I have studied for my PhD in engineering physics at Lund University in Sweden. The focus of my research is to develop thermodynamic databases for relevant materials systems for growth of semiconductor nanostructures. I perform CALPHAD assessment, DFT calculations and experiments. Currently, I am on a research visit at KTH Royal Institute of Technology.

First-principles Calculation Assisted Thermodynamic Modeling of B-Ta and B-C-Ta System

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Tantalum carbide ceramics are difficult to densify and leads to entrapped porosity. TaB2 and B4C have been widely used in Tantalum carbide ceramics to promote the densification and improve material sintering performance. The systems TaC-TaB2 and TaC-TaB2-B4C can combine advantageous properties of each of the composing phases, significantly modify microstructure and properties, provide the potential for their tailoring, and broaden the application spectrum .

The thermodynamic re-assessment of B-Ta system using CALPHAD method is performed by considering the latest experimental data and the results from first-principle calculations of the formation enthalpies for TaB2, Ta3B4, TaB, Ta3B2, and Ta2B. The sublattice model of (Ta, B)0.333(Ta, B)0.667 has been used to describe the homogeneity range of TaB2, while other four intermetallic compounds are treated as stoichiometric compounds. Compared with the previous thermodynamic description for the B-Ta system [1], noticeable improvement is achieved in the present work. The current thermodynamic parameters can well reproduce the newly published experimental data. Combining the thermodynamic parameters of the C-Ta [2] and B-C [3] systems available in literature with the re-assessed B-Ta system, the thermodynamic assessment of the ternary phase diagram of B-C-Ta system is carried out. The reliable experimental information is satisfactorily accounted for the present thermodynamic description.

Keywords: B-Ta system; B-C-Ta system; CALPHAD technique; Thermodynamic modeling.

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Interface energy at the limit radius in metallic system

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At the previous Calphad meeting held at Awaji, Prof. Kaptay gave a stimulating talk on the interface energy [1]. At the very beginning of his talk, I felt an unstability. After a while, I noticed that the discomfort is rooted in the different point of views on the interface energies. His is continuum, but mine is discrete. On this talk, I will show you the reason of the strangeness by discussing extreme behaviours of interface energies at the two limits of the radius, r =0 and ∞.

The starting point is the parabolic dependency of interface energy on radius, where ∞ at r =0, and 0 at r =∞. In the discrete atomistic systems, those are different. At first, we will see the limit of r =0. As the similarity with the other physics problems, we have to avoid the infinity divergence. In case of the heterogeneous metallic alloy system, the typical interface is observed in the particles precipitated in matrix. When we change the number of the atoms in precipitate clusters, we can calculate the size dependency of the interface energy. The limit of the small size should be not zero but one, which means that the dilution limit is the answer for the maximum limit of interface energy in the metallic systems.

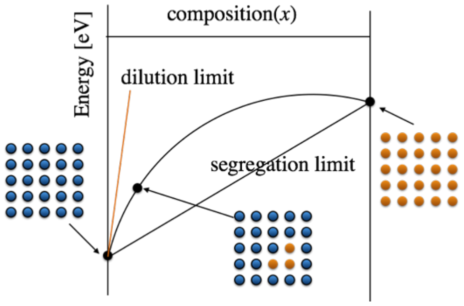

Fig.1 Schematic illustration between dilution limit and interface energy at small radius limit.

For the other limit of r =∞ , we will explore in the homogeneous system, the energy of small angle symmetrical tilt interface. Although the energy approaches to zero, the problem is the angle dependencies of it. The classical theory of the small angle tilt boundary energy was derived by Read and Shockley, and is described by the equi-spaced dislocations aligning on the interface. The important derivation of this theory is that the tangents of (100) tilt boundary near 0 and 90 degrees are different due to the difference of Burger's vectors. This is confirmed by the computer simulations with the interatomic potentials, but the experimental results show different tendency, where the tangent lines at 0 and 90 degree limits show the same slope[5]. We will report the first principles results and discuss where this inconsistency comes from.

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Temperature and concentration dependent solid/liquid interfacial energies

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Microstructural evolution during solidification is strongly influenced by the solid/liquid interfacial energy, which thus has a direct impact on the materials properties. Despite their importance, experimental determination of interfacial energies is rarely undertaken, and documented values in the literature are limited to pure substances [1] or eutectic alloys [2,3]. During solidification of alloys, the temperature at the interface and thus the concentration of the solid and liquid phase at the interface vary with time. Considering the high experimental effort for determining solid/liquid interfacial energies, their temperature and concentration dependence should rather be calculated than experimentally determined. Models for the prediction of the interfacial energy require the melting enthalpy (e.g. Turnbull [1]) and/or the melting entropy (Gránásy [4]) and/or the mixing entropy (Miedema [5]) as input parameter. So far, all models neglect the variation of these thermodynamic entities. For the calculation of temperature and concentration dependent interfacial energies, their change needs to be considered. CALPHAD-type thermodynamic databases offer the possibility to introduce temperature and concentration dependent values for the calculation of the solid/liquid interfacial energy of alloys in the entire solidification interval. Under the assumption of local equilibrium at the solid/liquid interface, different models of the interfacial energy for binary alloys from the literature are extended and employed to calculate the temperature and concentration dependent interfacial energies between binary and multicomponent solid solutions or intermetallic phases and their respective liquids. [6]

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Dr. Stephanie Lippmann

Stephanie works as a research associate in the Metallic Materials group of Prof. M. Rettenmayr at Friedrich Schiller University Jena with a focus on phase transformations. Within this field she studies aspects of the dynamic processes in temperature gradient (e.g. liquid film migration, nucleation) or the influence of interfacial processes during solid state phase transformations that determine the transition from diffusion controlled to massive transformation.

Modeling of metastable phase formation diagrams for sputtered thin films

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During energetic vapour phase condensation (for example by magnetron sputtering and cathodic arc deposition), the system is extremely far from equilibrium and the formation of metastable phases is often observed. Metastable phase formation diagrams for thin films can be compiled based on phase formation data from individual deposition experimentsor from combinatorial thin film synthesis experiments. Compared to phase diagrams (which can readily be calculated with the CALPHAD approach), metastable phase formation diagrams for thin films cannot directly be calculated.

In the present work, the metastable phase formation of the Cu–W thin films has been studiedusing combinatorial depositions and characterization techniques including 3D atom probe tomography (APT). A method to estimate the activation energy for surface diffusion during magnetron sputtering based on experimental metastable phase formation data has been developed [1]. The so obtained activation energies are consistent with diffusion activation barriers determined by *ab initio* calculations.A modeling strategy (including *ab initio*calculations, CALPHAD and one key experiment) to predict metastable phase formation diagrams has been proposed [2]. Metastable phase formation diagrams for the Cu–W and Cu–V thin films are predicted and validated by further combinatorial magnetron sputtering experiments.

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Calculation of phase diagrams with epitaxial orientations in Co-based binary alloy thin films

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The properties and performances of metallic Co-based alloy thin film such as magnetic anisotropy, magnetization reversal processes and domain wall magneto-resistance, are crucial for spintronic devices. However, the traditional phase diagrams can only give the thermodynamic phase stability without considering the crystallographic orientations of each phase, which cannot be used for design of the thin film with structural anisotropy. Strain-engineering, i.e. a technique that makes use of film-substrate misfit strain to grow epitaxial film, has recently been employed to improve the various properties of thin films [1].By tuning the lattice constants of the substrate artificially, the elastic field and the thermodynamic state of the film could be correspondingly manipulated. Thus, develop a new method that can calculate the phase diagrams containing the information of the crystallographic orientations of the phases could be important for fabrication of thin films more precisely and efficiently.

Based on CALPHAD method and our previous model for pure metal films[2], a comprehensive model for thermodynamic description of alloy thin films with structural anisotropy were proposed in the present work. The total free energy of the epitaxial film, including chemical free energy, elastic strain energy and surface energy, were calculated to predict the stable crystallographic structures and orientations. Phase diagrams of Co-based binary alloy thin films are calculated to describe relationships between the thermodynamic stable phases and such corresponding conditions as concentration, crystallographic orientations, temperature and film thickness. The phase diagrams with epitaxial orientations are expected to shed light on utilizing strain-engineering to fabricate desirable stable Co-based alloy thin films with specific crystal orientations.

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Thermodynamic study on grain boundary segregation

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A simple physical model of grain boundary is often employed in discussing the segregation behavior in iron, stating that the grain boundary has a constant thickness and that Gibbs energy can be assigned to the boundary material. Under this assumption, a common tangent does not denote the equilibrium between the boundary and the bulk, as in phase equilibrium, but the grain boundary concentration is defined by the tangent to the Gibbs energy of the grain boundary parallel to that for the bulk at the bulk concentration [1]. The Gibbs energy of the grain boundary is sometimes expressed as that of the liquid phase. It seems unusual to apply the Gibbs energy of a liquid to a grain boundary; however, it could be reasonable when considering the structural analogy between an amorphous phase and a grain boundary composed of simple structural units [2]. In fact, the calculated segregation coefficients of some elements in Fe agree fairly well with the experimental values. On the basis of this background, the present study aims to construct grain boundary structures by means of the molecular dynamics (MD) method, and to compare the properties of structures such as size and shape distribution of polyhedral with those observed in amorphous metals.

For the procedures, two tilted cells, where one cell is tilted by 15 degrees clockwise while the other is also tilted by 15 degrees anticlockwise, were created in MD framework. After that they were pasted at the boundary, and furthermore, one of the cells was twisted by 14 degrees toward the direction perpendicular to the cells in order to give a randomness in the atomic configuration. Then the structure was annealed at 300K to relax a distortion accumulated in the boundary. The Fe polyhedral structures were extracted from the grain boundary layers, and distribution for diameters of vacancies contained in the polyhedral was studied. To calculate segregation energy, some region around a polyhedral was cut in the shape of sphere, and compare the energies between the cases where the solute is inside and outside the polyhedral using the first principles calculation.

[1] M. Hillert: Lectures on the theory of phase transformations, H. I. Aaronson (ed.), AIME, New York (1975), 36–44.
[2] M.F. Ashby, F. Spaepen, and S. Williams: Acta Metall. 26 (1978), 1647–1663.

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My original research field is the calculation of phase diagram based on the thermodynamic analysis of experimental results for phase boundaries and thermodynamic properties. Our most recent research topic is on the construction of theoretical phase diagrams using genetic algorithm and convex-hull method.

A new thermodynamic database of Ti(C,N)-based cermets and its application tothe control of grain growth

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Ti(C,N)-based cermets are TiC, TiN and Ti(C,N) refractory materials embedded in the ductile binder phase such as (Co,Ni)-based metals and Ni3Al. The knowledge of thermodynamic data is the basis of quantitative description of microstructure, as well as the key of process parameter optimization and materials design. However, the complete thermodynamic description for multi-component Ti(C,N)-based cermets is still lacking. In the present work, a new thermodynamic database of Ti(C,N)-based cermets is developed by means of CALPHAD approach and key experiment. The assessed parameters can describe the experimental data of each sub-systems reasonably. Moreover, based on the presently modified solid-liquid interfacial energy model, an accurate prediction for solid-liquid interfacial energies is realized. The grain growth behavior of the ceramic phase in Ti(C,N)-based cermets during sintering process was simulated by using TC-PRISMA software applied to the thermodynamic and kinetic databases as well as the model predicted solid-liquid interfacial energies.

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The director for both Sino-German cooperation group "Microstructure in Al alloys" and Science Center for Phase Diagrams & Materials Design and Manufacture of CSU.
Research fields include thermodynamics, phase diagram, cemented carbide, diffusion, coating and first-principles calculation.

Thermodynamic assessment of the C-Zr system

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The carbon-zirconium system was assessed in 1995 by A. Fernández Guillermet [1] and has shown remarkable longevity in that it is an example of an assessment done with very little experimental data and some theoretical knowledge, that has survived in wide usage until now without any openly published modifications. However, the use of first principles calculations of thermodynamic quantities has recently become important in understanding the behaviour of phases such as those in this system, which allow the potential for new insights.

An analysis of the defect formation energy in the thermodynamic assessment was conducted recently [2], showing that it is easy to add more physical information to an existing assessment without reducing the extent to which the phase diagram reproduces the experimental data.

Following an extensive literature review, we have collected recent experimental data that suggests changes to the invariant eutectic point and liquidus phase boundary in the zirconium-rich region where previously no experimental data was available.

Taking into consideration this experimental data, a new assessment of the carbon-zirconium system is presented that also evaluates the thermodynamic quantities calculated purely by first principles methods [3] and considers the temperature-dependent formation energy of vacancies on the carbon sublattice.

[1] A. Fernández Guillermet, Journal of Alloys and Compounds, 217, 69–89, 1995.

[2] T. Davey et al., CALPHAD XLV, Awaji Island, Japan, 2016.

[3] A.I. Duff et al., Physical Review B, 91, 214311, 2015.

Theresa Davey

Doctoral thesis title: Thermodynamic assessments of the (Zr,Hf) carbides revisited and informed by the calculation of defect-formation energies in ZrC, supervised by Profs. M.W. Finnis and W.E. Lee at Imperial College London, UK.
Recent publications: A.I. Duff et al., Physical Review B, 91, 214311, 2015.
Further publications in preparation.

From ternary experiments back to binary modeling: Li-Si-C example

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Phase equilibria and thermodynamic properties of the ternary Li-Si-C system are crucial for developing new anode materials containing Si and/or C for Li-ion batteries. The ternary phase diagram may be calculated from combining previously established assessments of Li-Si [1,2], Li-C [3], and Si-C [4] with standard Calphad extrapolation. However, the key three-phase equilibrium of Li_2C_2+SiC+Li_7Si_3 around 640°C determined by our extensive experiments, see Fig. 1, disagrees with that calculation. Ternary phases or ternary solid solubilities in the intermetallics are excluded experimentally. Thus, revision of one or more binary assessments is inevitable. The present work demonstrates that significant revision of all three binary thermodynamic descriptions is required to obtain consistency of the ternary data with all the binary data. That makes Li-Si-C a prime example of the occasional need to revert the general Calphad strategy from binary to multicomponent assessments. The present significant revisions of the three binary edge systems result in the consistent thermodynamic description of the complete Li-Si-C ternary system.

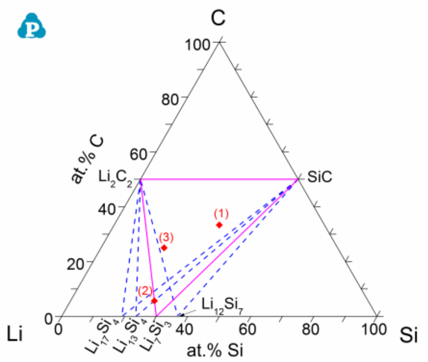

Fig.1. Ten samples with three key alloy compositions studied by long time annealing experiments confirmed the key three-phase equilibrium indicated by the solid tie-triangle. Potential alternative phase assemblies were investigated by various starting phases, shown by the dashed triangles. The same equilibrium assembly was attained independent of different starting phases.

[1] P. Wang et al. Intermetallics, 42 (2013) 137-145.
[2] M.H. Braga et al., J. Alloys Compd., 616 (2014) 581-593.
[3] A. Kozlov et al., Int. J. Mater. Res., 104 (2013) 1066-1078.
[4] J. Gröbner et al., Calphad, 20 (1996) 247-254.

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Modelling the Gibbs energy of Ag-Ni, Ag-Ge and Ag-Ge-Ni by calphad approach

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In this work, constitutional and thermodynamic information pertaining to Ag-Ge-Ni and its subsystems are generated by experiments, MD simulation and SQS. These in-house generated data along with the information amassed from the literature for Ag-Ni, Ag-Ge and Ag-Ge-Ni are used to model the Gibbs energy by a calphad approach.

Ag-Ni is a simple and important system with immiscible liquids and (Ag,Ni) phases. Earlier, this system has been thermodynamically modelled utilizing certain thermochemical and phase equilibria information based on the conjecture. Information that are missing due to experimental difficulty aregenerated in this study. The boundaries of the liquid miscibility gap at high temperatures are determined using a pyrometer. The temperature of the liquid ⇌(Ag) + (Ni) eutectic reaction is measured using the DTA. The tie-lines of the Ag-Ni system at 1023 K and 1473 K are measured using an EPMA. The enthalpy of mixing of the liquid at 1773 K and the (Ag,Ni) at 973 K is calculated by the MD simulation using LAMMPS. These results along with the information from literature are used to model the Gibbs energy of the liquid and (Ag,Ni) by a calphad approach. This Gibbs energy description is utilized in modelling the Ag-Ge-Ni system.

Ag-Ge is an elementary eutectic system with an intricate thermodynamic behaviour. In the Ag-Ge system, solidus for Ag rich alloys is measured employing the DTA and energy of mixing of (Ag,Ge) phase is calculated by SQS. The Gibbs energy of Ag-Ge system is remodelled with the new information along withliterature data. The Gibbs energy description of Ge-Ni is from [1]. Also, isothermal section of the Ag-Ge-Ni system at 1223 and 673 K is determined using an EPMA. These information along with the liquid miscibility gap boundary measurement at 1723 K from the literature is used to model the Gibbs energy ofAg-Ge-Ni system. Liquidus projection and the reaction scheme forAg–Ge–Ni system is then calculated and presented.

[1] S. Jin et. al., Calphad 38 (2012) 23–34.

Dr. V. B. Rajkumar

In 2015, Dr. V. B. Rajkumar received his Ph.D. degree from the Indian Institute of Technology Madras, India. Since 2015, He is a post-doctoral researcher working with Professor. Sinn-wen Chen at National Tsing HuaUniversity, Taiwan. His research interests are determination of phase diagram by experiments, calphad and physics based methods: SQS, Cluster expansion, *ab-initio* calculation, MD simulation, Monte-Carlo simulation assisting calphad.

Calphad XLVI - Tuesday, June 13, 2017, 15:00 - 15:15 **[O33]**

Thermodynamic modelling of Long Periodic Stacking Ordered (LPSO) phases in Mg-Gd-Al ternary system

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Long Periodic Stacking Ordered phases (LPSOs) are important for Mg alloys. In this work, thermodynamic modelling of the LPSO phases in the Mg-Gd-Al ternary system wascarried out using first-principles calculations and available experimental data. A sublattice model was developed which includes the different stacking polytypes such as 10H, 18R, 14H and 24R LPSO phases with L1$_2$ clustering of Gd/Al solute atoms with or without centered interstitial atomsinthese L1$_2$ clusters. The thermodynamic properties of these LPSOs were predicted using both the phonon method and the Debye model with inputs from first-principles calculations. Debye temperatures were estimated based on Debye-Gruneisen parameter calculations since the shear and Young's modulus of the LPSO increases significantly compared to pure magnesium (α-Mg). Calculated phase diagrams are in good agreement with existing experimental data. It is observed that the 14H and 18R LPSO phase regionshave little solubilities with different Gd/Al ratios.

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Phase equilibria of Pb-Sb-Se-Sn quaternary system

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Thermoelectric materials and modules, primarily because of their abilities to convert heat into electricity directly, have attracted very intensive research interests.Various compounds in thePb-Sb-Se-Snquaternary system, such asPbSe, Sb_2Se_3 and SnSe, havevery good thermoelectric properties. Phase diagrams are fundamentalinformation and are important formaterials development and materials process routes optimization.Although the Pb-Sb-Se-Sn quaternary system is important, there are only limited Pb-Sb-Se-Sn-related phase equilibria data available. Phase equilibria of Pb-Sb-Se-Snquaternary system are thus investigated in this study.

The phase equilibria data of its constituent binary and ternary systems are examined in this study. Among its six constituent binary systems, in addition to the liquid phase and four terminal phases, there aresix binary compounds, Sb_2Se_3, Sb_2Sn_3, SbSn, SnSe, $SnSe_2$, and PbSe. No ternary compound is found in the Pb-Sb-Sn [1] and Pb-Se-Sn [2] ternary systems. Three ternary compounds, $Pb_6Sb_6Se_{17}$, $PbSb_2Se_4$ and $Pb_2Sb_9Se_9$, in the Pb-Sb-Se ternary system, and two ternary compounds, $Sb_9Se_9Sn_2$ and Sb_2Se_4Sn in the Sb-Se-Sn ternary system are observed. The $Pb_2Sb_9Se_9$ and $Sb_9Se_9Sn_2$phases are newly foundand have not been reported before.

Thermodynamic modelling of theSb-Se-Sn-Pb quaternary system is carried out using the CALPHAD approach. The CALPHAD-type thermodynamic descriptions of the six constituent binary systems are reviewed and adopted with very limited revisions. The thermodynamic descriptions of the Pb-Sb-Snand Pb-Se-Sn ternary systems are developed based on those models available in the literatures and limited phase equilibria results in the literatures [1,2].Ternary thermodynamic descriptions of theSb-Se-Pb and Sb-Se-Sn systems are developed based on those as mentioned and the liquidus projections and 400^oC isothermal sectionsexperimentally determined [3]. The phase diagrams of those of thermoelectric applications interests in the Sb-Se-Sn-Pb system are calculated using the developed CALPHAD-type models.

[1] H. Ohtani, K. Okuda and K. Ishida, J. Phase Equilib., Vol. 16, pp. 416-429 (1995).
[2] S. Dal Corso, B. Liautard and J. C. Tedenac, J. Phase. Equilib., Vol. 16, pp. 308-314, (1995).
[3] Jui-shen Chang, Ph.D. thesis, National Tsing Hua University, Taiwan (2017).

Sinn-wen Chen

Dr. Sinn-wen Chen is a Senior Vice President and Distinguished Professor of National Tsing Hua University in Taiwan. He received his Ph.D. degree in Materials Science from the University of Wisconsin-Madison in 1990, and took a faculty position in National Tsing Hua University in 1992. He has been working on phase diagram determinations, solidification and interfacial reactions of electronic solders and thermoelectric materials.

Phase relations in the ZrO_2-TiO_2-Al_2O_3 system: experimental study and thermodynamic assessment

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The corundum and corundum-carbon bonded materials are proposed as filter materials for improving properties of steel and Al alloys. To improve corrosion resistance the filter surface is proposed to be modified by addition of TiO_2 and ZrO_2. Therefore the aim of this work is to derive thermodynamic description of ZrO_2-TiO_2-Al_2O_3 system which is necessary to model phase relations in the filter materials and interaction between filter and steel/Al alloy. The literature data [1, 2] for melting relations indicated two ternary eutectic reactions and one transitional reaction while the measured temperatures and compositions for invariant reactions reveals substantial scatter. Therefore experimental investigation of the system is of interest.

Samples were prepared by co-precipitation method from aqueous solutions of $Zr(CH_3COO)_4$, $Ti_2(SO_4)_3$ and $Al(NO_3)_3$ mixed in the desired ratios and dropped into water containing NH_4OH at pH above 9. After filtration and pyrolysis samples were heat treated at temperatures between 1250 and 1600°C in air. Phases were identified by XRD and microstructures were investigated by SEM/EDX. Melting relations were studied using DTA. The observed heat effects were attributed to invariant reactions based on XRD and SEM/EDX investigations before and after DTA.

Based on the obtained results isothermal sections at 1284, 1430 and 1624 °C and liquidus surface were constructed. Three ternary eutectic reactions were indicated in the system: $L \leftrightarrow Al_2O_3 + Al_2TiO_5 + ZrO_2$ at 1705°C, $L \leftrightarrow ZrO_2 + Al_2TiO_5 + ZrTiO_4$ at 1654°C and $L \leftrightarrow TiO_2 + Al_2TiO_5 + ZrTiO_4$ at 1636°C. Temperatures were determined using DTA and compositions of liquid in eutectic reactions were measured using SEM/EDX. The results obtained in the present work are in better agreement with [2] than [1].

Experimental data obtained were used to derive thermodynamic description of the ZrO_2-TiO_2-Al_2O_3 system.

[1] Berezhnoi A. S. and Gul'ko N. V.,Dopov. Akad. NaukUkr. RSR, 1(1955) 77-80.
[2] Pena P. and DeAza S.,Ceramica (Florence), 33 (1980) 23–30.

Olga Fabrichnaya

Academic degrees are MSc in Chemistry Department of Moscow State University, Russia and PhD in Uppsala University, Sweden. Presentposition is project leader and lecturer in Technical University Bergakademie Freiberg, Germany. The scientific interests are phase equilibrium investigations, thermal analysis, calorimetry and thermodynamic modelling of oxide system.

Thermodynamic properties of oxide compounds estimated from polyhedron method

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Polyhedron model was first introduced by geochemists to estimate the thermodynamic properties of silicate mineral phases. The basic assumption of polyhedron method is that the thermodynamic properties and molar volume of mixed oxides (mostly silicates) can be described as linear combinations of the fractional thermodynamic and molar volume properties of their constituent polyhedra. In this study, the polyhedron model was overviewed. Based on thermodynamic properties of 48 silicate and 19 titanate compounds collected from the critically evaluated and optimized FactSage database, thermodynamic properties of 18 polyhedra were optimized by weighted multiple linear regression analysis. The optimized properties of constituent polyhedra accurately reproduced the entropy, enthalpy and molar volume of all compounds, and were used for the prediction of thermodynamic properties of ternary oxide compounds in titanate systems. Considering that *ab inito* calculations are still less satisfactory to predict the thermodynamic properties of complex oxide phases, the polyhedron model can be a suitable option for CALPHAD community to estimate/predict the thermodynamic properties of oxide compounds which have not been experimentally determined.

In-Ho Jung

He joined McGill University in 2007 after he experienced various industrial process developments in South Korea. He is currently an associate professor. His main research interests are the CALPHAD-type thermodynamic database development for oxide and metallic systems, and applications to process optimization and new material design. He is also co-developer of the FactSage thermodynamic computing system.

Integrated experimental and thermodynamic modelling research on the multicomponent Pb-Cu-Fe-Zn-Ca-Si-O system

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Integrated experimental and modelling research program is under way on the phase equilibria and development of thermodynamic databases of the lead and copper metallurgical slag / matte / metal systems. The research on the Pb-Cu-Fe-Zn-Ca-Si-O system is the focus of the presentation, which is a part of the overall program also including Al, Mg, S, As, Sb, Bi, Sn, Ag, Au, and Platinum group metals.

Experimental studies involve I) high temperature equilibration of the synthetic samples in controlled gas atmospheres, II) rapid quenching and III) direct measurement of the compositions of equilibrium phases using electron probe X-ray microanalysis (EPMA) equipped with Wavelength Dispersive Detectors. Thermodynamic modelling (using FactSage package) is closely integrated with the parallel experimental research. Initial thermodynamic assessments are used to identify priorities for experiments. Experiments are planned to provide specific data for thermodynamic optimisation as well as for the multi-component systemsthat can be used directly by process operators. New experimental data are then used to re-optimise thermodynamic database.

PreviousPb-Fe-Zn-Ca-Si-O databasehad been developedusing experimental data and modelling capabilities available at that time [1]. Significant advances have been achieved in recent years in experimental and modelling methodologies.Primary phase substrate is used in experiments on the slag samples in equilibrium with metallic Pb, which is of particular importance to Fe-containing slags having variable oxidation state [2]. Thermodynamic modelling incorporates flexibility in the position of maximum short range ordering within the Modified Quasichemical Formalism (MQF), flexibility to use Kohler, Toop, Muggianu extrapolations of binary parameters in any combination, the combination of MQF, Bragg-Williams and other model parameters. The integration is achieved through the experiments and modelling undertaken in parallel iteratively and simultaneously. Significant improvement in the accuracy of the phase equilibria description is achieved.

[1] E. Jak at al., Metal.Trans. B 31(2000) 621-630.
[2] M.Shevchenko et al., 10th Intern. Conf. MOLTEN16, Seattle, USA 2016, 1229.

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M.Sc. in Chemistry (Kiev, Ukraine, 2012). A co-author of >50 papers, mostly in calorimetry and thermodynamics of binary and ternary metallic systems, a result of work at Frantsevich Institute for Problems of Materials Science, Kiev, Ukraine (2009-2015).

Since 2015, a PhD student at PYROSEARCH, UQ, Brisbane, Australia, studying phase equilibria and thermodynamics of complex metallurgical slag systems.

Thermodynamic investigation of the Cr-O-U and Cr-O-Zr systems

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During severe accidents in nuclear reactors, the core is partly melted. With time the temperature increases and more parts of the reactor are melted creating a very complex mixture, including many elements. This mixture is often referred to as corium.If the reaction is allowed to go on long enough, the vessel can brake causing the corium to flow out onto the floor creating ex-vessel corium. One of the aims of the TAF-ID project [1] is to be able to predict the thermodynamic properties of the corium to aid in the prevention of severe accidents.

One of the elements whose behaviour in the corium is not well known is chromium. Chromium can be introduced to the system through stainless steel that can be used both for the vessel itself and the cladding of the controlrods. In this work two of the key systems involving chromium, i.e. Cr-O-U and Cr-O-Zr, have been studied using the Calphad method.New experimental work has also been performed using equilibrated alloys at 1600 and 1800 °C.

[1] “OECD NEA/NSC: Thermodynamics of Advanced Fuels – International Database (TAF-ID).” [Online]. Available: https://www.oecd-nea.org/science/taf-id/. [Accessed: 08-Feb-2017].

Standard Enthalpies of Formation of Select Cu_2YZ Compounds

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Enthalpies of formation for Cu_2YZ–(Y = Ce, Dy, Er, Gd, Hf, Ho, La, Lu, Mn, Nd, Pr, Sc, Sm, Ti, Tb, Tm, Y, and Zr)(Z = Al, Ga, In)–compounds were experimentally measured using high temperature direct reaction calorimetry[1][2]. These compositions were selected for investigation via screening against Materials Project[3], Springer Materials[4], and the OQMD[5], databasesas part of a broader search fornew multifunctional Heusler structured materials. Formation enthalpies for structures not present in the databases were calculated using Density Functional Theory as implemented in the Vienna Ab Initio Simulation Package (VASP) software.Crystal structures and lattice parameters were determined from Rietveld refinement of powder x-ray diffraction profiles via the GSAS-II crystallographic data analysis software[6]. Composition and microstructure were investigated via scanning electron microscopy with energy dispersive x-ray spectroscopy. Ferromagnetic compounds produced were subjected to modified simultaneous differential scanning calorimetry and thermogravimetric analysis in a magnetic field to determine Curie Temperature.

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Philip Nash

Philip Nash is the Finkl Chair in Metallurgical and Materials Engineering and Director of the Thermal Processing Technology Center at Illinois Institute of Technology, Chicago, USA. His research interests are in the thermodynamics and physical properties of intermetallic compounds and phase diagrams of metallic systems.

Calorimetric determination of the formation enthalpy of ZnSb

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After a critical review of literature data on the enthalpy of formation of ZnSb, discrepancies between various experimental studies are highlighted. Moreover, experimental values disagree with values calculated by ab-initio method. As many of the experimental methods used suffer from some serious drawbacks, a new determination of the formation enthalpy of ZnSb by an alternative calorimetric method, drop solution calorimetry in liquid tin, has been performed. Two different synthesis methods have been used to obtain pure ZnSb phase and drop solution experiments were performed at 665 and at 974 K. The formation enthalpy derived from these experiments is -6.39 ± 0.73 kJ/mol of atoms for ZnSb sample prepared by ball milling and -7.85 ± 0.42 kJ/mol of atoms for ZnSb sample prepared by melting. These results are compared to literature data.

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(PhD) CNRS Research Engineer at IM2NP, Marseille (France) involved in chemical thermodynamics studies of nuclear and inorganic materials at high temperature by thermal methods: calorimetry and thermal analysis.

Gaseous phase thermodynamics of organometallics: a TaN-precursor study

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For various industrial applications, there is a growing interest in producing thin films by means of the gaseous phase deposition methods such as Atomic Layer Deposition (ALD). In this work is explored the gaseous phase behaviour of the precursor (the penta dimethyl amino tantalum) used to obtain TaN thin films [1]. The thermodynamic study of the precursor vaporization and its thermal cracking of has been performed using Knudsen cell and tandem cell, respectively, coupled with a mass spectrometer [2]. The results make it possible to propose reactions diagrams occurring at the time of the deposit of TaN in ALD reactor and to determine the structural and thermodynamic properties of identified molecules. These data are used in the various approaches of thermodynamic modeling of processes of growth that starts from a gas phase [3].

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[2] P. Violet et al., Rapid Communications in Mass Spectrometry 24 (2010) 2949-2956.
[3] E. Blanquet et al. ECS Transactions, 33 (2010) 321-332.

Ioana NUTA

I.Nuta, chemical engineer, is research scientist at the “Materials and Processes Science and Engineering” Laboratory in Grenoble since 2006. There, she works on thermodynamics of the gaseous phase using Knudsen effusion method coupled with mass spectrometry and calorimetry. Her research activity in the deals with the study of the thermochemical properties of compounds mainly for energy production and storage.

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Thermodynamic Vaporization Studies of Lead Oxide and Sodium Oxide with Knudsen Effusion Mass Spectrometry

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Modern sensors and solid state memories are widely consisting of oxides with perovskite structure and ferroelectric transitions. The stability in time and temperature of those compounds can be deduced by the thermodynamic activity. The determination of the activity of a compound is based on the comparison of its chemical potential in a sample and in its reference form. References for oxide systems containing lead or sodium are lead oxide (PbO) and sodium oxide (Na_2O). The vapor phases over these pure oxides are controversial discussed in literature. The vaporization studies of the yellow PbO(c) and Na_2O(c) were carried by Knudsen effusion mass spectrometry. Gibb's energy, equilibrium constants and sublimation enthalpies could be obtained.

This presentation will show the results of the comprehensive vaporization studies of these oxides in order to understand the vapor phase and to establish them as a reference state for thermodynamic activity determination.

The vaporization of pure PbO(c) was studied at temperatures, covering the range 810 – 1040 K. Only Pb(g), O_2(g) and PbO(g) were the molecules representing the vapor phase over PbO(c). Equation (1) and (2) describe e.g. thesublimation processes.

PbO(c) ⇔PbO(g) $\Delta_{sub}H^0_{930K} = (221.8 \pm 12)\ kJmol^{-1}$ (1)
PbO(c) ⇔Pb(g) + 0.5 O_2(g) $\Delta_{sub}H^0_{930K} = (205.3 \pm 11)\ kJmol^{-1}$ (2)

Sodium oxide Na_2O(c) is very reactive and has, even in its purest commercially form, up to 20% traces of sodium (Na), sodium hydroxide (NaOH), and mostly sodium peroxide (Na_2O_2) and, even sodium carbonate (Na_2CO_3) depending on way of the synthesis.

Here we describe the way to handle Na_2O(c) for the studies under equilibrium conditions. Only the species Na(g), Na_2O(g) and O_2(g) were observed in the vapor phase between 900 – 1100 K in accordance with eqs. (3) and (4).

Na_2O(c) ⇔ Na_2O(g) (3)
Na_2O(c) ⇔ 2 Na(g) + 0.5 O_2(g) $\Delta_{sub}H^0_{1000K} = (242 \pm 2.3)\ kJmol^{-1}$ (2nd law)
$\Delta_{sub}H^0_{1000K} = (240 \pm 1.7)\ kJmol^{-1}$ (3rd law) (4)

The ion intensity of Na_2O^+ was too weak to evaluate eq. (3).

Unprepared sodium oxide has impurities that have significant effect on the content and properties of the vapor phase. Thus the vapor over Na_2O(c) would be dominated by the sodium containing impurities, like Na, NaOH and Na_2O_2, which have a higher thermodynamic activity of sodium than in traces-free Na_2O(c). Molecules, such as NaO(g) and NaO_2(g) were only be observed over unpurified sodium oxides.

Thirty (30) temperature dependent vaporization studies on Na_2O(c) were intrinsically consistent and have given data for a particularly suitable reference.

A container-less electrochemical method to evaluate the thermodynamic properties of molten oxides and liquid alloys

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The materials at the basis of our modern society would not be available without processes operated in the molten state. Developing novel processes that adopt green chemistry principles calls for a substantial scientific effort to inform the thermodynamic and transport properties of this state of matter. In particular, providing faster experimental access to the thermodynamic and physical-chemical properties of molten systems at very high temperature is necessary[1].

Electrochemical methods are of key importance in such endeavor, though most methods to date require a container or a membrane (separator). Herein, a novel method developed for molten oxides systems is presented. Using a floating-zone furnace and a three-electrode configuration, Gibbs free-energy for molten oxides or liquid alloys are shown to be accessible at temperatures in excess of 2000°C. The performance of the method is inherited from the absence of a container, an extremely stable temperature profile and the use of alternative current (AC) technique for the precise identification of electrochemical potentials. The results show that methods unpractical in the solid state can perform efficiently in the molten state, paving the way to a faster experimental access to essential thermodynamic properties.

