

The background of the cover is a scenic photograph of Lake Bled in Slovenia. The upper half shows the turquoise lake with the Bled Island church in the distance, surrounded by forested mountains. The lower half, separated by a diagonal line, shows a close-up of Bled Castle with its red-tiled roofs and stone walls, situated on a hillside with autumn-colored trees.

# TOFA

## BOOK OF ABSTRACTS

**20<sup>th</sup> DISCUSSION MEETING ON  
THERMODYNAMICS OF ALLOYS**

**20 - 24 September 2026**

**BLLED - SLOVENIA**



UNIVERSITY  
OF LJUBLJANA

**NTF**

Faculty of Natural Sciences  
and Engineering

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# PREFACE

## Dear Colleagues and Friends,

It is our great pleasure to welcome you to the 20<sup>th</sup> Discussion Meeting on Thermodynamics of Alloys (TOFA 2026), which will take place from 20 to 24 September 2026 in Bled, Slovenia.

Nestled at the foot of the Julian Alps and renowned for its spectacular lake, island church, and medieval cliff-top castle, Bled is one of the most recognizable and attractive destinations in Central Europe. For centuries, visitors have been drawn to its unique natural beauty, rich cultural heritage, and welcoming atmosphere. Surrounded by mountains and forests, and located close to the Triglav National Park, Bled provides an inspiring environment for scientific discussion, professional networking, and the exchange of new ideas.

Since its establishment, TOFA has served as a distinguished international forum for researchers, scientists, engineers, and students working in the field of alloy thermodynamics and related disciplines. The conference has played an important role in advancing scientific understanding and fostering collaboration between experimental and computational communities, while continuously attracting participants from academia, research institutions, and industry.

TOFA 2026 continues this tradition by providing an environment that encourages scientific excellence, open discussion, and the sharing of insights. The conference programme includes invited lectures by internationally recognised experts, selected oral presentations, and poster sessions presenting the latest developments in thermodynamic modelling, phase equilibria, materials design, process metallurgy, and emerging applications supporting sustainable technologies and the green transition.

As always, TOFA offers a valuable opportunity for all generations of scientists to meet, interact, and build new collaborations. We are particularly pleased to welcome young researchers and students, whose enthusiasm and fresh perspectives will help shape the future development of our field.

We would like to express our sincere gratitude to all authors, participants, members of the Scientific and Organising Committees, sponsors, and supporting institutions whose contributions have made this conference possible. Most importantly, we thank you, the participants, for bringing your expertise, enthusiasm, and commitment to scientific progress.

We hope that TOFA 2026 will provide an inspiring forum for exchanging knowledge, establishing new collaborations, strengthening existing partnerships, and enjoying the hospitality and beauty of Bled.

We wish you a stimulating and successful conference and an enjoyable stay in Slovenia.

On behalf of the Organising Committee,

**Jožef Medved**



**Maja Vončina**



# COMMITTEES

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| PROGRAMME     |                                             |                                                                    |                                                                                |                                                                           |                                           |  |
|---------------|---------------------------------------------|--------------------------------------------------------------------|--------------------------------------------------------------------------------|---------------------------------------------------------------------------|-------------------------------------------|--|
|               | Sunday,<br>20 <sup>th</sup> September       | Monday,<br>21 <sup>st</sup> September                              | Tuesday,<br>22 <sup>nd</sup> September                                         | Wednesday,<br>23 <sup>rd</sup> September                                  | Thursday,<br>24 <sup>th</sup> September   |  |
| 8:00 - 9:00   |                                             | Registration                                                       | Registration                                                                   |                                                                           |                                           |  |
|               |                                             | Session 1                                                          | Session 4                                                                      | Session 6                                                                 | Session 9                                 |  |
|               |                                             | Chair: Klaus Richter,<br>Jožef Medved                              | Chair: Maja Vončina,<br>Andreas Leineweber                                     | Chair: Suzana G. Fries,<br>Boštjan Markoli                                | Chair: Olga Fabrichnaya,<br>Tilen Balaško |  |
| 9:00 - 9:40   |                                             | Invited: Suzana G. Fries                                           | Invited: Frank Stein                                                           | Invited: Joonho Lee                                                       | Invited: Klaus Richter                    |  |
| 9:40 - 10:00  |                                             | Andreas Leineweber                                                 | Min-Kyu Paek                                                                   | Tatsuya Tokunaga                                                          | Joo Hyun Park                             |  |
| 10:00 - 10:20 |                                             | Konatsu Yamada                                                     | Jérôme Andrieux                                                                | Ondřej Zobač                                                              | Se Hyeon Nam                              |  |
| 10:20 - 10:40 |                                             | Adam Grajcar                                                       | Karthikeyan Mohankumaramangalam                                                | Viera Homolová                                                            | Sylvie Chatain                            |  |
| 10:40 - 11:10 |                                             | Coffee break                                                       | Coffee break                                                                   | Coffee break                                                              | Coffee break                              |  |
|               |                                             | Session 2                                                          | Session 5                                                                      | Session 7                                                                 | Session 10                                |  |
|               |                                             | Chair: Mitja Petrič,<br>Michel Bénédicte                           | Chair: Viera Homolová,<br>Frank Stein                                          | Chair: Min-Kyu Paek,<br>Jérôme Andrieux                                   | Chair: Jaka Burja,<br>Aurélie Jacob       |  |
| 11:10 - 11:30 |                                             | Boštjan Markoli                                                    | Pedro N. Ferreira                                                              | Przemysław Fima                                                           | Olga Fabrichnaya                          |  |
| 11:30 - 11:50 |                                             | Cláudio G. Schön                                                   | Pavel Brož                                                                     | Jaka Burja                                                                | Michel Bénédicte                          |  |
| 11:50 - 12:10 |                                             | Aurélie Jacob                                                      | George Kaptay                                                                  | Luanna C. de Souza                                                        | Satyam Vankayala                          |  |
| 12:10 - 12:30 |                                             | Felicia Larsson                                                    | Yang Hu                                                                        | Hans Flandorfer                                                           | Danilo A. de Abreu                        |  |
| 12:30 - 12:50 |                                             | Lunch<br>12:30 - 14:00                                             | SP - Martin Sečar (Altium)<br>SP - Derek Black (Setaram)                       | Lunch<br>12:30 - 14:00                                                    | Jožef Medved                              |  |
| 13:30 - 14:00 |                                             | Session 3                                                          | Lunch<br>12:50 - 14:00                                                         | Session 8                                                                 | Closing                                   |  |
|               |                                             | Chair: George Kaptay,<br>David Bombač                              |                                                                                | Chair: Przemysław Fima,<br>Sylvie Chatain                                 | Lunch<br>13:00 - 14:00                    |  |
| 14:00 - 14:20 |                                             | Satoshi Minamoto                                                   | Optional Excursions<br><br>Meeting point<br>Hotel Riklí Balance Lobby at 14:30 | Grega Klančnik                                                            |                                           |  |
| 14:20 - 14:40 |                                             | Hai-Lin Chen                                                       |                                                                                | Yun Jin Kim                                                               |                                           |  |
| 14:40 - 15:00 |                                             | Karoline E. Borowski                                               |                                                                                | Agustin Flores                                                            |                                           |  |
| 15:00 - 15:20 |                                             | Sara Guerrucci                                                     |                                                                                | Ádám Végh                                                                 |                                           |  |
| 15:20 - 15:40 |                                             | Swathi M. Dikonda                                                  |                                                                                | SP - Haris Salihagić Hrenko (Talum)<br>SP - Keith Racman (Mettler Toledo) |                                           |  |
| 15:40 - 16:00 |                                             | SP - Nina Rejc (AstrinexLab)<br>SP - Andre Schneider (Thermo-Calc) |                                                                                | Viera Homolová - TOFA 2028                                                |                                           |  |
| 16:00 - 18:00 | Registration                                | Coffee break and poster session                                    |                                                                                |                                                                           |                                           |  |
| 18:00 - 20:00 | Opening Ceremony<br>and Welcome<br>cocktail |                                                                    | Evening programme with a walk up to Bled Castle<br>and the gala dinner.        | Meeting point<br>Hotel Riklí Balance Lobby at 18:00                       |                                           |  |
|               | Arnold Foyer                                |                                                                    |                                                                                |                                                                           |                                           |  |

# ORAL PRESENTATIONS



# AL ALLOYS BEFORE AI, A LONG STORY OF EXPERIMENTS AND MODELING

Suzana G. Fries<sup>1</sup>, Philip Spencer<sup>2</sup>

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(Corresponding author: [Suzana.G.Fries@ruhr-uni-bochum.de](mailto:Suzana.G.Fries@ruhr-uni-bochum.de))

Main topic: Phase diagrams and phase equilibria

Secondary topic: Computational thermodynamics

Abstract:

# VACANCIES IN PHASES OF THE FE-AL AND FE-AL-SI SYSTEMS

Andreas Leineweber<sup>1</sup>, Lukas Richter<sup>1</sup>, Ulrich Meier<sup>1</sup>, Stefan Martin<sup>1</sup>, Paul Lafaye<sup>2</sup>

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Main topic: Phase diagrams and phase equilibria

Secondary topic: Phase transformations and kinetics, solid state diffusion

Abstract:

Like many binary systems formed from “late” transition metals and aluminium, the Fe-Al system features a bcc-superstructure phase of the B2 type with a wide homogeneity range (“FeAl”). Like in similar phases with Ni and Co, thermal vacancy formation gets easier with increasing Al content, although the B2 phase in the Fe-Al system lacks a clear region of constitutional vacancy formation above 50 at. % Al. The crystal structures of the more Al-rich intermetallic phases as Fe<sub>5</sub>Al<sub>8</sub>, FeAl<sub>2</sub>, Fe<sub>2</sub>Al<sub>5</sub>, Fe<sub>4</sub>Al<sub>13</sub> and the metastable FeAl<sub>6</sub> but also the newly discovered Fe<sub>3</sub>Al<sub>13</sub> are often simply described as “complicated”. However, a common view on the  $\gamma$ -brass-like Fe<sub>5</sub>Al<sub>8</sub> is that it is a 3 x 3 x 3 superstructure of the bcc structure with 2 vacancies and 54 – 2 = 52 Fe + Al atoms.

Upon more closely inspecting the crystal structures of the other mentioned Fe-Al phases, it is now shown that also these can be described as vacancy-containing bcc-derivative structures, opening up thus a new way to describe their crystal structures on a common basis. The structure principle appears fulfilled for a couple of Al-rich ternary Fe-Al-Si phases:  $\tau_1$ ,  $\tau_2$ ,  $\tau_3$ ,  $\tau_4$ ,  $\tau_6$ ,  $\tau_{10}$ , and  $\tau_{11}$ . More importantly, it will be demonstrated based on own experimental and theoretical evidence, but also in view of data from the literature that there is not only a common (geometric) structure principle, but that this principle allows rationalizing a series of thermodynamic, mechanical and microstructural observations associated with these phases.

Keywords: Vacancies, Crystal structure, Aluminium, Microstructure

# CRYSTAL STRUCTURE, PERITECTOID REACTION TEMPERATURE AND COMPRESSIVE DEFORMATION BEHAVIOR OF $\text{Ta}_2\text{Co}_7$ IN THE CO-TA BINARY SYSTEM

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Main topic: Phase diagrams and phase equilibria

Secondary topic: Phase transformations and kinetics, solid state diffusion

Abstract:

The Co-Ta binary system is both fascinating and complex, with several notable intermetallic phases. Among these,  $\text{Ta}_2\text{Co}_7$  is of particular interest, as it has been established that  $\text{Nb}_2\text{Co}_7$  in the Co-Nb binary system exhibits unique mechanical properties through a kink formation mechanism. However, the literature reports considerable variation regarding the crystal structure and peritectoid reaction temperature of  $\text{Ta}_2\text{Co}_7$ , depending on the research group. Furthermore, the deformation behaviour of  $\text{Ta}_2\text{Co}_7$  under compression remains insufficiently understood. To clarify the crystal structure, peritectoid reaction temperature, and deformation behaviour under uniaxial compression of this phase, the present study involved preparing Co-21.8 at. % Ta alloys, which were subjected to prolonged isothermal heat treatments of up to 10,000 hours, followed by detailed experimental analyses.

SEM observations of the samples after isothermal heat treatment indicate that those heat-treated at 850 °C for 10,000 hours, at 900 °C for 10,000 hours, and at 1000 °C for 1,000 hours have all reached equilibrium. XRD analysis reveals that the crystal structure after heat treatment at 900°C for 10,000 hours does not correspond to  $\text{Ta}_2\text{Co}_7$ ; instead, the rhombohedral  $\beta\text{-Co}_3\text{Ta}$  structure (space group: 166, R-3m) is identified. DTA measurements show endothermic peaks associated with the peritectoid decomposition of  $\beta\text{-Co}_3\text{Ta}$  when the samples were previously heat-treated isothermally below 994 °C, whereas no endothermic peaks are observed after heat treatments above 996 °C. It is therefore concluded that the peritectoid reaction temperature of  $\beta\text{-Co}_3\text{Ta}$  is  $995 \pm 1$  °C. Compression tests reveal that the sample containing  $\beta\text{-Co}_3\text{Ta}$  is plastically deformable. However, no kinks were found after the compression tests in the samples containing  $\beta\text{-Co}_3\text{Ta}$ , suggesting that the deformation behaviour of  $\beta\text{-Co}_3\text{Ta}$  involves a different mechanism from kink formation.

Keywords: Co-Ta binary system, Peritectoid reaction,  $\text{Ta}_2\text{Co}_7$ ,  $\beta\text{-Co}_3\text{Ta}$

References:

1. T. Horiuchi et al: "Compressive Deformation Characteristics of  $\text{Nb}_2\text{Co}_7$  as Crystalline Mille-Feuille Structured Material", Mater. Trans. **64** (2023) 1622-1630.

# EFFECT OF PLASTIC DEFORMATION ON SUPERCOOLED AUSTENITE DECOMPOSITION IN ADVANCED MULTIPHASE STEELS

Adam Grajcar<sup>1</sup>, Firew Tullu Kassaye<sup>1</sup>, Adam Skowronek<sup>2</sup>, Aleksandra Kozłowska<sup>1</sup>, Pawel Nuckowski<sup>2</sup>, Krzysztof Matus<sup>2</sup>, Oguz Gulbay<sup>3</sup>, Alexander Gramlich<sup>3</sup>, Ulrich Krupp<sup>3</sup>

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Main topic: Phase diagrams and phase equilibria

Secondary topic: Computational thermodynamics

Abstract:

The decomposition of supercooled austenite plays a critical role in controlling the microstructure and mechanical properties of advanced multiphase steels. The present study systematically analyzed isothermal transformation kinetics of three low-alloyed steels containing 0.3 wt. % Mo and 1.0 wt. % Cu with a base composition of 0.17C-4Mn-0.8Al-0.5Si (wt. %). The decomposition of austenite during isothermal holding (TTT) was calculated using the JMatPro software (General Steels Module v11.2). Dilatometric experiments were also employed to compare the transformation kinetics during time-temperature-transformation (TTT) and deformation-time-temperature-transformation (DTTT). The results revealed that prior plastic deformation and alloying with Mo and Cu significantly influence the decomposition of austenite. The TTT and DTTT diagrams were the basis for further analysing the supercooled austenite decomposition under conditions of multi-step quenching and partitioning (Q&P) treatments. Based on this, QP parameters were optimized to produce a mixed microstructure of high-strength martensite with ductile film-like retained austenite (10-15%). The microstructure evolution was characterized after isothermal and Q&P treatments using electron backscatter diffraction (EBSD) and transmission electron microscopy (TEM). As a result, some relationships between the stability and volume fraction of retained austenite determined by XRD and deformation, alloy composition, and QP parameters were established.

Keywords: Advanced steels, Quenching and partitioning, Thermodynamic calculation, Austenite decomposition, Microstructure evolution

Acknowledgements: The study was funded by National Science Centre, Poland under the OPUS call in the Weave programme, grant no. 2021/43/I/ST5/02658 and by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – 504849602.

# SIMULATION AND EXPERIMENTAL INVESTIGATION OF PHASE EQUILIBRIA IN THE QUASICRYSTALLINE FORMING AL-MN-SI-(X) SYSTEM

Boštjan Markoli<sup>1</sup>, Borut Dremelj<sup>2</sup>, Iztok Naglič<sup>1</sup>, Matej Zupančič<sup>1</sup>, Adam Zaky<sup>1</sup>

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Main topic: Industrial applications of thermodynamics

Secondary topic: Phase diagrams and phase equilibria

Abstract:

Comprehensive understanding of phase equilibria is essential for accelerated design of high-strength, low-density alloys which should exhibit corrosion resistance and recyclability as well. Al-based alloys that can form quasicrystals, that act as reinforcing agents, appear to be promising candidates for structural applications in automotive, aircraft, and space industry [1]. However, their practical use has been hindered by the trade-off between mechanical performance and inability to operate at elevated temperatures and poor castability for intricate structural parts [2].

Using a combination of advanced characterisation techniques, including optical microscopy, scanning electron microscopy (SEM) with EDS, and differential scanning calorimetry (DSC) combined with Thermo-Calc, the study demonstrated the relationship between casting conditions, microstructure, and phase formation during high-pressure die casting (HPDC) and comparative casting in steel and copper moulds. We demonstrated how both casting conditions and changes in the alloy's chemical composition initiate different heterogeneous equilibria and thus influence the constitution of the alloys. The synthesised alloys contained a dominant  $\alpha$ -Al matrix,  $\text{Al}_6\text{Mn}$ ,  $\text{Al}_2\text{Cu}$ , and traces of  $\text{Al}_2\text{CuMg}$ ,  $\text{Al}_4\text{Mn}$ , and  $\text{Mg}_2\text{Si}$ . Nonequilibrium solidification of the investigated alloys led to the formation of different phases, such as icosahedral quasicrystalline phases (IQC), decagonal (DQC),  $\beta$ -AlMnSi, and their approximants, e.g.  $\alpha$ -AlMnSi. Finally, we confirmed the presence of different heterogeneous equilibria that existed simultaneously during the solidification of the investigated alloys.

