CALPHAD XLVIII

Conference on Computer Coupling of Phase Diagrams and Thermochemistry

June 2nd - June 7th, 2019
Singapore
Agenda and Abstracts

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Computer Coupling of Phase Diagrams and Thermochemistry

June 2nd - June 7th, 2019

Singapore
Preface

Dear participants,

Welcome to the 48th CALPHAD International Conference. We stick to the CALPHAD tradition of a single session throughout the 5-day conference, so that every speaker has the full attention of all the participants. Each speaker is equivalent to an invited speaker defined in other conferences. Thus, we hope to facilitate the formation of new ideas and collaborations in CALPHAD development, and to expose newcomers and students to the state-of-art advancements and new strategic research directions.

Singapore is a metropolitan city state, and an island links the Strait of Melaka to the South China Sea, therefore, its Maritime & Offshore industry plays an important role to Singapore economy. In order to benefit both Singapore and the CALPHAD community, the local conference organization committee secured funds from the National Research Foundation Singapore to co-fund a workshop/software demo on thermodynamics for maritime applications. We hope to bridge the gap between CALPHAD and maritime techniques.

Last year, we witnessed outstanding research activities reported at the CALPHAD Mexico conference. To continue the promising trend, we selected 71 oral and 107 poster presentations. These presentations are covered under three traditional and new CALPHAD techniques; (1) Classical Calpahd (CC) – phase diagrams and thermodynamics properties, (2) Advanced CALPHAD (AC) – combined with complementary techniques like DFT, AI and Phase Fields, and (3) Functional CALPHAD (FC) – calculation of physical/functional properties from CALPHAD database/solutions. About 60%, 30% and 10% of the selected presentations are respectively from the CC, AC and FC techniques. It will be interesting, in the future conferences, to look out the progress in each of these three CALPHAD sub-categories. To facilitate the formation of new ideas and strategic research directions, a panel discussion session is set up before the closure of the conference on Friday.

Finally, we are grateful to all the supporters and sponsors. With this, we would like to warmly welcome you to Singapore. We sincerely hope that you will enjoy your time and your fruitful exchanges here.

Ping WU
We would like to cordially acknowledge our sponsors

Thermo-Calc Software

HERMFACT

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NATIONAL RESEARCH FOUNDATION
PRIME MINISTER’S OFFICE
SINGAPORE

micress

LANDAT

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The Spencer Group Inc.

GT-TECHNOLOGIES
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<tr>
<td>List of participants</td>
<td>208</td>
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</table>
## CALPHAD XLVIII Organizing Committee

<table>
<thead>
<tr>
<th>Role</th>
<th>Name</th>
<th>Institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chair</td>
<td>Prof. Ping Wu</td>
<td>Singapore University of Technology and Design, Singapore</td>
</tr>
<tr>
<td>Honorary Chair</td>
<td>Prof. Zi-Kui Liu</td>
<td>Pennsylvania State University, USA</td>
</tr>
<tr>
<td>Member</td>
<td>Prof. Yuan Ping Feng</td>
<td>National University of Singapore, Singapore</td>
</tr>
<tr>
<td>Member</td>
<td>Dr. Kewu Bai</td>
<td>Institute of High Performance Computing, Singapore</td>
</tr>
<tr>
<td>Member</td>
<td>Dr. Anariba Franklin Edwin</td>
<td>Singapore University of Technology and Design, Singapore</td>
</tr>
<tr>
<td>Member</td>
<td>Prof. Pinaki Sengupta</td>
<td>Nanyang Technological University, Singapore</td>
</tr>
<tr>
<td>Member</td>
<td>Dr. Michael Sullivan</td>
<td>Institute of High Performance Computing, Singapore</td>
</tr>
<tr>
<td>General Secretary</td>
<td>Ms Magdelaine Tan</td>
<td>Singapore University of Technology and Design, Singapore</td>
</tr>
</tbody>
</table>
# Scholarships

## Recipients of the Larry Kaufman Scholarships

<table>
<thead>
<tr>
<th>Name</th>
<th>University/Institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boon Teoh Tan</td>
<td>Singapore University of Technology and Design, Singapore</td>
</tr>
<tr>
<td>Chenyang Zhou</td>
<td>University Science and Technology Beijing, China</td>
</tr>
<tr>
<td>Qisheng Feng</td>
<td>Shanghai University, China</td>
</tr>
<tr>
<td>Roncallo Giacomo</td>
<td>University of Genoa, Italy</td>
</tr>
<tr>
<td>Schorne Pinto Juliano</td>
<td>Institut National Polytechnique de Toulouse, France</td>
</tr>
<tr>
<td>Rodrigo Tolosa Martín</td>
<td>Universidad Nacional de Tucumán, Argentina</td>
</tr>
<tr>
<td>Gu Qing</td>
<td>Illinois Institute of Technology, USA</td>
</tr>
<tr>
<td>Shao-yu Yen</td>
<td>National Cheng Kung University, Taiwan</td>
</tr>
<tr>
<td>Elerbrock Borowski Karoline</td>
<td>University of São Paulo, Brazil</td>
</tr>
<tr>
<td>Bajenova Irina</td>
<td>National University of Science and Technology, Russia</td>
</tr>
<tr>
<td>Jayshri Milind Dumbre</td>
<td>Monash University, Australia</td>
</tr>
<tr>
<td>Kim Hong Yeun</td>
<td>Pennsylvania State University, USA</td>
</tr>
<tr>
<td>Anna Vasileva</td>
<td>Saint-Petersburg Mining University, Russia</td>
</tr>
</tbody>
</table>

## Recipients of the Y. Austin Chang-PANDAT Scholarships

<table>
<thead>
<tr>
<th>Name</th>
<th>University/Institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dobosz Alexandra</td>
<td>Institute of Metallurgy and Materials Science of the Polish Academy of Sciences, Poland</td>
</tr>
<tr>
<td>Lebedev Andrei</td>
<td>Singapore University of Technology and Design, Singapore</td>
</tr>
</tbody>
</table>
Conference Site and Accommodation

Grand Mercury Roxy Hotel, Singapore, located in the charming East Coast region of Singapore, 15 minute drive from both Changi Airport and the Singapore City Centre, 10 minute drive from Singapore Sports Hub, National Stadium and the Marina Bay Cruise Centre, also walking distance to East Coast beach, well-known shopping malls, and popular food centres.

50 East Coast Road, Roxy Square, Marine Parade Road, Singapore 428769
Phone: +6563448000
Conference Excursion and Banquet

Conference banquet will be held at 18:00 pm on June 6, 2019. You will have a wonderful time with delicious Chinese food and local music performance.

You will be invited to take part in a social tour at 13:00 pm on June 6, 2019 to the Gardens by the Bay, a huge, colourful, futuristic park in the bay area of Singapore. There are many attractions, such as Flower Dome, Cloud Forest, Supertree Groves, Floral Fantasy, and Heritage Gardens. We believe that you will fill up your cameras storage with amazing pictures.
## Conference Program of CALPHAD XLVIII 2019

### Sunday  June 2

<table>
<thead>
<tr>
<th>Time</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>14:00 - 18:00</td>
<td>Registration</td>
</tr>
<tr>
<td>18:00 - 20:00</td>
<td>Cocktail Reception</td>
</tr>
</tbody>
</table>

Venue: Grand Mercury Roxy Hotel, Singapore
<table>
<thead>
<tr>
<th>Time</th>
<th>Session/Chair</th>
<th>Topic</th>
</tr>
</thead>
<tbody>
<tr>
<td>08:40</td>
<td>OPENING</td>
<td>Ping Wu</td>
</tr>
<tr>
<td>09:00</td>
<td>SESSION 1</td>
<td>Modeling &amp; Theory</td>
</tr>
<tr>
<td></td>
<td>Chairs:</td>
<td>J.-M Joubert, Sergei A Decterov</td>
</tr>
<tr>
<td>09:00</td>
<td>O01 Zi-Kui</td>
<td>CALPHAD modeling, machine learning, and information</td>
</tr>
<tr>
<td></td>
<td>Liu</td>
<td></td>
</tr>
<tr>
<td>09:20</td>
<td>O02 Taichi</td>
<td>Magnetic contributions to the vacancy formation in pure</td>
</tr>
<tr>
<td></td>
<td>Abe</td>
<td>elements</td>
</tr>
<tr>
<td>09:40</td>
<td>O03 S. G. Fries</td>
<td>Discussion on the implementation of the Effective Bond</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Energy Formalism (EBEF)</td>
</tr>
<tr>
<td>10:00</td>
<td>O04 M. Selleby</td>
<td>Third generation of thermodynamic descriptions</td>
</tr>
<tr>
<td>10:20</td>
<td></td>
<td>Coffee-break</td>
</tr>
<tr>
<td>10:40</td>
<td>SESSION 2</td>
<td>Modeling &amp; Optimization - 1</td>
</tr>
<tr>
<td></td>
<td>Chairs:</td>
<td>Zi-Kui Liu, C.G. Schön</td>
</tr>
<tr>
<td>10:40</td>
<td>O05 Ping Wu</td>
<td>Entropic Models for Surfaces and Interface Research</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A general &quot;geometric&quot; thermodynamic model for</td>
</tr>
<tr>
<td></td>
<td></td>
<td>multicomponent solutions</td>
</tr>
<tr>
<td>11:00</td>
<td>O06 Sergei A. Decterov</td>
<td>Thermodynamic assessment of the KF-BeF$_2$, KCl-BeCl$_3$,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BeF$_2$-BeCl$_3$ and KF-KCl systems towards an investigation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>on the K, Be//F, Cl reciprocal phase equilibria</td>
</tr>
<tr>
<td>11:20</td>
<td>O07 Kun Wang</td>
<td>Using extent of reaction in CALPHAD modeling</td>
</tr>
<tr>
<td>11:40</td>
<td>O08 P. Koukkari</td>
<td>Lunch</td>
</tr>
<tr>
<td>12:00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13:40</td>
<td>SESSION 3</td>
<td>Modeling and Optimization - 2</td>
</tr>
<tr>
<td></td>
<td>Chairs:</td>
<td>Qing Chen, Taichi Abe</td>
</tr>
<tr>
<td>13:40</td>
<td>O09 R. Schmid-Fetzer</td>
<td>Combining Python and Pandat to assess kinetic and alloy</td>
</tr>
<tr>
<td></td>
<td></td>
<td>design parameters for precipitation simulation</td>
</tr>
<tr>
<td>14:00</td>
<td>O10 Yu Zhong</td>
<td>The CALPHADPLUS approach for multicomponent ionic</td>
</tr>
<tr>
<td></td>
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<td>solid solution oxides</td>
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<tr>
<td>14:20</td>
<td>O11 Shenglan Yang</td>
<td>OpenIEC: An open-source code for interfacial energy</td>
</tr>
<tr>
<td></td>
<td></td>
<td>calculation in alloys</td>
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<tr>
<td>14:40</td>
<td>O12 Aurélie Jacob</td>
<td>Thermodynamic modeling of G-phase for applied</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CALPHAD in Fe-based alloys</td>
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<tr>
<td>15:00</td>
<td>O13 Chuan Zhang</td>
<td>CALPHAD-based modeling of cooling rate influence on</td>
</tr>
<tr>
<td></td>
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<td>solidification microstructure in magnesium alloys</td>
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<tr>
<td>15:20</td>
<td></td>
<td>Coffee-break</td>
</tr>
<tr>
<td>15:50</td>
<td>SESSION 4</td>
<td>Modeling and Simulation -1</td>
</tr>
<tr>
<td></td>
<td>Chairs:</td>
<td>Chuan Zhang, Aurélie Jacob</td>
</tr>
<tr>
<td>15:50</td>
<td>O14 Qing Chen</td>
<td>A general simplified growth model for multicomponent</td>
</tr>
<tr>
<td></td>
<td></td>
<td>precipitation and its implementation in TC-PRISMA</td>
</tr>
<tr>
<td>16:10</td>
<td>O15 C.G. Schön</td>
<td>Diffusion paths in highly concentrated alloys: is there such</td>
</tr>
<tr>
<td></td>
<td></td>
<td>a thing as a ‘sluggish diffusion’?</td>
</tr>
<tr>
<td>16:30</td>
<td>O16 A. Kwiatkowski da Silva</td>
<td>Thermodynamics of grain boundary segregation and</td>
</tr>
<tr>
<td></td>
<td></td>
<td>interfacial spinodal: A CALPHAD-based modeling</td>
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<tr>
<td></td>
<td></td>
<td>approach and near-atomic scale characterization</td>
</tr>
<tr>
<td>16:50</td>
<td>O17 Hong Mao</td>
<td>Phase field simulation of 6XXX Al-Mg-Si alloys during the</td>
</tr>
<tr>
<td></td>
<td></td>
<td>whole ageing process and its experimental verification</td>
</tr>
<tr>
<td>17:10</td>
<td>O18 K. Abrahams</td>
<td>Generalized pair-diffusion model for multi-principal</td>
</tr>
<tr>
<td></td>
<td></td>
<td>element alloys</td>
</tr>
<tr>
<td>18:30</td>
<td></td>
<td>Posters &amp; Drink Session (P01-P53)</td>
</tr>
<tr>
<td>Time</td>
<td>Session</td>
<td>Topic</td>
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<tr>
<td>08:40</td>
<td>SESSION 5</td>
<td>Modeling and Simulation - 2</td>
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<tr>
<td></td>
<td></td>
<td>A model for assessing grain boundary thermodynamics based on the available bulk thermodynamics data</td>
</tr>
<tr>
<td>09:00</td>
<td></td>
<td>Role of materials informatics in computer-based design of Ni-Co-based single crystal superalloys</td>
</tr>
<tr>
<td>09:20</td>
<td></td>
<td>High throughput screening of alloy catalysts for PEMFC and machine learning prediction of chemisorption</td>
</tr>
<tr>
<td>09:40</td>
<td></td>
<td>Modelling of vacancies in the compound-energy formalism</td>
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<tr>
<td>10:00</td>
<td></td>
<td>High-throughput alloy design platform for Al-Si-Mg casting alloys driven by computational thermodynamics &amp; phase-field modeling</td>
</tr>
<tr>
<td>10:40</td>
<td>SESSION 6</td>
<td>Modeling and Simulation - 3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bayesian uncertainty quantification and information fusion in CALPHAD-based thermodynamic modeling</td>
</tr>
<tr>
<td>11:00</td>
<td></td>
<td>Modeling of Os-Pt system under high hydrostatic pressure</td>
</tr>
<tr>
<td>11:20</td>
<td></td>
<td>Thermodynamic stability of substitutional elements in potential new permanent magnet compounds R(Fe,X)_{12} using Special Quasirandom Structures</td>
</tr>
<tr>
<td>11:40</td>
<td></td>
<td>Lunch</td>
</tr>
<tr>
<td>13:40</td>
<td>SESSION 7</td>
<td><em>Ab initio</em> Calculations</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Melting parameters from <em>ab initio</em> using the fast statistical sampling TOR-TILD approach: Applications to Al and Ni</td>
</tr>
<tr>
<td>14:00</td>
<td></td>
<td>Improving Al wettability on B_{12}C by transition metal doping: A combined DFT and experiment study</td>
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<tr>
<td>14:20</td>
<td></td>
<td>First-principles-only phase diagram for the Al-Ni system</td>
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<tr>
<td>14:40</td>
<td></td>
<td><em>Ab initio</em> phase stability and electronic conductivity of the doped-Li_{2}Ti_{2}O_{5} anode for Li-ion batteries</td>
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<tr>
<td>15:00</td>
<td></td>
<td>Coffee-break</td>
</tr>
<tr>
<td>15:50</td>
<td>SESSION 8</td>
<td>Thermodynamic Assessment</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Thermodynamic assessment and experimental study of the Cu-Cr-O system</td>
</tr>
<tr>
<td>16:10</td>
<td></td>
<td>Thermodynamic assessment and experimental investigations of the Al–Fe–Mn–Ni system</td>
</tr>
<tr>
<td>16:30</td>
<td></td>
<td>Thermochemistry of the CaO-TiO_{2} and SrO-ZrO_{2} system: From enthalpies of formation and heat capacities of the compounds to the phase diagram</td>
</tr>
<tr>
<td>16:50</td>
<td></td>
<td>The fast silver ion conducting solid-state electrolytes for deriving thermodynamic data</td>
</tr>
<tr>
<td>17:10</td>
<td></td>
<td>The intermetallic compound Co–Ta and high-temperature phase equilibria in the Co–Ni–Ta system</td>
</tr>
<tr>
<td>18:30</td>
<td></td>
<td>Posters &amp; Drink Session (P54-P107)</td>
</tr>
<tr>
<td>Time</td>
<td>Session</td>
<td>Title</td>
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<td>--------------------------------------------</td>
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<tr>
<td>08:40</td>
<td>O25</td>
<td>First principles study of oxygen self-diffusion and thermal expansion in zirconia</td>
</tr>
<tr>
<td>09:00</td>
<td>O48</td>
<td>BCC-HCP-FCC multiple martensitic transformations in Fe-Co-Cr-Mn high entropy alloys</td>
</tr>
<tr>
<td>09:20</td>
<td>O49</td>
<td>Crystal structures and phase equilibria of RE-Mn-based alloys</td>
</tr>
<tr>
<td>09:40</td>
<td>O70</td>
<td>Insight into the thermodynamic and kinetic stabilities of compositionally complex high entropy alloys of Ni-Cr-Fe-Co-Al-Ti-Cu via a pseudo binary phase diagram models</td>
</tr>
<tr>
<td>10:00</td>
<td>O51</td>
<td>Quantified uncertainty in CALPHAD for materials design</td>
</tr>
<tr>
<td>10:20</td>
<td></td>
<td><strong>Coffee-break</strong></td>
</tr>
<tr>
<td>10:40</td>
<td>O52</td>
<td>Thermodynamic re-assessment of pure chromium using modified segmented regression model</td>
</tr>
<tr>
<td>11:00</td>
<td>O53</td>
<td>Thermodynamic reassessment of actinide-iron systems</td>
</tr>
<tr>
<td>11:20</td>
<td>O54</td>
<td>Thermodynamic modeling of Fe-Mn-Si-C system</td>
</tr>
<tr>
<td>11:40</td>
<td>O55</td>
<td>Calculation of grain boundary segregation in steels by CALPHAD method</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>Lunch</strong></td>
</tr>
<tr>
<td>13:40</td>
<td>O56</td>
<td>FeB-12wt.%AlO$_3$FeNiCoCr cermet coating deposited by AC-HVAF and its corrosion resistance to molten zinc</td>
</tr>
<tr>
<td>14:00</td>
<td>O57</td>
<td>Synthesis of pure intermetallic phases in temperature gradient</td>
</tr>
<tr>
<td>14:20</td>
<td>O58</td>
<td>Design of new weldable TiAl-based alloy with the CALPHAD tools</td>
</tr>
<tr>
<td>14:40</td>
<td>O59</td>
<td>Corrosion properties of Al-Mg and Al-Mg-Si coated steel (I)</td>
</tr>
<tr>
<td>15:00</td>
<td>O60</td>
<td>Thermal barrier coatings phase stability and in service degradation: Thermodynamic and experimental study of CMAS corrosion on Ansaldo Energia’s materials</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>Coffee-break</strong></td>
</tr>
<tr>
<td>15:50</td>
<td>O61</td>
<td>Designing of low-cost titanium alloy based on the assessment of Ti-Al-Fe-V system</td>
</tr>
<tr>
<td>16:10</td>
<td>O62</td>
<td>Development of the ballast water sterilization system in ships using computer simulations</td>
</tr>
<tr>
<td>16:30</td>
<td>O63</td>
<td>CALPHAD-based sensitivity analysis for alloy composition design in alloy additive manufacturing</td>
</tr>
<tr>
<td>16:50</td>
<td>O64</td>
<td>Calculation of phase diagrams for one component macro- and nano-systems taking into account the effect of surface melting</td>
</tr>
<tr>
<td>17:10</td>
<td>O65</td>
<td>Application of phase equilibria in smelting reduction of titaniferous magnetite</td>
</tr>
<tr>
<td>18:30</td>
<td>22:00</td>
<td>Marine Offshore and Software DEMO in Roxy 1 room</td>
</tr>
<tr>
<td>19:00</td>
<td>21:00</td>
<td>CALPHAD Board Meeting in Roxy 2 room</td>
</tr>
</tbody>
</table>

**Wednesday June 5**
Marine Offshore and Software DEMO
18:30-22:00, Roxy 1 room
Partially funded by the National Research Foundation, Prime Minister’s Office, Singapore under its Marine Science Research and Development programme

Chairs: Sang Sub Kim, Kewu Bai

Dr. Jae-In Jeong  Corrosion properties of Al-Mg and Al-Mg-Si coated steel (II)  18:30
Prof. Hideyuki Kanematsu  Interaction between metallic materials and extracellular polymeric substances for biofouling - from the viewpoint of materials protection  19:00
Dr. Qing Chen  Thermo-calc  19:30
Dr. Chuan Zhang  Pandat  20:00
Richard A. Otis  PyCalphad and ESPEI  20:30
Dr. Sergei Decterov, Dr. Moritz Moritz to Baben  FactSage  21:00

Software demo  21:30
### Thursday June 6

#### SESSION 9: Alloys and Oxides - 3

**Chairs**: V.B. Rajkumar

<table>
<thead>
<tr>
<th>Time</th>
<th>Paper ID</th>
<th>Name</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>08:40</td>
<td>O38</td>
<td>Yanglin Wang</td>
<td>Study on the phase equilibria of the Au-Pt-Co system</td>
</tr>
<tr>
<td>09:00</td>
<td>O39</td>
<td>M.J. Kriegel</td>
<td>Modelling of the pressure-dependent phase stability in the binary Ti–Fe system</td>
</tr>
<tr>
<td>09:20</td>
<td>O40</td>
<td>Scott J. McCormack</td>
<td>In-Situ phase diagram determination of the HfO₂-Ta₂O₅-temperature system up to 3000 °C</td>
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<td>09:40</td>
<td>O41</td>
<td>M. Ilatovskaia</td>
<td>Heat capacity of Al₂MnO₄ and thermodynamic assessment of the Al₂O₃-MnO system</td>
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<td>10:00</td>
<td>O42</td>
<td>S. Sineva</td>
<td>Experimental study of the slag/matte/spinel/gas equilibria in the “Cu₂O”-“FeO”-SiO₂-S-Al₂O₃-MgO-CaO system</td>
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#### SESSION 10: Experiment - 2

**Chairs**: M. Ilatovskaia, Yong Du

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<td>I. Fartushna</td>
<td>Experimental study of the phase equilibria in the Co-Fe-La system</td>
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<td>11:00</td>
<td>O44</td>
<td>P. Brož</td>
<td>Experimental study and thermodynamic re-assessment of the Co-Sb system</td>
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<td>11:20</td>
<td>O45</td>
<td>V.B. Rajkumar</td>
<td>Experimental investigation and thermodynamic modeling of Cu-Si-Zr and Ni-Si-Zr integrating ab initio calculation</td>
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#### SESSION 15: Modeling and Experiment
**Chairs:** Zi-Kui Liu, Yong Du

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<td>H. Ohtani</td>
<td>A thermodynamic study on the formation process of Z-phase in heat resistant steels</td>
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<td>O67</td>
<td>G. Kaptay</td>
<td>Extension of the thermodynamics of Gibbs to model interfacial energies for interfaces between any two bulk or nano solution phases</td>
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<td>09:20</td>
<td>O68</td>
<td>Andrei Lebedev</td>
<td>Carbon-doped BiNbO₄ nanoparticles: Urea-assisted synthesis and visible light photocatalytic applications</td>
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<td>O69</td>
<td>In-Ho Jung</td>
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<td>10:00</td>
<td>O47</td>
<td>O. Chizhko</td>
<td>Decomposition of titanium oxides. The systems Ti-U-O and Ti-W-O</td>
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#### SESSION 16: Modeling and Simulation - 5
**Chairs:** Zi-Kui Liu, Ping Wu

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</table>
Abstracts for Oral Presentations
CALPHAD modeling provides thermodynamic and kinetic data of multi-component materials for their engineering design and computational simulations. First-principles calculations based on density functional theory (DFT) have made significant contributions to enhance the robustness of CALPHAD modeling and enable the development of high throughput approaches of CALPHAD modeling with uncertainty quantifications using machine learning techniques. The development of high entropy alloys and the advancement of additive manufacturing, particularly the functionally graded materials, desire more accurate phase stability at the center of multi-component materials systems. This calls for more efficient approaches in generating thermochemical, phase equilibrium, and other property data, performing CALPHAD modeling, and unitizing data from CALPHAD modeling for discovery and design of materials. Machine learning can and is increasingly playing more and more important roles in all these aspects. In this presentation, the author’s perspectives on CALPHAD modeling and machine learning are presented along with connections among data ecosystem (Figure 1), entropy, and information.

Figure 1. Schematic chart of data ecosystem including proto data (experiment, first-principles calculations, and machine learning), processed data (Modeling: CALPHAD with pycalphad and ESPEI), materials manufacturing, materials service, and materials recycling. It was designed and drawn by John Shimanek based on a draft of the author.

References

Biographical Note
Zi-Kui Liu is a distinguished professor at The Pennsylvania State University and has been the Editor_In_Chief of the CALPHAD journal since 2001. His current research activities are centered on first-principles calculations, modeling of thermodynamic, kinetic and other properties, and their integration in understanding defects, phase stability, and phase transformations, and designing and tailoring materials processing and properties.
Magnetic Contributions to the Vacancy Formation in Pure Elements

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Key words: Magnetic transitions, Monovacancy, Thermodynamic database

We have discussed thermodynamic descriptions of the monovacancy and vacancy complexes; the results were partly presented in the last CALPHAD conference [1-3]. In some elements such as Fe, Co, and Ni, however, magnetic contributions play an important role at lower temperatures than its transition temperature, and thus must be considered in the thermodynamic descriptions of vacancies. Although effects of the magnetic transitions on properties of vacancies has been examined in recent years based on ab initio calculations and experimental measurements, it is not yet formulated within the CALPHAD framework.

In the present work, based on the SGTE unary database version 5.0 and Inden model for the magnetic transitions, the effects of the magnetic excess Gibbs energy on the monovacancy formation was discussed and compared to experimental and theoretical data.