[1] A. Allanore, *Journal of The Electrochemical Society*, 162 (1), 13, (2015)

Antoine Allanore

Prof. A. Allanore joined MIT in 2010 after several years in the steel industry at ArcelorMittal R&D in France. His research group at MIT investigates the thermodynamic and transport properties of the molten state, particularly molten oxides and sulphides, in the prospects of developing novel processes with higher selectivity and that adopt green chemistry principles.

On the Quaternary System Ce-Ni-Zn-B

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Although (i) addition of Zn to the Ni-B coating on steels was found to improve the crystallinity, mechanical properties, and corrosion resistance and (ii) the Ce-Zn(Ni) system is an important part of the high strength lightweight multinary Mg-based alloy system Mg-Zn-Mn(Ni)-RE for automotive applications, nothing is yet known on the influence of boron additions as grain refiners and/or boride precipitates and no phase diagrams have yet been reported for systems RE-Zn-Ni-B. Therefore the present work for the first time provides detailed information on phase relations and crystal structures in the quaternary system Ce-Ni-Zn-B at 800°C elucidated by electron microprobe analysis, x-ray powder and single crystal diffraction and transmission electron diffraction (TEM).

The isothermal section and compounds for the system Ce-Ni-B have been confirmed [1]. Whereas the system Ce-Zn-B shows the absence of ternary compounds and negligible mutual solid solubilities of binary phases, a reinvestigation of the system Ce-Ni-Zn at 800°C reveals large fields of liquid phase near the Zn and the Ce-corner and several novel compounds as well as extended solid solution phases characterize the phase relations. H. Stadelmaier [1] reported four ternary compounds in the system Ni-Zn-B (labelled as τ, ϕ, ψ, and χ) all except τ with unknown structure types. Our investigation of the entire isotherm at 800°C revealed six ternary compounds for which structure types have all been determined from X-ray single crystal diffractometry and TEM analyses. Phase relations have been revised accordingly and heat of formation data as well as the electronic DOS and chemical bonding has been elucidated by DFT calculations (density functional theory).

Physical properties have been derived for various Ni-Zn-B ternaries including thermal expansion, elastic moduli and hardness (up to 15 GPa), magnetic susceptibility, electrical resistivity and Seebeck coefficient.

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Determination of phase equilibria in Fe-C-Mn-Al alloys for 3rd generation duplex steels

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Fe-Mn-Al-C alloys based on medium Mn, medium Al steel grades with duplex structure are promising candidates to obtain lightweight automotive structures combining high-strength and high formability. The knowledge of the corresponding quaternary phase diagram serves as a roadmap for the choice of compositions and the elaboration conditions optimization. A reliable and precise thermodynamic database is therefore required.

The objective is to obtain an accurate characterization of the phases in equilibrium, typically ferrite (α), austenite (γ) and carbide $(Fe,Mn)_3AlC$ (κ), their compositions and proportions using thermodynamic calculations coupled with experiments. In order to determine the annealing duration for the establishment of the thermodynamic equilibrium at the investigated temperatures, the development of microstructures is studied for Fe-0.2C-5Mn-2Al (mass %) at 800°C between 2 min and 4 months. A kinetic model (DICTRA) is proposed to support the experimental evolution of phase fractions and compositions.
Some selected alloys are characterized between 700 and 1000°C in order to specify the stability fields of γ and κ by the determination of the α/γ, α/κ, α/γ/κ tie-lines. Characterization is done by using X-ray diffraction (XRD), scanning electron microscopy (SEM), field emission gun scanning electron microscopy (FEG-SEM) and electron probe microanalysis (EPMA-WDS). Due to the low C content, particularly in the α-phase, a specific methodology for EPMA measurements of this element is applied according to the standard ISO16592:2006 [1]. Our new experimental data are used to obtain a better set of consistent parameters for the thermodynamic description of the quaternary system.

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Alloy phase stability under electric currents

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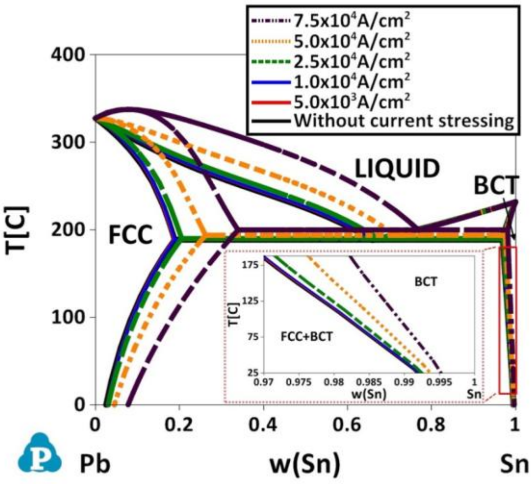
The effects of electric currents upon materials have been one of the most intriguing physical phenomena and thus have been extensively investigated since the 19th century. The phenomena involving thermic reactions are Joule heating and thermoelectric effects, and those involving atomic motions are known to be the electromigration (EM) effect; however, there are still some abnormal experimental observations, which cannot be explained with the existing theories. For instance, in electronic devices, electric currents pass through solder joints. A new physical phenomenon – the supersaturation of solders under high electric currents – has been observed. It involves (1) un-expected supersaturation of the solder matrix phase, and (2) the formation of unusual “core-shell” grains. A plausible explanation of these phenomena based on the changes in the phase stability of Pb-Sn solders is proposed based on *ab initio*-aided CALPHAD modelling. The electric current-induced stress is converted into the excess Gibbs free energies of the phases; hence, the phase equilibrium can be shifted by current stressing. As shown in the figure, the Pb-Sn phase diagrams with and without current stresses clearly demonstrate the change in the phase stabilities of Pb-Sn solders under current stressing [1]. On the other hand, recent theories of EM are based on the unbalanced electrostatic and electron-wind forces exerted on metal ions. However, none of these models have coupled the EM effect and lattice stability. Here, we elucidate the fundamental driving force of EM and validated with *in situ* current-stressing experiments using synchrotron X-ray diffractometry and scanning electron microscopy and *ab initio* calculations based on density functional theory [2]. A new insight of alloy phase stability under electric currents is uncovered.



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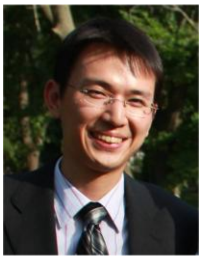

Shih-kang Lin

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Uncertainty quantification in ternary interpolation methods for thermodynamic properties of liquid alloys

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A methodology is presented that allows the measurement and model uncertainty to be explicitly accounted for in the derivation of binary interaction parameters and in the extrapolation to higher-order systems with the Kohler and Toop geometric methods. This allows for an assessment of the necessity of additional interaction parameters in light of the inherent uncertainty originating from the measurement data and the data treatment. The method is applied to thermodynamic property estimation of ternary melts with information from its limiting binary systems.

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Modelling thermochemical and thermophysical properties of liquids

Thermodynamic modeling and experimental investigations in the H_2O – HNO_3 – $Sm(NO_3)_3$ – $Eu(NO_3)_3$ – $(C_4H_9O)_3PO$ system

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The purpose of the present work is a development of a thermodynamic approach to the separation of rare earth elements (REE) by solvent extraction. Traditionally the solution of this problem is based on the experimental selection of optimal conditions for the extraction process. Due to the large number of components in the system it is almost impossible to solve the problem by exhaustively searching all the parameters. As an alternative the thermodynamic model of the multicomponent system may be constructed.

For the demonstration of the suggested method the system formed by water, nitric acid, samarium nitrate, europium nitrate and tributyl phosphate (TBP) was chosen as the object of the research. All the experimental literature data concerning thermodynamic properties and phase equilibria in the system under investigation and its subsystems were used for the thermodynamic modeling. In addition thermodynamic properties of aqueous ternary solutions were investigated by transpiration method and liquid-liquid equilibrium data were determined for the multicomponent systems.

The electrolyte version of the generalized local composition model (eGLCM) was proposed for describing the Gibbs energy of the system. The main advantage of this model is an ability to represent complex aqueous-organic immiscible solutions [1]. Additional Debye-Huckel and polynomial Pitzer-type terms allow to describe properties of electrolyte solutions. Thereby eGLCM is particularly suited for the thermodynamic modeling of rare earth elements separation by solvent extraction.

As a result the thermodynamic model of the water – nitric acid – samarium nitrate – europium nitrate – TBP system was constructed. This model may be used as a basis for an engineering of rare earth elements separation technology.

This work was performed under financial support of URALCHEM and RFBR (research project No. 16-33-01038 mol_a).

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Phosphoric acid and sodium phosphate: Extending the limit of aqueous electrolyte modelling

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Phosphorus-containing materials have diversified industrial applicationswhichare primarily based on phosphoric acid and phosphate salts.Thetwo most noted and representative applications arefertilizer manufacture and boiler-water treatment insteam power cycle. The former requires obtaining pure or concentrated phosphoric acid to produce the final high grade fertilizer; the latter involvespresence of sodium phosphate in high temperature water near its critical point, which is the most challengingconditionfor solution chemistry.

Thermodynamic modelling provides a powerful tool to provide insightsfor understanding mechanisms of such processes. In this work, we apply the previously developed thermodynamic model, the mixed-solvent electrolyte (MSE) model [1], to two practically important systems relevant to these applications: H_3PO_4 + H_2O and NaOH-H_3PO_4-H_2O to represent the chemical and phase equilibria over a wide range of conditions. The lattersystem encompasses aqueous mixtures containing Na_3PO_4, Na_2HPO_4, and NaH_2PO_4 with varying ratio of Na/P.We have particularly extended the model to represent the liquid-liquid immiscibility in aqueous sodium phosphate systems at temperature conditions pertinent to the steam generators [2].

In this presentation, challenges in modelling such systems due to complex chemical speciation (association of aqueous ions and formation of multiple solid phases) and phase behavior (VLE, SLE, LLE) will be discussed, and model results will be demonstrated. Specifically, phase equilibrium results (VLE and SLE) for mixtures of H_3PO_4 + H_2O will be shown over extended temperature (-85°C~ 250°C) and acid concentrations(xH_3PO_4= 0~1). Results for liquid-liquid immiscibility (LLE) in aqueous sodium phosphate systems at high temperatures(above 280°C)will also be presented, together withsolubilities(SLE) of various sodium phosphate salts at varying temperatures and concentrations of acid (H_3PO_4) and base (NaOH).

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Peiming Wang

Peiming Wang is a senior scientist at OLI Systems. She obtained her Ph.D. in physical chemistry from Brigham Young University, and worked as a postdoctoral fellow at Lawrence Berkeley Laboratory prior to joining OLI. Her research activitiesfocused on development, implementation, and validation of thermodynamic and transport property models in OLI's Mixed-Solvent Electrolyte (MSE) framework. She also provides expertise in thermodynamics and modeling techniques for a wide range of OLI clients' applications.

DFT/CALPHAD mixed method for the prediction of the thermal transport properties within aluminium electrolysis cells

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Thermal conductivity, describing the heat transport within materials, is involved in the optimization and control of many industrial processes. Unfortunately, for many compounds and solutions, there is a severe lack of experimental data on thermal conductivity and thermal diffusivity and their temperature dependence as well as microstructural parameters (porosity, grain size, microstructure type...) for solid phases. To alleviate this lack of data, we developed, in the recent years, a novel mixed Density Functional Theory/CALPHAD-like method in order to predict the thermal conductivity of microstructures as a function of temperature. Although the thermal conductivity and thermal diffusivity are not, in a strict sense, equilibrium properties, it has been shown that they can be described via equilibrium properties. The proposed model is based on a suitable formulation of the density of the lattice vibration energy and the mean free path of the phonons, and its parameters are obtained from a simultaneous optimization of heat capacity, thermal expansion and adiabatic bulk modulus as a function of temperature. Where data is missing, the density of the lattice vibration energy and the mean free path of the phonons are obtained via DFT calculations. This method was also extended to take into account fundamental microstructural parameters, allowing predictions to be made for solid solutions for which the thermal conductivity shows a drastic decrease, even with the addition of a little amount of solute. Similarly, another methodology, also based on the prediction of the “quasi-lattice” vibration energy and the mean free path of the phonons, was developed for predicting the thermal transport properties of molten mixtures. As a case study, we first present a prediction of the thermal conductivity of various components in aluminium electrolysis cells and in molten electrolyte used to dissolve alumina. Ultimately, the purpose of this work is to assist the aluminum industry, utilising finite element analysis to predict and control the thickness of the sideledge formed, attaching itself to the sides of the cells.

Aimen E. Gheribi

Aimen Gheribi was born in La Seyne sur Mer in the south of France. He studied Physics and Material Science at the “École superieure de Physique de Marseille”, obtaining his Phd. in 2006 at IN2MP in Marseille. After doing a postdoc at SIMAP in Grenoble with Prof. Alain Pasturel, he moved to Canada where he has been a Research Associate at the École Polytechnique de Montréal since 2008, working with Prof. Arthur Pelton and Prof. Patrice Chartrand.

Engineering applications of CALPHAD – some examples

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CALPHAD was introduced about 50 years ago and may be regarded as the first materials genome [1]. It offered the first systematic approach to represent thermodynamic information as self-consistent building blocks that could be used to extract various items of practical interest, e.g. phase diagrams, reaction heats and driving forces. The methodology was later extended to include also diffusional kinetics [2] and is now extended to include e.g. interfacial properties.

An important driver for this development has been the complexity of materials engineering problems where CALPHAD has offered an indispensable tool to allow less but more precise experimental work. CALPHAD has thus become a corner stone of Integrated Computational Materials Engineering (ICME).

Some examples of CALPHAD used in engineering problems will be discussed. These examples involve equilibrium calculations as well as dynamic processes in steels, super alloys and cemented carbides.

[1] L. Kaufman and J. Ågren,Scripta Materialia,70 (2014) 3-6.
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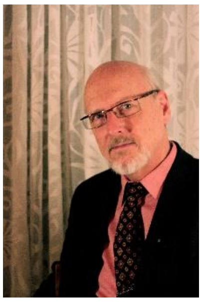

John Ågren

Dr Ågren is professor in physical metallurgy at the Royal Institute of Technology in Stockholm, Sweden. His main research interest is thermodynamics and kinetics of phase transformations in metallic materials.

The formation of magnesiowustite in steelmaking slag evaluated experimentally and via computational thermodynamics

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MgO containing additions are used in steelmaking processes to protect refractories. Solid MgO is fully miscible both with FeO and MnO. Thus, formation of magnesiowustite is possible in oxidizing slags. In the EAF slags, magnesiowustite saturation is believed to play a critical role in foaming. In Converters, this phase is believed to affect slag splashing/coating processes. Previous work indicated that the dissolution of MgO containing additions may be hindered by the formation of solid layers on their surfaces. Thus, thermodynamics alone may not be sufficient to support the assumption that magnesiowustite or other solid solutions will be present on saturation. In this work the evolution of MgO containing phases was followed through sampling converter slags at different stages of the process. The samples were analysed and the observed phases fractions and compositions were compared to equilibrium phase distribution calculated using different computational thermodynamics databases. The experimental results are analysed considering possible dissolution mechanisms and barriers, while the agreements and limitations in calculations with different databases are discussed. Finally, the impact on magnesiowustite formation and steelmaking process is discussed.

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Keywords: steelmaking, slag, magnesiowustite, dolomite, magnesia.

Thermodynamic features of the Al–Mo and Al–Mo–Ti systems

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Materials based on the binary Al–Mo and the ternary Al–Mo–Ti system are promising candidates for high-temperature applications. In order to overcome their brittleness at ambient temperature, the positive effect of a fine and lamellar structure on the mechanical properties can be utilized. This has already been shown for binary $AlMo_3$ + Al_8Mo_3 two-phase alloys that are formed by the eutectoid decomposition of the bcc-type AlMo phase [1]. Due to the difficulties caused by the retention of the AlMo phase even after water quenching, contradictory information concerning the crystal structure of this high-temperature phase and the formed phase equilibria can be found in literature. In the present work, the phase equilibria in the binary Al–Mo and the ternary Al–Mo–Ti system were studied experimentally at 1673 and 1773 K. The binary AlMo phase was successfully quenched and it has been demonstrated that the ternary bcc-type β continuous solid solution and the binary high-temperature bcc-type AlMo phase are connected.This is in accordance with the experimental work of Nino et al. [2] and the latest thermodynamic description for the Al–Mo–Ti system performed by Cupid et al. [3]. Moreover, the structural investigations using XRD confirmed the disordered nature of the AlMo phase (bcc/A2) which was already proposed by Rexer [4]. In addition, TEM/SAED micrographs revealed diffuse scattering indicative for a trend to form the omega phase in quenched A2-type AlMo, whereas superstructure reflections indicative for occupational ordering in the A2 structure were not detected.

Starting from the binary Al–Mo system microstructural investigations were performed to study the phase equilibria at 1523, 1673 and 1773 K with β and a newly detected phase at compositions around 62Al-24Mo-14Ti. Based on the obtained results, partial isothermal sections at 1523 and 1673 K, the liquidus projection and a Scheil reaction scheme was constructed.

[1] R. Nino et al., Intermetallics 9(2) (2001) 113-118.
[2] R. Nino et al., Intermetallics 11(6) (2003) 611-623.
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New assessment of the Al-Fe system

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The heat capacity of all intermetallic phases epsilon, zeta, eta and theta was measured up to their respective melting points. The heat capacity of B2 was studied up to 1620 K for the compositions 35, 40 and 45 at.% Al including the A2/B2 transition. The phase diagram between 50 at% Al and 90 at.% Al was studied by annealing and quenching experiments and by DTA. The homogeneity ranges of the intermetallic phases were determined.

Based on the above mentioned experiments and the results from [1] and [2], an assessment of the Al-Fe system was done with focus on modelling the correct liquidus between 50 at.% Al and 80 at.% Al, and reproducing homogeneity ranges and measured cp of epsilon, zeta, eta and theta intermetallics. The A2/B2 ordering on the Fe-rich side is described using a two-sublattice model. The A2/B2 transition temperature is accurately reproduced as well as the first order transition between A2 and B2 at 23.9 at.% Al around T = 890 K. It was not possible to reproduce the measured non-linear increase of heat capacity of the A2/B2 transition with the two-sublattice model. A better way to describe heat capacity of the order/disorder reaction will be discussed.

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[2] Han,K. et al., Journal of Alloys and Compounds, 668(2016) 97-106

Tilo Zienert

Studied Material Science and Technology at TU Bergakademie Freiberg, since 2011 scientific stuff within the project CRC 920 'Multi-Functional Filters for Metal Melt Filtration'. Scientific interests are experimental investigation of phase diagrams with focus on cp measurements, CALPHAD type modelling, combining description of metallic and ceramic systems to study interactions between metallic melts and ceramic materials of metallurgical interest.

A thermodynamic database for cast iron

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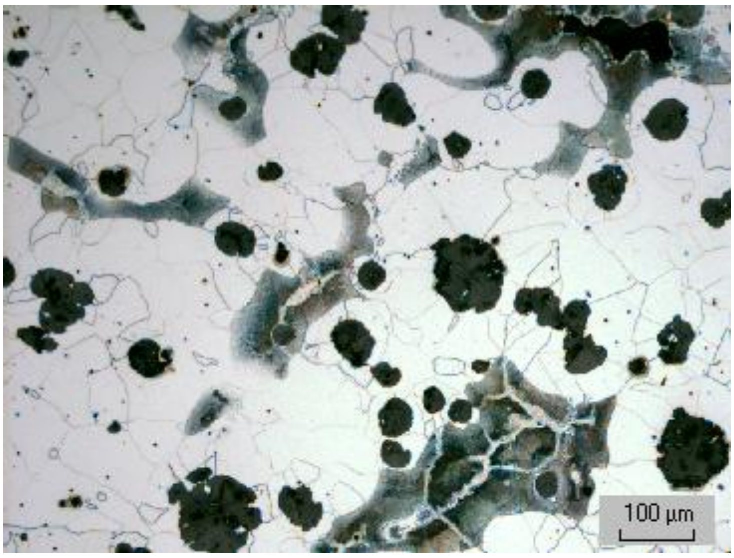
As a presumably "low-tech" material cast iron does not receive much attention in current research. At the same time the physical metallurgy of cast iron is complex. Nodular cast irons are used in e.g. wind turbines where they represent a fairly large fraction of the total mass. To further increase the power and efficiency of wind turbines further development of nodular cast irons is necessary. Using Si as a solid solution strengthener in ferritic nodular cast iron it is possible to reach a yield strength of 500 MPa at an elongation of 10%. This is on par with comparable steels at a much lower cost for the finished part. The amount of Si is limited to about 4 wt.%. Above that level ordered bcc phases, such as B2 and $D0_3$, start to appear, leading to embrittlement.In ferritic cast iron the presence of pearlite and other carbides should be avoided, since they reduce toughness and fatigue strength. At present it is not clear which levels of carbide forming elements, such as Cr, Mn, Mo, V and Nb can be tolerated. To be able to simulate carbide formation during the solidification and pearlite formation during the austenite transformation a database for cast iron was constructed containing the elements, Fe, Cr, Cu, Mg, Mn, Mo, Nb, Ni, Si, Ti, V, C and N. This database is based on an earlier database for alloyed cast iron [1] and a recently developed database for precipitation in high-Mn steels [2]. In this presentation the construction of this database will be described.



Nodular cast iron; mostly ferritic, but with some amount of pearlite and other carbides.

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Experimental study and modeling of thermodynamic properties of the Ag-Cu system for the third generation of thermodynamic databases

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The Ag-Cu is the most fundamental and essential system for the jewellery industry, high-temperature solders applications and active metal brazes. This has led to consequently huge interest for both experimental and theoretical study of this system. Due to recent activities focused on the development of the third generation of Calphad databases, we proposed a new thermodynamic description for the Ag-Cu system. Our current study using Differential Scanning Calorimetry analysis of the Ag-Cu system showed a very negative delta Cp of mixing in the Ag-Cu liquid which is inconsistent with data from previous assessments [1]. Based on this new experimental information, the Ag-Cu system has been reassessed.
Measurements of heat capacity of pure silver, copper and three binary alloys were conducted in the graphite crucibles under a flow of argon using Setaram LabSys Evo 1600 calorimeter. For the fitting procedure of published and new experimental values of the heat capacity Cp, we used models suggested at the Ringberg 95' workshop [2]. The Einstein model was chosen to describe thermodynamic properties of crystalline phase down to 100 K [3] and two state model was used to represent data for liquid phase [4]. The PARROT module in the ThermoCalc software was used for parameter optimization. The results will be presented and discussed.

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Phiri Albina

Albina is pursuing her PhD degree in Materials Science at National University of Science and Technology "MISIS" and working as an Engineer at the Thermochemistry of Materials Scientific Research Centre. Her thesis involves the development of thermodynamic and phase diagram data for the Ag-Cu-Ge-O-S system under the supervision of Dr. Alexandra Khvan.

On the temperature dependence of excess Gibbs energy of solutions

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The history and state of the art of the subject is discussed[1], specifically:

- the classical linear model, the high-temperature artefact [2]and its root reason [3],
- the exponential model [3] with some of its applications without any artefact [4-17],
- the possible low-temperature artefact and the false claim on the Mg-Si system[18],
- the high-temperature boundary condition [19],
- the complex linear-exponential model [20],
- the LET-functions [21]with their inconsistent properties compared to experimental data,
- theimproved exponential model with attached low-T polynomialand its properties [1].

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George Kaptay

MSc in metallurgical engineering (Leningrad, 1984), PhD in metallurgical engineering (Leningrad, 1988), habilitation (Miskolc, 1998), DSc in materials science (Hungarian Academy of Sciences, 2005), corresponding member of the Hungarian Academy of Sciences (2016). With the University of Miskolc (since 1987), as head of departments (since 1996) as a Dean (1998-2006) and as full professor (since 1999). Principal scientist at Bay Zoltan Ltd for Applied Research (since 2006).President of the Hungarian Society of Materials (since 2015). Recipient of the best Calphad paper award (2015).

Modelling thermal vacancies within the CALPHAD approach

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A physical model is proposed to enable a unified thermodynamic treatment of the vacancy-bearing solid and the gas. It also solves the long-standing controversy in modeling the vacancies in solids within the CALPHAD approach. The model parameters are related to quantities that can be calculated by first-principles or measured experimentally. The vapor pressure of tungsten is calculated using the proposed model and methods, achieving satisfactory agreement with experimental data. It is pointed out that the site fraction is an order parameter in the present model that can be used to describe sublimation.

[1] P. W. Guan, Z. K. Liu, Scripta Materialia 133, 5-8 (2017).

Pin-Wen Guan

Ph.D. candidate,Materials Science and Engineering,Pennsylvania State University. He is currently interested in thermodynamic modeling of solar materials.

Thermodynamic descriptions of pure Sn, Pb, Bi and Bi-Sn system from 0K using two state model for the liquid phase.

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This work is a part of a project focused on the development of new descriptions of thermodynamic data for pure non-ferrous elements which are of interest in the development and use of lead free solders. This work addresses not only data for pure elements but also the behaviour of the new models to represent the data during extrapolation into binary and multicomponent systems. For these purposes the Bi-Sn and Sn-Pb systems were revisited in the present work.

The Einstein model has been used for the description of the heat capacity of the crystalline phase and the two state model for the description of the liquid phase heat capacity. The theoretical basis for the models used in the new database was developed during the Ringberg workshop in 1995 and was later published in the proceedings of the workshop [1]. These models have been used for only a very few cases until recently [2] and not systematically for low melting point elements.

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Scientific Interests: Computational Thermodynamics, High Temperature Calorimetry, Phase Diagrams

About the limits of applicability of the Alkemade theorem for the construction of ternary liquidus surfaces

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The Alkemade theorem goes back to a very fundamental paper on the graphical description of thermodynamic equilibrium problems from 1893 [1]. It is one of the most helpful implements for the construction of the liquidus surface of ternary phase diagrams. In its original form, it allows to find the direction of falling or increasing temperature along the univariant reaction lines forming the boundaries of the primary crystallization fields. The theorem is valid for systems with any number of phases; however, its geometrical construction rule is only defined for the case of stoichiometric phases and it is not clear how to apply the theorem in case of phases with extended homogeneity ranges. Some examples of ternary, transition-metal-based systems containing phases with large homogeneity ranges are presented and the usefulness and limits of applicability of the theorem are discussed.

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The Calphad Method – the Scientific use of Metastability

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Ever since Larry Kaufman proposed the use of lattice stabilities for the end points of the Gibbs energy curves for solution phases there has been discussions and questions about the validity of such an approach. Today we have software and databases for multicomponent alloys and other materials based onthis concept and it is clear that the proposal was a very useful one. The Calphad method has become a tool used daily for many scientific and industrial applications. But many users are probably not aware of all the data hidden behind a calculated phase diagram or a simulation of a transformation or even a simple list of a calculated equilibria. And there is always the question, how accurate are the results?

As I have worked with thermodynamic calculations for 40 years I would like to share some of the experiences developing models, software and databases and give a few examples that may show the volatility of data but also the possibility to make reliable predictions of many complex phenomena. Some of these can also be found in the book by Leo, Suzana and myself [1].

[1] H Leo Lukas, Suzana G Fries and Bo Sundman, Computational Thermodynamics, Cambridge University Press (2007)

Bo Sundman

Understanding Physical Metallurgy and Computational Design of High Entropy Alloys: Atomistic Simulation and CALPHAD

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High-entropy alloys (HEAs) are attracting an explosive academic interest with promising and unique properties as structural materials. Particularly, the CrCoFeMnNi HEAs are reported to possess an excellent balance between strength and ductility, corrosion resistance and thermal stability. Strong solid solution effect, micro-twinning, high content of Cr and sluggish diffusion are mentioned as probable reasons for the unique HEA properties. However, exact mechanisms are not clearly known yet, and the fact that the physical metallurgical mechanisms related to individual properties are mostly not clarified limits wider industrial applications of HEAs even with the good combination of engineering properties.

In the present talk, the effect of individual elements on the solid solution strengthening, the mechanisms for the low temperature deformation and the sluggish diffusion will be clarified based on an atomistic simulation. An alloy design of new fcc HEA [1], based on the CALPHAD approach and literature phase diagram study will also be introduced, together with experimental results.

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Developer of the Second Nearest-Neighbour (2NN) MEAM interatomic potential formalism and 2NN MEAM interatomic potentials for various elements and alloy systems.

The fcc solid solution stability in multi-component system: towards high entropy alloys design

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For a long time, development of alloys was restricted to one principal element, or rarely two, with minor elements added for properties and performance optimization. In 2004 [1,2], an equimolar Co, Cr, Fe, Mn and Ni alloy was produced and was unexpectedly found to be single-phase. A new concept of materials was born: multi-component alloys forming a solid-solution and in which all components are very concentrated. By definition this new material concept should make it possible to explore an almost infinite field of chemical compositions. But in the meantime, the thermodynamic stability of these systems is poorly known and severely limits the choice of alloy compositions.

In this context, the objective of this study is to fully determine the composition range of existence of a unique fcc solid solution within the multi-component Co-Cr-Fe-Mn-Ni system. To address this problem, the phase stability was theoretically and experimentally investigated. Using the Calphad approach and a new database (TCHEA1), the stable phases of 10 626 compositions could be calculated, at several temperatures. 11 alloys were also processed and characterized by XRD, SEM-EDS and EBSD. The comparison between calculation and experimental results indicates that the fcc solid solution is accurately described by the TCHEA1 database but the σ phase is more stable than the predictions. It was shown that the fcc phase is stable over a wide range of composition, which was completely described. Now, it is possible to choose a priori a composition which will form a solid solution within the Co-Cr-Fe-Mn-Ni system. Finally, the heat of mixing of the fcc, bcc and hcp phases were compared between density functional theory (DFT) and Calphad calculations in order to improve the description of this system.

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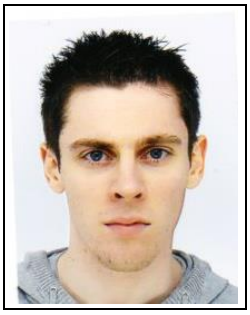

Guillaume Bracq

Second year PhD student at the ICMPE in MCMC and CMTR teams. These teams have an expertise in the fields of thermodynamics, elaboration and mechanical behaviour. My thesis allows to study jointly thermodynamics and mechanical properties of the Co-Cr-Fe-Mn-Ni system, in a multi-scale approach combining simulation and experimentation.

A Constraint Satisfaction Problem Approach to High-Entropy Alloy Design

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High-entropy alloys (HEAs) are multi-principal element alloys at near-equiatomic concentrations that can have superior properties such as high irradiation resistance, high fatigue resistance, and high temperature usage, compared to conventional alloys. This gives HEAs potential application to industries such as nuclear, aerospace, medical, and electronic. However, the design and discovery of HEAs has been largely limited to trial and error methods, therefore only a fraction of the possibilities have been produced. A computational alloy design methodology using the Constraint Satisfaction Problem (CSP) approach [1] is proposed to accelerate HEA design and discovery. This approach consists of three major steps: mapping design requirements into mathematical constraints and using computational thermodynamic calculations to implement them, sampling the HEA space of composition and temperature within the constraints to search for solutions, and describing the final solution space using machine learning methods. Ultimately, the CSP approach enables the identification of all regions in composition space that satisfy material design requirements. A Thermo-Calc database was verified against experimental data [2] to be implemented for phase stability calculations. With kinetic considerations, about 71% of the 216 evaluated alloys showed good agreement between experiments and calculations using the database. This database was used to map out single-phase solid solution regions for the known CoCrFeMnNi HEA and all of its subsequent near-equiatomic quaternary and ternary systems. Afterwards, regions of possible precipitation hardening potential were determined in Al-HEA systems. The results demonstrate the CSP approach's capability to search HEA thermodynamic space and to accelerate HEA design and discovery.

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Anas Abu-Odeh

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Phase stabilities of Ti materials with a focus on the thermodynamic modelling of metastable microstates

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Ti and it's alloys have become of great interest for a variety of applications including biomedical and aerospace. Based on the application, the phasesin Ti alloys become quite important. In biomedical applications, it is seen that Ti in the bcc phase lowers the Young's modulus while retaining the strength which is desired. In order to improve alloy selection and tailoring,the present work built a thermodynamic database for the Ti-Mo-Nb-Sn-Ta-Zr system using an integrated first-principles and CALPHAD modelling approach. The focus of the present work is on the phase stability of the equilibrium bcc phase as well as formation of the metastable microstates ω in hexagonal phase (space group P6/mmm)and α” in orthorhombic phase (space group Cmcm).The enthalpies of formation were systematically calculated for the pure elements, Ti-containing binary and ternary alloys in the bcc phase. These results as well as available experimental results were used to evaluate or build a thermodynamic description for the Ti binary and ternary alloys in the system. The completed database was still insufficient for predicting the formation of the metastable microstates that form. For this, the Ti-Nb binary alloy was studied. The partition function approach was adapted to calculate the configurational entropy produced due to the competition between the metastable microstates. This allows for calculation of phase fraction formed. The predictions were then compared with results from neutron scattering data. Two sets of Ti-Nb samples were arc melted. Each set of samples was composed of four different samples with different compositions. The sets of samples were heat treated differently so that one set formed the ω phase while one set of samples formed the α” phase. The phase fractions obtained both experimentally and computationally were then used to predict the mixed force constants to plot the phonon density of states and compare with the phonon density of states plotted from the neutron scattering data.

Cassie Marker

Cassie Marker is a Ph.D. student at The Pennsylvania State University. Her research is on the development of a thermodynamic and elastic database for the Ti-Mo-Nb-Sn-Ta-Zr system. Cassie is a National Science Foundation fellow. She was a recipient of the Department of Energy Graduate Student Research Award, the Student Excellence award for her service and leadership as well as the Materials Science and Engineering safety award at Penn State. She served as the President of the Penn State Chapter of the Materials Research Society as well as the Chair of the Laboratory Safety managers.

Crystal structure relations among variants of the ω phase in titanium alloys and their modeling

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The ωTi structure (*P6/mmm*, *hP*3) is stable at low temperatures near 0 K or at high pressures above 20 Kbar [1]. Metastable solutions based on ωTi were observed to form in many binary systems such as Ti-Mo, Ti-V and Ti-Nb and even higher order systems such as Ti-V-Sn [2].

In the crystallographic viewpoint, the ω structure can be derived from the bcc_A2 structure via the so-called ω collapse [3]. The frequently observed translational ω'' phase (*P-3m1*) is the product of an incomplete collapse. The other translational ω' phase (*P-3m1*), however, is merely a hypothetical structure.

In a binary system, the ω collapse with atom rearrangements may result in the C32 type structure, which can be regarded as an ordered version of ωTi. The resulting phase could also be of the $B8_2$ type, which is a further ordered structure of C32, especially if the parent phase is the B2 type [3]. Complexly ordered structures [4] may occur in Titanium alloys, such as the $D8_8$-type Sn_3Ti_5 [5], and the Ga_4Ti_5 type phase [6]. Complication exists in systems such as Co-Sn-Ti, where the Sn_3Ti_5 phase extends into the ternary system and transforms to the Ga_4Ti_5 type at the composition of $Ti_5Sn_3Co_1$, where Co occupies all the Ti octahedra [7]. The terms of "athermal ω" and "thermal ω" [4] are empirical and are not related to specific structures.

In the modeling, the solid solution based on ωTi is modeled as a substitutional solution, so is the translational ω'' solution. The C32 type and the $B8_2$ type are modeled with a 2-sublattice model and a 3-sublattice model, respectively. The $D8_8$-type structure and its filled variant, the Ga_4Ti_5 type, are described with a 4-sublattice model as the same phase.

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Characterizing uncertainty of CALPHAD assessment. The Au-Pd case

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It is well known that the results of CALPHAD assessments may be not unique even when based on divergent set of experimental data, including both phase equilibria and thermodynamic measurements.

We examined the possibility of explicit formulation of uncertainty of results of computer assessment. As first example the Au-Pd binary [1] was chosen, being sufficiently simple (only liquid and fcc phases are stable) and rather well studied (two investigations of phase equilibria, three calorimetric works and 3 measurements of partial Gibbs energies).

At the first stage we tested mutual agreement of experimental data using statistical procedures known as 'jackknife' or 'cross-validation' [2]. That consist of a series of calculations in every of which one peace of data is omitted. The results of the calculation should reasonably well restore omitted data. Data which did not passed this test were excluded from the dataset as not being in agreement with others.

For more detailed analysis we calculated the hessian of approximation, *i.e.* matrix of 2nd derivatives of sum of squared residues by parameters of models. The regions of uncertainty of parameters were then found as suggested in [3]. In addition, analysis of the hessian using SVD (singular value decomposition) enabled us to determine which parameters and/or their combinations are defined best and worst. Analogous analysis of “partial” hessianes restricted to particular datasets permitted us to determine an informativity of those ones, *i.e.* parameters and/or their combinations most (and least) influenced by every dataset.

The results are compared with other approaches to characterization of uncertainty of results, *f.e.* with so-called linear error model suggested by Rudnyi [3].