Keywords: Al-Mn-Si-(X), Phase equilibria, Quasicrystals, HPDC

References:

1. J-M. Dubois: Properties- and applications of quasicrystals and complex metallic alloys, Chemical Society Reviews **41(20)** (2012) 6760-6777.
2. J-M. Dubois: Useful Quasicrystals, World Scientific, London, 2005.

# MICROSTRUCTURAL CHARACTERIZATION OF TATINBZR MEDIUM ENTROPY ALLOY AND IN TATINBZRFE HIGH ENTROPY ALLOY PRODUCED BY VACUUM ARC MELTING

Thais Kaori Yazawa Ito<sup>1,2</sup>, Nathanael Wagner Sales Moraes<sup>2</sup>, Hugo R. Z. Sandim<sup>3</sup>, Jesualdo L. Rossi<sup>2</sup> Isolda Costa<sup>2</sup>, Cláudio Geraldo Schon<sup>1</sup>

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Main topic: Phase diagrams and phase equilibria

Secondary topic: Thermodynamics of high-entropy alloys

Abstract:

High-entropy alloys (HEAs) are a collective designation for near-equiatomic alloys containing five or more components. It is generally assumed that the large entropy of mixing characteristics of these systems should prevent the precipitation and/or decomposition of the solid-solution phases formed during casting. However, this simplistic view has been challenged [1] and subsequently disproved [2] by one of the present authors.

The binary systems Ti-(Nb, Ta, Zr) and Nb-(Ta, Zr) form a large field of BCC solid solution. In contrast, the binary systems Fe-(Nb, Ti, Ta, Zr) exhibit miscibility gaps for the BCC solid solutions. All Fe-containing binary systems have at least one eutectic point.

Two 10 g ingots of TaTiNbZr (TTNZ) and TaTiNbZrFe (TTNZF) alloys were cast using electric-arc melting. The TTNZ alloy ingot was heat-treated at 1273 K for 24 h, and the TTNZF alloy ingot was heat-treated at 1173 K for 24 h (to avoid the possibility of liquation at higher temperature).

The results show that the cast TTNZ sample exhibits a two-phase microstructure composed of a Ta, Nb-rich BCC phase and a Zr, Ti-rich HCP phase. The as-cast TTNZF sample additionally exhibits a single BCC solid solution. The heat-treated TTNZ alloy microstructure remained unchanged compared with the as-cast sample. In contrast, the heat-treated TTNZF sample shows a complex four-phase equilibrium, including the formation of an intermetallic with (Ta,Nb,Ti)<sub>3</sub>Fe stoichiometry.

These results confirm that the thermodynamics of these highly concentrated alloys are more complex than the concept of HEAs assumes.

Keywords: High entropy alloys, Refractory alloys, Experimental

References:

1. C. G. Schön et al: "Probing the entropy hypothesis in highly concentrated alloys" *Acta Mater.* **148** (2018) 263-279.
2. C. G. Schön et al: "A proof of concept: thermodynamics of aluminum – transition metal highly concentrated alloys" *J. Alloys Compounds* **781** (2019) 595-605.

# INFLUENCE OF BINDER CHEMISTRY ON THE FCC-HCP PHASE BALANCE: IMPLICATIONS FOR STACKING FAULT ENERGY

Anne-Marie Bastide<sup>1</sup>, Patricia Grausgruber<sup>2</sup>, Raquel De Oro Calderon<sup>2</sup>, Aur lie Jacob<sup>1</sup>

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Main topic: Experimental and theoretical thermodynamics – new results and techniques

Secondary topic: Co-binder, Phase stability

Abstract:

Cemented carbides based on WC-Co are widely used as wear-resistant and cutting materials, where the mechanical performance is strongly governed by the properties and deformation mechanism of the cobalt binder. In this work, we develop an extended Co-WC thermodynamic database incorporating Ru. Although Co-Ru binders are already employed industrially and Ru is known to influence the solubility of W and Cr in the binder phase, a consistent thermodynamic description enabling reliable phase stability predictions is still lacking.

We evaluate existing thermodynamic database against experimental data and produce a series of Co-based alloys with and without Ru to assess its effect on phase stability and deformation behaviour. The resulting experimental characterization is used to optimize the missing thermodynamic parameters. The refined database is then applied to quantify the influence of Ru on the stacking fault energy of the binder phase, providing insight into its role in controlling hardness and mechanical performance in cemented carbides.

Keywords: Cemented carbides, Phase stability, Thermodynamics, Stacking faults

# STACKING FAULT ENERGY IN FE-MN STEELS: BRIDGING THE GAPS BETWEEN DFT, EXPERIMENTS AND THERMODYNAMIC MODELLING

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Main topic: Experimental and theoretical thermodynamics – new results and techniques

Secondary topic: Computational thermodynamics

Abstract:

Stacking fault energy (SFE) governs the deformation behaviour of metastable face-centred cubic (fcc) alloys, particularly Fe-Mn steels exhibiting twinning-induced plasticity (TWIP) and transformation-induced plasticity (TRIP). Accurate SFE values are essential for predicting the balance between dislocation glide, mechanical twinning, and strain-induced martensitic transformation [1,2]. However, significant discrepancies exist between experimentally derived and ab initio calculated SFE values. Experimental approaches based on force-balance models typically yield positive SFE values, whereas density functional theory (DFT) calculations often predict negative values due to the thermodynamic instability of the fcc phase relative to the hexagonal close-packed (hcp) phase [3].

This work addresses this inconsistency using thermodynamic modelling of the Fe–Mn system. Third-generation CALPHAD descriptions are applied to evaluate the Gibbs energy difference between fcc and hcp phases and estimate SFE via the Olson–Cohen relation. The assumptions of experimental force-balance methods are reassessed, and the influence of the interfacial energy term is examined.

The results aim to reconcile experimental and theoretical SFE values, improving predictive capability for deformation mechanisms and supporting the design of advanced TWIP/TRIP steels.

Keywords: CALPHAD, Thermodynamic modelling, Stacking fault energy, Metastable fcc steels

References:

1. O. Grässel et al: “High strength Fe–Mn–(Al, Si) TRIP/TWIP steels—development, properties, application”, Int. J. Plast. **16** (2000) 1391-1409.
2. D.T. Pierce et al: “The influence of manganese content on the stacking fault and austenite/ε-martensite interfacial energies in Fe–Mn–(Al–Si) steels investigated by experiment and theory”, Acta Mater. **68** (2014) 238-253.
3. X. Sun et al: “Can experiment determine the stacking fault energy of metastable alloys?”, Mater. Des. **199** (2021) 109396.

# STRUCTURE-DEPENDENT EXCESS VOLUME DESCRIPTORS FOR LATTICE PARAMETER PREDICTION IN HIGH-ENTROPY ALLOYS

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Main topic: Thermodynamics of high-entropy alloys

Secondary topic: Machine learning of thermodynamic properties of alloys

Abstract:

The lattice parameter and mixing volume of high-entropy alloys (HEAs) are essential quantities for discussing phase stability, density, elastic response, and thermodynamic modelling. Vegard's law provides a simple reference based on linear mixing of elemental atomic volumes [1], while Alonso extended King's volume size factor concept to cubic HEAs and demonstrated the importance of excess-volume corrections [2,3].

Building on these established models, this study develops a structure-dependent excess volume descriptor for HEAs. Volume size factors are reconstructed from first-principles data of binary intermetallic compounds, mainly with B2 and L1<sub>2</sub> structures, using Materials Project, OQMD, and additional VASP calculations. Deviations from Vegard-type volumes are used to describe excess volume arising from chemical interactions and local coordination environments.

Pairwise volume size factors are further decomposed into element-specific parameters, enabling rapid prediction of mixing volume and lattice parameter for arbitrary HEA compositions, including non-equiatomic alloys. Validation using reported cubic HEAs, including data considered in the Alonso-type framework, shows accuracy comparable to or better than conventional Vegard- and Alonso-type descriptions. The proposed framework links first-principles alloy data, excess volume, lattice strain, and thermodynamic modelling, and may provide useful descriptors for machine-learning-based models of multicomponent alloys.

Keywords: High-entropy alloys, Excess volume, Vegard's law, Volume size factor, First-principles calculations

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# VALIDATION AND REFINEMENT OF AN ML-BASED FRAMEWORK FOR PREDICTING CCT DIAGRAM, PHASE FRACTIONS, AND STEEL HARDENABILITY

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Main topic: Phase transformations and kinetics, solid state diffusion

Secondary topic: Machine learning of thermodynamic properties of alloys

Abstract:

We present a general hybrid machine learning framework for predicting microstructure evolution, phase fractions, and hardness in continuously cooled steels, based on composition and austenitisation conditions. The framework includes specialised Artificial Neural Networks (ANNs) for predicting transformation start and finish temperatures, phase fractions of ferrite, pearlite, bainite, and martensite, hardness, and other key transformation characteristics. To improve model accuracy and generalisation, the ANN models are integrated with Thermo-Calc calculations and principles of physical metallurgy. A robust algorithm has been developed to enable rapid generation of Continuous Cooling Transformation (CCT) diagrams, detailing transformation temperatures and critical cooling rates, for arbitrary steel compositions and austenitisation conditions. Recent experimental data, not used during model development, have been used for independent validation of the models. Predicted transformation behaviour, phase fractions, and hardness are systematically compared with experimental results across a wide range of steel grades. The validation results demonstrate the strengths of the current framework while identifying areas for further improvement, providing a basis for targeted model refinement. The framework has been implemented as a web-based application that enables rapid generation and visualisation of CCT diagrams, together with phase fraction and hardness estimations. The tool provides valuable guidance for optimising steel heat-treatment processes and achieving desired microstructures and mechanical properties.

Keywords: Artificial neural networks, Machine learning, Continuous cooling transformation diagrams, Hardness, Heat treatment

# DESIGN OF METALLIC PHASE CHANGE MATERIALS BY CALCULATION AND EXPERIMENTAL CONFIRMATION: PRELIMINARY RESULTS

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Main topic: Experimental and theoretical thermodynamics – new results and techniques

Secondary topic: Computational thermodynamics

Abstract:

Phase change materials (PCMs) undergo phase transitions at specific temperatures and are primarily studied for energy storage. They cycle between liquid and solid states, storing and releasing thermal energy as sensible and latent heat. While most PCM research focuses on solar energy storage, they also have domestic, electronic, and vehicle applications. Common PCM materials include salt hydrates, organic compounds, and metallic alloys (MPCMs). Though not as widely used, MPCMs are appealing due to greater enthalpy of fusion per volume and higher thermal conductivity, which reduces the need for complex heat transfer systems [1]. In order to maximize the thermal energy that can be stored in a PCM and avoid chemical segregation, isothermal transformations are ideal, such as eutectics [2]. This work aims to identify suitable MPCMs for solar energy storage in multi-component systems using the CALPHAD approach and high-throughput calculations to select compositions for synthesis and characterization. A TC-Python® based approach using single-equilibria calculations was developed to perform high-throughput calculations of eutectic and congruent compositions. 51 elements within 5 commercial databases were used to identify over 5000 isothermal melting compositions in binary, ternary, quaternary, quinary and senary systems. An initial analysis based on price and enthalpy stored was used to select MPCM candidates in different ranges of temperature. The gathered best candidates were then separated in groups based on their compositions for further exploration. Experimental work has started, confirming or not the good assessment of some systems, with the discovery of new quaternary eutectics. Next steps are focused on calorimetry experiments.

Keywords: Phase-change materials, Phase diagrams, Eutectic alloys, CALPHAD

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# SYNTHETIC, STRUCTURAL, THERMODYNAMIC AND THEORETICAL INVESTIGATION OF ALKALI METAL SELENIDES

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Main topic: Experimental and theoretical thermodynamics – new results and techniques

Secondary topic: Phase diagrams and phase equilibria

Abstract:

Alkali elements play a crucial role in improving the performance of CIGS (Cu(In,Ga)Se<sub>2</sub>) solar cells [1], although the underlying mechanisms remain unclear. This has motivated the investigation of alternative alkali-containing compounds such as alkali selenides (Ak<sub>2</sub>Se), which may serve as precursors or dopants in future applications. In this work, a reactive flux synthesis route [2] was developed using a home-made tantalum tube device, following literature procedures [3,4]. The synthesis unexpectedly yielded shiny, colourful crystals. The samples were characterised by laboratory and synchrotron XRPD and SEM-EDS, confirming phase purity and enabling monitoring of air-induced degradation. The Cp was measured by DSC using a Labsys-Evo instrument equipped with a 3D Cp rod sensor in step-by-step mode. The unusual appearance prompted further investigation by Raman spectroscopy, supported by simulated spectra confirming the phases. The synthesis and characterisation proved challenging due to the high air sensitivity of the compounds. The availability of these pure phases provides new opportunities for controlling the synthesis of more complex alkali selenides and improving the understanding of Ak-Se phase diagrams. From a theoretical perspective, DFT electronic structure calculations confirmed the insulating character of the investigated selenides, with Li<sub>2</sub>Se showing an indirect gap. The valence band is dominated by Se 4s and 4p states, indicating a significant ionic contribution to the bonding, further supported by the calculated Mulliken and Löwdin charges, consistent with electronegativity differences.

Keywords: Reactive flux synthesis, Alkali metal selenides, Heat capacity, CIGS

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# EXPERIMENTAL INVESTIGATION OF PHASE EQUILIBRIA IN NI-CE-CR SYSTEM

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Main topic: Phase diagram and phase equilibria

Abstract:

Rare earths, comprising 17 elements including the lanthanides along with Sc and Y, are important for modern engineering applications because of their unique magnetic, optical, chemical, and structural properties. They are extensively studied for improving high-temperature properties such as tensile strength, creep, oxidation, and wear resistance. Even minor additions can significantly influence alloy behaviour through phase stabilization and property enhancement. However, their application in structural alloys remains limited due to the scarcity of reliable phase equilibria data, particularly for systems involving technologically important metals such as Fe, Cr, Ni, Nb, and Ta.

Among rare earths, Ce is the most abundant and has gained attention for its promising high-temperature characteristics. Ni and Cr are widely used alloying elements because of their excellent strength, oxidation, and corrosion resistance at elevated temperatures. The Ce–Cr–Ni system is therefore of considerable interest, especially for nuclear reactor applications, where Ce is produced as a fission product and may interact with Ni–Cr–Fe-based cladding materials to form potentially harmful intermetallic compounds [1]. Understanding phase equilibria in this system is thus essential for predicting material behaviour and improving cladding reliability.

A literature survey revealed that no experimental phase equilibrium study is available for the Ce–Cr–Ni ternary system. The present work addresses this gap through experimental investigation of selected alloys focusing on microstructure, phase constitution, and phase composition. Alloys were synthesized by vacuum arc melting, heat treated to attain equilibrium, and characterized using XRD, SEM, EDS, EPMA, and DSC.

Keywords: Phase equilibria, Rare earths

References:

1. P. C. Tortorici et al: "Interdiffusion of cerium in Fe-base alloys with Ni or Cr," Journal of Nuclear Materials **204** (1993) 165-172.

# GENERATING ALLOY THERMODYNAMIC AND THERMOPHYSICAL DATA USING CALPHAD

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Main topic: Computational thermodynamics

Secondary topic: Thermochemistry, thermodynamic properties (liquids, solids, amorphous materials)

Abstract:

Numerical simulation of solidification processes requires accurate alloy property data as functions of temperature and composition. CALPHAD databases have long been a trusted source for thermodynamic properties and, more recently, for thermophysical data, including thermal conductivity, liquid viscosity, surface tension, elastic properties, and more. In the last years, Thermo-Calc has been developing models for thermophysical properties and integrating them into its software and databases.

While phase-specific property descriptions are foundational, accurate modeling of alloy properties also hinges on selecting assumptions that best reflect the state of the alloy. For very slow cooling rates, one can assume the alloy is in thermodynamic equilibrium, and overall thermophysical properties can be calculated using phase fractions and compositions by rules of mixture.

For faster cooling rates, solidification becomes a non-equilibrium process. In this case, a popular choice to obtain the state of the alloy is the Scheil solidification model, which enables solute micro-segregation to be accounted for. Enforcing interstitial equilibrium, incorporating solute back-diffusion in the primary solid, and allowing decomposition of delta-ferrite in steels to further improve the accuracy and applicability of the Scheil model. Calculating thermophysical properties from a Scheil solidification simulation again requires applying rules of mixture, with the added complexity due to composition variation in the primary solid phase.

Both equilibrium and Scheil assume thermodynamic equilibrium at the solid-liquid interface. For extremely rapid cooling rates, such as those encountered in additive manufacturing, this assumption breaks down. Advanced models, including solute trapping and dendrite tip undercooling, are required to accurately capture the effects of these extreme conditions on solidification.

This work examines the models used to describe thermophysical properties as functions of temperature and alloy chemistry.

Keywords: CALPHAD, Thermophysical Data, Solidification

# ABOUT THE KINETICS OF SOLID-STATE PHASE TRANSFORMATIONS INVOLVING INTERMETALLIC PHASES

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Main topic: Phase transformations and kinetics, solid state diffusion

Secondary topic: Phase diagrams and phase equilibria

Abstract:

Published values for phase transformation temperatures often vary greatly, and the effects of the transformation kinetics have only rarely been considered. The reaction rates at which different phase transitions proceed in solids can vary by several orders of magnitude. This in many cases makes the experimental investigation of such transformations very difficult or even impossible. The range extends from extremely rapid, instantaneous transformations that cannot be suppressed even by rapid quenching, to very slow ones that lead to metastable states that persist for long periods of time. Examples from our work on different types of phase transformations in several systems with experimentally accessible kinetics from fast to slow will be presented and discussed. For the construction of a phase diagram, the precise determination of the equilibrium transformation temperatures is one of the most important tasks. Using a special example of a peritectoid decomposition of an intermetallic phase, it is shown that ignoring or incomplete consideration of the kinetics can lead to errors in the range of several 10 K.

