TOFA

19th DISCUSSION MEETING OF THERMODYNAMICS OF ALLOYS

23 - 27 September 2024

LYON - FRANCE

Abstract book

https://tofa2024.univ-lyon1.fr/en tofa2024@univ-lyon1.fr

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Welcome

Dear Colleagues and Friends,

The 19th Discussion Meeting on Thermodynamics of Alloys will take place in Lyon, France from September 23 to September 27, 2024. Lyon is the second-largest metropolitan area of France. It is located at the confluence of the rivers Rhone and Saone, 391 km (243 mi) southeast of Paris, 278 km (173 mi) north of Marseille, 113 km (70 mi) southwest of Geneva. The capital of the Gauls during the Roman Empire, Lyon became a major economic hub during the Renaissance. The city is recognized for its cuisine and gastronomy, as well as historical and architectural landmarks; as such, the districts of Old Lyon, the Fourvière hill, the Presqu'ile and the slopes of the Croix-Rousse are inscribed on the UNESCO World Heritage List. Lyon was historically an important area for the production and weaving of silk. Lyon played a significant role in the history of cinema since Auguste and Louis Lumière invented the cinematograph there. The city is also known for its light festival, the Fête des Lumières, which begins every 8 December and lasts for four days, earning Lyon the title of "Capital of Lights".

The home of three renowned universities and several higher education schools, Lyon is the second-largest student city in France, with a university population of nearly 200,000 students within the Metropolis of Lyon.

As usual TOFA 2024 will be an opportunity for all generations to meet. Researchers, scientists and students in the field of thermodynamics of alloys are welcome to join this international conference. TOFA 2024 will be a single session conference based on invited lectures, selected oral presentations and poster session.

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Chair of TOFA 2024

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Program

	Monday September 23	**Tuesday September 24**	**Wednesday September 25**	**Thursday September 26**	**Friday September 27**
08:00		**Registration**			
08:30			**Registration**		
		Session 1	Session 4	Session 6	Session 9
	Chairs:	J.M. Joubert & S. Lippmann	A. Antoni & F. Stein	C. Pascale & S. Delsante	O. Dezellus & G. Kaptay
9:00		S1.O1 Stein (invited)	S4.O14 Arroyave (invited)	S6.O23 Lippmann (invited)	S9.O36 Delsante (invited)
9:40		S1.O2 De Abreu	S4.O15 Benigni	S6.O24 Chatain	S9.O37 Schmitt
10:00		S1.O3 Bizot	S4.O16 Jacob	S6.O25 Vaubois	S9.O38 Simonin
10:20		S1.O4 Richter	S4.O17 Lee	S6.O26 Segondy	S9.O39 Tumminello
10:40		Coffee break	Coffee break	Coffee break	Coffee break
		Session 2	Session 5	Session 7	Session 10
	Chairs:	P. Benigni & R. Arroyave	J. Andrieux & J. Medved	G. Deffrennes & J-H. Lee	M. Perrut & O. Fabrichnaya
11:10		S2.O5 Zobac	S5.O18 Joubert	S7.O27 Voncina	S10.O40 De Villoutreys
11:30		S2.O6 Fabrichnaya	S5.O19 Lesage	S7.O28 Dupin	S10.O41 Desseaux
11:50		S2.O7 Chang	S5.O20 Desmarchelier	S7.O29 Eleno	S10.O42 Führer
12:10		S2.08 Kriegel	S5.O21 Charvet	S7.O30 Lomello-Taffin	S10.O43 Gossé
12:30		Lunch: 12:30-14:00	S5.O22 Liu	Lunch: 12:30-14:00	**Closing**
			Lunchbox		Lunchbox
		Session 3		Session 8	
	Chairs:	I.Nuta & P. Fima		R. Chiriac & K. Richter	
14:00		S3.O9 Guéneau		S8.O31 Fiorani	
14:20		S3.O10 Medved		S8.O32 Crochetet	
14:40		S3.O11 Fischer		S8.O33 Maugis	
15:00		S3.O12 Garcia-Arango	**Visits of Lyon** **From 15:00** **&** **Conference Dinner** **20:00 - 23:00**	S8.O34 Naciri	
15:20		S3.O13 Yang		S8.O35 Machajdíková	
	Registration **Welcome Cocktail** **18:00 - 20:00**	**Coffee Break** **&** **Poster Session** **15:40 - 18:00**		**Coffee Break** **&** **Poster Session** **15:40 - 18:00**	

Monday, September 23

17:00 - 18:00 **Registration**

18:00 - 18:30 **Opening**

18:30 - 20:00 **Welcome Reception**

Tuesday, September 24

S1

9:00 O-1 **Frank STEIN** Ternary liquidus surfaces and the predictive power of the Alkemade therorem

9:40 O-2 **Danilo Alencar DE ABREU** Phase Equilibria in the Li2O-SiO2 and MnOx-SiO2 systems

10:00 O-3 **Quentin BIZOT** Active learning approach and atomistic simulations for the prediction of the enthalpy of mixing in the liquid

10:20 O-4 **Klaus RICHTER** Solid-Vapor diffusion couples as a source of phase diagram data: a case study of the Ni-Zn system

10:40 - 11:10 **Coffee break**

S2

11:10 O-5 **Ondrej ZOBAC** Experimental and theoretical description of binary system Ge-Mg

11:30 O-6 **Olga FABRICHNAYA** Phase equilibria in the Li2O-MnOx system

11:50 O-7 **Keke CHANG** Surface damage mechanisms and new system design of Cermets

12:10 O-8 **Mario KRIEGEL** Experimental Investigation of the Mn–Ni–Ti System

12:30 - 14:00 **Lunch**

S3

14:00 O-9 **Christine GUENEAU** Measurement of phase diagram data in the SiO2-ZrO2-UO2 system for severe accident application

14:20 O-10 **Jozef MEDVED** Investigation of the Al-Mg-Si-In and Al-Mg-Si-In-Bi alloys

14:40 O-11 **Lukas FISCHER** Semi-liquid anodes Li-ion batteries: constitution and thermodynamics of the systems Li-Zn and Li-Sn-Zn

15:00 O-12 **Nicolás GARCíA ARANGO** The beta-alpha transformation in 6063 aluminum alloy; in-situ experimental results and computational analysis

15:20 O-13 **Yang YANG** Recent developments of CALPHAD databases for aluminum alloys

15:40 - 18:00 **Coffee break & poster session**

Wednesday, September 25

S4

9:00 O-14 **Raymundo ARROYAVE** Uncertainty Quantification and Propagation in CALPHAD and CALPHAD-based Frameworks

9:40 O-15 **Pierre BENIGNI** Thermodynamic description of unary glass forming liquids using 2-state models

10:00 O-16 **Aurélie JACOB** Computational thermo-kinetic simulation of MX phase in HSLA steel: the importance of thermodynamic parameters

10:20 O-17 **Joonho LEE** In-Situ Al-7075/Al3Ti Metal Matrix Composites Formation by Stir Assisted Ultrasonic Melt Processing Under Dynamic Nucleation

10:40 - 11:10 Coffee break

S5

11:10 O-18 **Jean-Marc JOUBERT**Crystal chemistry of the solid solutions based on Beta-Mn

11:30 O-19 **Louis LESAGE** Investigation of equilibrium conditions in liquid metal dealloying by in-situ X-ray diffraction

11:50 O-20 **Hugo DESMARCHELIER** New Experimental Data on Zr-Fe-O

12:10 O-21 **Romain CHARVET** Thermodynamic modelling and experimental study of protective barriers against carbon diffusion during SPS

12:30 O-22 **Yuheng LIU** Synergistic study of ordering mobility in D03-Fe3Al through experimental observation and phase-field simulation

12:50 - 14:00 Lunchbox

Visits of Lyon from 15:00
&
Conference Dinner from 20:00 - 23:00

Thursday, September 26

S6

9:00 O-23 **Stephanie LIPPMANN** Developing new methods for alloys characterizing employing temperature and concentration gradients

9:40 O-24 **Sylvie CHATAIN** Vaporization study of cesium molybdates by Knudsen cell mass spectrometry

10:00 O-25 **Thomas VAUBOIS** New Nickel Based Superalloys Reinforced By Gamma Double Prime Precipitation

10:20 O-26 **Sandra SEGONDY** Calorimetric studies of alloys at high temperature

10:40 - 11:10 Coffee break

S7

11:10 O-27 **Maja VONCINA** Thermodynamic assessment of the effect of Ce and La additives on alloys of the system Al-Fe

11:30 O-28 **Nathalie DUPIN** The effective bond energy formalism

11:50 O-29 **Luiz ELENO** Thermodynamic models to unravel superconducting physical properties and parameters

12:10 O-30 **Marc LOMELLO-TAFIN** Experimental contribution to the determination of the In-Zr system for severe nuclear accident assessment

12:30 - 14:00 Lunch

S8

14:00 O-31 **Jean Marc FIORANI** NACEF applied to the FCC ordering based on the four sublattice model

14:20 O-32 **Adrien CROCHETET** Measurement of the enthalpy and heat capacity of corium components at very high temperatures

14:40 O-33 **Philippe MAUGIS** Phase Stabilities in Mechanically Stressed Body-Centered Fe-C Solid Solutions: Are Ferrite and Martensite the Same Phase ?

15:00 O-34 **Kaoutar NACIRI** Thermodynamic Analysis of the K2MoO4-Li2MoO4 System: Towards Potassium Impurity Removal from Li2MoO4 Crystals

15:20 O-35 **Tereza MACHAJDíKOVá** Study of phase equilibria in Sn-3Ag-0.5Cu-xNi (x=0.05 - 4 wt.%) alloys

15:40 - 18:00 Coffee break & poster session

Friday, September 27

S9

9:00 O-36 **Simona DELSANTE** Comparison of the Sm and Gd alloying behaviour for RE-Ni-Al ternary systems

9:40 O-37 **Lisa-Yvonn SCHMITT** Primary phase solidification of a Pt-based glass forming alloy for the use in Additive Manufacturing

10:00 O-38 **Alexandre SIMONIN** An experimental study of the Rh-Zr binary system

10:20 O-39 **Silvana TUMMINELLO** The case of diffusion reaction in multilayer electrical contacts for Mg-Si-Sn based thermoelectric devices

10:40 - 11:10 Coffee break

S10

11:10 O-40 **Eloi DE VILLOUTREYS** Experimental study and thermodynamic modeling of the (Ce-Nd)-Fe-B system for substituted permanent magnets

11:30 O-41 **Mathias DESSEAUX** HP-HT modelling of Fe-Mg system: A comparison of CALPHAD-compatible models and data acquisition

11:50 O-42 **Markus FüHRER** Investigating the influence of boron alloying on the thermodynamics of the Fe-B-N-C system

12:10 O-43 **Stéphane GOSSé** Thermodynamic modelling of the solubility of minor additive elements in liquid metallic coolants

12:30 - 12:50 Closing

12:50 - 14:00 Lunchbox

Poster list

P01 EXPERIMENTAL AND THEORETICAL DESCRIPTION OF THE Ge-Mg-Sn TERNARY SYSTEM
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P02 EXPERIMENTAL STUDY OF PHASE EQUILIBRIA IN THE CR-IR BINARY SYSTEM BELOW 1375K
V. Homolová, L. Čiripová, A. Zemanová, O. Zobač, A. Kroupa

P03 EXPERIMENTAL STUDY OF THE Sb-Zn SYSTEM
Przemysław Fima, Agnieszka Bigos, Anna Góral, Tomasz Czeppe, Ondřej Zobač

P04 MIXING ENTHALPIES OF LIQUID ALLOYS FROM Cu-Mg-Ti SYSTEM: EXPERIMENT VS. THERMODYNAMIC MODELING
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P05 MOLECULAR DYNAMICS STUDY OF PHASE TRANSFORMATIONS IN NITICU SHAPE MEMORY ALLOYS
Won-Seok Ko , Jae Hur , Jea-Young Hwang, Young-Bum Chun

P06 SNS$_2$/SI - COMPOSITE ANODES FOR LI- ION BATTERIES: PHASE DIAGRAM INVESTIGATIONS IN THE LI-SN-S AND SI-SN-S SYSTEMS
Thangamalar Bhaskaran, Hans Flandorfer, Damian M Cupid

P07 THERMODYNAMIC AND KINETIC SIMULATIONS FOR MICROSTRUCTURE EVOLUTION OF DIRECT-QUENCHED STEELS DURING INTERCRITICAL ANNEALING
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P08 THERMODYNAMIC CONSIDERATION ON THE REACTIONS BETWEEN MGAL$_2$O$_4$ REFRACTORIES AND A LIQUID FERROMANGANESE METAL
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Ioana Nuta, Christian Chatillon, Francois Chombart, Amélie Moreau

P10 A DATA-DRIVEN STUDY OF THE ENTHALPY OF MIXING IN THE LIQUID PHASE
Guillaume Deffrennes, Bengt Hallstedt, Taichi Abe, Quentin Bizot, Evelyne Fischer, Jean-Marc Joubert, Kei Terayama and Ryo Tamura

P11 MACHINE LEARNING METHODS TO HELP CONSTRUCT PHASE DIAGRAMS
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P12 MICROSTRUCTURE EVOLUTION UPON ANNEALING OF BRAZING CU-P LAYERS BETWEEN AG-C ELECTRICAL CONTACTS AND CU SUBSTRATES
Josias Amovin-Assagba, Annie Antoni-Zdziobek, Fiqiri Hodaj, Sophie Roure, Corinne Durand, Céline Pascal

P13 PROCESSING OF A ZR-BASED BULK METALLIC GLASS
Manon Bornand, Marc Fivel, Guillaume Deffrennes, Damien Tresallet, Alexis Lenain, Laura Mangourny, Bruno Lavisse, Quentin Delafolie, Rémi Daudin

P14 SCIENCE OF DIRTY ALLOYS: IMPROVING THE RECYCLABILITY OF AL ALLOYS
Paul Chatron-Michaud

P15 DEVELOPMENTS AND APPLICATIONS OF THE GHEA THERMODYNAMIC DATABASE FOR CALPHAD MODELLING OF AL-C-CO-CR-FE-NI-R (R = MO, TA, W) SYSTEMS
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P16 THE STABILITY OF THE CALPHAD METHOD IN FRONT OF NEW MATERIALS
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P17 PHASE TRANSFORMATIONS IN LEAD-FREE NANOCOMPOSITE SOLDER JOINTS
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Manuel Löffler, Maren Lepple and Olga Fabrichnaya

P19 EFFECT OF THE ADDITION OF NI AND CU ON THE SOLIDIFICATION AND MICROSTRUCTURE OF AL-5SI-0.5MG ALLOYS
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P20 PUREALLOYS: DESIGNING NEW ULTRA-RADIOPURE, HIGH-STRENGTH ELECTROFORMED CUCRTI ALLOYS, FOR RARE EVENT SEARCHES
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P21 ADDITIVE MANUFACTURING OF WC-CO CERAMIC/METAL COMPOSITES USING BINDER JETTING: FROM POWDER TO SINTERED PART PROPERTIES
Erwan Marciano, Olivier Dezellus, Xavier Boulnat, Sébastien Dezecot, Alexis Burr

P22 ON THE SIZE AND SHAPE DEPENDENCE OF INTEGRAL AND PARTIAL MOLAR GIBBS ENERGY, ENTROPY AND ENTHALPY OF NANOPHASES
George Kaptay

Social program

Wednesday, September 25

Guided tours of Lyon
&
Conference Dinner

Old Lyon & Traboules | **Fourvière Hill** | **Musée des Confluences**

All guided tours from 3 P.M.

The **gala dinner** will take place on

Wednesday September 25th

(from 8 P.M.)

The Saint-Exupéry Boat-restaurant

(2h30 tour on the Saône)

Boarding at 13 bis Quai Rambaud - 69002 Lyon - France

Venue

Université Lumière Lyon 2

Palais Hirsch

18 quai Claude Bernard, 69007 Lyon, France

Orals

TERNARY LIQUIDUS SURFACES AND THE PREDICTIVE POWER OF THE ALKEMADE THEOREM

Frank Stein [1], **Cuiyun He** [2]

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Keywords: Alkemade theorem, phase diagrams, liquidus surface, solidification path

A crucial factor that determines the behaviour of alloys for structural and functional applications is the microstructure of the material resulting from the production process. In most cases, such kind of materials are produced by solidification from the liquid state, e.g., by a casting process or by additive manufacturing. The corresponding solidification path then is the most important factor that determines how the microstructure of the material will look. The complete information about the solidification path is available from the liquidus surface of the phase diagram of the corresponding alloy system. In the case of ternary systems, the three-dimensional liquidus surface is determined by a set of lines that define the monovariant equilibria and divide the surface into the different fields of primary crystallization of the individual phases. The exact position of the lines in turn is defined by the composition and temperature of the monovariant equilibria. While it is experimentally comparably easy to find the position of such lines, it is usually very difficult to determine the temperature change along the boundary lines, where the temperature can both increase and decrease. This knowledge about the increase or decrease of temperature is essential to predict the solidification path of an alloy, and exactly this information can be provided by the so-called Alkemade theorem. This theorem goes back to a very fundamental paper on the graphical description of thermodynamic equilibrium problems from 1893 [1]. It is valid for systems with any number of phases. However, its geometrical construction rule is only defined for the case of ‘point phases’ (i.e., phases without homogeneity range), the compositions of which can be connected by so-called Alkemade lines. It is not clear how to apply the theorem in the case of phases with extended composition ranges, where such an Alkemade line is no longer defined and is degenerated into a kind of Alkemade region [2]. Some examples from a ternary, transition-metal-based system containing phases with large homogeneity ranges will be presented, and the usefulness and limits of applicability of the theorem will then be discussed.

References:

1. A.G. van Rijn van Alkemade: Z. Phys. Chem. 11 (1893) 289-327
2. F. Stein, C. He: J. Phase Equilib. Diffus. (2024), https://doi.org/10.1007/s11669-024-01097-9

S1-O2

PHASE EQUILIBRIA IN THE Li2O-MnOx SYSTEM

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Keywords: Li recycling, CALPHAD approach, Thermodynamic modeling and Phase diagram.

The importance of recycling of valuable transition metals (such Co, Ni) and Li from Lithium-Ion Batteries (LIBs) increased in the recent years. Application of pyrometallurgical methods such as smelting reduction make it possible separate transition metals which are reduced to metal and dissolved in metallic alloy while Li2O and partially Mn oxides are dissolved in slag [1]. In this context, Li_2O reacts with slag, forming $LiAlO_2$ or spinel solid solution. Different slag compositions have been studied in the literature for concentration of Li in oxide compounds. The understanding phase relations in the Li_2O-MnO_x-SiO_2-Al_2O_3 system can lead to an optimization of the Li recycling process [1]. It should be noted that melting in this system was not investigated so far. In the frame of CALPHAD approach following thermodynamic models were applied to describe the Gibbs energy of phases: $LiMnO_2$ and Li_2MnO_3 phases were modelled as stoichiometric compound, compound energy formalism (CEF) was applied for cubic and tetragonal spinel phases and two-sublattice partially ionic liquid model for liquid phase. In the present study orthorhombic phase $LiMnO_2$ was synthesized and its heat capacity was measured. Thermodynamic parameters for phases in the Li_2O-MnO_x system were assessed based on literature data for phase equilibria [2,3] and experimentally determined thermodynamic properties [5-7]. Li^{+1} was introduced both in tetrahedral and octahedral site of cubic spinel $(Li^{+1},Mn^{+2})_1(Li^{+1},Mn^{+2},Mn^{+3},Mn^{+4},Va)_2O_4$. Homogeneity range and decrease of Li/Mn ratio in spinel was successfully reproduced. Li dissolution in Mn_3O_4 tetragonal spinel was modelled considering possibility of Li occupation of interstitial sites. Solubility of Li in Mn_3O_4 was reproduced, while appearance of tetragonal spinel with $LiMn_2O_4$ composition was not reproduced. It should be mentioned that there is contradiction in literature about stability of this phase in literature [2,3] and [7].

References:

[1] Xiao, S. et al. Recovery of valuable metals from spent lithium-ion batteries by smelting reduction process based on MnO–SiO_2–Al_2O_3 slag system. J. Sustain. Met., 3, 703 (2017).
[2] Paulsen, J.M., Dahn, J.R. Phase diagram of Li-Mn-O spinel air. Chem. Mater., 11, 3065 (1999).
[3] Thackeray, M.M. et al. The thermal stability of lithium-manganese-oxide spinel phases. Mat. Res. Bul., 31, 133 (1996).
[4] Cupid, D.M. et al. Enthalpy of formation and capacity of Li_2MnO_3. J. Ceram. Soc. Japan 124, 1082 (2016).
[5] Cupid, D.M. et al. Enthalpy of formation of $Li_{1+x}Mn_{2-x}O_4$ ($0<x<0.1$) spinel phases. Thermochim. Acta, 599, 35 (2015).
[6] Wang, M., Navrotsky, A. $LiMO_2$ (M=Mn, Fe, and Co): energetics, polymorphism and phase transformation. J. Solid State Chem., 178, 1230 (2005).
[7] Luo, C., Martin, M., Stability and defect structure of spinel $Li_{1+x}Mn_{2-x}O_{4-\delta}$: In situ investigations on stability field of spinel phase. J. Mater. Sci. 42, 1955 (2007).

S1-O3

ACTIVE LEARNING APPROACH AND ATOMISTIC SIMULATIONS FOR THE PREDICTION OF THE ENTHALPY OF MIXING IN THE LIQUID

Quentin Bizot[1], Noel Jakse[1], Ryo Tamura [2,3], Guillaume Deffrennes[1]

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Keywords: enthalpy of mixing, active learning, atomistic simulations, liquid alloys

The enthalpy of mixing is an important thermodynamic property for predicting phase transformations. For the screening of new alloys, it is of great interest to be able to estimate this property in a large compositional space for different phases. This is particularly true for high entropy alloys [1]. Currently, the solutions to achieve this are to rely on Miedema's model for the liquid phase [2], or on density functional theory calculations with a tradeoff between accuracy and computation cost for solid phases [1]. A promising alternative is to predict the enthalpy of mixing using machine learning (ML).

We collected a large amount of experimental data from over 400 binary liquids in order to build a first ML model. We will present a first ML model that performs better than Miedema's model. In order to improve our model, the collection of new data is crucial. This is particularly true for certain alloy families where no experimental measurements are available (notably refractory materials). We have chosen to collect new data through atomic-scale simulations. Ab-initio molecular dynamics (AIMD) is a particularly interesting technique, as it enables us to simulate the liquid phase of a wide variety of binary alloys while guaranteeing high accuracy. However, the computation time required for this type of simulation is extremely high. It is therefore necessary to restrict the number of binary alloys to be simulated.

In order to optimize our models with a minimum number of simulations, we have developed an Active Learning (AL) approach. Its purpose is to find the binary systems and the compositions where the acquisition of new data would most improve the accuracy of our models. Different AL processes will be presented as well as their efficiency. The selected AL process is used to identify the most informative AIMD simulations of binary liquids, which will also be presented.

References:

[1] Chen *et al.*, "A map of single phase high entropy alloys", Nature Communications, 14 (2023)
[2] Miedema, A.R., *et al.* "Cohesion in alloys - fundamentals of a semi-empirical model", *Physica B+C,* 100 (1980): 1

S1-O4

SOLID-VAPOR DIFFUSION COUPLES AS A SOURCE OF PHASE DIAGRAM DATA: A CASE STUDY OF THE Ni-Zn SYSTEM

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Keywords: Phase Diagram, Diffusion Couple, Solid-Vapor Reaction, Intermetallic Compounds

Phase diagrams of systems combining elements with highly different melting/boiling points are particularly difficult to investigate experimentally, due to various problems occurring during equilibration and homogenization. In these cases, it can be advantageous to employ direct solid-vapor reaction to prepare well-defined, equilibrated samples. On the other hand, the diffusion profiles developing during solid-vapor synthesis also allow evaluation similar to solid-state diffusion couple experiments. To our knowledge, the potential of this technique was not studied systematically yet.