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Thermodynamic modelling of Cr-Fe-Nb-Sn-Zr system

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Zirconium alloys are widely used as fuel cladding materials in Light Water Reactors (LWR). In order to improve accident tolerance in these reactors, new claddings are being developed. One of the promising candidates for alternative cladding materials is Cr-coated zirconium alloy.

In this framework, it is necessary to have a better understanding on phase transformations occurring in these alloys. Thus, a new thermodynamic database dedicated to Zirconium alloys is being developed using the Calphad approach coupled with systematic DFT and SQS (Special Quasirandom Structure) calculations.

In this work, the five following elements Zr, Cr, Fe, Nb, Sn are considered. Since no experimental data were available for the Cr-Fe-Sn, Cr-Nb-Sn, Cr-Sn-Zr and Fe-Nb-Sn ternary systems, new experimental data are provided, within this study, on the isothermal sections of these systems at different temperatures. In addition to these experimental data, DFT calculations are carried out in order to determine formation enthalpies of the stable and metastable phases. At last, the SQS method is jointly used with DFT calculations in order to predict the mixing enthalpies of the binary solid solutions. Finally, these experimental and calculated data in addition to the data obtained from literature, are used as input data for the Calphad modelling of the Cr-Fe-Nb-Sn-Zr quinary system.

We report here the Calphad modelling of all the binary and ternary sub-systems of the Cr-Fe-Nb-Sn-Zr quinary system. A last part is dedicated to comparisons between predictions obtained with our new database and new experimental results on Cr-coated claddings.

Paul Lafaye

I am a 3rd year PhD student at SRMA (CEA Saclay), ICMPE (CNRS) and Paris-Est University (UPE). My research project consists in designing a new thermodynamic database for Zirconium alloys. I have been working for three year on this subject, first during my MSc internship then my PhD with Jean-Marc Joubert, Jean-Claude Crivello researchers at ICMPE, and Caroline Toffolon-Masclet researcher at CEA Saclay.

A New Approach of the CEF applied to the sigma phase modeling : Application to the thermodynamic re-assessment of the Nb-Al system using new experimental data.

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[b] EEL/USP – Escola de Engenharia de Lorena, Universidade de São Paulo. Estrada Municipal do Campinho, s/n, Lorena, SP, 12600-000, Brazil.
[c] IEM/UNIFEI – Instituto de Engenharia Mecânica, Universidade Federal de Itajubá. Avenida BPS, 1303, Itajubá, MG, 37500-903, Brazil.
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The σ phase is a hard brittle phase present in a lot of technologically important systems. Because of its brittleness, it should generally be avoided. A careful control of its presence in multicomponent systems could in principle be achieved after calculations conducted with the CALPHAD method.

One of the main features of the σ phase is its non-stoichiometry. Among the intermetallic phases, it is probably the phase having the broadest range of existence among the different systems. An extensive analysis of the literature data concerning the CALPHAD modeling of the σ phase has been made by [1]. The author shows that the thermodynamic description of the sigma phase needs a five-sublattice model having a mixing of both elements in all sublattices as follows:

$$(A,B)_2^{2a}\,(A,B)_4^{4f}\,(A,B)_8^{8i_1}\,(A,B)_8^{8i_2}\,(A,B)_8^{8j}$$

In order to reduce the number of parameters, some simplifications who consist in reducing the number of sublattices must be made. In a classical CALPHAD approach based on the CEF, a major problem is that the various simplifications adopted in the choice of the model are not compatible with each of the others. We propose in this work a new approach of the CEF that allows making compatible all of them. This new approach is illustrated through the thermodynamic re-assessment of the Nb-Al system using new experimental data concerning the solubility limits of the intermetallic phases obtained by EPMA measurements.

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Thermodynamic study on microstructure evolution during aging process in the Al-Cu binary alloy

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Aging phenomena in the Al-Cu binary alloy have been investigated from both of experimental and theoretical points of view. It is well known that the hardness of the alloy increases accompanied by the formation of GP zone and succeedingly decreases when a metastable fluorite-type θ' phase precipitates. However, it still remains an unsolved problem how the metastable phase forms during aging treatment.

Recently, we reported the tendency of phase separation in the Al-Cu binary fcc phase. [1] In addition, several groups reproduced the microstructure of the GP zone by means of combining the first-principles calculations and the Monte Carlo method.[2-4] Nakagami et al. [4] concluded that the formation mechanism of the GP zone would be regarded as a kind of order-disorder transformation on fcc lattice.

On the basis of this background, we assumed that the formation process of the θ' phase could also be described as a kind of order-disorder transformation in the fcc-based matrix. To confirm this hypothesis, we attempted to evaluate the free energy curves of the fcc-based structure with different lattice constant of c-axis using the first-principles calculation. Configuration entropy was taken into account by means of the cluster expansion and cluster variation method at finite temperatures.

The calculated result indicates the existence of a continuous transformation path of the θ' phase from the fcc matrix. This transformation path is expressed as a rearrangement of Al, Cu, and vacancies which yields a contraction along the c-axis. According to these results, the evolution of microstructure during the aging treatment in this system does not proceed by nucleation, but is rather caused and accelerated by the spinodal decomposition for minimizing the free energy of the whole system.

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Phase diagrams of binary alloys under pressure

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The phase diagrams of binary alloys can vary significantly with pressure. Within the framework of solution-type models, the variation is controlled by the pressure dependence of the elemental end members, which is relatively well known, and that of the excess interaction, which is unknown. We develop an exact thermodynamic relationship for the pressure dependence of the excess interaction in an alloy solution and relate it to the composition dependence of the density and sound velocity measured at ambient pressure. The effect of composition on the sound velocity and density was studied for the isomorphous binary alloy Bi-Sb and the eutectic systems Bi-Sn, Bi-Pb and Pb-Sn, and the pressure dependence of the excess interaction was evaluated. On the basis of these results, the pressure dependence of these binary alloy phase diagrams was calculated and found to agree well with the experimental data in the literature

[1] M. Emuna et al., Journal of Alloys and Compounds, 687 (2016) 360.
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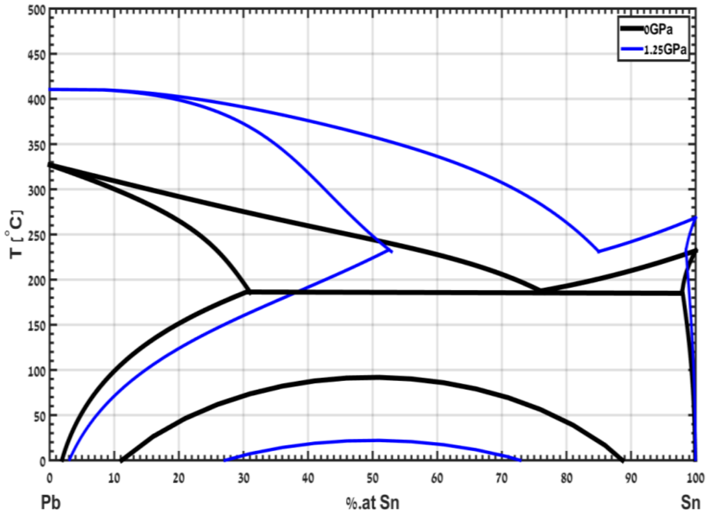

Effect of pressure on the binary phase diagram of Pb-Sn as calculated in the present study [1]

Guy Makov

Associate Professor of Materials Engineering at Ben-Gurion University of the Negev in the field of Materials Physics. Scientific education includes B.Sc. in Chemistry, Ph.D. in Chemical Physics at Tel Aviv University; postdocs and sabbaticals at Cambridge University, FZ Julich and King's College London. Guy's research aims to understand materials behavior under extreme conditions from a physical viewpoint, in particular equilibrium properties. Specific interests include the liquid state andeffect of pressure on phase diagrams.

Thermodynamic description of the lithium manganese oxide as cathode materials for lithium-ion batteries

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Lithium manganese oxide is a highly promising cathode material forrechargeable lithium ion batteries because of its low cost, high power density and environmental friendliness [1].The large number of structure types that exist in the Li–Mn–O system, like the spinel structured λ-MnO_2, $LiMn_2O_4$, $Li_4Mn_5O_{12}$, $Li_2Mn_4O_9$, orthorhombic or monoclinic structured $LiMnO_2$, and monoclinic structured Li_2MnO_3, offers a wide selection of cathode materials[2, 3].The composition of the active electrode material in the Li–Mn–O phase diagramplays an important role in controlling and designing battery performance. Therefore, the aim of the present work is to develop a reliable thermodynamic description of Li–Mn–O systemby means of the CALPHAD method.

All of the experimental data available in the literature were critically reviewed and assessed using thermodynamic models for the Gibbs energies of the individual phases. Two of the ternary compounds, $LiMnO_2$ and Li_2MnO_3, were modeled as stoichiometric phases. The spinel phase showed extensive solid solubility and was modeled as anon-stoichiometric compound. According to the practical application, twosets of sublattice formula were employedto describe the different solubility of the spinel phasewithinthe λ-MnO_2–$LiMn_2O_4$–$Li_4Mn_5O_{12}$ and $LiMn_2O_4$–$Li_4Mn_5O_{12}$–$Li_2Mn_4O_9$ triangles.Thecalculated phase diagrams and thermodynamic properties using the present thermodynamic descriptionare consistent with the literature information. Additionally,self-made $LiMn_2O_4$ samples were chemically delithatied and the enthalpies of formation of the metastable compounds were measured using high temperature oxide melt drop solution calorimtery for the fist time. The results of these measurements are compared to the thermochemical calculations from the dataset.

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Weibin Zhang

I received mydoctoral degreein Materials Science from Central South University in June 2015. I am working at Karlsruhe Institute of Technology (KIT) as a postdoc now. My research topic is the combination of the thermodynamic modeling and key experiments to develop the novel cathode materials for lithium-ion batteries.

Thermodynamics on Developing Earthquake Resisting High-Strength Reinforcing Steel Bars

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Due to rapidly increasing earthquake damage, seismic design construction becomes more important than ever. Especially, reconstruction of old town in Korea requires high-rise and seismic design construction, many attentions have been paid to high strength seismic reinforced steel bar. In the present presentation, thermodynamic issues are summarized for developing next-generation seismic reinforced steel bars. Thermodynamic equilibria of alloying elements between molten slag and molten steel are discussed. Alloy design based on computational thermodynamics are introduced as well. On the other hand, it is considered that grain size refinement by the controlled rolling and low-temperature transformation structures formed by the accelerated cooling are effective to obtain acceptable mechanical properties with high strength. Finite element simulation analysis is also useful to understand plastic deformation by rolling, internal and external heat transfer, and corresponding phase transformation of austenite phase to various low-temperature transformation structures.

This work was supported by the Industrial Strategic technology development program “Development of Earthquake Resisting Reinforced Concrete using Grade 700MPa Reinforcing Bars for Enhancement of Seismic Safety (10063488)“ funded by the Ministry of Trade, industry & Energy (MI, Korea). This presentation is based on our recent publication [1].

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Joonho LEE

Dr. Joonho LEE received PhD from the University of Tokyo in 2002. He joined Department of Materials Science and Engineering, Korea University in 2005 as Assistant Professor and became Full Professor in 2013. He has worked as POSCO Affiliated Professor from 2007, contributing industrial technology developments based on thermodynamics. He is a member of Steel Forum, Korea National Assembly. He is Organizer of TOFA 2018 and Calphad LIV.

A CALPHAD approach tomodelling of slag viscosities

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Viscosity as a function of temperature and composition is of practical importance for the description of slag flow behavior, for examplein entrained flow gasifiers or combustion power plants but also in many metallurgical applications. The viscosity essentially depends on the structure, a comprehensive description of structural dependence is therefore required for the development of a new viscosity model.In the framework of the HotVeGas project, astructure based model developed for the fully liquid system SiO_2-Al_2O_3-CaO-MgO-Na_2O-K_2O-FeO-Fe_2O_3-P_2O_5 has beenused to describe the viscosity of the system in the Newtonian range. The structural treatment of the various oxides in multicomponent oxide systems is discussed on the basis of the underlying non-ideal associate species model that was used to describe the Gibbs energy of the liquid.

To obtain an effective structural dependence of the viscosity, it is linked to theassociate species distribution. With this principle, both the temperature- and composition-induced structural changes of oxide melts can be described with a set of monomeric associate species in combination with the critical clusters induced by the self- and inter-polymerizations. With the new model, one of the challenges of the viscosity behavior in SiO_2-based binary systems, the so called lubricant effect, is well described. The viscosity behavior when substituting one network modifier for another at constant SiO_2 contents is also well described. Moreover, the Al_2O_3-induced viscosity maximum is described, in which the position and magnitude of the viscosity maximum as a function of temperature and composition (charge compensation effect) are properly predicted. The new model is self-consistent and gives a reliable prediction over the whole range of compositions and a broad range of temperatures using only one set of model parameters, which all have a clear physico-chemical meaning.

The essential steps to arrive at the thermophysical property viscosity when starting from the thermochemical property Gibbs energy will be outlined. Trends among the viscosity parameters will be discussed and high-lights of the viscosity prediction for real world systems will be demonstrated. Finally, 3D-relationships between liquidus surfaces and viscosity surfaces will be shown.

Thermodynamics of Actinide Alloys in the upcoming New Edition of the Pu Handbook

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A new edition of the “Pu Handbook – A Guide to the Technology” is close to completion. The last two-volume handbook was first edited in 1967, and reedited in 1980 by O. J. Wick with a minor update. One (Chapter 7) among several chapters in the handbook that related to topics close to those of interest to the CALPHAD community was entitled “Alloying Behaviour of Plutonium” authored by F. H. Ellinger, C. C. Land, and K. A. Gschneidner, Jr. Being the lead author on this revisited chapter (that will have a slightly different title, TBD), the presentation will give a brief overview of the entire Pu Handbook before focusing on the content of one section dedicated to Pu-based alloy phase diagrams, both experimental and theoretical. One point to make though is that despite a very limited number of studies carried out on Pu-based alloys after the mid-sixties, like for many other classes of materials, including the other actinides, very little experimental work has been done to augment our knowledge for this class of alloys, and subsequently to improve the thermodynamic assessment. After a general survey on experimental phase diagrams that are currently approximately known, CALPHAD modelling of Pu-based alloys will be discussed. Needless to say, more experimental and modelling work needs to be done, and in conclusion, the emphasis will be put on those systems that impact nuclear materials science and their application to fuels.

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Keywords: phase diagrams, *ab initio* calculations, thermodynamic modeling, materials for energy, actinide alloys, nuclear materials

CALPHAD approach: a complementary way to determine the corrosion path way of PuAl alloys stabilized in δ-phase

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In order to improve our knowledge of plutonium oxidation related to safe and long term storage, the reactivity of metastable δ-Pu alloy was studied under controlled atmosphere composed of dry O_2 at different temperatures. The originality of this work lies in the complementarity between CALPHAD approach and in situ X-ray diffraction (XRD) analysis performed during the oxidation process, enabling the phase identification as well as the characterization of the oxides growth kinetics.

In situ XRD analyses were performed under dry O_2 atmospheres with different isothermal holds, using a temperature chamber mounted θ/θ diffractometer inside a glove box. The oxide surfaces were also examined by scanning electron microscopy at the end of exposure. In order to be able to analyze the microstructure of Pu oxides, the recorded diffraction diagrams were analyzed using a novel method based on a modified Rietveld refinement.

Once again some CALPHAD calculations performed by adding oxygen into the thermodynamic description of the system from literature data [1-3] helped to determine the corrosion path way. They highlighted, like for martensitic reversion [4,5], a strong dependence of the solute effect. Indeed, the calculated ternary diagram Pu-Al-O at 500K exhibits the coexistence of pure plutonium oxides with plutonium-aluminum compounds, requiring a solute diffusion process during the oxidation pathway, with a final state consisting of a PuO_2 and Al_2O_3 mixture.

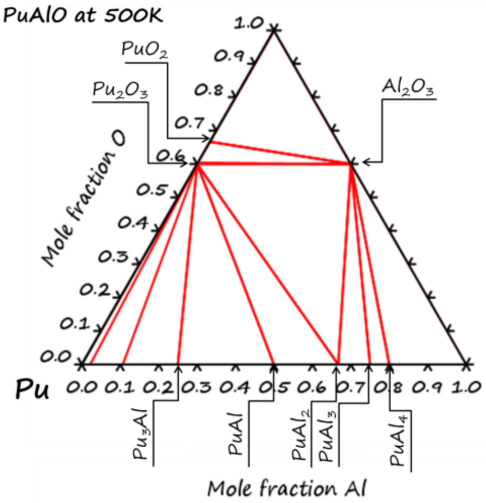

Fig. 1. Isothermal section of the ternary diagram of the PuAlO system at 500K.

With this simple example, we underline the powerful approach made by coupling CALPHAD method and experimental data to come through the plutonium complex behaviour and the role played by the solute diffusion process.

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PdZn Intermetallic compound: A pseudoelement of Cu for catalysis

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An intermetallic compound, PdZn has been verified to have similar valence electronic structure as pure Cu by hard X-ray photoelectron spectroscopy and energy band calculation[1,2]. In the mean time, the catalytic function was shown to be similar for the PdZn and Cu. An important principle has been derived in this study that an intermetallic compound can fully replace a metallic element without changing catalytic function. In other words, an intermetallic compound could be treated as a pseudoelements in terms of catalysis. A number of catalytic reactions such as steam reforming of methanol ($CH_3OH + H_2O \rightarrow 3H_2 + CO_2$) and NO+CO have been testified for the PdZn and Cu. The detail of electron structure and its contribution to catalytic properties will be described in the presentation.

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Design of grain growth inhibitors and analysis of mechanical properties in ultra-fine WC-10Co cemented carbides based on thermodynamic calculations

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A material with multiphase implicates complex thermodynamic phenomena in preparation of cemented carbides, which have many factors influencing microstructure and properties of cemented carbides, such as composition, sintering time, temperature and atmosphere and so on. The thermodynamic calculations provide a theoretical guidance to reasonably design the composition of ultrafine WC-10Co-Cr_3C_2-TaC cemented carbides, predicting the formation of phases and the solubility of grain growth inhibitors in cemented carbides.

According to our thermodynamic database of multi-component cemented carbides [1], the stability of Cr_7C_3 brittle phase and the segregation of (Ta,W)C cubic phase formation can be predicted. It is well known that cemented carbides must avoid the formation of these phases during cooling, which might be formed through the gradual replacement of tough binder phase [2]. The effect of Cr_3C_2 and TaC contents on microstructure and mechanical properties of WC-10Co based cemented carbides has been systematically studied by integrating the calculations and key experiments. This hybrid approach has shown to be a powerful tool for processing advanced materials in cemented carbides, which is more efficient on composition and process parameters optimization compared with expensive and time consuming experimental methods.

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[2] Zackrisson J et al. Int J Refract Met H., 16(1998) 417.

Haixia Tian
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Supervisor: Professor Dr. Yong Du
Research field:
- Design of grain growth inhibitors and analysis of property in cemented carbides bases on thermodynamic calculations.
- Real microstructure-based simulation of residual stress and crack propagation in cemented carbide by FEM.

Thermodynamic and Kinetic Modeling Applied to Hardmetals

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Hardmetals were invented in Germany in the 1920's and industrial production started shortly thereafter in several countries. The advances and scientific developments in powder metallurgy and in physical metallurgy that were made at the beginning of the century were important for this development [1]. Hardmetals consist of hard carbides embedded in a softer binder phase, where the binder is often Co and the carbide is the simple hexagonal WC carbide. However alternative metallic binders, alloying additions to Co for grain size control, and other carbides, for example TiC, or other cubic carbides, are common. Hardmetals are produced from powder and sintered at temperatures where the binder is liquid and the carbides are solid, and the microstructure that results from sintering is therefore close to what can be predicted from a CALPHAD type calculation of the phase equilibria. By applying diffusion calculations effects of sintering atmosphere and time, or compositional variations can be assessed. Since the 1970's thermodynamic modelling has been applied as a tool in hardmetal development, and has contributed to a better understanding of factors affecting the microstructure development [2,3]. By applying diffusion modelling, gradients formed on sintering have been understood and predicted [3]. A review of thermodynamic and kinetic modelling applied to hardmetals is presented. Methods to address the lack of relevant experimental information for these relatively new types of materials are discussed. The most important alloy systems, the main challenges, and some suggestions for future developments are presented.

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Thermodynamicmodeling of long-term precipitation kinetics in heat-resistant alloys

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There is an urgent need to improve the thermal efficiency of fossil fuel power plants by raising the operation temperature and pressure in order to reduce CO_2 emission as well as the cost of fuel. Plant operation at higher temperatures inevitably requires the development of heat-resistant alloys with a higher creep strength. There has recently been an increasing interest in applying advanced heat-resistant alloys to fossil fuel power plants in order to raise their operation temperature. The important role of precipitation in the achievement of good creep properties of heat-resistant alloys has long been recognized.

One of the most effective ways for improving the creep properties is to uniformly distribute fine precipitates with a good long-term stability at elevated temperatures.The experimental investigationof the long-term precipitate evolution behavior in heat-resistant alloys have not often been performed, although it is important inunderstanding the creep properties.In addition to experimental approaches, there have recentlybeen a few attempts to simulate the precipitation kinetics in heat-resistant alloys.

The purpose of this study is to simulate the long-termprecipitate evolution in various heat-resistant alloys such as ferritic/martensitic and austenitic steels and nickel alloys using a numerical model based on theclassical nucleation theory and evolution equations derived fromthe thermodynamic extremum principle that maximizes thedissipation rate of the total Gibbs energy of the system.The simulation results, such as the precipitation sequence and theprecipitate size, will be compared with experimental observations.

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Analysis of the phase equilibria and phase transformations in the region Al-Al_3Zr during slow cooling rate solidification and long-time annealings below the solidus

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Two separate groups have been investigating experimentally the phase transformations of alloys of different compositions in the Al-Al_3Zr region during solidification at slow cooling rates using DTA, SEM, TEM, XRD, EPMA analysis of as-cast and annealed samples.

The formation of eutectic type colonies on the boundaries of the dendrites cells was detected in the examined samples.

DTA analysis using slow heating rates at 0.25, 0.5 and 1 K/min detected a thermal arrest at a temperature of 659°C. Additional DTA analyses using pure aluminium as a references confirmed that the invariant reaction in the analysed sample is at a lower temperature then the melting point of pure aluminium.

Analysis of primary crystal formation showed 3 morphological types of intermetallic phase formation, one of which corresponds to the typical formation of Al_3Zr. The grain-boundary particles are detected as the DO23 Al_3Zr phase.

Long-time anneals at just below solidus temperatures, did not lead to the dissolution of the “eutectic phase” which confirms it’s stability. They also showed decomposition of the primary intermetallic phases and indicated that the solubility of Zr in Al is somewhat lower than previous experimental data implied.

Ab initio density functional theory has been used to predict the partial enthalpy of solution of Zr in fcc Al with a view to gain further understanding of the solubility of Zr. Tentative results indicate that a revision of the phase diagram for Al-rich compositions is required.

PA

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Actual position: Director of the Thermochemistry of Materials SRC
Scientific degree: PhD in Physical Metallurgy
Scientific Interests: Computational Thermodynamics, High Temperature Calorimetry, Phase Diagrams

Thermodynamic Optimization of Ni-Ti-V Ternary System

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A thermodynamic description of the Ni-Ti-V system is obtained by combining results of first-principle total energy calculations with the CALPHAD approach. The enthalpies of formation of binary intermediate phases are calculated by first-principle method, which are compared with the experimental data. The energy of formation of hypothetical end-members due to the sublattice model used for modeling the ternary solubility in the binary phases Ni_3Ti, NiTi, Ni_3V, and sigma are also calculated by first-principle method and incorporated in the modeling of those phases. Based on the crystallographic details, sigma phase is described with three sublattice model. The contradictory phase boundary of Ni-Ti-V ternary alloys at 900 [1, 2] and 1000°C [3] are studied by employing optical microscopy, X-Ray diffraction, Scanning electron microscopy and EDAX. Gibbs energy parameters for equilibrium phases in the Ni-Ti-V system are obtained by optimization with present experimental information along with published experimental data, by combining it with thermodynamic descriptions of the limiting binaries from the literature. The isothermal and vertical sections are calculated and compared with corresponding experimental information.

Acknowledgment: This research work was funded by Department of Science and Technology, India, under fast track scheme (SERC/ET-0345/2012).

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Computational Study of Atomic Mobility in HCP Mg-Al-Zn Ternary Alloys

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Mg-Al-Zn alloys stand among the most popular Mg alloys for structural applications. Both Al and Zn have good solubility in Mg, and form intermetallic precipitates ($Mg_{17}Al_{12}$, MgZn and $Al_5Mg_{11}Zn_4$), leading to an optimum combination of strength and ductility, through solid solution strengthening and precipitation hardening [1]. Thus, there is a strong interest to further improve the microstructure and properties of these alloys and virtual processing and virtual testing strategies [2-5] are starting to be used that requires reliable kinetic information. In the current work, the diffusion experimental data in the literature for the hcp phase of the Mg-Al-Zn ternary system have been critically reviewed. Based on the concentration profiles in the literature, the diffusion coefficients have been re-extracted from the ERFEX (Error Function Expansion) represented diffusion profiles using the Hall method, the Sauer-Freise and the Whittle-Green strategies. Moreover, extra interdiffusion coefficients were obtained from the "Darken-type" couples, which presented relative maxima or/and minima at the concentration profiles. This information was assessed to obtain an atomic mobility, by means of DICTRA software in conjunction with the CALPHAD thermodynamic description that could reproduce the diffusion couple experiments. Comprehensive comparisons between the calculated results and experimental values showed an excellent agreement not only for the diffusion coefficient data, but also for the concentration profiles and the diffusion paths.

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Master, Computational thermodynamics and kinetics, Shanghai University (Shanghai, China), 2013-2015, Supervisor: Prof. Xiaogang Lu
Research assistant, Computational alloy design, IMDEA Materials Institute (Madrid, Spain), 2015, Supervisor: Dr. Yuwen Cui
Research topic: The bulk anisotropic diffusion in hcp Mg-Al-Zn alloys and the influence of alloying elements on the micromechanical properties of Mg alloys

High-throughput Investigation of Diffusion and creep Micro-Mechanical Properties in Mg alloys

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High-throughput diffusion approach has emerged as a novel tool for advanced materials design. Starting from inexpensive raw bulk materials, annealing of diffusion couple/multiple at elevated temperature [1][2][3][4] allows the composition variation to span in the micron scales, that in turn results in the blended spectra of microstructures and physical/ mechanical properties. By doing so, a single diffusion specimen can provide an enormous amount of data for database construction of novel alloys, including properties such as lattice parameter, phase diagram, microstructure and physical and mechanical properties.
In this work, a high throughput diffusion research was conducted by incorporating advanced micromechanical characterization techniques to survey the micro-mechanical properties over the composition arrays of diffusion-couple specimen.For specific, the Mg/Mg-2.2at.%Zn diffusion couple was fabricated following a conventional solid-state diffusion-couple technique at 673 K. The composition profiles within the diffusion zone, resulting from high-temperature interdiffusion were characterized and acquired by high-spatially resolving electron probe micro-analysis (EPMA), whereas the corresponding grain orientations were mapped by the electron back-scattered diffraction (EBSD).It was followed by a survey of local mechanical properties (inc. creep) by nano-indentation over the arrays of composition and grain orientation. Furthermore, the deformation mechanisms around the indentations were screened and discerned by the focused ion beam (FIB) and transmission electron microscopy (TEM). As a whole, all the results were processed and analyzed together to rapidly delineate a full composition-microstructure-micromechanical properties relationship with Mg-Al-Zn to prototype the conventional magnesium alloys.

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Research skills:
1.Design and fabrication of Mg/Mg-Zn,Mg/Mg-Al and Mg/Mg-Al-Zn diffusion couples to obtain an diffusion zone with composition gradients
2.Quantify the composition-microstructure-micromechanical properties

A study of the Mg-Al-C system: synthesis and thermal stability of the Al_2MgC_2 ternary carbide

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The Al_2MgC_2 ternary carbide was first characterized 25 years ago [1] and may be obtained when a magnesium-rich Mg-Al alloy is in contact with carbon at temperatures above 723 K [2]. In the case of aluminium-rich alloys, the Al_4C_3 carbide would be obtained. The formation of Al_2MgC_2 at the fibre/matrix interfaces of a C/Mg-Al MMC strongly influences the mechanical properties of the composite by changing the fibre/matrix bonding strength [3]. Furthermore, carbon addition methods have become the major industrial grain refinement technique for Mg-Al alloys [4]. The mechanism behind this grain refinement, which has raised many conflicting hypothesis over the last 15 years, have been recently attributed to the formation of Al_2MgC_2 particles in the melt which would lead to the heterogeneous nucleation of Mg grain in a later stage [5]. However, despite this interest, the carbide phase is presently not described in any thermodynamic database for Mg alloys [6]. Therefore, extensive determination of phase equilibria in the Mg-Al-C, and equilibrium involving the Al_2MgC_2 carbide in particular, as well as determination of the decomposition reaction and temperature of the carbide, are of interest to sustain the development of grain refined Al-Mg alloys as well as Mg-Al/C Metal Matrix Composites.

In the present study, an experimental procedure to work with magnesium at temperatures up to 2000°C and to synthesize the Al_2MgC_2 carbide has been developed. Several practical difficulties, including relatively high vapour pressure and high affinity of Mg with oxygen, as well as a rapid hydrolysis of Al_2MgC_2 in ambient air, have been overcome.

In a first time, this experimental study aim at proposing new isothermal sections at temperatures of 1000°C or higher for the Mg-Al-C system as well as determining the decomposition temperature of Al_2MgC_2 by SDTA. In a second time, the purpose of this study is to perform a thermodynamic assessment of the Mg-Al-C ternary system.

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Integration of Phase Equilibrium Calculation and Kinetic Simulation

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Few materials are in global thermodynamic equilibrium state. But local equilibrium is one of main assumptions in simulating materials properties during a kinetic process. Thermodynamic properties and physical properties of phases, which are available in an equilibrium calculation, are important inputs for a kinetic simulation. This presentation will show how the phase equilibrium calculation from PanEngine (a phase equilibrium calculation engine) is integrated with kinetic simulations, such as diffusion, solidification and precipitation, to understand the kinetic processes. PanEngine is a dynamic linked library (DLL) and interacts with the kinetic simulation modules through its interface call functions. It can load thermodynamic and kinetic databases, and calculate phase equilibrium, thermodynamic properties as well as kinetic parameters, which are required by the kinetic simulation modules. A special data structure is designed to increase the speed of kinetic simulations. Examples will be given on those kinetic simulations.

Shuanglin Chen

Dr. Shuanglin Chen graduated from Dept. of Materials Science and Engineering at University of Wisconsin-Madison, USA. He is the major developer of Pandat software.

Influence of W and Mo on the phase equilibrium and diffusion behaviour of Ni-Co-Al ternary system

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Thermodynamic and kinetic knowledge on the Ni-Co-Al ternary system plays an important part in developing both Ni-base and Co-base superalloys. Besides, addition of refractory elements, such as W and Mo, in superalloys also acts as a critical role during the service process. On the one hand, Liu et al. [1] has recently reassessed the thermodynamic description of Ni-Co-Al ternary system and reproduced the phase equilibrium relationship especially among fcc, $L1_2$ and B2. On the other hand, Wang et al. [2] investigated the interdiffusion and diffusion mobility of fcc Ni-Co-Al alloys based on the thermodynamic parameters of Liu et al. [1]. However, few researchers have done research with the influence of refractory elements on the phase equilibrium relationship and diffusion behaviour of Ni-Co-Al ternary system.

The present work has investigated the phase equilibrium relationship among fcc, $L1_2$ and B2 by preparing Ni-Co-Al-W, Ni-Co-Al-Mo and Ni-Co-Al-Mo-W alloys which were annealed at the temperature range from 1523 to 1173K for 7 to 60 days. Besides, diffusion couples were prepared to study the diffusion behaviour of fcc Ni-Co-Al, Ni-Co-Al-W, Ni-Co-Al-Mo and Ni-Co-Al-Mo-W alloys at 1473K for 75hours to further exploring the influence of refractory elements on the diffusion behaviour.

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Yang Wang
Thermodynamic and Kinetic research of Ni-Co-based superalloys

Jiangsu University of Science and Technology (Sept. 2008-June.2012)
Major: Metal Materials Engineering (B.E.)

Shanghai University (Sept.2013-Now)
Major: Materials Science and Engineering (Ph.D. Candidate)
Supervisor: Prof. LU Xiao-Gang

Aqueous Salt Hydrates: Unconventional Deep Eutectic Solvents

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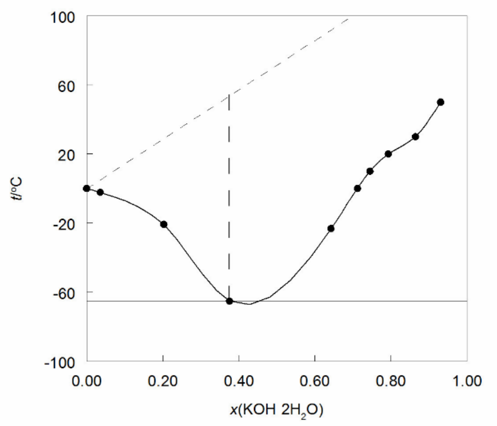
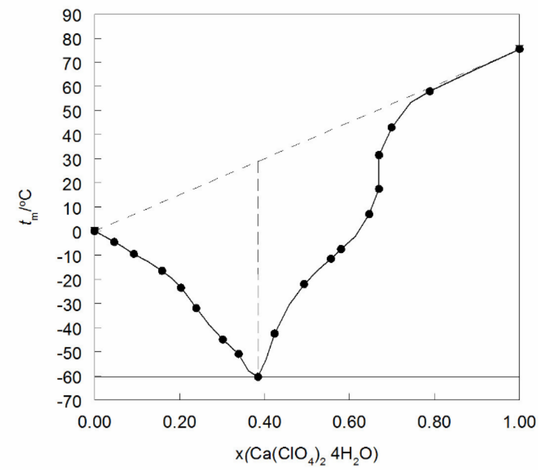
Some aqueous salt hydrates, i.e., mixtures of ice and certain salt hydrates, form liquid eutectics at low temperatures that may be deemed ‘deep eutectic solvents’ (DES). They feature properties that commonly used or proposed DES should have: they are definitely non-flammable, they are non-toxic (heavy metal salts are avoided), they are inexpensive (expensive metal salts are avoided), and are readily reconstituted after use. So far few applications of such DES are known, dissolution and treatment of cellulose being one such use.

The phase diagrams of aqueous salt hydrates feature the eutectic and in many cases the melting point of the congruently melting salt hydrate. Phase diagrams are shown for two aqueous salt hydrate DES that have large eutectic distances, water + $KOH\cdot 2H_2O$ with $\Delta T = 119.5$ K and water + $Ca(ClO_4)_2\cdot 4H_2O$ with $\Delta T = 89.6$ K.

The liquidus curves can be modeled according to the Brunauer-Emmett-Teller (BET) method [1,2].





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Yizhak Marcus

Professor emeritus of chemistry at the Hebrew University of Jerusalem. The research centers on liquids and solutions, aqueous, non-aqueous and mixed, including ionic liquids and supercritical fluids, their properties and the interactions leading to these properties.

High pressure-high temperature phase diagram using electrical resistancemeasurements in a “Paris-Edinburgh” large volume press

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We present a novel experimental design for high sensitivity measurements of the electrical resistance of samples at high pressures (0-6GPa) and high temperatures (0-1000K) in a ’Paris-Edinburgh’ type large volume press [1]. Uniquely, the electrical measurements are carried out directly on a small sample, thus greatly increasing the sensitivity of the measurement. The sensitivity to even minor changes in electrical resistance can be used to clearly identify phase transitions in material samples. Electrical resistance measurements are relatively simple and rapid to execute and the efficacy of the present experimental design is demonstrated by measuring the electrical resistance of Pb, Sn and Bi across a wide domain of temperature-pressure phase space and employing it to identify the loci of phase transitions. Based on these results, the phase diagrams of these elements are reconstructed to high accuracy and found to be in excellent agreement with previous studies. In particular, by mapping the locations of several well-studied reference points in the phase diagram of Sn and Bi, it is demonstrated that a standard calibration exists for the temperature and pressure, thus eliminating the need for direct or indirect temperature and pressure measurements. The present technique will allow simple and accurate mapping of phase diagrams under extreme conditions and may be of particular importance in advancing studies of liquid state anomalies.

[1] Shlomi Matityahu et al., Review of Scientific Instruments ,86 (2015) 043902.

Moran Emuna

Ph.D. studentand teaching assistant in the department of Materials Engineering, Ben Gurion University of the Negev Beer Sheva, Israel.
The research topic is "Pressure, phase diagram and physical properties of liquid metals and alloys".
Scientific interests:
Measurement of physical properties of liquid metals and alloys, the relations between the phase diagram and the anomalous physical properties of binary liquid alloys, in particular sound velocity and prediction of the properties of liquid metals and alloys under extreme temperature and pressure conditions.