In Table 1, parameters used in the calculations are listed where $T_C$ is the transition temperature, $\beta$ is magnetic moment, $G'_{Va}$ is Gibbs energy of an empty end-member, $L^{(0)}_{Fe,Va}$ is zeroth Redlich-Kister term between Fe and Vacancy (Va) and $T_m$ is the melting temperature (for Fe it is 1811K in the Unary database). For vacancies, $\beta$ and $T_C$ were set zero. The lattice stabilities were taken from SGTE Unary 5.0 database. The magnetic excess Gibbs energy was given by Inden model with Hillert-Jarlf modification. In Fig. 1, the temperature dependency of the monovacancy fraction is presented where the black and gray lines are the fractions of the monovacancy in the BCC-Fe without magnetic transition and with ferromagnetic transition. Due to the magnetic excess Gibbs energy, the monovacancy fraction in ferromagnetic state becomes smaller than that in the non-magnetic (paramagnetic) state.

Details of the descriptions and results will be given in the presentation.

References

Table 1 Parameter set (J/mol) for a BCC Fe with vacancies. The lattice stability were taken from SGTE Unary 5.0 database.

\[
\begin{align*}
G'_{Va} &= +10RT \\
L^{(0)}_{Fe,Va} &= +10RT_m - 2RT - G'_{Va} \\
\beta_{Fe} &= +2.22 \\
T_C &= +1144 \text{ K} \\
\beta_{Va} &= 0 \\
T_C^{Va} &= 0 \text{ K}
\end{align*}
\]

Fig. 1 Monovacancy fraction in a BCC-Fe with and without magnetic transition as a function of the reciprocal temperature.

Biographical Note
Taichi ABE is a senior research of NIMS from 1993 to Present, working on CALPHAD-type thermodynamic assessments and creating various thermodynamic databases. For alloy systems, TDB files can be downloaded from an open database named CPDDB (Computational phase Diagrams DataBase) at http://cpddb.nims.go.jp/index_en.html. Another database for vacancies will be released soon.
Discussion on the Implementation of the Effective Bond Energy Formalism (EBEF)

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Key words: TCP phases, Modelling

The EBEF is a new formalism recently proposed [1] in order to describe complex phases in the CALPHAD approach close to their crystallography. Its use for the sigma phase in the Mo-Ni-Re has shown its good ability to extrapolate from binary ab initio results. The optimum use of this formalism for the sigma phase, however, deserve more exploratory work. While the determination of the effective pair energies in the Mo-Re system where the sigma phase is stable was rather easy, the cases of the two other binary systems Mo-Ni and Ni-Re showing a miscibility gap at low temperatures were more difficult. The expansion of the effective pair energies performed in the Mo-Ni-Re did not take into account the actual number of pairs between the different crystallographic sites. The use of tools developed for decades within First-principles (F-P) approach will be tested and compared to the results obtained using the Open CALPHAD optimizer. The impact of different F-P result for a given binary system will be shown. This work will finally report extrapolated phase diagram sections in two ternary systems Cr-Ni-Re and Mo-Ni-Re having a shared subsystem.

References

Biographical Note
Suzana G. Fries is a researcher in ICAMS, Ruhr University. She is responsible for the CALPHAD Method course in the Master in Materials Modelling and Simulation and for the Group Computational Thermodynamics: CALPHAD.
Third Generation of Thermodynamic Descriptions

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Key words: CALPHAD, thermodynamic, database, modelling

The thermodynamic databases commonly used in CALPHAD are now approaching maturity and thus there is a need for rejuvenation, i.e., a new set of unary descriptions based on new and updated thermodynamic models. Since the start of the Hero-m project at KTH, work has been performed to develop the corner stones of these new descriptions.

An important contribution, on which the work is based, is the description of pure Fe developed by Chen and Sundman [1], using the recommendations of the 1995 Ringberg workshop. Based on their work, several elements have been evaluated at KTH: Al, C, Co, Cr, Mn, Ni, and additional elements by other groups.

To extend the descriptions to binaries, and eventually to higher order systems, the models must be tested for validity in binary assessments. In Chen and Sundman, the heat capacity of the solid was extrapolated to reach that of the liquid at some high temperature. With this extrapolation technique, the melting temperatures of the elements are still visible in the calculated heat capacity of alloys, however not as markedly as when using the SGTE extrapolation scheme. Therefore, in the present work, the extrapolation of the solid over its melting temperature and of the liquid below, has been given a lot of attention by attempting different methods.

For the liquid/amorphous phase, the two-state model has been used [2], again testing different extrapolation methods compared to [1] for the heat capacity of the liquid at high temperatures.

Also, a simple method to describe metastable states of the elements using the difference in entropy, as given, e.g., by the SGTE lattice stabilities or DFT calculated values, to estimate the Einstein temperature for the metastable state has been attempted as suggested by Dinsdale [3].

Models to describe the interaction in binary and higher order systems have been tested. In order to fully obey the third law of thermodynamics, the linear temperature term of the chemical interaction parameter was recalculated to interaction parameters of the Einstein temperature after a suggestion by Dinsdale [3]. The revised magnetic model by Xiong et al. [4] is also tested in higher order systems together with the new descriptions of the elements.

DFT calculations are used to validate and to guide the models and also to calculate, e.g., Einstein temperatures and heat capacities for stable as well as metastable end-members and compounds.

Figure 1. The heat capacity of pure Ni using the new description and new extrapolation method. Experiments from Desai 1986.

Acknowledgement

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References


Biographical Note

Malin Selleby is professor in Computational Thermodynamics at KTH Royal Institute of Technology in Stockholm, Sweden. Her main research interest is thermodynamic modelling of metallic systems using the CALPHAD technique.
Entropic Models for Surfaces and Interface Research
--an example of Functional CALPHAD technique

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Key words: Entropic force, Chemical mechanics, Marine anti-fouling, Corrosion

Entropic force driven intelligence is best demonstrated by the GO matches between AlphaGo and Lee Sedol in 2016. It sent shock waves over the world on how artificial intelligence can beat human intelligence in the fields of intuitive, creative and strategic thinking, by data statistical and numerical techniques. Although of AlphaGo’s powerful number and policy crunching abilities, the decisions it made are not necessarily consistent with physical laws. In this research, we aim to explore physics-based entropic models to aide in surface and interface engineering research. By analyzing the Helmholtz free energy, surface wetting properties are calculated from system entropies. We further demonstrated new entropic models for anti-marine fouling to “cheat” nature intelligence.

Entropy, as a typical thermodynamic property, is widely applied in the study of nature intelligence. Many nature intelligent processes are already explained, at least partially, by entropy principles. In particular, an equation to connect intelligence and entropy maximization is reported by Wissner-Gross of MIT, by which a causal generalization of entropic forces is used to simulate two defining behaviors of human- tool use and social cooperation. Similarly, the present speaker has demonstrated that maximizing causal entropy has correspondence to real physical systems like water wetting, metal corrosion and materials stretch [1-4]. In this presentation, entropic force (or changes) based models for surface and interfaces will be reviewed, and opportunities in surface and interface research, by using combined artificial and physical intelligence approaches, will thus be highlighted.

References

Biographical Note

Figure 1. A strain engineering approach for Mussel fouling control.
A General "geometric" Thermodynamic Model for Multicomponent Solutions
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Key words: thermodynamic models, multicomponent systems, miscibility gaps

Estimation of thermodynamic properties of a multicomponent solution from optimized data for its binary subsystems has been discussed since the beginning of CALPHAD. For estimating the properties of a ternary solution, several "geometric" models have been proposed. The most common are the Muggianu, Kohler, Kohler/Toop, and Muggianu/Toop models. The latter two are "asymmetric" in that one component is singled out, whereas the first two are "symmetric". The difference between estimations based on symmetric and asymmetric models becomes more drastic as the excess Gibbs energies for the binary subsystems increase.

The current tendency in the CALPHAD community is to use the symmetric Muggianu model for nearly all solutions. The use of a symmetric model when an asymmetric model is more appropriate can often give rise to errors, such as spurious miscibility gaps, as will be shown in a few examples. Correcting qualitatively wrong Gibbs energy functions by introducing ternary terms can be very difficult, if at all possible, resulting in a poor fit of experimental data. The popularity of the symmetric Muggianu model is mostly due to the fact that it gives particularly simple equations for the Gibbs energy of a multicomponent system if the excess Gibbs energies of binary subsystems are expressed by Redlich-Kister polynomials. However, simplicity of the equations presents no tangible benefits to modern thermochemical software packages. Furthermore, the Muggianu model does not require the use of Redlich-Kister polynomials, and, conversely, Redlich-Kister polynomials can be used with all other "geometric" models. Figure 1 shows a ternary liquidus surface calculated with two different "geometric" models. As can be seen from the figure, selection of a "geometric" model has a particularly strong effect on the extrapolation of the MgO-B$_2$O$_3$ binary miscibility gap into the ternary system and on formation of a ternary miscibility gap in Fig. 1b.

Very general and flexible equations are programmed in FactSage, which allow calculating the thermodynamic properties of an N component solution (N>3) in a rational manner while permitting complete flexibility to choose any Kohler Muggianu Toop model for any ternary subsystem [1]. Hence, ternary systems that were optimized using different "geometric" models can be combined in one database, where both binary and ternary terms are appropriately extrapolated into the multicomponent solution. These general extrapolation methods can be used in combination with any model, in particular with the Modified Quasichemical and Compound Energy Formalisms.

Figure 1. Liquidus surface in the Na$_2$O-MgO-B$_2$O$_3$ system calculated with two different "geometric" models.

References

Biographical Note
Sergei A. Decterov is a Research Professor and one of FactSage developers. His research interests are mostly related to thermodynamic modeling of oxide and sulfide systems and database development.
Thermodynamic Assessment of the KF-BeF$_2$, KCl-BeCl$_2$, BeF$_2$-BeCl$_2$ and KF-KCl Systems towards an Investigation on the K, Be// F, Cl Reciprocal Phase Equilibria

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Key words: molten salt; phase diagram; thermodynamics; first-principles

First-principles calculations based on various DFT (Density Functional Theory) methods (multiple combinations of Pseudopotentials and Exchange-Correlation Functionals) were employed to predict the thermodynamic properties of intermediate compounds (K$_x$BeF$_3$, K$_x$BeF$_4$, KBeF$_3$, KBeF$_4$, K$_x$BeCl$_3$, K$_x$BeCl$_4$ and KBeCl$_3$) and rocksalt solid solution (special quasirandom structure for KFCl$_2$) in the ternary reciprocal KF-BeF$_2$-KCl-BeCl$_2$ system. These predicted data in company with all the assessed experimental information available in the literature were adopted to perform a complete exhaustive thermodynamic modeling of the ternary reciprocal system. The Modified Quasichemical Model in the Quadraplet Approximation (MQMQA) was used for the molten salt solution where both of the First-Nearest-Neighbor (FNN, cation-anion) and Second-Nearest-Neighbor (SNN, cation-cation and anion-anion) Short-Range Orderings (SRO) are taken into account. The KF-KCl rocksalt solid solution was modeled using the Compound Energy Formalism (CEF). The gas phase was treated as an ideal mixture of species with evaluated thermodynamic properties. All the intermediate compounds were described to be stoichiometric, with their heat capacities estimated by the Neumann-Kopp rule. The calculated results can well reproduce most of the experimental and theoretical data for all the binary systems within error limits. By merging the Gibbs energies for relevant phases in all binary systems, several isothermal and isoplethal sections were predicted in the ternary reciprocal KF-BeF$_2$-KCl-BeCl$_2$ system, which is used industrially for beryllium extraction and nuclear reactors.

![Image](image_url)

Fig.1 Some quadruplets within the MQMQA for the molten salt

![Image](image_url)

Fig.2 The predicted isothermal sections in the reciprocal system at 1000°C
Using Extent of Reaction in CALPHAD Modeling

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Key words: driving force, affinity, extent of reaction, phase change

For non-equilibrium systems with internal entropy producing processes the combined first and second law of thermodynamics includes the driving force \((D)\) as an intensive state variable. Following Hillert [1], the Gibbs free energy of an open system is then written as

\[
\begin{align*}
\frac{dG}{dP} &= -SdT + VdP + \sum_{j=1}^{N_C} \theta_j dN_j - Dd (1)
\end{align*}
\]

where the components \((N_i)\) refer to exchange of matter with the surroundings and advancement of the internal processes is denoted with \(\xi\). At equilibrium \(D = 0\). For systems with non-equilibrium chemical reactions the driving force equals the thermodynamic affinity and \(\xi = \xi_0\) being the extent of the reaction \(r\). As noted by Hillert, the driving force \(D\) yet has a much wider applicability for any kind of internal process. The last term \(Dd\xi\) of equation (1) drops off at equilibrium \((D=0, d\xi=0)\) and \(\xi\) is a dependent variable, determined by the equilibrium conditions of the system. With \(D=0\) and \(d\xi=0\), the system is in constrained equilibrium (‘freezing-in condition’) and \(\xi\) is an independent variable.

In the Constrained Gibbs Free energy minimization (CFE) method, introduced by Koukkari and Pajarre [2] the conjugate pair of \(Dd\xi\) appears as a key concept for the calculation procedure. As the CFE method often is applied for non-equilibrium systems and for partial equilibria, the driving force may be either given as a target input or is received as the result of the calculation. The advancement of the internal process is either given as an external constraint (independent variable) or becomes defined from the internal conditions of a metastable system and acts as a dependent variable of the system.

The constraints related to the advancement of the internal processes must be incorporated into the conservation matrix of the Gibbs’ian system as massless (virtual) system components and virtual phases. For systems with chemical reactions, the reaction matrix is translated into an enlarged conservation matrix that includes both mass balance and reaction constraints, where the latter apply to explicit (kinetically slow) reactions. Respectively, for paraequilibrium solidification systems the constraint is deduced from the ratio of substitional components in the mother phase and defined along this ratio as virtual components affecting each stoichiometric phase that may be appear stable in the Gibbs’ian calculation.

With the conditions set the CFE calculation then is used to apply the CALPHAD method for complex systems including those with non-equilibrium chemical reactions, metastable ‘superequilibria’ as well as e.g. para-equilibrium conditions in solidifying matter. The driving force is received from the \(\min(G)\) calculation in terms of the ‘constraint’ potentials of the virtual components. Thus, e.g. the affinities of a system with chemical and phase changes are received as function of the extents of the chemical reactions [3]:

![Figure 1. Affinities and phases in a CO₂ absorbing system (left), simulated reaction path as affinity diagram (right).](image)

The procedure may further be developed to be used for Calphadian path analysis for reactive systems eventually reaching equilibrium as well as be applied for potential and phase diagrams describing metastable and non-equilibrium conditions.

References

Biographical Note
Pertti Koukkari is Research Professor of Chemical Systems at VTT, Technical Research Centre of Finland. He is the developer of the internationally awarded Constrained Gibbs Free energy method and co-author of several process simulation software products including the widespread ChemSheet and KihlSimu programs.
O09

Combining Python and Pandat to Assess Kinetic and Alloy Design Parameters for Precipitation Simulation

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Key words: Pandat, Python, Precipitation simulation, Kinetic and process parameters

Coupling of PanPrecipitation with a custom Python program supports assessing a wide range of kinetic and process parameters by automated simulations.

In precipitation simulation of age hardening alloys we need to distinguish material parameters and alloy design parameters. Material parameters comprise the thermodynamic and atomic mobility database, assumed to be known from prior CALPHAD assessment, as well as “kinetic” parameters, such as the well known atomic spacing or the – hard to determine – interfacial energy. Here we also include parameters used in the strengthening model applied to calculate yield strength and hardness of the alloy. All simulation tools are seamlessly integrated in the PanPrecipitation module \(^1\) of the software package Pandat \(^2\).

Alloy design parameters comprise the alloy chemistry as well as all process parameters since only this combination determines microstructure and properties. For age hardening the entire heat treatment profile is most important with many process parameters, such as heating/cooling ramps, duration, temperature, or multi-stage treatments. Simulations using Pan Precipitation are a powerful tool for alloy development and process optimization, e.g. \(^3\). Many alloy design parameter variations can be assessed within weeks or even days. The time to be invested for carrying out optimization procedures, including crucial or problematic kinetic parameters, can be further reduced by coupling a custom Python program to PanPrecipitation \(^4\).

The custom Python program generates batch files with parameters from a user defined search area and starts the simulation calculation in PanPrecipitation’s console mode. After PanPrecipitation finished the simulation, the simulation results are taken by the Python program, assessed and archived for further evaluation by the researcher.

This work presents the results of using this combination of PanPrecipitation and Python for the purpose of assessing the interfacial energy of one single and two concurrent phases of precipitates in Cu-based Cu-Co-Ni-Si alloys. By conducting a brute-force parameter test in a wide search area, the effect of various parameter combinations on the simulation results has been studied. In conclusion, values for interfacial energy have been found, which fit well to experimental results.

![Figure 1. Effect of the kinetic parameter “interfacial energy” of (Ni,Co)2Si precipitates in Fcc (Cu) on the standard deviation between simulated hardness and measured hardness across twelve ageing processes.](image)

References


Biographical Note

Rainer Schmid-Fetzer is professor emeritus with Clausthal University of Technology and guest professor with Central South University, Changsha.
The classic CALPHAD approach models complex phase equilibria in multicomponent alloys through computer coupling of phase diagrams and thermochemistry. Its theoretical basis is the thermodynamic description of individual phases, including the stoichiometric compounds and solution phases. This general approach can be used to describe the gas phase, liquid phase, and also the solid solution phases. In general, the Gibbs energy can be fixed by fitting the phase stability data, including liquidus, solidus, etc., and the thermochemical data, including enthalpy, entropy, heat capacity, etc.

However, there is a big difference to model multicomponent ionic solid solution oxides, i.e. the additional factor, defect chemistry, need to be considered. It has been repeatedly proved that only the models which represent the defect chemistry of oxide solution phases can match the experimental data. The role of defect chemistry in ionic oxides is so important that it deserved a different name, which is called CALPHADPLUS in the current work.

In the current talk, the process of database development for the multicomponent perovskite will be used as examples to show the important role of the defect chemistry. In addition, applications like quantitative Brouwer diagrams, electrical conductivities, etc. will be covered.
O11

OpenIEC: An Open-source Code for Interfacial Energy Calculation in Alloys

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Key words: Interfacial energy, Coherent interface, Solid/liquid interface, Ni alloys, Al alloys

Interfacial energies play an extremely important role in controlling microstructure evolution in various materials processes, such as nucleation, dendritic growth, coarsening/ripening and so on. Moreover, input of accurate interfacial energy is thus a prerequisite in the quantitative phase-field simulation of microstructure evolution at the meso scale. Despite its profound significance, the current supply of reliable interface energy data is still unsatisfactory. As a consequence, there is an urgent need to remedy this situation.

Many approaches including Lifshitz-Slyozov-Wagner (LSW) coarsening theory and its variants, grain boundary groove method, molecular dynamics (MD) and Monte Carlo (MC) simulations, first-principle calculations and the classic nearest-neighbor broken-bond (NNBB) approach, have been developed to evaluate interfacial energies. However, these methods are sophisticated for multicomponent alloys.

Very recently, Kaptay developed a thermodynamic approach for evaluating the isotropic interfacial energies of the solid/solid as well as liquid/liquid coherent interfaces and solid/liquid interfaces in alloys. The reliability of the predicted interfacial energies in different systems has also been validated by comparing with the experimental data available in the literature and applications in phase-field simulations of microstructure evolution. In general, there are three advance features in this thermodynamic approach, including i.e., (i) that the input of massive parameters are avoided in the thermodynamic approach, and the predicted interface energies are composition- and temperature-dependent; (ii) that this thermodynamic approach can be conveniently extended to the multicomponent systems; and (iii) that it is very easy to realize the programming and automation of interface energies calculations by coupling with the CALPHAD-type thermodynamic and molar volume databases.

Consequently, an Open-source code for Interfacial Energy Calculation (OpenIEC) was developed by following Kaptay’s models. The coupling with the CALculation of PHAses Diagram (CALPHAD) thermodynamic and molar volume databases was facilitated in OpenIEC for providing the necessary thermodynamic information. With OpenIEC, the temperature- and composition-dependent interfacial energies in alloys with any arbitrary number of components can be conveniently evaluated. In order to demonstrate the applicability and validity of OpenIEC, the benchmark tests in several model alloys in Ni and Al alloys were carried out, and the calculated interfacial energies were found to be in good agreement with the literature data. After that, the OpenIEC was applied to predict the temperature- and composition-dependent interfacial energies of coherent γ'/γ interfaces in two Ni-based superalloys, including ternary Ni-Al-Cr and quaternary Ni-Al-Cr-Re alloys, as well as the temperature- and composition-dependent solid/liquid interfacial energies in Ni-Al-Cr and Al-Cu-Li alloys.

We would like to share our latest progresses in development and application of OpenIEC code as well as the method of interfacial energy calculation. Comments and cooperation are warmly welcome. One can visit the website (https://github.com/openiec) for the code and the latest information of OpenIEC.

Figure 1. Framework of the OpenIEC code

References


Biographical Note
Shenglan Yang is now a Ph.D. candidate at Central South University in China. She is interested in the CALPHAD modeling of different thermophysical parameters, as well as the quantitative phase-field modeling of microstructure evolution.
Thermodynamic Modeling of G-phase for Applied
CALPHAD in Fe-based Alloys

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Key words: G-phase, Model development, DFT, Precipitation Kinetic

The G-phase – a silicide phase with a general formula Mn\textsubscript{n}Ni\textsubscript{o}Si\textsubscript{7} – is technologically important due to its precipitation in duplex stainless steels (DSS) by thermal ageing \cite{1} and its possible relevance for reactor pressure vessel (RPV) steels by either radiation-enhanced or radiation-induced precipitation \cite{2}. Our previous compound energy formulation (Ni\textsubscript{n}CrFeMn)\textsubscript{6}Si\textsubscript{7} contained questionable site occupancies resulting in an underestimation of Fe and Cr solubilities. These elements represent the major constituents of the considered steels. In order to evaluate the competition between thermodynamic and kinetic control (e.g. irradiation-modulated diffusivities) on G-phase precipitation in different steel grades by applied CALPHAD in MatCalc thermokinetic simulations, an appropriate thermodynamic CALPHAD description in terms of compound energies and associated element solubilities is required. We present a revised G-phase description and discuss assessed site occupancies and solubilities based on experimental and first-principles (DFT) input data.

G-phase silicide is thermodynamically stable in Ni-Si based ternary systems such as Ni-Mn-Si, Ni-Ti-Si and Ni-Nb-Si at high temperature (i.e. T=800-1000°C), whereas the phase is metastable in the Ni-Cr-Si and Ni-Fe-Si ternaries. Equilibrium phase diagram and molar enthalpies of Ni-Mn-Si G-phase are considered in the revised model, together with metastabilities of respective Fe- and Cr-containing end-member compounds and Fe- and Cr-site occupancies, as determined by first-principles analysis. In addition, excess energy was fitted in order to reproduce experimental phase compositions.

The extension of our thermodynamic description to multicomponent systems shows consistency with experimental G-phase dissolution temperatures and compositions \cite{1,3,4}.

Based on the present successful thermodynamic modeling, a kinetic simulation of G-phase precipitation in DSS and RPV was carried out. The resulting precipitate sizes, fractions and compositions compare well with experimental data \cite{1}. The presented thermokinetic modeling and simulation approach sets a physics-based framework for further simulative predictions of complex materials thermally aged for several decades at high temperature (~300°C and above) or used in nuclear power plant. Extension of the simulation setup, including considerations of irradiation effects on precipitation is on the way.

References


Biographical Note

Dr. Aurélie Jacob obtained her PhD in the development of thermodynamic database for high Cr steel in Germany after she finished her studies in chemistry in France. She is now working as research assistant at TU Wien since 2016 and as thermodynamic database developer for Matcalc Engineering GmbH. Her research topic is focusing on the thermodynamic modeling for technological applications where CALPHAD is used in kinetic simulation for prediction of precipitation.
O13

CALPHAD-based Modeling of Cooling Rate Influence on Solidification Microstructure in Magnesium Alloys

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Key words: Solidification, Cooling rate, Magnesium alloys, CALPHAD

Magnesium (Mg) alloys are among the lightest structural materials and offer significant weight saving potential. The vast majority of Mg applications in vehicles (>90%) are high pressure die casting, which affords tremendous design flexibility and opportunities for component integration, thereby lowering “system” cost [1].

Casting is a solidification process of liquid material in a mold. The solidification behavior of an alloy is determined by its solidification path, which describes the phase formation sequence during solidification. Therefore, it is critical to obtain an accurate solidification path for understanding and controlling the solidification process of the alloy. Phase diagrams are frequently used to understand the solidification path of an alloy cooled from the liquid state to room temperature. For multicomponent industrial alloys, their solidification paths can be simulated via the CALPHAD approach based on two approximate models, equilibrium (lever-rule) and non-equilibrium (Scheil-Gulliver) models, in a simple and efficient way without evoking complex kinetic calculations. Both models assume complete mixing in the liquid. In the solid, the lever-rule model assumes the solute diffusivity is infinity, while the Scheil model assumes that the solute diffusion in the solid phase is small enough to be negligible. As one can see, these two models describe the two extreme cases. While in almost all practical situations, the solidification occurs under non-equilibrium conditions but does not follow either of the two models. There is usually finite diffusion in the solid, the so-called “back-diffusion”, which is a function of cooling rate and plays an important role in the alloying element segregation as well as the final as-cast microstructure. Thus, the solute back diffusion within the solid under different cooling conditions needs to be considered in order to accurately predict the solidification microstructure.

Based on the previous work of Yan [2], the PanSolidification module of Pandat™ software is developed by coupling a solidification micro-model with PanEngine. This micro-model is basically a modified Scheil model and incorporates the back-diffusion, undercooling, and dendrite arm coarsening. This micro-model can predict the secondary arm spacing (SDAS), microsegregation, types and amounts of non-equilibrium phases in the solidification microstructure of multicomponent alloys by incorporating back-diffusion in the solidified primary phase, as well as the undercooling and dendrite arm coarsening during solidification.

In the present work, the microstructural evolution and microsegregation of a series of magnesium alloys (Mg-Al, Mg-Al-Ca and Mg-Al-Sn) at various cooling rates were investigated using the PanSolidification module. Experimental validations were also carried out in a wide range of cooling rate (0.12 ~ 55 K/s) using both directional solidification and die casting techniques. Good agreements have been achieved between the simulated and measured solidification microstructure parameters (phase fraction and secondary dendrite arm spacing) and microsegregation within the primary α(Mg) dendrites. This modeling approach demonstrated the reliability of the CALPHAD-based models for the prediction of solidification microstructure of magnesium alloys and their applicability for the optimization of magnesium castings.