Keywords: Solid-state phase transformations, Kinetics, Equilibrium reaction temperatures

# DEVELOPMENT OF THERMODYNAMIC DATABASE USING MODIFIED QUASICHEMICAL MODEL

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Main topic: Computational thermodynamics

Secondary topic: Databases development

Abstract:

Various thermodynamic databases have been developed using the regular solution model to construct phase diagrams. However, the CALPHAD approach without considering strong interactions among the metallic elements and gaseous impurities shows a poor predictability for the practical conditions of liquid alloy refining and inclusion evolution in solid steels during casting and heat treatment. To ensure the accuracy of liquid solution properties and phase diagrams for various steel grades, thermodynamic evaluation and optimization of all available experimental data for the ferrous system, including impurities such as C, O, N, P, and S, were performed. The liquid solution properties of the core system and the effects of impurity elements were described using the Modified Quasichemical Model (MQM). In this model, the strong attraction force was evaluated as the negative Gibbs free energy of the formation of pairs in the pair approximation. The modification of configurational entropy in this model reduces the temperature dependence of the excess Gibbs energy term in the liquid solution. It can also affect the stability of all solid phases by altering the Gibbs energy balance for adjusting both liquidus and solidus. This database is stored in the current version of the FSStel database in FactSage thermochemistry software. Examples of nitride and oxide inclusion formation and phase stability will be presented.

Keywords: Liquid alloy, Short range ordering, Modified quasichemical model, Impurity behavior

References:

1. M.K Paek et al: "Aluminum deoxidation equilibria in liquid iron", Met. Mater. Trans. B **47B** (2016) 2837-2847.

# TAILORING METAL MATRIX COMPOSITES VIA GLOBAL REACTIVE SYNTHESIS: THERMODYNAMIC INSIGHTS

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Main topic: Computational thermodynamics

Secondary topic: Phase transformations and kinetics, solid state diffusion

Abstract:

The Global Reactive Synthesis (GRS) route has emerged as a method for producing Aluminium Matrix Composites (AMCs) [1-4]. Using thermodynamic predictions to guide controlled chemical reactions, we synthesize AMCs with the in-situ formation of both the matrix and reinforcement phases, overcoming traditional challenges such as interphase formation or interface contamination. This approach has been successfully applied to conventional AMCs like Al-TiC and Al-TiB<sub>2</sub>, as well as to innovative systems such as Al-T3 (Al<sub>3</sub>B<sub>48</sub>C<sub>2</sub>), where the ternary borocarbide phase offers reinforcement capabilities close to Al-B<sub>4</sub>C AMC. The key advantage of GRS lies in its ability to tailor microstructures through a deep understanding of alloy thermodynamics and diffusion paths. For instance, the nature of the reinforcements, the interfacial characteristics of reinforcements, and the size can be tuned by adjusting reaction parameters, directly driven by the system's thermodynamic stability.

This talk will describe different AMCs obtained in this way. We will also detail the ongoing research: firstly, the adaptation of GRS to Laser Powder Bed Fusion (LPBF) [5,6], where rapid thermal cycles and high cooling rates are managed to achieve dense, near-net-shape AMCs with interesting microstructures; secondly, the ageing of such AMCs with temperature and time related to industrial applications. In both cases, this work will try to highlight the synergy between the reactive synthesis, the AMC microstructure and the thermodynamics of the systems.

Keywords: Aluminium matrix composites, Global reactive synthesis, Thermodynamics, Chemical reactivity

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# THERMODYNAMIC MODELLING OF AL-C-NB SYSTEM

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Main topic: Databases development

Secondary topic: Ab initio calculations, Thermochemistry, thermodynamic properties (solids)

Abstract:

The Al-C-Nb ternary system has gained considerable technological interest due to the presence of MAX phases. MAX phases are layered compounds with combined metallic and ceramic properties. They are represented by the general formula  $M_{n+1}AX_n$  where M denotes early transition metals and A is an element from group 13 to 16, and X is typically C, N or B. The Al-C-Nb system is reported to contain two MAX phases  $Nb_2AlC$  and  $Nb_4AlC_3$ , along with a cubic  $Nb_3Al_2C$  phase. These phases exhibit excellent high-temperature stability and fracture toughness [1]. MXenes derived from them are also recognized because of their attractive optoelectronic and photothermal properties [2]. Moreover, Al-C-Nb system forms one of the bounding ternaries of microalloyed steels. A thorough understanding of phase equilibria is essential for alloy design and process optimization. Previous studies reported the 1000 °C isothermal section [3] and thermal properties of  $Nb_2AlC$  [4] and  $Nb_4AlC_3$  [5]. However, the available thermochemical data are limited, and no thermochemical data have been reported for  $Nb_3Al_2C$ ; consequently, no CALPHAD thermodynamic assessment of the Al-C-Nb system has been reported to date. Although Density Functional Theory (DFT) databases provide formation energy ( $\Delta_f H^\circ$ ) of these phases, inconsistencies with the experimentally accepted C-Nb phase diagram and deviations in  $\Delta_f H^\circ$  of NbC raise concerns regarding their direct applicability.

In this work, various exchange–correlation functionals are systematically examined to identify DFT settings that reproduce experimentally observed stability trends. Using the selected settings,  $\Delta_f H^\circ$  of ternary carbides are calculated, and finite-temperature thermodynamic properties are obtained using phonon calculations within the Quasi-Harmonic Approximation (QHA). Structural vacancies and partial substitutions at M, A, and X sites are investigated to establish reliable sublattice models, and Special Quasi-random Structures (SQS) are employed to model random occupations. Experimentally, MAX phases are sintered using Spark Plasma Sintering (SPS). Heat capacity measurements are performed using Physical Property Measurement System (PPMS) at low temperatures and Differential Scanning Calorimetry (DSC) at high temperatures. The present work reports thermodynamic modeling of the Al-C-Nb system using newly generated experimental data together with literature data.

Keywords: CALPHAD, MAX phases, DFT, Finite temperature calculations, Calorimetry

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5. C. Hu, et al: "Nb<sub>4</sub>AlC<sub>3</sub>: A New Compound Belonging to the MAX Phases", Scripta Mater. **57.10** (2007) 893-896.

# AB INITIO THERMODYNAMIC MODELLING OF DISORDERED SOLID SOLUTIONS MADE SIMPLE

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Main topic: Computational thermodynamics

Secondary topic: Ab initio calculations

Abstract:

We present an *ab initio* thermodynamic framework for modelling chemical disorder in solid solutions. Based on the extended generalized quasichemical approximation (EGQCA) [1], this approach enables the prediction of composition-dependent properties using only a small number of small supercell calculations. It therefore offers a simple and efficient route to *ab initio* thermodynamic modelling of disordered crystalline systems. In this contribution, we will demonstrate applications of EGQCA to a broad range of systems, including intermetallics, hydrides, borocarbides, and oxides, showing its versatility for the study of complex alloys and solid solutions. A central advantage of the framework is that it captures the effects of configurational disorder and vibrational entropy with modest computational effort, making it well suited for practical materials exploration and screening. We will also present a surrogate version that reduces the computational cost of treating complex solid solutions by orders of magnitude, while preserving the predictive power. In combination with machine-learning interatomic potentials, this allows us to accelerate the entire workflow, from configurational sampling and energetics to thermodynamic modelling and property prediction. Altogether, this approach provides an efficient route toward high-throughput design and optimization of disordered materials, combining physical accuracy with computational simplicity.

Keywords: Thermodynamic modeling, Solid solutions, Ab initio calculations

References:

1. P. N. Ferreira et al: "Ab Initio Modeling of superconducting alloys" Materials Today Physics **48** (2024) 101547.

# EXPERIMENTAL AND THEORETICAL STUDY OF THE Nb-Sb SYSTEM

Pavel Brož<sup>1</sup>, Jan Vřešťál<sup>1</sup>, Vitaliy Romaka<sup>2</sup>, Xinlin Yan<sup>3,4</sup>, Peter Rogl<sup>3,4</sup>, Jiří Buršík<sup>5</sup>,  
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Main topic: Phase diagrams and phase equilibria

Secondary topic: Computational thermodynamics

Abstract:

The Nb-Sb system is known for the existence of intermetallic phases and the importance of discovering highly efficient multicomponent thermoelectric materials. A good knowledge of phase relations in this system is therefore crucial for understanding phase stabilities in higher-order systems. This system was recently studied by Melnyk et al. [1] and Failamani et al. [2], but the region of Nb<sub>3</sub>Sb phase stability (preliminarily reported as 1750 ± 25 °C by Myzenkova et al. [3]) was not covered due to the need for high-temperature measurements.

In this work, the peritectic temperature of the Nb<sub>3</sub>Sb phase was precisely determined by high-temperature DTA. During the measurements, the temperatures of the other peritectic reactions, including the Nb<sub>5</sub>Nb<sub>4</sub> and NbSb<sub>2</sub> phases, were revised. This, together with the determination of a narrow homogeneity region for Nb<sub>3</sub>Sb, limited Sb solubility in Nb at 950°C, and *ab initio* calculations of the heats of formation of all intermetallic phases, led to a thermodynamic assessment of this binary system using the CALPHAD approach.

Keywords: Nb-Sb, Thermal analysis, Phase analysis, Ab-initio calculations, Thermodynamic modelling

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# COMPARISON OF MODEL EQUATIONS FOR SIZE- AND SHAPE-DEPENDENT INTEGRAL AND PARTIAL MOLAR GIBBS ENERGIES OF NANO-PHASES TO FIND THE CORRECT ONE

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Main topic: Thermodynamics of low-dimensional systems (surfaces and interfaces, nanomaterials)

Secondary topic: Computational thermodynamics

Abstract:

Equations for the integral molar Gibbs energy of nano-phases and the partial molar Gibbs energy of components dissolved in nano-phases have been derived here by extending the classical thermodynamics of Gibbs to nano-sizes in three different ways, found in the literature: according to Kelvin, the nano-effect is proportional to the curvature of the phase; according to Searcy (and later to Lee and Sim and recently to Wong and Wong), the nano-effect is proportional to  $dA/dV$  (where  $A$  and  $V$  are the surface area and the volume of the nano-phase respectively); according to the previous papers of the present author (and recently to Xue) the nano-effect is proportional to the specific surface area of the nano-phase defined as  $A/V$ . It has been shown in many experiments that for all possible shapes of all nano-phases their molar Gibbs energies are inversely proportional to their characteristic sizes, such as to the radius of a nano-sphere, to the side length of a nano-cube or to the thickness of a thin film. It is shown that the approaches due to Kelvin (curvature) and Searcy ( $dA/dV$ ) lead to some controversial results vs experimental evidence, so they are excluded here. Moreover, they both contradict the nucleation theory of Gibbs, providing the same equations for the equilibrium size of a spherical nano-phase and for the critical size of the spherical nucleus, being the second reason to exclude these equations. Moreover, the model by Searcy contradicts the nucleation theory of Gibbs, providing the same equation for the equilibrium size of a cubic nano-phase and for the critical size of the cubic nucleus, being the third reason to exclude this equation. Moreover, the model by Searcy supposes that the surface area of a nano-phase and the amount of matter in it are proportional quantities, while they are independent state variables according to the thermodynamics of Gibbs. The surface area and the amount of matter in a phase are independent when the shape of the phase is changed or when the phase is divided into smaller pieces. It is also shown that the previous approach by the author ( $A/V$ ) is free of such contradictions, so it is suggested for further use here. This approach will also be extended to the question of electrochemical synthesis diagrams.

Keywords: Nanophases, Chemical thermodynamics; Kelvin vs. Gibbs

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# OPTIMAT ALLOYS: A FAIR, LIVING DATABASE OF MULTI-PRINCIPAL ELEMENT ALLOYS ENABLED BY A CONVERSATIONAL AGENT

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Main topic: Machine learning of thermodynamic properties of alloys

Secondary topic: Thermodynamics of high entropy alloys

Abstract:

Thermodynamic databases for multi-principal element alloys (MPEAs), especially high-entropy alloys (HEAs), remain inherently limited in coverage: the combinatorial composition space far exceeds what any curated repository can pre-compute, and each new alloy design question introduces entries that no curator has anticipated. We present OptiMat Alloys, a FAIR living database of MPEA properties that expands on demand. Instead of providing a static dataset, OptiMat Alloys combines a large language model (LLM) conversational agent with a backend of molecular dynamics simulations driven by foundational machine-learning interatomic potentials with near-DFT accuracy. HEA random solid solutions are modelled using special quasi-random structures (SQS), and users issue requests in natural language, for properties such as formation energy and mixing energy at 0 K, Gibbs free energy at finite temperature, lattice parameter, elastic constants, etc. Each alloy composition can be evaluated with multiple potentials and SQS realisations to quantify uncertainty, and all results are added to the shared database with full provenance. We demonstrate the database on the Cantor-family CoCrFeNi alloy and its six-component Co–Cr–Fe–Mo–Ni–W extension, showing parity with DFT and experimental references. The SQS-based mixing enthalpies, finite-temperature Gibbs free energies, and molar volumes are directly suitable as inputs for fitting Gibbs-energy models in open CALPHAD frameworks such as pycalphad and ESPEI. By extending the FAIR principles from pre-computed repositories to on-demand knowledge generation, OptiMat Alloys makes computational alloy screening accessible to all materials scientists. A public demonstration is available at <https://youtu.be/IQzuorkzPMc>.

Keywords: High-entropy alloys, Living database, Molecular dynamics simulations, Universal machine-learning potentials, LLM agent

# INTERFACIAL THERMODYNAMICS OF TRAMP ELEMENTS IN SCRAP-BASED STEELS: ORIGINS OF SURFACE HOT SHORTNESS

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Main topic: Industrial application of thermodynamics

Abstract:

This presentation addresses the growing challenge of tramp element accumulation in scrap-based steelmaking, framed within the broader transition toward a circular economy. As the steel industry increasingly prioritizes resource efficiency and closed-loop material cycles, electric arc furnace (EAF) production of steel plates relies on high scrap utilization. Under these conditions, tramp elements such as copper inevitably accumulate, raising critical concerns regarding surface hot shortness during high-temperature processing.

In this presentation, a mechanistic framework is suggested that links bulk composition, oxidation behavior, and interfacial phase stability. Through a combination of high-temperature oxidation experiments and thermodynamic calculations, it is demonstrated that copper preferentially segregates to the steel/oxide interface, where it forms a Cu-enriched liquid phase with a depressed melting temperature. This liquid phase promotes intergranular penetration and facilitates crack initiation, providing a direct physical origin for surface hot shortness.

The analysis of industrial EAF steel compositions reveals current accumulation trends of tramp elements under circular material flows, motivating the introduction of a copper-equivalent parameter to capture their combined effects.<sup>1</sup> Based on this approach, a critical compositional threshold for the onset of liquid phase formation and hot shortness is established.

Beyond copper-specific effects, the results highlight the broader role of interfacial thermodynamics in governing high-temperature degradation phenomena in multicomponent alloys. In the context of a circular economy, the proposed framework offers practical guidelines for managing tramp element accumulation and provides a predictive basis for designing robust, high-scrap steelmaking processes without compromising material performance.

Keywords: Circular economy, Electric arc furnace, Steel scrap, Surface hot shortness, Tramp element

References:

1. M. Cho et al: "Formation and Stability of Cu-Enriched Liquid Phases at the Steel/Oxide Interface: Implications for Surface Hot Shortness in EAF Steels", Metall. Mater. Trans. B (2026) in press.

# THERMODYNAMIC ANALYSIS AND EXPERIMENTAL INVESTIGATION OF PHASE EQUILIBRIA IN THE (GE, PB)–(SE, TE) SYSTEM

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Main topic: Phase diagrams and phase equilibria

Secondary topic: Phase transformations and kinetics, solid state diffusion

Abstract:

IV-VI compounds, such as the chalcogenides of germanium, tin, and lead, exhibit relatively high thermoelectric performance. In recent years, nanostructured bulk thermoelectric materials containing nanoparticles formed by phase separation of the FCC\_B1-type phase in the PbSe-PbTe system have been developed [1]. Nanostructuring that utilises phase separation contributes to enhancing the ZT values of IV-VI compounds; however, information on phase equilibria in IV-VI compound systems has largely been limited to pseudo-binary systems. Therefore, to further utilise phase separation as a nanostructuring technique, it is useful to obtain information on phase equilibria in multicomponent IV-VI compound systems. In this study, a thermodynamic analysis of phase equilibria in the (Ge,Pb)–(Se,Te) pseudo-quaternary system was carried out based on the CALPHAD method, using thermodynamic quantities obtained from first-principles calculations in this work and reported data on phase boundaries. In addition, to validate the calculated phase diagram of the pseudo-quaternary system, XRD measurements and SEM-EDS analyses were performed on samples prepared by heat treatment of mechanically alloyed (MA) powders.

The calculated phase diagrams of each pseudo-binary system generally reproduced the phase boundaries of the experimental phase diagrams. However, the calculated phase equilibria in the pseudo-quaternary system at 540 °C showed discrepancies compared with the reported experimental phase diagram [2]. In the calculated phase diagram at 500 °C, three-phase separation in the FCC\_B1-type phase was predicted, and experimental results from MA-treated and heat-treated samples also suggested the occurrence of three-phase separation.

Keywords: Chalcogenide, Phase separation, CALPHAD, First-principles calculations

References:

1. M. S. Kim et al: “Spinodally decomposed PbSe-PbTe nanoparticles for high-performance thermoelectrics: Enhanced phonon scattering and unusual transport behavior”, ACS Nano 10 (2016) 7197-7207.
2. L. E. Shelimova et al: “The ternary mutual system GeTe + PbSe  $\leftrightarrow$  GeSe + PbTe”, Inorg. Mater. 4 (1968) 1643-1646.

# PHASE EQUILIBRIA IN LA-NI-(AL, IN, SN) TERNARY SYSTEMS WITH HYDROGEN

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Main topic: Phase diagrams and phase equilibria

Secondary topic: Thermodynamics of energy storage materials

Abstract:

Hydrogen storage materials allow hydrogen to be incorporated into their structure through chemisorption, forming metal hydrides. One of the well-known compounds with hydrogen storage properties is the binary phase LaNi<sub>5</sub>. Formation of LaNi<sub>5</sub>H<sub>7</sub> hydride by absorption of hydrogen has suitable reaction energy and relatively fast kinetics for technical application. However, thermodynamic and kinetic properties of hydrogenation and dehydrogenation need to be optimized by addition of third element [1].