Ab initio study of the phononic origin of negative thermal expansion

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Negative thermal expansion is an uncommon phenomenon of theoretical interest. Multiple hypotheses regarding its microscopic origins have been suggested. In this paper, the thermal expansion of a representative semiconductor, Si, and a representative metal, Ti, are calculated *ab initio* using density-functional perturbation theory. The phonon modes contributions to the thermal expansion are analyzed and the negative thermal expansion is shown to be dominated by negative mode Grüneisen parameters at specific points on the Brillouin zone boundaries. Thus, the elastic (Debye) theory for negative thermal expansion is shown to be irrelevant for these phenomena. The anomalous behavior of these modes in Ti is shown to be unaffected by an electronic topological transition as previously suggested, instead it arises from complex interplay of atomic displacements of the anomalous mode.

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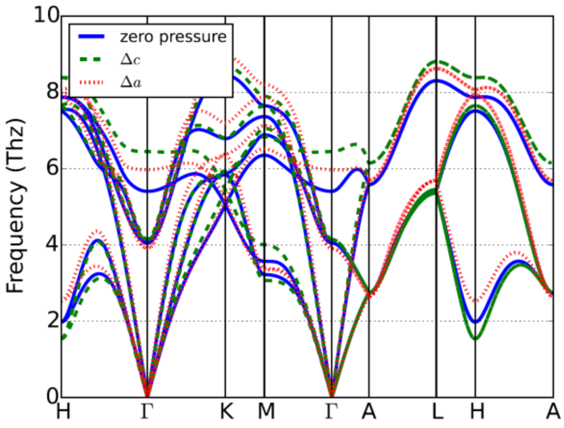

Phonon spectra at several lattice parameters for α-titanium around zero pressure. The curves denoted by Δc and Δa represent compressions of 2% in the c and a directions, respectively.

Uri Argaman

I am a Ph.D. student at Ben-Gurion University of the Negev, Beer-Sheva, Israel. My main interest is in ab-initio calculation for thermodynamic and transport properties using phonon calculations.

Al-B-C ternary compounds : synthesis, structure, composition and thermal stability

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The Al-B-C ternary system present some interest in the synthesis of Metal Matrix Composites because of the high hardness of B_4C phase and the low densities of both the Al-matrix and the carbide reinforcement [1]. Review of phase equilibria clearly indicates that boron carbide and Al are not in thermodynamic equilibrium until an unknown but very high temperature (above 1400°C) [2]. However, some ternary carbides such as τ_3-$Al_3B_{48}C_2$ are reported to have properties similar to boron carbide while being also characterized by a low density. As a consequence, extensive determination of phase equilibiria in the Al-B-C ternary system, especially at high temperature, is of interest not only to bring new insights in a unknown domain but also to sustain the development of synthesis processes of Al-based composites reinforced by B-rich particles.

In the present study, several Al-B-C ternary phases such as τ_1-$Al_{2.1}B_{51}C_8$, τ_2-$AlB_{40}C_4$$\tau_3$-$Al_3B_{48}C_2$, $\tau_{□}$-Al_3BC_3 and τ_5-Al_3BC have been synthesized. Phase structure was characterized by X-Ray diffraction (both on powder and single crystals) and Raman spectroscopy while their composition was determined by EDX analysis performed on single crystals. Moreover, the thermal stability and more precisely the decomposition temperature and reaction of the ternary compounds were also determined by SDTA and isothermal experiments at high temperature.

This experimental study allows us to propose new isothermal sections at high temperature as well as an upgrade version of the reaction scheme initially proposed by Grytsiv and Rogl [1]. In the future, the present results will be used to perform a thermodynamic assessment of the Al-B-C ternary system.

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PhD on reactive wetting mechanisms of liquid metals on ceramics with N. Eustathopoulos (2000).From 2002 to now, Assistant Professor at Laboratory for Multimaterials and Interfaces of the University Lyon 1 (France).

Research domains: liquid metals, wetting, thermodynamic, reactivity, Metal Matrix Composite

Comparison of various DTA methods for liquidus determination in Ag-Cd-In alloys

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The 80 wt. % Ag, 15 wt. % In, 5 wt. % Cd alloy is used as absorber material in most PWR reactors. During a severe accident at low pressure, the absorber rod failure occurs at temperature greater than 1200°C. It leads to significant release of gases and Ag, In and Cd aerosols into the primary circuit. This release strongly impacts chemistry of iodine which is the main contributor to the short-mid radiological dose. Accurate knowledge of Ag-Cd-In ternary phase diagram is necessary to predict the release during the degradation of the absorber rod.

The literature review showed that the Ag-Cd-In ternary diagram remains largely unknown, particularly for the case of equilibria involving the liquid phase which are relevant for the analysis of severe accident. Only two isopleth sections of the ternary have been partly investigated by thermal analysis. In this work, thermal analysis is performed for various compositions using a DSC instrument to check and extend the existing data. Emphasis is put on the accurate determination of the liquidus temperatures of the alloys by DTA using different protocols. The results thus obtained are compared and the advantages and drawbacks of the different procedures are discussed. Finally, for the first time, a thermodynamic modeling of the ternary system taking into account these results as well as mixing enthalpy data previously obtained in our lab is presented.

Kasi Visweswara Siva Sai GAJAVALLI (Arial 12pts)

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Research Interests : Nuclear Safety, Material Science, Thermodynamics

Thermodynamic modelling of the Al-Co-Pd system, aluminium rich corner of the phase diagram

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This work is focused on a study of phase equilibria in the Al-Co-Pd ternary system by CALPHAD method. The Al-Co-Pd system is complex system with a lot of ternary phases (W, V, F, U, Y_2, C_2). Thermodynamic description of the system has not been known up to now.

The latest assesment for the Al-Pd system with nonstechiometric model for Al_3Pd (ε) phase from literature [1] were used in present work. Thermodynamic parameters for binary Al-Co and Co-Pd systems were taken from the literatures [2], [3] and the data for pure elements were taken from Dinsdale [4].

The experimental results collected from the literature, were used in the optimization of the thermodynamic parameters. Good agreement between experimental results and calculations was achieved.

[1] L. Ďuriška, I. Černičková, R. Čička, J. Janovec, Jounal of Physics: Conference Series, in press
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Acknowledgement: The work was supported by Slovak Research and Development Agency under project No. APVV-15-0049.

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Career/Employment: since 2000 Scientist, IMR SAS, Košice Slovakia
The research topics: Thermodynamic modeling by CALPHAD method

Thermodynamic modelling of Fe-Cr-Ni and its implication forthe calculation of multicomponent systems

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Thermodynamic open-licensed Fe-base database (mc_fe [1]) is predictinga too low equilibrium phase fraction of ferrite in duplex stainless steel,e.g. steel grade 2205 compared to experiments[2]. Since the Fe-Cr-Ni system is highly governing phase relations in stainless steels, a revision of the Fe-Cr system and associated extension to Fe-Cr-Ni is made. The presented Fe-Crre-assessmentshows an improvement of mixing behaviour and phase boundaries of all phases in the system. In the framework of application of duplex steels, the austenitic-ferritic transformation is reproducedcorrectly. The present thermodynamic modelling of the Fe-Cr-Ni system is based on available experimental data and ab initio data of the enthalpy of mixing of bcc and fcc [3]. Re-assessment ofalloy phase stabilities in Fe-Cr-Ni does not solve the stability problem of ferrite in the multi-component extension. Additional stabilising / destabilising interactions in Mn-, Mo-, and Si-containing subsystems were deciphered, which required re-adjustments. As a result, the revised mc_fe delivers correct stabilities of the high-temperature delta-ferrite phase of various stainless steels, and composition-dependent austenite / ferrite fractions in duplex and super duplex steel grades.

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[3] J.S. Wróbel et al. Physical Review B - Condens. Matter Mater. Phys. 91 (2015).

Influencing factors of atomic order in binary sigma phases

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Sigma phase is a non-stoichiometric intermetallic compound designated as tetragonal structure (space group $P4_2/mnm$) with 30 atoms distributed on five inequivalent sites (2a, 4f, $8i_1$, $8i_2$, 8j) [1]. There are numerous researches [1-3] on the crystal structure and atomic order (i.e. atomic constituent distribution or site occupation on inequivalent sites of a crystal structure) of the sigma. Joubert [1] have explained the experimental site occupations by taking size factor and valence electrons into consideration based on the early publications. However, only considering these two above factors, we cannot explain all experimental facts.

The present work brings new insights into the influencing factors on atomic order of binary sigma phases. We have calculated the volumes and atomic charges of the constitutive elements of 32 stoichiometric end-member compounds of several binary sigma phases by using the first-principles approach. The calculation results show that besides size factor and the number of valence electrons, the total number of electron shells is another factor that affects the atomic order of a sigma phase. Moreover, the calculation results indicate that atoms with small number of valence electrons (SMe) or small total number of electron shells (SMs) prefer to occupy larger coordination number (CN) sites (4f, $8i_1$, 8j) and atoms with large number of valence electrons (LAe) or large total number of electron shells (LAs) prefer to occupy smaller CN sites (2a, $8i_2$). Furthermore, we have respectively discussed the effect of the three factors on atomic order of the sigma phase combining with the measured site occupations from the literature.

[1] Hall E O, Algie S H. Metall Rev, 11(1966) 61-88.
[2] Joubert J M. Progress in Materials Science, 53 (2008) 528-583.
[3] Sluiter M, Paturel A. Physical Review B, 80 (2009) 134122.

LIU Wei

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Research topics:

- The investigation on physical properties and site occupations of TCP phases combined with the CALPAHD approach and the DFT calculations.

PA

First-principles Calculation Assisted Thermodynamic Modeling of B-Ta and B-C-Ta System

Xuemei OuYang[a,b], Fucheng Yin[a,b,*], Jingxian Hu [a,b], Zhaohui Long[a,b]

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Tantalum carbide ceramics are difficult to densify and leads to entrapped porosity. TaB2 and B4C have been widely used in Tantalum carbide ceramics to promote the densification and improve material sintering performance. The systems TaC-TaB2 and TaC-TaB2-B4C can combine advantageous properties of each of the composing phases, significantly modify microstructure and properties, provide the potential for their tailoring, and broaden the application spectrum .

The thermodynamic re-assessment of B-Ta system using CALPHAD method is performed by considering the latest experimental data and the results from first-principle calculations of the formation enthalpies for TaB2, Ta3B4, TaB, Ta3B2, and Ta2B. The sublattice model of (Ta, B)0.333(Ta, B)0.667 has been used to describe the homogeneity range of TaB2, while other four intermetallic compounds are treated as stoichiometric compounds. Compared with the previous thermodynamic description for the B-Ta system [1], noticeable improvement is achieved in the present work. The current thermodynamic parameters can well reproduce the newly published experimental data. Combining the thermodynamic parameters of the C-Ta [2] and B-C [3] systems available in literature with the re-assessed B-Ta system, the thermodynamic assessment of the ternary phase diagram of B-C-Ta system is carried out. The reliable experimental information is satisfactorily accounted for the present thermodynamic description.

Keywords: B-Ta system; B-C-Ta system; CALPHAD technique; Thermodynamic modeling.

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Experimental Investigation and Thermodynamic Calculation of Phase Equilibria in the Sn-Zn-Co Ternary System

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Due to the concerns of environmental and health, European Union has formulated legislation to restrict the use of Pb[1]. Sn-Zn-based alloys are of technical importance to optimize lead-free solder alloys. Co has been considered to be a possible alloying element and as the diffusion barrier layer in UBM (Under Bump Metallurgy)[2-3]. Moreover, Co can effectively reduce the degree of undercooling of the Pb-free solders[4]. Hence, knowledge of the Sn-Zn-Co phase equilibria is significant for developing the Sn-Zn-based solders. The purpose of present work is to investigate isothermal sections of the Sn-Zn-Co system.

Wang et al.[5] have determined partial isothermal sections of the Sn-Zn-Co system at 250 °C and 500°C. In the present work, the 650°C isothermal section of Sn-Zn-Co system have been investigated experimentally using x-ray diffraction (XRD) and scanning electron microscopy (SEM) coupled with energy-dispersive spectroscopy (EDS). A self-consistent thermodynamic description of the Sn-Zn-Co system is obtained by considering the huge amount of experimental data from the literature and this research using the CALPHAD(Calculation of Phase Diagrams) method. Good agreement between calculated and experimental results is achieved.

Key words: Sn-Zn based alloys; Thermodynamic modeling; Phase diagram

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Phase equilibria, Thermodynamic Assessments and Microstructure Development of Mg-Alkaline Earth-Rare Earth Systems

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The phase equilibria relations of Mg–Alkaline Earth–Rare Earth (AE=Ca, Sr; RE=Nd, Gd) ternary systems at the Mg-rich corner are investigated via microstructure examination, chemical and phase constitution analysis and DSC measurement on the equilibrated ternary alloys. The stability of the Mg–RE (Rare-Earth elements) intermetallic compounds in the above ternary systems is predicted by using First Principles (FP) calculations, with especial focus on the $Mg_{41}RE_5$ compound. By comprehensive evaluating the key experimental data, thermochemical properties of intermetallic compounds in the family of Mg–RE systems, the thermodynamic assessments of the Mg–AE–RE ternary systems in the context of the CALPHAD approach are carried out for the first time. The Ca and Sr elements have the ability to effectively increase the stability of $Mg_{41}RE_5$ or Mg_5RE. The generation of ternary intermetallic compound of $Mg_{41}(AE, RE)_5$ or $Mg_5(AE, RE)$ doesn't narrow the composition window for phase and microstructure tuning but enriches the combination of precipitate hardening in heat treatment. Meanwhile, the solid-state reaction introduced $Mg_{41}(AE, RE)_5$ never serves as a primary crystal thus would not do effects on the as-cast microstructure. The CALPHAD type thermodynamic database enables the prediction of panoramic phase diagrams for the above ternary systems at the Mg-rich corner and clarifies the systematic trends of the phase relationships for the series Mg–AE–RE systems.

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Guanglong Xu

Dr. Guanglong Xu is an assistant professor at Nanjing Tech University. He got his PhD at La Universidad Politécnica de Madrid in 2016. Before joining Nanjing Tech, he was also a research assistant at the IMDEA Materials Institute, Spain. Dr. Xu has expertise in experimental phase diagram determination and diffusion research, computational thermo-kinetics, molecular dynamic and mesoscale Landau/phase field simulations.

Investigation of the ternary Ag–Ga–Sn phase diagram

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Due to existing environmental policies and green trends in industry lead-free solders are attracting considerable attention over the last decade. In frame of COST Action (0602 and 0531) a large number of ternary systems were studied. Alloys based on the Ag–Sn system are promising replacement for Pb–Sn alloys but seeking for free-lead solder alloy with lower melting point is still required. Adding a Ga to Ag-Sn alloys can significantly decrease the melting points and also improve the mechanical properties and the wetting ability.Up to now a complete description of the ternary Ag-Ga-Sn system is not proposed and experimental data of this system are important in orderto obtain the necessary knowledge of the phase diagram and themelting behavior of the Ag–Ga–Sn alloys. Generally speaking, knowledge of thermodynamic parameters and phase diagrams of solder alloys is crucial for soldering process.To date, only two studies of this system could be found in the literature [1,2]. These studies are related to the measurement of partial and integral enthalpies of mixing at 803 K along the seven sections [1], isothermal section at 0 ^{0}C and two vertical sections, one with constant amount of Ag (30 at. %) and the other with 30 at. % Sn [2].

The descriptions of three vertical sections Ag–$Ga_{50}Sn_{50}$, Ga–$Ag_{50}Sn_{50}$, Sn–$Ag_{50}Ga_{50}$ and isothermal section at 100 ^{0}C have been presented in this work. Phase transitionTemperatures were investigated by using Differential Thermal. Microstructure of the selected samples at 100 ^{0}C was analyzed by scanning electron microscopy and energy dispersive X-ray spectrometry.

Based on available information in the literature and present experimental results, a thermodynamic description of the ternary Ag-Ga-Sn system has been developed by using CALPHAD method. A reasonable agreement between experimental data and the calculated phase diagrams is reached. The liquid projection and invariant equilibria have been calculated by using present thermodynamic parameters.

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Milena Premović

Obtaining PhD in the field of Metallurgical Engineering in 2015 at University of Belgrade of Serbia. Currently she is one postdoc at Central South University in P.R. China in the group of Prof. Y. Du and also lecturer at University of Priština of Serbia. She is interested in experimental techniques for the characterization of materials, Calphad assessment, bulk and nano phase diagrams and crystallography.

Experimental investigation and phase equilibria of Al-Zn-Cu system

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The Al-Zn-Cu alloys attract considerable attention as the simultaneous achievement of high damping capacity, shape memory effects and super elasticity [1]. However, the phase relationship of Al-Zn-Cu system is still uncertain and in doubt at the Al-Zn rich side [2].

In the present work, phase equilibria of Al-Zn-Cu system at the Al-Zn rich side at 360 ºC was experimentally determined by investigating 16 samples in the annealed states, by means of X-ray diffraction measurement and electron probe microanalysis. Thermal analysis was carried out to check the invariant temperature. Five single-phase regions and seven two-phase regions as well as three three-phase region, i.e. (Al) + θ-Al_2Cu+τ'-Al_4Cu_3Zn, (Al) + τ'-Al_4Cu_3Zn + ε-$CuZn_4$ and (Al) + ε-$CuZn_4$ + (Zn), were determined. In the present work, the phenomenon that solid solution phase (Al) would easily decompose through natural aging was analyzed. Our results implied that (Al) would decompose into ε-$CuZn_4$, (Zn) and α′ (Al) at the ambient temperature in the early stages. Subsequently, ternary phase τ′-Al_4Cu_3Zn would form and ε-$CuZn_4$ would disappear gradually along with the extension of time. Finally, the isothermal section of Al-Cu-Zn at 360 ºC at the Cu-poor corner was constructed in this work.

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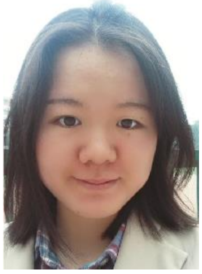

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Research field:

Phase diagram measurements and thermodynamic modeling

Experimental investigation and thermodynamic modeling of Co-Ge system

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Due to the limited knowledge on Co-Ge phase diagram, the Co–Ge system has been reinvestigated with a series of key alloys over the whole composition range by means of differential thermal analysis, X-ray diffraction, optical microscopy and electron probe microanalysis. The system contains one congruently melting intermetallic compound βCo_5Ge_3 (1210 °C), and five incongruent melting compounds Co_3Ge, Co_2Ge, CoGe, Co_5Ge_7 and $CoGe_2$. The previously reported Co_5Ge_2 phase is not found in the present work. The compound Co_3Ge has been determined to be an ordered fcc-cubic phase and observed to be stable at 750 °C. The liquidus of Co-rich and Ge-rich portions has been measured for the first time. A revised Co–Ge phase diagram is presented based on the present experimental results and reliable literature data. Thermodynamic modeling is done for this system based on our new experimental data as well as the assessed data from the literature. The sublattice model: $(Co,Va)_1$:$(Co)_1$,$Ge)_1$ [1] is employed to describe βCo_5Ge_3 with $B8_2$-structure. CoGe is modeled by a two-sublattice: $(Co,Ge)_1$:$(Co,Ge)_1$. According to the present experimental data, Co_3Ge is described as a L_{12} phase and modeled by the order and disorder transformation [2]. Other intermetallic compounds were described as stoichiometric phases because of their narrow homogeneity ranges or unknown crystal structure. A set of self-consistent thermodynamic parameters is finally obtained.

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Research field:

- CALPHAD approach;
- Experimental measurement of phase diagram.

A thermodynamic study of the WC-(Fe,Co,Ni) hardmetal

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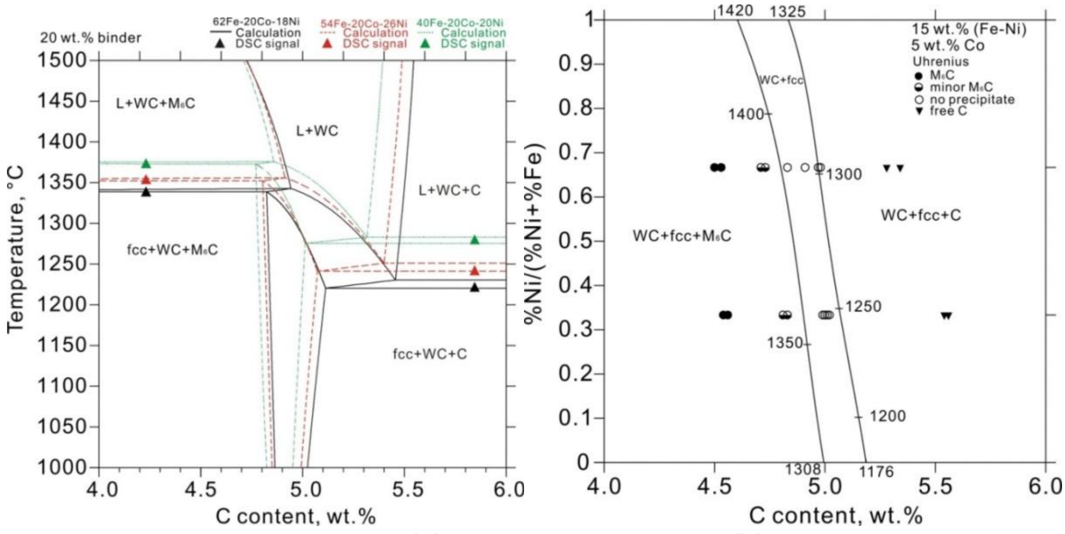
Using DSC analysis of 34 WC-(Fe,Co,Ni)-C(or W) alloys, the invariant reaction temperatures of four-phase equilibria, i.e. L+fcc+WC+graphite(orM_6C), for WC-based hardmetals with alternative binders are obtained. Based on the present experimental result and the reliable literature data, thermodynamic parameters from C-Fe-W, C-Ni-W, C-Co-Fe-W, C-Fe-Ni-W, and C-Co-Ni-W are re-assessed. A reliable thermodynamic database for the C-Co-Fe-Ni-W quinary system is then developed based on the thermodynamic parameters of the subsystems. The calculated phase diagrams agree well with the present DSC data and the literature data. The carbon windows of cemented carbides with alternative binders are well reproduced by the present calculation, as shown in Fig.1.



(a) (b)

Fig. 1 Calculated (a) vertical section, and (b) WC+fcc two-phase regions at different temperatures in the C-Fe-Co-Ni-W system at 20 wt.% (Fe,Co,Ni) with the experimental data.

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Phase Equilibria and Thermodynamic Modelling in the System Ni-Sn-Zr

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In continuation of our optimization of NiSn{Ti,Zr}-based thermoelectrics, we herein determined experimentally the constitution of the system Ni-Sn-Zr (liquidus surface and isothermal section at 950^{o}C) employing X-ray powder diffraction (XPD) and electron probe micro analyses (EMPA) of about 80 ternary alloys in as cast and annealed state.

The system is characterized by the existence of four ternary compounds labeled τ_1 to τ_4. At 950 ^{o}C no significant homogeneity regions are found for the compounds τ_1-NiSnZr (half Heusler phase, MgAgAs-type), τ_2-Ni_2SnZr (Heusler phase, $MnCu_2Al$-type) and τ_4-$NiSn_2Zr_6$ (K_2UF_6-type. ordered Fe_2P-type), but τ_3-$Ni_{2+y}Sn_{1-x-y}Zr_{2+x}$ exhibit a significant solution range.

Extended solid solutions starting from binary phases at 950 ^{o}C have been evaluated for Sn_4Zr_5 and Ni_5Zr. From differential thermal analysis (DTA) measurements in oxide crucibles under argon a complete liquidus surface has been elucidated revealing congruent melting for τ_1-NiSnZr (at 1466 ^{o}C) and τ_2-Ni_2SnZr (at 1541 ^{o}C), but incongruent melting for τ_3-Ni_2SnZr_2 (at 1406 ^{o}C), and for τ_4-$NiSn_2Zr_6$ (at 1124 ^{o}C).

For the thermodynamic CALPHAD assessment of the ternary diagram we relied on binary boundary systems data as modelled in the literature. As thermodynamic data in the ternary system heat of formation data were suplied by our DFT calculations for NiSnZr, Ni_2SnZr, Ni_2SnZr_2 and $NiSn_2Zr_6$. For these phases DFT calculations also provide details on electronic properties and bonding.

Thermodynamic calculation was performed with PANDAT software and resulted in a reasonably good agreement for all the 29 invariant reaction isotherms involving the liquid.

This work was 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)).

Phase equilibria of Sn-Ag-In-Zn quaternary system

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Soldering is among the most important joining technologies in electronic products. Pb-Sn solders were the most frequently used electronic solders. Due to environmental and health concerns, the RoHS regulation requires that the electronic products do not contain Pb except for a few exemptions. Sn-Ag-Cu alloys are currently the most widely used Pb-free solders. Additionally, the Sn-Ag-In-Zn alloys have been recently examined among various promising Pb-free solders.Phase equilibria ofthe Sn-Ag-In-Zn quaternary system arethusinvestigated in this study.

Phase equilibria data of the constituent binary and ternary systems of the Sn-Ag-In-Zn quaternary system are examined. In addition to the liquid phase and the four terminal phases, there are thirteen binary compounds,ζ-(Ag_4Sn), ε-(Ag_3Sn), β-(In_3Sn), γ-($InSn_4$), α'-(Ag_3In), β-(Ag_3In), ζ-(Ag_3In), γ-(Ag_9In_4), $AgIn_2$, β-(AgZn), ζ-(AgZn), γ-(Ag_5Zn_8), and ε-($AgZn_3$) phases.No ternary compound is found in the Sn-Ag-In-Zn quaternary system.

Thermodynamic models of the Sn-Ag-In-Zn quaternaryaredeveloped by using the CALPHAD approach.The CALPHAD-type thermodynamic descriptions of the six constituent binary systems and those ofSn-Ag-In, Sn-Ag-Zn, and Sn-In-Zn ternary systemsin the literatures are reviewed and adopted with limitedrevisions. [1-3]. The 500^{o}C isothermal section and liquidus projection of the Ag-In-Zn ternary system are experimentally determined in this study, and thermodynamic modelling of the Ag-In-Zn ternary system is developed based on the related phase equilibria results in the literatures and these obtained in this study[4]. Thermodynamic models of the Sn-Ag-In-Zn quaternary system are developed based on those of the four constituent ternary systems with no quaternary interaction parameters, and the phase diagrams of electronic soldering applications interests are calculated using the developed models.

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Thermodynamic and TEM investigations of Si poisoning effects on grain refinement in Al-Ti-Si and Al-Nb-Si systems

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Grain refining is a vital practice to improve the mechanical properties of Al-Si cast alloys. Unfortunately, silicon can severely reduce the grain-refining efficacy of the commercial Al-5Ti-B master alloy when its concentration is above 3 wt.%. [1, 2]. Recently, Al-Nb-B master alloys were developed and presented good anti Si-poisoning property [2-4]. However, the underlining mechanisms for anti/Si-poisoning effects of these two types of master alloys remain unclear, which would hinder the improvement of their grain-refining efficacies. In this work, CALPHAD-type thermodynamic investigations on phase formations within the casting temperature range (500~700 °C) were performed for Al-Ti-Si and Al-Nb-Si systems, respectively. Totally eight Al-Ti-Si and Al-Nb-Si equilibrium alloys and two diffusion couples (Al-10Si/Ti and Al-10Si/Nb) were used to clarify the phase equilibrium relationships in the Al-Si rich region (Ti or Nb ≤ 50 at.%). It was found that the phase in equilibrium with liquid/fcc-Al and MAl_3 (M=Ti or Nb) at 500~700 °C in Al-Ti-Si system was ternary silicide τ_2 (($Ti(Si_{1-x}Al_x)_2$ ($0.15 \le x \le 0.3$), $ZrSi_2$-type orthogonal), and that in Al-Nb-Si system was $NbSi_2$ ($CrSi_2$ type hexagonal) with ternary solubility of Al. Moreover, the edge-to-edge matching degrees at $\tau_2/TiAl_3$, τ_2/fcc-Al, $NbSi_2/NbAl_3$, and $NbSi_2$/fcc-Al interfaces were investigated by both edge-to-edge matching (E2EM) model and high-resolution transmission electron microscopy (HRTEM). Based on the calculated phase equilibria at 500~700 °C, and the heterogenous nucleation potencies of MAl_3 to $\tau_2/NbSi_2$ and $\tau_2/NbSi_2$ to fcc-Al, insights into the anti/Si-poisoning effects in Al-Nb-Si and Al-Ti-Si systems were given.

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Yang Li

I am a PhD student in School of Materials Science and Engineering, Shanghai University. I am interested in poisoning effects of Si, Cr, Zr, et al., on the grain refinement of aluminium alloys. I also devote myself to developing the anti-poisoning grain refiners with the aid of computational thermodynamics and advanced characterization techniques. Now I have published four papers on *Scripta Materialia*, *Materials & Design*, and *Journal of Chemical thermodynamics*.

Isothermal sections of Mg-La-Zr system in Mg-rich corner at 300,400 and 500°C

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Through alloying with rare earth(RE) element, the precipitation-strengthened magnesium–rare earth (Mg–RE) alloys have been developed to raise the operating temperature as well as to improve the creep resistance and strength [1]. The Mg-La-Zr phase diagram was investigated through the experimental methods. One diffusion couple of Mg and $La_{84.6}Zr_{15.4}$ was analysed to investigate the phase relations at 400°C. Three Mg-La-Zr alloys were prepared to measure the three isothermal sections at 300°C, 400°C, and 500°C in Mg-rich region. All alloys were detected by X-ray diffraction (XRD) and scanning electron microscopy (SEM) equipped with energy dispersive spectrometer (EDS) or the electronic probe microanalysis (EPMA). No ternary compound has been observed in the temperature from 300 to 500°C. Furthermore, the Mg-rich regions in the measured temperature range are all consist of three three-phase equilibria, that is, (Mg)+$LaMg_{12}$+(αZr), $LaMg_{12}$+La_2Mg_{17}+(αZr) and $LaMg_3$+La_2Mg_{17}+(αZr). The solubility of Zr in the Mg-La intermetallics ($La_{12}Mg$, La_2Mg_{17}, and $LaMg_3$) are less than 0.1 at.%, which can be negligible. The solubility of La in the Mg was also very little, which is about 0.3at.%. Based on the Calphad (calculation of phase diagram) method, the thermodynamic database of Mg-La-Zr system is established. Comprehensive comparisons between the calculated and the measured phase diagrams show that the present thermodynamic modelling is reliable.

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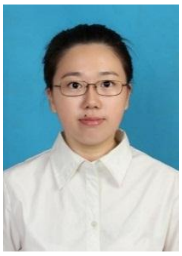

WenFei Zhu

I am studying for a master's degree at the Shanghai University. The ongoing research work is characterized with experimental investigation and thermodynamic assessment of Mg-Zn-RE-Zr alloys in mg-rich region.

Phase Equilibria of 540°C Isothermal Section of Fe-Al-Zn-Ce System

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The isothermal section of the Fe–Al–Zn–Ce system at 540 °C with Al fixed at 42at.% have been determined by means of scanning electron microscopy coupled with energy dispersive spectroscopy and X-ray powder diffraction. Eight four-phase regions and eight three-phase regions have been confirmed experimentally, and five more four-phase regions have been inferred in this section (as seen in Fig. 1). Two ternary compounds τ_1 and τ_2 existing in the Al–Zn-Ce system [1-2] and one ternary compound Ψ_1 existing in the Fe–Al–Ce system[3] have been identified in the system. No quaternary compound has been found. The maximum solubility of Zn in these phases has been determined.

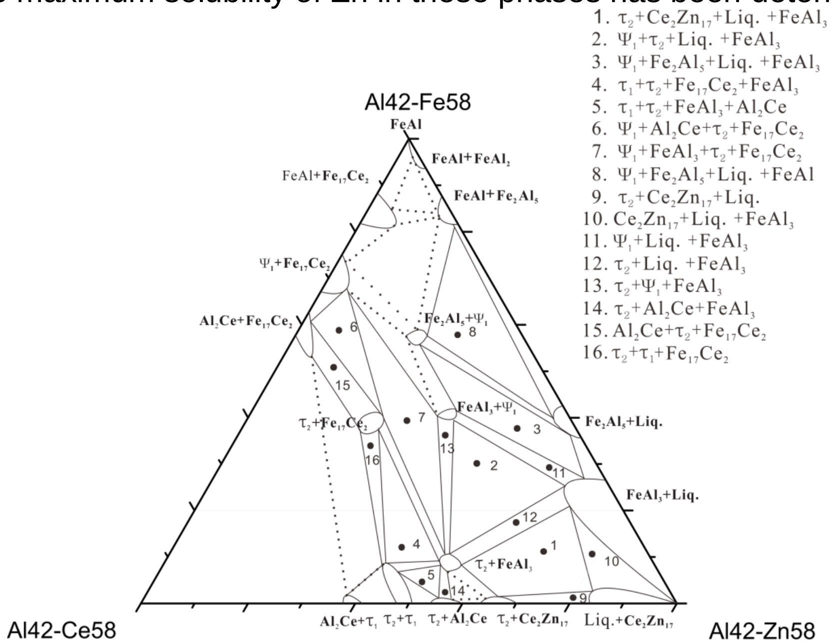

Fig. 1. The isothermal section of Fe–Al–Zn–Ce quaternary system at 540 °C with Al being fixed 42 at.%

Acknowledgments

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Phase stability of ternary compounds in Cu-Li-Sn system and path hysteresis in Cu_6Sn_5 electrode

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Cu_6Sn_5 compound is a promising alternative material for commercial anode in Li-ion batteries []. Phase evolution and stability of the Li-Cu-Sn systems in the lithium insertion/extraction process is a key problem. We used a combined experimental and computational method to construct ternary phase diagrams of Li-Cu-Sn system, and the polarization effect of Cu_6Sn_5 electrode during charge and discharge are elucidated from thermodynamics and kinetics point of view.

In order to confirm the stability of the ternary phases at low temperature, the isothermal sections of ternary Cu-Li-Sn system at 120 ºC and 180 ºC are determined using various equilibrated Cu-Li-Sn alloys. Three ternary phases, i.e. $CuLi_2Sn_2$, $CuLi_2Sn$ and Cu_2LiSn, were measured to be stable at 120 ºC and 180 ºC, but $Cu_6Li_3Sn_4$ was only detected at 180 ºC. First-principles calculations were used to construct the phase diagram of Cu-Li-Sn at 0 K, which is consistent with our experimental work at the low temperature (120 ºC). Our calculations further confirm that $Cu_6Li_3Sn_4$ is metastable at 0 K and stable above 149 ºC when vibrational free energy contribution were considered, which is also in agreement with the experimental results. After this, we discussed the path hysteresis of Cu_6Sn_5 electrode during charge and discharge processes. Our work indicates that the path hysteresis is attributed to a difference in reaction path between charge and discharge. For discharge process, the electrochemical reaction prevents the formation of Li-deficient phase due to the sluggish mobility of Cu. For charge process, the large diffusivity of Li promotes the formation of Cu-deficient phases and it will cause the reaction path to deviate from the equilibrium condition. Therefore, we think that the real reaction path of Cu_6Sn_5 electrode in Li-ion batteries would achieve a balance between thermodynamic and kinetic factors.

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Thermochemistry of some Bismuth –Transition metal compounds by high temperature direct synthesis calorimetry

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The standard enthalpies of formation of some Bismuth and Transition metal (TR) compounds have been measured by high temperature direct synthesis calorimetry at 1273±2K.The following values are reported in kJ/mole of atoms:
ScBi (-83.8 ± 2.1); Ti_2Bi (-15.2 ± 3.2); MnBi (-4.4 ± 3.0); NiBi (-6.0 ± 2.0); Y_5Bi_3 (-81.7 ± 2.5); ZrBi (-47.3 ± 3.1); RhBi (-17.2 ± 2.8); PdBi (-30.2 ± 3.1); PtBi (-17.8 ± 2.9).
The results are compared with available thermodynamic data from the published literature [1,2] and with predicted values from both Miedema's semi empirical model and from ab initio calculations [3].
This work is still in progress.

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S.V.Meschel earned a PhD in chemistry from the University of Chicago. Current position is Adjunct Associate Professor at Illinois Institute of Technology. Current research interests are thermodynamics of alloys, Lanthanide compounds, shape memory alloys.