The Ni-Zn system is ideal for such a study, as the melting point of Ni (1726 K) is far higher than even the boiling point of Zn (1180 K) [1]. The Ni-Zn phase diagram is considered as well understood with the currently accepted phase diagram assessment given by Nash and Pan [2] in 1987, citing all relevant literature until 1984. It contains a broad solid solution of Zn in Ni (up to 39% Zn) and phase fields β/β_1 (45.5-52% Zn), γ (74-85% Zn) and δ (89% Zn). Only few new experimental results have been reported since then, but several thermodynamic assessments based on the work of Nash and Pan were published; e.g. [3, 4].

In the current work we studied more than 50 solid-vapor diffusion couples obtained by direct reaction of Ni foil with Zn vapor at different temperatures, reaction times and final overall composition. The results were used to systematically explore the potential of this method as supplementary technique for phase diagram evaluation for systems combining elements with extremely different vapor pressures. The diffusion behavior is discussed in comparison with bulk diffusion experiments in Ni-Zn; e.g. [5, 6], and changes of the Ni-Zn phase diagram in the β/β_1-region are suggested based on our results.

References:

[1] J. Emsley, The Elements, Clarendon Press, Oxford, 1989.

[2] P. Nash, Y.Y. Pan, The Ni−Zn (Nickel-Zinc) system, J. Phase Equilib. 8(5) (1987) 422-430.

[3] J. Miettinen, Thermodynamic description of the Cu–Ni–Zn system above 600∘C, Calphad 27(3) (2003) 263-274.

[4] W. Xiong, H. Xu, Y. Du, Thermodynamic investigation of the galvanizing systems, II: Thermodynamic evaluation of the Ni–Zn system, Calphad 35(3) (2011) 276-283.

[5] V.I. Dybkov, Regularities of Reactive Diffusion and Phase Formation in Ni — Bi, Ni — Zn, and Co — Zn Binary Systems, Powder Metallurgy and Metal Ceramics 40(7) (2001) 426-431.

[6] S. Murakami, M. O, M. Kajihara, Compound Growth due to Reactive Diffusion between Solid-Ni and Liquid-Zn, Mater. Trans. 59(12) (2018) 1872-1877.

EXPERIMENTAL AND THEORETICAL DESCRIPTION OF BINARY SYSTEM GE-MG

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Keywords: Ge-Mg system, SEM-WDX, CALPHAD, ab-initio, phonon spectra

The Ge-Mg system consists of the liquid phase, magnesium (HCP_A3) with negligible solid solubility of Ge, Ge terminal solid solution with very low solubility of Mg, and the intermetallic stoichiometric phase Mg2Ge (anti-fluorite cubic structure, space group $Fm\overline{3}m$) [1996Gro]. There are three invariant equilibria in this system: the eutectic on the Ge-rich side (39 at.% Mg, 687°C), the eutectic on the Mg-rich side (~99 at.% Mg, 635.6°C) and the congruent melting point of Mg2Ge (66.67 at.% Ge, ~1117°C) [1971Rao].

During the experimental study of the ternary Al-Ge-Mg phase diagram [2023Zob], we encountered an inconsistency within the binary Ge-Mg phase diagram, where the binary intermetallic phase $GeMg_2$ showed a relatively high solubility (up to 5%). However, in the scientific literature this phase is perceived as stoichiometric. Due to the lack of experiments targeting the non-stoichiometricity of the $GeMg_2$ phase, we decided to carry out our own experimental investigation on this topic, complemented by a theoretical approach using ab-initio methods at 0 K and at higher temperatures by including phonon spectra.

The samples were prepared from pure elements melted in an arc melting furnace in an inert Ar6N atmosphere. Long-term annealing was carried out in an evacuated quartz glass ampoule. Samples annealed at higher temperatures were placed in a tantalum crucible under an inert Ar6N atmosphere, which was then placed in a quartz ampoule.

Samples were quenched in liquid nitrogen and then placed in an oven to prevent condensation of water vapor on the sample surface. The metallographic treatment was performed using anhydrous isopropanol as a coolant. The chemical composition of the phases and the overall composition of the samples were measured using SEM-WDX methods. The structure of the phases was verified by XRD.

The results of the analyses showed the existence of magnesium solubility in the structure of the intermetallic phase $GeMg_2$. The highest magnesium concentration was found in samples annealed at 600°C. The solubility of germanium in the GeMg2 structure was not observed.

The binary phase diagram has been modelled by the CALPHAD approach. The modelled phase diagram is based on a known experimental phase diagram, enthalpy of formation of the $GeMg_2$ phase calculated by ab-initio methods and heat capacity calculated with phonon spectra. The agreement is very good.

References:

[1971Rao] Rao Y.K., Belton G.R., Metall. Trans., 2(1971), 2215.
[1996Gro] Grosch G.H., Range K.J, J. of Alloys and Compd, 235(1996), 250-255.
[2023Zob] Zobač O., Karpíšková L., Kroupa A., J. Phase Equilib. Diffus., 44(2023), 127-136

PHASE EQUILIBRIA IN THE Li2O-SiO2 AND MnOx-SiO2 SYSTEMS

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Keywords: Li recycling, CALPHAD approach, Thermodynamic modeling and Phase diagram.

The importance to recycle and recover valuable transition metals (such Co, Ni) and Li from Lithium-Ion Batteries (LIBs) increased in the recent years. Application of pyrometallurgical methods such as smelting reduction make it possible the direct recovery of transition metals from their respective oxides while Li2O and partially Mn oxides are dissolved in slag [1]. In this context, Li_2O reacts with slag, forming $LiAlO_2$ or spinel solid solution [2]. Different slag systems have been studied in the literature and the understanding phase relations in the Li_2O-MnO_x-SiO_2-Al_2O_3 system can lead to an optimization of the Li recycling process [3]. Using the CALPHAD approach and two-sublattice partially ionic liquid model for liquid description, investigations of pseudo-ternary and pseudo-binary systems among these oxides have been performed by our research group [4-5]. Phase equilibria for the Li_2O-SiO_2 system were experimentally investigated with Li_2O and SiO_2 as starting materials, and the samples were characterized using SEM and XRD. The temperature of the $L \leftrightarrow Li_4SiO_4 + Li_2SiO_3$ eutectic reaction at 1289K was experimentally determined by DTA, while the heat capacity of the Li_8SiO_6 phase was obtained by DSC. Four stoichiometric phases ($LiSiO_6$, Li_4SiO_4, Li_2SiO_3, and $Li_2Si_2O_5$) were considered to be stable in the Li_2O-SiO_2 system. The metastable liquid miscibility gap on the SiO_2-rich side was reproduced. A preliminary thermodynamic description for the MnO_x-SiO_2 system was also derived, accounting for the available experimental data in the literature. Two stoichiometric compounds, $MnSiO_3$ (rhodonite) and Mn_2SiO_4 (tephroite), are stable in equilibrium with metal Mn. At air oxygen partial pressure, the Mn_7SiO_{12} (braunite) phase has a homogeneity range extension in the Mn_2O_3-enriched compositions, while the stability ranges of $MnSiO_3$ and Mn_2SiO_4 phases are substantially reduced. The nature of invariant reactions and thermodynamic properties were well reproduced for both systems and the phase diagrams were calculated.

References:

[1] Schnickmann A. et al. Stabilization of Mn4+ in synthetic slags and identification of important slag forming phases. Minerals.14(4), 368 (2024).

[2] Schirmer, T. et al. Li-distribution in compounds of the Li2O-MgO-Al2O3-SiO2-CaO system - A first survey. Metals, 10, 1633 (2020).

[3] Xiao, S. et al. Recovery of valuable metals from spent lithium-ion batteries by smelting reduction process based on MnO–SiO2–Al2O3 slag system. J. Sustain. Met., 3, 703-710 (2017).

[4] De Abreu, D.A., et al. Experimental Investigation and Thermodynamic Modeling of the Li2O–Al2O3 System, J. Phase Equilib. Diff., 45, 36-55 (2024).

[5] Ilatovskaia M, and Fabrichnaya O. Critical assessment and thermodynamic modeling of the Al-Mn-O system. J. Alloy. Compd., 884, 161153 (2021).

S2-O7

SURFACE DAMAGE MECHANISMS AND NEW SYSTEM DESIGN OF CERMETS

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Keywords: CALPHAD, cermets, materials design, corrosion resistance

Cermets (ceramic-metal composites) combine the high hardness of the ceramic phase and the high toughness of the metallic bonding phase, and are widely used in fields such as underwater exploration, shield machines, and metal processing. The severe environment of highly coupled multiple factors (high temperature, wear, corrosion, impact, etc.) has put forward an urgent demand for the integrated enhancement of high strength, high toughness, high temperature resistance, wear resistance, and corrosion resistance of cermets. This work has developed methods coupling first-principles calculations, molecular dynamics, CALPHAD (CALculation of PHAse Diagrams), and machine learning to investigate the surface damage mechanisms of metal ceramic materials under the action of coupled multiple factors. Based on this, new systems were designed through data-driven composition and structure regulation to achieve enhancement of key performance. The newly developed material components have been validated in deep drilling applications.

References:

[1] M. Lou, L. Chen, K. Xu, G. Zhang, K. Chang, Tribocorrosion of TiC-based composites incorporating Ni and Co binders in saline solutions, ***International Journal of Refractory Metals and Hard Materials*** 119 (2024) 106519.

[2] X Xiao, K Chang, K Xu, M Lou, L Wang, Q Xue, Efficient prediction of corrosion behavior in ternary Ni-based alloy systems: Theoretical calculations and experimental verification, ***Journal of Materials Science & Technology*** 167 (2023) 94-106.

[3] T Tang, X Xiao, K Xu, M Lou, X Hu, S Li, W Zhang, Z Fan, K Chang, Corrosion-resistant WC-Co based cemented carbides: Computational design and experimental verification, ***International Journal of Refractory Metals and Hard Materials*** 110 (2023) 106044.

[4] Z Zheng, J Lv, M Lou, K Xu, L Chen, J Zhang, Y Du, W Zhang, K Chang, Macro-gradient structures generated in Ti (C, N)-based cermets with supersaturated WC: an experimental and thermodynamic investigation, ***Materials Research Letters*** 11(2) (2023) 152-158.

[5] M. Lou, X. Chen, K. Xu, Z. Deng, L. Chen, J. Lv, K. Chang, L. Wang, Temperature-induced wear transition in ceramic-metal composites, ***Acta Materialia*** 205 (2021) 116545.

S2-O8

EXPERIMENTAL INVESTIGATION OF THE MN–NI–TI SYSTEM

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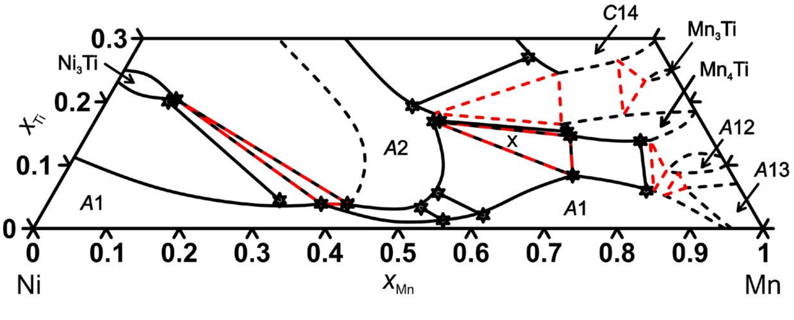
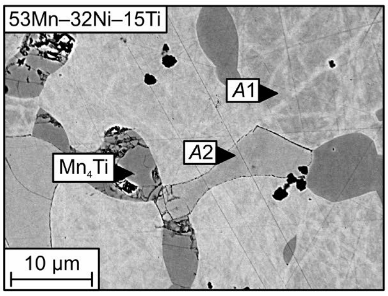
Keywords: Phase diagram, Constitution, Shape-memory alloys, Diffusion couple

The ternary Mn–Ni–Ti system plays a remarkable role in the development of a wide variety of materials ranging from precipitation or transformation strengthened alloys and steels to shape memory alloys (SMAs). In particular, for the Al–Fe–Mn–Ni based SMAs, Ti additions have been found to improve several technologically relevant properties and effects, such as the quenching sensitivity and the initiation of abnormal grain growth. To fully understand these phenomena and to further improve the properties of Fe-based SMAs, reliable phase equilibria data of the corresponding multicomponent systems are crucial.

In the course of the extension of the quaternary Al–Fe–Mn–Ni Calphad database [1] by the element Ti, the phase diagram of the Mn–Ni–Ti system at temperatures above 1000°C was investigated experimentally. The phase diagram has been studied mainly by SEM analyses of the microstructures of as-cast samples, heat-treated and quenched alloys and diffusion couples. Since the current experimental phase diagram data in the Mn–Ni–Ti system is rather scarce [2], diffusion couple experiments are an efficient means of studying large compositional regions in a single sample, which significantly reduces the experimental efforts required to determine isothermal sections. The location of interesting regions in the phase diagram, e.g., three-phase triangles, can be detected and further investigated by a targeted production and heat treatment of additional alloys.

Complementary investigations by DTA, EPMA, EBSD and XRD were conducted to determine the reaction temperatures, chemical composition of the phases and their crystal structures. Particular emphasis was placed on the accurate determination of phase equilibria in order to provide a solid and in-depth basis for a future Calphad assessment of the Mn–Ni–Ti system. The following figure shows the partial isothermal section of the Mn–Ni–Ti system at 1000 °C, together with selected experimentally determined phase equilibria data of the present work, as well as an SEM/BSE image of the heat treated and quenched alloy 53Mn-32Ni-15Ti (nominal composition in at.%, marked with "x" in the partial isothermal section), indicating a three-phase *A*1+*A*2+Mn_4Ti microstructure.





References:

[1] A. Walnsch, M.J. Kriegel, O. Fabrichnaya, A. Leineweber, Calphad 66 (2019) 101621.
[2] K.P. Gupta, J. Phase Equilib. 24 (2003) 371–372.

S3-O9

MEASUREMENT OF PHASE DIAGRAM DATA IN THE SIO2-ZRO2-UO2 SYSTEM FOR SEVERE ACCIDENT APPLICATION

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Keywords : Chernobylite, Thermodynamics, Laser heating, Severe accident

During a severe accident, UO2 fuel can react at high temperature with the Zr alloy cladding and steel vessel to form what is known as “in-vessel corium”, a complex mixture of solid and liquid phases. At a later stage, these phases may interact with the concrete to form the so-called “ex-vessel corium”. One of the main phases is the silicate phase Chernobylite (Zr,U)SiO4 [1] found in the Chernobyl lava. To understand and model the heat transfer that occurs during the corium-concrete chemical interaction, the thermodynamic properties of the SiO2-ZrO2-UO2 system need to be well understood. In this work, the ATTILHA laser heating set-up [2] was used to measure liquidus temperatures in the SiO2-ZrO2-UO2 system. The molten zone was characterized using SEM, EDS, WDS and EBSD. The experimental set-up will be described. The microstructure of the samples will be presented together with thermodynamic calculations used to interpret the observations.

References:

[1] E.B. Anderson et al, Radiochimica Acta 60 (1993) 149
[2] A. Brunel et al, Calphad 79 (2022) 102490

INVESTIGATION OF THE Al-Mg-Si-In AND Al-Mg-Si-In-Bi ALLOYS

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Keywords: Thermodynamic, Al-In alloys, Solidification, Forming properties

The Al-Mg-Si alloys (6XXX series) are precipitation-hardening alloys known for their moderate strength and strength-to-density ratio, good ductility, weldability, and corrosion resistance. However, machining these alloys can be challenging as they tend to form long, continuous strips that may cause disruptions in the machining process. The study includes a comparative investigation of the solidification sequence of Al-Mg-Si alloys modified with the addition of In and In-Bi master alloys. Some aluminium alloys contain tin, bismuth, and indium as substitutes for lead in various combinations, with the In. The objective of this experiment was to evaluate the potential suitability of indium, either alone or in combination with bismuth, as a substitute for toxic lead in free-machining aluminium alloys. This was carried out to investigate whether a low-melting-point phase formed in the microstructure of these alloys could potentially improve machinability. Thermodynamic analyses and microstructural characterizations were also performed to clarify the solidification sequence and microstructure evolution. Thermodynamic analysis was carried out using Thermo-Calc software, supplemented by differential scanning calorimetry (DSC) experiments. The microstructure of these modified alloys was characterized using SEM–EDS analysis.

The results provide valuable insights into the formation of different phases and eutectics within the alloys studied. The results represent an important contribution to the development of innovative, lead-free aluminium alloys suitable for machining processes. One of the most important findings of this research is the promising suitability of indium as a viable alternative to lead. This potential stems from indium's ability to avoid interaction with other alloying elements and its tendency to solidify as homogeneously dispersed particles with a low melting point. In contrast, the addition of bismuth does not improve the machinability of magnesium-containing aluminium alloys. This is primarily due to their interaction, which leads to the formation of the Mg_3Bi_2 phase, which solidifies as a eutectic with a high melting point.

References:

1. Santos, M.C., Jr.; Machado, A.R.; Sales, W.F.; Barrozo, M.A.S.; Ezugwu, E.O. Machining of aluminum alloys: A review. *Int. J. Adv. Manuf. Technol.* **2016**, 86, 3067–3080. https://doi.org/10.1007/s00170-016-8431-9.
2. Varshney, D.; Kumar, K. Application and use of different aluminium alloys with respect to workability, strength and welding parameter optimization. *Ain Shams Eng. J.* **2021**, *12*, 1143–1152. https://doi.org/10.1016/j.asej.2020.05.013.
3. Timelli, G.; Bonollo, F. Influence of tin and bismuth on machinability of lead free 6000 series aluminium alloys. *Mater. Sci. Technol.* **2011**, *27*, 291–299.
4. He, C.; Luo, B.; Zheng, Y.; Bai, Z.; Ren, Z. Effect of Sn on microstructure and corrosion behaviors of Al-Mg-Si alloys. *Mater. Charact.* **2019**, *156*, 109836. https://doi.org/10.1016/j.matchar.2019.109836
5. Abdelhakim, N.A.; Shalaby, R.M.; Kamal, M. A Study of Structure, Thermal and Mechanical Properties of Free Machining Al-Zn-Sn-Bi Alloys Rapidly Solidified from Molten State. *World J. Eng. Technol.* **2018**, *6*, 637–650. https://doi.org/10.4236/wjet.2018.63040
6. Faltus, J.; Karlík, M.; Haušild, P. Influence of the chemical composition on the structure and properties of lead-free machinable AA 6023 (Al-Mg-Si-Sn-Bi) alloy. In Proceedings of the 13th International Conference on Aluminum Alloys (ICAA13): TMS (The Minerals, Metals & Materials Society), Pittsburgh, PA, USA, 3–7 June 2012; pp. 1545–1550.

7. Rečnik, S.; Medved, J.; Kevorkijan, V.M.; Žist, S. An Advanced Industrial Methodology for Optimizing the Properties and the Process of Homogenization for Extruded AA2xxx and AA6xxx. In *Light Metals*; Eskin, D., Ed.; The Minerals, Metals & Materials Series; 2022; https://doi.org/10.1007/978-3-030-92529-1_31
8. Rečnik, S.; Bizjak, M.; Medved, J.; Cvahte, P.; Karpe, B.; Nagode, A. Mechanism of the Mg_3Bi_2 Phase Formation in Pb-Free Aluminum 6xxx Alloy with Bismuth Addition. *Crystals* **2021**, *11*, 424. https://doi.org/10.3390/cryst11040424

S3-O11

SEMI-LIQUID ANODES FOR Li-ION BATTERIES: CONSTITUTION AND THERMODYNAMICS OF THE SYSTEMS Li-Zn AND Li-Sn-Zn

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Keywords: Li-Sn-Zn, phase equilibria, enthalpy of mixing, miscibility gap

The ever-increasing demand for energy and the need for constant availability of both portable and stationary power sources is driving the need for continuous improvement in energy storage devices like batteries. One promising cell technology is the lithium-ion battery, which has several advantages, including high specific energy, low self-discharge rate and high operating voltage. However, high performance characteristics for electric vehicle propulsion or load leveling of power grids can only be achieved based on new electrode and electrolyte materials. Conventional carbon-based anodes, such as graphite, are abundant, relatively cheap and durable, but suffer from low specific capacities (372 mAhg^{-1}). Alternatives include intermetallic anodes based on Si, Sn, Sb or Zn. Tin is an excellent electron conductor and has a high theoretical capacity of 994 mAhg^{-1} during lithiation. A major disadvantage, however, is the formation of cracks during repeated charge/discharge cycles caused by large volume changes during lithiation and de-lithiation, which leads to relatively rapid degradation of the electrode material and hence low cyclability.

Healing of cracks based on partially liquid electrode materials is one solution to overcome this problem. The melting regime of the anode material must be lowered by addition of other relatively low-melting elements such as e.g., Zn, to introduce this effect at application temperatures of Li-ion batteries or slightly above.

Phase diagram investigations of the systems Li-Zn and Li-Sn-Zn based on XRD and thermal analysis were performed in order to understand the respective electrode alloys and their lithiation. Phase equilibria in the binary system Li-Zn, as well as in the ternary system Li-Sn-Zn at 623 K, were studied. Previously known ternary phases [1, 2] and a new Li-rich ternary compound were identified by single crystal X-ray diffraction. In addition, enthalpies of mixing were investigated in the system Li-Zn and in the system Li-Sn-Zn along nine sections using drop calorimetry at 823K [3]. The binary data is in good agreement with literature [4]. Seven of the ternary sections indicate multiple-phase regions and the obtained data were compared with a calculated isothermal section [5]. Thereby a supposed liquid miscibility gap was experimentally confirmed. The ternary data located in the fully liquid monophasic region was fitted based on a Redlich-Kister-Muggianu polynomial including ternary interactions. Our results will contribute to an improved CALPHAD data set for the Li-Sn-Zn system.

References:

[1] W. Pobitschka, H.-U. Schuster, Zur Kenntnis intermetallischer Phasen des Lithiums mit Zink (bzw. Cadmium, Indium) sowie Zinn oder Blei/A Contribution to the Knowledge of Ternary Intermetallic Lithium-Phases with Zinc (resp. Cadmium and Indium) and Tin or Lead, Zeitschrift für Naturforschung B 33 (1978) 115. https://doi.org/10.1515/znb-1978-0123.

[2] S. Stegmaier, T.F. Fässler, Lithium-stuffed diamond polytype Zn–Tt structures (Tt= Sn, Ge): the two lithium–zinc–tetrelides Li3Zn2Sn4 and Li2ZnGe3, Inorganic Chemistry 52 (2013) 2809. https://doi.org/10.1021/ic3011037.

[3] L. Fischer, H. Flandorfer, Calorimetric study of the enthalpy of mixing in the liquid systems Li-Zn and Li-Sn-Zn, Journal of Molecular Liquids 396 (2024). https://doi.org/10.1016/j.molliq.2024.123978.
[4] A. Dębski, W. Gąsior, Calorimetric measurements of the Li–Zn system. Direct reaction method and mixing enthalpy, The Journal of Chemical Thermodynamics 98 (2016) 111. https://doi.org/10.1016/j.jct.2016.03.017.
[5] P. Turchi, Thermodynamic Assessment of the Ternary Alloy System Li-Sn-Zn, (2014). https://www.osti.gov/servlets/purl/1130035.

S3-O12

THE β-α TRANSFORMATION IN 6063 ALUMINUM ALLOY, IN-SITU EXPERIMENTAL RESULTS AND COMPUTATIONAL ANALYSIS

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Keywords: particle transformation, synchrotron radiation, computational simulation

The cast state of common industrial Aluminum 6xxx alloys contains large primary phases that are deleterious for the material's performance. During homogenization, whenever Fe (and Mn) is present, the primary needle-shaped β-Al_5FeSi particles located near the grain boundaries transform into the more favorable round-shaped α-$Al_{12}(Fe,Mn)_3Si$ phase [1], [2]. Experimental studies quantifying the β→α transformation have mostly relied on ex-situ optical microscopy measurements, where the shape factor determined the nature of the particle and its relative fraction within the volume [3], [4].