References:

Biographical Note
Chuan Zhang is a principal materials scientist of CompuTherm, LLC where he joined in 2010 after five years of Ph.D study at University of Wisconsin-Madison.
A general simplified growth model for multicomponent precipitation and its implementation in TC-PRISMA

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Key words: Precipitation, Para-equilibrium, NPLE, Simulation, CALPHAD

A general simplified model for the growth of particles in a multicomponent system has been developed. The model takes into account of the effects of cross diffusion, high-supersaturation, and finite interface mobility. It can be applied in a straightforward way to treat precipitation under the condition of para-equilibrium (PE) or non-partitioning local equilibrium (NPLE) without resorting to a usually difficult and time-consuming solution of the coupled flux balance and local equilibrium equations under the influence of the Gibbs-Thomson effect. The model has been implemented in TC-PRISMA and applied to simulate the precipitation of carbides in steels. A few case studies will be shown and discussed.

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Diffusion Paths in Highly Concentrated Alloys: Is There Such a Thing as a ‘Sluggish Diffusion’?

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Key words: cluster variation method, diffusion, ordering, high entropy alloys

Diffusion paths in multicomponent alloys.

In recent works [1,2] two of the present authors investigated the thermodynamics of multicomponent alloys in the range of heavy concentrations, of what is usually called 'high entropy alloys' (HEAs). In general, the conclusions of the two works suggest that the unusual properties reported in these alloys are not attributed to the high value of the configurational entropy, but rather to complex thermodynamics in which short-range order parameters, i.e. opposite to high entropy, play a significant role.

It has often been reported that diffusion in HEAs is anomalously slow, an effect that would be quite technologically important if it were true. The effect is usually attributed to the high configurational entropy. This is contradictory to the accepted idea that sluggish diffusion is caused by various ordering phenomena.

Diffusion and thermodynamics are linked by the fact that gradients of chemical potentials are the true driving forces for diffusion [4]. The composition dependence of the chemical potential introduces influences which either enhance or reduce the action of the diffusion mobilities, introducing potential non-linear effects, which are particularly strong in “special” regions of the phase diagram (second-order boundaries and stoichiometric points or lines). This effect can be described by multiplicative factors, which were called “thermodynamic forces for diffusion” in ref. [1].

The results of ref. [1] show that the diffusion flux of a given element with respect to its own chemical potential composition dependence can lead either to the increase or to the decrease in of the flux relative to what is expected from the mobilities (referred to as the diagonal contribution), as it occurs with any binary concentrated alloy. More important than this, however, the influence of the chemical potential composition dependence of one element over another one’s diffusion flux (the non-diagonal contribution) may be as strong or even stronger.

The present work tests this hypothesis. First DICTRA simulations, based on established mobilities and thermodynamic databases, are performed for various HEA systems. Secondy a cluster variation method algorithm, capable of simulating diffusion paths in multicomponent alloys, is used. As test subject the present work simulates a diffusion couple between alloys VNb2WAI and VNbWAl using ab initio interactions taken from ref. [2] and assumed mobilities.

The results show that the multidimensional diffusion path is highly non-linear.

If diffusion is simplified, by treating this diffusion couple as a pseudo-binary alloy, this introduces an “effective” diffusion constant for Nb which indeed shows a reduced flux. This is supposed to be the origin of the “sluggish diffusion” effect.

The results, hence, prove that diffusion in multicomponent alloys is extremely complex and should be properly modeled using consistent thermodynamic models.

References


Biographical Note

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Thermodynamics of Grain Boundary Segregation and Interfacial Spinodal: A CALPHAD-based Modeling Approach and Near-atomic Scale Characterization


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Key words: grain boundaries, CALPHAD, segregation, interfacial spinodal, atom-probe tomography

Grain boundary segregation, embrittlement and phase nucleation are interconnected phenomena that are often treated separately, which is partly due to limitations of the current models to predict grain boundary segregation in non-ideal solid solutions. Here, a simple model is introduced to predict grain boundary segregation in solid solutions by coupling available CALPHAD bulk thermodynamic data with a mean-field description of the grain boundary character. The concept is first described for regular solid solutions (following the Fowler-Guggenheim model) and later extended to magnetic solid solutions which are exemplified here by the Fe-Mn binary alloy. The model is confronted with experimental results obtained in Fe-Mn alloys analyzed by atom probe tomography. This model successfully predicts a first order transition or a discontinuous jump in the composition of the grain boundary which kinetically implies the formation of spinodal Mn fluctuations that tend to grow further with time within the segregated region. The increase in solute concentration at the grain boundary leads to an increase of the enthalpy of the boundary and to its embrittlement at lower temperatures. Another important consequence of the model is that spinodal segregation provides a non-classical, i.e. chemistry-driven pathway for the heterogeneous nucleation of a second phase (e.g., austenite). This effect sheds new light on the heterogeneous nucleation mechanism which is usually associated only with the advantage of interface energy provided by the grain boundary. The new model shows that heterogeneous nucleation at interfaces can be also promoted by spinodal composition enrichment, i.e. precursor states at the grain boundary which do not necessarily occur in the adjacent bulk. This means that a grain boundary can assist nucleation in a twofold manner, through its available interface portion and through its interface-specific chemical working point which may enable phase precursors not found in the bulk.

Figure 1. Segregation isotherms at different temperatures for the Fe-Mn system assuming metastable local diffusional equilibrium between the BCC bulk phase and the grain boundary (GB).

References

Biographical Note
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Phase Field Simulation of 6XXX Al-Mg-Si Alloys during the Whole Ageing Process and its Experimental Verification

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Key words: Al-Mg-Si alloys, Multi phase field model, Stoichiometric precipitation, Elastic field

The age hardening of 6XXX Al-Mg-Si alloys is a frequently discussed topic, which has been studied by a wide range of techniques over years. In the present work, for the first time the combination of phase field crystal (PFC) and multi component multi phase field model (MPF) is used to simulate the whole aging process of Al-Mg-Si alloy with the experimental verification. At early stage of aging, PFC model at atomic scale is used to study the nucleation and growth mechanisms of early clusters in Al alloys. In addition, some studies focus on the mechanism of dislocation and solute enrichment region under external stress. Moreover, the number density, solute ratio and average solute number of atomic clusters in the early stage of aging have been determined by 3-dimensional atom probe (3DAP). The composition, size, number density have been determined by transmission electron microscopy and verified by 3DAP. For the later stage of aging process, the MPF model, which is coupled to elastic field and CALPHAD(CALculatin of PHAse Diagrams)-type databases, was used to simulate the growth and coarsen process of the stoichiometric precipitation β”Mg2Si6 in Al-Mg-Si alloy. The simulated results agree reasonably with the experimental data.

Figure 1. Comparison between phase field crystal simulation results (a) and High Resolution Transmission Electron Microscopy (HRTEM) images results (b)

Figure 2. Simulation of Needle-like precipitation Morphology by Multi-phase Field Model

Acknowledgments

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Reference


Biographical Note

Hong Mao, a PH.D student in Central South University, Changsha, Hunan province, PR China. He is supervised jointly by Prof. Yong Du and Assoc. Prof. Yi Kong. He is interested in phase field modeling of microstructure evolution.
Generalized Pair-diffusion Model for Multi-principal Element Alloys

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Key words: pair-diffusion model, interdiffusion, radiotracer diffusion, high-entropy alloys

In recent years, high entropy alloys, multicomponent alloys with (near-) equiatomic composition, are investigated and special interest focuses on diffusion, due to the initial assumption of a sluggish diffusion effect.

Since these alloys do not have a main element which can be used as reference, a generalized multicomponent diffusion model was developed which treats diffusion in a pair-wise manner. Considering the change between the frames of reference, a symmetric description of the chemical mobility for each pair is derived and related to the atomic mobilities of all elements. In the binary case and in the dilute solution limit this generalized model can be directly related to the DICTRA model \cite{1,2}.

The main advantage of the new model is its consistent description of interdiffusion and self-diffusion, which will be shown for a CoCrFeMnNi diffusion couple. Additionally, traditional tracer diffusion at the ends of the couple are evaluated in a constant concentration and in the interdiffusion zone in the center of the sample with non-constant concentration. A comparison between experimental and simulated results are shown in Fig. 1 \cite{3}.

In agreement with the CALPHAD approach the model is extended to multiple sublattices. The derivation of the diffusion equations using a consistent treatment of pairs of elements not only describes diffusion on one sublattice but also gives a kinetic term for the exchange of elements between different sublattices. The model is also extended to diffusion of interstitial elements for a wide-spread applicability. Again, a comparison between experimental and simulated results will be shown for CoCrFeMnNi with additional amount of carbon.

References

\begin{enumerate}
\end{enumerate}

Biographical Note

Katrin Abrahams is a doctoral candidate at ICAMS, Ruhr-University Bochum, Germany. Her research focuses on the development of a generalized diffusion model valid for all kinds of alloys and the development of an automated assessment software for diffusion data.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Comparison between interdiffusion and tracer-diffusion measurements and simulations using the pair-diffusion model in CoCrFeMnNi diffusion.}
\end{figure}
A Model for Assessing Grain Boundary Thermodynamics Based on The Available Bulk Thermodynamics Data

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Key words: Grain Boundary Thermodynamics; Grain Boundary Segregation; Grain Boundary Phase Transition

Direct assessment of the grain boundary thermodynamics properties is a difficult task due to the intrinsic complexity of the grain boundaries. An alternative approach can be assessing the grain boundary thermodynamics based on the available bulk thermodynamics. In the current study, a physically-sound framework has been proposed that allows an approximation of the grain boundary thermodynamics properties based on the bulk thermodynamics data [1]. In this model, a relative density field parameter (and its gradients), with respect to the corresponding bulk material, is introduced to distinguish and describe the grain boundary and its relevant thermodynamics properties.

Using the current model, the equilibrium phase diagram and segregation behavior of a grain boundary were studied in a binary alloy. Different regimes of segregation are identified and the coexistence of the bulk and grain boundary phases are discussed for the simple Pt-Au alloy system (An example grain boundary in this system is exemplified in Figure 1). Furthermore, the relationships between the grain boundary density, energy and misorientation angle are established that enable studying the grain boundary tendency for segregation as a function of initial grain boundary energy and misorientation angle.

Finally, an application of the current model in materials design is discussed. The current model is readily applicable for thermodynamics assessment and studying phase equilibria in grain boundaries.

Figure 1. Equilibrium phase diagram and coexistence compositions of the bulk and a grain boundary (GB) in Pt-Au system.

References

Biographical Note
Reza Darvishi Kamachali is a Heisenberg Fellow of German Research Foundation (DFG), currently hosted by the MPIE. He was a Research Group Leader (2014—2017) in ICAMS. He obtained his PhD on Modelling of Microstructure Evolution in Polycrystalline Materials. His research interests are Grain-Boundary Thermodynamics &Kinetics, Chemo-mechanical Coupling and Precipitation.

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Key words: mechanical properties, high throughput CALPHAD-calculations, superalloys, alloy design

In this work, we will present some applications of material informatics for the identification of statistically sound correlations between materials chemistry, thermodynamic, microstructure and mechanical data of single crystal Ni- and Co-based superalloys. Here, such important aspects, as the selection of the most appropriate modeling strategy and effective database structures for storage and management of experimental and simulation data will be discussed in details on two examples.

First, we will focus on the development of mechanical properties database [1] and physically-based data-driven creep models (s. Fig.1-I) supported by image mining of TEM/SEM images from interrupted tests.

Then, the application of regression-based approach for the construction of a fast sensitivity model of mechanical properties will be reported [2]. This model allows to take into account the scattering of the element concentration that are unavoidable during an alloy production and consider it in numerical alloy-by-design. Here, the estimation of parameter values and selection of the most appropriate regression model have been performed based on high-throughput CALPHAD calculations with the Thermotech TTNi8 database using Thermo-Calc software. The proposed model has been integrated into optimization tool MultOpt++ [3]. Moreover, the influence of each alloying element and its variation on sensitivity and the values of thermodynamic properties has been analyzed (s. Fig.1-II).

This work has been performed in cooperation with Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany in the frame of SFB/Transregio 103 “From atoms to turbine blades – a scientific basis for a new generation of single crystal super alloys” [4].

References

I) comparison of fitted and experimental creep curves of Co-based alloy
II) normalized standardized regression coefficients of elements and their variations (%C in wt%): results for sensitivity (a) and property values (b).

Notation:
\( \gamma\): gamma prime phase fraction, \( T_\gamma\): temperature of \( \gamma\) phase, \( T_{\text{SS}}\): solid solution strengthening index, \( T_{\text{sol}}\): solidus temperature, \( \delta\): misfit \( \gamma \)/\( \gamma'\), \( T_{\text{liq}}\): liquidus temperature, \( W_p\): heat treatment window, p: price, \( \rho\): density

Figure 1. Partial applications of material informatics in SFB/Transregio 103.

Biographical Note
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High Throughput Screening of Alloy Catalysts for PEMFC and Machine Learning Prediction of Chemisorption

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Key words: Fuel Cell, Electrocatalyst, DFT, High-throughput Screening, Machine Learning

Much progress has been made in hydrogen production and its utilization through fuel cell application to exploit this renewable energy source without any limitation from diurnal variation in local insolation. For rational design of new cathode catalysts for sluggish oxygen reduction reaction (ORR), theoretical approaches using density functional theory (DFT) have provided comprehensive explanations for enhanced performance of new catalysts. Based on solid concepts in heterogeneous catalysis, we conducted high-throughput screening of L1_2-type alloys for proton-exchange membrane fuel cell (PEMFC) application to find a new ORR electrocatalyst. In this study, we introduce a highly durable & active catalyst candidate and describe its chemistry on the corresponding surface by higher-level of calculations for verification.

In general, many computational screening studies have been done by fixing the surface structure without changing symmetry because of its simple construction of model surfaces and a limitation from the computing capacity. Here, however, we carried out symmetry-unconstrained screening to find a new Ag-based ORR catalyst for the anion-exchange membrane fuel cell (AEMFC). We considered not only the catalytic activity but also the phase stability from each phase diagram and heat of formation to secure the durability of catalysts. A further systematic approach to move closer towards optimal alloying design escaping from a known database, such as the Materials Project, is also discussed.

Given that one has a proper size of the database for a specific property, prediction through machine learning can be a good choice. Here, using a large database from the screening we had performed above, we trained an artificial neural network (ANN) to predict surface – adsorbate interaction to estimate the catalytic performance within an error range of < 0.2 eV. In this way, one can reduce computational cost significantly and broaden the screening window for materials exploration. Also, we will show how the accuracy of the machine learning model and types of input features depend on the size of a training set.

Biographical Note
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Modelling of Vacancies in the Compound-energy Formalism

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**Key words:** Vacancy, Gibbs energy, Substitutional solution, Two-sublattice model

The role of vacancies in thermodynamic models based on the compound energy formalism, CEF, is studied by application to a binary phase with two sublattices where the two components occupy one sublattice each. The variation in constitution is illustrated with a square-shaped diagram with corners representing the end-members. On two sides, the model degenerates to substitutional models of vacancies in either component. They meet in a corner representing only vacancies. For consistency, it would seem that all three models should there represent the same physical state which does not seem to be true. The conflict was resolved by studying the molar Gibbs energy expressions of the models.

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High-throughput Alloy Design Platform for Al-Si-Mg Casting Alloys Driven by Computational Thermodynamics & Phase-field Modeling

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Key words: composition design platform; Al–Si–Mg casting alloys; Scandium; Microstructure;

A high-throughput alloy design platform for Al-Si-Mg casting alloys based on computational thermodynamics and phase-field modeling is established in this paper. On one hand, based on the well-established thermodynamic database, the Scheil-Gulliver simulations for a series of alloy compositions can be automatically computed using the platform, from which the solidification diagram can be constructed and the optimal alloy composition can be effectively designed. On the other hand, the phase-field simulations coupled with accurate thermodynamic and atomic mobility databases are performed for the solid solution and aging process in the Al-Si-Mg casting alloys. The solidified microstructure can be read as the initial input of the phase-field simulation. From the phase-field simulation results, the optimal solid solution and aging mechanisms can be designed.

The established alloy design platform is then applied to the Sc-additional Al-Si-Mg casting alloys. In the first step, the optimal Sc-additional amounts for the Al-Si-Mg casting alloys over the wide composition range, including A356, A357, A360 and A380, are designed. Based on the designed optimal alloy compositions, the optimal solid solution and aging mechanisms, like temperature and time, are then chosen. The designed alloy compositions and heat treatment mechanism are validated by key experiments. It is finally found that the prepared series of Sc-additional Al-Si-Mg alloys, i.e., Sc-additional A356, A357, A360 and A380, according the designed compositions and heat treatment mechanisms show much improvement in strength and toughness.

References

Figure 1. Optimal Sc contents for series Al-Si-Mg casting alloys designed by the present high-throughput alloy design platform.

Figure 2. Comparison of mechanical properties between the designed Sc-additional Al-Si-Mg casting alloys and traditional commercial Al-Si-Mg casting alloys:(a) Ultimate tensile strength; (b) Yield strength; (c) Elongation.

Biographical Note
Jianbao Gao is now a Ph.D. candidate supervised by Prof. Lijun Zhang at Central South University, China. His research interest lies in alloys design driven by computational thermodynamics and kinetics.
Bayesian Uncertainty Quantification and Information Fusion in CALPHAD-based Thermodynamic Modeling

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**Key words:** CALPHAD Modeling, Uncertainty Quantification, Information Fusion, Bayesian Frameworks

Uncertainty quantification (UQ) is the process of identifying different sources of uncertainty and developing the corresponding mathematical representations for the error bounds of quantities of interest (QoIs). Uncertainty in QoIs arises from different sources, including: the random/stochastic nature of the physical system in question; uncertainty in the values of the variables used to parameterize models; lack of sufficient or accurate data to parameterize the models; and incomplete knowledge of the model structure, due to excessive simplifications, wrong assumptions and/or incomplete representation of the underlying physics/chemistry in the model.

For over a decade, uncertainty quantification (UQ), its propagation (UP), and the overall uncertainty management (UM) have been recognized as essential components to any effort in which simulations assist the discovery and design of materials. Perhaps the general area in the field of computational materials science that has experienced a comparatively slow rate of development—in the context of UQ/UP/UM—that is at odds with its importance in the entire ICME edifice is the CALculation of PHAsed Diagrams (CALPHAD) method. In this work, we present novel approaches to UQ and UP in CALPHAD modelling.

As a manner of illustration, a thorough probabilistic assessment of the CALPHAD model parameters is performed against the available data for a Hf-Si binary case study using a Markov Chain Monte Carlo sampling approach. The plausible optimum values and uncertainties of the parameters are thus obtained, which can be propagated to the resulting phase diagrams. Using the parameter values obtained from deterministic optimization in a computational thermodynamic assessment tool (in this case Thermo-Calc) as the prior information for the parameter values and ranges in the sampling process is often necessary to achieve a reasonable cost for uncertainty quantification. This brings up the problem of finding an appropriate CALPHAD model with high-level of confidence which is a very hard and costly task that requires considerable expert skill. A Bayesian hypothesis testing based on Bayes' factors is proposed to fulfill the need of model selection in this case, which is applied to compare four recommended models for the Hf-Si system. However, it is demonstrated that information fusion approaches, i.e., Bayesian model averaging and an error correlation-based model fusion, can be used to combine the useful information existing in all the given models rather than just using the best selected model, which may lack some information about the system being modelled.

![Figure 1. Uncertainty propagation: from uncertainty in CALPHAD model parameters, through free energies, to phase boundaries.](image)

**References**


**Biographical Note**

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First-principles Study of Oxygen Self-diffusion and Thermal Expansion in Zirconia

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Key words: ZrO₂, Diffusion, Thermal expansion, First-principles, Phonon

The diffusion of oxygen in ceramics is very important because it has extensive effects on materials properties such as phase stability, mechanical property, heat resistance and so on, which are usually critical to their applications in industry. Zirconia is an important industrial materials with three phases. With decreasing of the temperature, the structure of zirconia transforms from cubic to tetragonal (2650 K) and then to monoclinic (1478 K). The cubic phase (c-ZrO₂) is dynamically unstable. The tetragonal phase (t-ZrO₂) is metastable, while the monoclinic one (m-ZrO₂) is stable. Since the diffusion is more prominent at high temperature, studying the oxygen diffusion of the high temperature phases in ZrO₂ is evitable.

The present work attempted a full first-principles calculation of the self-diffusion coefficient for t-ZrO₂ combining the electronic structures, phonon vibration spectrum and transition state theory (TST)³⁴. In order to tackle the difficulty of the phonon imaginary frequency resulted from the dynamically instability due to vacancy in t-ZrO₂, an extended local harmonic approximation (LHA) that captures the most important vibrations adjacent to the migration atom is proposed in this work based on the LHA³⁵, then the atom jump frequencies along a-axis and c-axis directions for the tetragonal lattice have been obtained respectively. The vacancy concentration can be estimated from the formation energy and vibration entropy difference for single oxygen vacancy, which incorporated the influence of the oxygen partial pressure³⁶.

The main results are summarized as following. (1) The effective atom jump frequencies in a-axis and c-axis of t-ZrO₂ are obtained as 13.2THz and 12.1THz respectively, which is consistent to the common knowledge of 10³–¹⁰⁴Hz. Fig.1 shows corresponding atomic jump frequencies in temperature range of 10⁰-3000K. (2) Fig.2 is the oxygen vacancy concentration under various oxygen partial pressures. It can been seen a linear dependence of logCᵥ to temperature, and an increase of Cᵥ with a decrease of oxygen partial pressures. (3) Fig.3 gives the exact values of correlation factors in the tetragonal lattice of t-ZrO₂ as the function of temperature along a-axis and c-axis. (4) Summarize up all above results, the self-diffusion coefficients for t-ZrO₂ along a-axis and c-axis can be derived under various oxygen partial pressures. Further considering the equilibrium state between ZrO₂ and metallic Zr, the specific values of the oxygen partial pressures at given temperatures could be decided, so that the oxygen self-diffusion coefficient can be obtained finally, as shown in Fig.4. Furthermore, the thermal expansion of the atomic jump distance and its effect on the diffusion coefficient have been also estimated. Particularly, the thermal expansion of the atomic jump distance and its effect on the diffusion coefficient have been also estimated.

References


Biographical Note

Ying Chen is a professor at the Fracture and Reliability Research Institute, School of Engineering, Tohoku University, Japan. Expertise in computational materials science, modeling and simulation using first-principles approaches combining DFT, phonon, CVM, and materials datamining.
Thermodynamic Stability of Substitutional Elements in Potential New Permanent Magnet Compounds R(Fe$_x$X)$_{12}$ using Special Quasirandom Structures

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Key words: permanent magnets, ThMn$_{12}$, stability

ThMn$_{12}$-type compounds such as NdFe$_{12}$ and SmFe$_{12}$ have been paid more attention in the permanent magnets research community in recent years due to the theoretical prediction of the high magnetization and magnetocrystalline anisotropy energy which are comparable to the current strongest permanent magnet Nd$_2$Fe$_{14}$B[1]. Experimentally, it shows that SmFe$_{12}$ can achieve better magnetic properties than Nd$_2$Fe$_{14}$B[2] but due to the thermodynamic instability it is fairly difficult to synthesize SmFe$_{12}$ in bulk quantity. Adding alloying elements usually improves the stability while reduces the magnetic properties. Finding suitable alloying elements that can stabilize the compound while maintains or reduces the magnetic properties as small as possible are the key to the new class of permanent magnets.

In this work, we focused on the effect of random mixing of the substitutional elements on the stability of NdFe$_{12}$ and SmFe$_{12}$ compounds, as an extension of previous work on 3rd element substitution on the specific sites. First-principles total energy calculations are performed using density functional theory (DFT) via Vienna Ab-initio Simulation Package (VASP). Special Quasirandom Structures (SQS) generated by Alloy Theoretic Automated Toolkit (ATAT) are used for modelling the random mixing of substitute elements in NdFe$_{12}$ and SmFe$_{12}$ structures. Figure 1 shows 156 atoms SQS of SmFe$_{11}$Ti.

The formation energy of NdFe$_{12}$ and SmFe$_{12}$ with respect to the pure elements are positive which indicates that these compounds are thermodynamically unstable. By substituting Fe with Ti or Co, both compounds are stabilized more or less. The calculated formation energies of Ti or Co doped structures show significantly different values according to the substitutional sites of the alloying element in the structure. SQS results gave the most stable energies, indicating the important of disordered substitution of alloying elements in solid solution phases. We also investigated the effect of multi-elements random mixing on stability at various compositions.

This work is supported by the Elements Strategy Initiative Center for Magnetic Materials (ESICMM) under the outsourcing project of Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

References


Biographical Note

Assistant professor at laboratory for functional design of nano-scale interface, Tohoku University, Japan. Expertise in computational thermodynamics focusing on 0K and finite temperature first-principles density functional calculations. Also experience in CALPHAD approach.
O27

Revisiting Cast Al-Cu Alloy with Advanced Characterization and Modern Supercomputing

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Key words: Al-Cu, θ΄-Al3Cu, interfacial energy, solute segregation, STEM, APT, supercomputing, DFT

Oak Ridge National Laboratory (ORNL) recently developed cast Al-Cu alloy that can withstand up to 350°C without losing its mechanical strength. Extensive characterization, scanning transmission electron microscopy (STEM) and atom probe tomography (APT), has revealed that the engineered interface of θ΄-Al3Cu via microalloying is the key to stabilizing this metastable phase at unprecedented high-temperatures. Inspired by this stimulating observation, we have performed massively parallelized first-principles density functional theory calculations with modern petascale supercomputing to further investigate the underlying mechanism [1]. Herein, we present two large DFT databases of solute segregation energy at the interface between the aluminum matrix and θ΄-Al3Cu, and partitioning of solutes within θ΄ via special quasirandom structures (SQSs) [2]. We also report highly accurate semi-coherent Al/θ΄ interfacial energy at under-investigated (110) orientation for the first time [3].

References

Biographical Note
Dongwon Shin got his Ph.D. from the Pennsylvania State University in 2007 and spent two years at Northwestern University as a post-doc before joined ORNL. His research expertise is CALPHAD and ab initio calculations, and recently became interested in modern data analytics and supercomputing for the design of high-temperature alloys.