Modelling solidification segregation in two Nb microalloyed steels

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Segregation during continuous casting of steels for structural, pressure vessel and oil country tubular goods (OCTG) has an important influence on the homogeneity of properties. Some of the effect is caused directly by the solute redistribution and its effect on structure and non-metallic inclusions and some is associated to the premature precipitation of microalloying elements during the final stages of solidification. In the present work, we simulate the segregation in two Nb microalloyed steels: one with normal manganese and carbon levels and the other with lower carbon and lower manganese that is able to avoid extensive peritectic transformation. Scheil simulation using Thermo-calc and diffusion simulation using DICTRA are presented and discussed. The results are compared to measurements performed with large scale EMPA. The simplified calculations performed with DICTRA agree well with the EMPA results. For the forecasting of the precipitation of microalloying carbonitrides a two-step approach was used: first, diffusion was modelled without the inclusion of carbonitrides as possible phases. Then, the results of the segregated liquid composition and temperature were used as input for equilibrium calculations to determine when conditions were appropriate for the formation of carbonitrides. The method is accurate to predict carbon, manganese and probably silicon segregation and to predict the solid fraction before the onset of carbonitrides precipitation, critical to define the amount of microalloying elements, in special Nb, that will be tied up in large particles that will not dissolve completely during further heat treatment before rolling.

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Keywords: solidification, diffusion, segregation, microalloying, steel, niobium

Experimental study of Al-Cu-Zn phase diagram

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The design of the experimental study of Al-Cu-Zn system was focused on questions which have not been satisfactorily resolved yet in the scientific literature and on the divergent results from different publications [1,2,3]. Our experimental study of the Al–Cu–Zn ternary system was mainly focused on a description of the mixing and solubility of γ_AlCu and γ_CuZn brass phases and on the experimental characterization of the ternary τ' phase and its relationship to ternary τ phase.

Samples of Al-Cu-Zn was prepared from the pure metals in evacuated quartz ampoules. Samples were long-term annealed in evacuated quartz ampules at 550 °C for more than 500 hours. A combination of dynamic and static methods was used for the phase diagram investigation. Overall and phase composition of metallographically prepared samples were analysed by scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM-EDX). X-ray diffraction (XRD) was applied to the structure determination of the intermetallic binary or ternary phases found in Al-Cu-Zn system. Temperatures of phase transitions was measured using high-temperature DTA equipment.

The results of this experimental study will be used for obtaining the overall goal of the proposed research, which is the creation of a robust and self–consistent thermodynamic description of the Al-Cu-Zn phase diagram based on published experimental data, the results from ab-initio calculations and on new experimental data.

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Thermodynamic investigations of Fe-Mn-Al-Ni shape memory alloys

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Iron-based shape memory alloys such as Fe-Ni-based and Fe-Mn-based alloys have attracted considerable attention in recent years. In order to show a fully reversible pseudoelastic behaviour, these alloys have to meet several requirements including an only small volume change upon martensitic transformation and the presence of fine coherent precipitates [1].

Among such Fe-based shape-memory alloys, Fe-Mn-Al-Ni alloys, and especially $Fe_{43.5}Mn_{34}Al_{15}Ni_{7.5}$, are of particular interest for promising areas of application, because of their outstanding pseudoelastic behaviour over a wide temperature range and due to an extremely low slope for the Clausius–Clapeyron equation [2]. Since for an effective alloy design, the microstructure of those shape memory alloys needs to be adjusted deliberately, thermodynamic calculations can enhance the understanding of the phase equilibria in this system.

A thermodynamic database for the quarternary Al-Fe-Mn-Ni-system is created to describe the phase equilibria, which are important for the pseudoelastic performance of these alloys. The ternary key system Al-Fe-Mn was initially adopted from Lindahl and Selleby [3]. For the sake of simplicity, the four-sublattice modelling of the bcc and fcc phases was modified to a two-sublattice model, which is capable of describing the B2 and $L1_2$ superstructures for bcc and fcc, respectively. The $L1_0$ and $D0_3$ phases are described as separate phases in that case.

Starting from the ternary Al-Fe-Mn-system, thermodynamic calculations were performed together with microstructural investigations using complementary methods such as SEM, EPMA, XRD and TEM in order to investigate the phase transition between the disordered alpha-phase (A2) and the ordered beta-phase (B2). Through additional alloying of Nickel, the microstructural changes between the ternary alloys and the quarternary alloys were investigated and taken into account in the assessment of the thermodynamic database.

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Optimization of compositions and physical properties of salt systems for latent heat storage in thermal solar energy applications

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Thermal solar energy installations are a promising source of renewable energy. In these installations the sun’s rays are focussed by mirrors to heat a working fluid which then is passed through heat exchangers to power turbines. For efficient operation, the excess heat produced while the sun shines must be stored for use when the sun is not shining. At present, latent heat storage materials, also known as phase change materials (PCMs), offer the most promising storage technique. The objectives and constraints that any PCM design should meet are:

1- Find a singular composition for which the system melts at a nearly constant temperature (i.e. a eutectic point or local minimum on the liquidus surface) slightly below the temperature of the working fluid
2- Maximize the enthalpy of fusion per unit volume
3- Maximize the specific heat per unit volume, in order to provide additional sensible heat storage
4- Maximize the thermal conductivity of both the liquid and solid phases to facilitate heat transfer.
5- Minimize the volume change upon melting
6- Long-term chemical stability
7- Minimize corrosion of the container tank by the PCM

Moreover, the materials must be available over the long term and their cost must be as low as possible. Until now, PCM design has not been efficient due to the lack of available data for phase equlibria, in particular the composition of the singular points upon the liquidus surface, and for thermophysical properties. The aim of this work is to present tools and methods to overcome these limitations and make possible the identification of optimal PCM compositions among multicomponent anhydrous salt systems. The proposed methodology couples (i) the FactSage thermodynamics software, (ii) reliable critically assessed thermodynamic databases, (iii) suitable models for thermophysical properties with proven predictive capacity, and (iv), a direct search method algorithm for optimization with multiple objective functions under specified constraints

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Aimen Gheribi was born in La Seyne sur Mer in the south of France. He studied Physics and Material Science at the “École superieure de Physique de Marseille”, obtaining his Phd. in 2006 at IN2MP in Marseille. After doing a postdoc at SIMAP in Grenoble with Prof. Alain Pasturel, he moved to Canada where he has been a Research Associate at the École Polytechnique de Montréal since 2008, working with Prof. Arthur Pelton and Prof. Patrice Chartrand.

Ternary diffusivity from both the intersection of two diffusion couple and single diffusion couple: application to the Cu-Ni-Sn ternary system

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A numerical inverse method has been developed to extract the interdiffusion coefficients from a single diffusioncouple internary systems.This new method is based on a finite difference scheme[1] considering both of constant interdiffusion coefficients and composition-dependent interdiffusioncoefficients. Its application to various diffusion couples inthe Cu-Ni-Sn ternary systems, tests performed on computed profiles demonstrate the improvements this procedure providescompared with the methods in[2]. What's more, the interdiffusion coefficient values are obtained along thewhole diffusion path, instead of only at the intersection point of independent paths or instead of mean coefficient values.

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The stability investigation of $Fe_{23}Zr_6$ in the Fe-Zr system

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The stability of $Fe_{23}Zr_6$ has long been a controversial problem in the Fe-Zr system[1-2] .To find out the major factors of its formation, the present investigation varied a series of experiment conditions for comparison, such as the specimen size, the quenching medium, the isothermal time and the isothermal atmosphere. The phase equilibria in the Fe-rich region was characterized by electron-probe microanalysis (EPMA), scanning electron microscope (SEM) and X-ray diffraction (XRD) at 1073K、1273K、1373K and 1473K. The experimental results pointed out that the the $Fe_{23}Zr_6$ was an equilibrium phase at the above temperatures , but not stabilized by oxygen. Fig.1 showed the edge area of the Fe-17.5 at.%Zr alloy (annealed at 1273K for 240h), which indicated the most influential factor of $Fe_{23}Zr_6$ formation was the quenching rate. Therefore, the Fe-Zr system was reoptimized by Calphad approach combined with the results of first-principle calculation.The thermodynamic description of the solution phases was made using a Redlich-Kister polynomial. The intermetallic compounds were described by the compound energy formalism (CEF) model. The optimized Fe-Zr phase diagram was presented as Fig.2.

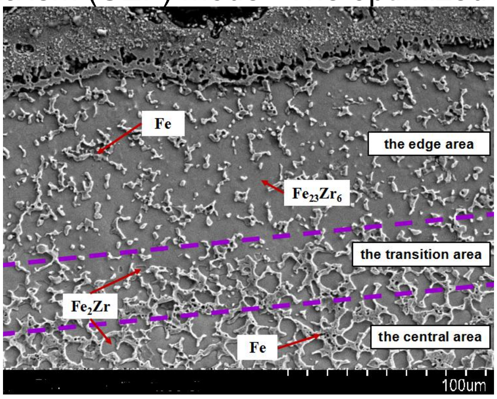

Fig.1 The scanning electron micrograph of the B3 alloy(17.5 at.%Zr), annealing at 1273K（240h）

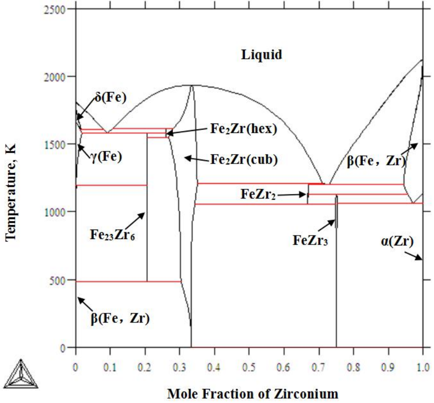

Fig.2 Calculated Fe-Zr binary phase diagram

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First principles study of hydrogen diffusion in iron

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The low hydrogen embrittlement susceptibility of epsilon martensite (HCP phase) in Fe-Mn-Cr-Ni steel has been reported previously [1]. This behavior is closely related to the diffusivity of hydrogen in the HCP phase, which affects the fatigue crack growth rate. However, it is difficult to determine the diffusion coefficient of hydrogen in the HCP phase experimentally, as it is a metastable phase with many structural defects. On the other hand, theoretical calculations are advantageous because it can provide an ideal situation. In particular, nudged elastic band (NEB) method and vibrational analysis have been suggested as effective methods to calculate the diffusion barrier [2]. In this study, the diffusion behavior of hydrogen in iron was investigated using the NEB method and vibrational analysis.

The stable interstitial sites of hydrogen in BCC and FCC phases, as determined by first-principles calculations, were consistent with previously reported results [3,4]. In the HCP phase, the octahedral site was found to be the stable interstitial site. The migration energy and the diffusion path of hydrogen in the BCC phase as estimated by the NEB method matched well with those reported in the literature [3]. In the case of diffusion in iron, the magnetic states need to be considered to get a complete understanding. Therefore, the migration energy of hydrogen in the FCC phase was calculated for the nonmagnetic and the antiferromagnetic states. A well-defined diffusion path between the octahedral sites mediated by the tetragonal site was observed in both the nonmagnetic and the antiferromagnetic states. The diffusion barrier was found to be at the same level in both the states, consistent with the experimental results. In the HCP phase, the diffusion path between the octahedral sites along the c-axis was confirmed to be stable. The value of the migration energy in the HCP phase was similar to that in the FCC phase, which was in accordance with the experimental results.

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Thermodynamic evaluations of the local ordering behaviors in the LPSO-forming Mg-Zn-Y system

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Recently, dilute Mg-Zn-Y alloys have attracted great attention because of their excellent mechanical properties, and their key microstructural feature strongly depends on long period stacking/order (LPSO) phase [1]. The LPSO structures consist of periodically inserted fcc stacking fault (fcc-SFs) in the hcp Mg matrix into which Zn and Y atoms segregate [2]. In addition, it is known that Zn and Y atoms form $L1_2$ ordered clusters at fcc-SFs [3]. Umebayashi et al. suggested that Zn and Y could segregate at fcc-SFs when fcc-SFs are introduced into hcp-Mg based on their thermodynamic calculation [4]. However, the contribution of $L1_2$ arrangement to the stability of the LPSO phases has not been reported. Thus, in this work, with the formation of $L1_2$ ordered clusters of Zn and Y segregated in the fcc-SFs in the LPSO phase was investigated based on CALPHAD method.

Thermodynamic parameters of the disordered fcc and hcp phases in the Mg-Zn-Y system were revised based on the first principles calculations performed by Umebayashi et al. using VASP [4]. The $L1_2$ and $L1_0$ ordering contributions in the fcc phases were evaluated based on the first principles calculations. Segregated compositions of Zn and Y in the fcc-SFs were calculated by the parallel tangent law proposed by Hillert.

Fig. 1 shows calculated metastable phase diagram of the Mg-Zn-Y system at 773 K. In this calculation, the Mg-1at.% Zn-2at.% Y hcp alloy (open circle) causes a segregation of Zn and Y in the fcc-SFs (solid circle), which results in phase separation between the $L1_2$ ordered clusters (solid square) and the Mg-rich disordered fcc matrix (open square). This corresponds qualitatively to the $L1_2$-cluster formation in the fcc-SFs of the LPSO structures.

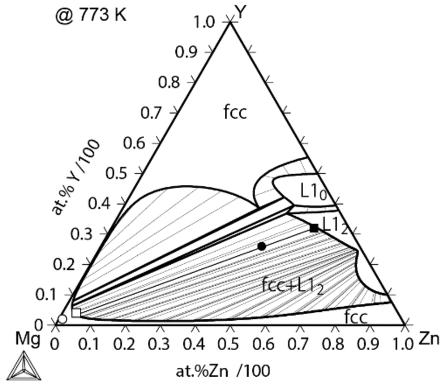

Fig. 1 Calculated metastable phase diagram of Mg-Zn-Y at 773 K.

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- Long period stacking/order

Thermodynamic re-assessment of the Al-Fe-Mn system

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Lightweight steels have attracted a growing interest in the field of automobile applications due to the weight reduction without the loss of high strength and excellent plasticity. In order to design and develop such steels, the understanding of thermodynamic properties and phase equilibria evolution of the alloy system is of the essence. As a core system for lightweight steels, the Al-Fe-Mn system has been assessed by Lindahl and Selleby [1] based on the experimental data on both the Al-rich and Fe-rich region. However, shortly after their work, the phase equilibria in the Al-rich part of the ternary system were experimentally investigated over the temperature range from 650 to 1070 ℃ by Balanetskyy et al. [2] and Priputen et al. [3]. Four stable ternary phases were found. Moreover, the extrapolation of the ternary experimental results indicated that the γ_1 phase was stable in the binary Al-Mn system. Therefore, the new experimental data necessitate the re-assessment of the Al-Fe-Mn system. In the present work, the γ_1 phase was introduced into the Al-Mn system to fit with the extrapolated experimental data. Then the Al-Fe-Mn system was re-assessed in the framework of the CALPHAD approach. Comprehensive comparison between the model-predicted and experimental data confirms that the present description can reproduce the experimental data over the whole composition range.

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Study of thermal stability of doped CoSb based skutterudites by Knudsen effusion mass spectrometry

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Study in the field of thermoelectric materials is of great importance because these materials are able to directly convert thermal energy into electrical energy (Seebeck effect, 1821; thermoelectric generator) and reversibly electrical energy into thermal energy (Peltier effect, 1835; thermoelectric heat pump or Peltier cooling). The current research, among other materials, is oriented on doped CoSb based skutterudites with high ZT-levels which can further be increased, e.g. by nano-structuring. Various ways in preparation of this kind of materials, as described e.g. in [1], [2], imply differences in thermoelectric efficiency which also depends on the thermal stability of the materials.

Thermal and phase stability of selected doped multicomponent CoSb based skutterudites from macrocrystaline to nano-structured form have been studied using methods of thermal analysis (TA) and Knudsen effusion mass spectrometry (KEMS). The measurements have been performed on a Netzsch STA 409 CD/3/403/5/G apparatus, a specially-adapted type of the commercial STA 409 CD - QMS 403/5 Skimmer Coupling Instrument, described in [3], [4]. The results of TA and KEMS measurements, including data on phase transformations and evaporation characteristics of volatile elements, supported by measurements of diffusion profiles are summarized and discussed in view of a full understanding of the degradation processes.

The work has been supported by the Czech Science Foundation under the project GA 17-12844S as well as by the project CEITEC 2020 (LQ1601) from the Ministry of Education, Youth and Sports of the Czech Republic under the National Sustainability Programme II.

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[4] Brož P. et al., International Journal of Mass Spectrometry, 383 (2015) 13-22.

Study of thermal stability of $CoSb_3$skutterudite by Knudsen effusion mass spectrometry

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CoSb based skutterudites, especially those containing targeted doping elements or in nanostructured form, play an importantrole in the development of high efficient thermoelectric materials, i.e. materials with high ZT- factor and hence with more efficient conversion of the waste heat to electricity [1]. However, these materials contain volatile elements (Sb, Sr, Yb, etc.), which can evaporate at operation conditions leading to structure changes, damaging the thermoelectric properties. The study of long term thermal stability of these materials is, therefore, of great importance.

Within our study on complex multicomponent CoSb based skutterudite systems thermal stability of primary $CoSb_3$skutterudite as a reference material, prepared by procedures described e.g. in [2], was investigated. The temperature and phase stability have been studied by means of thermal analysis (TA) and Knudsen effusion mass spectrometry (KEMS) performed on a Netzsch STA 409 CD/3/403/5/G apparatus, a specially-adapted type of the commercial STA 409 CD - QMS 403/5 Skimmer Coupling Instrument [3], [4]. Results of phase transformation processes and vapour pressure measurements of antimony as well as those from microstructure observations and measurements of diffusion profiles, as essential data for evaluation of the long term thermal stability, are discussed.

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Contribution to the experimental determination of the Ti-Al-W phase diagram

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Intermetallic alloys are an emerging class of structural materials. Some of them such as TiAl (commonly referred to as γ alloys) happen to have interesting specific properties, like creep resistance, and have been recently introduced as turbine blades in new aeroengines such as the CFM-LEAP. However, further development is required to design new γ alloys that are able to withstand higher operating temperatures (from 650-725°C to 800°C).

One way to achieve this goal is to include β stabilizer refractory elements, such as niobium or tungsten, in the composition of γ alloys. From an experimental perspective, the impact of tungsten additions on the properties of γ alloys has already been partially studied and is promising. However, the lack of reliable thermodynamic data severely hinders the optimization of such alloys. Despite a good knowledge of the binary system Ti-Al and of some ternary systems like Ti-Al-Nb [1] or Ti-Al-Cr [2], the ternary system Ti-Al-W remains rather unknown, as only few isothermal sections have been published [3] and the description of this phase diagram using the CALPHAD method [4] needs to be improved.

We present some new experimental data based on alloys containing at least 2 at.% of tungsten. Using microstructural characterization and diffusion multiples we aim to progress towards a new experimental determination of this ternary system. We also focus on the behavior of the element W, in terms of segregation during the solidification and diffusion during solid-solid phase.

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Mixing enthalpy measurements of liquid Li-Pb-Sb alloys

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New high capacity reachable batteries, with long lifespan and low cost, are crucial for industry. The alloys from the Li-Pb-Sb system are potential electrode materials for novel rechargeable liquid metal batteries (LMB) [1-3]. However, there is no information regarding thermodynamic properties and phase diagram of this ternary system.

This work presents the partial and integral molar mixing enthalpies of liquid Li-Pb-Sb alloys determined using the drop calorimetry technique. The measurements were taken at twelve different series of fixed molar ratios, respectively, Pb/Li = 9/1, 3/1, 3/2, 1, 2/3, 1/3, Pb/Sb = 3/1, 1, 1/3 and Sb/Li = 4/1, 3/2, 1 at 923 K and 1023 K. The integral molar mixing enthalpy of liquid Li-Pb-Sb alloys has negative values in the entire concentration range and obtained values are convergent near the points of intersection of experimental series.

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Sylwia Terlicka

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Phase equilibria, thermodynamics and microstructure simulation of metastable spinodal decomposition in metastable c-TiAlN-based coatings

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Metastable TiAlN-based coatings with cubic (c) structure are well acknowledged in automotive and aerospace industries. The age hardening around 900 °C resulting from the coherent strain between nano-scale c-TiN- and c-AlN-rich domains via spinodal decomposition plays an important role for their successful industrial applications. However, the metastable c-AlN-rich phase will transform into its stable structure hexagonal (h) AlN during further annealing treatment which can cause a rapid deterioration of mechanical properties. To alleviate this problem, there have been numerous attempts to stabilize the metastable c-AlN phase. One successful method is to add a third metal, such as Cr, Zr, and so on, to c-TiAlN.

Based on the experimental equilibrium data on spinodal decomposition in the literature together with the presently measured data, metastable phase equilibria for metastable c-TiAlN, c-TiAlCrN and c-TiAlZrN systems were constructed in the present work, from which self-consistent thermodynamic descriptions for respective systems were then established by means of CALculation of PHAse Diagram (CALPHAD) method with the aid of first-principles computed free energies. By coupling with the CALPHAD thermodynamic databases, quantitative numerical simulations of microstructure evolution in metastable c-TiAlN, c-TiAlCrN and c-TiAlZrN coatings during spinodal decomposition were performed using the Cahn-Hilliard model. The simulated microstructure evolution during spinodal decomposition and composition wavelengths at different temperatures were found to agree well with the experimental data in respective systems. Based on the numerical simulation results, the effect of additional third metals, i.e., Cr and Zr, on the spinodal decomposition was then analyzed in detail. Moreover, the effect of the composition fluctuation on the microstructure evolution during spinodal decomposition was also comprehensively investigated.

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The research topics and scientific interests:
- Numerical simulation of microstructure evolution during spinodal decomposition in alloys.
- CALPHAD-type modeling of thermodynamic and other properties.

Cluster ordering of Mg-LPSO

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Two possible scenarios, solute ordering and stacking fault induced, have been discussed for the formation mechanisms of the long period stacking ordered (LPSO) structure in Mg based alloys. Very recently, the authors have reported the solute ordering of mini clusters [1]. In this talk, we will show the first principles calculations of the interaction energy between a $L1_2$ cluster and a mini cluster, and discusses the diffusion mechanism of this mini cluster.

The target mini cluster was reported by Kiyohara et al.[2], where the horizontally split $L1_2$ cluster shows relatively stable energy in the hcp lattice. The distance dependency of interaction energy between a $L1_2$ cluster and a mini cluster are calculated by VASP. The calculated models are shown in Fig.1. The marks in the top view indicate the equivalent site of the location of a mini cluster in a- and c- layers of hcp stacking.

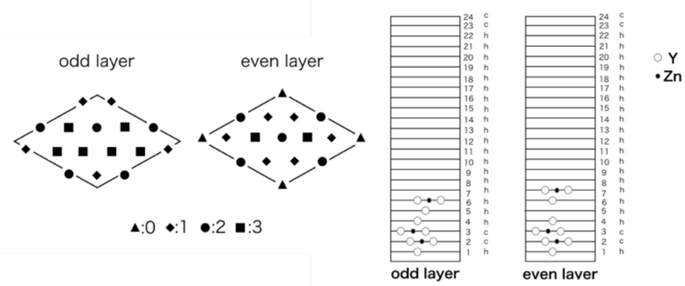

Fig.1 Schematic drawings of slab models.

Fig.2 shows the total energy changes depending on the vertical distance between $L1_2$ cluster and a mini cluster. A mini cluster shows a minimum around 4-5 layers, which is about 0.1eV lower than the far end. This energy minimum indicates that the solute ordering is a strong candidate to induce the formation of the LPSO structure.

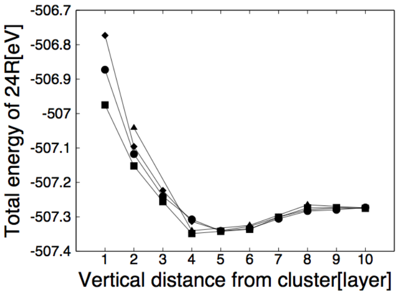

Fig.2 Energy dependency on vertical distance between $L1_2$ and mini clusters.

If we accept the energetic stability of solute ordering by a mini cluster, we have to discuss the kinetics of the solute movement. For two possibilities of an isolated solute diffusion or a cluster diffusion, we are calculating the stability of the vacancy and multi-vacancies around the mini cluster.

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[2] M. Kiyohara, et al., proceedings of PRICM, (Kyoto 2016), p.805.

Shinya Morishita, Mr.

He is a graduate student of Department of Informatics, Kwansei Gakuin Univ. He is studying the formation mechanism of LPSO structure, revealing from an energetic point of view with VASP. He also possesses practical skills on Ruby programming, web development by Ruby on Rails, and system configuration by Chef.

Thermodynamic descriptions of the quaternary Al-Si-Mg-RE (RE=Sc, Ce) systems and their application to design RE-containing cast aluminium alloys

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Using published experimental phase equilibria, self-consistent thermodynamic databases of the Al-Si-Mg-RE (RE=Sc, Ce) quaternary systems in the Al-rich corner were established by means of the CALPHAD (CALculation of PHAse Diagram) technique. Their reliability was validated in several model cast alloys by comprehensive comparison of their experimentally measured solidified microstructure characteristics and phase transition temperatures with the calculated ones. Scheil-Gulliver simulations were performed, allowing construction of solidification diagrams for Sc- and Ce-additional A356 alloys to examine the influence of Sc and Ce levels on the solidification behaviors of cast A356 alloys. With the aid of theoretical analysis on solidified microstructure and its qualitative relationship with mechanical properties, the optimal amounts of additional Sc and Ce in A356 alloys were accurately determined. The subsequent mechanical property measurements and microstructural characterizations confirmed that the A356 alloys with optimal Sc and Ce additional amounts exhibit the best comprehensive mechanical performance.

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ExperimentalInvestigation of the Fe-Co-Ce System

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Rare-earth – transition metal compounds form an interesting group of magnetic materials and are important for making permanent magnets. It has been found [1, 2] that substitution of Co for Fe can increase the Curie temperature and the saturated magnetostriction. However, there is only rather limited published information about the kind of phase equilibria and phase transformations that may take place. The goal of the present research was to study phase equilibria in the Fe-Co-Ce system over the whole concentrationregion.

Hardly any information on the phase equilibria in the Fe-Co-Ce system is available. In this work phaseequilibria in the Fe-Co-Ce system over thewhole concentrationregionhas been studied using DTA, SEM, electron probe microanalysis and X-ray diffraction data. The liquidus and solidus projections and a melting diagram have been constructed.

The isostructural compounds $Fe_{17}Ce_2$ and $Co_{17}Ce_2$ ($Zn_{17}Th_2$-type structure, *hR57-R-3m*) were shown to form a continuous solid solution $(Fe,Co)_{17}Ce_2$ at the solidus temperature. The Laves phase Fe_2Ce and Co_2Ce ($MgCu_2$-type structure, *cF24-Fd-3m*) also form a continuous solid solution $(Fe,Co)_2Ce$ at the solidus temperature.

The liquidus surface of the Fe-Co-Ce system is characterized by fields of primary crystallizationof (γFe,Co), (δFe), (δCe), (γCe) and the binary-based phases $(Fe,Co)_{17}Ce_2$, $(Fe,Co)_2Ce$, Co_5Ce, $Co_{19}Ce_5$, Co_7Ce_2, Co_3Ce and $Co_{11}Ce_{24}$. In the solidus surface five three-phase fields are present:(γCe) + $(Fe,Co)_2Ce$ + $Co_{11}Ce_{24}$, $(Fe,Co)_{17}Ce_2$ + $(Fe,Co)_2Ce$ + Co_3Ce,Co_5Ce + $Co_{19}Ce_5$ + Co_7Ce_2, $(Fe,Co)_{17}Ce_2$ + Co_5Ce + Co_7Ce_2 and $(Fe,Co)_{17}Ce_2$ + Co_7Ce_2 + Co_3Ce. The first three-phase field at the solidus surface results from an invariant eutectic four-phase equilibria $L_E \rightleftarrows (\gamma Ce) + (Fe,Co)_2Ce + Co_{11}Ce_{24}$. The remaining three-phase fields form via U-type reactions.

Among the binary compounds, Co_3Ce has the widest homogeneity region and at the solidus temperature dissolvesup to 50 at.% Fe. This phase is located along the isoconcentration line of 25 at.%Ce due to mutual substitution of the Fe and Co atoms. The homogeneity regions of the remaining phases are smaller.

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Present work: Investigation of phase equilibria in the Fe-{C, Co, Ni}-{La, Ce} and Ti-{Si,Sn}-{V, Nb, Cr, Mn, Fe, Co, Ni, Al, Gaetc.} ternary systems.
Fields of interests: Phase equilibria and phase transformations.

Experimental investigation and thermodynamic re-assessment of the ZrO_2–TiO_2 system

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High alloyed austenitic stainless TRIP-steel (Transformation Induced Plasticity) reinforced by Mg-PSZ (Partially Stabilized Zirconia) exhibits extraordinary high specific energy absorption in compression [1] and is the base of TRIP-Matrix-Composite material. It was revealed that a minor addition of titanium improves the densification of the matrix material and the bonding between the zirconia particles and the TRIP steel matrix that improves mechanical properties of the composite [2]. Therefore the aim of this work is a database development for the ZrO_2-TiO_2 system which can be used in combination with steel database to describe interfacial reactions between the matrix and reinforcing particles.
Phase relations in the ZrO_2–TiO_2 system has been studied experimentally. Samples were prepared using the co–precipitation method by dropping the mixture of aqueous solutions of $Zr(CH_3COO)_4$ and $Ti_2(SO_4)_3$ to the aqueous solution of NH_4OH. Phase assemblages stable after long time annealing of specimens have been identified by X-ray powder diffraction (XRD). Temperatures of invariant reactions have been determined by differential thermal analysis (DTA). Sample microstructures have been investigated using scanning electron microscopy combined with dispersive X-ray spectrometry (SEM/EDX). Chemical composition of phases and eutectic composition have been determined using EDX. Heat capacity of β-$ZrTiO_4$ has been measured using heat-flux differential scanning calorimetry (DSC) method in the range 250-1260 K. The formation enthalpy of β-$ZrTiO_4$ has been measured using drop solution calorimetry method in the sodium molybdate solvent at 973 K. Thermodynamic dataset of the ZrO_2–TiO_2 system have been derived using CALPHAD approach based on available literature data summarised by [3] and new experimental results of this work.

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Stability and defect chemistry analysis of Cu-doped Ceria by computational thermodynamic modelling

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Fluorite-structured Ceria has been proposed as a promising oxygen storage material in solid oxide fuel cells, due to its high oxygen storage capacity (OSC) [1]. Via doping by transition metal elements such as Cu, its catalytic efficiency is increased. The lower oxidation states of Cu compared to Ce cause the formation of charge-compensating oxygen vacancies in the phase [2]. Whereas numerous experimental studies on the kinetics of catalytic reactions are found, the thermodynamic stability of the defect-chemical Cu-doped Ceria has not been determined by means of Calphad modelling. We present the thermodynamic assessment of the CeO_2-CuO system, focusing on the fluorite phase stability and defect chemistry based on new experimental phase diagram data and results from X-ray photoelectron spectroscopy (XPS) on the prevailing oxidation states of Ce and Cu. The data set for the thermodynamic model parameterisation of Ce-Cu-fluorite is complemented by first-principles analysis of the thermodynamic stability of oxidised and reduced compounds. Previous modelling of the Ce-O system [3] strongly underestimated the occurrence of Ce^{3+} in the fluorite phase compared to our XPS results, resulting in insufficient accuracy of the calculated defect concentrations in the ternary fluorite phase. The optimised model description containing all prevailing ionic species is used for calculations of phase stabilities and defect concentrations as function of temperatures and oxygen partial pressure.

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Phase equilibria of binary Cr-Os system: experimental measurement and thermodynamic assessment

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Very recently, diffusion coefficient of Os in Ni-based superalloys was experimentally observed to be even lower than that of Re in our research group, and Os was thus regarded to be a potential alternative element of Re in Ni-based super-alloys. In order to perform the design of novel Ni-based superalloys with Os-addition, their accurate phase equilibira are the prerequisite, which however are usually missing in the literature.

In the present work, the Cr-Os binary system was chosen as the target. Based on the assessment of the phase equilibria and thermodynamic properties available in the literature, five decisive alloys were prepared. The alloys were annealed at 1573 K, 1373 K and 1173K for 10 days, 35days and 45 days, respectively, followed by water–quench. After standard metallographic technique, all the annealed alloys were analyzed using X-ray diffraction (XRD), optical microscopy, differential Scanning Calorimetry (DSC) and electron probe micro-analyzer (EPMA). Based on the assessed literature information and the presently experimental data, the thermodynamic optimization for the Cr-Os system was performed by using CALPHAD technique. The sublattice model was employed to describe Cr_3Os and Cr_2Os. A set of self-consistent thermodynamic parameters was finally obtained. Comprehensive comparisons show that the calculated phase diagram and thermodynamic properties agree well with the experimental ones.

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- Thermodynamics and kinetics investigation of Ni-based superalloy.
- Phase-field simulation and property prediction of Ni-based superalloy.

Modeling of the Mn-Ni-Pd alloy system

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Mn-Ni-Pd alloys were considered by Rhys et al.[1] for brazing materials for high temperature applications. While there is fairly comprehensive experimental information on phase equilibria in the Mn-Ni-Pd system [2], a thermodynamic description of this system was not published yet. In the present work we construct a thermodynamic model of the Mn-Ni-Pd ternary based on published models of the included binary systems [3,4,5]. The model for the Mn-Pd binary was revised substantially by use of a four-sublattice description of the FCC_A1 phase and the related ordered L10 and L12 phases. Also, the description of the ordered B2 phase was unified with that of the BCC_A2 phase. In the adjustment of model parameters, more weight was given to fitting experimental calorimetric data and activity measurements than to ab-initio calculations. The ternary model was completed by amending the extrapolation form binary systems through addition of few ternary interaction parameters.
The results of the modelling reproduce the small reduction in the melting temperature that might be achieved through adding small fraction of Pd to Mn-Ni alloys.

Calculated liquidus projection of the Mn-Ni-Pd system

[1] Rhys et al., Metallurgia, 66 (1962) 223-263
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Thermodynamic modelling of the B-Mn-V system

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This work is focused on a study of phase equilibria in the B-Mn-V ternary system by CALPHAD method with the aim of creating a reliable theoretical thermodynamic dataset for calculation of the phase diagram of the ternary system. Boron is modelled as an interstitial element in all solid solutions of vanadium and manganese. Thermodynamic parameters for binary B-V, B-Mn and Mn-V systems were taken from the literatures [1], [2], [3] and the data for pure elements were taken from Dinsdale [4]. The experimental results collected from the literature, were used in the optimization of the thermodynamic parameters. Very good agreement between experimental results and calculations was achieved.The main result of this work is an optimized thermodynamic dataset for the B-Mn-V ternary system allowing the phase diagram and thermodynamic properties to be calculated.

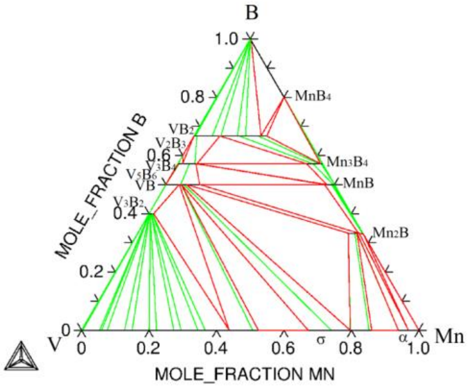

Fig.1 Isothermal section of the B-Mn-V phase diagram at 973 K.

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Experimental and computational study of diffusion between Fe-Cr-Al and Fe-Ni alloys at 800°C and 1000°C

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Fabrication of engineering components suitable for high temperature applications normally involves welding of alloys that differ considerably in composition. At high temperatures, diffusion of alloying elements across the dissimilar welds can occur and results in formation of deleterious phases. One can investigate the propensity of phase formation in dissimilar welds as a function of time using simulation tools such as DICTRA, which can help in determining the lifetime of such components. This, however, requires reliable thermodynamic and mobility databases.

Over the decades, increasing demands on high temperature properties have led to the development of many steel grades with higher Ni content. This means that the thermodynamic and mobility databases traditionally used for doing calculations in iron-base alloys should be augmented to deal with higher Ni content than normal. In the present work, diffusion experiments were carried out between Fe-Cr-Al alloys and Fe-Ni alloys at 800°C and 1000°C, in order to validate the reliability of appropriate databases from Thermo-Calc Software AB. The phase formation and diffusion profile across the interface was characterized using Electron Probe Micro Analyser. The results are compared with calculations performed using Thermo-Calc and DICTRA.

Rohit Ojha

Rohit is a Metallurgical and Materials Engineer working at Sandvik Materials Technology for 8 years in the field of material characterization and computational thermodynamics. He is currently pursuing Doctoral degree at Indian Institute of Technology Madras, India.