The current study obtains new experimental results from the β→α particle transformation. In-situ synchrotron radiation is used to analyze the microstructure evolution of a 6063 Aluminum alloy from its as-cast state up to the homogenization temperature (560 ºC), using two heating rates, 4 K/min and 20 K/min; the characteristic high brilliance of the incoming beam and the detection features of the experiment enabled a time-resolved study, which revealed the sequence behind the β→α transformation by evaluating the change in the diffractograms during the specified heat treatment.

In addition, using the MatCalc software with its latest thermodynamic and diffusion databases, a simulation of the phenomena is included; this allows the combination of published and new experimental results to a thermokinetic computational analysis, including the effect composition and temperature have on the nucleation and dissolution driving forces of α-$Al_{12}(Fe,Mn)_3Si$ and β-Al_5FeSi, respectively. The objective of this study is, therefore, to broaden the understanding of how and why the material microstructure evolves during the first stages of the alloy's processing.

References:

[1] I. Todd, W. Kool, I. S. van der Zwaag, and I. NCW Kuijpers, "Intermetallic phase transformations during homogenisation of 6xxx Al alloys A literature review," 2000.
[2] N. Bayat, T. Carlberg, and M. Cieslar, "In-situ study of phase transformations during homogenization of 6060 and 6063 Al alloys," Journal of Physics and Chemistry of Solids, vol. 130, pp. 165–171, Jul. 2019, doi: 10.1016/j.jpcs.2018.11.013.
[3] I. G. Aguilar, J. T. Torres, A. F. Valdés, and A. A. F. Saldivar, "The Effect of Interrupted Homogenization on β-Al5FeSi → α-Alx (Fe and Mn) Si Transformation in the A6063 Aluminum Alloy," Metals (Basel), vol. 12, no. 12, Dec. 2022, doi: 10.3390/met12122117.
[4] S. Zajac, B. Hutchinson, A. Johansson, and L.-O. Gullman, "Microstructure control and extrudability of Al-Mg-Si alloys microalloyed with manganese," 1994.

S3-O13

RECENT DEVELOPMENTS OF CALPHAD DATABASES FOR ALUMINUM ALLOYS

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Keywords: CALPHAD, Aluminum alloys

Aluminum alloys are widely used across industries, from structural components in aerospace and automotive sectors to packaging foils in food industry. By alloying with elements such as Mg, Si, Cu, Zn etc., aluminum alloys can be heat-treated to enhance strength, workability, thermal/electrical conductivity, and corrosion resistance, all while maintaining a lightweight profile.

CALPHAD is a key approach to accelerate the understanding and design of materials with a demanding balance of different properties. By incorporating thermophysical properties such as molar volume, electrical resistivity, thermal conductivity, viscosity, and surface tension of liquid into our CALPHAD database, we enable a more comprehensive design of new alloys and/or processes.

In this talk, the recent development of a 48-element thermodynamic and properties database (TCAL9) will be presented. TCAL9 includes all stable phases in the assessed subsystems alongside crucial metastable precipitates observed in industrial Al-alloys. Coupled with its compatible mobility database (MOBAL8), this framework allows for studying multiple phenomena, including diffusion-controlled phase transformations and precipitation kinetics. It will here be exemplified how simulations can be used to aid alloy design and process optimization of aluminum alloys.

S4-O14

UNCERTAINTY QUANTIFICATION AND PROPAGATION IN CALPHAD AND CALPHAD-BASED FRAMEWORKS

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Uncertainty quantification (UQ) is the process of identifying different sources of uncertainty and developing the corresponding mathematical representations for the error bounds of quantities of interest (QoI). Uncertainty in QoIs arises from different sources, including the random/stochastic nature of the physical system in question; uncertainty in the values of the variables used to parameterize models; lack of sufficient or accurate data to parameterize the models; and incomplete knowledge of the model structure representative of the physical model due to excessive simplifications, wrong assumptions and/or incomplete representation of the underlying physics/chemistry in the model. For over a decade, uncertainty quantification (UQ), its propagation (UP), and overall uncertainty management (UM) have been recognized as essential components to any effort in which simulations assist the discovery and design of materials. Perhaps the general area in the field of computational materials science that has experienced a comparatively slow rate of development—in the context of UQ/UP/UM—that is at odds with its importance in the entire ICME edifice is the CALculation of PHAse Diagrams (CALPHAD) method. In this work, we present novel approaches to UQ and UP in CALPHAD modelling. In this talk, I will present some of the most recent advances in UQ and UP in CALPHAD and CALPHAD-based frameworks. I will provide some examples in which rigorous approaches have been used to quantify the factors most responsible for uncertainty in CALPHAD modeling. I will also discuss how we can use Bayesian methods to evaluate models, fuse model predictions as well as assess the quality of competing thermodynamic models. I will finally discuss some approaches to propagate uncertainty through CALPHAD models into Phase Field models and beyond.

THERMODYNAMIC DESCRIPTION OF UNARY GLASS FORMING LIQUIDS USING 2-STATE MODELS

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Keywords: Calphad, Unary, Liquid, Glass, 2-state model

The 2-state model, or Two-Level System (TLS), is a well-known tool in statistical physics for describing specific heat anomalies in crystals at low temperatures. With the recent development of the 3rd generation Calphad thermodynamic databases, these models are enjoying renewed interest, as they have been adopted to describe the configurational part of thermodynamic functions in the liquid phase.

The basic equations of the two-state model, in its simplest version analogous to an ideal binary solution formalism, will be presented. The analogy with the ideal binary solution is not complete, however, as the composition variable here is an internal thermodynamic variable and not an external variable that can be imposed from outside the system. We will also try to clarify the physical meaning of the functions, variables and parameters involved in the equations, in relation to the phenomenology of supercooled liquids and the glass transition.

It is worth noting that the ideal 2-state model is exclusively used for describing the liquid phase in 3rd generation Calphad work. However, not all types of liquids can be described using an ideal 2-state model and for liquids qualified as fragile, which show a dramatic decrease in entropy as the temperature drops from melting point to glass transition, a regular 2-state model appears to be a more promising modelling solution.

The formalism, phase diagram and main characteristics of the regular 2-state model will be illustrated through a parametric study and the test case of water taken from a literature work. Compared to its ideal counterpart, the regular 2-state model may represent a valuable complementary modeling tool that considerably broadens the spectrum of phenomena that can be described. This model should only be used if it significantly improves the description compared to the ideal model, and its applicability in a multicomponent system should also be verified.

References:

Benigni, P. (2023). Interest of the regular 2-state model for the description of unary liquids: Presentation of the formalism. Calphad, 83, 102627. https://doi.org/10.1016/j.calphad.2023.102627

Benigni, P. (2021). Calphad modeling of the glass transition for a pure substance, coupling thermodynamics and relaxation kinetics. Calphad, 72, 102238. https://doi.org/10.1016/j.calphad.2020.102238

S4-O16

COMPUTATIONAL THERMO-KINETIC SIMULATION OF MX PHASE IN HSLA STEEL: THE IMPORTANCE OF THERMODYNAMIC PARAMETERS

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Keywords: MX, thermodynamic modeling, interfacial energy, kinetic precipitation

The microstructure of microalloyed steels are controlled by small concentrations of the elements Nb, Ti and V, forming carbonitride phases with a FCC structure, MX. To control the distribution and size of precipitate, it is important to have accurate knowledge of the thermodynamic of the Fe-(Nb,Ti.V)(C,N) systems.

In the present work, we review and assess the thermodynamic modeling of the MX phases. Within this work, it was found that some binary alloy (such as Fe-Nb, Nb-C, Nb-N) systems as well as M-(C,N) (M standing for metal) needed to be re-optimized in order to get accurate descriptions for multicomponent extensions with relevance for microalloyed steels. The reassessed description was then used to calculate the interfacial energy [1], representing an important property for classical nucleation theory and kinetic precipitation simulation. Via practical examples, we demonstrate the importance of the model parameters for the calculation of precipitation (i.e. Time-Temperature-Precipitation) and recrystallization kinetics [2].

References:

[1] A. Costa e Silva, Challenges and opportunities in thermodynamic and kinetic modeling microalloyed HSLA steels using computational thermodynamics, Calphad Comput. Coupling Phase Diagrams Thermochem. 68 (2020) 101720. doi:10.1016/j.calphad.2019.101720.

[2] E. Sobotka, J. Kreyca, R. Kahlenberg, A. Jacob, E. Kozeschnik, E. Povoden-karadeniz, Metals (Basel). 13 (2023) 884. doi:https://doi.org/10.3390/met13050884.

S4-O17

IN-SITU AL-7075/AL3TI METAL MATRIX COMPOSITES FORMATION BY STIR-ASSISTED ULTRASONIC MELT PROCESSING UNDER DYNAMIC NUCLEATION

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Keywords: In-situ casting, In-situ composite, Ultrasonic cavitation, Heterogeneous nucleation, Strengthening mechanisms, Fractography

Owing to the high propensity for particle agglomeration, the fabrication of aluminum matrix composites with uniform distribution using casting routes is extremely difficult. In this study, the in-situ development of the Al3Ti reinforcing phase by employing stir-assisted ultrasonic treatment was utilized to improve the homogeneity, wettability, and thermodynamic stability of the reinforcing particles in an Al-7075 alloy matrix. The in-situ Al3Ti particles acted as heterogeneous nucleation sites and facilitated grain refinement to form a non-dendritic globular structure compared with the dendritic cells of the base alloy. The grain size of the α-Al dendrites reduced from 160 μm to 65, 50, and 40 μm with the addition of 2, 5, and 7 wt% Al_3Ti, respectively. The reduction in the porosity of the composites and the improvement of the particle homogenization were due to cavitation-induced de-agglomeration and the degassing effect. The formation of a robust and clean interface between the Al3Ti particles and Al alloy via ultrasonic vibration improved the integrity of the composites compared with that of the base alloy. The thermal expansion mismatch between the Al3Ti particles and Al alloy contributed significantly to the improved mechanical properties of the composites. The present work was reported in ref. [1].

References:

[1] S. V. Sujith, Hansoo Kim, Rahul S. Mulik, Hyeonwoo Park, Joonho Lee, Metals and Materials International (2022) 28:2288–2303.

S5-O18

CRYSTAL CHEMISTRY OF THE SOLID SOLUTIONS BASED ON β-MN

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Keywords: β-Mn, Rietveld, Calphad, Site occupancies, DFT

Mn is a special element because of its 4 allotropic forms. Among them, α and β forms distinguish by their crystal structures typical of those of intermetallic compounds rather than of pure elements. Binary solid solutions based on β-Mn have been systematically investigated from a structural point of view [1]. The site occupancies of the substitutional solute elements Al, Co, Fe, In, Ir, Ni, Os, Ru, Si, Sn and Zn on the two distinct sites of its crystal structure have been determined experimentally by Rietveld refinement of X-ray or neutron powder diffraction data. The atomic distribution is discussed in light of the changes of lattice parameters in the solution and compared between the different chemical systems. A systematic analysis of the volume change within the complete binary systems has been carried out. Anomalies are observed and explained for the first time. The study is complemented by a detailed DFT investigation of the different systems demonstrating a problem with the description of the Mn atom by traditional first-principles calculations. The importance of the ordering of the solute element for the Calphad modeling is discussed and the use of a two-sublattice model for the description of β-Mn solid solutions in agreement with the presence of two different Wyckoff positions, instead of the conventional disordered solution model, is highly recommended.

References:

[1] J.-M. Joubert and J.-C. Crivello, Acta Mater. 267 (2024) 119738.

S5-O19

INVESTIGATION OF EQUILIBRIUM CONDITIONS IN LIQUID METAL DEALLOYING BY IN SITU X-RAY DIFFRACTION

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Keywords: Dealloying, Thermodynamic equilibria, In situ X-ray diffraction, Synchrotron, Rietveld analysis

Liquid metal dealloying (LMD) is a novel technique[1] applicable on a wide range of metals to elaborate bicontinuous micro and nano composite and porous materials. It consists in the selective dissolution of an element (Ni) from a precursor alloy (Fe-Ni) into a metallic liquid bath (Mg). Upon dissolution of Ni, Fe reorganises into a porous connected structure. This project aims at applying LMD to elaborate micro-porous metallic powders. Powders being the key ingredient of metallic additive manufacturing, the study and modification of their properties is therefore essential to improve these new manufacturing processes. This study focuses on the elaboration of porous Fe-based powders where Ni has been dissolved.

To elaborate dealloyed powders, Invar ($Fe_{65}Ni_{35}$) and solvent Mg powders were mixed. This mixture was then heated and the melting of Mg triggered the dealloying reaction. Utilising a powder mixture enabled precise control over the size of the Mg bath relative to the amount of precursor. Thus, the saturation of the Mg bath in Ni could be obtained, yielding partially dealloyed powders with a core-shell structure (Fig. 1). However, questions lingered about the role of intermetallic compounds in the dealloying reaction, the parameters influencing the ligaments composition and the kinetics of the reaction. To reach a better understanding of the dealloying reaction, it was monitored using in situ X-ray diffraction at the ID11 beamline of the European Synchrotron Radiation Facility.

The various phases present throughout the dealloying reaction were monitored and quantified via Rietveld analysis, as depicted in Fig. 2. The results were rationalised in light of the phase-diagram of the system, thereby revealing the role of the Mg_2Ni intermetallic on the dealloying reaction. These observations demonstrated how adjusting the thermodynamic conditions of the reaction (FeNi/Mg ratio, temperature) allows tailoring the microstructure of dealloyed powders, leading to the formation of core-shell structures with ligaments of predictable composition.

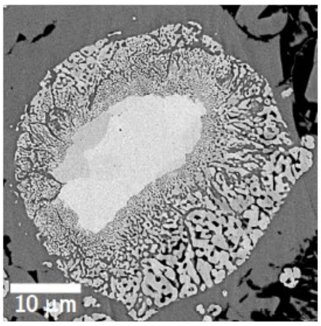

Figure 1: Partially dealloyed Invar powder

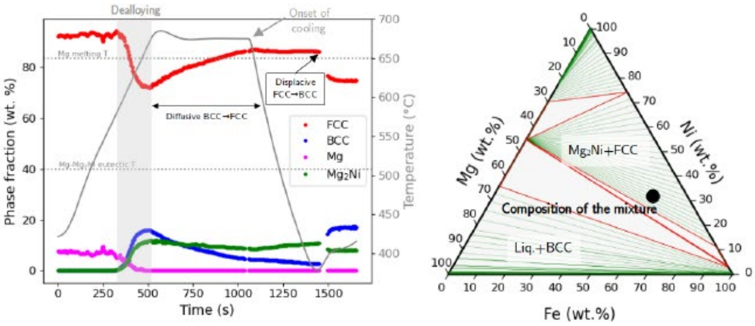

Figure 2: Evolution of phase fractions during the dealloying process compared to a simplified FeNiMg phase diagram[2]

1. Wada T. et al. Materials Letters. 2011 Apr 15;65(7):1076–8.2.
2. Wang P. et al. International Journal of Materials Research. 2011 Jan 1;102(1):6–16.

S5-O20

NEW EXPERIMENTAL DATA ON Zr-Fe-O

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Keywords: Zr-Fe-O ternary system; Corium

During severe accidents in water-cooled nuclear reactors, such as Pressurized Water Reactors (PWR) or Boiling Water Reactors (BWR), coolant failure leads to core overheating and potential meltdown [1]. Core components relocate, forming corium, a complex molten substance with stratified liquid phases. In-vessel retention (IVR) strategy aims to cool corium within the reactor vessel to prevent further escalation [2]. However, interphase reactions alter corium composition, potentially compromising IVR effectiveness. Improving simulations and modeling of corium, particularly the U-Zr-Fe-O system, through accurate thermodynamic characterizations is crucial to accurately predict vessel performance and improve nuclear safety [3]. Despite extensive research efforts [4], databases remain incomplete, and uncertainties persist regarding the chemical composition of the metallic and oxide liquids and their thermal behaviour, which can have a significant impact on predictions of vessel performances. In this context, the aim of this work is the investigation of the Zr-Fe-O ternary subsystem, which has been relatively underexplored in its entirety [5] as well as the Zr-Fe binary system, which has been studied but in which uncertainties remain [6–8]. In addition, experimental thermochemical data are lacking for several phases, essential to enhance the precision of calculations and the quality of simulations for a better thermodynamic characterization of the in-vessel corium system. We have evidenced a new eta-carbide phase, not referenced in the literature within the ternary system: Zr3Fe3O0,75, fully characterized using Powder X-Ray and Neutron Diffraction. We clarified the nature of the Zr6Fe23O phase, which was still under discussion [6–8], confirming its oxygen-stabilized composition and justifying its inclusion in the ternary system. We conducted measurements of the enthalpy of formation and heat capacity for both ternary phases obtained (Zr3Fe3O0,75, Zr6Fe23O) as well as on Zr4Fe2O0,67, never determined before. Additionally, we acquired thermodynamic data (ΔHf and Cp) for Zr3Fe, in the binary system.

References:

[1] H. Tuomisto, T.G. Theofanous, Nucl. Eng. Des. 148 (1994) 171–183. https://doi.org/10.1016/0029-5493(94)90108-2.
[2] O. Kymäläinen, H. Tuomisto, T.G. Theofanous, Nucl. Eng. Des. 169 (1997) 109–130. https://doi.org/10.1016/S0029-5493(96)01280-0.
[3] Y. Jiang, Y. He, W. Zheng, J. Zhang, D. Zhang, X. Lu, J. Nucl. Mater. 574 (2023) 154180. https://doi.org/10.1016/j.jnucmat.2022.154180.
[4] M. Fukasawa, S. Tamura, J. Nucl. Sci. Technol. 44 (2007) 1210–1219. https://doi.org/10.1080/18811248.2007.9711364.
[5] O. Fabrichnaya, D. Pavlyuchkov, Metall. Mater. Trans. A 47 (2016) 152–159. https://doi.org/10.1007/s11661-015-2805-8.
[6] F. Stein, G. Sauthoff, M. Palm, J. Phase Equilibria 23 (2002) 480–494. https://doi.org/10.1361/105497102770331172.

[7] P. Lafaye, C. Toffolon-Masclet, J.-C. Crivello, J.-M. Joubert, J. Alloys Compd. 821 (2020) 153200. https://doi.org/10.1016/j.jallcom.2019.153200.
[8] Z. Du, L. Zou, C. Guo, X. Ren, C. Li, J. Iron Steel Res. Int. 28 (2021) 1375–1389. https://doi.org/10.1007/s42243-021-00570-w.

S5-O21

THERMODYNAMIC MODELLING AND EXPERIMENTAL STUDY OF PROTECTIVE BARRIERS AGAINST CARBON DIFFUSION DURING SPS

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Keywords: SPS, carburization, DICTRA simulation, solid state diffusion

The elaboration of metallic parts by powder metallurgy techniques such as Spark Plasma Sintering (SPS), represents a relevant alternative to conventional manufacturing processes (casting, forging, etc.) [1]. This technique allows the elaboration in a single stage of dense and high-performance materials with high mechanical properties [2,3]. The powder is inserted into a mold, and densified by Joule heating and uniaxial pressure. The sintering time is limited, due to the use of high heating and cooling rates (of the order of several hundred of °C·min^{-1}) [4,5]. One of the major problems during SPS of metallic powders is the carbon diffusion from the graphite tooling and/or from the graphite foils inserted between the powder and the mold (punches and die) to the powder. If the carburization is not blocked, it can lead to a degradation of the properties of the sintered material and to the formation of surface composition gradients. Up to now, only few studies addressed this issue [6].

In a previous work [7], it has been demonstrated that a titanium coating (about 1 µm thick) deposited by Physical Vapor Deposition directly on the graphite foil was efficient in avoiding carburization of pure iron during sintering. In the present study, thermodynamic simulations were performed using the ThermoCalc® DICTRA module in order to estimate the penetration depth of carbon in the titanium coating and the sintered iron. By imposing a thermal profile, the diffusion problem was coupled to a temperature history characteristic of the SPS cycle (1050°C-10 min- 70 MPa), in order to understand the role of solubility of carbon in iron and in the protective coating, carbide stability, and respective diffusivities. In each case, simulations were compared with experimental investigations, allowing to validate the modeling results.

To study the mechanisms of phase transformations induced by carbon and iron diffusion inside the titanium coating during sintering, SPS interrupted tests were performed. Carbon and iron diffusion inside the titanium film were simulated for each temperature and compared to microstructural characterizations.

The modeling method used in the present work can be extended to different protective coatings, helping to quickly select the most promising ones to be tested.

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References:

[1] H.W. Zhang et al., Scripta Mater. 53 (2005) 863-868.
[2] A. Bolsonella et al., J. Alloys Compd. 856 (2021) 157869.
[3] S. Akhtar et al., Mater. Today Proc. 5 (2018) 18649-18655.
[4] Z.A. Munir et al., J. Mater. Sci. 2006, 41 (3), 763-777.
[5] V. Mamedov et al., Powder Metall. 2002, 45 (4), 322-328.
[6] K.E. Smetanina et al., J. Alloys Compd. 973 (2024) 172823.
[7] M.R. Ardigo-Besnard et al., Solids 2(4) (2021) 395-406.

SYNERGISTIC STUDY OF ORDERING MOBILITY IN *D*0$_3$-Fe$_3$Al THROUGH EXPERIMENTAL OBSERVATION AND PHASE-FIELD SIMULATION

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Keywords: Ordering mobility; Antiphase boundary; Fe$_3$Al; Phase-field simulation; Transmission electron microscopy

The presence of antiphase boundaries (APBs) can significantly impact the properties of materials. For instance, superelasticity with a recovery stain of as high as 5 % has been reported in the *D*0$_3$-ordered Fe$_3$Al alloys due to the interactions between the dislocations and APBs [1]. The temperature range for superelasticity in Fe$_3$Al is approximately 250 K (from –50 °C to 200 °C), broader than that observed in superelasticity originating from the martensitic transformation and makes Fe$_3$Al a potential shock-absorbing material. However, the superelasticity of Fe$_3$Al can only be found in single crystals and is closely related to the antiphase domain (APD) size. Recently, the fabrication of 316L stainless steel single crystals using laser powder bed fusion (L-PBF) has been successfully achieved [2], and its application to Fe$_3$Al single crystals is currently underway. On the other hand, the attempts for evaluating the ordering kinetics in *D*0$_3$-structured Fe$_3$Al and controlling the APD size has been made since the 1970s [3]. However, the determined ordering kinetics to date exhibit significant discrepancies, and no synergistic studies have been conducted.

The present study addressed the long-standing challenge of determining the growth kinetic of *D*0$_3$-ordered Fe$_3$Al APDs by the combination of phase-field (PF) simulations and transmission electron microscopy (TEM) observation. The “shape coefficient” which correlates the growth rate of APD with 3-dimensional intricate shape and the shrinking rate of 2-dimensional circular APBs was assessed through a comparative analysis of PF simulations using 2D- and 3D-models. Simultaneously, the increase rate in APD size in bulk samples after heat treatment was measured using TEM. By incorporating the calculated shape coefficient and experimental data on APD growth rates, we successfully derived accurate values of mobility for forming *D*0$_3$ type ordered structure [4]. This finding lays the foundation for optimizing heat treatment conditions to regulate APD structure and enhance the superelasticity of Fe$_3$Al. This methodology can be extended to estimate the ordering mobility of other intermetallic.