![Graph](image)

Figure 1. The effective change in room temperature Vickers hardness of conventional and ORNL alloys as a function of preconditioning temperatures, 200-hour exposure at the respective temperature to allow the evolution of the microstructure.
Melting Parameters from \textit{ab initio} Using the Fast Statistical Sampling TOR-TILD Approach: Applications to Al and Ni

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\textbf{Key words:} \textit{ab initio}, melting, thermodynamic integration, confidence interval

The melting point and melting entropy of materials have been always essential ingredients for CALPHAD to determine the lattice phase stabilities of unary materials, which provide the fundamental basis for all multicomponent phase diagram calculations. The phase stabilities of the metastable unaries, for which neither the melting point nor the melting entropy are experimentally accessible, were derived by an indirect procedure \cite{1}. The melting points of the metastable phases were obtained utilizing phase boundary extrapolations from binary alloys \cite{2}. Based on these estimated melting points the melting entropies of the metastable phases were obtained from the observed relationship between the melting entropy and melting point of stable phases. Since these developments the CALPHAD approach was successfully applied to a huge range of multicomponent materials. However, both the extrapolation to the metastable melting points and the correlation between melting points and melting entropy introduce uncertainties.

Recently, we have proposed a new methodology, TOR-TILD (two-optimized references thermodynamic integration using Langevin dynamics) \cite{3} to efficiently calculate melting points and melting entropies of materials with \textit{ab initio} accuracy, which can serve as a reference database for CALPHAD. TOR-TILD is based on the \textit{ab initio} free energy approach, but it overcomes the two main challenges of traditional free energy approaches, the high computational cost and the reliance on a good reference system for calculating the liquid free energies. We have applied TOR-TILD to fcc Cu with both the generalized gradient approximation (GGA) and the local-density approximation (LDA), which give a reliable \textit{ab initio} confidence interval for the melting point and melting entropy. TOR-TILD is not limited to calculate the melting properties of unary, stable and nonmagnetic phases. With certain extensions, it can be straightforwardly applied to magnetic materials, binaries or higher order systems. Most importantly, it can be applied to metastable and dynamically unstable phases.

Although TOR-TILD has significantly improved the computational efficiency, its application involves five successive steps and the knowledge of numerous technical details. To improve the application of TOR-TILD, we have implemented the full TOR-TILD simulation protocol into our in-house framework pyiron (http://pyiron.org) to automatize the procedure. In this work, we have applied the automatized TOR-TILD to fcc Al with both of GGA and LDA. In addition, we have extended TOR-TILD to magnetic materials. Specifically, we consider ferromagnetic Ni, where the magnetic contribution to the liquid free energy has been considered. The reliable \textit{ab initio} confidence intervals from both GGA and LDA are obtained for Al (Figure 1) and ferromagnetic Ni compared to their experimental melting properties.

Figure 1. Gibbs free energies of the liquid and the solid phase of Al as a function of temperature calculated with our \textit{ab initio} approach (TOR-TILD). GGA and LDA results give a reliable \textit{ab initio} confidence interval for the experimental melting point of Al.

\textbf{References}

\textbf{Biographical Note}
In 2009 Li-Fang Zhu received her PhD degree from the institute of physics, Chinese Academy of Science in Beijing. Since then she works as research scientist at Max-Planck-Institute for Iron Research with focus on \textit{ab initio}-based thermodynamics and developing new approaches for investigating melting properties.
O29

Improving Al Wettability on B₄C by Transition Metal Doping: a Combined DFT and Experiment Study

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**Key words:** B₄C/Al; DFT; wettability; work of adhesion; PDOS

B₄C/Al metal matrix composites (MMC) is one of the most potential neutron-shielding materials. Liquid stirring casting technology, at an elevated temperature, is the latest and most efficient method applied to manufacturing of such MMC. However the poor wettability of B₄C/Al interface damages the mechanical properties [¹], adding Al-Ti alloy into liquid Al to enhance the wetting is widely used in industry [²]. First-principles calculations based on density functional theory (DFT) can accurately provide the detailed atomic, electronic structures of the interface and quantitatively predict the work of adhesion [³]. To understand the alloying (or doping) effects in improving the wettability of B₄C/Al interfaces, we investigated the Al(111)/AlB₂(0001) and Al(111)/TiB₂(0001) interfacial structures via a combined approach of experiment and DFT calculations. We find a larger work of adhesion (Wad) on the Al(111)/TiB₂(0001) than the Al(111)/AlB₂(0001) interfaces. The subsequently calculated partial density of states (PDOS) of doped-diborides show fewer anti-bonding states in Al(111)/TiB₂(0001) than in Al(111)/AlB₂(0001), which contribute to a stronger bonding between Ti-3d and B-2p states and lead to a higher Wad and better wetting. Furthermore, we predicted improved wettability of Al/B₄C by V-doping, because of the fewer anti-bonding states in vanadium-boron molecular orbitals.

This first-principles CALPHAD result verifying with systematic experiments achieved a design of controllable complex interface of B₄C/Al composite. This result integrated with magnetic-mechanical stirring have successfully guided the manufactured of 31%wt.B₄C/Al composites with the B₄C particles distributed relatively homogeneously in matrix. These MMC products are being applied to spent fuel storage projects of China nuclear power plants.

The same approach developed in this study may be applied for general design of alloy elements to improve the interfacial wetting of alloy-semiconductor systems.

![Figure 1. Partial density of states of Ti-AlB₂ systems: partial Al, B, Ti density of states and total density of states of Ti-AlB₂ (the vertical lines indicate the Fermi level E_F)](image)

**References**


**Biographical Note**

Li Qiulin is an associate professor in Graduate School at Shenzhen, Tsinghua University. His areas of specialization include new materials for nuclear energy, preparation technology of metal matrix composites and external field effect on materials.
First-principles-only Phase Diagram for the Al-Ni System
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Key words: first principles, DFT, CEF, ordered phases, CVM

Phase diagrams calculated entirely from first principles have the potential to reduce time and expense in investigations for materials design by providing important thermodynamic information on new material systems at the prediction stage. However, it is still difficult to create a thermodynamic description of most systems using only calculated data and conventional methods. An approach is proposed that considers several theoretical techniques to inform a CALPHAD-based thermodynamic description derived only from first principles data.

Commonly, thermodynamic descriptions made using the CALPHAD approach use the Bragg-Williams approximation to describe the configurational entropy of a solid, which is a point correlation model ignoring the pair and higher order interactions [1]. Generally, other entropy contributions are indirectly contained within the excess energy terms that have optimized parameters fitted to experimental data. The Bragg-Williams entropy model with pure computational data does not give a proper description of the phase diagram, which is partially attributed to the lack of consideration of short range ordering. Other theoretical techniques, such as the Cluster Variation Method (CVM) [2], allow consideration of higher order configurational entropy contributions, and can be shown to produce phase diagrams with topology consistent with the real physical case.

In this work, various techniques have been implemented to modify the Gibbs energy of the CALPHAD descriptions of the fcc and bcc phases, such as by using reciprocal interaction parameters in a structure based on the compound energy formalism (CEF) [3,4]. These Gibbs energy models are then populated directly with data calculated from first principles, without any optimization.

Al-Ni was taken as a prototype system to compare various thermodynamic models and test the proposed new approach for calculating phase diagrams. First principles calculations for ordered phases include Density Functional Theory (DFT) ground state calculations, electronic energy contributions, and vibrational energy contributions up to 2500K from phonon calculations (quasiharmonic approximation) and the Debye-Grüneisen model. In addition to the known stable solid phases, various unstable phases were also considered.

We show that the effects of short range ordering are introduced with this framework, and further configurational entropy contributions can be directly included by comparison with other theoretical techniques such as the CVM.

Figure 1. Enthalpy of formation of all considered structures at 0K from DFT calculations.

A satisfactory solid phase diagram that reproduces all primary topological features of the experimental phase diagram is produced, using a CALPHAD platform and only first principles data.

Comparing the descriptions produced from each type of theoretical data, the computational accuracy required for a thermodynamic description without experimental insight is considered.

References

Biographical Note
Theresa Davey is an assistant professor at Tohoku University, Japan. Her work is themed around directly introducing information relating to physical quantities in CALPHAD descriptions. She completed her PhD in 2017 at Imperial College London, UK, with a thesis considering calculated structural defect-related properties directly within CALPHAD assessments of ultra-high temperature ceramics.
**O31**

*Ab initio* Phase Stability and Electronic Conductivity of the Doped-\(\text{Li}_4\text{Ti}_5\text{O}_{12}\) Anode for Li-ion Batteries

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**Key words:** lithium-ion batteries, \(\text{Li}_4\text{Ti}_5\text{O}_{12}\), phase stability, *ab initio* calculations

The \(\text{Li}_4\text{Ti}_5\text{O}_{12}\) (LTO) defect spinel is a promising anode material for lithium-ion batteries (LIBs), but it shows an intrinsic insulating property and poor electrochemical kinetics. Doping is a direct approach to manipulate the electronic conductivity of LTO. However, doping may induce multiple effects influencing the overall electrochemical kinetics, e.g., changing the size of particles and the ionic and electronic conductivities. Here we systematically investigated the phase stability, electronic conductivity, and electrochemical kinetics of M-doped LTO (M = Na, K, Mg, Ca, Sr, Al, and Ga). With both *ab initio* calculations and experiments, the mechanism of electron transport within LTO is elucidated, the desired type of dopants for improving electronic conductivity of LTO is clarified, and the role of electronic conductivity in the electrochemical kinetics of LTO is revealed. These results provide mechanistic insight into the doping approach to LTO and would guide the development of a variety of electrode materials.

![Graph](image)

*Figure 1. The enhancement of electronic conductivity as well as the role of electron transport in electrochemical kinetics are demonstrated for doped \(\text{Li}_4\text{Ti}_5\text{O}_{12}\)*

**References**


**Biographical Note**

Dr. Shih-kang Lin is an associate professor in dept. Mater. Sci. Eng. at National Cheng Kung University in Taiwan. His researches focus on computational thermodynamics-assisted design of advanced processes and materials, including Li-ion and solid-state batteries, lead-free solders, steels and multi-principal element alloys. He currently serves as the vice chairperson of the Alloy Phase Committee of TMS, an advisor as well as a guest editor for JOM, and the vice director of Hierarchical Green-Energy Materials (Hi-GEM) Research Center, NCKU.
Defect Phase Diagrams: Concepts and Applications

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Key words: defect phase diagrams, density functional theory

The enormous progress in aberration corrected transmission electron microscopy and atom probe tomography opened up the opportunity to systematically study with atomic resolution phases and phase transitions that form at extended defects such as dislocations, grain boundaries or interfaces. In contrast to common expectations, experiments and theory showed a much more complex behavior: Enhanced segregation can lead to spinodal decomposition and spatially confined phases can form around the defect that are thermodynamically unstable as bulk phase. Using first principles calculations, as well as empirical potentials, together with thermodynamic concepts we have started to develop a framework that allows us to construct defect phase diagrams. In the presentation we will give a brief overview over (i) the fundamental concepts, (ii) the type of complex simulation protocols and the tools we developed to handle them [1], as well as (iii) recent applications in dislocation and grain boundary engineering and hydrogen embrittlement [2, 3, 4].

Figure 1. Excess hydrogen per unit length, \( c_{H}^{\text{bulk}} \), in a straight edge dislocation as a function of hydrogen concentration \( c_{H}^{\text{bulk}} \) and temperature \( T \). The contours show that the transition between the hydride forming and the non-hydride forming regime is a sharp function of \( c_{H}^{\text{bulk}} \) and \( T \). Inset are equilibrium hydrogen structures at \( T=300K \) and two different bulk hydrogen concentration regimes.

References


Biographical Note

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O33

Thermodynamic Assessment and Experimental Study of the Cu-Cr-O System

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Key words: Cu–Cr–O system, phase diagram, delafossite CuCrO2, CALPHAD

The Cu-Cr-O system has technological applications in the development of catalytic compounds and transparent conductive films. The thermodynamics of this system was reviewed in 2010 [1], highlighting a lack of knowledge about phases equilibria, thermodynamic properties and possible non-stoichiometry of the ternary oxide phase spinel (CuCr2O4). In the present work, a model based on the CALPHAD method was developed with the available literature information and some additional measurements. The resulting phase diagram is shown in Figure 2.

The subsystems Cu-O, Cr-O and Cr-Cu were partially reassessed from the previous optimization of [2,3,4], respectively. The liquid phase, covering the whole composition range, was described with the modified quasichemical model [5] according to (Cu+, Cu2+, Cr+, Cr2+, Cr3+) (O2−, Va2−), with interaction parameters in the ternary system set with the liquidus data from [6]. The thermodynamic properties of the compound CuCrO2 were established according to our recent assessment (see J. Schorne Pinto et al., this conference), and the main information on solid phase equilibria were taken from [7–9].

Figure 2. Calculated Cu-Cr-O diagram in air with experimental data [this work and 6]

In situ HT-XRD (High-temperature X-Ray Diffraction) analyzed with Rietveld refinement method as well as TGA/DTA measurements were used to provide thermo-structural information in the temperature range 50 to 1100 °C for various compositions in the system (see Figure 2). These new experimental data were included in our description of the stability region and phase equilibria of the Cu-Cr-O system.

Acknowledgments
The authors wish to thank Toulouse INP for its financial contribution to academic visits at CRCT Montreal (L. Cassayre, J. Schorne Pinto), as well as Région Occitanie for PhD funding (J. Schorne Pinto).

References

Biographical Note
Juliano Schorne Pinto is a Ph.D. student at Université de Toulouse and research associate at the CIRIMAT and Laboratoire de Génie Chimique.
Iron-based shape memory alloys (SMAs) have attracted the attention of many research groups in recent years due to promising advantages compared to conventional NiTi-based alloys in several application fields like damping in constructions for the civil infrastructure and actuation for aerospace applications. [1,2] The main advantages are low materials costs and easy manufacturing due to the good cold workability. Moreover, iron-based SMAs provide the pseudoelastic effect over a wide temperature range due to the low slope of the Clausius-Clapeyron equation, which describes the temperature dependence of the superelastic stress [1]. For a further improvement of these properties, a thermodynamic description of the Al–Fe–Mn–Ni system can be used to adjust the chemical composition and to improve heat-treatment procedures.

The present thermodynamic assessment is based on reliable literature data, as well as comprehensive experimental investigations including conventional heat treated and subsequently quenched alloys, as well as diffusion couple experiments. The sample selection focused especially at the phase equilibria, which are important for the application of iron-based SMAs, including the phases A1, A2 and B2. The prepared samples were analyzed by means of scanning electron microscopy, wavelength dispersive electron probe microanalysis and transmission electron microscopy.

For both, the conventional heat treated and quenched samples, as well as the diffusion couples, the experimentally observed phase equilibria were reproduced very accurately by thermodynamic calculations. The measured tie-lines of three alloys heat treated at 1175°C and subsequently quenched are illustrated in the isoconcentration section at \( x_{\text{Mn}} = 0.20 \) in Figure 1 (a). Exemplarily the diffusion path of one of the diffusion couples, heat treated at 1000°C, is illustrated in the isoconcentration section at \( x_{\text{Mn}} = 0.08 \) in Figure 1 (b).

![Figure 1. Calculated partial isoconcentration sections of the Al–Fe–Mn–Ni system at (a) \( T = 1175°C \) for \( x_{\text{Mn}} = 0.20 \), together with the measured tie-lines of the conventional heat treated and quenched samples and (b) \( T = 1000°C \) for \( x_{\text{Mn}} = 0.08 \), together with the diffusion path given as the red line, the two-phase field (A1 + B2) covered by the diffusion couple illustrated with the red marked area and the experimentally measured local phase equilibria in the diffusion couple.]

References

Biographical Note
Alexander Walnsch studied Material Science and Technology and received the diploma degree in 2016 at the TU Bergakademie Freiberg. Since 2017 he works as research associate in the Institute of Materials Science (TU Bergakademie Freiberg). Research interests are experimental investigation and modelling of phase diagrams of metallic systems.
O35

Thermochemistry of the CaO - TiO$_2$ and SrO-ZrO$_2$ System: From Enthalpies of Formation and Heat Capacities of the Compounds to the Phase Diagram

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**Key words:** Ruddlesden-Popper compounds, calorimetry, thermodynamics, CALPHAD

Reliable thermodynamic and phase diagram data of the CaO - TiO$_2$ and SrO-ZrO$_2$ system are of interest for the optimization of synthesis and applications of functional and high temperature structural ceramics. The publications on the phase relationships and thermodynamic properties of these systems are unfortunately scatter and confusing. This work prepared the Ruddlesden-Popper compounds $\mathrm{A}_n\mathrm{B}_x\mathrm{O}_{3n+1}$ ($\mathrm{A}=$Ca, Sr; $\mathrm{B}=$Ti, Zr) with $n=3, 2$ and $1$ by solid state reactions and determined their heat capacities from 573 to 1273 K by differential scanning calorimetry and enthalpies of formation at 298 K by high temperature oxide melt solution calorimetry. Their thermodynamic functions and the corresponding systems are then critically evaluated by CALPHAD technology. This work would like to demonstrate how to set up the Gibbs energy function of the compounds based on the experimental thermodynamic data, how to identify and resolve the inconsistency between various kinds of experimental data and then to explain the literature information based on the phase diagram and thermodynamic properties. This is a prerequisite for accurate predictions of the relationships among the composition, temperature and microstructure of relative complex functional and structural materials.

**References**


**Biographical Note**

Weiping Gong is a Prof. Dr. of Materials Physics. She is director of Laboratory of Electronic Functional Materials, Huizhou University. Her main research interests have been the thermodynamics and microstructure of materials, including the molten salts and electronic functional ceramics. She has produced over 60 international publications.

![Figure 1. From Enthalpies of Formation and Heat Capacities to the Compounds to the Phase Diagram](image-url)
The Fast Silver Ion Conducting Solid-state Electrolytes for Deriving Thermodynamic Data

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Key words: EMF-method, solid electrolyte, silver iodide, thermodynamics

Reliable thermodynamic data are essential for accurate quantitative modelling of the stabilities of materials and their chemical behavior in the presence of other equilibrium phases. These thermochemical data support process improvement, in the extractive metallurgy of valuable metals, as well as product development work, in the design of novel multi-component functional materials.

Major groups of experimental methods to determine thermodynamic properties of materials are calorimetry, vapor pressure measurements and electromotive force (EMF). Calorimetry is a very convenient method to determine enthalpy values precisely. In the vapor pressure methods, the partial pressures of individual components can be measured and thermodynamic activities and partial Gibbs energies can be derived. In the case where partial pressures are obtained as a function of temperature, partial enthalpies and entropies can be calculated, although these derived quantities are usually less accurate than the directly measured partial Gibbs energies. The EMF method has proven to be direct, effective, and the most accurate method for determining the Gibbs energy of formations, chemical potentials, thermodynamic activities and partial pressures in equilibrium conditions. Furthermore, the entropies and enthalpies of reactions can be calculated from the EMF versus temperature relations of the electrochemical cell [1].

This work reviews, updates and discusses the EMF method that employs the fast Ag⁺ ion conducting solid electrolytes. The important experimental procedures for a successful measurement of the EMF of different galvanic cells in a certain temperature range and determination of the thermodynamic properties of chemical compounds from the obtained EMF values were discussed. A typical galvanic cell arrangement in a furnace is presented in Figure 1. The pure Ag⁺ ion conducting solid electrolytes were discussed in detail. The ionic conduction mechanisms in relation to the crystal structure are also studied. Superionic conductors in different temperature ranges were identified. Finally, the effect of pressure on ionic conductivity and the application of the solid electrolytes in the EMF cells are discussed.

We have also conducted EMF measurements using the fast Ag⁺ ion conducting solid state electrolyte. A solid electrolyte Ag₃GeS₂ glass and the cathode material Ag₃HgSe₂ were synthesized and electrochemical cell was assembled to measure the activity of Ag in the quaternary phase: (−)C | Ag | Ag₃GeS₂ glass | Ag₃HgSe₂ | C(+), where C is graphite and Ag₃GeS₂ glass is the fast purely Ag⁺ ions conducting electrolyte. The linear dependencies of the EMF of the electrochemical cell on temperature were used to determine the standard thermodynamic properties of Ag₃HgSe₂.

References

Biographical Note
Dr. Fiseha Tesfaye is a Senior Researcher in the Johan Gadolin Process Chemistry Centre (PCC) at Åbo Akademi University, Finland. He received his Master’s degree in materials processing technology in 2009 from Helsinki University of Technology and PhD degree in metallurgy in 2014 from Aalto University, Finland.
The Intermetallic Compound Co₃Ta and High-temperature Phase Equilibria in the Co–Ni–Ta System

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Key words: Cobalt-based superalloys, Phase stability, Scanning electron microscopy, X-ray diffraction

Nickel and tantalum are two basic constituent elements of Co-based superalloys and the addition of them can increase the solvus temperature and enhance the stability of γ'. Hence, the Co–Ni–Ta system is an important subsystem for Co-based superalloys.

Recently, the isothermal sections of the Co–Ni–Ta system have been constructed by Shaipov et al. [1] for 1200 and 1375 K and Zhu et al. [2] for 1073 and 1173 K. However, these isothermal sections indicate an unusual phenomenon that the intermetallic compound Co₃Ta (also called as Co₂Ta₃ in the former literature) has such a large Ni solubilities in the Co–Ni–Ta system. Besides, the crystal structure of Co₃Ta was still uncertain in the Co–Ta system. Therefore, further experiments on Co₃Ta are required.

![Figure 1. Predicted liquidus surface projection](image)

**Figure 2. Isothermal section at 1473 K**

References


Acknowledgements

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Study on the Phase Equilibria of the Au-Pt-Co system

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Key words: Au-Pt-Co, order-disorder transition, phase diagram, CALPHAD

Due to their high catalytic activity and good corrosion stability, Au-Pt-based alloys have important applications in the field of electrocatalysts\(^1\). In this work, we intend to study how the transition metals affect the phase equilibria of the Au-Pt-based alloys.

As the phase diagram of the Au-Pt-Co ternary system has never been previously studied, the first step of this work is to predict the Au-Pt-Co ternary phase diagrams by CALPHAD calculation based on the binary thermodynamic assessments of Au-Pt\(^2\), Au-Co\(^3\), and Co-Pt\(^4\). After that, two typical Au-Pt-Co ternary alloys with 16 at.% Au were selected. The alloy samples were prepared by arc melting under an Ar pressure of 0.5 mbar. The ingots were annealed at 850 °C for 7 days to promote homogeneity, and then were annealed at 650 °C for 20 days. The diffusion couple technique is also used in this work. The diffusion couple was prepared by the pure Au, Pt and Co, and were annealed at 850 °C for 30 days.

The alloy samples and the ternary diffusion couple were analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM) coupled with energy dispersion spectroscopy (EDS). As a result, the isothermal sections of the Au-Pt-Co ternary system at 650 °C and 850 °C have been established, together with the CALPHAD results of this system, as shown in Figure 1. Figure 1(a) shows that, at 650 °C, both the ordered L1\(_0\)-CoPt and L1\(_2\)-CoPt\(_3\) can dissolve a certain amount of Au and can get equilibrium with the disordered fcc phase (Au). While at higher temperatures, the ordered phases in the Co-Pt system disappear, and there exists a continuous solid solution (Co,Pt) with fcc_A1 structure. As shown in Figure 1(b), the (Co,Pt) phase can dissolve very slight amount of Au, and a ternary miscibility gap between the disordered fcc phases of (Co,Pt) and (Au) forms.

Figure 1. Isothermal sections of the Au-Pt-Co ternary system at 650 °C (a) and 850 °C (b)

References


Biographical Note

Yanglin Wang is a Ph.D. student at the College of Materials Science and Engineering, Northeastern University. Her research interests focus on the phase diagrams of precious metals, including experimental determinations and thermodynamic calculations.
Modelling of the Pressure-dependent Phase Stability in the Binary Ti–Fe System

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Key words: phase diagram, CALPHAD, high pressure torsion, thermal stability

Titanium-rich Ti–Fe alloys are promising candidates for development of new engineering materials, as they possess excellent mechanical properties and good corrosion resistances. The adjustment of the microstructure, e.g., through the mechanical and thermal treatment, improves further the properties of these alloys. The key parameters are the amount and distribution of the low-temperature α-Ti phase, the high-temperature β-Ti phase and the high-pressure α'-Ti phase. In order to better understand the formation behavior of the α-Ti phase different initial states of the samples were produced. Heat-treatments were performed at 470 and 800°C. In the present work, severe plastic deformation by high-pressure torsion (HPT) was applied to refine the grains and to initiate the α-Ti formation.

The phase fractions, the distribution of individual phases and their orientation relationships in the initial and HPT processed alloy (Ti-4Fe) were analyzed using X-ray diffraction (XRD), electron microscopy (SEM, (HR)TEM) and electron diffraction (EBSD, SAED). The thermal stability of the α phase was investigated by means of thermal analysis, and in situ XRD. The experimental results were compared with the results of thermodynamic calculations performed with the Thermo-Calc software and taking the effect of the hydrostatic pressure into account.

The alloys quenched from the bcc β-(Ti,Fe) solid solution show a martensitic microstructure for Fe contents below 2 ma.% and the formation of the athermal α phase at approximately 4 ma.% Fe. Alloys annealed at 470°C exhibit a two-phase α-Ti + TiFe microstructure. During HPT, the sample were partially or completely transformed to α-Ti, depending on the Fe content and the initial phase composition. The maximum amount of α-Ti was found at 4 ma.% Fe quenched from 800°C and minimum amount at 10 ma.% Fe annealed at 470°C. Differences in the thermal stability of the HPT-induced α-Ti phase were detected in the alloys.

The thermodynamic modelling of the pressure-dependent phase stability was performed, first for the unary systems titanium (see Figure 1) and iron. Thereby, experimental as well as ab initio data regarding the heat capacities, molar volumes, thermal expansions and bulk moduli were utilized to model the phases in these unary systems. The modelling of the binary Ti–Fe system was based on the assessment of Ref. [1]. However, the modelling of the intermetallic phases TiFe and TiFe₂ was modified. Both compounds were modelled as separate phases taking into account experimental heat capacity and heat of formation. Finally, the system was re-optimized and extrapolating calculations were performed to predict the phase equilibria in the Ti–Fe system at high pressures.

Thermodynamic calculations of the Tₚ-lines were performed to describe the diffusion-less transformations of the high-temperature β phase into the low-temperature α' and the athermal α phases and to predict the maximum Fe solubility in these phases.