On the configurational entropy of nano-solutions

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Configurational entropy of nanoscale solutions is discussed in this poster. As follows from the comparison of the exact equation of Boltzmann and its Stirling approximation (widely used for both macroscale and nanoscale solutions today) the later significantly over-estimates the former for phases smaller than 16 nm in diameter. On the other hand, the exact Boltzmann equation cannot be used for practical calculations, as it requires the calculation of the factorial of the number of atoms in a phase and those factorials are so large numbers that they cannot be handled by commonly used computer codes (as an example: Microsoft Office EXCEL 2007 can handle factorials of numbers below 171). Therefore, a correction term is introduced in this paper for the Stirling approximation, which is a continuous function of the number of atoms / molecules and the composition of the binary nano-phase. This correction becomes negligible for phases larger than 16 nm. However, the correction term does not cause mathematical difficulties even if it is used for macro-phases. This correction will be useful for future nano-Calphad calculations[1-14].

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Thermodynamic Modelling of the Al-Mn-C system

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Excellent combinations of strength and ductility paired with the possible weight reduction motivates the research of high manganese TWIP or multi-phase steels. The development of alloying concepts to achieve the goals required for safety relevant applications in e.g. automotive applications for these steels depend on finely adjustable material properties by thermo-mechanical treatment and thus demand accurate thermodynamical description for efficient theoretical alloy design. A possible design concept for such steels is the formation of finely dispersed intermetallic phases, such as the κ phase (structure type E21, $(Fe,Mn)_3AlC$).

As a sub-system of the quaternary Fe-Mn-Al-C, the Al-Mn-C system is fundamental for the design of high manganese and aluminium alloys. New experimental data by Bajenova et al. [1,2] give new insights into the composition range and solubility of Al-Mn-C alloys at temperatures above 1000 °C where previously no data was available. Both liquidus and solidus temperatures along with isothermal sections at 1100 °C and 1200 °C have been recorded. It is shown that the κ phase melts congruently and has a wide field of primary crystallization. In addition, previous isothermal sections at 700 °C and 1000 °C were used [3].

In the work presented, the Al-Mn-C system is thermodynamically modelled using the new experimental data. The results about the κ phase indicate that previous modelling as a stoichiometric compound is not suitable given the large homogeneous region and its shape. Therefore, the stoichiometric compound is compared to a four sub-lattice model of an ordered fcc structure and previous modelling of the system [4].

[1] Bajenova, I. et al., Journal of Alloys and Compounds 700 (2017), pp. 238–246.
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Ph.D. student in research groups (i) “thermodynamic modelling” at IWM, RWTH Aachen and (ii) collaborative research center “SFB 761” on high manganese steels.

Recent work:

C. Haase et al., On the deformation behavior of κ-carbide-free and κ-carbide-containing high-Mn light-weight steel, Acta Mat122 (2017),332–343.

F. Tang et al., Using the PARROT module of Thermo-Calc with the Cr–Ni system as example, Calphad 55 (2017), 260-269.

Phase equilibria of the Gd-Mn-Ge/Si ternary systems and magnetic properties of $GdMn_2(Ge,Si)_2$ compound

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The rare-earth(RE)-transition metal compounds in the RE-Mn-X(X=Ge, Si) system have been investigated because of their interesting magnetic properties, resulting from the interesting interplay between the 3d and 4f magnetism and the strong dependence of the magnitude of the Mn moment and the magnetic state of the Mn sublattice on the Mn-Mn interatomic distances [1,2]. The intermetallic compounds $REMn_2X_2$ show magnetocaloric effect and $REMn_6X_6$ compounds have magnetoresistive properties, while REMnX compounds show magnetoelasticity [3,4]. Phase equilibria and crystal structures of intermetallic compounds in the RE-Mn-X systems are contributes to understand the relationships between crystal structure, phase transformation and physical properties.

In this work, phase equilibria of the Gd-Mn-Ge and Gd-Mn-Si systems at 673/873 K were investigated by means of X-ray diffraction (XRD), scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDS) and electron probe microscopy (EPMA). On the other hand, the crystal structure, magnetic properties and magnetocaloric effect of $GdMn_2(Ge,Si)_2$ compound were studied by XRD and Physical Property Measurement System (PPMS). The maximum magnetic entropy change and the relative cooling power (RCP) of the compound were obtained.

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[2] J.L. Wang, L. Caron, S.J. Campbell, S.J. Kennedy, M. Hofmann, Z.X. Cheng, M.F. Md Din, A.J. Studer, E. Brück, S.X. Dou, Phys. Rev. Lett. 110 (2013) 217-211.
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Experimental study and thermodynamic calculation of Mn-RE (RE=Nd, Gd, Ho, Dy) binary systems

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Ternary intermetallic compounds with rare earth elements and transition metals in the RE-Mn-X (X=Si, Ge, Sn etc.) ternary systems show interesting magnetic properties [1-3]. As key sub-binary systems of the RE-Mn-X (X=Si, Ge, Sn etc.) ternary systems, the information of phase euqibira and thermodynamic properties of the Mn-RE (RE=Nd, Gd, Ho, Dy) binary systems are indispensable to explore the RE-Mn-X (X=Si, Ge, Sn etc.) alloys with better magnetic properties.

In this work, the experimental data of phase equilibria and thermodynamic properties of the Mn-RE (RE=Nd, Gd, Dy) binary systems in the published literature were reviewed firstly. Some key Mn-RE binary alloys were prepared and examined by X-ray diffraction (XRD), scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDS). Based on the available experimental information, thermodynamic calculation of phase equilibria of the Mn-RE (RE=Nd, Gd, Ho, Dy) binary systems was performed using the CALPHAD method. Self-consistent thermodynamic parameters of all phases were obtained, which would be necessary to develop the self-consistent and compatible thermodynamic database of the RE-Mn-based alloy systems.

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[3] Y.Y. Gong, L. Zhang, Q.Q. Cao, D.H. Wang, Y.W. Du, J. Alloys Comp. 628 (2015) 146-150.

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Jiang Wang

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Development of a new thermodynamic database for slag relevant oxide systems containing P_2O_5

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Thermodynamic properties of complex oxide systems can be described and predicted by thermodynamic modelling on the basis of reliable experimental data and appropriate Gibbs energy models for various phases. An oxide database containing SiO_2, Al_2O_3, alkali, earth-alkali, P_2O_5, CrO_x, FeO_x, MnO_x with addition of sulphates/carbonates of alkali and earth-alkali oxides and metal sulphides has been created for the modelling of a complete coal ash (slag) and gas system. The corresponding systems have been thermodynamically assessed using all available experimental data on phase diagrams and thermodynamic properties. Self-consistent datasets have been obtained covering experimental information on binary, ternary, and quaternary subsystems. The present work describes the extension of the database with respect to P_2O_5. The interaction of phosphorous oxide with potassium oxide as well as with CaO, MgO and ZnO is considered. The binary and ternary sub-systems will be discussed.

The Gibbs energy of the liquid phase has been modelled using a non-ideal associate solution approach. The corresponding binary and ternary compounds were introduced as constituents in the liquid phase along with the basic component oxides. The Gibbs energy of the stoichiometric compounds is presented in form of simple G(T) functions. The solid solutions have been described using sublattice models.

The ternary systems K_2O-MeO-P_2O_5 (Me=Ca, Mg, Zn) are characterised by a large number of ternary stoichiometric compounds and by solubility between K_3PO_4 and ternary compounds with the general formula $(K_2O)_3(MeO)(P_2O_5)$ and $(K_2O)_2(MeO)(P_2O_5)$ with Me=Ca, Mg. The solid solutions have been treated using a simple sublattice approach according to the formula $(K_2O)_2(P_2O_5)(K_2O, MeO, K_2MeO_2)$. The corresponding solid solution parameters have been found to obtain adequate representations of the available experimental data. The pseudo-binary sections in the framework of the ternary systems are calculated. The ternary phase diagrams including sub-solidus equilibria are proposed.

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Electronic state entropy: informing thermodynamic and transport properties of the molten state.

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While an important state for major metallurgical processes, the molten state is still often considered as a mere extension of the solid state, following statements from thermodynamicists [1]. As a matter of fact, predictions of miscibility in the molten state remain a challenge, along with predictions of transport properties. Herein, a quantitative theoretical connection between the thermopower and electronic state entropy of molten systems is presented, and tested for molten semiconductors and metallic materials [2]. For molten semiconductors such as binary metal-chalcogenides, the connection quantitatively predicts the entropy of mixing and its temperature dependence in agreement with physics phenomenological models [3].

Quantification of the electronic state entropy allows the definition of the conditions for miscibility in the molten state [4], which in turn informs the range of electronic properties that this state can exhibit. Electronic state entropy is also shown to be pertinent in explaining the deviation from Richard's rule for certain systems, and is therefore put forth as an important thermodynamic function for understanding ordering in high temperature liquids and solid-liquid phase transitions.

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Antoine Allanore

Prof. A. Allanore joined MIT in 2010 after several years in the steel industry at ArcelorMittal R&D in France.His research group at MIT investigates thethermodynamic and transport properties of the molten state, particularly molten oxides andsulphides, in the prospects of developing novel processes with higher selectivity and that adopt green chemistry principles.

Solidus surface projection of Fe-Sn-S system

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Peter the Great St. Petersburg Polytechnic University

Information about phase transformations in high temperature range of Fe-Sn-S system is necessary for detailed knowledge and control of pyrometallurgical processes. The Fe-Sn-S system is very complicated for thermodynamic calculation due to the absence of proper thermodynamic models, which is connected with deficiency of experimental data about phase equilibria and thermodynamic properties of compounds. Perhaps, serious lackof experimental data about this system is caused by the peculiarities of the system, namely high partial pressure of tin, sulphur and their compounds as well as miscibility gap in liquid state, occupied the wide composition range. Thus, indicated lack of information about phase equilibria in Fe-Sn-S system has motivated us to provide the detailed research.Our scientific team has developed special technique of preparation and investigation samples by DSC method, enablesus to overcome these difficulties. This technique was examined under construction of phase diagrams for sulphur-metallic systems [1].
With the use of beam section of Gibbs triangle more than 80 experimental compositions were chosen for synthesis and further research.To study phase equilibria we decided to use the complex of modern analytical techniques such as DSC, SEM/EPMA and XRD methods.
The liquidus surface projections of Fe-Sn-S system and pseudobinary FeS-SnS section were presented before [2]. At CAPLHAD 2017 Conference solidus surface projection and Sheil scheme of phase equilibria with determined nonvariant reactions will be presented.

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Phase Equilibria of the Fe-Al-Zr System at 600℃

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The phase equilibria of the Fe-Al-Zr ternary system at 600℃ has been investigated using a combined methods of scanning electron microscopy coupled with energy dispersive x-ray spectroscopy, and x-ray diffraction. Five ternary compounds are found, and fourteen three-phase regions have been determined (as seen in Fig. 1). A new ternary compound λ_1 is generated, when the solubility of Al in $ZrFe_2$ is more than 20 at.%. Another new phase λ_2 is found, while Al contents between 52 and 59.6 at.% in $ZrFe_2$. It was confirmed that the maximum solid solubility of Fe in Zr_3Al_2 is 3.16 at.%, and the solubility of Al in Zr_3Fe is up to 2.09 at.%. There are almost no solid solubility of Zr in the FeAl, $FeAl_2$, Fe_2Al_5, and $FeAl_3$.

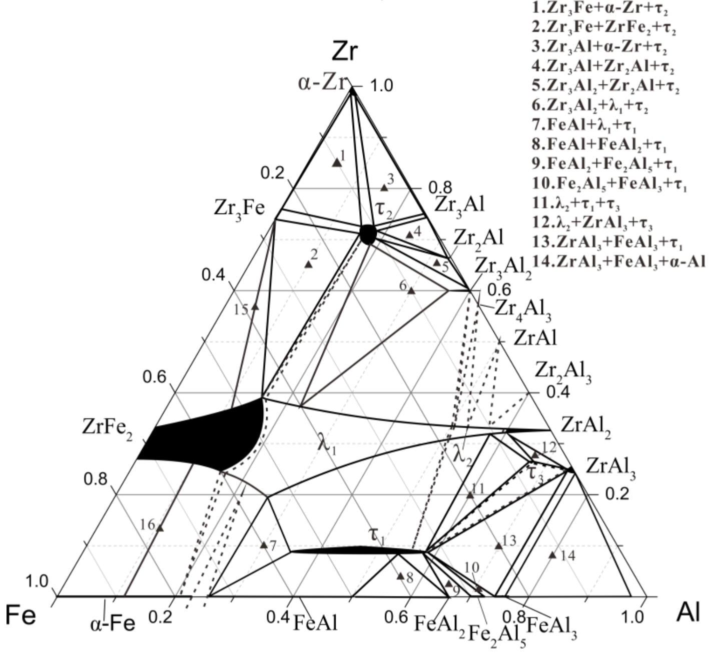

Fig. 1. Experimentally determined isothermal section of the Fe-Al-Zr system at 600℃

Acknowledgments
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Experimental study on the Fe-C-La System

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There are three main roles for rare-earth metals in steels: modification of inclusions, deep purifying steel and alloying. However, the mechanism of the influence of the rare-earth additions on the property of the steel is still not clear. Thus, an investigation of the phase diagram for the Fe-C-La system is of some interest for the processing of steels as lanthanoids are frequently used in the refinement of steel melts. It therefore has great practical importance for the steel industry.

There is little published information on the phase equilibria in the Fe-C-La system. Two ternary compounds $La_{3.67}[Fe(C_2)_3]$ and $La_2Fe_{14}C$ had been found [1-3]. In [2] the compound $La_{3.67}[Fe(C_2)_3]$ was reinvestigated by X-ray powder diffraction, and $La_2Fe_{14}C$ in [3]. But, neither the temperature nor the method of forming the ternary compounds was established.

In this work phase equilibria in the Fe-C-La system have been studied for the first time. The liquidus and solidus projections and a melting diagram over whole concentration region have been constructed using DTA, SEM, electron probe microanalysis and X-ray diffraction data. The compound $La_{3.67}FeC_6$ (τ) was found in equilibria with the liquid.

The liquidus surface of the Fe-C-La system is characterized by primary crystallization regions of the following phases, (C) graphite, (γFe), (δFe), (αFe), βLaC_2, La_2C_3, (βLa), (γLa) and $FeLa_{3.67}C_6$ (τ). The miscibility gap in the liquid state is well established. The two liquid phases, Fe rich (L_1) and La rich (L_2), coexist over a wide composition range. The experimental results from this study have been used as input for the CALPHAD modeling of data for this system.

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Thesis works involve Thermodynamic modelling and experimental study of R-TM-X systems.

Wetting and interfacial reactivity in the Al_3Ti-SiC system

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SiC based Ceramic Matrix Composites (CMCs) are considered as very promising materials in the aerospace field. This is due to thefavorable combination of their properties: high thermal, mechanical and chemical stability as well as low weight. The process parameters to obtain reliable SiC-SiC joints, using Al_3Ti as filler material, have to be defined.To reach this goal, the Al_3Ti-SiC system has been evaluated in terms of wetting and interfacial reactivity. The use of Al_3Ti allows to form phases such as $Ti_3(Al,Si)C_2$ that gives excellent properties for the joint performances.

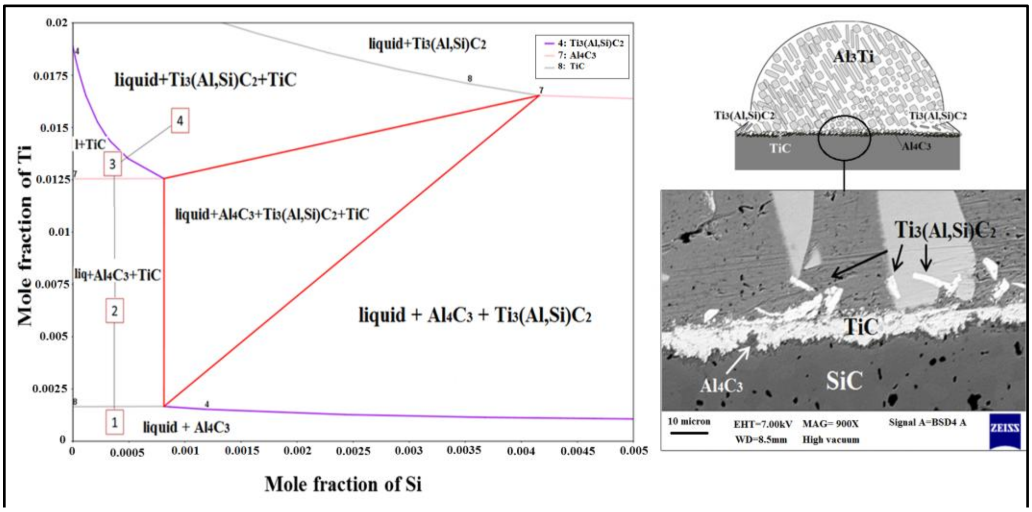

Fig. 1- Thermal history of the system represented in the Al-C-Ti section at 1200°C (1wt% of C fixed) and schematic image of the Al_3Ti/SiC interfaceobtained by sessile drop wetting test at the same temperature.

An home-made Al-C-Si-Ti database has been implemented by merging and adapting interaction parameters assessed in literature for the binary and ternary subsystems: Al-C-Si [1], Al-C-Ti [2], Al-Si-Ti [3], C-Si-Ti [4].Combining the experimental results (EDS,DSC) to the thermodynamic calculations, pathway of the liquid through the ternary system during brazing can be explained and the joining parameters optimized.

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Experimental study of phase equilibria of the La/Y-Fe-B ternary systems

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$Nd_2Fe_{14}B$-based permanent magnets are used for a wide variety of applications because of the high energy products [1-3]. Heavy rare earth elements (e.g. Dy, Tb) were added to improve the coercivity of Nd-Fe-B magnets. On the other hand, the crystal structure of $RE_2Fe_{14}B$ with light rare earth elements (e.g. $Ce_2Fe_{14}B$) is similar with its $Nd_2Fe_{14}B$. In order to understand better effect of the light rare earth elements on alloy composition, phase transformation and microstructure of the Nd-Fe-B alloys, phase relations of the related RE-Fe-B ternary systems are necessary.

In this work, the La-Fe-B and Y-Fe-B alloys prepared by arc melting were annealed and then were investigated by means of X-ray diffraction (XRD) and scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDS). According to the XRD and SEM/EDS results and experimental information reported in the literature, phase equilibria of the La-Fe-B and Y-Fe-B ternary systems were determined.

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Jiang Wang

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Thermodynamic optimization of Al-B-N system using *ab initio* calculations

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We report the thermodynamic modelling of Al-B-N system along with improved thermodynamic descriptions of the limiting binaries Al-N and B-N. Previous assessment of Al-N system by [1] was improved by including revised Gibbs energy function for stable polymorph and new functions for the metastable polymorphs of AlN. The thermodynamic descriptions for B-N system by [2] was also improved in a similar manner. The functions were obtained using estimated finite temperature thermodynamic quantities from *ab initio* phonon calculations.

The Al-B-N system was optimized using experimental constitutional data from literature [3] and *ab initio* thermochemical data obtained in this work. An attempt is made to estimate the mixing energies as a function of temperature using special quasirandom structures for metastable polymorphs of AlN and BN. The calculated quasibinary sections for the metastable polymorphs with be of technological importance in designing microstructures for tribological applications.

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Soumya Sridar

I am currently a PhD research scholar in IIT Madras. My research interest is developing thermodynamic databases using Calphad method coupled with 0 K energetics and finite temperature thermodynamic properties obtained from *ab initio* calculations.

Prediction of heat capacity

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The heat capacity is a basic property of a material as well as a basic function for a correct thermodynamic modelling. Heat capacity is linked with elastic properties and volume of a material. For the description of new thermodynamic databases starting from zero Kelvin, heat capacity, elastic constants and volume should be correctly described for enhancing the thermodynamic description. These information can be derived from experiment or ab-initio calculations. In most cases experiments are only possible in a limited temperature range and time consuming. On the other side DFT calculations can be easily done for T = 0 K, but need long calculation times by extending to high temperature ranges.

A model approach is presented which allows one to predict heat capacity of a material from zero Kelvin up to high temperatures based on zero-Kelvin properties. The accuracy of results can be increased by taking experimental data on volume, thermal expansion or bulk modulus into account. It is shown that cp without electronic contribution, volume and thermal expansion is reproduced within experimental error. The predictions works good for elements. However, for intermetallics and ceramics the mentioned experimental data should be taken into account.

The presented algorithm is based on Debyes description of heat capacity [1] and thermodynamic relations [2][3]. It allows one to calculate the described properties between zero Kelvin and 2000 K within a few minutes on a normal desktop computer which can be used as a starting point of an thermodynamic assessment or for further studies.

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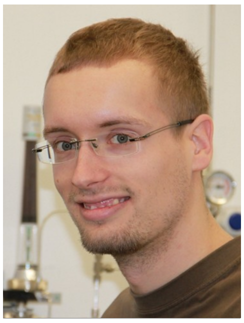

Tilo Zienert

Studied Material Science and Technology at TU Bergakademie Freiberg, since 2011 scientific stuff within the project CRC 920 'Multi-Functional Filters for Metal Melt Filtration'. Scientific interests are experimental investigation of phase diagrams with focus on cp measurements, CALPHAD type modelling, combining description of metallic and ceramic systems to study interactions between metallic melts and ceramic materials of metallurgical interest.

Thermodynamic study and assessment of the fluorine-iron system

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UF_6 molecule is utilized for enrichment of fissile uranium for nuclear power plant fuel. However, corrosion of steels structural materials can occur in UF_6 production plants. Corrosion of steels in fluoride atmospheres leads to formation of iron fluorides FeF_2 or FeF_3 [1]. In order, to understand and then to model the corrosion mechanism, thermodynamics of the fluorine-iron system is required. A literature review on the phase diagram data and thermodynamic properties of this chemical system has pointed out the lack of reliable thermodynamic data:
- the melting temperature of FeF_2 has to be confirmed;
- the enthalpy of formation measurements of FeF_3 are scattered;
- the only phase diagram proposed in the literature is limited to the FeF_2-FeF_3 part [2];
- and the Fe_2F_6 gaseous dimer has no available thermodynamic properties.

Thus, both experimental and computational works were carried out to improve the thermodynamic knowledge of this system. In this study, differential thermal analysis experiments were performed to measure the liquidus temperatures in the FeF_2-FeF_3 part and to determine transition temperatures in the Fe-FeF_2 part. Moreover, calculations using the Density Functional Theory method permitted to obtain thermodynamic properties of Fe_2F_6 gaseous molecule.

Finally, CALPHAD method, taken into account the previously obtained data and a former database, has been used to improve the thermodynamic description of the system Fe-F.

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Effects of Ni-doping on various properties of NbH phases: A first-principles investigation

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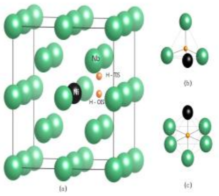
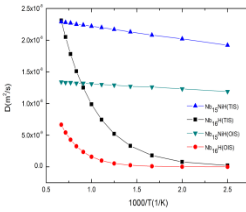
Employing a first-principle method, we have studied effects of Ni-doping on the stability, H-diffusion properties, and mechanical properties of NbH phase. Calculated results reveal that single H atom is energetically favorable sitting at the tetrahedral interstitial site (TIS) instead of octahedral interstitial site（OIS）, the preferential path of H diffusion is from TIS-TIS, followed by TIS-OIS in both $Nb_{16}H$ and $Nb_{15}NiH$ phases. Ni-doping (in $Nb_{15}NiH$ phase) would lower energy barrier of H diffusion, enhance H-diffusion coefficient (D) and mechanical properties of $Nb_{16}H$ phase. D value will increase with the increasing of temperature, and the difference of D resulted from the alloying with Ni would weaken clearly with the increase of temperature. At a typical operating temperature of 400 K, $Nb_{15}NiH$ (TIS) has a bigger D value ($1.90\times10^{-8} m^2/s$), which is about 88.6 times more than that of $Nb_{16}H$(TIS) ($2.14\times10^{-10} m^2/s$). The calculation suggests that the Ni-doping will greatly improve the diffusion properties of H in Nb.





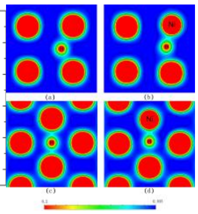


Fig.1 Schematic illustrations of (a)$Nb_{15}NiH$, (b)tetrahedral interstitial site(TIS), and (c)octahedral site (OIS). The green and black balls represent Nb and Ni atoms, respectively. The orange small balls stand for various sites of H atom.Fig.2 Diffusion coefficient of H as a function of reciprocal temperature.Fig.3 The valence charge density distribution of $Nb_{16}H$ and $Nb_{15}NiH$ with TIS case (a, b) and OIS case (c, d).

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Effects of Mo alloying on the structure and hydrogen-permeation properties of Nb metal

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Effects of alloying Nb with Mo on the structure and hydrogen permeation properties of Nb metal have been investigated by XRD analysis, PCT measurements, and three-point bending tests. The results indicate that all the as-prepared $Nb_{100-x}Mo_x$ (x= 2, 7, 14) alloy samples are Nb-based solid solutions with a BCC structure, which are hydrogenated into their corresponding hydrides with the $NbH_{0.95}$ phase after hydrotreatment. The lattice deformations of the BCC structure and $NbH_{0.95}$ phase are due to the difference in size between Nb and Mo atoms. The $Nb_{86}Mo_{14}$ sample has a higher hydrogen-diffusion coefficient value (1.84×10^{-9} cm/s), higher hydride-formation enthalpies (- 35.8 kJ/(mol·H_2)) with the maximum force and displacement before/after the hydrotreatment, indicating that alloying with Mo can greatly improve the hydrogen-diffusion behavior and anti-bending properties of Nb metal.

Keywords: Alloying, Nb metal, Lattice deformation, Hydrogen-diffusion coefficient (DH), Mechanical property.

This work is supported by the National Natural Science Foundation of China (51471055, 51261003), the Natural Foundations of Guangxi Province (2016GXNSFGA380001).

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Evaluation of empirical rules on the phase formation of the multi-principal element alloys through Calphad approach

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Multi-Principal Element Alloys (MPEAs), which is also widely known as High Entropy Alloys (HEAs) or Compositionally Complex Alloys (CCAs), has become one of the hottest topic in development of new alloy systems. The main feature of the MPEAs is that near equiatomic multi-components constitute a disordered solid solution phase which exists in an alloy as a single phase or a main matrix phase, or two solution phases with close amounts as dual phase structure. Several empirical rules, mainly based on Hume-Rothery rule and the estimated thermodynamic properties, have been proposed to predict the formation of solid solution phases. But in these empirical rules, the enthalpy of mixing is estimated by Miedema's model, and the entropy of mixing is only considered the configurational part. In the present work, we calculate the thermodynamic properties of a series of high entropy alloys using Calphad approach based on self-consistent developed databases. Fig. 1 shows an example of a typical high entropy $AlCo_xCrFeNi$ alloy that the disordered fcc single phase region does not appear in the region with "highest entropy", which was regarded as the most important core effect of high entropy alloys. The application and limitation of other empirical rules will also be evaluated and discussed.

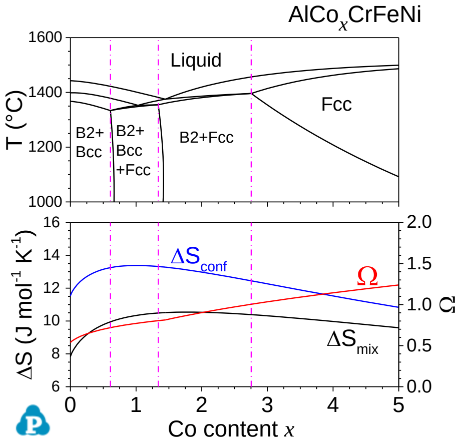

Fig.1 Calphad calculated vertical section of $AlCo_xCrFeNi$ (top) and example parameters used in empirical rules (bottom). The significance of the parameters is defined as follows:

ΔS_{conf} : Configurational entropy of disordered mixing.

ΔS_{mix}, Calphad calculated entropy of mixing at the liquidus temperature (T_L) refers to liquid phase of the elements.

$\Omega = T_L \Delta S_{mix} / |\Delta H_{mix}|$ proposed in [1] with

ΔH_{mix}: Calphad calculated enthalpy of mixing at the liquidus temperature (T_L) refers to liquid phase of the elements.

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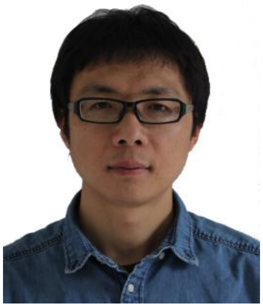

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Ab initio calculations of the intermetallics in Ni-Zr system

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Zirconium is an important alloying element in Ni-base superalloys. Intermetallics of the Al-Ni-Zr system have been found to have excellent creep and oxidation resistance [1]. Furthermore, this system is considered the base system for a variety of metallic glass. Hence, it has become crucial to examine the Ni-Zr system with more detail.

Substantial scatter has been observed in thermodynamic data obtained experimentally. This has been attributed to the high oxidization of Zr and contamination with Hf [2]. Additionally, it is necessary to ascertain the reliability of the heat capacity data from [3] as they have not characterized the phases formed. It is hoped that the current results will be beneficial in improving the Calphad description of the Ni-Zr system.

Ab initio calculations so far have dealt with only 0 K properties [4,5]. In this work, we calculate formation enthalpies of the intermetallics at 0 K along with finite temperature thermodynamic quantities like heat capacity. The vibrational contribution is obtained using the quasi-harmonic approximation as implemented in Phonopy [6]. The electronic contribution is calculated separately and added to the vibrational contribution.

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Thermodynamic modeling of the Co-Cr-Ta system

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Co-Cr based alloys are the basic of high-temperature alloys, biomedical alloys and magnetic recording materials. The addition of Ta will have an influence on the phase composition of Co-Cr based high-temperature alloys.

The phase equilibria of Co-Cr-Ta system were experimentally investigated in [1]. Three isothermal sections at 800, 900 and 1100°C were published. No ternary compound was detected. The thermodynamic optimization of the Co-Cr-Ta system is carried out by using CALPHAD approach. The interaction parameters of three binary systems were mainly obtained from the literature [2-5] with several modifications. In particular, DFT calculations of the 0 K enthalpies of the pure elements in C14, C15 and μ phases [6,7] have been considered in this work. C14, C15 and C36 have been described separately by a two-sublattice model, while the μ phase has been modeled using four sublattices in agreement with the structural analysis by [8]. Assessment procedure and the obtained results will be presented and discussed.

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Experimental research on thermo-stability of the ternary compounds and related phase transformation in the Mg-Zn-Gd system

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Magnesium alloys, as the lightest metallic structural materials, have received increasing attention because of their good potential use in automotive and aerospace application. Thermo-stability of the ternary compounds and relative phase transformation in the Mg-rich corner of Mg-Zn-Gd system have been researched through the equilibrated alloy method by using differential scanning calorimetry, scanning electron microscopy assisted with energy dispersive spectroscopy of X-ray, electron probe microanalysis, X-ray diffraction and transmission electron microscopy. It has been shown that the icosahedral quasicrystals could be obtained in the as-cast Mg-based alloys of the Mg-Zn-Gd system, and could be in equilibrium with Mg-based solid solution at the temperature below 427.5^{o}C. So the icosahedral quasicrystal phase in the Mg-Zn-Gd system is not metastable, but thermodynamically stable. The ternary compound Z, H, W could also be in equilibrium with Mg-based solid solution. The phase transformation (Mg)+H→W+Liquid occurs at $443\,^{o}$C.

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Remodelling of Hf-V system

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The structural and energetic characteristics of the C14, C15 and C36 Laves phases as well as of the tetragonal and orthorhombic phase were studied using ab initio approaches. The experimentally found heat of formation is compared with ab initio results. It turns out that various theoretical approaches provide different description of stability of C15 Hf-V Laves phase.

The ab initio data were used for thermodynamic modelling of phase equilibria. Our results show that we are able to describe correctly the phase transformation from orthorhombic HfV_2 structure to cubic C15 Laves phase, which occurs in Hf-V system during heating at about 115 K. Our method of extension of the thermodynamic unary SGTE data down to zero Kelvin temperature [1], which may be applied also to complicated intermetallic phases, is utilised here. Data concerning the recent thermodynamic assessment of the Hf-V system (valid for temperatures above 298.15 K) [2] are reassessed. The calculated phase diagram and the approach employed will be presented and discussed.

PB

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Thermodynamic Evaluation and Optimization of the NaF - KF - ZnF_2 System

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We have developed a quantitative thermodynamic description of the NaF-KF-ZnF_2 system. This salt system is of great importance for the recycling of aluminium alloys with Zn as the main alloying element such as the Series 7000 alloys, which are mainly used in aeronautics. The liquid phase was modelled using the Modified Quasichemical Model in the Pair Approximation [1,2]. Based on Raman spectroscopy data available for liquid solutions [3], three compositions of maximum short-range-ordering were introduced for the AF-ZnF_2 liquid : A_2ZnF_4, $A_2Zn_2F_6$, and $A_2Zn_6F_{14}$ (where A = Na, K). This better represents the polymerization of ZnF_2 in the ZnF_2-rich region of composition.
The model parameters were obtained by critical evaluation and optimization of all available thermodynamic and phase equilibrium data for the binary systems NaF-ZnF_2 and KF-ZnF_2. The intermediate solid compounds $NaZnF_3$(s_1, s_2), $KZnF_3$ and K_2ZnF_4 were taken into account. The NaF-KF system, which exhibits a KF-rich solid solution, has previously been modelled [4]. The calculations for the AF-ZnF_2 systems satisfactorily reproduce the experimental data from the literature, without the use of any composition-dependent interaction parameters. This lends support to the proposed liquid model. The NaF-KF-ZnF_2 liquidus projection was predicted from the binary model parameters using a standard asymmetric interpolation method, with ZnF_2 as the asymmetric component. A negligible solid solubility was assumed between $NaZnF_3$(s_1, s_2) and $KZnF_3$, based on the available crystal structure data. The developed thermodynamic model will be merged with the previous model for the NaCl-KCl-$ZnCl_2$ system [5] in order to obtain a thermodynamic model for the chloro-fluoride reciprocal system (Na, K, Zn // F, Cl).

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Master’s research project : Acid/base model for aqueous salt systems (from pure water to the pure anhydrous salts), from a perspective of fertilizer process optimization

Thermodynamic modelling of key metallic sub-systems for the treatment of mid-level wastes

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The metallic waste resulting from the synthesis of mixed (U,Pu)O_2 oxides fuel is characterised by a mid-level contamination and needsto be treated before disposal. A possible process designed for this problem consists in melting such metals and then mixing them together witha SiO_2-Na_2O silicatemelt in order to accommodate actinides into astable glass matrix.

Because of the large number of alloying elements involved in this process, the Calphad method is used to predict the thermodynamic behaviourof the metallic phase and the reactions between the metallic and oxide liquids at high temperature.This work focuses on the thermodynamic modelling of severalmetallic sub-systems of interest that may form during the processing of waste.

A particular attention will be paid to the main elementspresent in the metallic waste: Al-Cu-Fe-Si-U. Differential Thermal Analysis coupled with Electron Microscopy are used to better document a variety of binary and ternary sub-systems. These new data are also used to validate the database under development,which eventually will be representative of the entire metallic melt.

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Thermodynamic description of the Ga-Li-Zn system

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The integral molar mixing enthalpy of liquid ternary Ga-Li-Zn alloys has been investigated using drop calorimetry method at different temperatures and along four intersections as follows: X_{Li}/X_{Zn} = 9/1 at 1006 K, X_{Ga}/X_{Zn} = 1/9 at 813 K, X_{Ga}/X_{Zn} = 1/1 at 1018 K X_{Ga}/X_{Zn} =9/1 at 1017 K. The available in the literature equations describing the excess Gibbs energy of binary Ga-Li, Ga-Zn and Li-Zn systems in the form of the Redlich-Kister relation and presented in this work experimental values of mixing enthalpy of liquid Ga-Li-Zn alloys were used for the calculation of ternary interaction parameters.

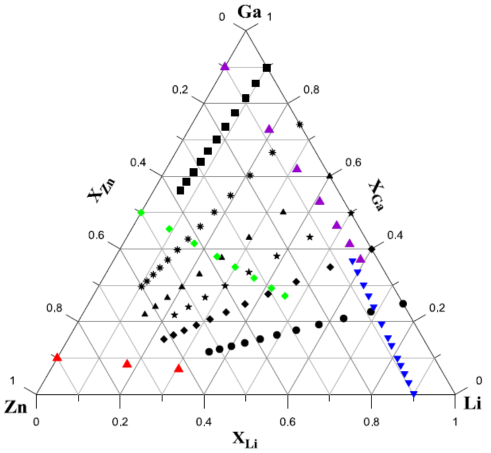

Fig. 1. The studied compositions of alloys of the Ga-Li-Zn system together with literature data - black symbols [1].

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After receiving the doctor's degree, his scientific interests were concentrated on metal alloys which can be applied as materials for hydrogen and energy storage (anodes for lithium batteries and accumulators).