References:

1. H.Y. Yasuda, K. Nakano, T. Nakajima, M. Ueda, Y. Umakoshi, Acta Mater. **51** (2003) 5101–5112.
2. Y. Liu, K. Nose, M. Okugawa, Y. Koizumi, T. Nakano, Mater. Trans. **64(6)** (2023) 1135–1142.
3. Y. Koizumi, S.M. Allen, Y. Minamino, Acta Mater. **56** (2008) 5861–5874.
4. Y. Liu, M. Watanabe, M. Okugawa, T. Hagiwara, T. Sato, Y. Seguchi, Y. Adachi, Y. Minamino, Y. Koizumi, Acta Mater. **273** (2024) 119958.

S6-O23

DEVELOPING NEW METHODS FOR ALLOYS CHARACTERIZING EMPLOYING TEMPERATURE AND CONCENTRATION GRADIENTS

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Keywords: experimental data mining, materials constitution, solid/liquid interfacial energies, rapid solid-state phase transformations

Experimental data on materials constitution, kinetic properties and physical parameter are requirements for alloy and database development, the prediction of microstructural evolution and materials properties. Considering the number of alloy systems and alloying elements, efficient experimental methods are needed to characterize metallic materials. Experiments with temperature and concentration gradients offer a high throughput. Widely known are methods with diffusions couples [1] and multiples [2-4] or thin films [5, 6]. Less common are methods that combine temperature and concentration gradients. At the university of Jena, methods for effectively obtaining thermodynamic, kinetic, and thermal data have been developed over the past 20 years. Initially, the methods are methodically based on directional solidification, where temperature gradients are used to adjust microstructures. In sample regions where solid and liquid phase co-exist, locally separated, temperature-dependent equilibria are formed and are accessible to subsequent characterization. In this way, large sections of solidus and liquidus lines in binary alloys or paths in multicomponent systems can be determined with a single experiment [7]. Later, a two-step experiment was introduced and used to determine solvus lines (paths) [8]. In addition to methods for the constitution of metallic materials, a method for characterizing chemical diffusion was also developed. Here, the frequency factor and activation energy for the Volume Diffusion are determined with a single experiment [9]. The presentation addresses the development of new experimental methods that use temperature and concentration gradients to either specifically establish a metastable state in metallic alloys, or to increase efficiency by considering multiple (thermodynamic) states simultaneously. By the combined approach of temperature and concentration gradients, solid/liquid interfacial energies of alloys are determined using non-equilibrium microstructures[10,11], pure intermetallic phases are synthesized as bulk materials for measuring and modelling heat capacities $c_p(T)$ [12,13] and temperature-dependent thermal properties, i.e., the thermal conductivity l(T) and thermal diffusivity a(T) are efficiently determined [14-16]. Recently, temperature and concentration gradients are also used to systematically study rapid phase transformations that cannot be described using phase equilibria predicted from the equilibrium phase diagrams [17-21]. This applies to the transition from diffusion-controlled transformation under kinetic effects to interface-diffusion-controlled massive transformation and diffusionless martensitic transformation in particular.

References:

[1]. J.C. Zhao, Combinatorial approaches as effective tools in the study of phase diagrams and composition-structure-property relationships, Progress in Materials Science 51 (2006) 557-631.

[2]. J.C. Zhao, A combinatorial approach for efficient mapping of phase diagrams and properties, Journal of Materials Research 16 (2001) 1565-1578.

[3]. J.C. Zhao, X. Zheng, D.G. Cahill, High-throughput diffusion multiples, Materials Today 8 (2005) 28-37.

[4]. J.C. Zhao, M.R. Jackson, L.A. Peluso, L.N. Brewer, A diffusion-multiple approach for mapping phase diagrams, hardness, and elastic modulus, Journal of the Minerals Metals & Materials Society 54 (2002) 42-45.

[5]. Ludwig, R. Zarnetta, S. Hamann, A. Savan, S. Thienhaus, Development of multifunctional thin films using high-throughput experimentation methods, International Journal of Materials Research 99 (2008) 1144-1149.

[6]. Ludwig, Discovery of new materials using combinatorial synthesis and high-throughput characterization of thin-film materials libraries combined with computational methods, npj Computational Materials 5 (2019) 70.

[7]. G. Zhao, M. Rettenmayr, Using directional solidification to determine solid/liquid equilibria in multicomponent phase diagrams, Journal of Crystal Growth 279 (2005) 540- 550.

[8]. H. Engelhardt, B. Hallstedt, M. Drüe, A. Löffler, M. Schick, M. Rettenmayr, Solvus composition paths in multicomponent alloys – Experimental approach and correlation with Calphad calculations for the example Al–Mg–Si, Advanced Engineering Materials 14 (2012) 319-323.

[9]. H. Engelhardt, M. Rettenmayr, Diffusion in a temperature gradient – A single cycle method to determine frequency factor and activation energy of solid diffusion coefficients in alloys, Acta Materialia 95 (2015) 212-215.

[10]. S. Lippmann, I.-H. Jung, M. Paliwal, M. Rettenmayr „Modeling temperature and concentration dependent solid/liquid interfacial energies“ Philosophical Magazine 96 (2016) 1–14.

[11]. S. Lippmann, C. Simon, S. Zechel, M. Seyring, U.S. Schubert, G. Wilde, M. Rettenmayr „Determining solid/liquid interfacial energies in Al-Cu by curvature controlled melting point depression” Acta Materialia 147 (2018) 113-121.

[12]. S. Lippmann, R. H. Kemsies, M. Schick, B. Milkereit, O. Kessler, M. Rettenmayr, K. Hack „Synthesis of pure intermetallic phases on the example of the ternary phase t1 in the system Al-Fe-Ni” Intermetallics 105 (2019) 107-112.

[13]. Saenko, H. Engelhardt, P. Hornig, O. Fabrichnaya, S. Lippmann “Specific heat capacity of the intermetallics e-Cu3Sn, h/h’-Cu6Sn5, Al3Ni and Al3Ni2” Calphad Journal, 74 (2021) 102294.

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

[15]. S. Wilhelmy, A. Zimare, R. Rettenmayr, S. Lippmann “Measurement of the Curie temperature based on temperature dependent thermal properties” International Communications in Heat and Mass Transfer, 124 (2021) 105239.

[16]. S. Wilhelmy, A. Zimare, S. Lippmann, M. Rettenmayr “A temperature gradient evaluation method for determining temperature dependent thermal conductivities” Measurement Science and Technology, 32 (2021) 105601.

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

[18]. T. Kaaden, P. Wutzler, S. Lippmann “Occurrence and morphology of martensite in β-Cu-Zn alloys with minor Al additions” Metallurgical and Materials Transaction A 51 (2020) 3403–3409.

[19]. T. Kaaden, M. Rettenmayr, S. Lippmann “Phase Identification in Multi-Phase Cu- Zn/Cu-Al Alloys with Macroscopic Concentration Gradients” Practical Metallography 58 (2021) 1-13.

[20]. T. Kaaden, V. Tympel, M. Kober, F. Schmidl, M. Rettenmayr, S. Lippmann "Electric pulse heating device for the analysis of solid/solid phase transformations” Review of Scientific Instruments, 92 (2021) 074703.

[21]. A. Walnsch, T. Kaaden, P.D.B. Fischer, M. Motylenko, M. Seyring, A. Leineweber, S. Lippmann „Formation of a nanoscale two-phase microstructure in Cu–Zn(–Al) samples with macroscopic concentration gradient“ Materials Characterization 192 (2022) 112229.

S6-O24

VAPORIZATION STUDY OF CESIUM MOLYBDATES BY KNUDSEN CELL MASS SPECTROMETRY

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Keywords: Cesium molybdates - Fission products - Knudsen cell mass spectrometry - Vaporization

Cesium and molybdenum play a key role in the fission product chemistry of irradiated fuel in the current generation of pressurized water reactors but also in some new generation reactors (Generation IV). They belong to volatile fission products and knowledge of their gas phase speciation is important in severe accident scenarios. The release kinetics of Cs depend on temperature, fuel oxygen potential, and burn up. It can react with Mo and form molybdates. In the mechanism of release of cesium molybdates, only the formation of Cs_2MoO_4 in the gas phase is mentioned and the existence of the molecule $Cs_2Mo_2O_7$ due to vaporization of the condensed phase $Cs_2Mo_2O_7$ is not confirmed [1, 2].

To verify the nature and stability of the gas phase above condensed $Cs_2Mo_2O_7$, we performed Knudsen cell mass spectrometry measurements. We present first the results obtained for $Cs_2MoO_{4(s,\ l)}$ for which the thermodynamic properties of the molecule are well known, and then for $Cs_2Mo_2O_{7(s,\ l)}$.

References:

[1] T. M. D. Do, S. Sujatanond, Y. Tachibana and T. Ogawa (2017) Vaporization and deposition of cesium dimolybdate, $Cs_2Mo_2O_7$, Journal of Nuclear Science and Technology, 54:3, 330-336, DOI: 10.1080/00223131.2016.1273146

[2] V. L. Stolyarova, V. A. Vorozhtcov, S. Lopatin, S. M. Shugurov, E. P. Simonenko, N. P. Simonenko, K. Masaki and D. Costa (2021) Vaporization and thermodynamics of the Cs_2O–MoO_3 system studied using high-temperature mass spectrometry, Rapid Communication in Mass Spectrometry, 35 :e9097, DOI: 10.1002/rcm.9097

NEW NICKEL BASED SUPERALLOYS REINFORCED BY GAMMA DOUBLE PRIME PRECIPITATION

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Keywords: alloy design, thermodynamics, CALPHAD, nickel alloys, gamma double prime

Designing new metallic materials able to withstand higher temperatures is one of the main challenges of the aeronautic industry. This new generation of alloys should entail better mechanical properties and a higher environmental resistance to be viable for future aero engines development. Nickel-based superalloys are widely used for many high temperature applications in aeronautics. Superalloys are generally reinforced either by the γ' or the γ'' phase. Although usually having better formability, the latter family of alloys, including materials such as Inconel 718, cannot be used at temperatures higher than 700 °C.

In this work, a focus is set on the design of nickel-based superalloys reinforced by a γ'' phase stable at higher temperatures. The main difficulty comes from the metastable nature of this phase over the δ phase. The relationship between these two phases is rather well reported in the literature [1] but the properties of γ'' phase are only partially described in commercially available thermodynamic databases.

Our goal is to design new alloys reinforced by a γ'' phase stable up to at least 800 °C using the CALPHAD *(CALculation of PHAse Diagrams)* method and previous experimental results [2,3]. First, a large composition set of about 500 000 alloys was analysed using the Thermo-Calc software with the TCNI10 database to identify compositions which would be favorable for γ'' formation.

Then, the most promising alloys were cast using an arc-melting furnace and characterized (X-Ray Diffraction, Scanning Electron Microscopy, Energy Dispersive X-Ray Spectroscopy,…) after different heat treatments. Micro-Hardness measurements were also carried out to study the stability of the γ'' phase over time as well as its reinforcing potential.

This presentation will focus on the design strategy as well as the agreement between thermodynamic simulations and experimental results.

References:

[1] S.Antonov et al., *Precipitate phase stability and compositional dependence on alloying additions in γ-γ′-δ-η Ni-base superalloys*, Journal of Alloys and Compounds, Volume 626, 2015, pages 76-86
[2] Finet, L., Esin, V.A., Maurel, V., Nazé, L. (2020). *Composition and Temperature Stability of η and δ Phases for Future Nickel-Base Superalloys for Turbine Disks Application*, Superalloys 2020. The Minerals, Metals & Materials Series. Springer, 2020.
[3] L. Finet, *Stabilité en composition et en température des phases η et δ dans les superalliages base nickel*, PhD Thesis, Université Paris Sciences et Lettres, 2019

CALORIMETRIC STUDIES OF ALLOYS AT HIGH TEMPERATURE

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Keywords: thermodynamic properties; drop calorimetry; heat flow DSC; high-temperature calorimetry

Alloys are predominant in numerous industries and topics, such as automotive, aerospace, nuclear and energy storage. Therefore, a need for improved materials has increased over the years. Depending on the application field, alloys with complex compositions need to be developed to have the most adequate characteristics possible (density, rigidity, thermal resistance, etc.). However, high temperature thermodynamic properties of such binary/ternary systems are not always well known, even though they are crucial to better evaluate their stability, reactivity and establish their phase diagram. High temperature calorimetry, such as drop calorimetry or heat flux DSC (HF-DSC), can be used to accurately measure heat capacities, heats of melting, enthalpies of mixing, standard formation enthalpies, as well as solidus and liquidus temperatures up to 1600 °C in a scanning or isothermal mode.

The goals of this presentation will be to give an overview of the existing techniques and to illustrate them through different examples. Drop calorimetry and HF-DSC will also be compared to more common techniques to highlight their pros and cons. As an example, heat capacity (Cp) measurements of steel with the Calvet DC apparatus equipped with the HF-DSC sensor from ambient temperature up to 1550 °C will be presented. Another example of Cp measurements made with the same sensor will be given for iron-based alloys for temperatures up to 1575 °C and enthalpy change and heat of fusion will be calculated [1]. Also, enthalpy of mixing evaluation will be illustrated in the case of binary and ternary systems (magnesium alloys) with the Calvet DC apparatus in the drop configuration [2,3].

References:

[1] Ľ. Drozdová, B. Smetana, M. Machů, V. Novák, J. Vontorová, S. Zlá, M. Kawuloková, L. Řeháčková, S. Sorokina, J. Mater. Res. Technol. 20 (2022) 4318–4332, https://doi.org.10.1016/j.jmrt.2022.08.159.

[2] A. Dębski, S. Terlicka, W. Gąsior, W. Gierlotka, M. Pęska, J. Dworecka-Wójcik, M. Polański, Materials 14 (2021) 680, https://doi.org.10.3390/ma14030680.

[3] W. Gozdur, W. Gąsior, M. Zrobek, A. Budziak, R. Dębski, W. Gierlotka, M. Pęska, M. Polański, A. Dębski, Materials 17 (2024) 1786, https://doi.org.10.3390/ma17081786.

S7-O27

THERMODYNAMIC ASSESSMENT OF THE EFFECT OF Ce AND La ADDITIVES ON ALLOYS OF THE SYSTEM Al-Fe

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Keywords: Thermodynamic, Al-Fe alloys, Lanthanum and/or cerium addition, Solidification, Forming properties

In this study, the thermodynamics assessment and microstructural constituents of Al-1.4Fe alloys (wt%) with different Ce and/or La additions were investigated. The addition of rare earths (RE) to aluminium alloys improves their microstructure in the as-cast state, enhancing both their corrosion resistance and mechanical properties over a range of temperatures.

Thermodynamic calculations were performed to assess phase formation and phase stability in the designed alloys. Thermal analysis of the solidification behaviour of the base alloy revealed three distinct reactions corresponding to the formation of α-Al, eutectic (α-Al + Al_xFe_y) and Fe intermetallic. Comparable reactions were observed in the Ce- and/or La-modified alloy, which occurred at slightly different temperatures, indicating changes in phase formation due to the Ce- and/or La-additions. In all scenarios, the microstructures were hypoeutectic, with primary α-Al and the eutectic (α-Al + Al_xFe_y). Grain refinement in the primary as-cast α-Al grains of the alloy was evident with the RE addition, with La showing the most pronounced effect. Although the RE additions did not noticeably affect the morphology of the eutectic Al_xFe_y phase, they were present in these phases. The addition of Ce and/or La led to the formation of (α-Al + $Al_{11}Ce_3$) and/or (α-Al + $Al_{11}La_3$) eutectics, although no Fe was detected in these eutectics. After the homogenisation Ce- and La-bearing phases agglomerated appropriately and preferentially influenced the forming properties of the designed Al-1.4Fe alloys.

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S7-O28

THE EFFECTIVE BOND ENERGY FORMALISM

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Keywords: Calphad, Thermodynamics, Bond, Compound, Modeling

The sub-lattice model [1,2] has been used for several decades to model the thermodynamics of many phases. Based on the fact that the crystallographic structure of many solid phases are often constituted of different kinds of sites, it considers the mixing of chemical species on different sub-lattices. The variables of the model to describe the Gibbs energy of the phases are the fractions of occupation of these sub-lattices by the different constituents. In addition to the configurational contribution given by these sub-lattice fractions, the formalism allows to describe different kinds of phases thanks to model parameters related to different occupations of the sub-lattices. In the reference term, parameters corresponding to pure compounds *i.e.* configurations where each sub-lattice is occupied by a single component are used. This feature made that the model has often been referred as the Compound Energy Formalism (CEF).

When applying this formalism to complex phases using each of the Wyckoff position as a sub-lattice of the thermodynamic model, the number of parameters increases dramatically and the quality of the extrapolation into high order systems is weak. These drawbacks have recently been addressed by the introduction of the Effective Bond Energy Formalism [3]. This new formalism differs from the CEF by the use, in the reference term, of parameters related to configurations where the occupation of some sub-lattices are undefined. A parameter where the single occupation of only two sub-lattices is given then corresponds to a bond energy. The term effective is added because the actual number of bonds between the sub-lattices is not taken into account. The use of such parameters allows to decrease the number of energetic parameters to describe the thermodynamics of a complex phase. Moreover, they contribute to all the configurations whatever the occupations of the other sub-lattices improving significantly the ability of extrapolation of the model.

The use of this new formalism has already been applied to complex cases [4]. Features of this formalism and know-how acquired up to now to use it will be reported.

References:

[1] M. Hillert, L. I. Staffansson, Acta Chem. Scand. 24 (10) (1970) 3618–3626.
[2] B. Sundman, J. Ågren, Journal of Physics and Chemistry of Solids 42 (4) (1981) 297–301.
[3] N. Dupin, U. R. Kattner, B. Sundman, M. Palumbo, S. G. Fries, Journal of research of the National Institute of Standards and Technology 123 (2018)
[4] J. C. Pereira Dos Santos, S. Griesemer, N. Dupin, U. R. Kattner, C. Liu, D. Ivanova, T. Hammerschmidt, S. G. Fries, C. Wolverton, C. E. Campbell, Journal of Phase Equilibria and Diffusion (2023) 1–28

THERMODYNAMIC MODELS TO UNRAVEL SUPERCONDUCTING PHYSICAL PROPERTIES AND PARAMETERS

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Keywords: EGQCA, Generalized Quasichemical Model, DFT calculations, Thermodynamics, Superconductors

Pursuing new, efficient superconductors has long been at the forefront of solid-state physics and chemistry research. The development of efficient approaches for modeling the thermodynamics of these systems while predicting their behavior, hence, is of utmost importance. In order to fill this gap, we propose an ab initio thermodynamic statistical model called Extended Generalized Quasi-Chemical Approximation (EGQCA), an adaptation of a well-established method used mainly in semiconductors [1-2] to investigate off-stoichiometric superconductors. Within EGQCA, one can predict any alloy's physical properties, such as the critical temperature in superconductors, as a function of composition and crystal growth temperature, evaluating the average of individual supercell properties weighted by their occurrence probability by minimizing the overall mixing Gibbs free energy. As a proof of concept, we apply EGQCA to the well-known Al-doped MgB_2, showing a remarkable agreement with the experimental data. We provide an open-access, user-friendly implementation of EGQCA, making it easily applicable to any 2D or 3D system. Our approach also enables the high-throughput screening of more complex high-Tc superconductors, providing simultaneously valuable insights into the interplay between synthesis and thermodynamics in these materials. In this vein, we also apply the method to Nb-V and Nb-Ti alloys, that also present superconducting properties, in order to further illustrate the range of applications of the EGQCA.

References:

[1] A.-B. Chen and A. Sher, Semiconductor alloys: physics and materials engineering, 1995.
[2] A. Sher, M. van Schilfgaarde, A.-B. Chen, and W. Chen, Phys. Rev. B 36, 4279 (1987)

EXPERIMENTAL CONTRIBUTION TO THE DETERMINATION OF THE IN-ZR SYSTEM FOR SEVERE NUCLEAR ACCIDENT ASSESSMENT

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Keywords: In-Zr system, Thermodynamics, Experimental, Absorber rod, Nuclear severe accident

A revised In-Zr phase diagram is proposed on the basis of detailed metallographic observations, XRD, DTA and bi-DTA, calorimetric techniques and literature data. The new version of the phase diagram will serve as a basis for a future CALPHAD reassessment of the system in the NUCLEA database which will also allow the internal consistency of the experimental results to be tested.

The existence of the intermetallic compounds (In_3Zr, In_2Zr, InZr, $InZr_2$ and $InZr_3$) previously reported by Schubert et al. [1, 2, 3] has been confirmed. An additional phase of In_3Zr_2 composition was found by SEM examination of 20-40 at.%Zr alloys after DTA. Existence of this phase is also supported by DFT calculations [4] but we have not been able to confirm it by XRD.

Using bi-DTA investigation, we showed that there is peritectic reaction, (In) $\leftrightarrow$ αIn_3Zr + Liquid, at low temperature (156.8 ± 0.3 °C). The peritectic decomposition of all the In-rich phases has been evidenced: $In_3Zr \leftrightarrow In_2Zr + L$ at 591.6 ± 2.4 °C, $In_2Zr \leftrightarrow In_3Zr_2 + L$ at 1132.9 ± 1.8 °C and $In_3Zr_2 \leftrightarrow InZr + L$ at 1279 ± 6°C. However, it was impossible to determine the phase transition temperature of αIn_3Zr to βIn_3Zr by DTA due to the quasi athermal character of the transition.

No information is available on the melting and invariant temperature of the compounds in the central region of the system.

On the Zr-rich side, the peritectoid reaction reported by Betterton and Noyce [5] was adopted. However, metallographic investigations on few alloys in this compositional range after DTA have surprisingly shown lamellar eutectoid-like microstructures. Future studies need to be done in order to draw a definite conclusion about the type of invariant reaction.

The experimental standard enthalpy of formation of In_3Zr and In_2Zr compounds have been determined by dissolution calorimetry at 1173 K. For In_2Zr, the enthalpy value obtained by dissolution calorimetry was further complemented by drop calorimetry at 1273 K. The values obtained for In_2Zr are consistent with the NUCLEA database, -38.3 $kJ.mol^{-1}.at^{-1}$ while the value obtained for In_3Zr is more exothermic than NUCLEA, -32.5 $kJ.mol^{-1}.at^{-1}$ [6]. The standard enthalpy of formation of In_2Zr determined by both direct reaction and dissolution calorimetry are consistent. The results obtained for In_2Zr are also in agreement with the experimental data [7, 8].

References:

[1]: Schubert, K., Meissner H.G., Raman A., Rossteutscher W., Einige Strukturdaten Metallischer Phasen (9). Die Naturwissenschaften. 51 (12): 287–287 (1964).

[2]: Schubert K., Frank K., Gohle R., Maldonado A., Meissner H.G., Raman A., et al.,Einige Strukturdaten Metallischer Phasen (8). Die Naturwissenschaften. 50 (2): 41–41 (1963).

[3]: Schubert K., Meissner H.G., Potzschke M., Rossteutscher W., Stolz E., Einige Strukturdaten Metallischer Phasen (7). Die Naturwissenschaften. 49 (3): 57–57 (1962).

[4]: Colinet C. “Private communication (2019)”.

[5]: Betterton J.O., Noyce W.K. The Equilibrium Diagram of Indium-Zirconium in the Region 0-26 At. Pct In. Trans. Metall. Soc. AIME. 212 (6): 340–342 (1958).

[6]: Fischer E., Thermodynamic database NUCLEA (IRSN) (2014).

[7]: Gajavalli J., Experimental Contribution to Thermodynamics of the Ag-Cd-In, In-Zr and In_2O_3-ZrO_2 Systems. PhD Thesis, Aix Marseille University (2019).

[8]: Meschel S.V., Kleppa O.J., Standard Enthalpies of Formation of Some Transition Metal Indium Compounds by High Temperature Direct Synthesis Calorimetry. J. Alloys Compd. 333:91–98 (2002).