Figure 1. Calculated pressure-temperature phase diagram of pure Ti

References

Biographical Note
Mario J. Kriegel studied Materials Science and Technology and received the doctoral degree in 2014 at the TU Bergakademie Freiberg. Since 2009 he works as research associate in the Institute of Materials Science (TU Bergakademie Freiberg). His research interests are experimental investigation and modelling of phase diagrams of metallic systems.
In-Situ Phase Diagram Determination of the HfO$_2$-Ta$_2$O$_5$-Temperature System up to 3000 °C
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Key words: Phase diagrams, In-situ High temperature X-ray diffraction, Hafnia, Tantalia,

Ceramic equilibrium phase diagrams have proven to be difficult to produce for materials above 1500 °C. We demonstrate that in-situ X-ray powder diffraction on laser-heated, levitated samples can be used to elucidate phase diagrams up to 3000 °C. In these experiments, solid spherical samples were suspended and rotated by a gas stream through a conical nozzle levitator, heated by a 400 W CO$_2$ laser at beamline 6-ID-D of the Advanced Photon Source at Argonne National Laboratory, Lemont, IL, USA. X-ray diffraction patterns suitable for Rietveld refinement were collected at 100 °C temperature intervals and were used to determine the phase fields of phases present. The temperature of each phase was determined based on thermal expansion data collected by powder diffraction in conjunction with the Quadrupole Lamp Furnace (QLF) at beamline 33-BM-C of the Advanced Photon Source. The liquidus temperatures were determined from levitation and laser-heated recalescence experiments. The crystal structures of new phases were solved using the charge flipping method from powder diffraction data. The HfO$_2$-Ta$_2$O$_5$ binary was investigated as an example system due to its high melting points and application in refractories and electronics.

Figure 1. HfO$_2$-Ta$_2$O$_5$-Temperature phase diagram built based on the observed equilibrium phases from in-situ X-ray powder diffraction and the Gibbs Phase Rule. The H subscript is referring to the compounds which exhibit a homologous series. The dashed lines in the O-Ta$_2$O$_5$ and the O-Hf$_6$Ta$_2$O$_{17}$ regime signify the potential homologous series of compounds. The eutectoid and peritectic tie lines would have to be adjusted based on the Gibbs Phase Rule to accommodate the homologous series. The homologous series lines drawn in the Hf$_6$Ta$_2$O$_{17}$ regime matches the predicted by the work of McCormack et al. Acta Cryst B (2019). The homologous series lines drawn for the Ta$_2$O$_5$ regime are simply a schematic and have not been determined experimentally or theoretically.

References

Biographical Note
Scott J. McCormack is a final year graduate student at the University of Illinois at Urbana-Champaign in the Department of Materials Science and Engineering. His research interests focus on the interplay between material symmetries and energetics that can extend our understanding of thermophysical and thermochemical properties of next generation ceramic materials.
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Heat Capacity of Al₂MnO₄ and Thermodynamic Assessment of the Al₂O₃-MnO System

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Key words: spinel, assessment, Al₂MnO₄, Al₂O₃-MnO, heat capacity

The Al₂O₃-MnO system is essential for steel industry. According to available experimental results, manganese is the main reactive alloying element in steel in combination with oxide ceramics. Thereby, the interactions between steel and alumina should be thermodynamically modelled, including the Al₂O₃-MnO system into ceramic materials description.

The Al₂O₃-MnO system has been thoroughly investigated. However, it is still unclear whether the MnAl₂O₄ spinel phase melts congruently or according to the peritectic reaction L + Al₂O₃ ↔ MnAl₂O₄. Moreover, the thermodynamic description of the Al₂O₃-MnO system has been performed several times. The first optimization of Eriksson et al. (1993) has been then improved [1] by correcting the Gibbs energy of MnAl₂O₄ from the original experimental data. In both works, Farina and Neto [2] who modeled the MnAl₂O₄ spinel phase using the three sublattice model and considering the Mn²⁺ and Al³⁺ distribution between tetra- and octahedral sites and Navarro et al. [3] who considered MnAl₂O₄ as a stoichiometric compound, the Gibbs energies of MnAl₂O₄ were not consistent with the experimental values. Recently, Chatterjee and Jung [4] re-modeled the Al-Mn-O system by taking into account various oxidation states for Mn and describing cubic spinel as (Mn²⁺,Al³⁺)₃(Mn²⁺,Mn³⁺,Mn⁴⁺,Al³⁺,Va)₃O₁₂. Their calculations showed that MnAl₂O₄ spinel melts with decomposition at reducing atmosphere.

Despite the presence of numerous studies performed to optimize the Al₂O₃-MnO system, the available data are partially contradictory. The aim of the present work is thus an experimental study of the Al₂O₃-MnO system, critical evaluation and optimization of all available data to get reliable thermodynamic description of the system.

The MnAl₂O₄ compound has been prepared by co-precipitation routine described well in Ref. [3] and then annealed at 1100°C followed by air-quenching. XRD confirmed the presence of pure MnAl₂O₄ spinel. Melting behavior of MnAl₂O₄ has been checked by DTA followed by SEM/EDX. Heat capacity measurements of the spinel compound have been carried out in the temperature range between -70°C and 600°C using DSC (Fig. 1). Obtained data fitted using Maier-Kelley equation:

\[ C_p, J/mol K^{-1} = 160.69 + 0.01444 T - 3.52381 \times 10^{-4} T^{-2}, \]

agree with results of Navarro et al. [3].

Results obtained in the present work and available thermodynamic data will be used to derive a new thermodynamic description of the Al₂O₃-MnO system. Using the CALPHAD approach by applying the Thermo-Calc software, liquid will be described by the two-sublattice model for ionic liquids while all solid solutions – using the compound energy formalism. A low inversion degree of spinel previously reported will be also accounted for the MnAl₂O₄ modeling.

![Figure 1. Heat capacity of Al₂MnO₄ spinel](image)

**References**


**Biographical Note**

M. Ilatovskaia is a researcher at TUBA Freiberg. Her main area of interest is the study of ceramic systems related to the filter materials used during steel and aluminum processing. She is also a Ph.D. student at SPbPU (Russia), where she finalizes her research on phase diagrams for non-ferrous metallurgy.
Experimental Study of the Slag/matte/spinel/gas Equilibria in the “Cu2O”-“FeO”-SiO2-S-Al2O3-MgO-CaO System

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Key words: copper smelting, phase equilibria, slaging elements, SEM-EPMA, quenching

Optimisation of the metallurgical primary and recycling operations needs accurate and reliable information on high temperature chemistry of increasingly complex slag/matte/metal/gas systems. The lack of data and reliable models exists due to difficulties in high temperature experiments and thermodynamic modeling. The authors of the project are continuously developing the integrated experimental and modeling research program for non-ferrous smelting and recycling systems. This program allows accurate determination of phase equilibria in complex systems at high temperatures and different gas atmospheres. Experimental and modeling studies are focused on the phase equilibria in “Cu2O”-“FeO”-SiO2-S multicomponent system with Al2O3, MgO and CaO slagging elements. The experiments involve high temperature equilibration in controlled gas atmospheres, rapid quenching and direct measurement of equilibrium phase compositions with quantitative microanalytical techniques including electron probe X-ray microanalysis and Laser Ablation ICP-MS. The thermodynamic modelling is undertaken using computer package FactSage with the quasi-chemical model for the liquid slag phase and other advanced models.

The current research is devoted to the improvement of the precision and accuracy of the results, obtained with the applying of experimental technique. Significant advances have been achieved through continuous developments of experimental methodologies [1 – 3]. Systematic analysis of all experimental steps including preparation of the initial mixture, achievement of equilibrium at desired conditions, quenching, EPMA uncertainties, etc. is done. Systematic analysis enables to identify a number of possible sources of uncertainties and to develop the ways to mitigate those shortcomings.

Achievement of equilibrium is the most important and common uncertainty in the phase equilibria studies. The key four-test approach is applied to ensure the achievement of equilibrium state. It will be discussed in details during the conference.

After equilibration experiment the sample is mounted in epoxy resin polished, and examined with SEM. The example of local phase equilibria area is given in Figure 1. EPMA analysis of compositions of coexisting phases gives the information about local phase equilibria.

The equilibration/quenching/microanalysis approach will be discussed applying to phase equilibria in the above mentioned system.

Figure 1. Example of BSE-image of the microstructure of equilibrium sample in the “Cu2O”-“FeO”-SiO2-S-Al2O3-MgO-CaO system at 1200°C, PSO2=0.25 atm and P O2 = 10−4.3 atm

References

Biographical Note
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Areas of interest: Experimental research of phase equilibria, Thermal Analysis, SEM/EPMA methods, Sulphide-metals systems, Pyrometallurgy of nonferrous metals.
Experimental Study of the Phase Equilibria in the Co-Fe-La System

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Key words: Co-Fe-La system, ternary compound, phase equilibria

Rare earth-transition metal alloys have been the subject of numerous investigations because of their magnetic properties. Co₁₂La has the largest 3d metal content of any known rare-earth intermetallic, resulting in a very large magnetization and a high Curie temperature and, accordingly, is of potential interest for various applications [1]. Co₃La has a relatively high magnetization, a strong uniaxial magneto-crystalline anisotropy field, and a high Curie temperature and therefore it is another promising candidate for permanent magnets [2]. Replacement of Co in Co₁₂La by Fe enhances the magnetic moment. Fe doping in Co₄La increases the saturation magnetization while improving the coercivity. However, information on phase equilibria in the Co-Fe-La system was limited to partial isothermal sections at 800 and 400°C [3]. A ternary compound (Co,Fe)₁₇₋₄La₂ (Th₂Zn₁₇-type structure, R-3m, a = 8.524-8.546, c = 12.370-12.400 Å) had been reported. It had also been reported that the ternary solid solution of Fe in Co₁₂La extends up to 35 at.% [3].

In this work, phase equilibria in the Co-Fe-La system at solidification and at 500°C have been studied for the first time. The liquids and solids projections and an isothermal section at 500°C over the whole concentration region have been constructed. It was shown that the ternary compound Co₄₋₃Fe₃La₂ (t) melts incongruently by peritectic reaction, has a rather wide homogeneity range and coexists with most of the phases based on the binary compounds.

The liquidus surface of the Co-Fe-La system (Fig. 1) is characterized by fields of primary crystallization of (γFe,Co), (δFe), (αFe), (γLa), (βLa), the binary-based phases Co₁₂La, Co₃Ca, Co₁₀La₅, Co₅La₂, Co₃La₂, Co₂La₇, Co₁₃ and also the ternary compound (Co,Fe)₁₇₋₄La₂ (t), separated by corresponding monovariant curves and participating in ten four-phase invariant equilibria.

The phases based on the binary compounds are substitution solid solutions. Of the binary compounds Co₁₂La has the widest homogeneity region.

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References

Biographical Note
Degree: PhD (physical chemistry), 2012.
Place of work: Thermochemistry of Materials Scientific Research Centre, NUST MISIS, Leninsky prosp. 4, 119049 Moscow, Russia.
Present work: Investigation of phase equilibria in the Fe-[C, Co, Ni]-[La, Ce] and [Ti, Zr]-[Si, Sn]-[V, Nb, Cr, Mn, Fe, Co, Ni, Al, Ga etc.] ternary systems.
Fields of interests: Phase equilibria and phase transformations.

Figure 1. Liquidus projection of the Co-Fe-La system
Experimental Study and Thermodynamic Re-assessment of the Co-Sb System

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Key words: Co-Sb system, differential thermal analysis, phase analysis, thermodynamic modelling

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The Co-Sb system is of a keen interest because of the existence of CoSb3 phase with skutterudite structure, which is the basis for doped CoSb3 based skutterudite thermoelectric materials. A good knowledge on phase relations in this binary system, including especially the CoSb3 phase, is therefore crucial for the study of the thermal and phase stability of the doped analogues.

This system has been studied experimentally and theoretically by many authors. Compared to other studies, the recent thermodynamic assessment published by Zhang et al. [1], leading to phase diagram shown in Figure 1, may not be necessarily fully correct as pointed out in a critical review by Okamoto [2]. A contradiction exists especially in the position of the liquidus line on the Sb-rich side of the phase diagram and for the eutectic reaction, liquid ↔ CoSb3 + Sb, the information on which can be found in Massalski [3]. Correct information on the phase equilibria in this part of the phase diagram is necessary for prediction of phase stability of the thermoelectric phase in higher order systems.

To obtain reliable data, experimental alloys in composition range from 80 to 100 at% Sb were prepared and investigated by differential thermal analysis (DTA) on a Netzsch STA 409 CD/3/403/5/G apparatus and by methods of phase analysis performed on a Tescan LYRA 3XMU FEG/SEM scanning electron microscope (SEM) with an XMAX 80 energy dispersive X-ray (EDX) analyzer by Oxford Instruments. The data were compared with existing literature information and thermodynamic re-assessment of this binary system based on CALPHAD approach, using software PANDAT and ThermoCalc, was done.

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

References


Biographical Note

Pavel Brož is associate professor at Masaryk University, Faculty of Science, Department of Chemistry and at CEITEC MU, Brno, working in experimental thermodynamics and CALPHAD calculations of metal systems. Present research activity is focused on thermoelectric materials and nanoalloys.
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Experimental Investigation and Thermodynamic Modeling of Cu-Si-Zr and Ni-Si-Zr Integrating ab initio Calculation

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Key words: ab initio, CALPHAD

This study attempts to systematically and theoretically investigate the Cu-Si-Zr and Ni-Si-Zr ternary systems. The graphical representation of the experimental research plan in this study is shown in Figure 1. These investigations are performed in the context to improve the Cu-based thermodynamic CALPHAD database and to generate information that are absent in the literature because of the experimental difficulties. The primary solidification phase analysis, ternary liquidus surface measurement, isoplethal and isothermal sections (1073 K) information for Cu-Si-Zr and Ni-Si-Zr ternary alloy compositions are performed and detailed in this study.

The primary solidification phase analysis is with the XRD and SEM. The ternary liquidus is measured in-situ during arc melting with the aid of pyrometer. Pyrometer is the only option to measure high melting temperature of oxidation prone Zirconium rich alloys. 16 ternary Cu-Si-Zr and Ni-Si-Zr alloy compositions each were heat treated at 1073 K for 40 days and their constitutional information were analyzed with the aid of XRD and EPMA. The transformation temperature for few Cu-Si-Zr alloys were measured with DSC whereas, Ni-Si-Zr alloys could not be used in the DSC because of its reaction with the DSC alumina crucible.

The Cu-Si-Zr (7) and Ni-Si-Zr (6) system consists of several ternary intermetallic compounds. Their energy of formation are calculated with the aid of ab initio calculation. Sublattice model was proposed for these intermetallic phases. The Gibbs energy modeling of Cu-Si-Zr and Ni-Si-Zr metallic system is accomplished by CALPHAD methodology. The results of this study and their comparison with the existing information would give a detailed insight of Cu-Si-Zr and Ni-Si-Zr system.

Figure 1. Graphical representation of the experimental plan

Biographical Note
Dr. V. B. Rajkumar’s research interest are in computational thermodynamics. This include the experimental and theoretical investigation of phase diagram of the metallic systems, CALPHAD, physics based techniques (ab initio calculation, MD and AIMD simulation) assisting CALPHAD modeling, diffusional studies and Phase field simulation.
Enthalpies of Formation of Some Laves Compounds as a Function of Composition

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Key words: Laves phase, Formation Enthalpy, Calorimetry

The standard enthalpies of formation of some Laves phases in ternary alloy systems have been measured by direct synthesis calorimetry. The measured compounds are NbAl(Fe, Ni or Cu) and FeAlTi. Since these compounds exhibit substantial homogeneity ranges, measurements have been made as a function of composition. The measured enthalpies of formation (in kJ/mole of atoms) of the Laves compounds will be discussed and compared with first principles computed values. The crystal structures of the Laves compounds were verified by X-ray diffraction analysis. Scanning electron microscopy (SEM) and energy-dispersive spectroscopy were used to verify the phase composition. The compounds are typically extensions of binary Laves phases with significant solubility in the ternary system. This offers the opportunity to measure the enthalpy of formation over a range of composition providing insight into the alloying and constitutional defect behavior.

Biographical Note
Qing Gu joined the group in 2017 for her Ph.D. degree in Materials Science and Engineering. She obtained her Master degree in Materials Physics and Chemistry from Beijing Normal University, China. Her research is focused on calculate the formation energy of metallic compounds with different composition in ternary systems and compare the experimental data with first principles computed values. The experimental data provides stability predictions and obtains standard formation energy for future alloy design. The enthalpy of formation is the major component of the Gibbs energy, particularly at moderate to low temperature and is equal to the Gibbs energy at 0 Kelvin.
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**Key words:** evaluation of mixing energy, oxide compound, tetrahedral constituent, substitutional solution

The oxide compounds of davidite minerals are generalized with the system Ti–U–O. The oxygen affinity of titanium is the cause of transformation of the octahedral constituents into the tetrahedral ones of rutile [1]. The reduction of uranium tri-oxide [2] is the consequence of thermal destabilization of the dodecahedral units [3]. Thus, the phase equilibria of the both oxides are directed to the building of the complexes of fourth valency. They are the partial compositions of the red and green fields, which are visualized at the figure 1.

The first interactions are resulted in the formation of TiWO₄ at the higher concentrations of TiO₂. At the prevalence of the tungsten tri-oxide, the building of the TiO₃ oxy-anions [4] is caused with the reaction ability of WO₂⁺.

Our systematization of experimental results introduces the statement that the oxide solutions are limited with concentrations of the stabilized constituents. The compounds transform their symmetries and decompose the structures, which are characterized with polymorphic bonding of units in the crystal cells.

**References**


**Biographical Notes**

1989-1995, I studied physics of metals and phase transformations of Fe-Ni (Ni-Nb) alloys in the National Technical University of Ukraine.
1998-1999, I researched ash fraction (Al₂O₃-SiO₂ slag) of the combustion products of coal and municipal waste in the University of Karlsruhe (Studium Generale).
1995-2000, I investigated electric conductivity of plasma body (the ionized area of dynamic pressure) and burning processes of energetic fuels for plasma generator in the Research Center of Chemical Technologies (Moscow region).
2000-2002, I was occupied with treatment of databases for geological information and environmental systems in the Research Institute of Mineral Resources.
2008, Delegate of International CODATA Conference 2003-2019, Association of German Engineers
BCC-HCP-FCC Multiple Martensitic Transformations in Fe-Co-Cr-Mn High Entropy Alloys

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Key words: martensitic transformation, phase stability, high entropy alloy

High entropy alloys (HEAs), defined as multi-component (five or more elements) solid-solution alloys with near-equiaxial ratios, have attracted increasing attentions because of its potential for structural materials. We investigated the phase transformations in Fe-Co-Cr-Mn alloys, which is a basis of HEAs.

Phase stability and martensitic transformations in Fe-Co-Cr-Mn alloys were investigated by optical microscopy, transmission electron microscopy (TEM), X-ray diffraction (XRD) and vibrating sample magnetometry (VSM).

A unique martensitic transformation from the bcc α parent phase to the hcp ε martensite phase was observed in Fe-Co-Cr-Mn alloys. Figure 1 shows the calculated vertical section diagram of Fe-20Co-20Mn-Cr (at%) using the TCHEA2 database and the optical micrograph of Fe-20Co-20Mn-24Cr alloy quenched from 1300 °C. Martensite plates are seen in the microstructure, and the crystal structure of the parent and martensite phases was identified by TEM and XRD to be the bcc and hcp, respectively. A high density of stacking faults was also observed in the martensite by TEM.

While the bcc (α) parent phase coexisted with the hcp (ε) martensite phase in as-quenched Fe-20.4Co-24Cr-20Mn alloy, the ε martensite was fully induced by cold-rolling. Furthermore, the fcc (γ) phase was obtained by heavy deformation by means of a converge mill. These results suggest the existence of multiple martensitic transformations from the bcc through hcp to fcc martensite phases, i.e., α→ε→γ. These three phases are ferromagnetic, the magnetization in the γ and ε phases at room temperature being lower than that in the α phase.

Multiple phase transformations can be qualitatively explained on the basis of thermodynamic considerations related to the $T_0^{α/ε}$ and $T_0^{α/γ}$ temperatures in the Fe-Co-Cr-Mn system, in disagreement with the calculation suggesting $α→γ→ε$, in which the stability of the ε phase is too low in the current database.

Figure 1. Calculated phase diagram of the Fe-20Co-20Mn-Cr system (α: bcc, γ: fcc, ε: hcp) and optical micrograph of 24Cr alloy.

Biographical Note
Toshihiro Omori is an Associate Professor at Tohoku University, Japan. His research interests include experimental investigation on phase stabilities and phase diagrams as well as CALPHAD.
Crystal Structures and Phase Equilibria of RE-Mn-based Alloys

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Key words: RE-Mn-based alloys, Crystal structure, Phase equilibria

The RE-Mn-based (RE=rare earth elements) ternary compounds with special crystal structure have been attracted much attention because of their interesting magnetic properties, resulting from the interesting interplay between the 3d and 4f magnetism and the strong dependence of the magnitude of the Mn moment and the magnetic state of the Mn sublattice on the Mn-Mn interatomic distances [1-3]. In particular, the intermetallic compounds in the RE-Mn-X (X=Si, Ge, Sn etc.) ternary systems were investigated experimentally to explore their complex magnetic behaviour [3]. For example, the intermetallic compounds REMnX2 show magnetocaloric effect and REMnX6 compounds have magnetoresistive properties, while REMnX compounds show magnetoelasticity. Phase equilibria and crystal structures of intermetallic compounds in the RE-Mn-based alloy systems are important to understand the relationships between crystal structure, phase transformation and physical properties.

In this work, phase equilibria of the Nd/Gd-Mn-Ge/Si ternary systems at 673/873 K were investigated by means of X-ray diffraction, scanning electron microscopy equipped with energy dispersive X-ray spectroscopy and electron probe microscopy. The crystal structure, magnetic properties and magnetocaloric effect of REMnX2 compound were also studied by X-ray diffraction and physical property measurement system.

References

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Biographical Note
Dr. Jiang Wang completed his studies as a PhD student in Central South University in 2008 and then joined as postdoctoral researcher in Swiss Federal Laboratories of Materials Science and Technology, Switzerland in October 2008. Since October 2011, he works as a research scientist in Guilin University of Electronic Technology, China. His research work focuses on phase equilibria, phase structure and physic properties of metal materials (e.g. Mn/Fe-based alloys) through both experiments and calculations.
Modeling of Os–Pt System under High Hydrostatic Pressure

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Key words: Os, Pt, Os–Pt, equation of state, pressure, DFT, phonon, thermodynamic optimization

The system Os–Pt is interesting for applications in catalysis and because materials based on this system exhibit outstanding properties such as high mechanical strength, resistance to oxidation and extremely high melting point. The modeling of this system at high pressure would help to understand the behavior of precious metals in the earth mantle and is interesting since osmium is considered as an analogue of hcp iron in the study of earth's core.

We used the model of Lu [1] to describe the system at high pressure/high temperature. Pure metals, hcp Os and fcc Pt, were modeled using available experimental compressibility and lattice expansion data. The liquid was described using measurements of the melting point as a function of pressure.

The metastable fcc Os and hcp Pt were modeled using DFT and quasi-harmonic phonon calculations.

The binary system was thermodynamically optimized at ambient pressure using experimental data and SQS-DFT calculations.

Finally, extrapolations in the CALPHAD framework allowed an efficient description of the complete system at high pressure and temperature (100 GPa, 6000 K).

A comparison was then made with recent experiments obtained at high hydrostatic pressure.

References

Biographical Note
Jean-Marc is Director of Research at the National Center of Scientific Research (CNRS) in France. He is head of the group 'Chemical Metallurgy of Rare Earths' at the East-Paris Institute of Chemistry and Materials Science in Thiais, in the Paris suburb. His primary research interests are intermetallic compounds, hydrogen-metal systems and thermodynamic modeling.

Figure 1. Os–Pt system at ambient pressure and 50 GPa.
Quantified Uncertainty in CALPHAD for Materials Design

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Key words: uncertainty quantification, materials design, Cu-Mg, visualization

The CALculation of PHAse Diagrams (CALPHAD) approach is a critical component in the design and development of new materials. CALPHAD users recognize that for any particular database, some regions of composition, temperature, and pressure (X-T-P) space are accurate and well defined, while others have a high degree of uncertainty. This uncertainty is not only apparent in the boundaries between phases, but also for invariant points and in the stability of entire phase regions. In the last several decades, this has spurred the development of uncertainty quantification (UQ) approaches for CALPHAD models [1]. Existing approaches directly quantify the uncertainty in phase boundaries and invariant features [2]. This results in several limitations, including ambiguity in the dependence of uncertainty on X-T-P, the inability to represent the uncertainty of the stability of phase regions and the non-trivial extension to systems with more than two varying X-T-P dimensions. In this work, we present a methodology to leverage Bayesian CALPHAD parameter estimation for the flexible representation of uncertainty in forms useful to materials designers [3].

Figure 1. Schematic illustrating the methodology for obtaining useful UQ results from the MCMC optimization Gibbs energy models.

Figure 1 illustrates our approach for quantifying the uncertainty in CALPHAD predictions. First, the multivariate distribution of CALPHAD model parameters is sampled through a Markov chain Monte Carlo (MCMC) calculation in the open-source ESPEI package [4]. The sampled sets of model parameters from MCMC are then directly employed to perform parallelized equilibrium calculations. The collation of results from the equilibrium calculations associated with each parameter set are then leveraged to perform the expected CALPHAD predictions with quantified uncertainty. These analyses include the direct superimposition of phase diagrams to represent their probability distribution and the calculation of the probability of invariant features residing in specified X-T-P regions. Furthermore, we can compute the probability of stability and the distributions of phase fraction, composition and Gibbs energy (in addition to other properties) for a selected phase at any X-T-P point, irrespective of the number of dimensions.

References


Biographical Note

Noah Paulson is a postdoctoral researcher at Argonne National Laboratory developing reduced-order models and uncertainty quantification approaches for thermodynamic and mechanical properties of industrially relevant materials. Noah received his Ph.D. in Mechanical Engineering from Georgia Tech in 2017.
Thermodynamic Re-assessment of Pure Chromium Using Modified Segmented Regression Model

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Key words: Pure Cr, Heat capacity, Thermodynamic properties, Segmented regression, Sigmoid function

Chromium is an important addition element that is well known for its unique magnetic properties and high corrosion resistance. It is considered to be an essential part of the stainless steel and chrome plating industries. However, there is an ongoing debate regarding some of its properties, especially its melting point value. Multiple studies have reported different melting point values that can vary by a range of about 65 K, from 2115 K to 2180 K, but most of the recent studies seem to agree on the value of 2136 K, rather than the value, 2180 K, that is currently used in the SGTE description [1].