The characteristic of Fe as a β–Ti stabilizer in Ti alloys

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Due to the excellent properties such as the light weight, the high corrosion resistance, high temperature performance and formability and the excellent mechanical properties, the titanium and its alloys have been widely used in various engineering fields including automobile and aerospace applications. It is well known that titanium can be alloyed with varieties of alloying elements to alter its properties, such as strength property, corrosion resistance, high temperature performance and formability. Fe[1,2] is proven to be a promising alloying element for suppressing the formation of α” phase and ω phase and an excellent β phase stabilizer. Although Fe as the β phase stabilizer has been extensively used in the designing titanium alloy experimentally, the physical origin is still unclear now.

Using first-principle calculations, we investigated the effect of dopant iron on the stability of β phase titanium and the phase transition between α, β and ω phase of titanium. Our results revealed the physical origin for Fe as a β phase stabilizer because the 3d orbital of Fe splitting into e_g and t_{2g} states which leads to the strong hybridization between Fe-d orbital and Ti-d orbital. The phase transition for Fe doped titanium for ω to β and α to β become much easier compared that for pure titanium. Our results show that one dopant Fe can lead at least 9 titanium atom from ω phase transition to β phase. Our results indicate that the Fe is an excellent alloying element with strong β phase stabilizing effect.

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Structure, elasticity and thermal decomposition of $Ti_{1-x}TM_xN$ alloysfrom first-principles study

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A systematic investigation concerning the effects of transition metals (TM = Y, Zr, Nb, Hf, and Ta) on the structure, elasticity and thermal decomposition of the TiN-based nitride coatings with a cubic rock-salt structure has been performed in terms of first-principles calculations. Calculated lattice parameters of $Ti_{1-x}TM_xN$ as a function of alloying concentration show positive derivations from the linearized Vegard's law, agreeing well with experimental and theoretical results. Positive enthalpies of mixing of $Ti_{1-x}TM_xN$ (TM = Y, Zr, and Hf) indicate the formation of these alloys is energetically unfavored with respect to the mixing of the cubic phases. The predicted consolute temperature of $Ti_{1-x}Zr_xN$ agrees reasonably well with previous theoretical findings. The miscibility gaps disappear in the case of alloying TiN with NbN and TaN. Predicted elastic stiffness constants C_{11}, C_{12}, and C_{44} together with the aggregate polycrystalline properties of $Ti_{1-x}TM_xN$ are determined by an efficient strain-stress method [1]. The present results indicate that the above nitride alloys are mechanical stable and addition of Nb and Ta increases the ductility, with Ta possessing the largest effect.It is found that, alloying Nb and Ta could reduce the resistance to shear and tensile strains, but ensure a high resistance to compression at the same time. The degree of elastic anisotropy of TiN-basd coatings increases with the increment of metallicity, which leads the inevitably presence of lattice distortion and micro-cracks during the preparation of these materials.These results could contribute to the explanation of experimentally-observed spinodal decomposition and serve as valuable information for the research of TiN-based ternary alloys at high temperatures.

Keywords: Nitride coatings; First-principles calculations; Thermodynamic properties; Elastic properties

Acknowledgments

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Reference

[1] P.Ou, J. Wang, S. Shang. et al.,Surface &Coating Technology 264 (2015) 41-48.

Calculation of mixing enthalpy in Mo–Pd–Rh–Ru system

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Molybdenum, palladium, rhodium and ruthenium are abundant fission products that form in oxide fuels of nuclear reactors. The resulting fission phases are known as white phases that form in the irradiated oxide fuel pellets. Because the conditions of prediction of these products are of high importance, a thermodynamic modelling is under development based on the quaternary Mo–Pd–Rh–Ru system using the Calphad method. In this framework, the ternary Pd–Rh–Ru system was recently investigated [1].

Due to the lack of experimental thermodynamic data, first principles method as the density functional theory (DFT) coupled with the special quasirandom structures (SQS) methods were used. The calculation allows to obtain the mixing enthalpy of all the binaries and all the ternaries resulting from the combination of the four elements in the three solid solutions: *fcc*, *bcc* and *hcp*.

The resulting thermodynamic description based on the present first principles calculations was used to obtain the binary and ternary interaction parameters of the all solid solutions and are compared to the few available data. These interaction parameters were used to compute the four different *ab initio* ternary sections. Moreover, they were coupled with experimental results from the literature to carry out the thermodynamic assessment of the binary systems of Mo–Pd and Mo–Rh.

[1] S. Gossé, N. Dupin, C. Guéneau, J.-C. Crivello, J.-M. Joubert, Journal of Nuclear Materials 474 (2016) 163–173.

Jean-Claude Crivello

Since his PhD study (University Paris XI, 2005), JCC has been working with first principles calculation of materials for energy storage applications. After a postdoctoral study in Tokai University, he was recruited as a researcher at the French National Center of Scientific Research (CNRS) in the ICMPE institute. In 2015, he spent a sabbatical leave in CMRI-IMR (Tohoku university).
With the help of DFT, his recent interest is combining several approaches (DFT, CEM, SQS, phonon…) to describe the phase equilibria of solid state.

Experimental and computational study on surface layer microstructure evolution in single crystal superalloys during solution heat treatment

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Single crystal superalloys are used in the hot sections of jet engines, particularly for their high resistance in creep and fatigue. Industrial processing involves solution heat treatments at elevated temperatures, high vacuum and argon atmosphere. They are aiming at homogenised microstructure free from microsegregation and other secondary solidification phases. Nevertheless, microstructural modifications beneath the surface have been observed after heat treatment. They involve formation of TCP phases and melting of surface layers [1-2]. The present study uses experimental and computational tools to explain these observations using CMSX-10 and example, for typical furnace conditions, such as the pressure and temperature. It is demonstrated that the loss of chemical elements is the cause of the observed modifications. The proposed mechanism is rationalised by thermodynamic modelling using CALPHAD type databases. Transport effects on the substrate response of the alloy are studied in detail.

[1] D'Souza, N., et al., Metallurgical and Materials Transactions A, 44 (2013) 4764.
[2] Wang, H., et al., Scripta materialia, 78-79 (2014) 45-48.

Experimental Determination of Phase Equilibria Related to Iron Silicides in the Fe-Si Binary System

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Iron silicides in the Fe-Si binary system have been widely investigated for electric applications due to the advantages of iron and silicon, for instance, a large amount of resources as well as their environment-friendly natures. In the literature, seven kinds of silicides including ordered-phases, denoted as α_1-Fe_3Si(D0_3), α_2- FeSi(B2), β-Fe_2Si, η-Fe_5Si_3, ε-FeSi, ζ_β-$FeSi_2$ and ζ_α-$FeSi_2$, were reported as stable phases [1-5]. Phase equilibria among the αFe(A2), α_1 and α_2 phases are re-examined in detail by Ohnuma *et al.* [5], in which miscibility gabs of α_1+α_2 and αFe+α_2 were recognized to appear along the B2/D0_3 second-order order-disorder transition boundary. In contrast, solubility ranges of the other iron silicides have not been precisely determined yet even though their microstructure control based on the phase diagram is very important to improve the electric properties. Moreover, phase equilibria reported in the literature have some uncertainties in the determination method, purity of raw materials, analysis equipment, and so on. In this study, therefore, phase equilibria related to iron silicides in the Fe-Si binary system were experimentally determined by alloying method and invariant reactions and transformation temperatures were re-examined, precisely.

High purity Fe (99.99%) and Si (99.999%) were melted to prepare Fe-Si alloys by a high frequency induction furnace using magnesia crucibles under high purity Ar (99.999%) atmosphere. Obtained samples were heat-treated at temperatures between 600°C and 1150°C after encapsulated in quartz tubes backfilled with Ar gas. Equilibrium compositions were measured by an FE-EPMA equipped with WDS. Transformation and invariant temperatures were determined from heating curves measured by DSC under a heating rate mainly at 10°C/min.

Figure 1 shows the phase diagram of Fe-Si binary system determined in this study. Solubility ranges of β-Fe_2Si and ζ_α-$FeSi_2$ were confirmed to be much narrower and to deviate to the Fe-rich side in comparison with those reported in the literature [1]. The higher stability of the η-Fe_5Si_3 phase was also newly confirmed from microstructure examinations, composition analysis and onset temperatures of DSC heating curves. The peritectoid temperature of β+ε→η is determined to be 1090°C, which is 30°C higher than the generally accepted temperature of 1060°C reported by Schurmann *et al.* [4].

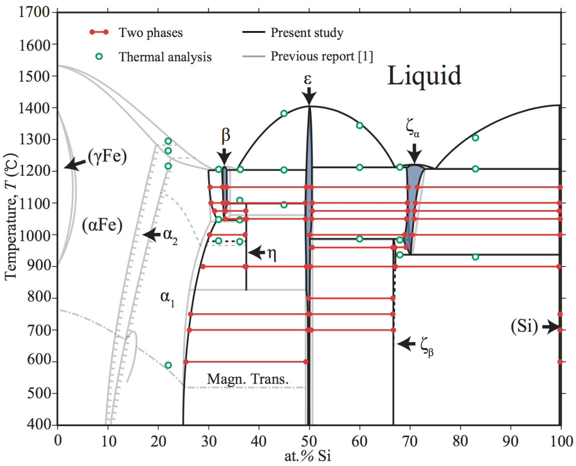

Fig. 1 Experimentally determined phase diagram of the Fe-Si binary system.

[1] O. Kubaschewski, Phase Diagram of Binary Iron Alloys, ed. by H. Okamoto, ASM International, Ohio, (1993) 380
[2] W. Koster, Trans. ISIJ 14 (1974) 393
[3] E. Wachtel, T. Manger, Z. Metallkde 62 (1070) 762
[4] E. Schurmann, U. Hesgen, Arch. Eisenhuttenwes. 51 (1980) 1
[5] I. Ohnuma, S. Abe, S. shimenouchi, T. Omori, R. Kainuma, K. Ishida, ISIJ Int., 52 (2012) 540

Theoretical study of hydrogen insertion in bcc metals

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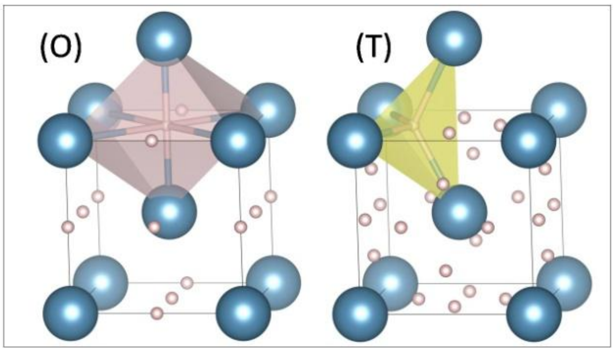
Modelling hydrogen insertion in body-centered cubic (bcc) metals is important both for the design of hydrogen storage alloys and to prevent structure embrittlement. In bcc host metals, hydrogen may settle on two types of interstitial sites: octahedral (O) or tetrahedral (T), whose multiplicity is 3 and 6, respectively. Nevertheless, the closeness of the sites prevents a total occupancy. For this reason, the interstitial sublattice in Calphad models has been usually limited to low multiplicities. However, the choice of the multiplicity is not obvious. Different values have been used, without common agreement [1].

The purpose of this study is to determine a physically based model for the interstitial sublattice. To this end, the Ising model based on atomic interactions represents an ideal tool to describe hydrogen interstitial solid solutions. Monte-Carlo simulation coupled with DFT calculations was applied to Cr-H, Fe-H, Nb-H and V-H systems. The calculations allowed to determine hydrogen site preference for each metal. Besides, the energy of mixing was estimated, based on the cluster expansion formalism [2].



[1] Joubert, J.-M., JOM, 64 (2012) 1438-1447.
[2] Sanchez et al., Phys. A, 128 (1984), 334-350.

Natacha BOURGEOIS

After graduating from a French Engineering School, I began my PhD in October 2014 at the ICMPE, institute of the French National Center of Scientific Research (CNRS). My thesis deals with the modelling of metal-hydrogen (*M*-H) systems using the Calphad method coupled with different calculation and simulation methods including DFT and phonon calculations, Cluster Variation Method and Monte-Carlo simulation.

Experimental investigation and thermodynamic calculation of the Al-Si-V system in the Al-rich corner

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Both experimental investigation and thermodynamic modeling were performed for the Al-Si-V system with available experimental data [1]. Alloys were selected and prepared using arc-melting method to measure the three isothermal section at 500 °C, 600 °C, and 654 °C in Al-Si rich region via a combination of X-ray diffraction (XRD) and scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectrometer (EDS). The detected phases, Al_3V, $Al_{45}V_7$, Fcc(Al), Liquid and (Si), could equilibrated with Si_2V. The temperatures of invariant reactions of the Al-Si-V system were measured by means of differential scanning calorimetry (DSC) measurements. Six invariant reactions between 500 °C and 1100 °C of the Al-Si-V system were determined and a new invariant reaction was determined by experiment. In the present modeling, the Si-V system was re-optimized to obtain the congruent melting point of Si_3V_5, which performed more consistently and reliably than previous results. The ground state energies values of end-members for Al-Si-V intermetallic compounds based on DFT calculations at 0 K were compiled for the thermodynamic description of the Al-Si-V system. A self-consistent thermodynamic description was obtained by a combination of experimental results and first-principles calculations.

[1] Beatrix Huber et al. Intermetallics, 18 (2010) 606–615.

Kang Li

I am a third year Master Candidate in the Materials Science and Engineering of Shanghai University. My research interest is composition design of hot-dip Al-Zn-Si coating from thermodynamic aspects.

CALPHAD assessment of the key ternary and quaternary systems in Ti alloys

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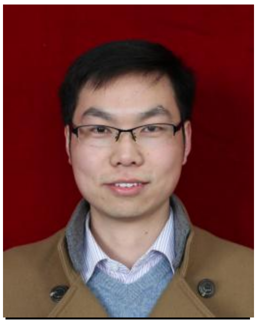
Titanium alloys have been widely used in aviation, aerospace, biomedical applications etc. due to their attractive properties. The design of Ti-based novel materials requires information about the phase equilibria and thermodynamic properties in the ternary and quaternary systems in Ti alloys. Based on the thermodynamic descriptions of constitutive binary systems as well as the experimental phase equilibria data of the ternary and quaternary systems available in the literature, some ternary and quaternary systems in Ti alloys have been evaluated using the CALPHAD approach. A set of self-consistent thermodynamic parameters for these systems is obtained [1,2]. Some isothermal sections and vertical sections are calculated. The complete liquidus projection is also presented. The present thermodynamic description can satisfactorily account for most of the reliable experimental data.

The financial support from the National Natural Science Foundation of China (Nos. 51501002 and 51601228), the China Postdoctoral Science Foundation (No. 2015M581972), and the Hunan Provincial Natural Science Foundation for Youth of China (No. 2016JJ3152) are greatly acknowledged.

[1] B. Hu, et al., Calphad, 55 (2016) 103-112.
[2] B. Hu, et al., J. Min. Metall. Sect. B-Metall., 2017, in press.



Biao Hu

Male, Ph.D., Associate Professor, Master Tutor, graduated from Central South University, China, majored in Materials Physics and Chemistry, main research: Phase Diagram Determination, Thermodynamics and Dynamics Calculations, Solidification Process of Alloys, et al.

Liquidus and solidus projections of the Fe-Co-S system

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Cobalt is extracted as a byproduct of oxidizing nickel and copper-cobalt ores during pyrometallurgical processing. Received mattes which contain up to 12 % mass of cobalt can be directly related to the Fe-Co-S system. Phase relations in the Fe-Co-S system were studied experimentally in Refs. [1-4]. Vogel and Hillner [1] reported liquidus projection and several vertical sections of the Fe-Co-S system. Three invariant reactions on the liquidus projection were detected [1,2] and then included to the scheil scheme reaction with some corrections [5]. Based on the literature data for the boundary binary systems, the Fe-Co-S was partially calculated thermodynamically [5,6]. Mainly isothermal sections at high temperatures (in the temperature range between 1100°C and 1350°C) were calculated. Nevertheless, the thermodynamic data have some contradictions with respect to the available literature data.

Thus, the aim of the present work is an experimental reinvestigation of the phase equilibria in the Fe-Co-S system with the subsequent possibility of thermodynamic calculation of the entire system. For this, about 90 different compositions of the system were prepared by melting in an induction furnace followed by quenching in water. Samples were examined by X-ray diffraction. The microstructure characterization was carried out using SEM/EDX. Phase transformations temperatures and melting behavior of the samples were studied by DTA. Combination of the obtained results and mathematical treatment of these for the liquidus temperatures allowed visualizing phase transformations of the Fe-Co-S system as the liquidus and solidus projections.

[1] Vogel R., Hillner G.F., Arch. Eisenhuettenwes., 1953, 24, pp. 133-141.
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[3] Chen Y.O., Chang Y.A., Metall. Mater. Trans. B, 1978, 9B, pp. 61-67.
[4] Soltanieh M., Toguri J.M., Sridhar R., Metall. Mater. Trans. B, 1997, 28B, pp. 647-650.
[5] Raghavan V., Phase Diagrams of Ternary Iron Alloys, Indian Institute of Metals, Calcutta, 1988, 2, pp. 93-106.
[6] Kongoli F., Pelton A.D., Metall. Mater. Trans. B, 1999, 30B, pp. 443-450.

Phase Equilibria of the Gd-Fe-B Ternary system at 873K and 1073 K

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The phase equilibria of the Gd-Fe-B ternary system at both 873 K and 1073 K have been investigated by means of powder x-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersion spectroscopy (EDS) techniques. The existence of ternary intermetallic compound $Gd_2Fe_{14}B$ with space group $P4_2/mnm$ as $Nd_2Fe_{14}B$ structure type, $GdFeB_4$ with space group Pbam as $YCrB_4$ structure type, $Gd_5Fe_2B_6$ with space group R-3m as $Pr_5Co_2B_6$ structure type and $Gd_{1.14}Fe_4B_4$ with space group Pccn as Re_{1+x} Fe_4B_4 structure type was confirmed. In the present work, it was found that the binary inermetallic compound $Fe_{23}Gd_6$ is not stable, while it decomposes into two phases $Fe_{17}Gd_2$ and Fe_3Gd and the ternary intermetallic compound $GdFe_2B_2$ is not observed. Both of the phase equilibria of the Gd-Fe-B ternary systems at 873 K and 1073 K consist of 16 single-phase regions, 33 two-phase regions and 18 three-phase regions.

G. Cheng

The research topics are the experimental determination of the binary and ternary phase diagrams and the investigation of the magnetic thin-film materials.

Next Generation CALPHAD Databases: Accurate approximation of the Debye model and its application for phase diagram calculations

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1 – Interdisciplinary Centre for Advanced Materials Simulation (ICAMS), Ruhr-Universität Bochum, Universitätsstraße 150, 44801 Bochum, Germany

2 – Engineering and Science Directorate, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109, USA

3 – Department of Mathematic, Institute of Statistics, Ruhr-Universität Bochum, 44780Bochum, Germany

4-State Key Laboratory of Powder Metallurgy, Central South University, 410083 Changsha, PR China

An accurate non-integral approximation of the Debye model of heat capacity has been developed. The approximation is based on segmentation in temperature and the linear combination of the Einstein function [1]. The method gives an accurate description of the Debye function and has been validated from a mathematical and physical point of view. The method is applied to the experimentally determined heat capacity data of pure Al, Cr, Fe, Ge, Ir, Mo, Nb, Ta, W and Ni. The proposed non-integral solution is accurate for the entire temperature range and can be easily integrated into the TDB format of thermodynamic databases. An example of thermodynamic calculation performed in the pycalphad open-source software [2] using the newly proposed approximation of the Debye model will be demonstrated.

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[2] R. Otis, Z.-K. Liu, pycalphad: Calphad-based computational thermodynamics in python, Journal of Open Research Software 5 (1).

Roslyakova Irina and Richard Otis

A short CV may be inserted here, summarizing the academic education and current position. The research topics and scientific interests may also be indicated in this frame. Text should be written using Arial 10 pts.

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The first principle calculation and experimental investigation of the $Ti_2(Al,Si)C$ solid solution

Kseniia Piven[a], Chengjie Lu[b], Jie Zhang[b], Gilles Hug[a] and Aurélie Jankowiak[c]

[a] ONERA-CNRS, LEM, France
[b] Harbin Institute of Technology, China
[c] ONERA-DMSC, France

Previous experimental studies of the brazing of the Ti_2AlC ceramic using an Al-Si eutectic filler alloy has revealed that a $Ti_2(Al,Si)C$ solid solution can be formed within the brazing joints although the Ti_2SiC ceramic, with the typical 211 structure of MAX phase, is unstable according to the known Ti-Si-C ternary phase diagram [1]. Using density functional theory (DFT) and quasi-harmonic approximation (QHA) the electronic structure and the vibrational spectra of the $Ti_2(Al,Si)C$ solid solutions are calculated at different concentrations. The thermal properties, (heat capacity, enthalpy and entropy) have been computed and the Gibbs free energy of the $Ti_2(Al, Si)C$ solid solution is interpolated at all concentrations using the ideal solution model tacking into account the configurational entropy. Finally, the comparison with the Gibbs free energy of the competition phases, including the Ti_2AlC, Ti_3SiC_2, $TiSi_2$ and $Ti_5Si_3C_x$ [2], allows to define the solubility limit of Si content in the $Ti_2(Al,Si)C$ phase. These predictions are compared with experimental processing of $Ti_2Al_{(1-x)},Si_xC$, at different Al/Si ratio (with x=0.25; 0.5; 0.75). The different powder mixtures of Ti, Al, Si and TiC were ball-milled using tungsten carbide media in ethanol. After drying (rotary evaporation), reactive hot pressing was performed with a heating rate of 5°C/min up to the final temperature, under 1 bar of Ar atmosphere and 30 MPa. Samples were characterized by X-ray diffraction and scanning electron microscopy methods in order to observe the formation of the MAX phase.

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[2] V.J. Keast, et al, Prediction of the stability of the $M_{n+1}AX_n$ phases from first principles, Phys. Rev. B 80 (21) (2009) 7.

Kseniia Piven

PhD student since November 2016 at Laboratory of Microstructural Investigations (LEM), ONERA-CNRS – The French Aerospace Lab. PhD project focusing on the synthesis and optimization of the properties of Ti_2AlC MAX phases for high temperature applications. Proposed materials are tested as protective coatings for TiAl-based alloys.

Experimental and thermodynamic study of Li-O and Li_2O-P_2O_5systems

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† Present address: Departments of Materials Physics, School of Physics and Optoelectronic Engineering, Nanjing University of Information Science & Technology, Nanjing, China

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As part of ongoing projects to develop oxide thermodynamic databases for designing and producing LFP-based cathode materials, thermodynamic evaluation and modeling of the Li – O and Li_2O – P_2O_5 is examined in this work. The Li – O and Li_2O – P_2O_5 binary systems have been assessed and optimized based on the available experimental and ab-initio data using the FactSage thermodynamic software. Thermodynamic optimization/modeling of Li_2O – P_2O_5 system was carried out for the first time. The Modified Quasichemical Model (MQM) with quadruplet approximation, which takes short-range ordering of first-nearest-neighbors (FNN) and second-nearest-neighbors (SNN) simultaneously into account, is used for the liquid phases in the Li – O and Li_2O – P_2O_5 systems. Optimized model parameters of the Gibbs energies for all the phases considered which reproduced all the reliable experimental data to satisfaction have been obtained for the Li – O and Li_2O – P_2O_5 binary systems. DSC-TGA experiments on the selected compositions of Li_2O – P_2O_5 system were carried out to verify/confirm the phase transition temperature reported in the literature.

Liling Jin

With Ph.D in thermodynamics, BSc and MSc in metallurgical engineering, I am working as research associate in the group of Prof. Patrice Chartrand, co-director of CRCT and FactSage developerat Ecole Polythnique de Montréal, Canada. The research interestsare: 1) thermochemical modeling and calculation of phase diagrams on metallic systems (Al, Mg, Rare earth alloys), oxide systems ($LiFePO_4$ battery), and fertilizer systems. 2) Related industrial applications or processes.

Thermodynamic description of spinodal decomposition in Ni-based superalloys

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[a] School of Metallurgy and Materials Engineering, University of Tehran, Tehran, Iran
[b] Department of Mechanical Engineering, University of California Riverside, Riverside, USA
[c] Department of Materials Science and Engineering (POSTECH), Pohang, South Korea

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The precipitation of ordered γ' phase in Ni-based superalloys has been extensively investigated in the last 50 years. However, a small portion of them has focussed in the investigating the early stages of precipitation of γ' inside the γ phase matrix. Some investigators have indicated that the formation of γ' occurs by classical nucleation and growth mechanism. On the contrary, others have recently indicated that spinodal decomposition is the responsible mechanism for γ' precipitation [1,2]. In the present investigation, thermodynamic modeling, complemented by experimental verification, have been used to explore the precipitation phenomena with the goal of resolving the controversy. The Gibbs free energies of γ and γ' phases for the reported Ni-based superalloys were calculated employing two sublattice model [3,4]. The possibility of spinodal decomposition was then determined from the curvature change in the Gibbs energy function of the FCC phase. The calculations also included the strain energy as well as gradient energy of interface in order to attain more accurate region for the spinodal decomposition. The calculation results confirm that both classical nucleation and spinodal decomposition are possible depending on the level of supersaturation of the FCC phase; lower supersaturations resulted in positive curvature while higher supersaturations resulted in negative curvature and spinodal decomposition. Furthermore, inspired by this description, specific experiments were conducted using Ni-Al binary system as a model alloy. 3-D atom probe tomography (APT) was utilized to determine γ' phase formation at the early stage of precipitation in Ni-18Al (at%). As expected from thermodynamic calculations, the APT analysis indicated spinodal decomposition of γ' phase formation inside γ matrix at higher supersaturations.

[1] G.B. Viswanathan et al., Scr. Mater., vol. 65 (2011), pp. 485.
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[3] I. Ansara et al., J. Alloys Compd., vol. 247 (1997), pp. 20.
[4] N. Dupin, Thesis, Institut Nationale Polytechnique de Grenoble, France, 1995.

Farsad Forghani

PhD Candidate in Materials Science and Engineering,
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Research interests:
Computational Materials Science, CALPHAD, Physical Metallurgy of Structural Materials

Isothermal section of the Phase diagram of the Co-Pt-Ho ternary system at 773K

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The solid-state phase equilibria in the Co-Pt-Ho ternary system at 773K were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersion spectroscopy (EDS) techniques. It is found that the 773K isothermal section consists of 23 single-phase regions, 43 two-phase regions and 21 three-phase regions. At 773K, it is observed that the maximum solid solubilities of Pt in $Co_{17}Ho_2$, Co_3Ho_4, Co_7Ho_{12} and $CoHo_3$ are all below 1 at.% Pt, while in Co_7Ho_2, Co_3Ho and Co_2Ho they are about 1.5, 1 and 1.5 at.% Pt, respectively. The highest solubilities of Ho in α_1-(Co, Pt), ε-(Co, Pt), α_2-(Co, Pt), CoPt, $CoPt_3$ and α-(Pt, Co) are all below 1.5 at.% Ho. The maximum solid solubilities of Co in $HoPt_5$, $HoPt_3$, Ho_3Pt_4, HoPt, Ho_5Pt_4, Ho_5Pt_3, Ho_2Pt and Ho_3Pt are less than 1 at.% Co, with uniquely being about 18.2 at.% Co in $HoPt_2$. No new ternary compounds were observed.

Y.S. Du

The research topics are the experimental determination of the binary and ternary phase diagrams and the investigation of the magnetic refrigeration materials.

Thermodynamic modelling of lead chalcogenide thermoelectricsfor optimized ZT

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[2]QuesTek Innovations LLC, Evanston, IL

Pb based chalcogenides are promising candidates for high efficiency thermoelectrics. The alloying of PbTe with PbS leads to a combination of nanostructures and point defects that help scatter heat-carrying phonons [1]. Alloying with PbSe allows for manipulation of the PbTe band structure as well as introducing point defect sites for scattering phonons [2]. The simultaneous addition of PbS and PbSe continues to increase the ZT value to approximately 2 [3]. It is clear that a firm understanding of this multicomponent system is an essential step in optimizing these promising materials.

The intrinsic defects in each of these binary semiconductors are doubly-ionizedvacancies and play a key role in their carrier concentrations. The modelling of vacancies in multicomponent databases has been a known issue and much work has gone into determining the best method. Based on the work of Rogal et al [4], a multicomponent database for these thermoelectrics has been built that accurately describes the intrinsic carriers of the systems. The end-members containing vacancies have been fixed to a structure specific value of 2.3RT. The system specific interaction parameters can then be related to the formation energy of the defect, which have been determined by first-principle calculations. The first-principle calculations are used as a starting point and the experimental data is well described without further interaction parameters. These thermodynamic descriptions, coupled with electronic and thermal conductivity modelling based on the Debeye-Callaway model, can then be used to determine the optimized composition and processing parameters.

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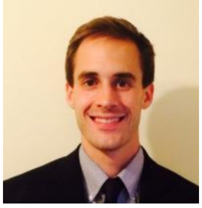

Matthew Peters

Matthew is a fourth year PhD student in Peter Voorhees's group at Northwestern University. His work involves building thermodynamic databases based on the CALPHAD method for industrial applications. Prior to graduate school, he taught 4th and 5th grade elementary school and recently finished an internship at SpaceX. Outside of research, he focuses on developing his leadership and communication skills as a weekend instructor for the Center for Talent Development at Northwestern.

Thermodynamic stability of substitutional- and interstitial-type of boron in fccFe

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It is well known that boron(B) atoms in steels tend tostrongly segregate tograin boundaries.[1] Even if the added amountis in the order of ppm, B brings significant effectsto the properties of steels such as hardening grain boundaries and improving mechanical properties.[2] On the other hand, excessive addition of the element leads to rather negative effects, for example, as causing steel embrittlement due toprecipitation of compoundsat grain boundaries.[3] Therefore,to improve the mechanical properties of steels,it is necessary to control the behaviors considering such complex characters of B. One of the most important issues in the features may be on the occupation sites of B in solid Fe. The behavior plays a key role in diffusion during segregation. However,experimental difficulties mainly caused by its low solubility prevents from precisely comprehending the behavior, and the question still remains an unsolved problem. On the basis of this background, we investigated the thermodynamic properties of Bin fccFeusingthe cluster expansion and cluster variation method(CE-CVM)based onthe first principles calculations.

Figure1 showsthe calculated freeenergy curvesfor the fcc Fe-B binary system at *T* = 1300 K. In this figure, we compared three types of B solution. A symbol ⋈ shows the case that B occupies only the substitutional site (S-site) in fcc structure, while ✕ is fortheoctahedral interstitial site (I-site). The case of existing in both sites at a ratio of 1:1 isdenoted by the symbol ⚠. According to the results,B atoms in the I-siteare more stable thanthose inthe S-site inlower concentration region. In contrast, as B contentincreases, mixed stateof solution becomes a dominant mode. This tendency can be explained by the effect of configurational entropy for solutionof B. We will also discuss the magnetic modelsused in the calculation as well as the temperature dependence of the free energy surfaces.

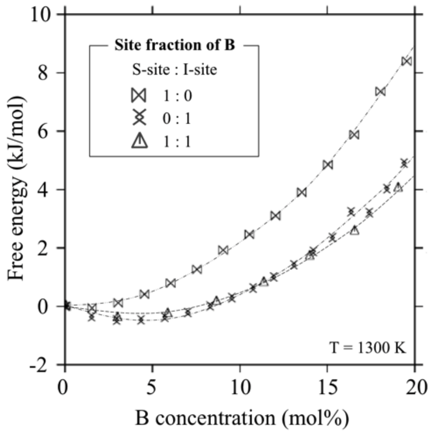

Fig.1 Free energies of fcc phase when changing the occupation sites of B in Fe.

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First-principles calculations and thermodynamic modeling of the Cu-Sn-S system relevant to CZTSSe photovoltaic materials

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Achieving sustainable penatration of solar photovoltaics (PV) at a scale to displace fossil fuels for electrcity production will require a PV absorber material that has a high absorption coefficient, incorporated into a high efficiency multijunction thin-film cell and be earth abundant. The chalcogenide $Cu_2ZnSn(S,Se)_4$ (CZTSSe) is a promising PV absorber material that shows promise for meeting these criteria. The material chemcistry of this 5-component system, however, is not well understood and depositing the kesterite phase with suitable doping and without secondary phases has proven difficult. Thus a self-consistent thermodynamic description of the CZTSSe system would be extremely helpful in developing a process depositing thin films of this material. This work examines the ternary Cu-Sn-S subsystem. Specifically, a thermodynamic description of the Cu-Sn-S system is developed using an integrated approach of density functional theory (DFT) based first-principles calculations along with the CALculation of PHAse Diagram (CALPHAD) method. The two binary systems Cu-S and Sn-S are revisited to correct for inaccurate thermochemical data of sulfides in the literature. To describe the predominant defect complexes, a solid solution model for the digenite phase is proposed, which uses first-principles calculations to estimate CALPHAD model parameters. This approach produces very good agreement between the experimental data, first-principles calculations, and the CALPHAD modeled properties.

Pin-Wen Guan

Ph.D. candidate,Materials Science and Engineering,Pennsylvania State University. He is currently interested in thermodynamic modeling of solar materials.

Design of Ti-Alloy by Integrating High Throughput Experiments and Calculations

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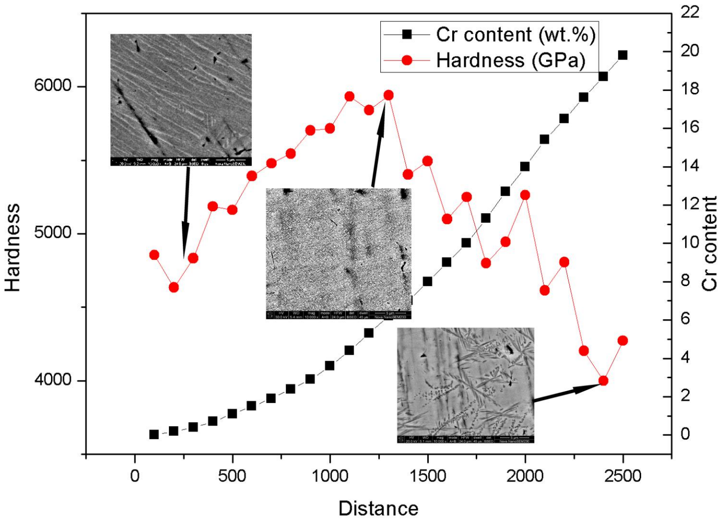
The speed for development of new materials is too slow has been emerging as the bottleneck for the innovation of the manufacturing technology. However, application of the computer and information technology to the materials science and engineering has made it possible for us to estimate the properties for single phases, model the microstructure evolutions, and predict the material properties. On the other hand, in order to verify the calculation results, we should develop and use the high throughput methods. In this talk, we introduce some new progress in materials calculation and high throughput experiments, especially the high throughput determination of the phase diagram, diffusion coefficients, and thermal-physical properties; and the high throughput verification of the response of the materials microstructure and properties to the compositions and heat treatment temperatures. Some preliminary results on the attempt of development of high strength and high toughness Ti alloy alloy has been introduced.



Composition-microstructure-properties relationship of the series Ti6Al4V-Ti6Al4V20Cr Diffusion Couple

Libin Liu

Fellow of Chinese Materials Research Society, Academic Member of the Phase Diagram Committee of Chinese Physical Society, Senior Professor and Deputy Dean of School of Materials Science and Engineering, Central South University. Liu's main research interests include: phase diagram, calculation thermodynamics, diffusion kinetics, and material design. He has published more than 100 scientific papers, which are widely cited by the scientist all over the world.

Phase relations of the Ce_2Co_{17}-Sm_2Co_{17} system

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The phase relations in the Ce_2Co_{17}-Sm_2Co_{17} system in a whole concentration range have been studied by means of X-ray powder diffraction (XRD), differential thermal analysis (DTA) and scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS). The XRD results reveal that all the alloys $(Ce_{1-x}Sm_x)_2Co_{17}$ (x = 0.0−1.0) belong to the rhombohedral structure type (space group R-3m) similar to the end member Sm_2Co_{17} in the presently investigated system. The continuous solid solutions were formed in the solid state. The DTA measurements show that the decomposition temperature of the $(Ce, Sm_x)_2Co_{17}$ phase increases gradually with increasing the Sm content. For the metallic alloys $(Ce_{1-x}Sm_x)_2Co_{17}$ with x=0.0−0.6, the reaction of $(Ce, Sm_x)_2Co_{17}$→L+Co and L+Co→L, is present, while for alloys $(Ce_{1-x}Sm_x)_2Co_{17}$ with x=0.6−1.0 phase transformation is a congruent melting when the temperature is increased. Curves of magnetic field thermo-gravity reveal that the Curie temperature (T_c) increase monotonically with the Sm content for the $(Ce_{1-x}Sm_x)_2Co_{17}$ alloys, which is similar to the temperature change of the polymorphic transformation α-$(Ce, Sm_x)_2Co_{17}$→β-$(Ce, Sm_x)_2Co_{17}$. On the basis of all the results obtained from the presently investigated samples, the tentative vertical section of Ce_2Co_{17}-Sm_2Co_{17} in the Ce−Sm−Co system has been constructed.