S8-O31

NACEF APPLIED TO THE FCC ORDERING BASED ON THE FOUR-SUBLATTICE MODEL

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Keywords : NACEF, 4SL model, FCC ordering, Order/Disorder transitions

There are many ordered structures based on the FCC lattice and most of them can be treated as separate phases with different Gibbs energy expressions based on the two-sublattice (2SL) model due to its simplicity and computational efficiency. On the other hand, regarding the description of the L12 and L10 phases, it is currently recommended to use a four-sublattice (4SL) model which allows to calculate these ordered intermetallic phases based on the FCC lattice, as well as their disordered phase associated, A1, with a single Gibbs energy function. The first attempt to use the 4SL model in the CEF framework was made by [1] in an assessment of the Au-Cu system. The formalism is presented in detail in several articules [2,3] and can be summarized as follows.

The formalism assumes a random mixture on each sublattice and the site-fractions are equivalent, i.e. $(A,B)_{0.25}.(A,B)_{0.25}\ .(A,B)_{0.25}\ .(A,B)_{0.25}$. The Gibbs energy of an A–B binary phase with the 4SL model based on the CEF is

$$G^{4\mathrm{sl}}(y_i)=\sum_i x_i\,{}^0G_i^{\mathrm{FCC}}+0.25\,RT\sum_s\sum_i y_i^{(s)}\ln y_i^{(s)}+{}^{\mathrm{E}}G(y_i)$$

$$\begin{aligned}{}^{\mathrm{E}}G(y_i^s)=&\sum_{i,j,k,l}y_i^{(1)}y_j^{(2)}y_k^{(3)}y_l^{(4)}\Delta G_{i:j:k:l}+y_{\mathrm{A}}^{(1)}y_{\mathrm{B}}^{(1)}\sum_{i,j,k}y_i^{(2)}y_j^{(3)}y_k^{(4)}\sum_{\upsilon=0}\left(y_{\mathrm{A}}^{(1)}-y_{\mathrm{B}}^{(1)}\right)^{\upsilon}\,{}^{\upsilon}L_{\mathrm{A,B}:i:j:k}+\ldots\\&+y_{\mathrm{A}}^{(1)}y_{\mathrm{B}}^{(1)}y_{\mathrm{A}}^{(2)}y_{\mathrm{B}}^{(2)}\sum_{i,j}y_i^{(3)}y_j^{(4)}L_{\mathrm{A,B:A,B}:i:j}+|\ldots\end{aligned}\qquad(1)$$

where $y_i^{(s)}$, $\Delta G_{i:j:k:l}$ and *L* are the site fraction of constituent *i* on the sublattice *s*, the compound energies referred to the pure elements in the fcc structure and the interaction parameters, respectively. Due to the crystallographic symmetry, the sublattices are identical and the permutation of the occupation between sublattices should not change the value of the parameter considered. Moreover, most of the model parameters can be related to nearest neighbour bond energies [2,4]. This lead to the following relations for the excess parameters:

$$\begin{aligned}&\Delta G_{\mathrm{A:A:A:B}}=\Delta G_{\mathrm{A:A:B:A}}=\ldots=\Delta G_{\mathrm{A3B}}=3\,UAB+U1\\&\Delta G_{\mathrm{A:A:B:B}}=\Delta G_{\mathrm{A:B:A:B}}=\ldots=\Delta G_{\mathrm{A2B2}}=4\,UAB\\&\Delta G_{\mathrm{B:B:B:A}}=\Delta G_{\mathrm{B:B:A:B}}=\ldots=\Delta G_{\mathrm{AB3}}=3\,UAB+U2\\&L_{\mathrm{A,B:A,B:*:*}}=L_{\mathrm{A,B:*:A,B:*}}=\ldots=L_{\mathrm{A,B:A,B:*:*}}=UAB+U3\\&{}^0L_{\mathrm{A,B:*:*:*}}={}^0L_{\mathrm{*:A,B:*:*}}=\ldots={}^0L_{\mathrm{A,B:*:*:*}}=U4\end{aligned}\qquad(2)$$

where *UAB* which is the bond energy between AB pairs and *Un* are adjustable parameters. To simplify the integration of an ordered FCC phase with a database where many systems have FCC phases without any ordering, the Gibbs energy is partitioned in an ordered and disordered part:

$$\begin{aligned}&G=G^{\mathrm{FCC}}(x_i)+\Delta G^{\mathrm{ord}}(y_i)\\&\Delta G^{\mathrm{ord}}(y_i)=G^{4\mathrm{sl}}(y_i)-G^{4\mathrm{sl}}(y_i=x_i)\\&G^{\mathrm{FCC}}(x_i)=\sum_i x_i\,{}^0G_i^{\mathrm{FCC}}+RT\sum_i x_i\ln x_i+{}^{\mathrm{E}}G^{\mathrm{FCC}}\\&{}^{\mathrm{E}}G^{\mathrm{FCC}}=x_{\mathrm{A}}\,x_{\mathrm{B}}\sum_{\nu=0}\left(x_{\mathrm{A}}-x_{\mathrm{B}}\right)^{\nu}\,{}^{\nu}L^{\mathrm{FCC}}={}^{\mathrm{E}}G(y_i=x_i)+x_{\mathrm{A}}\,x_{\mathrm{B}}\sum_{\nu=0}\left(x_{\mathrm{A}}-x_{\mathrm{B}}\right)^{\nu}L\nu\end{aligned}\qquad(3)$$

As given by Eq. (3), the disordered interaction parameters for the disordered FCC-A1 state are expressed as follows [2,4,5]:

$$\begin{aligned} {}^{0}L^{\mathrm{FCC}} &= 13.5\,UAB + U1 + U2 + 1.5\,U3 + 4\,U4 + L0 \\ {}^{1}L^{\mathrm{FCC}} &= 2\,U1 - 2\,U2 + L1 \\ {}^{2}L^{\mathrm{FCC}} &= -1.5\,UAB + U1 + U2 - 1.5\,U3 + L2 \end{aligned} \tag{4}$$

where the interaction parameters for the disordered FCC phase are related to the ordering parameters and where *L0*, *L1* and *L2* are adjustable parameters independent of the ordering and are fitted to experimental data. Finally, the Gibbs energy for the $L1_0$ and $L1_2$ compounds are:

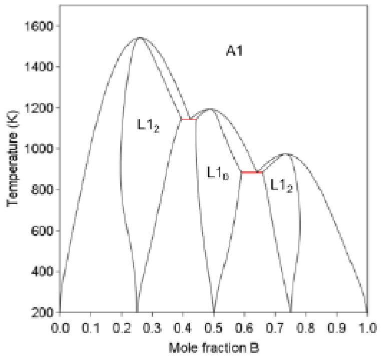
$$\begin{aligned} \Delta G(\mathrm{L1_0\text{-}AB}) &= 4\,UAB + \tfrac{1}{4}(L0) \\ \Delta G(\mathrm{L1_2\text{-}A_3B}) &= 3\,UAB + U1 + \tfrac{3}{16}\left(L0 + \tfrac{1}{2}L1 + \tfrac{1}{4}L2\right) \\ \Delta G(\mathrm{L1_2\text{-}AB_3}) &= 3\,UAB + U2 + \tfrac{3}{16}\left(L0 - \tfrac{1}{2}L1 + \tfrac{1}{4}L2\right) \end{aligned} \tag{5}$$

From the new approach to the compound energy formalism (NACEF) recently proposed by [6], we present in the present work an analysis of FCC ordering based on the 4SL model which highlights certain important points such as for example that the parameters used in CEF may not be independent. This can be illustrated by the different sets of parameters given in Tab. 1 and which provide the same equilibrium phase diagram shown in Fig. 1.

Tab. 1: CEF parameters in kJ/mol.

	#1	#2	#3	#4
UAB	-10	-9		-7.5
U1	-2	-2	-2	-2
U2	2	2	2	2
U3	1		-9	-1.5
U4		1	10	2.5
L0	40	24	-120	
L1	2	2	2	2
L2	2	2	2	2

Fig. 1: Calculated phase diagram in an A-B system from parameters given Tab. 1.



References :

[1] B. Sundman, S.G. Fries, and W.A. Oates, CALPHAD, 22 (3) (1998) 335–354
[2] H. L. Lukas, S. G. Fries and B. Sundman, Computational thermodynamics: Cambridge University Press; (2007). ISBN 978-0521868112
[3] Sundman, B., Chen, Q. & Du, Y., J. Phase Equilib. Diffus. 39, (2018) 678–693
[4] A. Kusoffsky, N. Dupin, B. Sundman, CALPHAD, 25 (2001) 549–565
[5] T. Abe, B. Sundman, CALPHAD, 27 (2003) 403–408
[6] J. M. Fiorani, et al., CALPHAD, 80 (2023) 102509

MEASUREMENT OF THE ENTHALPY AND HEAT CAPACITY OF CORIUM COMPONENTS AT VERY HIGH TEMPERATURES

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Keywords: Enthalpy, measurement, high temperature, Aerodynamic Levitation

Corium is a multiphasic and multi-component substance initially formed by the partial or total melting of the nuclear fuel and the mixing with materials structures such as stainless steel (second barrier) and concrete (third barrier). In case of containment failure, radioactivity release to the environment could occur. To prevent such accidents, or limit their impact by mitigation tools, it is essential to better know this complex corium mixture and especially its thermophysical properties. However, the very high temperature reached by corium (T>2500K), its complexity and the fact that its composition changes with each accident scenario makes its study complicated. To overcome these difficulties, simulation of thermophysical properties of corium by Molecular Dynamic or Butler field phases is an approach currently under development. Nevertheless, this approach raises a new problem: the lack of data on the thermodynamic properties of corium materials, and materials in general, at very high temperatures (> 2000 °C).

The goal of this work, part of the NEEDS – PROTECT* project, is to provide new thermophysical measurements using innovative devices, particularly the enthalpy and heat capacity of some liquid oxides constituting corium. To this end, a very high-temperature drop calorimeter is being developed at the CEMHTI. This device uses an aerodynamic levitator and CO_2 lasers to heat oxide-based droplet. Once melted, the sample can then be dropped inside a calorimeter. Parallel to the experimental development, the cooling of the droplet during its fly is numerically simulated to assess its experimental parameters, such as initial temperature when it arrives in the calorimeter. Additionally, the heat exchange between the sample and the calorimeter is numerically evaluated in order to correct instrumental bias and to optimize the calorimeter design. The first tests are being made on pure alumina to validate the experiments and high-temperature enthalpy and heat capacity will be evaluated and compare with thermodynamics databases and standards. Once validated, next experiment will be carried out on pure zirconia.

* : NEEDS : NEEDS : Nucléaire : Energie, Environnement, Déchets, Société, PROTECT PROpriétés ThErmohysiques du Corium en Température

PHASE STABILITIES IN MECHANICALLY STRESSED BODY-CENTERED FE-C SOLID SOLUTIONS: ARE FERRITE AND MARTENSITE THE SAME PHASE?

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Keywords: carbon steels, elasticity, long-range ordering, mean-field modeling

The low-temperature Fe-C solid solution consists of a body-centered host lattice incorporating C interstitial atoms on the three sublattices of octahedral sites. When no stress is applied, carbon atoms are evenly distributed over the three interstitial sublattices of the ferrite phase, leading to the bcc structure, whereas carbon atoms occupy preferentially one sublattice of the martensite phase, leading to the bct Zener-ordered structure.

Our goal is to quantify theoretically the influence of applied stress or strain on the state of carbon ordering in the Fe-C solid solution, and to rationalize the possible phase transitions between ferrite and martensite. For this purpose, we developed the elasto-chemical meanfield model of carbon-carbon and carbon-strain interaction in the body-centered lattice. By introducing two long-range order parameters, we obtained a unified description of both the ferrite phase and the martensite variants through a unique Gibbs energy function.

We studied numerically the thermodynamic stability of the three possible crystalline forms of carbon-supersaturated body-centered iron, namely bcc, bct and bco, and their orientational variants. The phase stabilities depend not only on temperature and solute carbon content, but also on the state of mechanical stress in the crystal.

Remarkably, the calculated phase diagrams exhibit a continuous transition between martensite (defined as the high-order phase) and ferrite (the low-order phase) through supercritical iron. We conclude that ferrite and martensite are actually two instances of the same phase: the body-centered orthorhombic iron.

Our diagrams intend to help understanding the spatial distribution of orientational variants in martensite nanocrystals and in Cottrell atmospheres around dislocations.

References:

[1] Maugis, P., “Effect of Mechanical Stress Tensor on Phase Equilibria in Body-Centered Interstitial Alloys: Case of Carbon-Supersaturated Iron”, J. Phase Equilib. Diffus. 43 (2022) 827–843.

S8-O34

THERMODYNAMIC ANALYSIS OF THE K2MOO4-LI2MOO4 SYSTEM: TOWARDS POTASSIUM IMPURITY REMOVAL FROM LI2MOO4 CRYSTALS

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Keywords: Li_2MoO_4, DSC-DTA, congruent vaporization, thermodynamic modeling

The Li_2MoO_4(LMO) single crystal has been the subject of numerous studies concerning its primary use in Heat Scintillation Cryogenic Bolometers (HSCBs) due to the presence of the ^{100}Mo isotope, essential for neutrinoless double beta decays. However, the reliability of results provided by HSCBs depends largely on the purity of the materials used, hence the importance of elaborating radiopure single crystals. In the case of LMO, background measurements show that K, Th, U are the most undesirable impurities in the crystal [1].

Our aim is to develop, using the CALPHAD approach, a thermodynamic database of Li-Mo-O-X system (X=K, U, Th) in order to establish the physicochemical and thermodynamic conditions required for perfect control of crystal synthesis and growth conditions, with the aim of optimizing crystal radio-purity, and then improving the detector signal-to-noise ratio.

A database of the Li-Mo-O ternary system is being developed, based on a critical evaluation of literature data and DFT calculations. This will be used to develop a more database of the entire Li-Mo-O-X system. Nevertheless, experimental input data is very scarce in other ternary and quaternary systems.

Starting with potassium impurity, further experimental data are being obtained using thermal and structural analyses. We have obtained promising preliminary results, proving the ternary quasi-congruence nature of LMO for vaporization behavior under neutral gas or air ($p(O_2)$ = 0.21), assuming no interaction with N_2. Then we experimentally redetermined a new phase diagram dataset for the Li_2MoO_4-K_2MoO_4 system as the only reported data are very old [2,3]. Our analyses reveal information on the solubility of potassium in LMO, the crystal structure of the intermediate compound $KLiMoO_4$, as well as the nature of vaporization in the quasi-binary system and its impact on the stability of LMO under controlled pO_2 atmosphere. A first version of the quaternary model describing the K-Li-Mo-O system can be presented as part of this work.

Future work also will include experimental exploration of the gas phase by means of Knudsen Cell Mass Spectrometry and the construction of defect equations to attempt at grounding the partition coefficient of each radio-impurity at the level of its building units. To conclude, our study aims to provide a solid basis for the design of high-purity materials for rare event searches detectors, paving the way for new discoveries in the field of (astro)particle physics.

References:

[1] Velázquez, M., et al. (2017). Solid State Sciences 65: 41-51.
[2] Hoermann, F. (1929). Zeitschrift für anorganische und allgemeine Chemie 177(1): 145-186.
[3] Belyaev, I. (1961). Zhurnal Neorganicheskoi Khimii 6(5): 1178-1188.

STUDY OF PHASE EQUILIBRIA IN Sn-3Ag-0.5Cu-xNi (x=0.05 - 4 wt.%) ALLOYS

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Keywords: SAC305, microstructure, phase composition, thermal behavior, computational thermodynamics

The use of Sn-Pb solder alloy in the electronic industry has been limited due to the toxicity of lead and that is why there is a goal to find a suitable replacement with the same or even better properties. One of the most used solders nowadays is the Sn-3.0Ag-0.5Cu (SAC305) alloy, however, the research has also focused on the influence of other elements added to Sn-based alloys. [1] The aim of this work is to study the phase equilibria in the solder system of Sn-3.0Ag-0.5Cu-xNi (0.05 - 4) mass % Ni, using computational and experimental techniques (scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction, differential scanning calorimetry). This alloy has the potential to improve the microstructure of the SAC305 solder, as well as its thermal and mechanical properties. [2-4] The results of the study show that the microstructure of SAC305 varies based on the amount of Ni present in the sample. With a small addition of Ni (0.05%), the microstructure is refined, consisting of β-Sn dendrites in the eutectic matrix (β-Sn + Ag_3Sn) and particles of Cu_6Sn_5 intermetallic phase, while Ni is dissolved in Cu_6Sn_5 phase. With the increasing amount of Ni (1% Ni) the Ni_3Sn_4 phase starts to form, at the expense of Cu_6Sn_5. Also, the microstructure becomes coarser, mainly Cu_6Sn_5 and Ni_3Sn_4 phases with cracks observed mainly in the later phase. Low values of undercooling during solidification were observed in comparison to SAC305 solder. A good agreement was found between experimental results – phase composition, eutectic temperature, enthalpy of phase transformation (eutectic transformation + melting of β-Sn dendrites), and thermodynamic computations in Thermo-Calc software.

References:

[1] Kotadia HR, Howes PD, Mannan SH. A review: On the development of low melting temperature Pb-free solders. Microelectr. Rel. 2014; http://dx.doi.org/10.1016/j.microrel.2014.02.025

[2] El-Daly AA, Hammad AE, Fawzy A, Nasrallh DA. Microstructure, mechanical properties, and deformation behavior of Sn-1.0Ag-0.5Cu solder after Ni and Sb additions. Mat. Des. 2013; https://doi.org/10.1016/j.matdes.2012.06.058

[3] Wang Y, Wang G, Song K, Zhang K. Effect of Ni addition on the wettability and microstructure of Sn2.5Ag0.7Cu0.1RE solder alloy. Mat. Des. 2017; https://doi.org/10.1016/j.matdes.2017.01.046

[4] Cheng H.K., Huang CW, Hsuan L, Wang YL, Liu TF, Chen CM. Interfacial reactions between Cu and SnAgCu solder doped with minor Ni. J. All. Comp. 2015; https://doi.org/10.1016/j.jallcom.2014.10.121

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S9-O36

COMPARISON OF THE Sm AND Gd ALLOYING BEHAVIOUR FOR R-Ni-Al TERNARY SYSTEMS

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Keywords: isothermal sections, intermetallic compounds

The investigation of phase equilibria (i.e. isothermal sections [1-4]) and thermodynamic properties (i.e. determination of $\Delta_f H°$ of binary and ternary phases [5,6]) of R-Ni-Al systems and boundary R-Ni and R-Al binary systems (R = rare earth elements) have been ongoing in our laboratory for a long time. In this presentation, the experimentally determined isothermal sections at 800°C for Sm-Ni-Al and Gd-Ni-Al will be described and compared to highlight observed similarities and differences.

Determining the phase equilibria in both systems has proven to be very challenging due to the large number of compounds, some of which having a very close composition. For this reason, the following well-concerted techniques have been employed: X–Ray Powder Diffraction analysis (XRPD), Light Optical Microscopy (LOM) and Scanning Electron Microscopy (SEM) coupled with Energy Dispersive Spectrometry (EDS). Synthesis of a high number of alloys has been performed starting from pure metals (> 99.9 %) taking into account the peculiarity of the elements (i.e. vapour pressure of Sm, reactivity toward oxygen of rare-earth elements) and then a variable annealing time (from 15 to 90 days) has been selected considering the global composition of the samples.

For the Sm-Ni-Al system the 30–100 at. % Al region has been studied whereas for the Gd-Ni-Al, the investigation was devoted to the 50–100 at. % Al range. The following ternary phase have been confirmed in both systems: $R_3Ni_5Al_{19}$ (o*S*108-$Gd_3Ni_5Al_{19}$), $R_4Ni_6Al_{23}$ (m*S*66-$Y_4Ni_6Al_{23}$), $RNiAl_4$ (o*S*24-$YNiAl_4$), $RNiAl_3$ (o*P*20-$YNiAl_3$), $R_3Ni_7Al_{14}$ (h*P*72-$Gd_3Ni_7Al_{14}$), $RNiAl_2$ (o*S*16-$CuMgAl_2$) and RNi_2Al_3 (h*P*18-YNi_2Al_3). An additional ternary phase in the Al-rich region, namely the RNi_3Al_9 (h*R*78-$ErNi_3Al_9$), has been found only in the Gd system, whilst, for the Sm-Ni-Al system were observed SmNiAl (h*P*9-ZrNiAl) and $Sm_3Ni_6Al_2$ (*cI*44–$Ce_3Ni_6Al_2$). For all phases crystal structures and lattice parameters have been investigated. In addition, along the 16.67 at. % Sm isopleth, the presence of two structurally related extended solid solutions have been studied.

References:

[1] S. Delsante et al., Intermetallics, 16 (2008) 1250-1257.
[2] S. Delsante et al., Intermetallics, 45 (2014) 71.
[3] S. Delsante et al., J. Phase Equilib. Diffus., 35 (2014) 421.
[4] S. Delsante et al., submitted to J. Phase Equilib. Diffus., (2024)
[5] G. Borzone et al., Intermetallics, 11 (2003) 1217.
[6] S. Delsante et al., J. Chem. Thermodyn. 65 (2013) 73.

S9-O37

PRIMARY PHASE SOLIDIFICATION OF A PT-BASED GLASS FORMING ALLOY FOR THE USE IN ADDITIVE MANUFACTURING

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Keywords: bulk metallic glasses, additive manufacturing, precious metal, crystallization

Bulk metallic glasses (BMG) are a class of metal alloys that can offer good corrosion resistance, high electrocatalytic activity as well as high yield strengths and elastic strain limits. This makes them attractive for a wide field of applications. Precious metal based BMGs have attracted interest for use in luxury goods, for sustainability energy and biomedical applications. However, alloy compositions with target properties for application and high glass-forming ability (GFA) need to be found.

Since high cooling rates must be achieved to prevent crystallization, casting is typically limited to thin sections. Adjusting the composition to improve particular properties leads to a loss of GFA. High cooling rates in the melt pool of additive manufacturing (AM) are attractive for the processing of BMGs, overcoming the size limit of conventional casting. Much research has already been done on AM of BMGs [1,2], but for precious metal alloys, only Pd-based systems processed by laser powder-bed fusion have been explored [3]. Sohrabi et al. demonstrated such alloys can be printed amorphous at high relative densities [3].

The present study investigates the additive manufacture of two Pt-based BMGs: Alloy A with 85 wt% Pt having a moderate GFA; Alloy B with 95 wt% Pt and marginal GFA. Both alloys are of interest for luxury goods due to their high precious metal content. Single tracks were conducted using different laser parameters and characterized by hardness measurement and metallographic investigation. Amorphous tracks were found in alloy A, but alloy B partially crystallized, with crystallites up to 1 µm in diameter. Scanning Transmission Electron Microscopy (STEM) was performed on a lamella prepared from a laser track of alloy B. Structural characterization and chemical mapping were performed to characterize the crystallites.

Understanding crystallization in the melt pool of marginal glass-forming alloys is important to the development of AM and its potential for developing BMGs with target properties for specific industrial applications.

References:

[1] Z. Yang, M. Markl, C. Körner, Predictive simulation of bulk metallic glass crystallization during laser powder bed fusion, Addit. Manuf. 59 (2022) 103121. https://doi.org/10.1016/j.addma.2022.103121.

[2] N. Sohrabi, J. Jhabvala, R.E. Logé, Additive Manufacturing of Bulk Metallic Glasses—Process, Challenges and Properties: A Review, Metals 11 (2021) 1279. https://doi.org/10.3390/met11081279.

[3] N. Sohrabi, J. Jhabvala, G. Kurtuldu, R. Frison, A. Parrilli, M. Stoica, A. Neels, J.F. Löffler, R.E. Logé, Additive manufacturing of a precious bulk metallic glass, Appl. Mater. Today 24 (2021) 101080. https://doi.org/10.1016/j.apmt.2021.101080.