Several attempts were made to improve the description of thermophysical properties of pure Cr [2,3,4]. One of the most recent re-assessment of pure Cr have been performed using the segmented regression (SR) model [4], which is valid from 0K up to the melting point. In order to expand the SR model beyond this region to high temperatures, a special logistic function has been utilized to modify the SR model without any additional fitting parameters. Such a modification of original SR model allows to change the melting point without the need for additional re-assessments. Moreover, in comparison to the recent SGTE description each phase would have a smooth description over the entire temperature range, even in regions where the phase might be metastable/unstable.

Additionally, two machine learning methods were developed and applied to calculate weights of datasets involved in assessment and to detect possible outliers. These automated methods can improve a quality of thermodynamic assessments and give a hint to unexperienced researches which datasets should be validated more precisely.

References

Figure 1. Comparison of the heat capacity of the modified SR model and other assessments for pure Cr.

Biographical Note
Abdulmonem Obaied is a doctoral candidate at ICAMS, Ruhr-University Bochum, Germany. His research focuses on developing and application of machine learning and data mining tools for property prediction of Co-based superalloys and relevant pure elements and binary systems.
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**Thermodynamic Reassessment of Actinide-Iron Systems**

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**Key words:** thermodynamic assessment, actinides, impurities

The interest in actinide elements extends across many nuclear applications; specifically, uranium and plutonium research is sponsored by many government entities, including the US Department of Energy (DOE). Our current work focuses on a common impurity, iron and its effect on actinide (Ac) phase formation, which has very small solubility in the actinides, but can easily form the stoichiometric composition U\(_x\)Fe and Pu\(_x\)Fe. The CALPHAD method is applied across various Ac-Fe compositions ranges, including U, Pu, Am and Np where particular interest is given to the \(\delta\)-stabilized Pu-Ga alloy and its interaction with the Fe-impurity. Figure 1 depicts the Pu-rich corner of the ternary Pu-Fe-Ga phase diagram. Previous models [1,2] are either lacking proper description of some important reactions or do not use the standard reference state to describe the stoichiometric compounds.

A reassessment of the iron-actinide thermodynamic model is carried out for complete consistency across the multi-component system. Ab-initio calculations are performed to validate the stability of the stoichiometric (U,Pu,Am,Np)\(_2\)Fe and (U,Pu,Am,Np)\(_6\)Fe compounds by computing their formation energies. Experimental suggestions are made where experimental data is missing.

Acknowledgements

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References


Biographical Note

Emily Moore is a post-doctoral researcher at LLNL, she completed her PhD in 2013 at the CEA Saclay in France. Her work has focused on the development of thermodynamic database for nuclear applications including actinide oxides, silicides and other alloy systems.
Thermodynamic Modeling of Fe-Mn-Si-C System

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Key words: High-Mn steel, Ferromanganese, Siliconmanganese, Modified Quasichemical Model

Recently, high Mn steels have received many attentions as next generation advanced high strength steels for automotive applications. Since large amount of ferromanganese or siliconmanganese alloys are added to molten steels as a manganese source in the final stage of the refining process, the demands of high purity ferroalloys are also increasing. In order to develop the efficient high Mn steelmaking process, accurate thermodynamic information of the Fe-Mn-Si-C system in both Fe-based steel region and Mn-rich alloys is required.

In the present study, thermodynamically consistent set of the database for the Fe-Mn-Si-C quaternary system was developed. The Gibbs energy and short range ordering (SRO) in liquid Fe-Mn-Si-C solution was well described by the Modified Quasichemical Model (MQM). In the MQM, the SRO exhibited in the liquid solution is accounted by the negative Gibbs energy change of the following pair exchange reaction.

\[(A-A) + (B-B) = 2 (A-B): \ \Delta g_{AB} \] (1)

The Gibbs energy of liquid solution was properly interpolated from binaries to ternary and higher order systems using so-called geometric interpolation method based on the symmetricity of thermodynamic properties of each ternary liquid solution. The optimization of solid solutions was performed using the Compound Energy Formalism (CEF).

In the Fe-Mn-Si-C quaternary system, two ternary systems, Fe-Mn-C \textsuperscript{[1]} and Mn-Si-C \textsuperscript{[2]}, were already optimized by the present authors. Two remaining subsystems, Fe-Si-C and Fe-Mn-Si systems, were newly optimized in the present study and integrated with the previous two ternary systems to describe the entire quaternary systems. The significant improvement was achieved for the descriptions of C solubility, partial enthalpy of mixing of C, peritectic temperature in Fe-Si-C system. In Fe-Mn-Si system, the liquid miscibility gap formation at Si-rich side was resolved by adopting Toop interpolation method at high temperature. The solid phase equilibria among FCC, BCC, CUB and Fe-Mn-silicide at Fe-rich corner were also reproduced well by considering the BCC order/disorder transition.

By combining all binary and ternary model parameters, without any additional parameter, the C solubility in Mn-Fe-Si-C melts of both lab scale and plant data were successfully reproduced over a wide range of Si concentration from graphite to β-SiC saturation condition as shown in Fig. 1.

The present model can cover the entire range of quaternary alloy composition and temperature. The new database can be used to predict the complex chemical reactions and phase diagrams for the various pyrometallurgical processes; refining of high Mn steel and high Si electrical steel, production of ferroalloys such as ferromanganese, ferrosilicon, siliconmanganese as well as cast iron alloys containing Mn and Si.

![Figure 1. Solubility of C in Mn-Fe-Si-C melt at 1500 °C.](image)

References


Biographical Note

Min-Kyu Paek is a postdoctoral researcher at Aalto University in Finland. His work focuses on the development of high alloy database using FactSage thermochemistry software; He has recently published the studies on the SRO behavior of liquid alloys in CALPHAD, JPEDAV and Metallurgical and Materials Engineering B.
Calculation of Grain Boundary Segregation in Steels by CALPHAD Method

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Key words: grain boundary segregation, parallel tangent law, TQ-Interface

It is well-known that alloying elements and impurities in steels segregate in the grain boundary (GB) of γFe and αFe, which causes great influence on the microstructure formation, mechanical properties, etc. of practical steels. It is suggested, for instance, that segregated B on GBs of γFe causes considerable reduction of the GB energy, which retards the formation of αFe and improve the hardenability of steels. Experimental studies on the GB segregation using atom probe tomography were performed and tremendous results of quantitative measurement of GB segregation were reported [1,2]. However, thermodynamic calculation of the GB segregation in practical steels containing multiple alloying elements and impurities has not been carried out yet. In the present study, calculation method and calculated results of the GB segregation in steels by CALPHAD method will be presented.

The parallel tangent law proposed by Hillert [3] was extended to the multicomponent system up to 5 alloying or impurity elements and applied to calculate the segregated compositions using the following conditions for the chemical potential of constituent elements:

\[ \mu_{Fe}^G - \mu_{Fe}^{\alpha or \gamma} = \mu_{X1}^G - \mu_{X1}^{\alpha or \gamma} = \mu_{X2}^G - \mu_{X2}^{\alpha or \gamma} = \ldots \]

X1, X2, … represent alloying or impurity elements such as Cr, Cu, Mn, Mo, Nb, Si, Ti, Zr, B, C, N, O, P, S, etc. The GB phase was supposed to have random structure which has the free energy identical to that of the liquid phase [4]. The Gibbs energy of the liquid, γFe and αFe phases was taken from Thermo-Calc using TCFE9 database via TQ-Interface and used for the calculation. The effect of volume fraction of the GB phase, i.e. the grain size dependency of the segregated composition, was also considered in the present calculation.

Fig. 1 shows calculated results on the effect of substitutional alloying elements M (M= Nb, Ti, Mo, etc.) on the segregation of B in (a) γFe and (b) αFe of Fe-0.001B-0.1M (at.%) alloys. Segregated compositions of B increase drastically with decreasing temperature. It is suggested that Nb, Ti and Zr addition enhances the B segregation considerably in comparison with the calculated B composition without substitutional alloying elements (black curves w/o M).

References

Biographical Note
I. Ohnuma is now a group leader of Computational Structural Materials Design Group in NIMS. His research interests focus on the experimental determination and thermodynamic evaluation of phase diagrams of structural and magnetic materials as well as alloy design and development of various practical materials using CALPHAD method.
FeB-12 wt.% Al<sub>0.25</sub>FeNiCoCr Cermet Coating Deposited by AC-HVAF and its Corrosion Resistance to Molten Zinc

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Key words: thermal spraying, corrosion, molten zinc, Fe–B alloy

In a continuous hot-dip galvanizing line, the parts and components of galvanizing equipment (e.g., bearings, sinks, stabilizing rolls etc.) are subjected to the corrosion by molten zinc [1]. As a cheap and common material for anti-corrosion application, 316L stainless steel is widely used for the production of these parts and components [2]. However, 316L stainless steel is not a material specially designed for galvanizing, so its corrosion resistance to molten zinc is debatable [3]. To extend their service life, a novel cermet coating of FeB-12 wt.% Al<sub>0.25</sub>FeNiCoCr is deposited on the surface of 316L stainless steel by AC-HVAF. In this work, the endurance of FeB-12 wt.% Al<sub>0.25</sub>FeNiCoCr coating in molten zinc are studied.

Powders of 2.9 wt.% Al, 24.06 wt.% Fe, 25.35 wt.% Ni, 25.35 wt.% Co, and 22.34 wt.% Cr are added to a ball mill. The ball milling time is 50 h, the rotation speed is 300 r/min, and the ball ratio is 10:1. After ball milling, the mixed powders are put into a furnace for vacuum sintering, then ground and sieved. Next, 12 wt.% Al<sub>0.25</sub>FeNiCoCr powders and 88 wt.% FeB powders are ball milled for 10h. FeB-12 wt.% Al<sub>0.25</sub>FeNiCoCr powders are obtained through the same process of Al<sub>0.25</sub>FeNiCoCr powders, except that the ball milling time is 10 h and the ball ratio is 3:1.

316L stainless steel is used as a substrate. The above powders are sprayed with AC-HVAF to obtain FeB-12 wt.% Al<sub>0.25</sub>FeNiCoCr coating. And then, coating samples are immersed in molten zinc bath at 450 °C for 1, 3, 5, 10, 15, 20 days. SEM-EDS and XRD are used to analysis the microstructures and phase compositions of coating samples immersed in molten zinc. The main experiment results and conclusions are as follows:

As is shown in Figure 1, the coating and molten zinc are contacted, wetted and corroded, and then peeled off. With the prolongation of immersion time, the coating thickness gradually decreases. Due to the difference in thermal expansion coefficient between the coating and the substrate, after immersion in molten zinc for a long time, micro-cracks gradually expand into macro-cracks. Along these cracks, molten zinc corrodes the inside of the coating further, which in turn accelerates the propagation of cracks, and the thickness of the coating is significantly reduced. During the corrosion process, a large volume of coating spalls and dissociates with corrosion products such as δ phase (91.9 wt.% Zn, 6.98 wt.% Fe, 0.33 wt.% Al, 0.52 wt.% Ni, 0.10 wt.% Co, and 0.16 wt.% Cr) into molten zinc. To a certain extent, they prevent molten zinc from further corroding the coating.

Figure 1. Cross-section morphologies of coating after immersion in molten zinc at 450 °C for different time (a) 1 day, (b) 3 day, (c) 5 day, (d) 5 day, (e) 10 day, (f) 15 day, (g) 20 day

References

Biographical Note
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Synthesis of Pure Intermetallic Phases in Temperature Gradient

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Key words: intermetallic phases, temperature gradients, heat capacity, Neumann-Kopp rule

Synthesizing intermetallics as single-phase materials may be challenging, e.g. for stoichiometric phases and/or incongruently melting phases and/or phases containing components with a high melting point or low boiling point. Densification of compressed powders by (spark plasma) sintering or electron beam melting are modern synthesizing techniques, but the single-phase character of the intermetallic phases may suffer from solute partitioning during solidification, the large surface to volume ratio of the powder that leads to an unknown oxide fraction, or a lack of knowledge about the precise phase composition.

Heat capacities are key input data for the thermodynamic description of intermetallics. Reliable measurements require samples of high purity and considerable quantities. Since the synthesis of pure intermetallic phases using conventional techniques is laborious and sometimes even impossible, the Neumann-Kopp rule is often used for the thermodynamic description of intermetallic phases. In many cases, this rule has shown to be a good first approximation, but its predictive power is limited for compounds with significant differences in the strength of the A-B bond in comparison with that of the pure substances, or for phases with a λ-transition (for specific examples see e.g. the workshop reports from Ringberg meeting 1995 published in CALPHAD Journal).

Synthesis of pure intermetallic phases can also be achieved, if samples are partially melted and subsequently resolidified in a temperature gradient [1,2]. In the temperature and concentration range of the solid/liquid two-phase equilibrium, intermetallic phases may form spatially separated during the resolidification of the mushy zone. For this, a suitable initial alloy composition must be chosen that is different from the composition of the desired final product. The choice of composition is crucial as it determines the minimum fraction of solid after partial melting, the liquidus temperature and thus the processing temperature range.

Calculated phase diagrams may help to select suitable initial compositions. However, additional information is needed, if the exact composition of the intermetallic phase or the melting range are not known precisely. In this case coarsening experiments and phase analysis of the coarsened phases can assist to identify a suitable initial composition.

Exploiting temperature gradients, it is possible to produce pure intermetallic phases far below their melting or decomposition temperature as bulk materials, independent of their congruent or incongruent melting characteristics. The samples provide information on temperature dependent phase equilibria and solubilities and offer the possibility of a comprehensive study of temperature dependent thermal properties [3,4].

Figure 1. Intermetallic phases formed by mushy zone resolidification in a temperature gradient; sequence of phases in (a), transition from two phase (formerly Al5Ni3+T12+liquid) to single phase region (formerly T12+liquid) in (b)

References

Biographical Note
Stephanie’s research focuses on phase transformations. Within this field, she studies aspects of the dynamic processes in temperature gradients or the influence of interfacial processes during phase transformations that e.g. determine the transition from diffusion controlled to massive transformation.
Design of New Weldable TiAl-Based Alloy with the CALPHAD Tools

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Key words: TiAl alloy, composition design, Relative Potency Factor, internal stress

TiAl alloys are characterized by a combination of high-temperature strength, elasticity modulus and lower density than that of nickel-based superalloys, considered to be suitable for next-generation turbine and launch vehicle. To be used as welding parts, the TiAl-base alloys need to minimize the solidification and liquidation cracking and sustain appropriate strength and ductility from cryogenic to solidus temperatures. In this work, novel weldable TiAl alloy was designed with the CALPHAD tools, with a particular focus on the composition and mechanical property of material.

Upon a thermodynamic database[1], the phase information, such as formation sequence, solidification paths and phase fraction ratio, were calculated by tuning the species and contents of alloying elements, inc. B, Cr, V, Nb, Ta, W, Mo. The favorable composition range was first outlined by evaluating three appropriateness’s, i.e.

1) the high-temperature thermodynamic stability of \(\gamma\) and \(\alpha_2\) phases promoted by the additives,

2) the equilibrium phase fraction ratio between \(\gamma\) and \(\alpha_2\) in full lamellae structure to maintain the ductility,

3) the reduced solidification temperature range to restrain fusion zone solidification cracking.

The absence of the peritectic products was then considered to reduce the segregation. A more precise control of the segregation was further carried out by assessing a Relative Potency Factor as the functionals of solidification temperature range, nominal composition, liquidus slope and partition coefficient, such that the relative effect of the alloying and impurity elements on weld solidification cracking susceptibility[2] was respectively addressed.

Boron was added to form TiB as the heterogeneous nucleation sites and grain refiner, however, the B addition was ensured to be completely consumed prior to the transformation of \(\alpha\rightarrow\gamma\) to minimize its detrimental effect on the liquation cracking in the heat affected zone (HAZ) during welding. Moreover, the thermal cyclic stress was estimated as the functional of lattice expansion resulting from the alloying and temperature change in the formalism of micro-elasticity phase field method[3,4]. The composition of the alloy was optimized by iterating through the above calculations.

The as-designed alloy was experimentally fabricated, and the cast exhibits a full lamellar microstructure of \(\gamma\) and \(\alpha_2\) with the average grain size of 25μm and the phase ratio of 8.1, in good agreement with the CALPHAD-type design. The mechanical properties of the alloy, like room-temperature ultimate tensile strength and ductility, are now being tested and validated in details.

Figure 1. Roadmap of composition design for the new TiAl based alloy.

References

Biographical Note
Dr. Guanglong Xu, an assistant professor at Nanjing Tech University, has expertise in experimental phase diagram determination, experimental diffusion research, application of computational thermo-kinetics in alloy design, and Landau/phase field simulation of phase transformation.
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Corrosion Properties of Al-Mg and Al-Mg-Si Coated Steel (I)

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Key words: Corrosion resistant coatings, Al-Mg alloy coatings, Heat treatment, Physical Vapor deposition

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In steel industry, the surface treatment of steel is one of major issues for increasing the lifetime of steel sheet. Hot dip coating and electroplating techniques have been applied to the surface treatment of steel for over last 100 years. There are several types of coated steel products, but mainly zinc-based coated steels are most common and used primarily for automotive, home appliances, and construction applications.

This paper presents the corrosion properties of Al-Mg and Al-Mg-Si coated steel prepared by physical vapor deposition (PVD)[1-2]. It is well known that Al coating has a good barrier property, however, it is lack of sacrificial properties for steel. Mg coating provides sacrificial ability for steel, but its surface is too sensitive to environment to be used commercially at this time. To achieve having both barrier and sacrificial properties, Al-Mg coatings have been investigated as an alternative coating material for Zn. It has been aimed that Al-Mg alloy coating can achieve two crucial properties of barrier protection and sacrificial ability for steel. The coatings have been prepared on a steel sheet using the magnetron sputtering.

Figure 1 shows the time to onset of red rust according to the magnesium contents of Al-Mg alloy coatings by salt spray test. Other coated specimens were tested together for comparison. For as-deposited Al-Mg alloy coatings, red rust was observed after SST from 150 to 220 hours according to the Mg contents. However, after annealing, the red rust was observed after SST from 300 to 520 hours. The annealing has enhanced the corrosion resistance of Al-Mg coatings. The optimum Mg content, which showed the highest corrosion resistance, was around 20wt%.

In this presentation the corrosion properties of Al-Mg alloy coatings together with Al-Mg-Si coatings will be presented.

References

Biographical Note
J.I. Jeong is a research scientist at RIST (Research Institute of Industrial Science & Technology). He is performing the research on plasma-induced deposition technology based on physical vapor deposition (PVD). He is also interested in corrosion resistant coatings on steel. The analysis and evaluation of the coated products is one of his main topics of research, too.
Thermal Barrier Coatings Phase Stability and in Service Degradation: Thermodynamic and Experimental Study of CMAS Corrosion on Ansaldo Energia’s Materials

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Key words: Gas turbine, Termal Barrier Coating, CMAS corrosion, CALPHAD method, thermodynamic assessment

Thermal barrier coatings (TBC) are materials used in gas turbines to protect metal substrates from high temperatures. For this reason, the materials used must have: high melting point, low thermal conductivity, high thermal expansion coefficient, microstructural stability, chemical compatibility with substrate and high oxidation and corrosion resistance. Normally, the material used is zirconia partially stabilized with yttria (6-8 wt%).

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

In this work, the second and most important interaction is studied by experimental tests and thermodynamic modelling.

Several samples were prepared to evaluate the interaction of two different TBC used by Ansaldo Energia (one with greater yttria content) with two different compositions of CMAS.

The specimens were exposed at high temperatures ranging between 1200 and 1400°C for different times and subsequently analyzed by different instrumental techniques (SEM-EDS and EBSD, and RX diffraction). The results allowed us to evaluate the interaction thickness and the microstructural modifications occurring in TBC after reaction with CMAS.

Moreover, a multi-component thermodynamic database (Al-Ca-Mg-Fe-Si-Y-Zr-O) is under development using the CALPHAD method in order to simulate the process.

The assessment of over 15 binary and 20 ternary systems will be necessary to have a database able to provide reliable calculations of the CMAS-TBC interactions and to predict the phenomena that take place during the exercise in the turbine.

Biographical Note
Ph.D. student at the University of Genoa, Italy working in Department of Chemistry and Industrial Chemistry, in collaboration with Ansaldo Energia, a company that produces gas turbines.
O61

Designing of Low-cost Titanium Alloy Based on the Assessment of Ti-Al-Fe-V System

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Key words: Ti-Al-Fe-V system, Low-cost titanium alloy, Computer modeling and simulation, Pseudobinary sections, Phase equilibria

The previous investigations for the thermodynamic descriptions of the sub-systems in the Ti-Al-Fe-V system were reviewed and summarized, then the thermodynamical database of this quaternary system was built up by directly extrapolating from four sub-ternary systems assessed by means of the CALPHAD approach. The pseudobinary sections with V:Fe=7.3:1 and Al=0.0, 3.0, 4.5 and 6.0 wt% were calculated, respectively. It may provide the theoretical support and the novel low-cost titanium alloys can be designed combining with the aluminum and molybdenum equivalent design criterion. The results showed that β, α+β, titanium alloy could be considered to design with the content of Al was 3%, 4.5%, 6%, respectively, when the ratio of V:Fe was determined to be 7.3:1. It not only avoid the appearance of some brittle phases, but also the use of ferrovanadium intermediate alloy can reduce the production cost.

Fig.1 The Fe-V system assessed by Tojo et al.[1]

Fig.2 The calculated pseudobinary section of 3 wt% Al and V:Fe=7.3:1

Fig.3 The calculated pseudobinary section of 4.5 wt% Al and V:Fe=7.3:1

Fig.4 The calculated pseudobinary section of 6 wt% Al and V:Fe=7.3:1

References


Biographical Note

My name is Feng Qisheng, I am a first year graduate student in Shanghai University, my research direction is calculation of phase diagram and my tutor is prof. Li Chonghe.
Development of the Ballast Water Sterilization System in Ships Using Computer Simulations

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Key words: sterilization, BWMS, electron impact, solution plasma

IMO(International Maritime Organization) has established the Convention for the Control and Management of Ships’ Ballast Water and Sediments(BWM Convention) in 2004 to prevent environmental problems caused by ships’ ballast water and sediments and the BWM Convention will enter into force on 8 September 2017, following the ratification of Finland in 2016. Many technologies have been developed and it has been approved by IMO. Among these technologies, the technology using solution plasma is economical because it does not need the additives for sterilization, and it can be treated by various self-generated factors such as OH radical, ultraviolet ray, shock wave, electric field, ozone generated and it is eco-friendly as it does not require additives for neutralization.

In this study, we studied the method using solution plasma for seawater sterilization. The electrode has been placed in point to point. The solution was taken from the coast of Busan and the volume of solution was 1L, and 8kV, 30khz voltage has been applied. A radiation of plasma has been analyzed during discharge using the Optical Emission Spectroscopy.

Meanwhile, in order to improve its performance, it is necessary to clarify the reaction in the processes, and the reaction in the solution should be controlled and monitored effectively. However, the reaction mechanisms of the organosilicon molecules in plasma have not been clarified due to its complexity. To understand the reactions in the plasma, it is necessary to investigate the electron impact dissociation of the monomers, which is one of the most fundamental processes in plasma. Therefore we introduce the solution plasma process using computer simulations, such as the dissociative ionization of the organosilicon molecules by electron impact phenomenon. However, there is a possibility that the dissociative ionization and neutral dissociation shows quite different behavior, i.e., X⁺ ionic radical production occurs but X radical production does not occur. Hence we describe only the dissociative ionization behavior in this work.

Electron impact dissociation phenomenon was investigated by using a quadrupole mass spectrometer (QMS : MSQ-400, ULVAC Japan). The pressure in the QMS unit became ~ 5.5x10⁻³ Pa at the reactant pressure in the chamber of 5 Pa. Electron impact ionization was carried out at 10 ~ 40 eV of electron energy. Bond dissociation energies for the molecules were estimated by a semi-empirical molecular orbital (MO) calculations with PM3 Hamiltonian. Each bond dissociation energy was calculated by difference of heat of formation between the reactants and the productants.

As a result, it was confirmed that OH radicals which are generated during discharge have a bactericidal action. Also during the experiment, samples were taken and cultured at 35 °C for 48 hours.

References

Figure 1. Sterilization results of electrolytic reduction treatment(S. aureus)

Biographical Note
Dr. Yongsup Yun is an associate professor in the Division of Marine System Engineering at Korea Maritime & Ocean University. He received his Ph.D degree in Materials Engineering from Nagoya University in 2007. From 2008 to 2009, he was a research fellow in Japan National Institute of Advanced Industrial Science and Technology(AIST). His research interest mainly focuses on plasma phenomena as well as water sterilizations, including thin films, molecular dynamics and diamond semiconductors, etc. Dr. Yongsup Yun has published more than 21 peer-reviewed journal papers in the field of material science.
O63

CALPHAD-based Sensitivity Analysis for Alloy Composition
Design in Alloy Additive Manufacturing
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Key words: ICME, Additive manufacturing, CALPHAD, Composition design, HSLA

Additive manufacturing (AM) of components applies the layer-by-layer fabrication concepts provides unique opportunities to materials science and metallurgical engineering in design and optimization. One grant challenge of the AM technique is the feedstock materials design, which can generate good process-structure-property relationships in different processing steps, and thus enhance the performance of the AM components. In the powder-based AM technique such as powder-bed laser melting, the practical composition sometimes can significantly deviate from the nominal composition range in both feedstock materials (e.g., alloy powders) production and laser melting process. This can directly lead to the failed builds with undesired microstructure. Therefore, it is critical to perform a sensitivity analysis identifying the proper composition range that meets property requirements. This can provide valuable guidance to the feedstock materials production.

In this work, a high-throughput sensitivity analysis was performed by using an in-house ICME model framework based on the process-microstructure models with 10,000 compositions close to the composition of the high-strength low-alloy steel, HSLA-115. Under such a high-throughput sensitivity analysis, the HSLA-115 steel composition has been further tailored for laser melting AM process. The required properties and microstructural attributes, such as critical phase transition temperatures, ductile-to-brittle transition temperatures (DBTT), phase fractions of strengthening precipitations, and printability are calculated in accordance with the roadmap in Fig. 1 to ensure that the alloys with desired microstructure for better mechanical properties. As a result, the developed ICME tool identifies the new average composition and its manufacturing uncertainty range with less detrimental phases and more desired strengthening precipitates. Figure 1 shows that the designed alloy owns a much higher probability of meeting all the requirements than the one defined empirically.

This study provides a strategy to efficiently optimize the alloy composition for additive manufacturing powder production, and it can be further extended for powder composition design.