Metal alloy samples were prepared from pure elements using a plasma furnace under an inert atmosphere of pure argon (6N) with Ti as a getter [2]. The metal samples were then sealed in quartz glass ampoules and annealed for an extended period at a specified temperature. The chemical composition was characterized using SEM-EDS methods, and the crystal structure was analyzed using powder XRD. The amount of the third element was optimized so that the LaNi<sub>5</sub> phase also coexists

The thermodynamic (de-)hydrogenation behaviour of the studied alloys was investigated using pressure-concentration isotherms (p-c-T curves) recorded during hydrogen absorption and desorption cycles. These measurements enabled the determination of the maximum hydrogen storage capacity, as well as the enthalpy and entropy associated with the reaction. The findings indicate that modification of the LaNi<sub>5</sub> binary phase by third element influences the thermodynamics and kinetics of hydrogen storage, while also affecting the maximum hydrogen storage capacity.

Keywords: LaNi<sub>5</sub> phase, Ternary systems Phase diagram, Hydrogen storage; p-c-T curves

Acknowledgment: This study is a part of the project No. CZ.02.01.01/00/22\_008/0004631 Materials and technologies for sustainable development within the Jan Amos Komensky Operational Program financed by the European Union and from the state budget of the Czech Republic.

References:

1. Mendelsohn et al: "LaNi<sub>5</sub>-xAl<sub>x</sub> is a versatile alloy system for metal hydride applications", *Nature* **269** (1977) 45–47.

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# EXPERIMENTAL INVESTIGATION OF PHASE EQUILIBRIA AND THERMODYNAMIC DESCRIPTION OF B-Nb-Ta SYSTEM

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Main topic: Phase diagrams and phase equilibria

Secondary topic: Databases development

Abstract:

The ternary B-Nb-Ta system is of considerable interest for the development of materials intended for the ultra-high temperature applications, particularly in environments where a combination of high melting point, mechanical strength, and chemical stability is required. In this work, phase equilibria in this system were investigated experimentally and combined with thermodynamic modelling to provide a consistent description of the ternary system.

B-Nb-Ta alloys were prepared by arc melting from high purity powders and subsequently long-term annealed at two different temperatures. Phase identification and structural characterization were carried out using X-ray diffraction and scanning electron microscopy coupled with energy-dispersive spectroscopy.

Based on the newly obtained experimental data, a thermodynamic description of the B–Nb–Ta system was developed using the CALPHAD method. Boron was modelled as an interstitial element in the BCC solid solution. Optimisation of some models and thermodynamic parameters in the B-Nb and B-Ta binary systems was also done. Very good agreement was achieved between the experimental results and calculations obtained with developed dataset. Consequently, the developed thermodynamic database provides reliable predictions of phase equilibria for B-Nb-Ta system across the entire composition range and over a wide temperature interval.

Keywords: Boride, Phase diagram, Thermodynamic modeling, Ternary system

Acknowledgement: This work was supported by the Scientific Grant Agency VEGA under the project No. 2/0069/24.

# EXPERIMENTAL STUDY OF THE IN-SB-ZN TERNARY PHASE DIAGRAM

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Main topic: Phase diagrams and phase equilibria

Abstract:

Following the recent liquidus projection study [1], the phase equilibria of the In-Sb-Zn ternary phase diagram were experimentally studied at the temperatures 473, 573 and 698 K. The alloys were prepared by melting in evacuated quartz ampoules, followed by several weeks of isothermal annealing ended with quenching in water. The annealed alloys were examined by scanning electron microscopy coupled with energy dispersive spectroscopy, and the phase composition of selected alloys was confirmed by powder x-ray diffractometry. The ternary phase  $\text{Zn}_5\text{Sb}_4\text{In}_2$  reported by the earlier studies [2,3] was found to be stable at all temperatures. In agreement with the binary phase diagrams, the solubility of In and Sb in the (Zn) phase is close to zero, while the (Sb) phase dissolves above 1 at. % of In and Zn. Binary phases InSb and  $\text{Zn}_4\text{Sb}_3$  show some remarkable solubility of the third element. The maximum solubility of Zn in the InSb is up to 6.3 at. %, while the maximum solubility of In in the  $\text{Zn}_4\text{Sb}_3$  phase on the expense of Zn is up to 8.9 at. %.

Keywords: In-Sb-Zn system, phase diagram, ternary phase

Acknowledgment: Authors gratefully acknowledge the Czech Academy of Sciences and Polish Academy of Sciences bilateral mobility project PAN-24-08. P. Fima acknowledges support from IMMS PAS under the Z-11.

References:

1. O. Zobač et al: "Liquidus projection of the In-Sb-Zn system", J. Mater. Sci. **61** (2024) 3030-3046.
2. Y. Wu et al: " $\text{Zn}_5\text{Sb}_4\text{In}_{2-5}$  - a Ternary Derivative of Thermoelectric Zinc Antimonides", Inorg. Chem. **48** (2009) 5996-6003.
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# INFLUENCE OF SULPHUR ON $\text{Al}_2\text{O}_3$ NON-METALLIC INCLUSION FORMATION IN FE-0.45%C STEEL

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Main topic: Thermochemistry of metallurgical processes

Secondary topic: Industrial applications of thermodynamics

## Abstract

Non-metallic inclusions significantly affect steel cleanliness, castability, and product quality. We noticed that alumina inclusions were the main culprit. Furthermore, we noticed that these problems mainly occur in high S steels. Industrial data collected from ladle furnace processing and continuous casting operations revealed an increased proportion of alumina inclusions following sulphur addition. This was partially assigned to the Ca-S interactions, but not all of the phenomenon could be attributed to S interfering with Ca. Furthermore, severe submerged entry nozzle (SEN) clogging was observed, with deposits consisting predominantly of alumina non-metallic inclusions adhering to the SEN refractory walls, leading to reduced casting stability and operational challenges.

To understand the relationship between the sulphur content and alumina inclusion behaviour, the interfacial phenomena governing inclusion attachment were examined. Surface tension effects and wetting characteristics were investigated using laboratory experiments conducted with a heating stage microscope. The wetting angle of Fe-0.45% C steel samples with different S contents on an alumina single crystal substrate was measured under controlled conditions to evaluate the influence of sulphur on steel–alumina interfacial interactions.

The results indicate that sulphur alters the interfacial properties of the steel melt, affecting the wettability of alumina surfaces and potentially promoting non-metallic inclusion formation. The combined industrial and experimental findings suggest that sulphur plays an important role in the mechanisms governing alumina non-metallic inclusion behaviour and SEN clogging. These insights contribute to a better understanding of inclusion control in Al-killed steels in industrial steelmaking.

Keywords: Steelmaking, Alumina non-metallic inclusions, Sulphur, Surface tension, Wetting angle

# NEW EXPERIMENTAL DATA ON THE FE-B-C TERNARY SYSTEM AT HIGH TEMPERATURES

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Main topic: Phase diagrams and phase equilibria

Abstract:

High-strength steel grades manufactured by continuous casting undergo controlled B addition (<0.004 mass%) to suppress liquid metal embrittlement and promote martensite formation during quenching. However, the presence of B is challenging for this casting process due to the metatectic reaction predicted for the Fe-B system at 1380 °C, transforming ferrite  $\delta$  into austenite  $\gamma$  and liquid [1]. During steel solidification, local remelting may cause slab defects. Although thermodynamic descriptions of systems including B have been updated [2,3], current steel databases still lack information on thermodynamic and phase diagram data for Fe-rich regions above 1000°C to support parameter improvements in continuous casting processes. The present study addresses these experimental gaps in the Fe-B-C ternary system by establishing new datasets on phase equilibria involving a liquid phase with boron ranging from 0.003 to 5 mass%. Owing to the experimental precision requirements due to the alloys' compositions, the alternative technique of electromagnetic phase separation is combined with differential scanning calorimetry (DSC) measurements. DSC analysis is supplemented by a thorough investigation of the resulting microstructures using XRD, SEM, and EBSD to deduce the solidification sequence. The compositions of each observed phase are characterized with chemical analysis techniques, including GD-OES, ICP-OES, SIMS, and EPMA-WDS. The results from the Fe-B-C ternary system are discussed and compared with previous findings on the Fe-B binary system.

The positions of univariant lines on a partial liquidus projection, and phase-field boundaries in the solid and liquid regions, are established at selected temperatures with boron concentrations up to 5 mass%. The study determines the locations of invariant reactions in terms of temperature and composition, as well as boron solubility in high-temperature ferrite and austenite solid solutions. A critical literature review, combined with new data, enables the refinement of the CALPHAD-type description of the Fe-B-C ternary system, particularly at low boron concentrations.

Keywords: Phase equilibria, Thermodynamics, DSC, Solidification path

References:

1. K.E. Blazek et al: "Boron effects on the solidification of steel during continuous casting", Rev. Metall. **105** (2008) 609-625.

2. J. Miettinen et al: "Thermodynamic description of ternary Fe–B–X systems. Part 7: Fe–B–C", Arch. Metall. Mater. **65** (2020) 923-933.
3. M. Enoki et al: "Thermodynamic Analysis of the Fe-B-C Ternary System and an Evaluation of the Grain Boundary Segregation Behavior of B and C", J. Phase Equilib. Diffus. **45** (2024) 1244-1259.

# THE THERMAL BEHAVIOR OF THE LI-ION BATTERIE CATHODE MATERIAL $\text{LiNi}_{0.5-x}\text{Mn}_{1.5+x}\text{O}_4$

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Main topic: Thermodynamics of energy storage materials

Secondary topic: Thermochemistry, thermodynamic properties (liquids, solids, amorphous materials)

Abstract:

$\text{LiNi}_{0.5-x}\text{Mn}_{1.5+x}\text{O}_4$  (LNMO) is a spinel structured oxide that is highly suitable as a cathode material for lithium-ion batteries. While Ni and Mn occupy either in ordered ( $T < \text{approx. } 650^\circ\text{C}$ ) or disordered manner octahedral sites, Li occupies one-eighth of the tetrahedral sites.

The structure can be electrochemically reversibly delithiated, whereby  $\text{Ni}^{2+}$  is oxidized to  $\text{Ni}^{4+}$  and a metastable  $\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$  structure is formed. During lithiation, significantly more Li-ions (theoretically up to 4 Li-ions per formula unit) can be incorporated. This is why this material exhibits a very high specific capacity in cathodes for Li-ion batteries. Due to the high potential of the  $\text{Ni}^{2+}/\text{Ni}^{3+}$  and  $\text{Ni}^{3+}/\text{Ni}^{4+}$  redox pairs ( $> 4.5\text{ V}$ ), the battery voltage against Li or even graphite as an anode is also very high, which in turn ensures high specific energy. However, this high cell voltage also requires special electrolytes, which, however, hinders the widespread use of such cathodes in practice.

Regarding safety, recycling, and disposal, the thermal behavior of battery materials is of great importance. Therefore, LNMO, both ordered and disordered, was investigated using TGA-DSC/MS, DTA, XRD and HT-XRD. The chosen atmosphere was air and Ar, respectively. The formation of a rock-salt structure, designated as Ni-rich  $(\text{Li},\text{Ni},\text{Mn})\text{O}$  and the release of oxygen at approx.  $700^\circ\text{C}$  could be confirmed. Mass spectroscopy under Ar could prove the evolution of oxygen. A selection of our results [1] is presented in detail here.

Keywords: Li-ion batteries, Cathode materials, LNMO, Thermal decomposition

References:

1. M. Reda et al: "Insights into the thermal decomposition of LNMO", *Ceramics International* (2026).

# CHROMIUM LOSSES DURING PRODUCTION OF HIGH-CR-STEEL SHOTS

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Main topic: Industrial applications of thermodynamics

Secondary topic: Oxides (Phase Diagrams, Corrosion)

Abstract:

The slag compositional changes in relation to the variation of  $\text{Cr}_2\text{O}_3$  in EAF slag were observed during the production of high-chromium melts for the applications of steel shots. The EAF is primarily used for scrap melting, composition and temperature adjustment, and impurity refining. In the present study, the chemical compositions of slags were analyzed and represented by using the  $\text{CaO-Al}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-MgO-FeO-SiO}_2$  multicomponent phase diagrams. A conventional process for means of furnace reducing slag formation and interpretation of slag behaviour was made for the first and second test of slag composition adjustment using the  $\text{CaO-Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$  (-10MgO-10FeO-10SiO<sub>2</sub>) slag system to show Cr reduction/oxidation efficiency. Additionally, the measured data were also expressed within the  $\text{CaO-FeO-Cr}_2\text{O}_3\text{(-Al}_2\text{O}_3)$  pseudo-ternary diagram, from which we observed the FeO mass fraction variations in each operation of slag preparation. In this paper, trajectories of slag compositions are shown from  $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ -based spinel saturated system close to the  $\text{Al}_2\text{O}_3$ -rich corner toward optimised compositions of the CaO-rich corner of predominantly  $\text{CaO-Al}_2\text{O}_3\text{(-SiO}_2)$  oxide system, achieving stable and fluid slag performance, limited refractory erosion, no-crust slag experience and limited Cr losses. Using a statistical approach, the chromium distribution was described with the most affecting linear regression parameters. The present study covers crusty  $\text{Al}_2\text{O}_3$ -rich slags (conventional) and emulsified CaO-rich (optimised) reduction slags under EAF virgin melting process for shots production in relation to control of  $\text{Cr}_2\text{O}_3$  and FeO content.

Keywords: FactSage, Slag, EAF, Chromium oxide, Reduction

# THERMODYNAMICS OF REFINING HIGH-NITROGEN STAINLESS STEEL BY $\text{CaF}_2$ - $\text{CaO}$ - $\text{Al}_2\text{O}_3$ - $\text{MgO}$ SLAG FOR ELECTROSLAG REMELTING

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Main topic: Thermochemistry, thermodynamic properties

Secondary topic: Thermochemistry of metallurgical processes

Abstract:

As global energy supply instability intensifies, nuclear power generation has regained attention for energy independence. Particularly, replacing conventional coal-fired power plants with small modular reactor (SMR) is being actively pursued to achieve carbon neutrality. Austenitic stainless steels are considered as candidate structural materials for SMR due to their high creep strength and excellent oxidation and corrosion resistance [1]. Nitrogen, which has a higher solid solubility than carbon, enables partial replacement of expensive nickel (Ni), thereby simplifying alloy composition and significantly reducing manufacturing costs while suppressing carbide precipitation and improving both strength and corrosion resistance [2].

Although high-nitrogen stainless steels (HNSS) exhibit excellent strength and ductility, the electroslag remelting (ESR) process is required to minimize porosity, inclusions and segregation. However, compositional inhomogeneity caused by the oxidation loss of reactive alloying elements such as Al and Si during ESR process remains an unresolved issue [3]. Nevertheless, studies on slag-metal equilibrium and desulfurization behavior in HNSS under ESR conditions remain limited.

Therefore, the present study aims to investigate the slag-metal equilibrium relationship between HNSS and the  $\text{CaF}_2$ - $\text{CaO}$ - $\text{Al}_2\text{O}_3$ - $\text{MgO}$  ESR-type slag, focusing particularly on optimizing the slag composition to maximize desulfurization and deoxidation efficiency. A commercial thermochemical computing package, FactSage (Ver.8.3), was used to design the  $\text{CaF}_2$ - $\text{CaO}$ - $\text{Al}_2\text{O}_3$ - $\text{MgO}$  ESR-type slags. Slag-metal experiments between HNSS and  $\text{CaF}_2$ - $\text{CaO}$ - $\text{Al}_2\text{O}_3$ - $\text{MgO}$  slag were conducted at 1773 K with varying  $\text{CaO}/\text{Al}_2\text{O}_3$  (=C/A) ratio and  $\text{CaF}_2$  content. By comparing thermodynamic predictions calculated *via* FactSage with experimental data, the effects of Al content on equilibrium Si content in the steel were evaluated. Furthermore, the sulphide capacity of the slag was intensively analyzed to elucidate its influence of slag chemistry on the desulfurization behavior of HNSS, thereby contributing to the establishment of optimal slag window for effective sulfur and oxygen removal.

Keywords: High nitrogen stainless steel, Electroslag remelting (ESR), Desulfurization, Deoxidation, Thermodynamics

References:

1. K. Kwon et al: "Precipitation Behavior and Mechanical Properties of High-Nitrogen Austenitic Stainless Steel According to Chemical Composition and Heat Treatment Temperature", Korean J. Met. Mater. **63** (2025) 143-151.
2. W. Simmons: "Overview: high-nitrogen alloying of stainless steels", Mater. Sci. Eng. A **207** (1996) 159.
3. S. Duan et al: "Investigation of the oxidation behavior of Ti and Al in Inconel 718 superalloy during electroslog remelting", Sci. Rep. **8** (2018) 5232.

# CALPHAD-ASSISTED DESIGN OF REDUCED CRITICAL RARE-EARTH PERMANENT MAGNETS

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Main topic: Computational thermodynamics

Secondary topic: Phase diagrams and phase equilibria

Abstract:

Rare-earth permanent magnets are essential for the efficient and compact operation of numerous electrical devices. Their use in automotive motors and wind turbine generators is a key breakthrough in the transition to carbon-free transportation and energy production. However, the limited availability of these critical materials directly impacts industrial sovereignty. To address this challenge, the CEA has deployed two parallel strategies: the partial substitution of strategical rare-earths in conventional Fe-Nd-B permanent magnets with more abundant and available elements, and the development of new generations (Fe-Sm) of permanent magnets with reduced critical rare-earth elements by design.

The first point addresses the introduction of cerium (Ce) into commercial Nd<sub>2</sub>Fe<sub>14</sub>B magnets to reduce their cost [1,2]. The Calphad method is used to tune the processing and subsequent heat treatments to avoid deleterious phases.

The second case deals with development of a new family of SmFe<sub>12-x</sub>M<sub>x</sub> permanent magnets (M = Ti, V) [3]. The primary magnetic phase of these magnets requires approximately 50% less rare-earth content than conventional Nd<sub>2</sub>Fe<sub>14</sub>B while maintaining comparable magnetic performance.

The thermodynamic modeling is an essential tool to define and optimize the manufacturing, processing, and recycling pathways for these emerging magnetic materials.