S9-O38

AN EXPERIMENTAL STUDY OF THE RH-ZR BINARY SYSTEM

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Keywords - 5 max: Zirconium, Rhodium, nuclear waste, phase diagram

M5® zirconium-base alloys are used as cladding material for fuel pellets in nuclear reactors. After their in-reactor life-time, irradiated fuel assemblies are taken care via specific processing operations. They are primarily sheared into sections called hulls, separated from the fuel by a dissolution step, rinsed and then compacted and packaged into CSD-C (French acronym for Standard Container of Compacted Waste). They are currently considered as Intermediate Level Waste Long Life (ILW-LL) in the French waste classification and will be stored in the CIGEO French geological disposal.

In the framework of the REGAIN project (French acronym for recycling of nuclear cladding), an alternative solution is being tested. This solution is based on an innovative approach, consisting in reducing the radiological source term of the hulls through successive decontamination operations to recover the Zr. Decontamination of the hulls with actinides and fission products constitutes one of them. Some of the fission products generated by the nuclear reaction can settle inside the Zr cladding and interact with it. Thus, it is of high interest to forecast the resulting microstructural evolutions.

Rhodium is one of the fission products encountered, thus in this framework, an experimental investigation of the Rh-Zr phase diagram has been conducted. Several samples were fabricated by arc melting from pure zirconium (Van Arkel grade) and rhodium plates (from Goodfellow) chosen in different part of the phase diagram and quenched in order to complete and or confirm the data from literature [1]. These samples have been characterized by scanning electron microscopy, energy dispersion spectroscopy, Microprobe analysis, X-ray diffraction and DTA confirming the presence of the five following intermetallic compounds: Zr_2Rh, ZrRh, Zr_3Rh_4, Zr_3Rh_5 and $ZrRh_3$ and providing the necessary data for the assessment of this system using the CALPHAD method.

This project is funded by the French government as part as France 2030. The REGAIN project consortium was built around the main industrial players in the French nuclear industry (Framatome and Orano) and leading research organizations in the field of energy (CEA and CNRS).

References:

[1] D. Arias and J. Abriata, “The Rh-Zr (Rhodium-Zirconium) System”, J. Phase Equilib, 14 (1), 1993), 110-117

THE CASE OF DIFFUSION REACTION IN MULTILAYER ELECTRICAL CONTACTS FOR MG-SI-SN-BASED THERMOELECTRIC DEVICES

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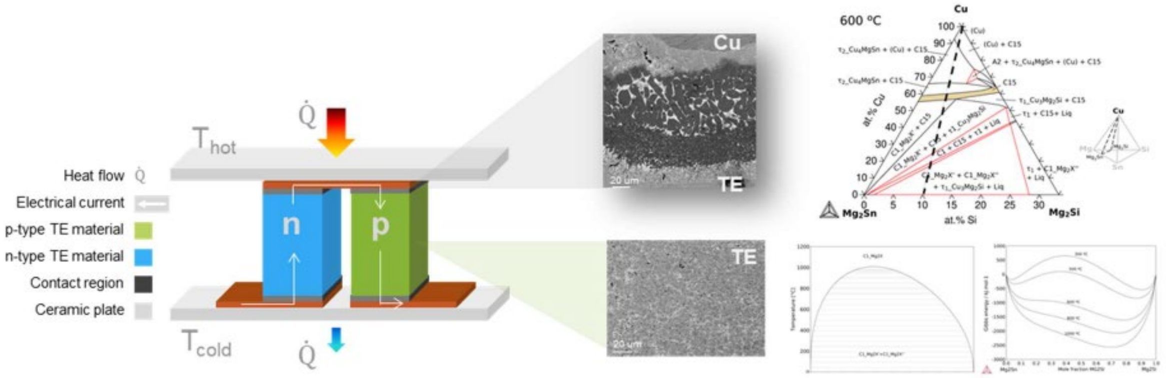
Keywords: Magnesium Silicide Stannide, Thermoelectric, CALPHAD, Diffusion.

Thermoelectric (TE) energy conversion is a versatile option for harvesting and recovering waste heat by direct conversion of thermal into electrical energy having important advantages such as absence of any harmful emission and moving parts. Yet, a crucial challenge in TE device technology is the contact between the TE material and the metallic bridge to build up a functional module for energy conversion [1]. Mg-Si-Sn-based compounds are suitable TE materials for high-temperature applications with non-toxic, abundant and inexpensive elements. In particular, the compositions $Mg_2(Si_{1-x}Sn_x)$ with x = 0.6, 0.7 lay within a miscibility gap of the $Mg_2(Si_{1-x}Sn_x)$ C1 solid solution phase, therefore susceptible of undergoing spinodal decomposition sensitive to diffusion, electrical or stress fields. This TE material is optimized for good performance, i.e. optimal Seebeck coefficient and electrical conductivity, in a tradeoff, by adding dopants (for p- and n-type semiconductor legs) and synthesized by ball milling and sintering to achieve good control of the composition. Electrical contacts are needed between the TE legs and a metallic electrode to build up TE devices. Typically, such devices have to work under a temperature gradient. Using Cu as a typical electrode, significant diffusion and reaction at the interconnection zone (IZ) has been observed, accompanied by changes in the Seebeck coefficient that compromise the mechanical strength of the contacts and functionality of the TE material.



We approach this technological problem with a CALPHAD-based computational framework, combining thermodynamics, diffusion and mechanical modeling. A thermodynamic description for the quaternary system Cu-Mg-Si-Sn was developed in a previous study [2] where the layer sequence in the IZ after the contacting process was calculated and confronted with experiments. In the quaternary system several phases are found in the IZ, Laves phase C15, τ_1-Cu_3Mg_2Si and C1-Mg_2Sn. Diffusion simulations with DICTRA [3,4] in C1-$Mg_2(Si_{1-x}Sn_x)$ solid solution are restricted by the lack of atomic mobilities in the C1 phase. Therefore, we initially transform the problem into a single FCC or HCP solid solution phase in contact with a stoichiometric C1 phase to set the design criteria for electrical contacts and extend them to other metallic electrodes. Additionally, diffusion couple experiments were carried out to determine interdiffusion coefficients in C1-$Mg_2(Si_{1-x}Sn_x)$ solid solution which can be used to assess the atomic mobilities in this phase.

References :

[1] Ying, P., et al. Nat Commun, 2021, 12, 1121.
[2] Tumminello S., et al., J. Mat. Chem. A, 2021, 9, 20436-20452.
[3] Andersson J.O., et al., Calphad, 2002, 26, 273-312.
[4] Larsson, H., Calphad, 2014, 47, 1-8

S10-O40

EXPERIMENTAL STUDY AND THERMODYNAMIC MODELING OF THE (CE-ND)-FE-B SYSTEM FOR SUBSTITUTED PERMANENT MAGNETS

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Keywords: Thermodynamics, permanent magnets, Rare Earths

Nd-based (Nd-Fe-B) permanent magnets find widespread application in the realm of new energies. Worldwide pressure on their supply is pushing manufacturers to develop new formulations with reduced Nd content, partially replaced by other less critical Rare Earths such as Ce or La [1]. Traditional Nd-based magnet are composed of two key phases: the main grain $Nd_2Fe_{14}B$ phase and the grain boundary Nd-rich phase. Both phases are necessary for achieving high coercivity in the magnet. In the Nd-Fe-B system, an equilibrium between these two phases allows to produce easily this microstructure through fast solidification processes. However, in the Ce-Fe-B system, the equilibrium between the 2:14:1 phase and the Ce-rich phase is broken due to the stability of the paramagnetic $CeFe_2$ phase. The formation of $CeFe_2$ can impact coercivity and thereby restrict the amount of Ce that can effectively substitute Nd.

In this work, the quaternary system (Ce-Nd)-Fe-B was studied through a combination of experimental techniques and the CALPHAD method. Long-term annealing at 750°C were conducted on the Ce-Fe-Nd, B-Ce-Fe and (Ce-Nd)-Fe-B systems. Microstructures were characterized by SEM-EDS, EPMA and XRD. The Ce-Nd system and the 80 at.% Fe isopleth of the Ce-Fe-Nd system were further explored through Differential Thermal Analysis (DTA). The solubility of Nd observed in $CeFe_2$ at 750°C was consistent with that found by Luo [4] at 500°C. Effects of undercooling arising from the kinetics of Nd_5Fe_{17} formation were also addressed. In addition, quasi-harmonic calculations were performed on the 2:14:1, 1:2 and 2:17 phases for both Ce and Nd end-members. Regarding these experimental and computational data, a thermodynamic model for the (Ce-Nd)-Fe-B system was developed.

In the synthesis of Ce-substituted magnets, one of the two strategies to deal with the $CeFe_2$ phase consists in avoiding its formation (the other is to confine the phase in specific grain boundaries). For this purpose, calculations were carried out and new compositions and treatment temperatures were proposed. The effects of rapid cooling on $CeFe_2$ formation were also studied using Scheil-type solidification calculations.

References:

[1] G. Delette, $Nd_2Fe_{14}B$ permanent magnets substituted with non-critical light rare earth elements (Ce, La): A review, Journal of Magnetism and Magnetic Materials. 577 (2023) 170768.

[2] K. Luo, X. Cui, J. Zhu, J. Liang, W. Qin, Phase Relationships in the Nd-Ce-Fe System at 773 K, J. Phase Equilib. Diffus. 41 (2020) 148–156.

S10-O41

HP-HT MODELLING OF FE-MG SYSTEM: A COMPARISON OF CALPHAD-COMPATIBLE MODELS AND DATA ACQUISITION

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Keywords: P-T modelling, Fe-Mg, LH-DAC, CALPHAD

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

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

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

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

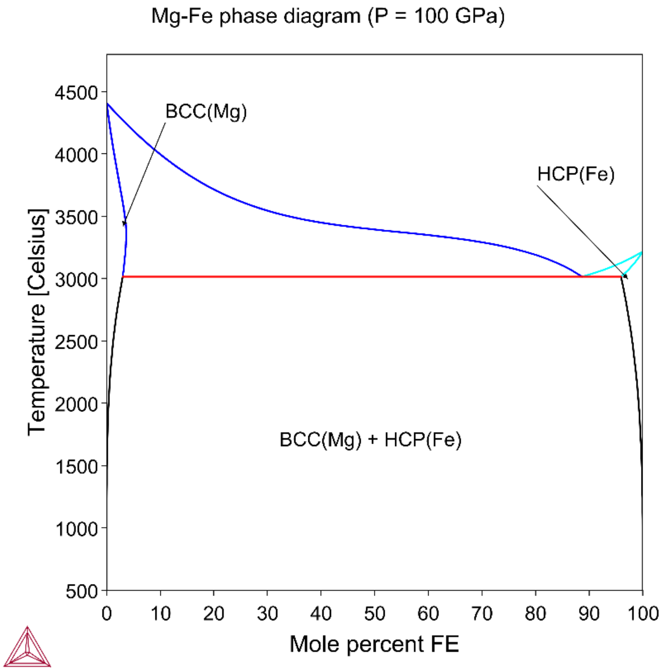

Figure 1. Fe-Mg phase diagram calculated at 100 GPa

References:

[1] Dubrovinskaia, N., et al. “Beating the Miscibility Barrier between Iron Group Elements and Magnesium by High-Pressure Alloying,” PHYSICAL REVIEW LETTERS, 95 (2004): 245502

[2] Brosh, E., et al. “Application of CALPHAD to high pressures,”, CALPHAD, 31 (2007): 173–185

[3] Joubert, J.M., et al.” Modification of Lu’s (2005) high pressure model for improved high pressure/high temperature extrapolations,”, CALPHAD, 74 (2021): 102304

[4] Gao, P., et al. “Iron–magnesium compounds under high pressure,” New J. Chem., (2019) 43, 17403

Biographical Note

(1) (Under review) Desseaux, M.; et al. “New measurements of Fe solubility in liquid Mg up to 1450°C and reassessment of the Fe-Mg system,” JPED (2024)

(2) Desseaux, M.; et al. "Fe-Mg Phase Equilibria under High-Temperature and High-Pressure Conditions: Experimental Investigation and Calphad Modeling," In Goldschmidt2023 abstracts; EAG: Lyon, France, 2023. https://doi.org/10.7185/gold2023.19239.

S10-O42

INVESTIGATING THE INFLUENCE OF BORON ALLOYING ON THE THERMODYNAMICS OF THE FE-B-N-C SYSTEM

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Keywords: Boron, microalloyed steel, solidus, BN

Boron is the most cost-effective hardenability promoter in microalloyed steel [1]. Boron being segregated at austenite grain boundaries inhibits the nucleation of ferrite and thus facilitates the formation of martensite by lowering the critical cooling rate [2]. Therefore, correctly describing the thermodynamics of the involved phases provides the basis for a proper thermokinetic simulation. This leads to a deeper understanding of the interplay of BN with other nitrides such as TiN or AlN, the quantification of dissolved boron in austenite, and the steel microstructure.

To date, Calphad modeling of BN lacks robust and consistent experimental data in microalloyed steel systems, with the boron concentration typically lying within 20 - 50 wt.-ppm. Moreover, a discussion of its thermodynamic properties is missing. Here, we reassess the Fe-rich corner of the subsystems Fe-B-N-C based on different experimental analyses in vacuum induction melted samples, focusing on the thermodynamic stability of BN and the solidus temperature of the system as a function of the boron concentration. We use electron probe microanalysis (EPMA) and atom-probe tomography (APT) to specify the segregation tendency of boron.

The obtained experimental results are used to critically evaluate the accuracy of thermodynamic steel databases. We found a far too strong effect of boron on the solidus temperatures. This problem is related to assessed parameters within the Fe-B and Fe-B-C subsystems, which were reassessed in an update of the available open-licensed Matcalc database mc_fe_v2.060.tdb. This database is now well applicable to microalloyed steels.

Giving the proper enthalpy, entropy, and heat capacity high weights in the description of BN, the phase has a much higher stability than experimentally observed. Elemental boron is strongly segregating to grain boundaries. Following an approach by Svoboda et al. [3], we evaluate the depth of the traps ΔE (trapping enthalpy) from chemical potentials of interstitial atoms. Using this approach, we analyze simulatively the influence of trapping enthalpy ΔE on the BN precipitation versus segregation of boron to GB with MatCalc [4]. It is shown that the experimentally observed BN stability is strongly controlled by segregation.

References

[1] D. Wipp, Boron Influence on Microstructural Evolution and Mechanical Properties in Micro-Alloyed Carbon Steels Precipitation and Segregation Behavior.
[2] M. Sharma, I. Ortlepp, W. Bleck, 1611-3683 90 1900133.
[3] J. Svoboda, Y.V. Shan, E. Kozeschnik, F.D. Fischer, 0965-0393 21 65012.
[4] Kozeschnik, Ernst. (2022) *"Mean-Field Microstructure Kinetics Modeling"*. In: Francisca G. Caballero (ed.), *Encyclopedia of Materials: Metals and Alloys*. vol. 4, pp. 521–526. Oxford: Elsevier

S10-O43

THERMODYNAMIC MODELLING OF THE SOLUBILITY OF MINOR ADDITIVE ELEMENTS IN LIQUID METALLIC COOLANTS

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Keywords: Bismuth, Calphad, Lithium, Lead, Solubility

Liquid metals and their alloys – particularly lead, lead-bismuth eutectic (LBE) and lithium – are fluid candidates for the primary or intermediary circuit of generation IV nuclear fast reactors (Lead-Cooled Fast Reactors) and accelerator driven transmutation systems (ADS).

As coolant materials, these liquid alloys exhibit advantageous thermohydraulic and neutronic properties as well as inherent safety. However, the compatibility of these liquid alloys with the structural materials is a key point regarding corrosion issues [1,2]. To address this problem, and in parallel to the iron-based alloys already studied, High Entropy Alloys (HEA) have recently been investigated as new the compatible materials. Several recent studies investigated their resistance to corrosion phenomena in these severe environments [3,4].

In this framework, the thermodynamic properties of several transition elements in interactions with the metallic liquids were reviewed. In parallel, a specific database was developed using the Calphad method [6] to assess the thermodynamic properties of some minor elements in the iron-based alloys and some HEA structural elements (Al-Co-Cr-Ni-Fe) in these metallic liquids [7]. This database aims at predicting the behavior of the alloying elements in the liquid metals and to provide fundamental data. These results can also be used to support the knowledge of the kinetic mechanisms and transport phenomena in the circuits.

References:

[1] L. Martinelli, T. Dufrenoy, K. Jaakou, A. Rusanov, F. Balbaud-Célérier, Journal of Nuclear Materials 376 (2008) 282–288

[2] L. Martinelli, F. Balbaud-Célérier, A. Terlain, S. Delpech, G. Santarini, J. Favergeon, G. Moulin, M. Tabarant, G. Picard, Corrosion Science 50 (2008) 2523–2536

[3] X. Huang, X. Gong, M. Song, J. Chen, F. Hu, Y. Yin, J. Xiao, H. Wang, H. Wang, H. Gong, Y. Deng, B. Pang, Y. Li, Journal of Nuclear Materials, Volume 528, 2020, 151859

[4] L. Martinelli, F. Balbaud-Célérier, A. Terlain, S.Bosonnet, G. Santarini, G. Picard, Corrosion Science 50 (2008) 2537–2548

[5] Scripta Materialia Vol. 194, 2021, 113652, X. Gong, C. Xiang, T. Auger, J. Chen, X. Liang, Z. Yu, M. P. Short, M. Song, Y. Yin

[6] H.L. Lukas, S.G. Fries, B. Sundman, Computational Thermodynamics: The Calphad Method, Cambridge University Press, 2007

[7] S. Gossé, Thermodynamic assessment of solubility and activity of iron, chromium and nickel in lead bismuth eutectic, Journal of Nuclear Materials 449 (2014) 122–131

Posters

P01

EXPERIMENTAL AND THEORETICAL DESCRIPTION OF THE Ge-Mg-Sn TERNARY SYSTEM

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Keywords: Ge-Mg-Sn ternary system, thermodynamic modelling, CALPHAD method

The aluminium-silicon based alloys are currently of great interest as they exhibits the combination of favourable material properties, e.g. good castability, low density, high specific strength and stiffness, outstanding corrosion resistance. Therefore they are of interest in the automotive and aerospace industry [1]. Further improvement of their material properties can be reached by addition of alloying elements. Recently, Mg, Ge and Sn are among those experimentally tested by scientists [2]. The alloying elements can influence the precipitation process in Al-Si-(Cu) based alloys and play an essential role in controlling alloy microstructure. The exploitation of those precipitates depends on the knowledge of relevant phase diagrams, in this case for the Ge-Mg-Sn system.

Two limiting binary systems of this ternary system contain the isostructural intermetallics Mg_2Sn and Mg_2Ge with anti-CaF_2 type cubic structure (space group $Fm\bar{3}m$) [3]. Existing experimental studies were focused on the pseudo-binary phase diagram Mg_2Sn-Mg_2Ge and mutual solubility of these isostructural phases [4]. Jung and Kim [5] presented thermodynamic modelling of the Ge-Mg-Sn system but the Modified Quasichemical Model for the liquid phase description was used, which is not compatible with commonly used liquid models. Therefore new experimental and theoretical study was carried out here.

Experimentally, samples have been prepared using Arc-melting method in the Ar-atmosphere. Long term annealing was performed in evacuated quartz glass. Overall and phase composition of metallographically prepared samples were analysed by SEM with WDX and EDX analysis. Results of experiments showed existence of the $Mg_2(Ge_xSn_{1-x})$ phase and described the solubility of third elements in binary intermetallic and solid solutions.

Consequently, the ternary phase diagram Ge-Mg-Sn was assessed by CALPHAD-type approach by the Thermo-Calc software using our own experimental data and ab initio calculation of the properties of binary intermetallics, ternary phase and published experimental data by [4]. The ternary phase was implemented into the phase diagram with respect to our experimental results and ab initio calculations. Also, solubility of Sn was found in the Mg_2Ge intermetallic.

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References:

[1] Costa T.A., Dias M., Gomes L.G., et al., *J. Alloys Compd.*, 683 (2016), 485–494.
[2] Dai S., Bian Z., Wu W. et al., *Mat. Sci. Eng. A*, 792(2020), 139838.
[3] Grosch G.H., Range K.J, *J. of Alloys and Compd*, 235(1996), 250-255.
[4] Makarov E.S., Muntyanu Sh., et al., *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 2(1966), 2116-211.
[5] Jung, I.-H.; Kim, J., *J. Alloy. Compd.*, 494(2010), 137-147.

P02

EXPERIMENTAL STUDY OF PHASE EQUILIBRIA IN THE CR-IR BINARY SYSTEM BELOW 1375K

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Keywords: phase diagram, Cr-Ir binary system, X-ray, DSC

Only limited experimental data are known about the phase stability of the Cr-Ir system. So far, experimental research on the system has focused only on the region above 1373 K. Furthermore, in the iridium rich area, there are discrepancies between published results [1, 2, 3]. The Cr-Ir system is important for Ni-base superalloys, which are the most used high-temperature materials in gas turbine and aircraft engines. Chromium is the primary alloying element in these superalloys, improving resistance to oxidation, sulphidation and corrosion. And the addition of iridium improves their resistance to creep and oxidation.

The present study has been focused on the investigation of phases, phase equilibria and phase transitions of the Cr-Ir system below 1375 K in order to complete and improve the phase diagram of the binary system. Several alloys from composition range 14 to 72 at.% Ir were prepared and investigated. X-ray diffraction and scanning electron microscopy equipped with EDX analyzer were used for determination of phase equilibria and composition of the coexisting phases in the alloys after long-term annealing at 1073 K and 873 K for 1220 h and 1800h, respectively. For equilibrated alloys with a chemical composition in the range of ~50-65 at.% Ir, differential thermal analysis was also performed to determine the temperatures of phase transitions below 1375 K. Subsequently, the phase diagram of the Cr-Ir binary system was established based on new experimental findings. The obtained results of the experimental study will be help to improve thermodynamic assessment of the Cr-Ir binary system in the future.

Acknowledgement:

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References:

1. H. Okamoto, JPED, Vol. 34, No. 6, 2013, p. 493
2. C. Zhang, J. Zhu, D. Morgan, Y. Yang, F. Zhang, W.S. Cao, and Y.A. Chang, CALPHAD, 2009, Vol. 33, p 420
3. R.M. Waterstrat and R.C. Manuszewski, J. Less-Common Met., 1973, 32, p 79.

P03

EXPERIMENTAL STUDY OF THE Sb-Zn SYSTEM

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Keywords: Sb-Zn, phase equilibria, thermal analysis, thermoelectric

Sb-Zn-based alloys are studied as potential materials for thermoelectric applications. Many authors studied the effect of various alloying elements on thermoelectric properties of SbZn and Sb_3Zn_4 intermetallic phases, mainly focused on a very narrow concentration range of the third, added element. Although thermoelectric studies were combined with structural or microstructural studies, their authors did not aim to study correlations between thermoelectric properties and microstructure. On the other hand, the few papers covering broader concentration range suggest that multi-phase alloys have lower thermal conductivity and thus higher figure of merit than any of component phases. Moreover, previous researches are often based on time-consuming and costly trial and error approach. Recently it was shown [1] that CALPHAD approach may be very useful in the design of novel thermoelectric materials. The available assessments of Sb-Zn phase diagram [2,3] differ in small details in the central section of phase diagram. However, most recent experimentally determined phase diagram [4] diverges with respect to concentration ranges of intermetallic phases and phase transition temperatures. We have studied Sb-Zn alloys with Zn content from 48 to 61 at.% i.e. in the concentration range corresponding to the range of existence of the Sb_3Zn_4 and SbZn phases. The alloys were prepared by melting pure components in quartz-glass ampoules and then annealed for a specified period of time at temperatures of interest. The alloys were analyzed by SEM/EDS, XRD and DSC.