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Figure 1. ICME roadmap for HSLA design (upper figure) and the comparison of the possibility of meeting multiple criterions between designed alloy and HSLA 115 (lower figure)

Biographical Note:
Xin Wang is a Ph.D. student at the Physical Metallurgy & Materials Design Laboratory, University of Pittsburgh (http://www.pitt.edu/~weixiong). Under the supervision of Prof. Wei Xiong, Mr. Xin Wang focuses on studying process-structure-property relationships in metals 3D printing, CALPHAD-based ICME modeling, and materials design.
Calculation of Phase Diagrams for One Component Macro- and Nano-systems Taking into Account the Effect of Surface Melting

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Key words: phase diagrams, nano-systems

Nano-Calphad provides a method to calculate phase diagrams for nano-systems [1]. The effect of size is significant only in nano-systems with at least one phase with at least one of its dimensions below 100 nm. The evaporation, the melting and the sublimation lines for nano-phases depend also on the number of atoms in nano-systems, not only on pressure, temperature and composition as is the case for macro-systems. In some macroscopic and nano-sized system with surface melting [2] there is a new transition line what is missing in unary phase diagrams. In macroscopic systems it is called surface melting transition (SMT) line, but in nanoscopic systems it is called solidus line. That means there is a new triple point on p-T phase diagram that is belong to SMT line. Solid and nano-thin liquid layer coexist between SMT line and bulk melting transition line (BMT) at a given pressure what is higher than pressure of triple point of SMT (Fig.1).

The nano-systems differ from macroscopic systems in that in nano-systems the size of the solid phase is comparable to the size of the liquid phase between solidus and liquidus transition line. The solidus and liquidus transition lines merge into one melting line on a critical size of nano-phase.

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References


Fig.1. Different lg(p/p₀) - T phase diagrams for an example element calculated at different fixed total mole of atoms in the system. The triple points merge into one triple point at the critical mole of atoms (2.3e-20 in this case).
O65

Application of Phase Equilibria in Smelting Reduction of Titaniferous Magnetite

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Key words: phase equilibria, liquidus temperature, ironmaking, FactSage

Titanomagnetite is a typical source for both titanium and iron. Smelting reduction of titanomagnetite can produce V-containing iron metal and TiO₂-bearing slag. Fluxes such as silica, dolomite and/or limestone can be used in the process and the slag chemistry can be represented by the system TiO₂-SiO₂-Al₂O₃-MgO-CaO. Optimal control of the slag chemistry is one of the key issues influencing efficient and stable operation of smelting process, and requires detailed knowledge of the slag liquidus and phase equilibria.

Phase equilibria in the system TiO₂-SiO₂-Al₂O₃-MgO-CaO were experimentally determined at low oxygen partial pressures. The experimental method used in the present study involves high temperature equilibration, quenching and electron probe X-ray microanalysis (EPMA). Approximately 0.2 g pelletized synthetic slag was placed in a graphite crucible which was suspended by Mo wire. Equilibration experiments were carried out in an atmosphere of ultrahigh purity Ar gas in a vertical furnace. After equilibration the samples were quenched into ice-cooled water. Liquid was converted to glass and all phase compositions were remained the same for EPMA examinations. The average accuracy of the EPMA measurements is within 1 wt%. Under experimental conditions used in the present study there may be Ti⁴⁺, Ti⁵⁺ and Ti⁶⁺ present in the samples. However, only the metal cation ratios can be measured by the EPMA; the phase compositions were recalculated to TiO₂ for presentation purpose.

The compositions of the liquid and solid phases present in the quenched samples were measured by EPMA. These data have been used to construct liquidus isotherms of the pseudo-ternary sections “TiO₂”-(CaO+MgO)-(SiO₂+Al₂O₃) with fixed MgO/CaO and Al₂O₃/SiO₂ weight ratios. TiO₂, SiO₂ and Al₂O₃ usually come from ore and coal/coke. CaO and MgO concentrations can be adjusted as fluxes according to the requirements. A number of pseudo-ternary sections have been investigated with MgO/CaO weight ratios of 0.20, 0.40 and 0.72 and Al₂O₃/SiO₂ weight ratios of 0.40 and 0.60. Main experimental phase fields include dicalcium silicate (Ca₂MgO·SiO₂); melilitite (CaMg(SiO₄)₂); anorthite (CaO-Al₂O₃·2SiO₂), perovskite Ca₃TiO₆, pseudobrookite Mg₃Ti₂O₆ and mullite 3(Al₂Ti₂O₇)/2SiO₂. Perovskite and pseudobrookite primary phase fields cover the common slag compositions for reduction of titanomagnetite.

Perovskite is nearly pure CaO-TiO₂. Pseudobrookite Mg₃Ti₂O₆ is a complex solid solution which can be expressed as 2Ti₃⁺,Mg²⁺,Al³⁺-Ti⁴⁺O₆. In perovskite primary phase field liquidus temperatures mainly increase with increasing basicity (CaO+MgO)/(SiO₂+Al₂O₃). In pseudobrookite primary phase field liquidus temperatures mainly increase with increasing (TiO₂+SiO₂+Al₂O₃). In addition, Al₂O₃/SiO₂ and MgO/CaO ratios in the slag also have significant effects on the liquidus temperature.

Figure 1 shows effect of TiO₂ on liquidus temperature. It can be seen that TiO₂ has complicated effects on liquidus temperature depending on primary phase field and MgO/CaO ratio. Increase of MgO/CaO ratio can decrease liquidus temperature 100 K between 20-30% TiO₂. FactSage calculations are compared with the experimental data to demonstrate the difference.

Figure 1. Liquidus temperatures for pseudo-binary section (CaO+MgO+SiO₂+Al₂O₃) “TiO₂” at (CaO+MgO)/(SiO₂+Al₂O₃)=1.0 and Al₂O₃/SiO₂=0.4

Biographical Note
Baojun Zhao specialized in pyrometallurgy, obtaining BS and MSc from Peking University, PhD from University of Queensland (UQ). Since 1994, he has started pyrometallurgical research at UQ and he is currently leading an active research group on experimental investigations of ferrous and nonferrous pyrometallurgy. He has developed a number of novel research techniques including experimental determination of phase equilibria and viscosity for complex slags under controlled atmosphere. A large number of experimental data have been produced to support industrial operations and development of thermodynamic and viscosity models.
A Thermodynamic Study on the Formation Process of Z-phase in Heat Resistant Steels

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Key words: cluster expansion method, Monte-Carlo simulation, two-phase separation, complex nitride

Introduction
In ferritic heat-resistant steels containing small amount of V, fine VN particles contribute to an improvement of high temperature strength. However, the creep strength rapidly decreases in long-term creep test. The phenomenon is due to decomposition of VN phase followed by a formation of the so called Z-phase and its rapid coarsening. The formation of the Z-phase is caused by Cr added for improving high temperature corrosion resistance. However, the formation process and its thermodynamic factors are not necessarily revealed. With this point as background, we investigated the phase equilibria in the Cr-V-N system based on the CALPHAD approach and attempted to confirm the formation process of the Z-phase in view of the phase separation from the VN phase.

Procedures
The Z-phase has a tetragonal structure and shows the periodic stacking consisting of VN and Cr layers. Crystallographic similarity is observed between this structure and NaCl-type VN phase. Therefore, for describing these two structures using the same thermodynamic model, the four-sublattice formalism as (Cr,V)<sub>0.5</sub>(V,Cr)<sub>0.5</sub>(N,Vac)<sub>0.5</sub>(Vac,N)<sub>0.5</sub> (where the symbol of Vac indicates vacancy) was adopted in this study. The free energy was calculated using the cluster expansion and cluster variational methods. The evaluated effective cluster interaction energies allowed to perform the Monte Carlo simulation to reveal the structure transition between the VN and Z-phase. Based on the information, a thermodynamic assessment was carried out by means of the CALPHAD method in focus to the equilibrium between these two phases.

Results
The calculated free energy curves showed a two-phase separation tendency between the VN and Z-phase. Figure 1 is the calculated phase diagram of the Cr-V-N ternary system at 1000K. According to the result, it is suggested that the formation of the Z-phase may probably be caused by the two-phase separation between these two phases. In addition, the Fe-Cr-V-N quaternary system was analyzed using the CALPHAD method. The previous study [1] showed that the Z-phase formed in the Fe-10wt%Cr-0.19wt%V-0.066wt%N alloy. Then an attempt was made to calculate the driving force of the Z-phase. The result shows that an addition of V makes the driving force for the formation of Z-phase in ferrite decreased. Thus, it is suggested that an increase of V content will increase the thermodynamic stability of VN and suppress the formation of the Z-phase.

Reference

Biographical Note
Dr. Ohtani’s original research field is the calculation of phase diagram based on the thermodynamic analysis of experimental results for phase boundaries and thermodynamic properties. The most recent research topic is on the study of theoretical phase diagrams calculation using genetic algorithm and convex-hull method.
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Extension of the Thermodynamics of Gibbs to Model Interfacial Energies for Interfaces between Any Two Bulk or Nano Solution Phases

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Key words: interfacial energy, general model, composition dependence, temperature dependence

Thermodynamics of Gibbs is extended to model the composition and temperature dependence of interfacial energies for interfaces between any two solution phases \cite{1}. Solution phases include: solid solutions, liquid solutions and vapors. Interfaces include: liquid/vapor, solid/vapor, solid/liquid, liquid/liquid, solid/solid, including grain boundaries. The equations for the interfacial energy are derived from the fundamental equations of Gibbs for systems containing only two bulk phases and systems containing also a flat interface between them, taking into account that in equilibrium the chemical potential of the same component should be equal in all bulk phases and in the interfacial region. This method leads to the two extended Butler-type equations, valid not only for liquid/gas surface (as originally suggested by Butler), but also for all possible surfaces and also to all interfaces between any two condensed phases. The method allows finding the composition of the interfacial region and the interfacial energy as function of temperature and average composition of the system at fixed standard pressure for binary and multi-component systems. To apply the method to the specific interface type information is needed on the structures of the two bulk phases and on the structure of the interface. Additionally, model equations are needed for partial molar volumes and partial excess molar Gibbs energies of the components in the two bulk phases as function of bulk compositions and temperature. For some interface types, additionally also the interfacial energies for one-component systems are needed. Models are also developed here to estimate these values. The method was also extended to interfaces between nano-phases or between a nano-phase and a macroscopic phase. As all types of interfacial energies are modelled within the same framework, a comprehensive set of model equations and predicted values are obtained for different types of interfacial energies and also for more complex quantities such as contact angles.

References


Biographical Note

Carbon-Doped BiNbO$_4$ Nanoparticles: Urea-Assisted Synthesis and Visible Light Photocatalytic Applications
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Carbon (C) has been universally accepted as an effective dopant to improve decomposition properties of pollutants in water. Previously, by computational methods [1] and by hands-on experiments to synthesize C-doped TiO$_2$ [2] and C-doped ZnO [3], it was demonstrated that (1) under oxygen-poor conditions carbon atoms effectively promote the formation of oxygen vacancies and (2) under oxygen-rich conditions carbon atoms tend to fill in the cation vacancies.

Here, for the first time we report fabrication of carbon-doped BiNbO$_4$ by tuning oxygen partial pressure using thermal decomposition of urea (U-BiNbO$_4$). The unique synthesis method included tube furnace unsealed from one side and sensor to monitor the concentration of ammonia (NH$_3$). The material was annealed at 700°C with the heating rate of 2 degrees/min which allowed to measure the amount of produced ammonia. The highest concentration of ammonia was recorded at 300-400 °C (40-50 ppm), corresponding to oxygen-poor conditions. The rest of the time the amount of produced ammonia was low (below 5 ppm) which corresponds to oxygen-rich conditions. The unique synthesis approach lead to surface modifications and formation of oxygen vacancies which was controlled by oxygen-poor atmosphere.

The photocatalytic properties of pristine BiNbO$_4$ and U-BiNbO$_4$ were investigated towards visible-light degradation of cationic methylene blue (MB) and brilliant green (BG) dyes. The results revealed that U-BiNbO$_4$ is about 1.5 times more efficient towards degradation of both MB and BG pollutants. Better degradation properties of U-BiNbO$_4$ were ascribed to (1) reduced band gap and (2) oxygen vacancies which lead to enhanced separation efficiency of photo-generated carriers. In summary, the unique synthesis method opens up new perspectives in non-metal doping, leading to lower costs and wider utilization of catalysts in solar and environmental industries.

References

Biographical note
Andrei Lebedev is a PhD student in Engineering Product Development (EPD) pillar at the Singapore University of Technology and Design. His research focuses on the development of new photocatalytic materials sensitive to visible and UV light with specific emphasis on the ability to predict their properties for water treatment purposes.
From CALPHAD to Smart Factory – Steelmaking
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Key words: Steelmaking, Smart Factory, CALPHAD database, Process simulation

Smart Factory is one of the hottest issues in manufacturing industry. Smart Factory is 4th industrial revolution based on combination of Big Data available in plant and Artificial Intelligent to improve the quality of product and production process efficiency.

CALPHAD database has been widely used for the alloy design and problem solving in industrial process. However, it is still less applied to process control or operation. As CALPHAD database is the pinnacle of critically evaluated and reliable thermodynamic experimental data for complex chemical reactions and phase diagrams, the CALPHAD database can be used as supplementary data for Big Data analysis in plant. In addition, CALPHAD database can be applied to industrial process simulation for leading Smart Factory project. Smart Factory is a new chance for CALPHAD community to contribute to data-driven industrial revolution.

Steelmaking process is very complex high temperature industrial process involving liquid steel, liquid slag, solid refractories, non-metallic inclusion, and gas phases. Therefore, the precise process control of this high temperature process is difficult but important for the production of good quality of steel. We have successfully linked the CALPHAD thermodynamic database with process kinetics to develop the process simulation model. This process simulation model is based on the so-called effective equilibrium reaction zone (EERZ) model [1], shown in Fig. 1. In this approach, the process kinetics is allowed to determine the volume of local equilibrium at the reaction interface and local equilibrium calculations are performed using the commercial thermodynamic database. We have applied this concept to develop many steelmaking operation units [1-4] and the model is now used for the study of process optimization and used for virtual twin factory in smart factory project.

In this presentation, the concept to link thermodynamic database to process simulation will be outlined. Several success stories of the simulation model in steelmaking industries and the future direction of our virtual steelmaking plant project will be presented.

![Reaction interface](image)

**Figure 1. Concept of the Effective Equilibrium Reaction Zone Model applied to a slag-metal reaction**

**References**

**Biographical Note**
Marie-Aline Van Ende is a research professor in Seoul National University (SNU). She got her PhD at KU Leuven and her major research topic is the application of CALPHAD database to steelmaking process simulation. In-Ho Jung is an associate professor at SNU, who is leading the FactSage Steelmaking Consortium Project, sponsored by the 11 steel producers around the world. His major research areas include the oxide and metallic database development and new materials and process design. Both are also working for FactSage software as associate member and co-developer.
Insight into the Thermodynamic and Kinetic Stabilities of Compositionally Complex High Entropy Alloys of Ni-Cr-Fe-Co-Al-Ti-Cu via a Pseudo Binary Phase Diagram Models

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Key words: high entropy alloys, pseudo binary diagram, CALPHAD, Gibbs model

A simplified pseudo phase diagram yet with well-calibrated thermodynamic and kinetic property of the alloys is an important to understand and design the compositionally complex high entropy alloys (CCA alloys). It is also prerequisite for the simulation of the microstructure of CCA alloys and prediction of the mechanical property of the alloys using the simulation technique such as phase field. In this paper, the similarity coefficients of the constituents in a ternary alloy system, widely used for the geometrical extrapolation of the excess Gibbs energy in a multi-component alloy system from that of its sub-binaries, are in turn used to quantify the chemical similarity between the constituents of a CCA alloy. It enables a thermodynamically unified approach to treat the chemical dissimilar components of the CCA alloys and to build pseudo phase diagram of the alloys. It is found that with simplified Ni-Al pseudo binary diagram and kinetic model, it is able to reasonably recreate the underlying thermodynamic and kinetic stability the light weight CCA alloys comprise of alloying elements Ni and Al at a fast speed and much lower computational cost. The calculation results provide insights into the significance of pseudo phase diagram as an important tool for designing the new generation of CCA alloy.

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References


Biographical Note

Dr. Bai Kewu, as a senior research scientist of Institute of High Performance Computing Singapore, has been focused on the research of the thermodynamic and kinetic properties of materials using CALPHAD technique and first principles molecular dynamics method.
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CALTPP: A General Program to Calculate Thermophysical Properties

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Key words: Thermophysical property; Diffusion coefficient; Interfacial energy; Thermal conductivity; Viscosity; Molar volume; CALPHAD modeling

A program CALTPP (CALculation of ThermoPhysical Properties) is developed in order to provide various thermophysical properties such as diffusion coefficient, interfacial energy, thermal conductivity, viscosity and molar volume mainly as functions of temperature and composition. These thermophysical properties are very important inputs for microstructure simulations and mechanical property predictions, including diffusion simulation, phase field modeling as well as finite element method. The general structure of CALTPP is briefly described, and fundamental equations describing these thermophysical properties are presented. A few case studies including (a) the calculation of bulk and grain boundary diffusion coefficient and optimization of atomic mobility in binary and ternary alloys, (b) the calculation of solid/liquid, coherent solid/solid and liquid/liquid interfacial energies in binary and ternary alloys [1], (c) the calculation of thermal conductivity in binary and ternary alloys [2], (d) the calculation of viscosity in binary and ternary alloys [3], and (e) the establishment of molar volume database in ternary and quaternary systems [4] are demonstrated to show the feature of CALTPP. It is expected that CALTPP will be widely used in both scientific research and education.

Acknowledgement

Financial support from National Natural Science Foundation of China (Grant Nos. 51671219, 51429101) is greatly acknowledged.

References


Biographical Note:

Dr. Yuling Liu, Central South University, Changsha, Hunan province, PR China. Her supervisor is Professor Yong Du. She is interested in CALPHAD approach; phase diagram, thermodynamics and diffusion as well as the simulation of the microstructure evolution.

Fig. 1. The general structure of CALTPP program

CALPHAD XLVIII, Singapore, June 2nd - June 7th 2019
Abstracts for Marine Workshop
Interaction between Metallic Materials and Extracellular Polymeric Substances for Biofouling - from the Viewpoint of Materials Protection

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Key words: biofouling, biofilm, Marine anti-fouling, Corrosion

Biofouling of various metallic materials in Marine environments are serious causes not only for deterioration of ship components and structures, but also for that of the whole off-shore and longshore structures. Particularly, metallic materials are critical for biofouling and corrosion, since they attract bacteria and react with polymeric substances derived from biofilms various bacteria produce cooperatively. In my presentation, I will talk about the background for biofilms and biofouling in marine environments, the theoretical aspects, mechanism, evaluation methods in the field, and also evaluation processes in the laboratory[1]-[8]. And some countermeasures from the alloy design and surface engineering etc. will be explained.

Fig.1 Schematic illustration of Biofilms and interaction with metal substrates.

References

Biographical Note
Dr. Hideyuki Kanematsu, FIMF (a Fellow of IMF: Institution of Materials Finishing, the United Kingdom) is a full professor of National Institute of Technology (NIT, KOSEN), Suzuka College (Department of Materials Science and Engineering). He is the former Deputy President of NIT, KOSEN, Suzuka College) and the Dean of Dept. MS and E in the college. He has been a researcher in Surface Science and Engineering of Materials. He is interested particularly in the interfacial phenomena between the metallic surface and organism from the environmental science. He holds a B.Eng. (1981), a M.Eng(1983) and a Ph.D in Materials Science and Engineering (1989) all from Nagoya University. He is active members, board members, editorial members of ASM International (for IMR & AM&P), National Association for Surface Fishing, the USA (N ASF), the Institute of Metal Finishing, UK(IMF) as well as the Minerals, Metals & Materials Society, USA(TMS), American Chemical Society (ACS), Electrochemical Society (ECS), the Japan Institute of Metals (JIM) and the Iron & Steel Institute of Japan (ISIJ) etc.
Corrosion Properties of Al-Mg and Al-Mg-Si Coated Steel (II)


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Key words: Corrosion resistant coatings, Al-Mg alloy coatings, Heat treatment, Physical Vapor deposition

In steel industry, the surface treatment of steel is one of major issues for increasing the lifetime of steel sheet. Hot dip coating and electroplating techniques have been applied to the surface treatment of steel for over last 100 years. There are several types of coated steel products, but mainly zinc-based coated steels are most common and used primarily for automotive, home appliances, and construction applications.

This paper presents the corrosion properties of Al-Mg and Al-Mg-Si coated steel prepared by physical vapor deposition (PVD)[1-2]. It is well known that Al coating has a good barrier property, however, it is lack of sacrificial properties for steel. Mg coating provides sacrificial ability for steel, but its surface is too sensitive to environment to be used commercially at this time. To achieve having both barrier and sacrificial properties, Al-Mg coatings have been investigated as an alternative coating material for Zn. It has been aimed that Al-Mg alloy coating can achieve two crucial properties of barrier protection and sacrificial ability for steel. The coatings have been prepared on a steel sheet using the magnetron sputtering.

Figure 1 shows the time to onset of red rust according to the magnesium contents of Al-Mg alloy coatings by salt spray test. Other coated specimens were tested together for comparison. For as-deposited Al-Mg alloy coatings, red rust was observed after SST from 150 to 220 hours according to the Mg contents. However, after annealing, the red rust was observed after SST from 300 to 520 hours. The annealing has enhanced the corrosion resistance of Al-Mg coatings. The optimum Mg content, which showed the highest corrosion resistance, was around 20wt%.

In this presentation the corrosive properties of Al-Mg alloy coatings together with Al-Mg-Si coatings will be presented.

References

Biographical Note
J.I. Jeong is a research scientist at RIST (Research Institute of Industrial Science & Technology). He is performing the research on plasma-induced deposition technology based on physical vapor deposition (PVD). He is also interested in corrosion resistant coatings on steel. The analysis and evaluation of the coated products is one of his main topics of research, too.
Abstracts for Poster Presentations
Variation of Interfacial Compositions with Increasing Reaction Time in Solid Fe / liquid Zn Diffusion Couples

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Key words: Hot dip galvanizing, Solid/liquid reaction, Intermetallic compound layer

Hot dip galvanizing is generally performed by simple dipping of steel sheets into molten Zn bath, and heat-treatment is optionally conducted to control mechanical properties of intermetallic compound (IMC) layers of the Fe-Zn binary system. It is well-known that mechanical properties of IMC layers depend on their microstructures [1], crystal structures [2] and chemical compositions [3]. Among these factors, interfacial compositions of IMC layers can be controlled by dipping time and temperatures. Especially, dipping time is very important because the heat-treatment temperature is fixed in the practical process. However, investigation of interfacial reactions was mostly performed to identify obtained phases or to determine phase equilibria. Furthermore, phase equilibria determined by the diffusion couple method were sometime incorrect due to experimental conditions such as reaction time, purity of alloying elements, etc. In the present study, therefore, the evolution of interfacial compositions with increasing reaction time in solid Fe/liquid Zn diffusion couples at 450 °C was investigated.

Fe sheet samples of 5 mm × 20 mm × 0.2 mm (or 0.5 mm) were cut from high-purity Fe sheets (99.99%), ground by silica paper and polished using diamond suspension (1µm). Each sample was encapsulated in a silica quartz tube together with high-purity Zn (99.99%) under Ar atmosphere. Firstly, Zn was melted at 450 °C for 1800 s in a vertical electric furnace. During that period, Fe sheet was fixed at the top of the quartz tube by a magnet and placed outside of the furnace for preventing surface oxidation. Then, the Fe sheet was carefully dipped into molten Zn for 10 s ~ 432 ks.

Interfacial microstructures of Fe/Zn diffusion couples were observed by FE-EPMA and chemical compositions were analyzed by WDS. WDS analysis were performed under two conditions of the acceleration voltage, 20 kV and 6 kV, in accordance with thick and thin width of IMC layers, respectively. Chemical compositions measured by 6 kV were calibrated using following equation.

$$x_{Zn} = x_{Zn}^{6kV} + 0.4022x_{Zn}^{6kV}(1 - x_{Zn}^{6kV})$$

IMC layers of the Γ-Fe2Zn9, δ1k-FeZn5 and ζ-FeZn3 phases in the Fe-Zn binary system were observed after reactions shorter than 30 s, then the δ1p-Fe12Zn30,8 and Γ1-Fe21Zn8 phases formed at the δ1p/ζ and Γ1/δ1k interfaces, respectively. In the relationship between the thickness of layers d and annealing time t; d = k·r^n, the value of the time exponent n of the total thickness of IMC layers was determined to be 0.5, which indicates that the growth of whole IMC layers is controlled by volume diffusion. However, the growth of each IMC layer was individually controlled by one of or mixture of interfacial reaction, volume diffusion or grain boundary diffusion.

Figure 1 shows the summary of interfacial compositions after various reaction times. In the early stage, the interfacial compositions of all the IMC layers tend to deviate from the equilibrium ones toward Fe-rich side. After 1000s, those of the ζ and liquid phases changed close to the equilibrium ones, 7.5 and 0.6 at.%Fe, respectively. However, those of the Γ1, δ1k and δ1p phases remained slightly deviated even after 5 days (432ks). Especially, those of the Γ phase deviated toward Fe-rich side after the Γ1 phase formed between the Γ1/δ1k interface.

![Figure 1 Variation of interfacial compositions.](image)

References

Biographical Note
The author is a postdoctoral researcher at Tohoku University (TU) in JAPAN after graduation of Ph. D course at TU. Phase equilibria, solid/liquid reaction, texture control, etc. are mainly studied nowadays.
Understanding the Formation of (Al,Si)$_3$Sc and AlSc$_2$Si$_2$ Phases in Novel Al-Si-Sc Alloys via the Use of CALPHAD, Electron Microscopy and Atom Probe Tomography

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**Key words:** Al-alloys, CALPHAD, Phase analysis, Precipitation

Scandium (Sc) additions result in a significant improvement of the strength of Aluminium (Al) alloys, particularly in AA5xxx and AA7xxx-series alloys. There is very little literature on the addition of Sc in AA6xxx series alloys and there are conflicting results in the literature on the impact of Sc in these alloys and this is due to the limited understanding of the interaction between Si and Sc and the formation of SiSc-containing phases that are deleterious to the mechanical properties [1]. Understanding the formation of SiSc-containing phases is the first step towards the design of high strength Al-Si-Sc alloys.