Keywords: Calphad, Permanent magnets, Rare-earth, Thermodynamics, Design

References:

1. G. Delette: "Nd<sub>2</sub>Fe<sub>14</sub>B permanent magnets substituted with non-critical light rare earth elements (Ce, La): A review", *J. Magn. Magn. Mater.* **577** (2023) 170768.
2. E. de Villoutreys et al: "Experimental investigations and thermodynamic modeling of the Ce-Fe-Nd system", *J. Alloys Compd.* **1058** (2026) 186934.
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# ON THE ELECTROCHEMICAL PHASE DIAGRAMS

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Main topic: Phase diagrams and phase equilibria

Secondary topic: Thermochemistry of metallurgical processes

Abstract:

The presentation focuses on electrochemical phase diagrams (ECPDs) and their potential practical applications in the electrochemical deposition of binary metal systems. The ECPD diagrams show which phases the metallic cations form on the cathode when galvanostatically deposited from an electrolyte consisting of compounds containing components A and B, as a function of temperature and electrolyte composition at constant pressure and low current density. During the presentation, the theoretical background for calculating ECPD diagrams based on electrochemical diagrams (ECD [1]) will be discussed. These diagrams can be easily correlated with the equilibrium phase diagrams calculated using the CALPHAD method [2], which is based on Gibbsian thermodynamics [3]. I will show the analytically solvable equations for the phase equilibrium curves found on the ECPD diagram in cases where the binary A-B system deposited on the cathode is a solid solution, involves phase separation, eutectic, or stoichiometric compounds. In addition, the ECPD diagrams for real binary metal systems will be shown, comparing them with experimental data found in the literature.

Keywords: phase diagram, binary co-deposition, galvanostatic, electrolyte, molten salts

References:

1. G. Kaptay: Electrochemical diagrams showing equilibrium cathodic phases and their compositions as function of electrolyte composition and type of alloy phase diagram. *Electrochimica Acta* 484 (2024): 144002.
2. HL Lukas, SG Fries, B. Sundman: Computational thermodynamics. The Calphad method. Cambridge, UK: Cambridge University Press; 2007.
3. J.W. Gibbs: On equilibrium of heterogeneous substances. *Trans Connect Academy*, 3 (1875–1876) 108-248 and 3 (1877-1878) 343-524.

# APPLICATION OF THERMODYNAMIC SIMULATIONS IN THE DEVELOPMENT OF ALUMINIUM ALLOYS FOR PACKAGING APPLICATIONS

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Main topic: Industrial applications of thermodynamics

Secondary topic: Phase diagrams and phase equilibria

Abstract:

Thermodynamic simulations have become an essential tool in the industrial development of aluminium alloys for packaging applications, enabling faster alloy optimization while reducing experimental trials and development costs. In the production of aluminium packaging materials, including aerosol cans, beverage cans and food cans, the chemical composition and processing parameters must be carefully balanced to achieve high strength, excellent formability, corrosion resistance and low material consumption. The study demonstrates how Thermo-Calc calculations, combined with thermal analysis, DSC measurements and microstructural characterization, were used to support the development of new aluminium alloys for continuously cast narrow strip intended for slug production.

Thermodynamic modelling was used to predict solidification behaviour, optimize alloy chemistry, and assess the influence of recycled material on castability and intermetallic phase formation. The simulations also supported the optimization of heat treatment and oxidation behaviour, particularly in Al–Mg alloys, improving process reliability

The simulation-guided alloy design resulted in alloys with more stable mechanical properties, higher deformation and bursting pressures, and improved potential for lightweight aluminium packaging through thinner can walls. These results demonstrate that thermodynamic simulations are an effective tool for accelerating the development of sustainable aluminium alloys for aerosol, beverage and food cans while increasing the use of recycled materials.

Keywords: Thermodynamic simulations, Aluminium alloys, Packaging industry, Aerosol cans, Alloy development

# THE VAPOUR-SOLID APPROACH TOWARDS CONTROLLED SYNTHESIS OF INTERMETALLIC NANOPARTICLES

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Main topic: Experimental and theoretical thermodynamics – new results and techniques

Abstract:

Intermetallic compounds are increasingly popular for heterogeneous catalysis, as the great variety of ordered crystal structures offers high potential for active site engineering [1]. Catalytic applications require high accessibility of catalytically active sites favouring the use of nanoparticles. However, the controlled synthesis of intermetallic nanoparticles is demanding. Bottom-up methods by various colloidal approaches are currently most used, but supported annealing approaches may offer the best routes regarding clean surfaces and limiting sintering [2].

The vapour-solid synthesis, recently developed in our lab, employs direct reaction of supported monometallic nanoparticles with the vapor of a second element, providing a clean and straightforward process and allowing for better control of the final particle composition than other methods. We systematically investigated this synthetic concept using different intermetallic systems (Pd-Zn, Ni-Te, Pt-Zn) on various support materials (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, carbon black). Sample characterization confirmed high compositional control and accessibility of many intermetallic compounds. Results for selected model reactions in electrocatalytic, photocatalytic and other heterogeneous catalytic reactor setups are given and future research directions are discussed.

Keywords: Intermetallic nanoparticles

References:

4. A. Dasgupta et al: "Intermetallics in catalysis: An exciting subset of multimetallic catalysts", *Catalysis Today* 330 (2019) 2-15.
2. B.P. Williams et al: "The impact of synthetic method on the catalytic application of intermetallic nanoparticles", *Nanoscale* **12(36)** (2020) 18545-18562.

# THERMODYNAMIC AND KINETIC APPROACH ON MANUFACTURING HIGH-ENTROPY ALLOY VIA COMMERCIAL FERROALLOYS FEEDSTOCK

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Main topic: Thermodynamics of high entropy alloys

Secondary topic: Thermochemistry of metallurgical processes

Abstract:

High-entropy alloy (HEA) comprises several principal elements, while most conventional alloys are based on one main element. Due to the high-entropy effect, a solid solution can be stabilized when numerous elements are mixed in an equimolar or near-equimolar fraction. This gives HEA unusual properties, such as outstanding strength and hardness, wear resistance, high-temperature strength, structural stability, and resistance to corrosion and oxidation. Meanwhile, the manufacturing methods *via* solid and liquid state processing also have a significant influence on the properties, and high-purity metallic elements are typically used as raw materials, which tends to increase production costs.

Alternatively, the commercial grade ferroalloys have been widely applied in steel industry as deoxidizers and alloying agents. Applications of ferroalloys in manufacturing of HEA are now receiving increasing attention because of: the scale of ferroalloy production; the higher price advantage compared with pure metallic elements; and the variety of ferroalloys, such as ferronickel (FeNi), high-carbon or low-carbon ferrochromium (HCFeCr or LCFeCr), high-carbon or low-carbon ferromanganese (HCFeMn or LCFeMn), silicomanganese (SiMn), ferrotitanium (FeTi), ferrovanadium (FeV), ferroniobium (FeNb), etc. available to produce HEA.

However, the presence of high levels of elemental impurities in the ferroalloys, including but not limited to oxygen, nitrogen, sulfur, etc. can influence the cleanliness of the produced alloys using the ferroalloys, and lead to further deterioration of the mechanical properties. Metallurgical slag plays a key role in the removal of impurities such as sulfur and oxygen as well as non-metallic inclusion (NMI) from a metal during melting, refining, and casting with high cost-effectiveness.

Hence, in the present lecture, the laboratory trials to produce HEA based on thermodynamic and kinetic principles will be discussed including a combination of several kinds of commercial grade ferroalloys for target HEA system, and an effective refining of harmful elements and NMI from alloy melt with fluid slagging method. The characterization of NMI and the effect of NMI on the mechanical properties of HEA will be discussed.

Keywords: High-entropy alloy, Ferroalloys, Slag, Thermodynamics, Kinetics

## References:

1. N. Choi et al.: "Characterization of non-metallic inclusions and their influence on the mechanical properties of a FCC single-phase high-entropy alloy", J. Alloys Compd. **763** (2018) 546-557.
2. S. Duan et al.: "Manufacturing an ultra-low-sulfur CoCrFeMnNi high-entropy alloy by slagging through induction melting with ferroalloys feedstock", J. Alloys Compd. **928** (2022) 167080.
3. S. Duan et al.: "Novel applications of ferroalloys for manufacturing of ultra-clean CoCrFeMnNi high-entropy alloy by slagging method", J. Alloys Compd. **939** (2023) 168692.
4. Y. Wang et al.: " Effect of Manufacturing Conditions and Al Addition on Inclusion Characteristics in Co-based Dual-phase High Entropy Alloy", Metall. Mater. Trans. A **54A** (2023) 2715-2729.
5. Y. Wang et al.: " Characterization and formation mechanism of non-metallic inclusions in single bcc-phase high entropy alloy", Mater. Charact. **25** (2023) 113299.
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7. Y. Su et al.: "Manufacturing ultra-low sulfur and oxygen (FeCrCoMnNi)<sub>100-xCx</sub> high-entropy alloys using a commercial ferroalloy feedstock via induction melting and slag refining", J. Mater. Res. & Technol. **42** (2026) 5181-5191.

# HIGH TEMPERATURE PHYSICAL CHEMISTRY OF SULFUR REMOVAL FROM NICKEL-BASED SUPERALLOY BY CAO-CAF<sub>2</sub>-AL<sub>2</sub>O<sub>3</sub>-MGO SLAG

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Main topic: Thermochemistry of metallurgical processes

Secondary topic: Thermochemistry, thermodynamic properties

Abstract:

Sulphur (S), a major impurity element in nickel superalloys, forms non-metallic inclusions, and can act as crack initiation sites under high temperature loading conditions [1]. Therefore, effective control of S is essential for producing high performance Ni-superalloys. In this study, thermochemical equilibrium experiments and kinetic experiments were conducted at 1823 K to investigate the effects of the CaO/CaF<sub>2</sub> ratio and Al<sub>2</sub>O<sub>3</sub> content in the CaO-CaF<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-MgO slag on the desulphurisation behaviour of a Ni-based alloy. At a fixed Al<sub>2</sub>O<sub>3</sub> content, the S distribution ratio ( $L_S = (\%S)/[\%S]$ ) increased with increasing CaO/CaF<sub>2</sub> ratio. In contrast, it generally decreased with increasing Al<sub>2</sub>O<sub>3</sub> content. This is because Al<sub>2</sub>O<sub>3</sub> acts as an acidic oxide in the slag, decreasing the slag basicity and thereby reducing the thermodynamic driving force for desulphurisation. By analysing the relationship among CaO activity ( $a_{CaO}$ ), S distribution ratio, and sulphide capacity ( $C_S^{2-}$ ), it was confirmed that CaO is the major factor with the greatest influence on desulphurisation capability. The kinetic analysis showed that Al<sub>2</sub>O<sub>3</sub> addition decreased the S removal rate, and the rate-controlling step of desulphurisation shifts from slag-phase or slag-metal mixed mass transfer to metal-phase mass transfer below 20 wt. % Al<sub>2</sub>O<sub>3</sub>. Based on the experimental results, considering both the slag melting rate and sulphur refining capacity, the Al<sub>2</sub>O<sub>3</sub> content should be controlled not more than 20 wt. % and there is no significant difference in terms of sulphur removal rate when the Al<sub>2</sub>O<sub>3</sub> content is 10% or less.

Keywords: Nickel superalloy, Desulphurisation, Slag, Thermodynamics, Kinetics

References:

1. D. Texier et al: "Short crack propagation from cracked non-metallic inclusions in a Ni-based polycrystalline superalloy", Acta Materialia **165** (2019) 241-258.

# THERMODYNAMIC REASSESSMENT OF FE-CR-NI SYSTEM

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Main topic: Databases development

Secondary topic: Phase diagrams and phase equilibria

Abstract:

Nickel-based superalloys are widely used in sectors such as aerospace, oil and gas, automotive, and power generation, particularly for components that require high-temperature strength and resistance to oxidation and corrosion. Commercial Gibbs energy databases face challenges in accurately predicting the stability range of topologically close packed (TCP) phases in superalloy grades such as Alloy 625, 718, and 925. This issue is likely due to the quality of the thermodynamic description of the Fe-Cr-Nb-Ni system. Another difficulty with most commercial databases is the coupled Gibbs energy model used in the thermodynamic description of  $\gamma$ - $\gamma'$  phases. Computations involving coupled  $\gamma$ - $\gamma'$  model in multicomponent systems tend to be slow and pose many numerical difficulties, especially in kinetic simulations. Therefore, a decoupled Gibbs modeling approach is preferred. The final goal of this research is to create a Gibbs energy database for the Fe-Cr-Nb-Ni system using the CALPHAD approach addressing the issues outlined above.

As a first step towards achieving this goal, the thermodynamic modelling of the Fe-Cr-Ni ternary system is revisited, incorporating all relevant data from literature as well as new phase equilibria data generated in the present work. Alloy compositions were selected based on information gaps identified in the collected literature data. Alloys produced by vacuum arc-melting, were examined to assess the extent of microsegregation. Homogenisation heat treatment was carried out at 1200 °C for 48 h to reduce microsegregation. Equilibration heat treatments at selected temperatures (i.e., 1100 °C and 1000 °C) for extended periods were conducted in a furnace under an argon atmosphere. Heat treated samples were analysed using SEM-EDS to obtain tie-line data. Eventually, the generated phase equilibria data along with data from literature is used in the thermodynamic assessment of the system

Keywords: CALPHAD, Fe-Cr-Ni, Vacuum Arc-Melting (VAM), Equilibration

# THE $\text{ZrO}_2\text{-HfO}_2\text{-Y}_2\text{O}_3$ SYSTEM: EXPERIMENTAL STUDY AND THERMODYNAMIC MODELLING

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Main topic: Experimental and theoretical thermodynamics

Secondary topic: Phase diagrams and phase equilibria

Abstract:

The system of  $\text{ZrO}_2\text{-HfO}_2\text{-Y}_2\text{O}_3$  presents interest for thermal barrier coating applications as well as solid state electrolyte. Thermodynamic functions of the  $\text{HfO}_2\text{-Y}_2\text{O}_3$  system [1] were re-assessed due to thermodynamic data change for the  $\text{HfO}_2$  and  $\text{Y}_2\text{O}_3$ . The same phase diagram data and thermodynamic properties obtained by high-temperature calorimetry and vapor pressure measurements as in ref. [1] were used. The heat capacity of  $\delta\text{-Y}_4\text{Zr}_3\text{O}_{12}$  phase was measured using differential scanning calorimetry (DSC) in the temperature range between 200 and 900 K. The enthalpy increment calculated using heat capacity measured in the present work is consistent with data obtained using transposed drop calorimetry [2]. The thermodynamic description of other phases in the  $\text{ZrO}_2\text{-Y}_2\text{O}_3$  system was accepted from [3] except for  $\text{Y}_4\text{Zr}_3\text{O}_{12}$  phase. The  $C_p$  data were used to describe the Gibbs energy of this phase, while enthalpy and entropy were optimized using phase relations and enthalpy of formation [2]. The ideal model was applied for solid and liquid solutions in the  $\text{HfO}_2\text{-ZrO}_2$  system. The database of ternary system  $\text{ZrO}_2\text{-HfO}_2\text{-Y}_2\text{O}_3$  was developed based on binary descriptions and using CALPHAD approach to optimize the thermodynamic parameters of ternary system to reproduce literature experimental data on isothermal sections, vertical sections and liquidus surface. Thermodynamic description of the  $\text{ZrO}_2\text{-HfO}_2\text{-Y}_2\text{O}_3$  system was derived, phase diagrams were calculated and compared with experimental data.

Keywords: Heat capacity, Calorimetry, Phase diagram, CALPHAD

References:

1. O. Fabrichnaya et al: "Phase relations in the  $\text{HfO}_2\text{-Y}_2\text{O}_3\text{-Al}_2\text{O}_3$  system", CALPHAD **29** (2005) 239-246.
2. T.A. Lee et al: "Enthalpy of formation of cubic yttria-stabilized zirconia", J. Mater. Res. **18** (2003) 908-918.
3. O. Fabrichnaya et al: "Up-date of a thermodynamic database of the  $\text{ZrO}_2\text{-Gd}_2\text{O}_3\text{-Y}_2\text{O}_3\text{-Al}_2\text{O}_3$  system for TBC applications", J. Phase Diagr. Diff. **32** (2011) 2-16.

# INVESTIGATION ON THE METAL-OXIDE PART OF U-PU-O SYSTEM AT HIGH TEMPERATURE

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Main topic: Experimental and theoretical thermodynamics

Secondary topic: Phase diagrams and phase equilibria

Abstract:

MOX fuel, made of uranium and plutonium oxides, is used to recycle nuclear fuel. Its behavior under severe accidents is still not well known, especially in the metal–oxide region of the U-Pu-O phase diagram. Thermodynamic calculations suggest a possible phase separation between U- and Pu-rich regions, which could increase the risk of recriticality of the damaged core. However, these predictions remain hypothetical due to a lack of high-temperature experimental data.

This study aimed at determining transition temperatures using laser heating experiments [1] with thermal arrest detection during cooling for compositions in the region of interest. A pyrometer and spectrometer were used to measure the sample temperature, while reflectivity changes helped identify phase transitions. This study showed that the larger the metallic fraction, the more the emissivity varies during the experiment, making its accurate measurement increasingly important for reliably determining transition temperatures. XRD and SEM-EDS analyses were also performed to refine the sample composition before and after laser shots.

Thermodynamic calculations using the NUCLEA database [2], developed using CALPHAD method, were also carried out to support the experiments by predicting target temperatures and interpreting results. These data also help to improve databases used in nuclear safety studies.

Keywords: U-Pu-O system, Thermodynamics, Laser melting, Metal-oxide domain

References:

1. D. Manara et al: “New techniques for high temperature melting measurements in volatile refractory materials via laser surface heating”, *Rev. Sci. Instrum.* **79.11** (2008) 113901.
2. B. Michel et al: “Merging NUCLEA and Mephista database: over three decades of building a European nuclear thermodynamic database for severe accident phenomenology”, paper **108** in: *ERMSAR 2026*, (2026)

# CHEMICAL INTERACTION BETWEEN URANIUM DIOXIDE (UO<sub>2</sub>), STAINLESS STEEL AND BORON CARBIDE (B<sub>4</sub>C)

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Main topic: Experimental and theoretical thermodynamics – new results and techniques

Secondary topic: Phase diagrams and phase equilibria

Abstract:

In some specific reactors core severe accidental scenarios (e.g., Unprotected Loss of Cooling Flow), the (U,Pu)O<sub>2</sub> fuel pellets can be in direct contact with the stainless-steel cladding of the boron carbide, B<sub>4</sub>C, neutron absorbers. In these conditions and depending on the local temperature in this specific region of the reactor, the B<sub>4</sub>C absorbers may initially interact with the internal surface of the stainless-steel cladding, leading to the formation of a liquid phase [1]. As the temperature rises, the liquid phase fraction can significantly increase and lead to the loss of the mechanical stability of the stainless-steel cladding. The liquid mixture may then be exposed and in direct contact with the ejected fuel pellets. Therefore, depending on the temperature and the stage of the accident, the fuel may be in contact with a stainless-steel - B<sub>4</sub>C based liquid mixture or alternatively with the external surface of the stainless-steel cladding.