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References:

[1] H.-J. Wu, P.-C. Wei, H.-Y. Su et al., ACS Appl. Energy Mater., 2 (2019) 7564-7571.
[2] J-B. Li, M-C. Record, J-C. Tedenac, J. Alloy Compd., 438 (2007) 171–177.
[3] W. Gierlotka, J. Min. Metall. Sect. B-Metall., 50 (2014) 149-155.
[4] C.-W. T. Lo, V. Svitlyk, D. Chernyshov et al., Dalton Trans. 47 (2018) 11512-11520.

P04

MIXING ENTHALPIES OF LIQUID ALLOYS FROM Cu-Mg-Ti SYSTEM: EXPERIMENT VS. THERMODYNAMIC MODELING

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

There are many industrially important materials based on three-component alloys. This is due to the ability of the new material to have unique properties not possible for individual components on their own. These also include those based on the Cu-Mg-Ti system, which is used, among others, in the space and aviation industry, and as biomaterials in medicine. Knowledge of the thermodynamic properties of the system is the first step in the development of alloys and future implantation for industry applications. Due to the lack of thermodynamic data on the Cu-Mg-Ti system in the existing literature, this work aims to conduct the first thermodynamic studies on these three-component liquid solutions. This work presents the results of the mixing enthalpy change ($\Delta_{mix}H$) of the liquid Cu-Mg-Ti solutions obtained from the high-temperature drop calorimetric technique. Based on the achieved results and the thermodynamic properties of binary systems, the liquid phase of the Cu-Mg-Ti system was described by symmetrical Muggianu [1] and asymmetrical Toop [2] models. To accomplish that, homemade software (TerGexHm) was used. The obtained results are the first stage of further investigation and evaluation of the thermodynamic properties of the copper-magnesium-titanium system.

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References:

[1] Muggianu, Y.-M.; Gambino, M.; Bros, J.-P. Enthalpies of Formation of Liquid Bi-Ga-Sn Tin Alloys at 723 K -The Analytical Representation of the Total and Partial Excess Functions of Mixing. *Journal de Chimie Physique*,1975, 72, 83–88.
[2] Toop, G. W. Predicting Ternary Activities Using Binary Data. *Transactions of the Metallurgical Society of AIME*,1965, 233, 850–855.

P05

MOLECULAR DYNAMICS STUDY OF PHASE TRANSFORMATIONS IN NITICU SHAPE MEMORY ALLOYS

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Keywords: Atomistic simulation; Shape-memory alloy; Martensitic phase transformation; Modified embedded-atom method; Ni–Ti–Cu

NiTiCu shape memory alloys have attracted much attention for their ability to reduce hysteresis, which is required fast responses in actuator and sensor applications, but the correlation between the properties and specific process of phase transformation is unclear. An atomic-level understanding of the detailed phase transformation behavior of NiTiCu shape-memory alloys is achieved based on a newly developed interatomic potential for the Ni–Ti–Cu ternary system. Free energy calculations based on the thermodynamic integration method faithfully reproduce reported experimental trends, such as the compositional dependency of different phase transformation paths. Further, large-scale molecular dynamics simulations performed on nanocrystalline alloys provide visual evidence of the detailed phase transformation process involving different martensitic transformation paths. Our results suggest that although both the composition and grain size can be adjusted to realize slim hysteresis, the effect of increasing the Cu amount is only significant if changes in the phase transformation modes are involved at relatively low Cu contents. When the material exhibits only a single phase transformation mode at relatively high Cu contents, the additional Cu is not highly effective in reducing the hysteresis. The established interatomic potential and MD simulation results presented in this study provide a theoretical basis for the future alloying design of shape memory alloys with specific desired properties.

SNS$_2$/SI - COMPOSITE ANODES FOR LI- ION BATTERIES: PHASE DIAGRAM INVESTIGATIONS IN THE LI-SN-S AND SI-SN-S SYSTEMS

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Keywords: Lithium-ion batteries, phase diagram, Li-Sn-S, Si-Sn-S, CALPHAD

The development of efficient and environmentally sustainable Li-ion batteries (LIBs) is pre-requisite in today's world. In the advancing renewable energy topic, LIBs look promising as a field with its associated research environment [1]. Our research supports the development and optimization of high-performance Si/SnS$_2$ nanocomposite anode materials for generation 3b LIBs. Silicon (Si) nanoparticles recovered from end-of-life solar panels are used as a source due to its high specific capacity (3579 mAh g^{-1}) which is about 10 times that of graphite, low cost, and high availability [2]. Recent research shows that Tin (Sn) based materials can be used to increase the capacity of anode by 20% in comparison to the traditional Graphite anodes [3]. The full lithiation of Sn results in the formation of Li$_{17}$Sn$_4$ at a theoretical specific capacity of 994 mAh g^{-1}. Although Si and Sn- based materials exhibit high specific capacities, they undergo large volumes of expansion during lithiation. To counter this, we use SnS$_2$ instead of pure Sn. After intercalation of Li and conversion forming Li$_2$S and Sn the alloying reaction starts, only the latter is reversible [4]. During lithiation of Si and SnS$_2$, due to the presence of inert Li$_2$S heterojunction interfaces will be generated to buffer the volume expansions of the Si and Sn nanoparticles which inhibits further agglomeration.

To study the processes and design new composite electrodes, phase equilibria, phase transformations, crystal structure and electrochemical properties of Si/ SnS$_2$ nanocomposites should be known. Therefore, the main aim is to clarify phase relations and thermodynamics of the ternary Li-Sn-S and Si-Sn-S systems. Also, to model the Gibbs free energy of the phases formed during the lithiation mechanisms of the nanocomposites.

In Cupid et.al [5], the equilibrium Li-Sn-S phase diagram was calculated based on the extrapolation of binary systems assessments applying CALPHAD. The calculated isothermal section showed no ternary solubilities of Li-Sn alloys. There was a direct equilibrium between the pure component Sn and the binary compound Li$_2$S from which the Li-Sn-S system can be split into two partial systems namely, Li$_2$S-S-Sn and Li-Li$_2$S-Sn. Based on this concept, experiments were performed having Li, Li$_2$S, SnS$_2$, Sn and S as starting materials to study the phase diagram of the ternary system Li-Sn-S. The ternary samples were then analyzed using powder X-ray diffraction. In the Si-Sn-S system, samples were prepared using the constituent elements as powders for solid-state synthesis. The known ternary compounds Li$_4$SnS$_4$, Li$_2$SnS$_3$ and SiSn$_2$S$_4$ in both the systems were tried to be synthesized phase pure under our scope of work. Thermal analysis and calorimetry will be performed to obtain thermochemical information, which will be subsequently used to optimize the Gibbs free energy descriptions of the systems in study.

References:

1. G., Strange, C., Yadav, M., & Li, S. (2021). Lithium-ion battery data and where to find it. In Energy and AI (Vol. 5). Elsevier B.V. https://doi.org/10.1016/j.egyai.2021.100081
2. P.U. Nzereogu, A.D. Omah, F.I. Ezema, E.I. Iwuoha & A.C. Nwanya, (2022) Anode materials for lithium-ion batteries: A review, Applied Surface Science Advances. https://doi.org/10.1016/j.apsadv.2022.100233

3. Lepple, M., Cupid, D. M., Franke, P., & Seifert, H. J. (2015). [O15] Thermodynamic modeling and experimental investigations of materials systems for lithium-ion batteries. Calphad, 51, 349–350. https://doi.org/10.1016/j.calphad.2015.01.022
4. Shan, Yuying & Li, Yan & Pang, Huan. (2020). Applications of Tin Sulfide-Based Materials in Lithium-Ion Batteries and Sodium-Ion Batteries. Advanced Functional Materials https://doi.org/10.1002/adfm.202001298
5. Cupid, D. M., Rezqita, A., Glibo, A., Artner, M., Bauer, V., Hamid, R., Jahn, M., & Flandorfer, H. (2021). Understanding and modelling the thermodynamics and electrochemistry of lithiation of tin (IV) sulfide as an anode active material for lithium-ion batteries. Electrochimica Acta, 375. https://doi.org/10.1016/j.electacta.2021.137936

P07

THERMODYNAMIC AND KINETIC SIMULATIONS FOR MICROSTRUCTURE EVOLUTION OF DIRECT-QUENCHED STEELS DURING INTERCRITICAL ANNEALING

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Keywords: low-carbon steels, intercritical annealing, ferrite-martensite microstructure, mechanical properties

In this study, we investigated the microstructure evolution and mechanical properties of direct-quenched low-carbon steels, focusing on the ferrite-martensite microstructures controlled by alloying elements and intercritical annealing (IA) temperatures. The low-carbon steels directly quenched before IA were found to determine the morphology and distribution of ferrite-martensite microstructures after IA. The volume fraction of martensite increased with the IA temperature, resulting in the formation of fine and fibrous martensite. At the maximum IA temperature, the carbon content in martensite decreased significantly leading to a reduction in disparity in nanoindentation hardness between ferrite and martensite. The addition of Cr and Mo reduced the volume fraction of martensite through the solute drag effect, particularly noticeable at low IA temperatures, with this effect being alleviated by increasing the IA temperature. To elucidate the impact of Cr and Mo additions on microstructure evolution during IA, simulations utilizing DICTRA™ software with the TCFE12 thermodynamic database and MOBFE7 mobility database were conducted. The simulations indicate a delay in the reverse martensite-to-austenite transformation at lower temperatures due to the solute drag effect induced by Cr and Mo. Nonetheless, at higher IA temperatures, this effect diminishes, resulting in simultaneous transformation irrespective of alloying elements. Moreover, DICTRA™ simulations illustrate variations in Mn concentration at the ferrite/austenite interphase boundary, influenced by the addition of Cr and Mo. This variation is attributed to the reduction in interphase boundary mobility due to the solute drag effect, leading to an increase in Mn concentration at the interphase boundary. In summary, our findings reveal the intricate interplay between alloying elements, IA temperatures, and microstructural evolution in low-carbon steels. Understanding these mechanisms is crucial for tailoring the mechanical properties of steels for specific applications, ranging from enhancing yield strength to improving elongation and toughness

References:

G. Miyamoto, K. Yokoyama, T. Furuhara, Acta. Mater. 177 (2019) 187-197; Q. Guo, H.W. Yen, H. Luo, S.P. Ringer, Acta Mater. 225 (2022), 117601

THERMODYNAMIC CONSIDERATION ON THE REACTIONS BETWEEN MGAL$_2$O$_4$ REFRACTORIES AND A LIQUID FERROMANGANESE METAL

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Keywords: Liquid ferromanganese metals, Spinel Refractories, High temperature Reactions, X-ray CT analysis, XRD

Recently, in Korea, the production of high Mn containing steel such as Twinning Induced plasticity (TWIP) steel is increasing [1-3]. PosLM(POSCO Liquid Manganese) has been introduced as one of the high manganese steel production processes. In PosLM, ferromanganese is supplied in a liquid form during the steelmaking process. A holding furnace is used to maintain high Mn (85%) in a liquid phase. $MgAl_2O_4$ refractories may be suitable candidates to improve corrosion resistance by trapping Fe and Mn ions in the high Mn melts. In this study, a reaction mechanism is suggested for two types of $MgAl_2O_4$ refractories; a $MgAl_2O_4$ and a MgO-rich $MgAl_2O_4$, which were reacted with a liquid ferromanganese metal. The finger rotating test was adopted and experiments were carried out at 1873K. After the experiments, each refractory was analysed by X-ray computed tomography, field emission scanning electron microscopy, energy dispersive spectroscopy, and X-ray diffraction. When the $MgAl_2O_4$ was in contact with the liquid ferromanganese metal, $MgMn_{21}Al_2O_{32}$ layer was formed at the surface of the refractory. It acted as a passive layer since manganese ions did not penetrate into the bulk of the refractory with increasing reaction time. However, when the MgO-rich $MgAl_2O_4$ was in contact with liquid ferromanganese metal, manganese ions selectively penetrated through the MgO grains, which led to the formation of a $(Mg_xMn_{1-x})O$ solid solution. The penetration depth increased both with increasing reaction time and rotating speed. The characteristics of the reaction layers were analyzed by XRD and EDX and, a possible mechanism to form these layers was suggested based on thermodynamic consideration.

References:

1. B. C. De Cooman, Y. Estrin, & S. K. Kim, Acta Mater., 142, 283 (2018) 336.
2. J. E. Jung, J. Park, J. S. Kim, J. B. Jeon, S. K. Kim, & Y. W. Chang, Met. Mater. Int, 20, 27 (2014) 338
3. M. Jo, Y. M. Koo, & S. K. Kwon, Met. Mater. Int., 21, 227 (2015) 3

4. V. Y. Dashevskii, & K. V. Grigorovich, Russ. Metall., 2007(8), 694 (2007) 344
5. R. J. Fruehan, The making, shaping and treating of steel (AISE Steel Foundation, Pittsburgh, 1998), P. 20

THERMODYNAMIC EVALUATION OF AG-CU-O DURING BRAZING PROCESS OF MEDIUM-VOLTAGE ELECTRICAL CIRCUIT BREAKERS

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Keywords: Vacuum Interrupters, Brazing, Thermodynamics, Vaporization, Condensation, Oxygen Transport

The thermodynamics of Ag-Cu-O during the vacuum soldering process of electrical vacuum bottles, also known as vacuum switches (VI)[1], is an important topic in the production of electrical components. This analysis[2] examines the behavior of oxygen, among the various impurities originating from VI components or vacuum technology, due to its tendency to form stable oxides. Throughout brazing cycles, vapors emanating from vacuum furnace resistors and VI materials, as well as from certain brazing components, serve as primary sources, partially escaping or depositing on cooler furnace surfaces. Evaluating vaporization and condensation processes[3], material flows are quantified, elucidating their interaction with residual oxygen through a delicate balance between oxygen supply from vacuum or neutral gas, and oxygen sources within processed components. The study also assesses the oxygen enrichment of VI materials and deposits[4], establishing the necessary vacuum conditions. The main conclusion suggests that current vacuum conditions facilitate correct brazing; however, during temperature transitions, oxygen tends to accumulate as oxides on the surface of parts or in furnace materials.

References:

1. Théoleyre, S., *Techniques de coupure en moyenne tension.* Techniques de l'ingénieur Réseaux électriques de distribution publique, 1999. base documentaire : TIB264DUO(ref. article : d4705).
2. I. Nuta, C. Chatillon, F. Chombart and A. Moreau, Thermodynamic evaluation of oxidation during brazing process of medium-voltage electrical circuit breakers, Metallurgical Research Technology 2016 Vol. 113 Issue 5 Pages 510-536. DOI: http://dx.doi.org/10.1051/metal/2016031
3. Luo, H.-T. and S.-W. Chen, *Phase equilibria of the ternary Ag-Cu-Ni system and the interfacial reactions in the Ag-Cu/Ni couples.* Journal of Materials Science, 1996. **31**(19): p. 5059-5067.
4. Assal, J., B. Hallstedt, and L.J. Gauckler, *Thermodynamic assessment of the Ag-Cu-O system.* Journal of Phase Equilibria, 1998. **19**(4): p. 351-360.

A DATA-DRIVEN STUDY OF THE ENTHALPY OF MIXING IN THE LIQUID PHASE

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Keywords: Enthalpy of mixing, Excess heat capacity, Liquid alloys, Machine learning

The enthalpy of mixing in the liquid phase is an important thermodynamic property for predicting phase equilibria, not only using the Calphad method, but also machine learning approaches [1]. Means to reasonably estimate this property are valuable for two reasons: first, so far, it has only been measured in at the very most a third of the binary systems, and second, it is not easily available from *ab initio* calculations. To estimate this property in binaries, the model developed by Miedema *et al.* in the 1980s [2] is still to this day considered the best. However, since it has never been systematically evaluated, the accuracy that can be expected from it is not well known. Combined with Muggianu's model [3], it can provide estimates in multicomponent liquids. Again, the accuracy of this extrapolation has never been systematically studied.

To address this, we collect a large amount of enthalpy of mixing data in binary liquids from a review of about 1000 thermodynamic evaluations. This allows us not only to develop a machine learning model applicable to 70 elements of groups 1 to 16 that performs significantly better than Miedema's model, but also to bring new insights on the dependance in temperature and composition of the enthalpy of mixing in the liquid phase, as well as on its extrapolation from binary to multicomponent systems [4].

References:

1. G. Deffrennes, K. Terayama, T. Abe, E. Ogamino, R. Tamura, A framework to predict binary liquidus by combining machine learning and CALPHAD assessments, Mater. Des. 232 (2023) 112111.
2. A.R. Miedema, P.F. De Châtel, F.R. De Boer, Cohesion in alloys — fundamentals of a semi-empirical model, Physica B+C 100 (1980) 1–28.
3. Y.-M. Muggianu, M. Gambino, J.-P. Bros, Enthalpies de formation des alliages liquides bismuth-étain-gallium à 723 k. Choix d'une représentation analytique des grandeurs d'excès intégrales et partielles de mélange, J. Chim. Phys. 72 (1975) 83–88.

MACHINE LEARNING METHODS TO HELP CONSTRUCT PHASE DIAGRAMS

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Keywords: Phase diagrams, active learning

Knowledge of phase diagrams is essential for materials design, and their determination is thus a central task. We have developed a method for efficiently determining phase diagrams called PDC (Phase Diagram Construction) [1]. This method based on uncertainty sampling selects the most uncertain point in the phase diagram for experimental validation. Once the experiment performed, uncertainty sampling is performed again on the increased number of data to select the next candidates. By repeating this, the number of experiments required to determine a phase diagram can be reduced by a factor of five compared with a random search. Phase diagram determination is further accelerated by using Gibbs' phase rule to reduce the search space and multiple-phase domains to generate additional data [2]. PDC was successfully used to determine an unexplored phase diagram for the deposition of Zn–Sn–P films by molecular beam epitaxy and the temperature-composition phase diagram of a crosslinked polymer [3,4]. To efficiently determine phase diagrams using the PDC algorithm, we have created a web application called AIPHAD [5]. It includes strategies to obtain multiple candidate points at a time for high-throughput batch experiments [6].

Component A: A
Range (Component A): 0.0 – 1.0
Component B: B
Range (Component B): 0.0 – 1.0
Component C: C
Range (Component C): 0.0 – 1.0
Step size (components): 0.1
*Please set 0 ≤ Range ≤ 1
Step size (temperature): 100
Range (Temperature): 300 – 700

References:

1. K. Terayama, R. Tamura, Y. Nose, H. Hiramatsu, H. Hosono, Y. Okuno, and K. Tsuda, Phys. Rev. Mater. 3 (2019) 033802.
2. K. Terayama, K. Han, R. Katsube, I. Ohnuma, T. Abe, Y. Nose, and R. Tamura, Scr. Mater. 208 (2022) 114335.
3. R. Katsube, K. Terayama, R. Tamura, and Y. Nose, ACS Mater. Lett. 2 (2020) 571.
4. W.-H. Hu, T.-T. Chen, R. Tamura, K. Terayama, S. Wang, I. Watanabe, and M. Naito, Sci. Tech. Adv. Mater. 23 (2022) 66–75.
5. https://aiphad.org/
6. R. Tamura, G. Deffrennes, K. Han, T. Abe, H. Morito, Y. Nakamura, M. Naito, R. Katsube, Y. Nose, and K. Terayama, Sci. Technol. Adv. Mater. Methods 2 (2022) 153-161.

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MICROSTRUCTURE EVOLUTION UPON ANNEALING OF BRAZING CU-P LAYERS BETWEEN AG-C ELECTRICAL CONTACTS AND CU SUBSTRATES

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Keywords: electrical contact, brazed joints, annealing, Cu-Ag-P phase diagram, microstructure.

Circuit breakers are the main applications of silver based electrical contact materials reinforced by carbon fibers [1]. They offer good thermal and electrical conductivity, thermal dissipation as well as mechanical strength. For some low voltage circuit breakers, Silver based electrical contact materials can be sintered and bonded in the same operation to a silver-plated copper substrate with the help of a Cu-P brazing underlayer. This process, called resistance sintering, combines effort and heating generated by Joule's effect thanks to an electrical current [2]. In this work, such assemblies are annealed at different temperatures (between 500 and 800°C) and different times (3-60 min) in a tubular furnace under argon atmosphere to simulate ageing and thermal stresses. Samples are quenched in water after annealing. Microstructural investigations are performed using FEG-SEM on metallographic cross-sections. Annealed microstructures for temperatures above 700°C reveal ternary Ag-Cu-Cu3P eutectic formation [3, 4] from both sides containing silver, and its progress through the Cu-P layer during the annealing. Quantitative EDX analyses on approximately 300 µm □ 300 µm zones reveals at 700°C, an increase of the silver content in the Cu-P underlayer until 15 min of annealing due to liquid formation and its diffusion through the whole underlayer. Then a decrease is observed after 30 and 60 min which can be explained by silver diffusion through the copper substrate once the silver coating is consumed. Moreover, numerous pores are observed inside the Cu-P underlayer, and their size increases with the annealing time and temperature. Analysis of obtained microstructures and porosity formation is a way of understanding and preventing occurrence of failures linked to weak bonding between contact tips and copper substrates.

References:

[1] P. SLADE, “Electrical contacts- Principles and Applications”, p741-743, Dekker edition, 1999“

[2] E. Brisson “*Etude expérimentale et numérique du frittage-assemblage d'un composite conducteur Ag-SnO2 par courants pulsés*“, PhD thesis 2014, Université de Bretagne-Sud, France

[3] H. Yu, Y. Sun, S. P. Alpay, M. Aindow, *“Microstructure effects in braze joints formed between Ag/W electrical contacts and Sn-coated Cu using Cu-Ag-P filler metal”*, J. Mater. Sci. vol. 15 (2015), pp. 324-333, https://doi.org/10.1007/s10853-014-8591-7

[4] T. Takemoto, I. Okamoto, J. Matsumura “*Phase diagrams of Cu-Ag-P and Cu-Sn-P ternary brazing filler metals”*, Transactions of JWRI, vol 16 (1987), pp. 302-307, https://doi.org/10.18910/6457

PROCESSING OF A ZR-BASED BULK METALLIC GLASS

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Keywords: Zr-based bulk metallic glasses, processing, defects

The lack of atomic long-range order provides bulk metallic glasses (BMGs) with very high mechanical resistance compared to more conventional crystalline metallic alloys. To prevent crystallization during solidification, very high cooling rates [1] must be achieved which also impede skrinkage and allows the production of near net-shape components. However, depending on the composition, the achievable size of a fully amorphous structure can vary and structural defects, such as isolated crystalline phases, can sometimes be found in the final part. Such crystalline inclusions can lower several properties such as the mechanical resistance but also their corrosion resistance or their capacity to be machined to reach the final shape.

In a context of industrialization, the rising VULKAM company leads the BPI-financed project “VULBAM” into which BAUD Industry and two academic laboratories, SIMAP (Grenoble, France) and LAMPA (Angers, France) are also involved. This project aims at ensuring the reliability of the produced components, developing innovative and eco-efficient machining technics as well as integrating recycling strategies to reduce the waste of material side-products.

The paper will present some of the first results of a PhD work addressing these objectives. For instance, the numerous steps of processing of the BMG part, from the raw material to the final component, has been investigated order to better understand the mechanisms [2] at the origin of the presence of undesirable crystalline phases such as spherulites [3]. Microstructural and chemical characterizations of the matter alloy at different steps allows the determination of the more stable crystalline phase. A coupled thermodynamic/experimental approach is considered to understand and suppress the appearance of such phases inside BMGs.

References :

[1] *H. Sun, K.M. Flores, Spherulitic crystallization behavior of a metallic glass at high heating rates, Intermetallics 19 (2011) 1538e1545*

[2] Gautier et al., « Critical aspects of Titanium-based Bulk Metallic Glasses for biomedical applications: an investigation on casting defects and corrosion sensitivity ».