Zhengfei Gu

The research topics are the experimental determination of the binary and ternary phase diagrams and the investigation of the permanent magnetic materials.

Experimental reinvestigation and thermodynamic description of Bi-Te binary System

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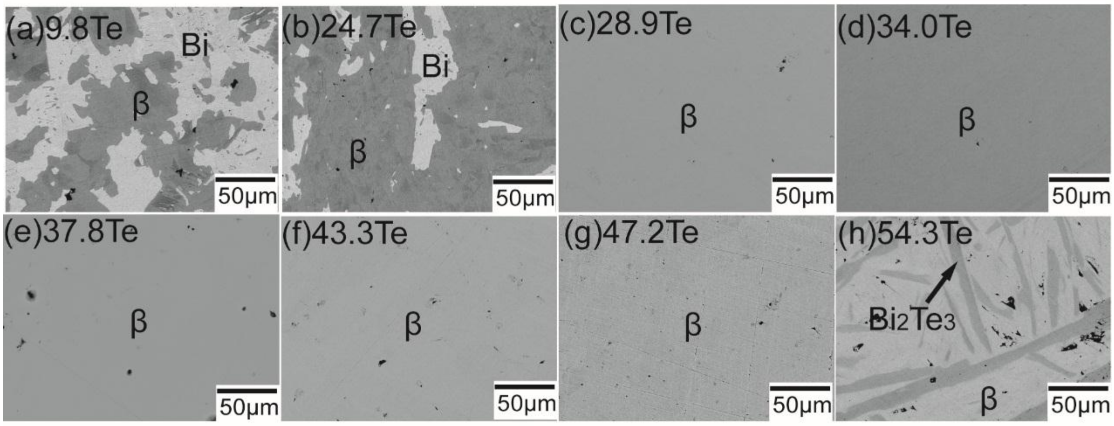
The Bi-Te alloys are well known for good thermoelectric properties at room temperature. Numerous efforts have been made to improve their thermoelectric performance. The performance of Bi-Te thermoelectric materials is strongly associated with the crystallographic structure, thermodynamic stability and phase transformation of Bi-Te compounds which can be readily extracted from the phase diagram and thermodynamic database of Bi-Te system. Thus, the construction of reliable phase diagram and the understanding of phase transformation in Bi-Te alloys are of importance to tune the chemical composition and phase constitution of Bi-Te alloys, thereafter advance the exploration of novel thermoelectric materials. Although the Bi-Te phase diagram has been studied experimentally in a number of works, hardly a consistent phase diagram has been achieved to cover all the available experimental findings.

The Bi-Te binary phase diagram were studied by the phase constitution and microstructure evolution of key alloy samples with 14 different compositions with the help of XRD, SEM, and DSC. The experimental microstructural features and composition distribution indicates the continuous solidus to form the broad solid solution β phase which corresponds to primary lenticular phase in our experiments. The thermodynamic model parameters for the binary system Bi-Te are evaluated on the basis of the experimental information of this work and the reported thermochemical experimental data.



Dr. Ligang Zhang

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Application of the CALPHAD approach and First-principles calculations to electrode materials in Li ion batteries

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Design and development of novel electrode materials is one of the hottest topics in studying Li ion battery. In recent years, density functional theory (DFT) based first-principlescalculations have played an important role for this purpose. The CALPHAD (CALculation of PHAse Diagrams) approach enables calculation of stable and metastable phase equilibria, as well as thermodynamic properties for various materials. The traditional trial-and-error method is being replaced by the integration of CALPHAD with first-principlescalculations, empirical methods and key experiments. The CALPHAD approach has been proved to be a powerful tool in studying electrode materialsin Li ion batteries, not only for calculation of phase equilibria and thermodynamic properties, but also for prediction of cell voltages, which allows for the design of future cathode materials with improved stability and efficiency[1-4]. Examples of the related material systems (including both anodes and cathodes) studied by applying the CALPHAD approach and first-principles calculations are presented.

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Experimental investigation and thermodynamic modelling of LiF-NdF$_3$-DyF$_3$ system

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Electrolysis of molten fluorides is one of the promising methodsforeseenfor the recovery and recyclingof rare earth metals from used magnets. In order to optimally design such processes, knowledge of phase equilibria and thermodynamics of LiF-DyF$_3$-NdF$_3$system is crucial. However,there is a dearth of such informationin the literature [1].In the present workwe reportthermodynamic optimization of LiF-DyF$_3$-NdF$_3$system using the CALPHAD approach. Gibbs energy modelling for LiF-NdF$_3$ system was carried out using the constitutional data from literature [2-4].*Ab initio* calculations were used to obtain enthalpy of formation of LiDyF$_4$,a phase that is found to exist in theLiF-DyF$_3$ system[5]. Along with the constitutional data available in the literature [1-3], thermodynamic modelling was carried out for this system.Liquidus and solidus temperatures and enthalpy of fusion at various compositions were measured usingdifferential thermal analysis (DTA) for the NdF$_3$-DyF$_3$ system. Subsequently, X-raypowder diffraction was employed to confirm the nature of the solid solution.The obtained information was used for modellingGibbs energy functions of equilibrium phases in this system. DTA was also used to obtain the constitutional data pertaining to different compositions inthe LiF-NdF$_3$-DyF$_3$ternary system. The Gibbs energy functions for limiting binaries determinedin this work, along with the experimental data, were used to obtain thermodynamic descriptions of all equilibrium phases in the LiF-NdF$_3$-DyF$_3$system.

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PhD research: “Electrochemical reduction of rare-earth oxides and their mixtures in molten salts” at Technical University of Delft
Master thesis: “Effect of sulfur and carbon content on surface tension of steel” at University of Toronto.
Master degree from Royal Institute of Technology, Stockholm

Thermodynamic properties of liquid In-Li solutions

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The integral molar enthalpy of mixing was determined by the drop calorimetric method for binary In-Li liquid alloys. The measurements were conducted at three temperatures, i.e. 653 K, 940 K and 994 K. A strong negative deviation from the ideal solution was observed, with the minimum value equal to -21.8 kJ/mol for X_{Li} = 0.6277. The analysis of the experimental data suggests that the integral mixing enthalpy of the In-Li liquid solutions is independent of temperature. The maximal differences between the experimental data of this study and the literature once are about 2 kJ/mol. Based on the lithium activity, measured with the use of concentration cell method, and calorimetric measurements of the mixing enthalpy change the equation of Redlich-Kister was determined and next the thermodynamic functions of the liquid In-Li alloys were calculated and compared with those from experiments. Additionally, the excess stability, structure partial factor Scc(0) and short range order parameter was counted and discussed. These investigations are a part of the research program on thermodynamics and phase diagram of the Ge-In-Li system.

Acknowledgements

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Ab-initio study of finite pressure-temperature phase stability for magnetic materials

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For the rational designing of novel functional materials, the phase diagrams with reliable information about the phase stability at finite temperature and pressure F(T, P) are valuable to guide experimental synthesis and to understand the thermodynamic properties of various materials. At the *ab initio* level, the main problem is how to obtain the Gibbs free energy G(P, T), with all entropy terms from lattice, electrons, and particularly magnetic ordering for magnetic materials, based on density functional theory (DFT) calculations. Comparing the CALPHAD modeling and molecular dynamics, where the interatomic potentials is demanding, moreover thermodynamic models based on DFT calculations have improved remarkably for determining properties at F(T, P), exhibit consistent agreements with experimental observations [1] and the calculated phase diagrams are also good agreement with the CALPHAD method [2].

In the present work, we consider *ab initio* strategy to determine the G (T, P) energies of magnetic $CaCo_2$ and $CaCo_5$ as a f(P, T) by performing DFT calculations, which is given by G(P, T)= H(V, T) + PV, where PV is enthalpy and H(V,T) is Helmholtz free energy as a f(T, V), is given by $H(V, T) = E_0 (V) + F_{lat}(V, T) + F_{ele}(V, T) + F_{mag}(V, T)$, where E_0 is the energy at 0K from DFT calculations, $F_{lat}(V, T)$ vibrational free energy, $F_{ele}(V, T)$ electronic excitation energy, and $F_{mag}(V, T)$ the magnetic free energy.

Based on the above theory, we characterize the phases diagram of Ca-Co system, focusing the phase stabilities at F(T, P). After obtaining the G(P, T) of the binary compounds and the Ca and Co elements, we evaluated the formation energy ΔH and formation enthalpy ΔG. Our calculations show that the ΔH and ΔG are negative at high pressure (25 GPa) and high temperature (1000K) for both the system. But the ΔH and ΔG are more negative for $CaCo_2$ than $CaCo_5$, which indicate that the synthesis of $CaCo_2$ from initial components is energetically more favorable. Additionally, we also determine the convex hall ($2CaCo_5 \rightarrow 2CaCo_2 + 6Co$), and found that the ΔH and ΔG are positive for $CaCo_5$ through the whole T and P range represent the existing of $CaCo_2$ only. Our theoretical results are in good agreement with the experimental evidences. Here, neglecting the magnetic and electronic contributions denotes that the lattice contribution is more dominanting in determining the phase stabilities.

[1] Zi-Kui Liu, *JPEDAV*, (2009), 30, 517.
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Harish Kumar Singh

I did my M.Sc. in Chemsitry from Indian Institute of Technology Roorkee. Curently, I am doing my Ph.D. in the Theory of Magnetic Materials group of Prof. Hongbin Zhang at TU Darmstadt, Germany.
My research topic is “Finite temperature phase diagram study of Magnetic materials based on CALPHAD method”. In addition I have research interests in computational materials designing for energy applications and spintronic devices.

Stability study of Ni_8V phase

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Ni_8V is a phase discovered by electrical resistivity measurements in the early 70ies [1]. Its stability is not well known and critical evaluation of Ni-V binary system presents it as a “dashed” phase indicating that more research is necessary to completely characterize this phase [2]. In the two available CALPHAD assessments for this system [3,4] this phase is not considered. Very recently High Throughput (HT) calculations using First Principles (FP), discuss its stability together with other compounds with the same stoichiometry [5].
In this work we do FP calculations with the objective to carefully investigate the ground state of this tetragonal phase. As a further objective we would like to associate this phase with Ni(V) FCC solid solution and understand the order-disorder transformation indicated by the earlier investigation of [1].

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[5] Taylor et al., Journal of the American Chemical Society, 132 (2010), 6851-6854.

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-Student assistant at the Department of Scale bridging Thermodynamics and kinetic Simulation.

-Interests: CALPHAD, Phase Field and Microstructure, *Ab initio* Calculations

Progress in the development of the OECD-NEA Thermodynamics Advanced Fuels – International Database (TAF-ID): Application calculations

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[f]Royal Military College of Canada, Kingston, Canada
[g]University of Ontario Institute of Technology, Oshawa, Canada
[h]Canadian Nuclear Laboratories, Chalk River, Canada
[i]Central Research Institute of Electric Power Industry, Tokyo, Japan
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[k]Korean Atomic Energy Research Institute, Deajeon, Korea
[l]Nuclear National Laboratories, United Kingdom
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The Thermodynamics of Advanced Fuels- International Database project (TAF-ID) was initiated in 2013 under the Nuclear Energy Agency (NEA) of the Organization for Economic Cooperation and Development (OECD) to make available a comprehensive, internationally recognised, and quality-assured database for the thermodynamic modelling of advanced nuclear fuels [1]. The database is being developed using the Calphad method. In its current state, it contains 41 elements and assessments for 204 binary and 66 ternary systems. The content of the database will be described andexamples of calculations using the database will be presented for several nuclear applications.

[1] www.oecd-nea.org/science/taf-id/

Assessment of NiO-SiO_2 System with Kapoor-Frohberg-Gaye Model

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[a]Research and Development Center - Villares Metals S/A
[b]Polytechnic School - São Paulo University

NiO-SiO_2 system is one of the important systems to understand metal-slag reactions during the elaboration process of Ni-based alloys by conventional melting practices like Electric Arc, Ladle and VOD (Vacuum Oxygen Decarburizing) furnaces as well by special process as ESR (Electro-Slag Remelting). During the elaboration process of Ni-based alloys by conventional melting process, silicon can be added as a de-oxidant for the alloys that allow this element in its composition or it can be added as a result of the reduction of SiO_2 from the slag by elements as titanium, aluminium or even magnesium. For the slags of ESR process, usually SiO_2 is added to control the fluidity as well the basicity of the slag and can be incorporated to the Ni-based alloy by reduction of SiO_2. Usually, the presence of silicon in the Ni-based alloy is deleterious, once this element improves the kinetic of precipitation of several TCP phases as μ and Laves phase [1-2]. So the control of the amount of this element on the Ni-based alloy is important to assure the quality of the final product.

NiO-SiO_2 system was already assessed by several authors [3-5], however none of the have used the Kapoor-Frohberg-Gaye model [6], which is necessary to use this system with the SLAG® database from Thermo-Calc® package.

This work presents the thermodynamic assessment of NiO-SiO_2 system using Kapoor-Frohberg-Gaye model coupled with PARROT® module from Thermo-Calc® package. As a result of the present work there were obtained the thermodynamic parameters to describe the phases of NiO-SiO_2 system.

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Alexandre Bellegard Farina

Graduation in Metallurgical Engineering,Master and PhD by Polytechnic School of São Paulo University.MBA in Industrial Management by FundaçãoGetúlio Vargas.Currently developing the Pos-PhD at Polytechnic School of São Paulo University. Work as Senior Researcher at Villares Metals with focus on the development of Ni-based alloys, thermodynamics, alloy design and phase transformations.

Development of cemented carbides through thermodynamic calculations

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Cemented carbide is a kind of multicomponent multiphase material and its manufacture process involves complex thermodynamics and kinetics phenomena. In order to provide theoretical basis for the development of cemented carbides, a thermodynamic database was established and the influence of various process parameters on the microstructure was studied by using a hybrid approach of designed key experiments and CALPHAD method, which can be summarized as following. i) General applications of thermodynamic calculations in the design of cemented carbides were illustrated. ii) The saturated solubility of various elements in Co binder phase and cubic phase was investigated through thermodynamic calculations and experimental verification. iii) With the aid of thermodynamic calculations, the spinodal decomposition process of cubic phase was studied and applied to the control of the formation of nano-scale second cubic grains, which can enhance the hardness and strength of cemented carbides. iv) Smaller grain size of cubic phase can be obtained by controlling the dissolution and precipitation process.

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Research Interests: Computational Thermodynamics; Materials Design; Hard Materials.

Prediction of Free Energy at Finite Temperatures by First-Principles Calculations and Statistical Mechanics

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Free energy such as Helmholtz energy and Gibbs energy of a structure is nowadays routinely predicted by first-principles and phonon calculations using the potential energy from zero Kelvin and used extensively in the CALPHAD community [1,2]. However, this approach fails in predicting anomalies at high temperatures such as the critical point, or instability. Recently we developed a new theory to predict critical phenomena and related property anomalies [3]. In the presentation, our further investigation of the theory will be presented in the framework of fundamental thermodynamics, Lennard-Jones potential, and statistical mechanics. It is anticipated that this theory can be used to predict a wide range of properties at finite temperatures.

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Development of lightweight high entropy alloys using coupled CALPHAD-DFT modeling

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High entropy alloys (HEAs) are a new class of multicomponent metallic alloys in (near) equal atomic percent with exceptional mechanical, chemical and magnetic properties. CALculation of PHAse Diagrams (CALPHAD) modeling and density function theory (DFT) calculations were used to design lightweight HEAs for structural applications. The new alloys were prepared using low-cost melting and casting processes for model validation and mechanical testing. Heat treatments were conducted based on CALPHAD modeling results. Advanced characterization techniques were used to identify phases in the alloy microstructures. The observed microstructures were used to validate the CALPHAD calculations. Mechanical tests were also performed to verify the results of DFT calculations. It has been demonstrated that the coupled CALPHAD-DFT modeling approach is an effective way in developing new lightweight high entropy alloys.

PB

Xuejun Huang

Xuejun Huang is currently pursuing his Ph.D. degree at The Ohio State University. He received his Bachelor of Science in Materials Science and Engineering also at OSU in 2015. He was honored with Mars G. Fontana Award for his achievement in the field of metallurgy research during undergraduate study. His research focuses on alloy design using computational tool, such as CALculation of PHAse Diagram (CALPHAD) and first-principles calculation. His current projects include development of lightweight high entropy alloys using CALPHAD.

Thermodynamic modeling of FeO-Fe_2O_3-Ti_2O_3-TiO_2 system

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A complete literature review, critical evaluation and thermodynamic optimization of phase diagrams and thermodynamic properties of the FeO–Fe_2O_3–TiO_2–Ti_2O_3 system at 1 atm pressure were performed. The molten oxide phase was described by the Modified Quasichemical Model considering the short range ordering in molten oxide, and the Gibbs energies of solid solutions (pseudobrookite, ilmenite and spinel) were described using the Compound Energy Formalism considering the crystal structure of each solid solution. A set of optimized model parameters of all phases was obtained which reproduces all available and reliable thermodynamic data and phase diagrams within experimental error limits from 25 °C to above the liquidus temperatures over the entire range of composition under the oxygen partial pressures from metallic saturation to 1 atm. The complex phase relationships in the system have been elucidated, and discrepancies among the experimental data have been resolved. The optimized thermodynamic database, together with existing liquid steel and other databases, can be used for the thermodynamic calculations related to titanium distribution between steel and slag; and oxide inclusion generation in high titanium steel production.

Sourav Kumar Panda

Sourav Kumar Panda is currently a PhD student (4th Year) with Prof. In-Ho Jung at McGill University, Canada. He is working on developing thermodynamic database of MnO_x-containing and TiO_x-containing multicomponent oxide systems for pyrometallurgical applications. He holds a master degree from the same group working on Ca-Mg-Mn-O system.

Analysis at high lateral resolution of Mo-Ni-Re system with the CAMECA SXFIVE FE

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The development of the Schottky emitter and its implementation as electron source in Electron Microprobe has significantly improved the characterization of materials in metallurgy.

The Field Emission (FE) Source allows major elements and trace elements analysis with high beam currents thanks to the high brightness of the source and the excellent stability of the beam current, trading off spatial resolution.

As X-rays are generated from a much larger diameter than the diameter of the incident electron beam, it is advised to work at low voltage and low beam current in order to take full advantage of the small spot sizes achievable with a Field Emission Source. Thus, at low beam voltage, the analytical resolution is not limited anymore by the beam diameter but only by the diameter of the X-ray emission volume.

One of the advantages of the FE Source is to obtain fine focused electron beam at low beam voltage (≤10 keV) while maintaining high and stable beam current. In these experimental conditions, the penetration depth of the primary electrons and thus the interaction volume- in which electrons are scattered and generate X-rays- decreases to sub-µm scale (compared to micron scale of the traditional Electron Microprobe at 15 or 20 keV).

Thanks to WDS spectrometers with sub 10eV energy resolution, accurate qualitative and quantitative analysis can be achieved even on sub-micron phases at low beam energy and high lateral resolution using L- and M-Lines for heavy elements.

The SXFive FE analytical capabilities will be illustrated by analysing several isothermal sections (1200°C & 1600°C) of the Mo-Ni-Re system [1]. X-ray maps and backscattered electrons (BSE) images acquired at low beam voltage will demonstrate the analytical resolution that can be achieved using the SXFive FE.

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Anne-Sophie Robbes

After obtaining my Ph.D. in composite materials at the Synchrotron Soleil and the French Neutron facility (LLB, CEA-Saclay), I joined CAMECA in 2012 as an Application Engineer on the EPMA tool (LEXES) dedicated to the semiconductor field. In 2016, I was put in charge of the instrument as Technical Product Manager and started working on the EPMA SX Five. I'm today Technical Product Manager of the LEXES and EPMA tools.

Thermodynamic properties of alloys of the binary Sb–Yb system

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The antimony alloys with lanthanides (Ln) and some transition metals (e.g., Mn) are used as magnetic and thermoelectric materials. The compounds in such systems, especially Ln_3Sb_4, are very refractory in comparison to the pure components. In the case of the Sb–Yb system, the melting temperature of most compounds are comparable to the boiling temperature of Sb and far exceed the boiling point of Yb. This makes a question of finding indirect methods of synthesis of these compounds actual, as well as investigation of their physicochemical properties. The thermodynamic modeling plays a large role here; however, it is impossible to conduct reliably until there is at least some minimum experimental information.
Mixing enthalpies of melts of the binary Sb–Yb system have been determined for the first time in the ranges $0<x_{Yb}<0.155$ at 960–1030 K and $0.89<x_{Yb}<1$ at 1140 K using isoperibolic calorimetry. The melts form with great exothermic effects: $\Delta\overline{H}_{\mathrm{Sb}}^{\infty}=-260$, $\Delta\overline{H}_{\mathrm{Yb}}^{\infty}=-205$ kJ/mol. An ideal associated solution (IAS) model [1] has been selected to describe the temperature and concentration dependences of thermodynamic properties of the melts, and the parameters of the model have been optimized through self-consistent analysis of the available data on the phase diagram. The model description allows to calculate the Gibbs energies and entropies of mixing of the melts, the activities of the components and the molar fractions of the associates, and the enthalpies and entropies of formation of the solid phases.
A good agreement of the liquidus curve of the Sb–Yb phase diagram with the data from literature is achieved, except the region of alloys high in Yb. Despite the differences of our results for liquidus coordinates from the studies and the model, their validity is confirmed with wider experimental information (including the enthalpies of mixing on the melts and the improved estimation of the enthalpies of formation of the intermetallics). However, further experimental investigations of the phase diagram are required to complete the thermodynamic description of this system.

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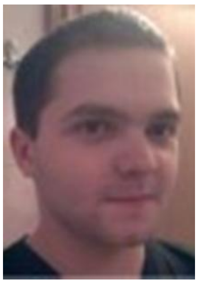

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Thermodynamic Assessment of Binary Subsystems of Al_2O_3-CaO-SiO_2-UO_2-ZrO_2 System Using Cell Model and Ionic Model

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Thermodynamic database is a useful tool for evaluating the progress in chemical reactions during molten core concrete interaction (MCCI), which are potentially ocuured at the last stage of severe accident of light water reactors, and the phase relations in MCCI-products. Japan Atomic Energy Agency (JAEA) and Nippon Steel & Sumitomo Metal Corporation (NSSMC) are collaborating to develop a thermodynamic database by combining their own nuclear- and steel/slag-databases, respectively. Thermodynamic database of Al_2O_3-CaO-SiO_2-UO_2-ZrO_2system is constructed using both of cell model and ionic moel by CALPHAD method. Phase diagrams of quasi-binary sub-systems between oxides are able to be drawn properly using the assessed interaction parameters. The phase boundaries are reasonably overlapped on the experimental data. Assessment of thernary sub-systems is ongoing.

Masaki Kurata

Dr. Masaki Kurata is a Division Head of Collaborative Laboratories of Advanced Decommissioning Science (CLADS) of JAEA.He is in charge of R&Ds on severe accident progression evaluation and the related thermodynamic databases in CLADS.

Computational thermodynamics of solid-solid phase change materials development for thermal energy storage in ternary system: Pentaglycerine - Tris(hydroxymethyl)-aminomethane - 2-amino-2-methyl-1,3-propanediol (PG-TRIS-AMPL)

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Materials development for energy conservation requires property optimization, system design, and integration, however computational methodologies for these types of materials have not been fully integrated. We propose a computational framework with a rather new "solvus projection calculation" concept for designing heterogeneous multi-component latent heat Phase Change Materials (PCMs) using CALPHAD thermodynamic calculations [1-7]. In this study our focus was on prediction of compositions of PG-TRIS-AMPL ternary solutions that have maximum latent heat storage capacity during solid-solid phase transitions. Predicted enthalpies showed good correlation with differential scanning calorimetry results, in which enthalpies (H) are extrapolated. In addition, calculated stable phases at various temperatures matched those determined by in-situ x-ray diffraction. It was found that the maximum latent heat storage, at constant pressure, in the ternary system in the four phase equilibria region. As a result, we discovered two types of four-phase equilibrium regimes with six pseudo-peritectoid in the isopleths not easily extracted using conventional methods. Calculations that lead to compositions that yield the maximum energies with stabilized phase transition temperature are described in this study.

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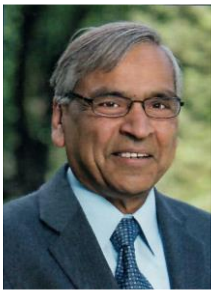

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The 600 ºC isothermal section of the La-Zn-Si system

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1. Introduction

The knowledge of phase stability and phase equilibria of the Zn-Al-Si-La system is important due to hot dip galvanizing industry. However, it is devoid of adequate theoretical studies and practical applications in these fields. Especially, no phase diagram has yet been established for the system La-Zn-Si. Therefore, the La-Zn-Si system were experimentally investigated in the present work.

2. Experimental methods

The phase relationships were determined using equilibrated alloys with the aid of diffusion couple approach. All equilibrated alloys were prepared using the 99.99% purity of the materials. Each alloy mixture was heated to 1200 °C and kept 14 h, followed by quenching in water. The samples were finally annealed at 600°C for 30 days respectively to ensure the establishment of an equilibrium state, and were then water-quenched at the end of the treatment. In order to prepare the (La-Si)/Zn diffusion couples, $La_{60}Si_{40}$ and $La_{54}Si_{46}$ (in at. %) alloy were re-melted five times in arc furnace under high purity argon atmosphere using a non-consumable tungsten electrode, and kept at 800°C for 8 days to improve their homogeneity. The ingot was cut into small pieces and then ground, polished, cleaned, finally sealed together with appropriate amounts of Zn blocks. The sealed specimens were annealed at 600°C, kept for 4 days and 2 days, respectively, then quenched in water. All the specimens were examined by SEM-EDS/WDS and some key ones of them were further studied by XRD.

3. Results and discussions

Based on the experiment data, sixteen three-phase equilibria of the La-Zn-Si system were well determined. Seven ternary compounds were found in this ternary system, and temporally designated τ1, τ2, τ3, τ4, τ5, τ6 and τ7, respectively. Two previously reported ternary compounds, viz. τ1 and τ2, were evidenced to exist at 600 ºC. Two newly ternary phase τ5 and τ6 were identified. The τ5 phase with the $CeZn(Zn_{1-x}Si_x)_2$-type was determined to have a composition range of 36.9-39.2 at.% Si at about 24 at.% La. The τ6 phase with the Al_3CeCu-type was found to have a composition range of 18.9-19.7 at.% La and 27.4-30.6 at.% Si. The crystal structures of τ3, τ4, and τ7 are still unknown. The solubility of Si in $LaZn_{13}$, $LaZn_{11}$, La_2Zn_{17}, La_3Zn_{22}, $LaZn_5$ are negligible, and that of Si in $LaZn_4$, $LaZn_2$ and Zn in $LaSi_2$, La_3Si_2 were determined to be up to 5.1 at.%, 2.3 at.%, 16.2 at.% and 3.8 at.%, respectively.

Experimental investigation of the intermetallic dross phases formed in galvalume baths

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There is usually a problem of slagging in galvalume production lines, which has a severe influence on the quality and productivity of galvalume. The addition of Si in the galvalume bath makes the intermetallic dross phase be more complex. Although the effect of Si for the structure and thickness of the galvalume coating has been studied by various authors, its information about the bath maintenance and dross formation is not fully explained. The reaction in galvalume process is actually Al-Fe-Si-Zn system. Due to its importance to the galvanizing industry. The Al-rich corner of Al-Fe-Si system at 600°C (based on the work of Maitra and Du), can not be used to complete explain the interface reaction in galvalume process. In order to obtain the accurately information of the reactive mechanism of Si for hot-dipping galvalume, the Al-Zn-rich side phase equilibria of the $Al_{0.55(1-x-y)}Fe_xSi_yZn_{0.45(1-x-y)}$ section in the Al-Fe-Si-Zn system at 600°C was experimentally determined in the present study.

The intermetallic dross phases formed in g alvalume baths containing 1.0～3.0 wt.% Si in the temperature range of 580～610°C have been studied detailedly. The intermetallic dross phases are considered to be the $FeAl_3$ phase and the τ_5 phase containing Zn. The Al-Zn-rich corners of $Al_{0.55(1-x-y)}Fe_xSi_yZn_{0.45(1-x-y)}$ section in the Al-Fe-Si-Zn system at 580～610°C have been constructed. It is intuitionistic to predict the change in the nature of the intermetallic dross phases present in galvalume baths for variations of Si content and temperature. For Si content dose not exceed 1.3 wt.%, the dross is solely the $FeAl_3$ phase, and the most Si content in the FeAl3 phase is 1.93 wt.% for 1.0～1.6 wt.% Si in baths. When Si content up to 2.0 wt.%, the intermetallic dross phase is solely τ_5 phase. In this study, $FeAl_3$ and τ_5 can co-exist when Si content is 1.6 wt.% in baths at the temperature range of 580～610°C.

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Isothermal section of Zn-rich corner of the Zn-Al-Mg-Si system at 450 °C

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Si in Zn-11Al-3Mg(Super Dyma) bath could inhibit the growth of Fe-Al intermetallic layer in Super Dyma coating. Although the microstructure of Super Dyma coating has been studied, the phase equilibrium of Zn-Al-Mg-Si system is still not clear. The isothermal section of Zn-rich corner of the Zn-Al-Mg-Si system at 450 °C was experimentally determined using scanning electron microscopy coupled with energy dispersive X-ray spectroscopy and X-ray diffraction. The experimental results reveal that liquid+α-Al+Mg_2Si, liquid+α-Al+$MgZn_2$, liquid +$MgZn_2$+Mg_2Si, liquid+α-Al+Si, liquid+$MgZn_2$+Si five three-phase equilibria and liquid+$MgZn_2$+Mg_2Si+Si, liquid+$MgZn_2$+Mg_2Si+α-Al two four-phase equilibria exist in Zn-Al-Mg-Si system. Mg_2Si、$MgZn_2$ and α-Al phase could coexist with liquid phase, respectively. Si is not dissovled in $MgZn_2$ and α-Al. The solubility of Al in Mg_2Si and $MgZn_2$ is 1.8at.% and 3.2at.%, respectively. The solubility of zinc in Mg_2Si is 6.1at.%. No ternary phase has been found.

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High Temperature Experimental Contribution to the Thermodynamic Modeling of Corium Pools

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During a severe accident in a Pressurized or Boiling Water nuclear reactor, extreme temperatures may be reached (T>2500 K). Under these conditions, the UO2 fuel may react with the Zircaloy cladding and with the stainless steel vessel, forming a mixture of solid-liquid phases called in-vessel corium.

To study these very high temperature interactions both experimental and Calphad modeling approaches are used. The simplified system (Fe-U-Zr-O) representative of a so-called prototypic corium was considered due to the complexity of the high temperature interactions of such mixtures. Nevertheless, there is a significant lack of high temperature data in this quaternary system.

For this reason, a specific facility was developed to address the measurement of phase equilibria up to 3000 K. To reach these high temperatures, this setup uses an aerodynamic levitation nozzle and a CO2 laser heating technique to melt metallic or oxide samples. This device makes it possible to observe in-situ the formation of miscibility gaps that form in such metal/oxide corium sub-systems.

The results from the experimental investigations: thermal arrest measurements and associated composition and microstructure analyses will be presented for some samples representative of prototypic in-vessel sub-systems. Thermodynamic calculations performed with the Fe-U-Zr-O database under development will be presented and compared to the available experimental data.

Stéphane Gossé

Stéphane Gossé is head of the Laboratory of Modelling, Thermodynamics and Thermochemistry within the Department of Physico-Chemistry of the Nuclear Energy Division of the French Alternative Energies and Atomic Energy Commission. He is involved in high temperature thermodynamics of nuclear materials and his current research combines thermodynamic modeling and experimental studies. His actual works mainly focuses on the thermochemistry of corium pools during severe accidents and on the behavior of insoluble fission products during the vitrification process of nuclear waste forms.

Explicit calculations of vacancy profile during interdiffusion in quaternary Ni-Pt-Cr-Al system for optimization of new γ – γ’ bond coating

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A numerical modelling of the diffusion under chemical potential gradients including the transport of vacancies was developed in order to anticipate Kirkendall voids formation during interdiffusion process. It was applied to the Ni-Pt-Cr-Al system. Indeed, interdiffusion of a Pt layer with a Ni-base superalloy is a way to form a Pt-enriched γ – γ’ layer as a bond-coating for thermal barrier coating systems [1]. The formation of this Al-rich coating without any aluminising step is possible thanks to the decrease of Al chemical activity due to Pt, which allows Al diffusion against its composition gradient [2]. However, these Pt-rich γ – γ’ coatings often include many pores that are attributed to Kirkendall effect. The uphill diffusion of Al during interdiffusion of Pt/Ni-Al has been previously modelised by Sundman *et al*. [3] using DICTRA calculations. However, the effect of Cr was not taken into account neither vacancies. The CALPHAD thermodynamic database used in this work has been enriched in the present work with Cr description. It enabled to implement the chemical potentials as explicit functions of local compositions in the calculations of fluxes. To be able to handle the vacancy flux in the calculations, a specific finite difference diffusion code “ABCV” was used to solve the diffusion equations of the chemical species and of the vacancies, which could be partly eliminated on bulk sinks and sources as done previously for the Ag-Cd-In-Sn system [4]. Calculations had been performed to reproduce short-term interdiffusion experiments at high temperature of an electroplated Pt coating with a γ-Ni(Al,Cr) alloy [5] which permitted to assess four coefficients for the mobility matrix. The composition of the coating and the location of Kirkendall voids could be accurately predicted without any others fitting parameters.

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- High Temperature Corrosion, oxidation kinetics
- Diffusion in solids, Study of diffusion mechanisms

Mechanical Properties of Non-Centrosymmetric $CePt_3Si$ and $CePt_3B$

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The first non-centrosymmetric heavy fermion superconductor $CePt_3Si$ [1], crystallizing with $CePt_3B$ -type, without an inversion symmetry (one of the key symmetries for Cooper pairing) shows a number of novel physical properties. In order to get insight into the pressure dependence of the strong electron correlations in these materials the present paper provides mechanical property data (elastic moduli and hardness both at room temperature as well as thermal expansion in the range from 4.2 to 670 K) for both single and poly-crystalline $CePt_3Si$ and its prototype compound $CePt_3B$.

The experimental data are backed by first-principles (*ab-initio*) calculation. Resonant ultrasound spectroscopy was used to determine elastic properties (Young's elastic modulus E and Poissons ratio ν). Bulk modulus and shear modulus were calculated from E and ν, and with Anderson's equation the respective Debye temperatures were derived. In addition, ab-initio DFT calculations were carried out for both compounds. A comparison with parameters evaluated from these first-principles computations with the experiments revealed, in general, good agreement.

Positive and negative thermal expansion values obtained from $CePt_3Si$ single crystal data are fairly well explained in terms of the crystalline electric field model, using CEF parameters derived recently from inelastic neutron scattering. The DFT calculations, in addition, demonstrate that the atomic vibrations keep almost unaffected by the antisymmetric spin-orbit coupling present in systems with crystal structures having no inversion symmetry. This is opposite to electronic properties, where the antisymmetric spin-orbit interaction has shown to distinctly influence features like the superconducting condensate of $CePt_3Si$.

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Kinetic simulation of alloying element partitioning in Q&P steels

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Understanding the carbon diffusion from martensite to austenite is a challenging task in quench and partitioned (Q&P) steels. Several numerical and analytical models exist to address this problem. One such model developed by Speer *et al*., called the 'constrained carbon equilibrium' (CCE), using which the end point of carbon partitioning can be found [1-3]. Based on this approach, the kinetic simulation was done on the selected Q&P steel of composition (in wt. %) C=0.26, Si=1.06, Mn=1.57, Al=0.98 by using the DICTRA coupled with Thermo-Calc software using the thermodynamic database TCFE7 and a mobility database MOBFE2 [4]. Assuming an immobile interface, the diffusion profile of C, Mn, Si and Al in the two phases (martensite-BCC and austenite-FCC) was simulated at 350 and 450°C for various partitioning time and the saturation time for elemental partitioning was found. The microstructural characterization was done using transmission electron microscope (TEM) and the Rietveld refinement was done on the X-ray diffraction (XRD) data to find the austenite volume fraction and carbon content present in it. The distribution of C, Si, Mn, and Al in martensite and austenite was analyzed using atom probe tomography (APT). Experimental data are compared with the simulated results.

Keywords
Quench and partitioned; Steels; Kinetics; Simulation; TEM; APT.

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