This study is focused on equilibrium and kinetics of reactions on chemical systems of interest for severe accident simulation codes. The aim is to obtain thermodynamic data on UO<sub>2</sub>-B<sub>4</sub>C-stainless-steel mixtures to understand the mechanisms leading to the dissolution of uranium in a liquid phase rich in iron, boron and carbon. Two kinds of experiments are conducted: heat treatments for one hour at 1900 °C and Knudsen Effusion Cell Mass Spectrometry measurements during a heating cycle up to 1900 °C. In both cases, the microstructure and the phases are analyzed. Vapor pressures at equilibrium above samples as well as the solidification paths are calculated using the TAF-ID and compared to the experimental data [2].

Keywords: Carboreduction, Sodium-Fast reactor, Severe accident

References:

1. F. Nagase et al: "Chemical interaction between B<sub>4</sub>C and stainless steel at high temperatures", J. Nucl. Mater. **245** (1997) 52-59.
2. C. Guéneau et al: "TAF-ID: International thermodynamic database for nuclear fuel applications", Calphad **72** (2021) 102212.

# PHASE RELATIONS IN THE $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Dy}_2\text{O}_3$ SYSTEM

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Main topic: Phase diagrams and phase equilibria

Secondary topic: Oxides

Abstract:

Phase equilibria in the  $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Dy}_2\text{O}_3$  system have an important role in the development of new high-entropy oxides (HEOs) for applications as thermal barrier coatings (TBCs) in aircraft and gas turbines [1]. To improve the understanding of phase relations in this crucial system, sample compositions were produced by solid state reaction and heat-treated either at 1573 K for 2160 h or at 1773 K for 100 h to derive isothermal sections at both temperatures. The microstructures were investigated experimentally by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). Differential scanning calorimetry (DSC) was used to determine the heat capacity of single-phase defect fluorite compositions  $(\text{Dy}_x\text{Y}_{1-x})_2\text{Zr}_2\text{O}_7$  ( $0 \leq x \leq 1$ ). The  $\text{ZrO}_2\text{-Y}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3\text{-Dy}_2\text{O}_3$  phase diagrams are adopted from [2,3], while the thermodynamic parameters were re-optimized in the framework of the CALPHAD method to calculate phase equilibria in the  $\text{ZrO}_2\text{-Dy}_2\text{O}_3$  system, aiming to achieve better consistency between parameters and models for high-order descriptions. The calculated isothermal sections at 1573 K and 1773 K reproduce the experimental findings within uncertainties.

Keywords: Phase diagram, CALPHAD, Isothermal section, Thermal barrier coating (TBCs), heat capacity

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3. M. Zinkevich: "Thermodynamics of rare earth sesquioxides", Prog. Mater. Sci. **52** (2007) 597-647.

# MODELLING AND CHARACTERIZATION OF A MODIFIED EN AW 7075 ALLOY FOR ADDITIVE MANUFACTURING

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Main topic: Experimental and theoretical thermodynamics – new results and techniques

Secondary topic: Thermochemistry of metallurgical processes

Abstract:

EN AW 7075 is a high-strength aluminium alloy from the 7XXX series, with zinc and magnesium as the principal alloying elements. Due to its high strength and fatigue resistance, it is widely used in aerospace and other demanding engineering applications. However, processing high-strength aluminium alloys by additive manufacturing remains challenging because of hot cracking, porosity, and microstructural instability.

This study aimed to improve the suitability of EN AW 7075 for Selective Laser Melting (SLM) through alloy modification and process optimisation. Thermodynamic calculations were performed using Thermo-Calc software to predict phase equilibria and solidification behaviour. In parallel, key SLM process parameters, including laser power, scanning speed, and preheating temperature, were systematically varied to evaluate their influence on microstructure and mechanical properties.

Initial experiments showed that conventional SLM processing of EN AW 7075 resulted in significant cracking and porosity. To improve processability, the alloy composition was modified by adding silicon. Thermodynamic modelling indicated that silicon addition altered the solidification path and reduced susceptibility to hot cracking. Experimental results confirmed the formation of a refined and more homogeneous microstructure with a significantly lower tendency for crack formation. Microstructural characterisation using Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), energy-dispersive spectroscopy (EDS), and synchrotron X-ray diffraction revealed a fine-grained microstructure with reduced porosity and no detectable cracks. The modified alloy exhibited a homogeneous microstructure and enhanced mechanical properties, achieving an as-built tensile strength of up to 480 MPa.

The results demonstrate that the addition of silicon enables stable SLM processing of a modified EN AW 7075 alloy, suppressing crack formation while maintaining high mechanical performance, thereby expanding the potential application of high-strength aluminium alloys in additive manufacturing.

Keywords: Thermodynamic modelling, EN AW 7075, Selective laser melting, Microstructural characterization

Acknowledgement: This research was funded by Slovenia's Agency for Research and Innovation (ARIS) under grant number ARIS project L2-3164: 'A Novel High-strength Aluminium Alloy developed for Selective Laser Melting and Lightweight Applications' and within the framework of the Slovene ARIS programme P2-0132, "Surface physics and chemistry of metallic materials", and the Programme for Advanced Metallurgy, grant number P2-0344(B)

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# POSTER PRESENTATIONS



## THERMAL DECOMPOSITION OF HEMATITE IN AIR: AN IMPROVED VERSION OF THE FE-O PHASE DIAGRAM

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Main topic: Experimental and theoretical thermodynamics – new results and techniques

Secondary topic: Oxides (phase diagrams, corrosion)

Abstract:

In this poster thermal decomposition of fine hematite ( $\text{Fe}_2\text{O}_3$ ) powder is experimentally studied in open air by measuring its mass loss at different temperatures (1300 ... 1600 °C) and holding times up to 48 hours. Only the sample at 1600 °C was found melted, while samples at and below 1550 °C were all found solid. The mass loss was found zero at 1300 and 1350 °C, but it had a finite value at 1363 °C after 24 hours, leading to about 1355 °C for the equilibrium dissociation temperature of hematite in 1 bar air. The equilibrium mass losses were estimated using Avrami kinetics as 3.22 wt.% at 1550 °C and as 2.98 wt.% at 1600 °C. XRD analysis proved that the ratio of magnetite was increasing, while the ratio of hematite was decreasing with increasing temperature and holding time. The oxygen-rich, high-temperature part of the Fe-O equilibrium phase diagram was re-constructed at 1 bar pressure of air (= 0.21 bar partial pressure of  $\text{O}_2$  gas) based on previous measurements, Calphad assessments and our new experimental data. Using Avrami kinetics it was shown that 90 % of maximum hematite decomposition is reached at 1600 °C within 21 minutes, while much longer times are needed for the same at 1550 °C and below. This is because at 1600 °C the iron oxides are liquid and the diffusion of oxygen ions out of this liquid is much faster than at and below 1550 °C from solid oxide particles. These results mean that partial reduction of iron ores (containing mostly hematite) can be achieved without any chemical reducing agent (carbon, hydrogen or methane) or electrochemical energy at 1600 °C in open air atmosphere within 10 ... 30 minutes, leading to the formation of liquid magnetite and releasing pure oxygen gas. Even deeper deoxidation of hematite is expected in vacuum.

Keywords: Hematite, Thermal decomposition, Avrami kinetics, Fe-O phase diagram

# MODELING AND EXPERIMENTAL STUDY OF IMC FORMATION AT SN/CU INTERFACE

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Main topic: Computational thermodynamics

Secondary topic: Experimental and theoretical thermodynamics – new results and techniques

Abstract:

As electronic devices continue to miniaturise, the integrity of solder joints has become increasingly dependent on the microstructural characteristics of the joint interface. While the initial formation of intermetallic compounds (IMCs) is essential for a strong metallurgical bond, their continued growth during a product's lifecycle is a major reliability concern [1]. As IMCs are inherently brittle and have higher electrical resistivity than bulk solder, excessive growth is detrimental to mechanical properties such as fatigue and shear strength, and often leads to premature joint failure [2,3]. Analysing solder/substrate interactions provides critical insight into interfacial evolution from a metallurgical perspective. Phase-field modelling has proven effective for simulating these soldering reactions, allowing detailed description of complex IMC evolution [1-4]. This study investigates the growth kinetics and morphology of  $\text{Cu}_6\text{Sn}_5$  and  $\text{Cu}_3\text{Sn}$  phases within the Sn/Cu system. A multi-phase field model was developed and coupled with the TCLSD thermodynamic database to simulate IMC growth at the Sn/Cu interface. Simulations were performed in one and two dimensions. The experimental work involved preparing Sn/Cu joints subjected to isothermal ageing at different temperatures (150 °C, 155 °C, and 180 °C) and times (50, 100, 250, 500, and 1000 h). The microstructure and chemical composition of the Sn/Cu interface were analysed using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). The thickness of the IMCs was measured using a convolutional neural network specifically trained for this system. Results showed that total IMC thickness follows a parabolic law, confirming that the process is diffusion-controlled across the temperature range. Thermal analysis was performed using differential scanning calorimetry (DSC) at 250 °C to observe IMC growth. DICTRA simulations were used to compute concentration profiles across the Sn/Cu interface. From these profiles, the individual thicknesses of phases were estimated and compared directly with experimental data obtained from DSC and SEM. This comparison enabled calibration of the phase-field kinetic parameters, ensuring the model accurately captures the diffusion-controlled growth observed in the experiments.

Keywords: IMC growth, Sn/Cu interface, Isothermal aging, Phase-field modeling

Acknowledgement: This work was supported by the Programme to support excellent teams of young researchers at STU under project 1366, by the Programme of young researchers at STU under project 1355

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# EXPERIMENTAL DETERMINATION OF THE CU-NI NANO ALLOY PHASE DIAGRAM

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Main topic: Thermodynamics of low-dimensional systems (surfaces and interfaces, nanomaterials)

Secondary topic: Phase diagrams and phase equilibria

Abstract:

The Cu-Ni alloys, besides their well-known use in corrosion-resistant and hard alloys, are of importance for the use in complex systems for lead-free soldering in electronics and for their catalytic applications. Their potential in these fields is further enhanced when bimetallic Cu-Ni nanoparticles are used. Nanoparticles, due to the large ratio of the surface area to the volume and hence increased surface energy in comparison to bulk materials, are reactive, highly catalytically active, and exhibit melting point depression (MPD), which is usable in specific catalytic reactions and in lead-free soldering.

The purpose of this contribution is to present the results of a study of the thermal stability of Cu-Ni nanoparticles prepared via wet synthesis and specified by a combination of a number of spectroscopic and microscopic methods, leading to the experimental determination of the Cu-Ni nano alloy phase diagram in the composition range of 0–50 at.% Ni via differential scanning calorimetry (DSC). As found, the results of our study [1] were in good agreement with the thermodynamic calculation of the Cu-Ni nano alloy phase diagram from our previous work [2], experimentally confirming its validity.

Keywords: Cu-Ni, Nano particles, Thermal analysis, Phase analysis

Acknowledgement: MUNI/A/1691/2024 and FSI-S-25-8787 Czech projects are gratefully acknowledged for the support.

References:

1. K. Blažek et al: "On the thermal stability and surface and catalytic properties of Cu-Ni nanoparticles" Mol. Catal., **582** (2025) 115188.
2. J. Sopoušek et al: "Cu–Ni nanoalloy phase diagram – Prediction and experiment", CALPHAD **45** (2014) 33-39.

# EXPERIMENTAL INVESTIGATION OF PHASE EQUILIBRIA IN THE CR-MO-SI TERNARY SYSTEM AT 1500 °C

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Main topic: Phase equilibria

Secondary topic: High temperature refractory alloys

Abstract:

Solid understanding of phase equilibria is essential for accelerated design of high temperature alloys which should possess a broad portfolio of properties. Though refractory alloys have been considered as perspective candidates for applications at ultra-high temperatures for decades, their practical use has been hindered by the trade-off between mechanical performance and oxidation resistance [1]. Outstanding combination of room temperature ductility, high temperature strength and corrosion resistance up to 1200 °C was recently discovered for a single-phase (Cr,Mo) solid solution (ss) in the Cr-Mo-Si alloy system [2]. However, experimental data on high-temperature phase equilibria especially above 1200 °C remain insufficient, which hinders the efficient development of these materials. This study aims to experimentally determine phase equilibrium in the Cr-Mo-Si system at 1500 °C focusing on the formation of sigma ( $\sigma$ ) phase in the Si-lean region.

Twelve alloys with selected compositions in the vicinity of the  $\sigma$  phase were manufactured by arc melting under argon atmosphere and annealed at 1500 °C for 200h followed by furnace cooling. Phase identification and composition analysis were performed using X-ray diffraction (XRD), scanning electron microscopy (SEM), and electron probe microanalysis (EPMA).

For the first time, the isothermal section at 1500 °C in the Si-lean region ( $x_{Si} \leq 25$  at. %) of the Cr-Mo-Si ternary is constructed. The equilibrium of the investigated samples was achieved after 200 hours. The presence of the  $\sigma$ -phase within 12.5–13.5 at. % of Si, 30.6–48.3 at. % of Mo and 38.7–56.8 at. % Cr is confirmed. The results indicate three single-phase region((Cr,Mo)<sub>3</sub>Si,  $\sigma$ -phase and (Cr,Mo)<sub>ss</sub>), three two-phase regions ((Cr,Mo)<sub>ss</sub> + (Cr,Mo)<sub>3</sub>Si,  $\sigma$  + (Cr,Mo)<sub>ss</sub> and  $\sigma$  + (Cr,Mo)<sub>3</sub>Si), and one three-phase region ( $\sigma$  + (Cr,Mo)<sub>ss</sub> + (Cr,Mo)<sub>3</sub>Si) in the studied isothermal section at 1500 °C.

Keywords: Cr-Mo-Si, Phase equilibria,  $\sigma$ -phase, Isothermal section

References:

1. J.H. Perepezko: "The Hotter the Engine, the Better", Science **326** (2009) 1068.
2. F. Hinrichs et al: "A ductile chromium–molybdenum alloy resistant to high-temperature oxidation", Nature **646** (2025) 331-337.

# EXPERIMENTAL AND THERMODYNAMIC ANALYSIS OF ADVANCED MEDIUM-MN STEELS CONTAINING CU AND MO TRAMP ELEMENTS

Firew Tullu Kassaye<sup>1</sup>, Adam Skowronek<sup>2</sup>, Aleksandra Kozłowska<sup>1</sup>, Alexander Gramlich<sup>3</sup>, Oguz Gulbay<sup>3</sup>, Ulrich Krupp<sup>3</sup>, Adam Grajcar<sup>1</sup>

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Main topic: Phase diagrams and phase equilibria

Secondary topic: Computational thermodynamics

Abstract:

Due to their excellent combination of strength and ductility, medium-Mn steels are suitable for automotive applications. However, tramp elements in steel scrap (Cu, Mo, Ni, and Sn) can influence the thermodynamic-kinetic behavior of these steels. The effects of 1.0Cu and 0.3Mo simulated tramp elements on phase transformation behavior in 0.17C-4Mn-0.8Al-0.5Si (wt. %) medium-Mn steels were investigated in this work. Thermodynamic calculation (Thermo-Calc) and experimental validation (high-resolution Bahr DIL805 dilatometer) methods were used. In addition, transformation kinetics under various thermal conditions were simulated using JMatPro software, and CCT and TTT diagrams were developed. Furthermore, microstructural characterization and hardness measurement were conducted. The predicted transformation kinetics were compared with experimentally obtained values. As a result, the simulations and experiments exhibited significant differences. This provided insights that thermodynamic calculations are very useful tools in optimizing the heat treatment schedules of modern steels, but it is necessary to experimentally verify the obtained results. In general, the results show that the tramp elements influence the decomposition of austenite. These findings provided a deeper understanding of the thermodynamic and kinetic mechanisms in medium-Mn alloys.

Keywords: Medium-Mn steel, Tramp elements, Phase transformation behavior, Thermodynamic calculation, Microstructure evolution

Acknowledgement: Firew Tullu Kassaye would like to acknowledge the Pro-quality program for support in starting scientific activities in new research topics as part of the Excellence Initiative – Research University program, grant no. 32/014/SDU/10-22-001.

References:

1. X. Zhang et al: "Enhancing the strength–ductility synergy of medium-Mn steel by introducing multiple gradient structures," *Materials Science and Engineering: A* **860** (2022) 144268.

# THERMODYNAMIC MODELING AND MICROSTRUCTURAL DESIGN OF LIGHTWEIGHT FE-MN-AL-C ALLOYS

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Main topic: Phase diagrams and phase equilibria

Secondary topic: Computational thermodynamics

Abstract:

Fe-Mn-Al-C alloys, commonly known as lightweight steels, have attracted considerable attention due to their favourable strength-to-weight ratio and promising mechanical properties. This study presents an integrated approach to the thermodynamic and microstructural design of six Fe-Mn-Al-C lightweight alloys of various C (0.04, 0.25 and 0.75 wt. %), Mn (1.6, 5.5, 8.5 and 12.5 wt. %) and Al (3.9, 5.5 and 8.0 wt. %) contents. Aluminium contributes to reducing alloys' density, which is caused by lattice expansion as well as by its lower atomic mass. Thermodynamic calculations, utilising ThermoCalc and JMatPro software, were employed to predict phase evolution and stability within the Fe-Mn-Al-C system. The thermodynamic calculations indicate that increasing the concentration of Al and C stabilizes the precipitation of detrimental  $\kappa$ -carbides; notably, Al increases the phase stability temperature. Furthermore, a high Al content (5.5 wt. %) stabilized  $\alpha$ -ferrite by reducing the  $\gamma$ -austenite loop, resulting in an expanded ferritic phase field. In contrast, increasing Mn content inhibited  $\kappa$ -carbide ((Fe,Mn)<sub>3</sub>AlC) formation and stabilized the austenitic phase. Discrepancies are pronounced between experimental results obtained from microstructural observation and dilatometry, and those predicted by thermodynamic calculations at higher concentrations of alloying elements. The findings demonstrate that a precise control of alloying elements and microstructure enables the tailored design of lightweight alloys for high-performance structural applications.