[3] Gránásy et al., « Growth and Form of Spherulites ». 2005

P14

SCIENCE OF DIRTY ALLOYS: IMPROVING THE RECYCLABILITY OF AL ALLOYS

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Keywords - Recycling, Aluminium, intermetallics, Characterization, Databases development

Theoretically, aluminum alloys, like most metal alloys, are infinitely recyclable. Moreover, in the case of aluminum, which is a very energy-intensive metal, the energy involved in the recycling process represents only 5% of the energy required for primary production from the ore. However, recycling presents some difficulties, as alloying elements from certain series are poisons to be avoided for others, and their mixing in the recycling process must be strictly limited, as such contamination leads to a reduction in the properties of so-called secondary aluminum, particularly ductility, which in turn reduces the potential applications for the use of this recycled aluminum. This decrease is usually attributed to the presence of Fe-rich intermetallic compounds (IMC).

The objective of this work is to improve the recycling sector's ability to produce alloys of interest for a wide range of applications, in particular by closing the loop on wrought grades such as alloys 5xxx and 6xxx without any cascade down to casting alloys.

To do so, the methodology relies on a combination of experimental approaches and thermodynamic calculations to better understand the impact of impurities on the microstructure and final properties of alloys. The microstructure of the alloys, and especially the nature, size, shape and distribution of intermetallic compounds, will be deeply investigated by advanced techniques such as Scanning Electron Microscopy, Energy Dispersive Spectroscopy, Electron BackScattered Diffraction, X-ray tomography, X-ray diffraction and chemical analysis. The influence of several processing parameters such as cooling rate or homogenizing heat treatment will be considered. Experimental results will be compared with numerical phase transformation models. Thermodynamics databases will be optimized in order to improve the predictive capacity of numerical simulation tools.

The main expected outcome is the definition of one, or more, robust aluminum alloy grades that can be obtained from a recycling process and whose properties can be adjusted to a large extent by means of a composition tolerant to the variations inherent in the recycling process, controlled solidification and a series of suitable heat treatments.

P15

DEVELOPMENTS AND APPLICATIONS OF THE GHEA THERMODYNAMIC DATABASE FOR CALPHAD MODELLING OF AL-C-CO-CR-FE-NI-R (R = MO, TA, W) SYSTEMS

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Keywords: Database building, High-Entropy Alloys, CALPHAD, thermodynamic modelling, experimental validation

The escalating global energy demand is pushing materials science towards the development of innovative materials capable of withstanding high temperatures while maintaining exceptional performance. In this context, High-Entropy Alloys (HEAs) represent a novel class of materials with particularly promising attributes [1].

The CALPHAD method is employed to predict thermodynamic equilibria in complex multi-component systems, allowing the selection of fewer key alloys for experimental investigation. This approach is particularly crucial for HEAs, given the vast number of possible elemental combinations.

Over the past nine years, the COMAT research group at the University of Genova has developed the Genova High-Entropy Alloys (GHEA) thermodynamic database. This comprehensive database includes 15 elements and over 200 different phases in 67 binary and 80 different ternary systems, meticulously modelled across the full range of temperatures and compositions. Key features and experimental validations of the GHEA database were showcased at the 2022 and 2023 CALPHAD conferences [2, 3].

In this past year, significant progress has been made by applying the database to Al-C-Co-Cr-Fe-Ni-R (R = Mo, Ta, W) systems. The database has been of fundamental importance in designing alloy compositions and treatments, as well as interpreting results of different experimental tests such as wettability measurements.
This communication will detail the recent improvements, expansion, and applications of the GHEA database, highlighting its critical role in experimental design and data interpretation. Examples of practical applications will be provided [4], emphasizing the database's role in advancing HEAs research.

References:

[1] Miracle, D.B., et al. “A Critical Review of High-Entropy Alloys and Related Concepts”, Acta Materialia, 122 (2017), pp. 448-511 - http://dx.doi.org/10.1016/j.actamat.2016.08.081.
[2] Fenocchio, L., et al. “Development of a Thermodynamic Database for High-temperature Materials”, O5, XLIX CALPHAD, Stockholm (2022).
[3] Fenocchio, L., et al. “**Validation and Application of the Genova High-Entropy Alloys (GHEA) Thermodynamic Database for Selected Multi-component Systems”, O20, CALPHAD L, Boston (2023).**
[4] Gambaro S., Fenocchio L., et al., “Combined experimental and CALPHAD investigation of equimolar AlCoCrFeNiX (X = Mo, Ta, W) High-Entropy Alloys” – Calphad 85, 2024 - https://doi.org/10.1016/j.calphad.2024.102702.

P16

THE STABILITY OF THE CALPHAD METHOD IN FRONT OF NEW MATERIALS

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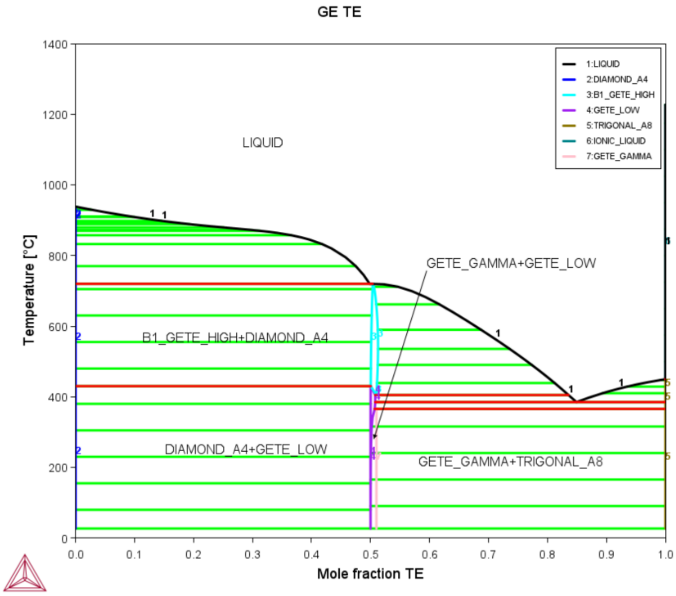
Keywords: CALPHAD, semiconductors, thermoelectrics

When a set of Gibbs energies is created in order to describe a system, not necessarily an application is given as motivation. It can be that the model able to reproduce the measured quantities offers a challenge for finding a satisfactory set of parameters or it can also be that there are samples in the laboratory that allow to investigate equilibrium between phases that are not well known and that instigate the curiosity of the researcher. Over the years, however, new applications are discovered, and, often, the system that was investigated, out of pure curiosity, becomes relevant information for technological development.

The Ge-Te binary system, in the figure, [1], was studied experimentally by a French-German group of scientists which became interested in thermodynamic modeling. The complexity of the liquid phase and the narrow range of solubility of two intermediate phases gave the impetus for the research.

It was just recently that, Germanium Telluride (GeTe) properties were discovered, like ultrafast ferroelectric transition, anomalous phonon anharmonicity as well as its use in thermoelectric applications. GeTe then attracts enormous interest in academia but also in industrial production [2]. As devices are created, the preparation the characterization, the behavior when use requires a deep knowledge to the Ge-Te phase diagram that now found its application.

Fortunately, the CALPHAD description was available in open and proprietary databases and is being intensively used in the last few years.



[1] Schlieper, A., Feutelais, Y., Fries, S. G., Legendre, B., Blachnik, R, CALPHAD, 1999, 23, 1.

[2] Li, M., Shi, X-L, Che,Z-G, Advanced Functional Materials, 2024,2403498.

PHASE TRANSFORMATIONS IN LEAD-FREE NANOCOMPOSITE SOLDER JOINTS

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Keywords: phase transformations, nanocomposite lead-free solders, nanoparticles, solder joints, microstructure

The Sn-based lead-free solders are important metal interconnection materials in electronic industry. Most of studies are mainly focused on the characteristics of the solders themselves, while the reliability of soldered joints is less evaluated. But information about the relationship between the structure, thermophysical and mechanical properties and the reliability of solder joints is extremely important to know and predict the behaviour of soldered components during operation in extreme thermodynamic conditions in a wide temperature range including subzero temperatures for application of specific electronic components, e.g., in aerospace conditions. The reliability of joints is mainly determined by the intermetallic compounds that form at the interface of the solder/substrate joint. Although a thin layer of the intermetallic compounds promotes better wettability between a solder and a substrate, its growth can weaken the joint due to its brittleness. As a result, there is an increased likelihood of brittle failure due to changing temperature conditions, such as thermal aging and thermal cycling processes, due to thermal expansion mismatches between components and substrates. As Sn-based solders have a higher melting temperature and a higher tin content that conventional Pb-Sn solders, the formation and growth of the intermetallic compounds layer in solder joints occurs faster, causing brittle fracture and a decrease in the durability of the joint due to thermal fatigue. To avoid these problems and improve the solder properties, various metal, carbon and ceramic nano-sized admixtures are added to the main matrix. We report the results and compare the influence of different nano-sized admixtures on phase transformations, structure, microstructure and properties of lead-free nanocomposite SAC305 and SAC387 solders and solder joints over a wide temperature range between elevated and subzero temperatures.

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P18

PHASE EQUILIBRIUM INVESTIGATIONS AND THERMODYNAMIC STUDY OF THE ZRO_2-HFO_2-TA_2O_5 SYSTEM

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

The ZrO_2-HfO_2-Y_2O_3-Ta_2O_5 system materials have attracted attention for their potential use as innovative thermal barrier coatings [1,2]. A fundamental understanding of the thermodynamics in this system is essential for future practical applications. This work focuses on the ZrO_2-HfO_2-Ta_2O_5 side system. A preliminary thermodynamic database was combined from thermodynamic descriptions of the ZrO_2-Ta_2O_5 and HfO_2-Ta_2O_5 systems published in ref. [3] and [4], respectively. Solid and liquid solutions in the HfO_2-ZrO_2 system are assumed to be ideal. The isothermal sections were calculated at 1673 K and 1873 K as well as the liquidus surface. The preliminary calculations were used for planning of experiments.

This study investigates phase and melting relations in the ZrO_2-HfO_2-Ta_2O_5 system using two methods: the equilibration method, which covers temperatures from 1673 K to 1873 K, and the DTA method, which extends up to 2473 K. The samples were obtained using the co-precipitation method. Phase identification was carried out using X-ray diffraction (XRD). Microstructure investigation and phase composition measurements were performed using scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDX). Special attention was given to the $(Hf,Zr)_6Ta_2O_{17}$ phase. The heat capacity of the $(Hf,Zr)_6Ta_2O_{17}$ phase was measured using differential scanning calorimetry (DSC) over the temperature range of 240 K to 1300 K for several compositions for Hf and Zr between $Hf_6Ta_2O_{17}$ and $Zr_6Ta_2O_{17}$. The experimental data were fitted to the Maier-Kelley equation. The temperatures of the monovariant eutectic and the peritectic reactions were measured using DTA as a function of composition. The influence of the composition on the microstructure was observed.

The thermodynamic database for the ZrO_2-HfO_2-Ta_2O_5 system obtained using the CALPHAD approach will be improved, accounting experimental data on the phase diagram and thermodynamic values obtained in the present study and literature [3,4].

References :

[1] Lepple, M. et al. “Enthalpies of formation of the solid solutions of $ZrxY_{0.5-x/2}Ta_{0.5-x/2}O_2$ ($0 \le x \le 0.2$ and $0.65 \le x \le 1$)”, *J. Mater. Res.* 34 (19) (2019)
[2] Pitek, F. Met al. “Opportunities for TBCs in the ZrO_2–$YO_{1.5}$–$TaO_{2.5}$ system”, *Surface and Coatings Technology* 201 (12) (2007)
[3] M. Löffler et al., Phase equilibrium investigations and thermodynamic modelling of the ZrO_2-Ta_2O_5 system, Journal of the European Ceramic Society (2023).
[4] M. Löffler, O. Fabrichnaya, Phase equilibrium investigations and thermodynamic modeling of the HfO_2–Ta_2O_5 system. International Journal of Applied Ceramic Technology, (2024) https://doi.org/10.1111/ijac.14648

P19

EFFECT OF THE ADDITION OF NI AND CU ON THE SOLIDIFICATION AND MICROSTRUCTURE OF AL-5SI-0.5MG ALLOYS

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Keywords: Al-5Si-0.5Mg alloys, Cu and Ni addition, solidification, phase formation

The need for lightweight vehicles and stricter fuel efficiency regulations in the automotive, aerospace, and other sectors are driving research to improve the high temperature strength of Al-Si alloys. However, unmodified Al-Si alloys do not have the strength required for demanding applications. This study investigates the development of high-strength, tough hypoeutectic Al-Si alloys by microalloying, a common method of improving their properties.

Microalloying elements influence the solidification, microstructure, and mechanical properties of Al-Si alloys. High-performance Al-Si-Mg alloys offer a good balance between weight reduction, properties, and cost. An effective alloy for high-temperature applications requires elements with specific properties, such as the formation of stable age-hardening phases and low solubility in the Al matrix. Elements such as Cu and Mg improve the mechanical properties, while Ni additions can increase the strength, i.e. the high-temperature strength by forming the δ-Al_3CuNi phase, but also lead to porosity and reduced ductility. Fe can further reduce ductility through the formation of the β-Al_5FeSi phase.

Microalloying with elements such as Ti, Zr and V is often combined with improved processing methods to create new high-strength Al-Si-Cu-Ni-Mg alloys. The high-temperature strength of these alloys depends on a network of intermetallic compounds such as ε-Al_3Ni, δ-Al_3CuNi and γ-Al_7Cu4Ni that transfer the load from the Al matrix.

In this study, the solidification and microstructure evolution of an Al-5Si-0.5Mg alloy with Cu and Ni additions are analysed using different techniques. The focus is on understanding how these elements influence the solidification process and microstructure, which is crucial for optimising the development of high-strength Al-Si alloys. A low Ni content leads to the formation of the $Al_9Fe_2Si_2$ phase after the (α-Al+β-Si) eutectic, while a higher Ni content promotes the solidification of the Al_9FeNi phase before the eutectic at higher temperatures. In addition, Ni appears to interact with Cu during phase formation, and both Cu and Cu-Ni additions increase the solidification range. Microstructural analysis shows the incorporation of Ni into the AlCuNi phase, and Ni also appears to form phases with Fe (AlFeNi) and Mg (Mg_2Si).

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PUREALLOYS: DESIGNING NEW ULTRA-RADIOPURE, HIGH-STRENGTH ELECTROFORMED CUCRTI ALLOYS, FOR RARE EVENT SEARCHES

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Keywords: electroforming, radiopurity, alloys, ICME

Immense progress has been achieved in understanding the Cosmos over more than 45 orders of magnitude in length. Alas, fundamental questions remain about the nature of; a) Dark Matter (DM); and b) neutrinos. Direct detection is considered the most prominent approach; aiming to observe DM from the Milky Way halo.

Copper is the material of choice for rare event searches. It can be procured at low cost and high purity, and it has no long lifetime isotopes. Alas, it may be contaminated during manufacturing and can be activated by fast neutrons from cosmic rays. Electroformed Cu (EFCu) enables even higher radiopurity, with favorable radiochemical, thermal, and electrical properties. This novel technique [1] leads to extreme radiopurities with contamination below 10^{-14} grams of ^{232}Th and ^{238}U per Cu gram. However, Cu is highly ductile and of low strength, limiting its use for moving mechanical, high-pressure, and load-bearing parts. This would improve the capability for experiments such as DarkSPHERE [2], a large-scale, fully electroformed underground, spherical detector operating under pressure to probe uncharted territory in the search for DM, and is vital for nEXO, a neutrinoless-double β-decay experiment.

The most promising element for strengthening of EFCu is Cr. It has been demonstrated that small additions of Cr, combined with heat treatment and aging, improve strength by 70% [3]. However, Cr additions lead to impurities, and a compromise between strength and radiopurity is required by exploring a complex parameter space of compositions and strengthening mechanisms [4]. Cr solubility in Cu is very limited and small additions of Ti can allow for improved mechanical strengthening due to reinforced precipitation. The Cr-Cu-Ti system has gained recently significant interest in the development of CuCrTi alloys for contact wires of high-speed, large-scale integrated circuit lead frames and electronic connectors [5].

PureAlloys aims to develop high radiopure CuCr and CuCrTi alloys with significantly higher strength compared to Cu. The project will deliver a novel approach based on the Integrated Computational Materials Engineering (ICME) framework enabling rapid design of new, application-specific alloys. Electroformation in additive-free bath is the focus of the project, which will push the boundaries in fundamental science and industrial applications.

References:

[1] NEWS-G Collaboration "Copper electroplating for background suppression in the NEWS-G experiment", *Nucl. Instrum. Meth. A,* 988 (2021): 164844

[2] NEWS-G Collaboration "Exploring light dark matter with the DarkSPHERE spherical proportional counter electroformed underground at the Boulby Underground Laboratory", Phys. Rev. D 108, (2023): 112006

[3] Overman N. et al. "Mechanical property anisotropy in ultra-thick copper electrodeposits", *Appl. Phys. A* 120 (2015): 1181

[4] Vitale A. et al. "A preliminary investigation into the electrodeposition and synthesis of radiopure Copper–Chromium alloys for rare-event physics detector systems", *Nucl. Instrum. Meth. A*, 1003 (2021): 165291

[5] Zhaokuo H. et al. "Mechanism investigation on high-performance Cu-Cr-Ti alloy via integrated computational materials engineering", *Mater. Today Commun.* 27 (2021): 102378

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ADDITIVE MANUFACTURING OF WC-CO CERAMIC/METAL COMPOSITES USING BINDER JETTING: FROM POWDER TO SINTERED PART PROPERTIES

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Keywords: Binder Jetting, Cemented carbides, Sintering, Dilatometry, Modeling

Cemented carbides are used in industry as cutting tools and wear parts *[1]*, thanks to their high hardness and wear resistance. Traditionally composed of tungsten carbide (WC) and a metal binder of cobalt (Co) *[2]*, these composites are manufactured by powder metallurgy and must have a density greater than 99.5%. Today's environment is prompting us to find ways of saving the materials needed to manufacture industrial products, through the use/development of innovative processes such as additive manufacturing, and more specifically binder jetting *[3]*. However, major technological and scientific hurdles remain: understanding the link between printing parameters, physico-chemical properties of powders, microstructures of printed parts and mechanical properties of sintered parts.
In this purpose, a number of mechanical tests (hardness, toughness, bending test) have been carried out to establish the link between microstructure and mechanical properties of sintered parts. Fine microstructural analysis (composition, grain size, phases present) and thermodynamic calculations in sintering windows (ThermoCalc) will help predict microstructure as a function of debinding/sintering conditions.
In addition, dilatometry tests on green parts printed by Binder Jetting have been carried out to quantify anisotropy, determine its cause and correct it if necessary. The aim of these tests is also to understand the specific features of liquid phase sintering, so as to feed a numerical simulation model of the sintering process *[4], [5]*. 19th Discussion Meeting on Thermodynamics of Alloys TOFA 2024, 23-27 September 2024, Lyon

References:

[1] « Evatec-tools ». [Online]. Available at: www.evatec-tools.com.
[2] J. M. Tarragó et al., « Microstructural effects on the R-curve behavior of WC-Co cemented carbides », Materials & Design, vol. 97, p. 492-501, mai 2016.
3] A. Lores, N. Azurmendi, I. Agote, E. Zuza, A review on recent developments in binder jetting metal additive manufacturing: materials and process characteristics, Powder Metall. 62 (2019) 267–296. https://doi.org/10.1080/00325899.2019.1669299.
[4] C. Manière, « Simulation des nouveaux procédés de frittage », thesis, Université de Caen Normandie, 2023. [Online]. Available at: https://hal.science/tel-04230055.
[5] O. Gillia et D. Bouvard, « Phenomenological analysis of densification kinetics during sintering: application to WC–Co mixture », *Materials Science and Engineering: A*, vol. 279, nₒ 1-2, p. 185-191, févr. 2000, doi: 10.1016/S0921-5093(99)00621-8.

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ON THE SIZE AND SHAPE DEPENDENCE OF INTEGRAL AND PARTIAL MOLAR GIBBS ENERGY, ENTROPY AND ENTHALPY OF NANOPHASES

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Keywords: Nano-phases; integral and partial molar; Gibbs energy; entropy; enthalpy

Nanomaterials are materials that contain nanophases. Nanophases are phases that have at least one of their dimensions below 100 nm. To calculate phase equilibria in nanomaterials, the size dependence of their molar Gibbs energy is needed. It was shown that the Kelvin equation is wrong [1]. Instead, the following equation was derived for he size dependence of molar Gibbs energy of nanophases ($G_{\mathrm{m},\Phi}$, J/mol) [2]:

$$G_{\mathrm{m},\Phi} = G^{o}_{\mathrm{m},\Phi} + A_{\mathrm{sp},\Phi} \cdot V_{\mathrm{m},\Phi} \cdot \sigma_{\Phi/g} \qquad (1)$$

where $G^{o}_{\mathrm{m},\Phi}$ (J/mol) is the standard molar Gibbs energy of the same macro-phase at same temperature and same pressure, $A_{\mathrm{sp},\Phi}$ (1/m) is the specific surface area of a nano-phase, $V_{\mathrm{m},\Phi}$ (m^3/mol) is the molar volume of the nano-phase, $\sigma_{\Phi/g}$ (J/m^2) is the surface tension of a liquid nano-droplet, or the surface energy of a solid nano-crystal. Five years later the same was extended to the chemical potentials (partial molar Gibbs energies) of components in nano-phases [3]:

$$G_{\mathrm{m,i}(\Phi)} = G^{o}_{\mathrm{m,i}(\Phi)} + A_{\mathrm{sp},\Phi} \cdot V_{\mathrm{m,i}(\Phi)} \cdot \sigma_{\Phi/g} \qquad (2)$$

where $X_{\mathrm{m,i}(\Phi)}$ is the same as $X_{\mathrm{m},,\Phi}$ defined above but refers to partial molar quantities of the components in nanophases. Further 7 years later the same was extended to the size dependence of the molar entropies and enthalpies as [6]:

$$S_{\mathrm{m},\Phi} \cong S^{o}_{\mathrm{m},\Phi} - \frac{C_{p,m,\Phi}}{H_{m,c,\Phi}} \cdot z_{\Phi} \cdot\ A_{\mathrm{sp},\Phi} \cdot V_{\mathrm{m},\Phi} \cdot \sigma_{\Phi/g} \qquad (3)$$

$$H_{\mathrm{m},\Phi} \cong H^{o}_{\mathrm{m},\Phi} + \left(1 - T \cdot z_{\Phi} \cdot \frac{C_{p,m,\Phi}}{H_{m,c,\Phi}}\right) \cdot\ A_{\mathrm{sp},\Phi} \cdot V_{\mathrm{m},\Phi} \cdot \sigma_{\Phi/g} \qquad (4)$$

where S and H refer to entropy and enthalpy, $C_{p,m,\Phi}$ (J/molK) is the molar het capacity of the nano-phase, $H_{m,c,\Phi}$ (J/mol) is the molar cohesion energy (negative) of the nanophase, $z_{\mathrm{s}} \cong 2$ for solid nano-particles and $z_{\mathrm{l}} \cong 1$ for liquid nano-droplets. Partial entropies and enthalpies are written by similar equations. The validity of the above equations (1-4) were confirmed by experimental data.

References:

1. G. Kaptay. The chemical (not mechanical) paradigm of thermodynamics of colloid and interface science. Adv Colloid Interface Sci 256 (2018) 163-192.
2. *G. Kaptay. The Gibbs equation versus the Kelvin and the Gibbs-Thomson equations to describe nucleation and equilibrium of nano-materials. J Nanosci Nanotech 12 (2012) 2625-2633.*
3. G. Kaptay. A new paradigm on the chemical potentials of components in multi-component nano-phases within multi-phase systems. RSC Adv 7 (2017) 41241-41253.
4. G. Kaptay. On the size- and shape-dependence of integral and partial molar Gibbs energies, entropies, enthalpies and inner energies of solid and liquid nano-phases. J Mater Sci (2024).

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