Keywords: Fe-Mn-Al-C alloys, Thermodynamic modeling,  $\kappa$ -carbide, Microstructural design, Phase stability

Acknowledgement: Tamiru Hailu Kori would like to acknowledge the Pro-quality program for support in starting scientific activities in new research topics as part of the Excellence Initiative – Research University program, grant no. 32/014/SDU/10-22-002.

# USING THERMODYNAMICS TO SOLVE CRYSTAL STRUCTURES OF TERNARY INTERMETALLICS IN THE FE-AL-SI SYSTEM

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Main topic: Phase diagrams and phase equilibria

Secondary topic: Phase transformations and kinetics, Solid state diffusion

Abstract:

As two of the most common materials in structural engineering, steel and aluminum are widely used together due to their complementary advantages in toughness and ductility. Upon joining these materials, they tend to form intermetallic phases via diffusion. Since silicon is a common alloying element in aluminum, the Fe-Al-Si system is particularly important. This system contains at least 11 known ternary intermetallics ( $\tau_1$ – $\tau_{12}$ , with  $\tau_1$  and  $\tau_9$  later identified as the same phase). Among these, the Al-rich phases  $\tau_{10}$  ( $\text{Fe}_{24}\text{Al}_{60}\text{Si}_{16}$ ) and  $\tau_{11}$  ( $\text{Fe}_{24}\text{Al}_{66}\text{Si}_{10}$ ) have now been structurally and thermodynamically characterized.

Microstructural analysis on arc melted, equilibrated and afterwards quenched alloys confirm, as it concerns the  $\tau_{10}$  and  $\tau_{11}$  phases, that only  $\tau_{10}$  occurs at 650 °C, that only  $\tau_{11}$  occurs at 800 °C, whereas at 727 °C both phases can occur in equilibrium, in spite of the rather similar compositions. Analysis of the respectively hexagonal crystal structures reveals that the unit cell of  $\tau_{11}$  is a 2 x 2 x 1 superstructure of that of  $\tau_{10}$ , containing, however, both Fe and Al/Si vacancies.

Due to the similar scattering factors of Al and Si, conventional X-ray diffraction methods largely fail to resolve their mutual ordering. Therefore, we have used density functional theory calculations to determine preferred sublattice occupations. This also allowed to conclude defect formation enthalpies, which were used to establish possible transition paths between  $\tau_{10}$  and  $\tau_{11}$ . The formation enthalpies of different structural variants were well described using a Compound Energy Formalism based on fully occupied or vacant sublattices.

It will be tried to draw a comprehensive picture of the thermodynamics and other properties of the  $\tau_{10}$  and  $\tau_{11}$  and how they are linked.

Keywords: Compound energy formalism (CEF), Density functional theory (DFT), Phase equilibria, Vacancies, Ordering

# ON THE PRACTICAL APPLICATION OF ELECTROCHEMICAL PHASE DIAGRAMS TO BINARY METAL DEPOSITION

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Main topic: Phase diagrams and phase equilibria

Secondary topic: Thermochemistry of metallurgical processes

Abstract:

This poster presents the practical application of electrochemical phase diagrams (ECPDs) to the interpretation and prediction of binary metal electrodeposition from molten salt electrolytes. While the theoretical basis of ECPDs is established through electrochemical and thermodynamic considerations, their real value lies in their ability to support the analysis of experimentally relevant systems and to identify the conditions (temperature and electrolyte composition) under which pure metals, solid solutions, two-phase regions, or intermetallic compounds may form on the cathode during galvanostatic deposition. The poster therefore focuses on representative literature examples of binary metallic systems deposited from molten salts and demonstrates how ECPDs can be used as an interpretive framework for these cases. The examples included in the poster is selected from recent studies on binary metallic systems co-deposited e.g. from molten fluoride and chloride electrolytes.

Keywords: Phase diagram, Binary co-deposition, Galvanostatic, Electrolyte, Molten salt

References:

1. A. Rudenko et al: "Synthesis of Al-Y Master Alloy via Electrolysis of Low-Temperature Fluoride-Oxide Melt", J. Electrochem. Soc. **172** (2025) 082503.
2. E. Brosh et al: "Phase diagrams for electrodeposition of alloys from molten chlorides", Electrochim. Acta (2026) 148411.
3. M.V. Erzhakov et al: "Electrochemical Behavior of Scandium Ions in the LiCl-KCl Eutectic Melt", J. Electrochem. Soc. **173** (2026) 092501.
4. E. Brosh et al: "Calculation of Littlewood predominance diagrams for metal electrodeposition from molten chlorides using CALPHAD software and databases", Electrochim. Acta **492** (2024) 144322.

# HIGH TEMPERATURE PHYSICAL CHEMISTRY OF SULFUR REMOVAL FROM NICKEL-BASED SUPERALLOY BY CAO-CAF<sub>2</sub>-AL<sub>2</sub>O<sub>3</sub>-MGO SLAG

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Main topic: Thermochemistry of metallurgical processes

Secondary topic: Thermochemistry, thermodynamic properties

Abstract:

Sulphur (S), a major impurity element in nickel superalloys, forms non-metallic inclusions, and can act as crack initiation sites under high temperature loading conditions [1]. Therefore, effective control of S is essential for producing high performance Ni-superalloys. In this study, thermochemical equilibrium experiments and kinetic experiments were conducted at 1823 K to investigate the effects of the CaO/CaF<sub>2</sub> ratio and Al<sub>2</sub>O<sub>3</sub> content in the CaO-CaF<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-MgO slag on the desulphurisation behaviour of a Ni-based alloy. At a fixed Al<sub>2</sub>O<sub>3</sub> content, the S distribution ratio ( $L_S = (\%S)/[\%S]$ ) increased with increasing CaO/CaF<sub>2</sub> ratio. In contrast, it generally decreased with increasing Al<sub>2</sub>O<sub>3</sub> content. This is because Al<sub>2</sub>O<sub>3</sub> acts as an acidic oxide in the slag, decreasing the slag basicity and thereby reducing the thermodynamic driving force for desulphurisation. By analysing the relationship among CaO activity ( $a_{CaO}$ ), S distribution ratio, and sulphide capacity ( $C_S^{2-}$ ), it was confirmed that CaO is the major factor with the greatest influence on desulphurisation capability. The kinetic analysis showed that Al<sub>2</sub>O<sub>3</sub> addition decreased the S removal rate, and the rate-controlling step of desulphurisation shifts from slag-phase or slag-metal mixed mass transfer to metal-phase mass transfer below 20 wt. % Al<sub>2</sub>O<sub>3</sub>. Based on the experimental results, considering both the slag melting rate and sulphur refining capacity, the Al<sub>2</sub>O<sub>3</sub> content should be controlled not more than 20 wt. % and there is no significant difference in terms of sulphur removal rate when the Al<sub>2</sub>O<sub>3</sub> content is 10% or less.

Keywords: Nickel superalloy, Desulphurisation, Slag, Thermodynamics, Kinetics

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# PHASE EQUILIBRIA IN THE AL-RICH CORNER OF THE AL-CR-LA TERNARY SYSTEM AT 600 °C

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Main topic: Experimental and theoretical thermodynamics

Secondary topic: Phase diagrams and phase equilibria

Abstract:

Phase equilibria in the Al-rich corner of the Al-Cr-La ternary system were investigated at 600 °C for compositions with a minimum aluminium content of 99.45 at.%. Equilibrium phases, transformation temperatures, and microstructural evolution were determined experimentally by isothermal annealing (600 °C for 600 hours) and differential scanning calorimetry (DSC), with comprehensive characterisation performed using scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDXS). In the region with increased Cr content, the equilibrium microstructure comprises the aluminium matrix (Al), the binary phase  $\text{Al}_{45}\text{Cr}_7$ , and the ternary phase  $\text{LaCr}_2\text{Al}_{20}$  while in the region with increased La content, it consists of (Al), the mixture (Al) +  $\text{Al}_{11}\text{La}_3$ , and the ternary  $\text{LaCr}_2\text{Al}_{20}$  phase. These results are consistent with existing literature and provide new, detailed experimental evidence regarding the composition and microstructure of these phases. Notably, this study demonstrates that the ternary  $\text{LaCr}_2\text{Al}_{20}$  phase forms readily, even with minor alloying additions as low as 0.03 at.% La and/or Cr. DSC investigations identified characteristic temperatures essential for planning effective heat treatments for newly developed aluminium alloys. The region with increased Cr content appears particularly promising for the development of high-performance aluminium-based materials; furthermore, as even small amounts of La promote the formation of the  $\text{LaCr}_2\text{Al}_{20}$  phase, this work highlights significant potential for economically viable alloy development.

Keywords: Al-Cr-La, Phase equilibria, Ternary phase system, Microstructure

Acknowledgment: We gratefully acknowledge the financial support of the Slovenian Research and Innovation Agency (ARIS) for funding under program grant P1-0195 (B).

# TRANSIENT PHENOMENA OF NMI-EVOLUTION OBSERVED DURING AL-KILLED MEDIUM CARBON STEELS

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Main topic: Industrial applications of thermodynamics

Secondary topic: Oxides (phase diagrams, corrosion)

Abstract:

The transient conditions of non-metallic inclusion (NMI) formation are possible to observe, mostly in relation to the design of melt chemical composition, slag formation, starting deoxidation practice, alloying and all within time scale consideration to reach sufficient interactions between NMI and melt as between slag and NMI. The time scale and effective slag mixing measurably change the chemical compositions of pre-existing NMIs. In the final refined steel melts, focus is given mostly on the presence of solid products: CaS, spinel ( $\text{MgAl}_2\text{O}_4$ ) and solid CA. In this study, examples are given by presenting the ternary elemental plots instead of pre-defined oxide or sulphide plots, as certain information is lost in the latter approach. The transient evolution of NMIs, especially in the finishing stage of secondary metallurgy, has gained more attention as understanding the kinetics considerably affects the knowledge of casting performance, especially under small-diameter nozzles (SEN) compared to large-diameter nozzles (slabs), where the stopper influences sensitivity in disturbing the casting operation. Therefore, time window adjustments for NMI modification can have a tremendous effect on clogging despite having the same strategy of NMI formation and modification from heat to heat. To observe the NMI nature of chemical variations, observed as a transient phenomenon in the desire to achieve target NMIs, was observed under automatic image analysis (AIA). The results reveal that under similar processing steps, different casting performance is experienced in relation to the evolution of NMIs, slag composition adjustment and melt-slag interactions. Among in-situ slag composition measurements, AIA, predicting the activities of oxides in refining slags in relation to elemental activities, is being more regularly used in the production environment, as shown in this study. Predominantly to predict the slag stability for late additions of stronger deoxidant and/or sulphur additions.

Keywords: Thermodynamic predictions, Al-killed steel, Transient NMI evolution, Deoxidation, Re-sulfurization

# INFLUENCE OF NICKEL CONTENT ON THE THERMAL STABILITY OF SPINEL LNMO CATHODE MATERIALS

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Main topic: Thermodynamics of energy storage materials

Secondary topic: Thermochemistry, thermodynamic properties (liquids, solids, amorphous materials)

Abstract:

Spinel structured lithium nickel manganese oxide (LNMO,  $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ ,  $x \leq 0.5$ ) is a promising candidate as cathode material for the next generation of lithium-ion batteries (LIBs). LNMO could enable LIBs with open circuit voltage of around 4.7 V and high specific energy/energy densities of up to  $300 \text{ Wh}\cdot\text{kg}^{-1}$  and  $750 \text{ Wh}\cdot\text{l}^{-1}$ . These materials show in general long battery cycle life stability (1000–6000 cycles) and their production is not reliant on the critical element cobalt [1,2]. Because of LNMOs stoichiometry ( $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ ,  $x \leq 0.5$ ), the redox potential of  $\text{Ni}^{2+/4+}$  can be fully used, while its spinel structure allows full electrochemical delithiation without any significant structural changes [3]. However, there are still many open questions regarding LNMOs thermal and structural stability, which are crucial properties regarding battery safety and performance. This conference contribution should address this and give an overview about the effects of the Ni/Mn ratio on the thermal stability of LNMO.

LNMO can crystallize in the disordered (SG  $Fd\bar{3}m$ ) or the ordered structure (SG  $P4_332$ ) in terms of Ni- and Mn-ion distribution [4]. Nickel-rich secondary phases with rock-salt structure can form during synthesis or on heat treatment, influencing the elemental composition of the remaining spinel phase. However, precise annealing methods can reduce the amount of these secondary phases, leading to more pure products [3,4]. Nickel and lithium content can vary from  $x = 0$  to  $0.5$  and  $y = 0$  to  $4$  regarding the formula  $\text{Li}_y\text{Ni}_x\text{Mn}_{2-x}\text{O}_4$  [1]. Our LNMO materials have been synthesized via a Sol-Gel route and investigated in terms of TGA-DSC/MS, powder-XRD, AAS and TXRF. In general, thermal decomposition starts at lower temperatures if LNMO has a disordered structure, a higher nickel, and a lower lithium content. In air  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  disintegrates at around  $700^\circ\text{C}$  under the release of  $\text{O}_2$  giving Ni-rich (Li,Ni,Mn)O and a Ni-poor LNMO. In argon the material decomposes at around  $670^\circ\text{C}$  under  $\text{O}_2$  evolution giving Ni-rich (Li,Ni,Mn)O,  $\text{Mn}_3\text{O}_4$  and  $\text{LiMnO}_2$ . Phase fractions of these products highly depend on the nickel content in the initial LNMO phase.

Keywords: Lithium-Ion Batteries, LNMO, Cathode Material, Thermal Behavior

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# INFLUENCE OF CERIUM AND LANTHANUM ADDITIONS ON AL-SI-MG ALLOYS

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Main topic: Industrial applications of thermodynamics

Secondary topic: Phase diagrams and phase equilibria

Abstract:

In recent years, considerable attention has been given to rare earth additions, as these elements can significantly influence grain refinement, phase distribution, and the solidification behaviour of aluminium alloys. The addition of elements such as lanthanum and cerium can improve strength, toughness, corrosion resistance, and wear resistance, primarily through microstructural modifications and the formation of new intermetallic phases.

In this study, the effects of rare earth additions, specifically lanthanum (La) and cerium (Ce), on the thermodynamic properties and microstructure of Silafont 36 and EN AW-6082 aluminium alloys were investigated. Differential Scanning Calorimetry (DSC) analysis of the Silafont 36 alloy showed that the alloy without rare earth additions exhibited the highest melting enthalpy of the main peak. The addition of lanthanum had a pronounced effect on the modification of the  $\alpha$ -Al +  $\beta$ -Si eutectic, resulting in a finer and more rounded eutectic morphology, whereas the influence of cerium was less significant. Microstructural analysis confirmed the presence of  $\beta$ -Si, eutectic  $Mg_2Si$ , and iron-containing eutectic phases, as well as polygonal  $Al_2Si_2RE$  phases formed by both La and Ce [1,2]. The results indicate that rare earth additions primarily affect microstructural modification and the formation of new intermetallic phases, with lanthanum having a more pronounced effect than cerium.

For the EN AW-6082 alloy, the addition of cerium caused a slight increase in the solidus temperatures of the first two eutectic reactions. The modifying effect of rare earth elements was less pronounced in this alloy than in Silafont 36, which can be attributed to its lower silicon content and the smaller fraction of the  $\alpha$ -Al +  $\beta$ -Si eutectic. Microstructural analysis revealed the presence of phases similar to those observed in Silafont 36, but with a substantially lower eutectic fraction. In addition, quaternary eutectics consisting of  $\alpha$ -Al,  $Mg_2Si$ ,  $\alpha-Al_{15}(Fe,Mn)_3Si_2$ , and  $\beta-Al_5FeSi$  phases were identified in the EN AW-6082 alloy [3].

Keywords: Al-Mg-Si alloys, Rare earths, Lanthanum, Cerium, Microstructure

Acknowledgment: We gratefully acknowledge the financial support of the Slovenian Research and Innovation Agency (ARIS) for funding under program grant P2-0344(B).

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# ANALYSIS OF SOLIDIFICATION HORIZONTALLY CONTINUOUSLY CAST STELLITE

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Main topic: Industrial applications of thermodynamics

Secondary topic: Thermochemistry of metallurgical processes

Abstract:

This study investigates the microstructural, phase, and solidification characteristics of Stellite 6, Stellite 12, and Stellite 21 alloys produced via horizontal continuous casting. The horizontal continuous casting achieves exceptionally high cooling rates and fine-grained microstructures compared to differential scanning calorimetry analysis (DSC). Thermodynamic calculations were performed to predict equilibrium solidification and were compared with experimental observations. Differential scanning calorimetry was utilized to analyze the phase transformation temperatures and solidification behavior, followed by a detailed microstructural analysis of the DSC samples to evaluate phase stability. Optical and scanning electron microscopy (SEM-EDS) revealed Co-rich dendritic grains surrounded by eutectic regions containing  $M_7C_3$ ,  $M_{23}C_6$ , and  $M_6C$  type carbides. X-ray diffraction (XRD) confirmed a dominant FCC Co matrix without HCP phase formation, which is attributed to the rapid cooling and solidification. The volume fraction of carbides increased with higher carbon content, directly influencing the mechanical properties. Vickers hardness measurements showed that Stellite 6 exhibited the highest hardness (508 HV10), followed by Stellite 12 (470 HV10) and Stellite 21 (345 HV10). The finer grain size and elevated carbide fraction in the high-carbon alloys contributed to enhanced hardness and structural uniformity. These findings demonstrate that horizontal continuous casting enables the production of fine-grained Stellite rods with a highly homogeneous composition, excellent structural integrity, and optimal properties for subsequent hard-facing applications in wear-resistant environments.

Keywords: Stellite, Horizontal continuous casting, Hard facing, Carbides

# DEFINING HOMOGENIZATION PARAMETERS FOR ENHANCED FORMABILITY OF EN AW-7020 ALUMINIUM ALLOY USING THERMODYNAMIC SIMULATIONS

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Main topic: Industrial applications of thermodynamics

Secondary topic: Phase diagrams and phase equilibria

Abstract:

The homogenization annealing parameters significantly affect the formability characteristics of aluminium alloy EN AW-7020. This study aims to identify the optimal combination of temperature and time for homogenization treatment using advanced thermodynamic modelling, enabling improved control of microstructural evolution and enhanced formability.

Thermodynamic simulations (Thermo-Calc) were essential for predicting phase transformations and guiding experimental design. These were complemented by differential scanning calorimetry (DSC), optical and scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS), and mechanical testing using a Gleeble 3500-GTC thermomechanical simulator. Cast EN AW-7020 samples were homogenized at 470 °C and 490 °C for durations ranging from 3 to 10 hours.

The results, supported by thermodynamic analysis, show that solidus temperature and yield strength increase with longer homogenization times and higher temperatures, accompanied by grain growth. Simulations accurately predicted the dissolution of the MgZn<sub>2</sub> eutectic phase after 6 hours and the fragmentation and spheroidization of Al<sub>9</sub>Fe<sub>2</sub>Si<sub>2</sub> phases, while confirming the stability of Al<sub>3</sub>(Ti,Zr) particles throughout all treatments.

Based on the combined experimental and simulation-driven approach, the optimal homogenization regime was determined to be 490 °C for 5 hours. This condition yields a solidus temperature of 611.5 °C, a yield strength of 42.71 MPa, and a grain size of 73.4 µm. The integration of thermodynamic simulations was essential in establishing the best balance between phase dissolution, solidus temperature, microstructure refinement, and low deformation stress, thereby defining optimal conditions for subsequent plastic deformation of the EN AW-7020 alloy.

**Keywords:** EN AW-7020 aluminium alloy, Homogenization, Microstructure, Formability, Thermodynamic modelling

**Acknowledgment:** We gratefully acknowledge the financial support of the Slovenian Research and Innovation Agency (ARIS) for funding under program grant P2-0344(B).

# EXPERIMENTAL AND THEORETICAL DESCRIPTION OF THE AL-LA-NI TERNARY SYSTEM

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Main topic: Experimental and theoretical thermodynamics – new results and techniques

Secondary topic: Experimental and theoretical thermodynamics – new results and techniques

Abstract:

This work is focused on thermodynamic modelling of the Al-La-Ni ternary system using the semi-empirical CALPHAD method. Materials based on La-Ni-M-H (M = Al, Cu, Co, Mg) are suitable for hydrogen accumulation, release, and transport, and for its subsequent use as an energy source. Hydrogen has a promising perspective as an energy carrier with the potential to be a clean and efficient energy source in various applications [1, 2], especially in a situation where, for example, the weight and/or insufficient capacity of electric batteries can be a limiting factor for energy storage in modern technologies, including heavy industry as well.

A combination of various sophisticated (theoretical and experimental) methods was used to obtain complex (thermodynamical, thermophysical, and kinetic) knowledge and description of the Al-La-Ni phase diagram. The morphology, overall and phase compositions of samples were analyzed by scanning electron microscopy combined with energy dispersive X-ray spectroscopy detector (SEM-EDX). The diffraction analysis was carried out using X-ray powder diffraction (XRD). Temperatures of phase transitions were measured using DSC equipment Netzsch 404 C. Consequently, the ternary phase diagram Al-La-Ni was assessed by a CALPHAD-type approach by the Thermo-Calc software, using our own experimental data and experimental data published by [3, 4].

Keywords: Al-La-Ni ternary system, Thermodynamic modelling, SEM-EDS analysis

Acknowledgment: This study is a part of the project No. CZ.02.01.01/00/22\_008/0004631 Materials and technologies for sustainable development within the Jan Amos Komensky Operational Program financed by the European Union and from the state budget of the Czech Republic.

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# SN-INDUCED TUNING OF AUSTENITE FINISH TEMPERATURE IN CU-AL-MN SHAPE MEMORY ALLOYS

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Main topic: Phase transformations and kinetics, solid state diffusion

Secondary topic: Thermochemistry, thermodynamic properties (liquids, solids, amorphous materials)

Abstract:

In Cu-Al-Mn shape memory alloys, minor alloying additions provide an effective way to tailor the martensitic transformation temperatures. This work examines the effect of Sn addition on the transformation behaviour and room-temperature phase state of as-cast CuAl9Mn9.5-based alloys. A Sn-free reference alloy and alloys with nominal Sn additions of 0.75, 1.5, and 2.5 wt.% were produced by arc melting and suction-assisted casting into a copper mould. Vickers hardness testing, differential scanning calorimetry (DSC), and optical microscopy were used to evaluate mechanical response, transformation temperatures, and microstructure. DSC showed that Sn progressively lowered the transformation temperatures, with the austenite finish temperature ( $A_f$ ) decreasing from 102.4 °C in the Sn-free alloy to -61.1 °C at 2.5 wt.% Sn. Optical microscopy confirmed the Corresponding phase-state change from martensitic plate/lath morphology in the Sn-free alloy to an austenitic equiaxed-grain microstructure in CuAl9Mn9.5Sn1.5. Vickers hardness increased from 180.5 to 260.6 HV1 with increasing Sn content, indicating that Sn also affected the mechanical response. These results show that Sn addition is an effective route for adjusting  $A_f$  and stabilising the austenitic phase at room temperature in as-cast Cu-Al-Mn shape memory alloys.

Keywords: Cu-Al-Mn shape memory alloys, Sn alloying, Transformation temperatures, Differential scanning calorimetry

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# THERMODYNAMIC STABILITY OF NUCLEI AT GRAPHITE NUCLEATION

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Main topic: Industrial applications of thermodynamics

## Abstract:

The presented study examines the composition and thermodynamic stability of graphite nuclei in spheroidal graphite cast iron produced under industrial conditions. Graphite nuclei were characterized using FE-SEM and EDS analyses, while thermodynamic equilibrium calculations were performed with Thermo-Calc to determine the stability of the phases involved in graphite nucleation.

The thermodynamic calculations showed that MgO is the most stable phase, exhibiting the lowest Gibbs free energy of formation. This indicates that MgO precipitates first in the liquid melt and serves as the primary substrate for graphite nucleation. The next most stable phase is (Mg,Ca)S, which forms after MgO and frequently surrounds the oxide particles. This sequence was confirmed experimentally, supporting a nucleation mechanism in which sulphides precipitate on previously formed MgO particles. Complex nitrides containing Mg, Al, and Si were also detected within some graphite nodules. However, they occurred less frequently and were not directly associated with sulphide particles, suggesting that their contribution to graphite nucleation is secondary.

The close agreement between thermodynamic predictions and microscopic observations demonstrates that the formation of graphite nuclei is largely controlled by the thermodynamic stability of Mg-containing inclusions. Since MgO and (Mg,Ca)S remain solid before solidification begins, they provide effective heterogeneous nucleation sites for spheroidal graphite growth. The study also found that varying the tin (Sn) content did not affect the composition, stability, or formation sequence of graphite nuclei, but only increased the pearlite fraction of the final microstructure.

Overall, the results indicate that graphite nucleation in Fe-C-Si alloys is primarily governed by the sequential formation of thermodynamically stable Mg-containing oxide and sulphide inclusions. While thermodynamic stability determines the order of phase formation, the authors conclude that the complete nucleation mechanism is also influenced by melt chemistry, magnesium treatment, inoculation practice, and solidification conditions.

Keywords: Nodular cast iron, Graphite nucleation, Thermodynamic stability of nuclei, MgO

# THERMAL CARBURISATION AND SURFACE HARDENING OF 92.5W-5.25NI-2.25FE ALLOY

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Main topic: Industrial applications of thermodynamics

Secondary topic: Thermochemistry of metallurgical processes

Abstract:

This study investigates a conventional thermal gas carburisation method to enhance the surface properties of a 92.5W-5.25Ni-2.25Fe tungsten heavy alloy. Guided by Thermo-Calc simulations, samples were exposed to a methane-argon gas mixture at 1100 °C in a vacuum furnace. Microstructural and SEM-EDS analyses confirmed a 42.6 µm deep carburised zone featuring a 7.5 µm thick, crack-free outer layer. Detailed phase characterization successfully identified unreacted tungsten grains enveloped by protective tungsten carbide (WC) shells, alongside complex intermetallic "eta-carbides" (Me<sub>6</sub>C). These phases formed as dissolved tungsten was heavily consumed from the local Ni-Fe binder phase near the surface, leaving it chemically depleted and distinct from the unaltered binder phase at the sample center. The results demonstrate that direct thermal gas carburisation is an effective, straightforward approach for synthesizing advanced, multi-phase protective surfaces on tungsten heavy alloys.

Keywords: Tungsten heavy alloy, Surface hardening, Carbides

# ELECTROCHEMICAL DECOMPOSITION OF WUSTITE (FeO) DISSOLVED IN MOLTEN CRYOLITE: TOWARDS A GREEN STEEL TECHNOLOGY

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Main topic: Experimental and theoretical thermodynamics – new results and techniques

Secondary topic: Oxides (phase diagrams, corrosion)

Abstract:

In this poster electrochemical decomposition of wüstite (FeO) dissolved in molten cryolite at 960 °C is discussed. Iron crystals are deposited on a carbon cathode (with, or without copper coating), while oxygen gas is released on inert anode (platinum or silver), so this is one of the ways of green production of iron, without emitting carbon dioxide into atmosphere. The final iron deposit is collected by re-melting some cryolite with the dispersed concentrated iron crystals. Different chemical side reactions are studied in details and the current efficiency is discussed. The measured electrochemical decomposition potential is used to find the partial molar Gibbs energy of wustite dissolved in the cryolite melt at 960 °C. At around 3 w% of FeO this value appeared close to the standard molar Gibbs energy of FeO, indicating that 3 w% of FeO is close to its solubility in liquid cryolite at 960 °C.

Keywords: Wüstite, Electrochemical decomposition, Solubility of FeO in molten cryolite

# EXPERIMENTAL RESULTS ON THE 1023 K AND 1223 K EQUILIBRIA IN THE NB-MO-ZR (NIOBIUM – MOLYBDENUM – ZIRCONIUM) SYSTEM

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Main topic: Experimental and theoretical thermodynamics – new results and techniques

Secondary topic: Phase diagrams and phase equilibria

Abstract:

Phase equilibria in the Nb-Mo-Zr system is key in the context of developing new metallic Uranium alloys for use as nuclear fuel. The issue is complicated by the fact that Zr has a phase transition from the low temperature hexagonal close packed phase (A3,  $\alpha$ -Zr) to the body centered cubic phase (A2,  $\beta$ -Zr) at 1143 K. Investigating the equilibria with A3 is desirable, but the low temperature is limiting, due to diffusion constraints. The present methodology requires the equilibration at 1223 K for 500 h followed by a seconds heat treatment at 1023 K for additional 500 h. This allows to obtain equilibrium from the as-cast microstructure in the first treatment and then obtaining the low temperature equilibria from this homogeneous microstructure. A second aim of the present work is to investigate the C14/C15 Laves phase equilibria in the system.

Keywords: Nuclear alloys, Refractory alloys, Phase equilibria

# THERMODYNAMIC ASSESSMENT OF THE FE-CO-C SYSTEM USING MODIFIED QUASICHEMICAL MODEL FOR HIGH-TEMPERATURE METALLURGICAL AND BATTERY RECYCLING APPLICATIONS

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Main topic: Phase diagrams and phase equilibria

Secondary topic: Databases development

Abstract:

Recently, cobalt-containing alloys and secondary battery materials have attracted considerable attention due to their importance in high-temperature alloy production and sustainable recovery of critical raw materials. In pyrometallurgical recycling processes, cobalt-bearing battery scrap and metallurgical residues are treated under highly reducing conditions, during which Fe-Co-based liquid alloys form in the presence of carbon. Therefore, accurate thermodynamic descriptions of the Fe-Co-C liquid system are essential for predicting phase equilibria, carbon behavior, and liquid-phase thermodynamic properties during extraction and refining processes.

In the present study, the liquid Fe-Co-C system was thermodynamically assessed using the CALPHAD approach by FactSage thermochemistry software. The liquid solution was modeled using the Modified Quasichemical Model (MQM) in the pair approximation to account for short-range ordering and asymmetry in the liquid phase. The phase equilibrium data available in the literature and our experimental results were critically reviewed and assessed as input values into the optimization procedure.

Particular attention was devoted to the thermodynamic behavior of carbon in the ternary liquid solution. The optimized parameters successfully reproduced the experimentally reported liquidus equilibria over a wide range of compositions. In addition, the MQM description provided significantly improved agreement with the partial enthalpy of mixing of carbon compared with the conventional Bragg-Williams random mixing model. The improved reproducibility indicates that short-range ordering in the liquid phase plays an important role in describing the thermodynamic properties of the Fe-Co-C system.

The developed thermodynamic description provides a reliable basis for further calculations involving cobalt-containing alloy systems and pyrometallurgical recycling processes of battery materials. The obtained parameters can improve predictions of liquid alloy behavior, phase stability, and thermodynamic properties relevant to sustainable recovery and process optimization of critical metals.

Keywords: Fe-Co-C system, Modified Quasichemical Model, Battery Recycling, Thermodynamic Assessment

#### References:

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# METASTABLE ORDERING AND NANODOMAIN FORMATION IN RAPIDLY SOLIDIFIED $\eta$ -Cu<sub>6</sub>Sn<sub>5</sub>

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Main topic: Experimental and theoretical thermodynamics – new results and techniques

Secondary topic: Computational thermodynamics and first-principles calculations

Abstract:

Rapid solidification can induce non-equilibrium atomic arrangements and nanoscale compositional modulations in Cu-Sn alloys [1]. Rapidly solidified Cu-75 at. % Sn alloys exhibit stripe-like nanodomain contrast within  $\eta$ -Cu<sub>6</sub>Sn<sub>5</sub> grains [2]. In this study, TEM, nanobeam diffraction (NBD), STEM-EDS analysis, first-principles calculations, and cluster expansion analysis were used to investigate nanodomain formation in melt-spun Cu–Sn ribbons.

TEM and HAADF-STEM observations revealed periodic Cu-rich and Cu-poor nanodomains in the as-quenched microstructure. NBD measurements showed that the forbidden 001 reflection of the parent h-Cu<sub>6</sub>Sn<sub>5</sub> structure appears selectively in Cu-rich domains but is absent in Cu-poor regions.

Cluster expansion calculations based on density functional theory were performed for the partially occupied Cu(2) sublattice in hexagonal h-Cu<sub>6</sub>Sn<sub>5</sub> [3]. Simulated diffraction patterns demonstrated that the 001 reflection emerges only when the Cu occupancies of the Cu(2) layers at  $z = 1/4$  and  $3/4$  are inequivalent. Comparison with experiment indicated that Cu-rich domains correspond to metastable high-occupancy ordered structures, whereas Cu-poor domains are associated with near-stoichiometric configurations.

The calculated ordering-energy landscape was globally convex and did not support solid-state spinodal instability within the h phase, suggesting that the stripe-like modulation originates from liquid-state compositional modulation inherited during rapid solidification [1]. High-occupancy h structures were thermodynamically unstable relative to decomposition into Cu<sub>3</sub>Sn and near-stoichiometric h phases [3], consistent with experimentally observed Cu<sub>3</sub>Sn precipitation during ageing [2].

Keywords: Rapid solidification, h-Cu<sub>6</sub>Sn<sub>5</sub>, Cluster expansion, Nanodomain, Metastable ordering

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1. D. Li et al: "The Cu–Sn phase diagram part II: New thermodynamic assessment", *Intermetallics* **34** (2013) 148–158.
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3. A. Leineweber, M. Löffler, S. Martin: "Stable and metastable phase equilibria involving the Cu<sub>6</sub>Sn<sub>5</sub> intermetallic", *Journal of Electronic Materials* **50** (2021) 5898–5914.

# LOW-CARBON AND CIRCULAR VALORISATION OF SECONDARY MATERIALS IN ELECTRIC FURNACES FOR HIGH-QUALITY STEELMAKING

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Main topic: Experimental and theoretical thermodynamics – new results and techniques

Abstract:

The CircSmeltSteel project funded by the European Union within the Clean Steel Partnership (Grant Agreement no. 101294187) validates the use of metallurgical by-products as secondary sources in low-carbon iron and steelmaking (Electric Smelting Furnace/ESF; Electric Arc Furnace/EAF). The project aims to clarify the impact of steel quality on product properties, while contributing to EU objectives related to net-zero manufacturing, sustainability, and competitiveness in the Net-Zero Industry Act, Clean Industrial Deal, Steel and Metals Action Plan.

The research encompasses the entire steelmaking value chain, from primary and secondary metallurgy and continuous casting to hot rolling, cold rolling and annealing. A low-CO<sub>2</sub> production route based on the ESF-EAF route and EAF as stand-alone recycling route is investigated using a system-level approach that incorporates metallurgical by-products as alternative feedstock at both, pilot and industrial scales. The resulting steel will be evaluated at elevated levels of tramp and residual elements including nitrogen, phosphorus, sulphur, copper, molybdenum and tin. Advanced experimental techniques, such as Gleeble simulations and dilatometry, will be employed to support the EU zero-defect manufacturing objectives.

CircSmeltSteel also supports the EU's zero-waste and industrial symbiosis goals by promoting classification of the ESF and EAF slags as secondary raw materials for use in other industrial sectors. In addition, a skills development strategy aligned with the Industry 5.0 paradigm will enhance societal readiness for the adoption of lower-quality materials in low-carbon steelmaking technologies.

All data and models generated within the project will be integrated into a digital platform, providing a robust data management framework for R&D projects in the steel industry. The consortium combines expertise in metallurgy, plant technology, process automation, and circularity, supported by leading scientific partners. CircSmeltSteel will increase awareness of the importance of utilizing lower quality metallurgical by-products in green steel production and facilitate their large-scale implementation, thereby contributing to a resource-efficient and competitive economy. The business potential is substantial, with an estimated 80 million tonnes of metallurgical by-product recycled annually through the ESF-EAF route and the potential to replace conventional blast furnace-based production routes in integrated steel plants.

Keywords: Green steelmaking process chain, low-quality metallurgical by-products, Electric Furnace, material and process modelling