In this project, CALPHAD was used to define a range of model alloys and heat treatments with the aim of maximising the formation of Si-Sc containing phases. For this purpose, the binary phase diagrams of Al-Sc, Al-Si and ternary phase diagram of Al-Si-Sc were constructed using Thermocalc™ with the use of TCAL-4 thermodynamic database. Thermocalc™ was also utilised for prediction of phases and to get the Scheil solidification curves which were then qualitatively compared with the microstructure of the model alloys prepared. The equilibrium phase diagrams were used to design a low-temperature annealing treatment at 350°C to form favourable (Al,Si)$_3$Sc nano-precipitates and high-temperature annealing treatments at 450°C and 550°C to form unfavourable V-phase (AlSc$_2$Si$_2$) precipitates.

We used a combination of electron microscopy techniques and atom probe tomography to study the formation of the V-phase and it was found that all the (Al,Si)$_3$Sc precipitates were replaced by the V-phase in our heat treatment conditions and this was accompanied with a sharp drop in hardness of the alloys. These results explain the detrimental effects reported in the literature and can be used to inform on the design of suitable compositions and heat treatments of Sc and Si containing aluminium alloys.

**References**


**Biographical Note**

Jayshri is a PhD research candidate at the Department of Materials Science and Engineering in Monash University since 2017 and her PhD focuses on the Sc-containing Al-Si alloys. She holds an M. Tech. degree in Process Engineering – Metallurgy from Indian Institute of Technology, Bombay (IITB), India and a Bachelor of Engineering (B. E.) degree in Metallurgical Engineering from College of Engineering, Pune (COEP), India. She also has an industrial experience of 10+ years on alloys and process developments.
P03

Uncertainties on Several Titanium Binary Diagrams

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Key words: Mo–Ti, Ti–V, Ti–W, phase diagrams, SQS-DFT

The binary phase diagrams based on titanium (hcp at low temperature, bcc at high temperature) and bcc elements of the vanadium and chromium columns (Ti–V, Ti–Nb, Ti–Ta; Ti–Cr, Ti–Mo, Ti–W) are very simple. Except in Ti–Cr, no compounds are formed and the phase diagrams show either:

- a complete solid solution in the bcc phase at high temperature and a lens between hcp and bcc at low temperature
- or a miscibility gap in the bcc domain and a monotectoid reaction bcc → bcc′ + hcp.

However, in certain cases, like for example the Mo–Ti or Ti–W systems, they are reported with a miscibility gap in the bcc phase whereas the DFT calculations of ordered phases show negative enthalpies of formation for bcc ordered structures. In addition, the SQS calculations show exothermic heat of mixing in the bcc phase. These results contradict the reported phase diagrams and the presence of a miscibility gap.

Furthermore, a careful study of the literature show also major contradictions between authors concerning the shape of the phase diagrams.

In the present work, a systematic SQS study of the bcc phase has been undertaken jointly with a complete literature review. These results will be presented in order to try to reconcile the experimental studies with the first-principles calculations.

Biographical Note

Jean-Marc is Director of Research at the National Center of Scientific Research (CNRS) in France. He is head of the group ‘Chemical Metallurgy of Rare Earths’ at the East-Paris Institute of Chemistry and Materials Science in Thiais, in the Paris suburb. His primary research interests are intermetallic compounds, hydrogen-metal systems and thermodynamic modeling.
P04

Toward the Generation of an Engineering-type Thermodynamic Database for Aluminum Heat Treatable Alloys Based on Fully Self-consistent DFT-based Thermodynamic Properties

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Key words: Aluminum alloys, Metastable phases, Density Functional Theory, Quasiharmonic approximation, Self consistent thermodynamic modelling

Aluminum-based heat treatable alloys are of prime importance for several highly technological aerospace applications. They present superior specific mechanical properties that are modulated by the controlled precipitation of stable/metastable phases via specific heat treatments. Being able to predict the phases that are precipitating under equilibrium or near-equilibrium conditions is a first step toward the optimization of their mechanical performance.

The thermodynamic properties of these metastable phases are experimentally difficult to assess; sets of thermo-physical data are often lacking for those phases. Fortunately, it is nowadays possible to estimate thermodynamic properties of metastable compounds or solutions using atomic simulations based on the Density Functional Theory (DFT). Accurate ground-state properties such as the 0K enthalpy of formation can be easily evaluated from DFT calculations for large sets of unary, binary and ternary ordered compounds with various crystallographic structures (L12, D022, D023 and FCC). Other thermodynamic properties such as the heat capacity at constant pressure can be estimated from these DFT ground-state calculations by applying a phonon-based treatment for the effect of temperature (i.e. the quantification of the thermal vibrational kinetic energy) using approaches like the Quasi Harmonic Approximation method (QHA).

The QHA relies on the parameterization of an equation of state (EOS) using the internal energy-deformation curves from DFT calculations. The estimation of the temperature dependence of several thermodynamic properties (such as heat capacities and thermal expansivities) and elastic properties (C11, C12, C44) can be obtained from this approach. It has been recently shown that the QHA is not necessarily self-consistent as it can violate some Maxwell's relations [1, 2, 3]. It was also highlighted that there is generally no systematic way of preserving self-consistency in the literature when applying the QHA. Moreover, the Gibbs free energy of solids predicted with the QHA is most of the time overestimated (few kJ/mol at melting) which could considerably impact phase equilibrium calculations.

The aim of this work is to alleviate the inconsistencies of the QHA method to obtain sets of fully self-consistent thermo-physical properties of Al-based binary and ternary ordered compounds. To do so, an iterative self-consistent scheme using state-of-the-art 0K DFT calculations is proposed. These thermodynamic properties are then used to parameterize the Compound energy formalism via the fine-tuning of the standard Gibbs energy of the different end-members defining each studied ordered solution. Several examples will be presented.

Figure 1. Comparison between calculated \( \omega_2 = 1 - \frac{\partial u}{\partial p} \cdot \left( \frac{1}{K^2} \frac{\partial K}{\partial T} \right)^{-1} \), for aluminium, with our procedure (blue line) and QHA method (black line). \( \omega_2 \) must be null to ensure the self-consistency between the thermodynamic properties.

References

Biographical Note
Javier A. Jofré is a member and Ph.D. candidate at the CRCT in Polytechnique Montreal. He obtained a master’s degree in chemical engineering during which he studied the energetic behavior of enzymes using molecular dynamics. His ongoing Ph.D work focuses on the development of the new generation of thermodynamic models of solid solutions.
Third Generation CALPHAD Database from 0K up to 6000K for 8 Transition Elements

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Key words: Thermodynamic properties, Heat capacity, Segmented regression, Sigmoid function

Novel physically-based description of thermodynamic properties from 0K up to 6000K has been derived in this work. The proposed model is a flexible extension of the segmented regression (SR) covering temperatures from 0K up to the melting point [1] to the high temperatures far above the melting point. It contains five model parameters to be estimated from experimental / DFT data, same as in original SR formulation and it enables the modification of the melting point value without the need for additional re-assessments, e.g., in case of pure chromium where the correct value of melting point is still under discussion.

The modified SR model has been successfully applied for the description of thermos-physical properties of eight transition elements, such as Ti, V, Ni, Fe, Mn, Cr, Nb and Mo. In all considered cases it shows a good agreement with available experiments. To estimate the accuracy of newly proposed SR model, a comprehensive review of recommended values for heat capacities, relative enthalpies, standard entropy, melting and Debye temperatures has been performed. The model performance has been evaluated in comparison to the existing alternative physically-based description valid from 0K [2-4].

References

Biographical Note
Abdulmonem Obaied is a doctoral candidate at ICAMS, Ruhr-University Bochum, Germany. His research focuses on developing and application of machine learning and data mining tools for property prediction of Co-based superalloys and relevant pure elements and binary systems.

![Graph a) Modified SR model fitted to experimental heat capacities in comparison to Desai’s recommended values [2] and Thurnay model [3]](image)

![Graph b) Comparison between calculated relative enthalpies using the modified SR model [1], Thurnay model [2] and recommended Desai’s values [3] with experimental data.](image)

Figure 1. Results for pure V using modified SR model.
New thermodynamic databases for pure elements and substances should provide accurate description of thermodynamic properties from 0 K well above the melting point, be based on critically assessed experimental data and have a good physical basis. Third generation CALPHAD approach obeys these principles and has already been used for the description of pure elements’ properties.

The aim of present work is to develop model representation of thermodynamic properties of crystalline and amorphous/liquid phases of SiO₂ and GeO₂ at ambient pressure. The extended Einstein model was used for modelling of crystalline phases. It allows to represent with different terms the input from harmonic lattice vibrations and effects from anharmonicity [1]. Planck-Einstein model [2] was used to obtain a better representation of properties at low temperatures and, in particular, the standard entropy at 298.15 K.

Two-state liquid model [3] describes the effects of melting and glass formation in terms of difference in Gibbs energy of “vibrational” (solid-like) and “translational” (liquid-like) atoms. Its application would be especially relevant to substances with experimentally studied properties of amorphous and liquid phase.

It was shown that the new model representation provide better descriptions of existing experimental data. On figure 1 are shown the modelled heat capacity curves for the crystalline phases of GeO₂ in comparison with [4].

The Planck-Einstein approach allows to increase accuracy in standard entropy calculation. However, two-state liquid model showed limitations in description of glass transition phenomenon.

Figure 1. Modelled heat capacity of crystalline phases of GeO₂

References

Biographical Note
I am a PhD student at National University of Science and Technology (MISIS) and engineer at SRC Thermochemistry of Materials, Moscow, Russia. My research interests include thermodynamic modelling of oxides and experimental determination of thermodynamic properties of elements and substances.
Thermophysical Properties of Liquid Alloys from the Ternary Ga-Sn-Zn System

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Key words: gallium alloys, Ga-Sn-Zn, liquid metals, viscosity

Liquid metal alloys are a new and exciting group of materials, gaining more and more importance in various fields of science and technology.

Non-toxic alloys with a low melting points are heavily researched for a number of different applications, including lead-free solders, soft and wearable sensors, stretchable electronics or as heat transfer fluids in Concentrated Solar Power Technologies [1,2]. Due to the outstanding thermal conductivity and the fact that these alloys remain liquid in a wide range of temperatures, including temperatures under room temperature, they are suitable candidates for thermal management in different systems, including cooling computer chips, Li-ion batteries, high power LEDs or in thermal management of nuclear reactors [2]. A number of liquid metal based on gallium have been proposed over the years, including Ga-In eutectic, Ga-In-Sn eutectic, also known as Galinstan, Ga-Zn and Ga-Zn eutectics. Here we study the Ga-Sn-Zn ternary system [3], which we believe could be a cheaper alternative to systems with indium, and could have a lower melting temperature compared to binary systems.

In order to successfully apply a material in any of the listed technologies, the basic properties of the alloy should be assed. In this study we aim at measuring the density, surface tension and viscosity of liquid alloys from the ternary Ga-Sn-Zn system using the discharge crucible method [4] in the temperature range of 323-823 K.

The alloys were prepared from pure elements in a glove box under the protective atmosphere of argon. The discharge crucible method, used in the experiment, allows the simultaneous measurement of the density, viscosity and surface tension. The measurements were conducted under argon atmosphere in order to minimize the risk of liquid metal oxidation. The experimental set-up used in the measurement is presented in Figure 1.

Across the analyzed temperature range, the density, viscosity and surface tension of the Ga-Sn-Zn alloys were determined. The obtained experimental values of the thermophysical properties were compared with the values calculated using appropriate models, including the Egry model for density, Sato, Kucharski, Melywen-Hughes, Kozlov, Romanov and Petrov, Schick and Gasior models in the case of viscosity and Kohler, Toop, Muggiano and Butler models for the surface tension.

Figure 1. Experimental set-up for density, viscosity and surface tension measurements

References

Biographical Note
Alexandra Dobosz completed her studies in Materials Engineering at the University of Science and Technology AGH, preparing her master thesis at the French Alternative Energies and Atomic Energy Commission. She started PhD studies on liquid metals at IMMS PAS (Cracow) in 2017. She gained experience during stay at RMIT University (Australia).
Thermodynamics of Alkali Oxides Using DFT Calculations

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Key words: alkali oxides, DFT, phonons

Alkali oxides are commonly observed in various industrially important materials such as fly ashes from coal or biomass combustion, cement clinkers or glass. Despite their relative importance, the Gibbs free energy of formation of most of the pure solid alkali oxides is poorly known. For example, the Gibbs energy of solid K₂O is completely estimated by analogy with Na₂O and Li₂O [1]. No experimental measurement is available!

DFT calculations are more and more reliable to predict the heat of formation of inorganic compounds at T=0K. This is particularly the case when using the recently developed SCAN (Strongly Constrained and Appropriately Normed) functional [2] as implement in the most recent version of VASP (Vienne ab-initio simulation package) [3].

In this contribution, we will present the results of DFT calculations for the solid compounds Alk₂O, Alk₂O₂ and AlkO₂ (Alk=Li, Na, K, Rb and Cs). The heat of formation is calculated with respect to the pure elements Alk and O₂(g) and the results will be compared to the available experimental information.

A special focus will be set on the thermodynamic properties of the compounds in the K-O and Na-O binary systems for which only very limited experimental data exist. In addition to the ground state properties obtained at 0K, we determine their temperature dependence using lattice theory. More specifically, the phonon spectra for Na₂O, NaO₂, K₂O, K₂O₂, and K₂O are calculated using the phonopy code [4]. With these data, one can calculate the heat capacity at constant volume in the harmonic approximation and the heat capacity at constant pressure in the quasi-harmonic approximation and then derive the standard heats and entropies of formation at 298K. All these theoretical data are compared to the Gibbs free energy data stored in thermodynamic databases (JANAF, SGSUB, FACTPS). As an example, the comparison between the calculated heat content and the measured one for Na₂O is presented in Figure 1.

As alkali oxides are rather volatile, new Gibbs free energy data of the solid phases will have an impact on the data for the gas species. As an example, the impact on K-O gas species will be discussed. The calculated phase diagram log(p(O₂)) vs 1/T using these new data will be compared to a calculated diagram using Gibbs free energy data for the solids from the commercial substance databases (FTPS & SGSUB).

This work is financially supported by the French research institute “Carnot” in the frame of the “énergie du futur” programme. Valuable discussions with colleagues in the frame of the French collaborative network GDR “ThermalIT” are acknowledged.

References

Biographical Note
Alexander Pisch is CNRS research fellow at SIMaP (Science, Engineering, Materials and Processes) in Grenoble, France since 1997 with a research focus on CALPHAD assessments, calorimetric measurements and DFT calculations.
Mo-Zr alloys are widely used in many applications because of their refractory nature and resistance to harsh environments. These alloys are also used in the fabrication of fuel cladding, channel boxes and other in-core structural components. Besides, Mo and Zr are used as alloying elements in several grades of Ni-base superalloys.

The four phases present in the phase diagram are BCC, HCP, LIQUID and the Laves (C15) phase. Domagala et al. [1] reported that the ideal stoichiometry of the Laves phase corresponds Mo:Zr, whereas Brauer et al. [2] reported that its homogeneity ranges from 32 to 40 mol% Zr. The diffusion study performed by Bhatt et al. [3], however indicates a somewhat narrow homogeneity ranges of 33.3 to 34.5 mol% Zr. Also, according to Perez et al. [4] there are considerable uncertainties regarding the exact position of the Mo-rich solidus and liquidus.

In this work, we report the thermodynamic optimization of Mo-Zr system using CALPHAD approach combined with ab initio calculations. The enthalpy of formation of Mo₂Zr is calculated using DFT. The finite temperature thermochemical properties are computed using phonon approach. These ab initio generated data are used as input along with the experimental thermochemical and constitutional data for the thermodynamic optimization of Mo-Zr system. The calculated phase boundaries are in good agreement with the experimental data as shown in Figure 1.

**Figure 1. Calculated phase diagram of the Mo-Zr system**

**References:**


**Biographical Note**

I am a 3rd year undergraduate student at the Department of Metallurgical & Materials Engineering in Indian Institute of Technology Madras. My research interests include CALPHAD and density functional theory.
P10

Thermodynamic Modeling of the U-Nb-Zr ternary System

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Key words: U-Nb-Zr, phase diagram, thermodynamic calculation, miscibility gaps, solvus projection

U-based alloys are considered as good candidates for nuclear fuels due to their high fissile density and thermal conductivity. Since the stability of bcc-γ phase influenced by Nb and Zr additions is considered as an important factor that decides the microstructures, thermal behaviors, and mechanical properties, an impetus is raised to get a good knowledge about the phase diagram information of the U-Nb-Zr ternary system. Although extensive work about experimental phase diagram of this system has been done in the literature, a thermodynamic modeling using the CALPHAD method is of great interest to the R&D of U-based materials.

In this work, a thermodynamic modeling of the U-Nb-Zr ternary system has been performed. The modeling describes solution phases, i.e. liquid, bcc, ort, tet, and UZr2, and covers the whole composition range and a temperature range from 450 to 2300 ºC. A set of self-consistent thermodynamic parameters have been developed. Comprehensive comparisons between the present calculations and measured phase diagrams show that the reliable experimental data are well accounted for by the present thermodynamic description. With regard to the bcc-γ phase, the evolution of miscibility gaps and phase relations concerned are satisfactorily reproduced by the present calculation. Based on this, the solvs projection and reaction scheme of the U–Nb–Zr system have been generated, thereby providing guidance for possible industrial applications.

Figure 1. Calculated liquidus and solidus projections of the U-Nb-Zr ternary systems.

Figure 2. Calculated isothermal sections of the U-Nb-Zr ternary systems at 620–450 ºC

References

Biographical Note
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Research interest: CALPHAD; cemented carbides, nuclear materials.
P11

Thermodynamic Investigation of the Oxidation of NiAl– (Cr, Mo) Alloys Used for Manufacturing Metal Matrix Composites

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Key words: Thermodynamic modelling, CALPHAD, NiAl-(Cr, Mo), Oxidation

In the last few decades Ni$_3$Al-based superalloys have been of interest as novel materials for elevated temperature structural applications such as turbines. Several attempts have been made to increase the operating temperature using NiAl-based alloys. However, NiAl has undesirable mechanical properties such as poor ductility and fracture toughness at room temperature and insufficient creep resistance and low strength at high temperature. To overcome these problems, lamellar and fibrous directionally solidified NiAl-based eutectics (Cr, Mo, etc.) are suggested.

These composites show much higher creep resistance \cite{1} and are promising candidates for high-temperature applications. As these alloys are in contact with combustion gases, oxidative corrosion processes will happen presumably. So far, the oxidation behavior of these metal matrix composites have been studied only by few groups. \cite{2,3}

In the present work oxidation processes are investigated using both experimental and advanced computational thermodynamics in the materials systems: NiAl–Cr–O, NiAl–Mo–O and, NiAl– (Cr, Mo) –O. Alloys with equimolar ratio of Ni: Al are the main focus.

Based on thermodynamic data such as isothermal phase diagrams, isopleths and oxygen activity diagrams from literature as well as datasets for the sub systems, a thermodynamic database for the system NiAl-(Cr, Mo)-O is established. This new dataset combines data for pure Ni, Al, Cr, Mo, O and corresponding binaries and ternaries. Thermodynamics of the relevant oxides and their equilibria with the metallic composites can be predicted, using the provided database.

The solution phases are modeled with the compound energy formalism, while the liquid is modeled with the ionic two-sublattice model to describe both the metallic and the oxide melts. Simple spinels within this system like Cr$_2$O$_3$, NiCr$_2$O$_4$ and NiAl$_2$O$_4$ are described using a four-sublattice model. Moreover, metastable oxides like γ-Al$_2$O$_3$ (with spinel structure), δ-Al$_2$O$_3$, θ-Al$_2$O$_3$, are included.

Experiments are performed to determine data for the missing relevant oxides. In order to investigate the oxidation behavior of NiAl–Cr and NiAl–Mo interfaces, samples were manufactured by embedding Cr and Mo wires in NiAl by using an arc-melter. Samples were oxidized under defined oxygen partial pressure in thermogravimetric analysis (TGA). Subsequently, the composition and the microstructure of the oxides formed at the surface were studied. Besides, the interface of NiAl and the Cr phase was investigated by electron backscatter diffraction (EBSD) as shown in figure 1. In addition, the oxidation products are investigated also by X-ray diffraction (XRD) and scanning electron microscopy (SEM) equipped with energy dispersive X-ray (EDX).

With the provided database from this work, Thermo-Calc software is used as a modern thermodynamic simulation method to anticipate the phase diagrams, isopleths, isothermal sections, heterogeneous phase reactions and thermodynamic functions.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{EBSD image of NiAl-Cr interface with oxide layers at the surface after oxidation at 1300°C in 0.13 bar O$_2$ in Ar for 50 hours.}
\end{figure}

References
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Biographical Note
Golnar Geramifard is currently a PhD candidate at Karlsruhe Institute of Technology where she is one of the members of Helmholtz Research School on “Integrated Materials Development for Novel High-Temperature Alloys”. Since 2016 she has been investigating the oxidation of NiAl-Based superalloys using CALPHAD approach based on experiments.
P12

L12 Cluster and Y Interaction in LPSO Mg-Zn-Y System

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1 Introduction

Mg alloy with LPSO(Long period stacking order) structure shows superior mechanical properties than ultra-super surlar mine in the ratio yield strength. The growth mechanism of LPSO structure. However, has not been clarified. Thus, we have performed the first principals’ calculations on this system. With two hypotheses.

1. the stacking fault initiation, or
2. the middle range ordering of solutes initiation

If the latter hypothesis stands, the solute atoms should be enriched at the middle range away from L12 clusters at the stacking fault region. Recently, Morishita revealed that the small size clusters show the middle range stability from L12 clusters at the stacking fault region. On the other hand, the model size, 18 layers of the slab, for the interaction between isolated solute atoms and L12 cluster, in the early research performed by our group, has appeared to be not enough long.

In this research, we checked the longer interaction between isolated solute atom, Y, and L12 cluster by the first principles calculations.

2 Method

We used VASP(Vienna ab initio simulation package) for the first principles calculation. The pseudopotentials for Mg, Zn, Y are PAW PBE with the energy cutoff of 300eV. The slab model with 24 layers of Mg and two stacking faults, is constructed as shown in Fig.1. An L12 cluster is located at one of the stacking faults. The sites of Y are illustrated in top and side views for Fig.1. After the outer shape and ionic relaxations with the break condition of -0.02, total energies are obtained by tetrahedron method with Bloch corrections with the k-space of 5x5x1.

Figure 1: Schematic illustrations of top and side view of the slab model with 24 layers. A Y atom is embedded at few sites separated from a specific layer away from L12 cluster at a stacking fault.

3 Results

Fig.2 shows the vertical distance dependency of interaction energy between isolated Y solute and L12 cluster. Some points at the same distance layer show the scattered values from the different sites. Each minimum energy at the vertical distance layer are connected for the eye guide. The energy decreases monotonously on the vertical distance from the L12 cluster, except 0.02eV minimum at the 6th layer. The small cluster dependency obtained by Morishita et al., which is simultaneously plotted for the comparison, show the obvious stability with 0.08eV drop at the 4th layer.

Thus, we concluded now that the isolated Y solute does not show the middle range ordering with L12 cluster at the stacking fault, but a small size cluster with 4 Y and 3 Zn atoms, reported by Morishita et al., shows the middle range stability at 4 layers away from L12 cluster. This middle range stability enforces the enrichment of solute atoms of middle range and initiate another stacking fault.

Figure 2: Vertical distance dependencies of interaction energies between small cluster and L12 cluster, and between isolated Y solute and L12 cluster.

References
P13

Thermodynamic Evaluation of Grain Boundary Segregation and Precipitation Behavior in Steels

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**Key words:** segregation, precipitation, boron, hardenability

Boron (B) is a commonly known as an alloying element that enhances the hardenability of steels, and this is most likely due to the suppression of the nucleation of ferrite at the austenite grain boundaries, where B segregates. The effect of B addition on hardenability is significantly influenced depending on the form of B atoms in steels, and solute B segregated at the grain boundaries inhibits the ferrite nucleation, in contrast, B becomes ineffective for hardenability by the precipitation of Fe\textsubscript{23}(C,B)\textsubscript{x}. In addition, it has been reported that hardenability of steels is synergically increased by the combined addition of B and Mo [1] and that of B and Nb [2]. In this study, the grain boundary segregation of B and alloying elements in steels has been investigated using the parallel tangent law proposed by Hillert. Furthermore, the grain boundary precipitation behavior has been also evaluated based on the TTT curves calculated by coupling the CALPHAD method with the Davies-Uhlmann kinetic approach, where the Gibbs energy of the grain boundary was expressed as that of the liquid phase, following a previous study [3]. The calculated grain boundary segregation behavior, including the co-segregation, was consistent with the reported experimental results. The tendency of the co-segregation of B and transition element may correlate with the boride formation ability of alloying element. The calculated TTT curves indicated that the precipitation of M\textsubscript{23}(C,B)\textsubscript{x} was suppressed with increasing Mo content up to 1 mass\%, whereas the nose of the TTT curves for FeMo\textsubscript{3}B\textsubscript{2} precipitation shifted to shorter times with increasing Mo content. These predicted results roughly reproduced the experimental results [1,4].

**References**


**Biographical Note**

Dr. Tatsuya Tokunaga is an associate professor at Kyushu Institute of Technology. He received B.S. and M.S. degrees from Nagoya University in Nuclear Engineering and his Ph.D degree from Kyushu Institute of Technology in Materials Science and Engineering. His main research interests are phase equilibria, phase transformation and computational thermodynamics in alloys based on the CALPHAD method and their applications to engineering materials.
P14

Thermodynamic Database of RE-Fe-B Magnetic Alloys

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Key words: Permanent magnets, Nd-Fe-B, Thermodynamic, CALPHAD

Nd-Fe-B permanent magnets with excellent magnetic properties have been used in the industrial applications including medical instruments, electrical motor and wind power [1,2]. In order to fully balance the application of rare-earth resource in magnetic materials and reduce the costs, it is necessary to introduce high abundant rare earth (RE) metals (e.g. La, Ce, Y) to Nd-Fe-B permanent magnets [3]. Phase diagrams and thermodynamic properties of the RE-Fe-B alloys are important to understand the effect of the abundant rare earth metals on microstructure and magnetic properties of Nd-Fe-B permanent magnets.

In this work, the RE-B, RE-Fe, RE-RE (RE=La, Ce, Y, Nd) sub-binary systems were assessed using CALPHAD method on the basis of experimental thermodynamic data and phase equilibria, and then thermodynamic database of the RE-Fe-B ternary systems is developed, which is fundamental to obtain the thermodynamic database of multi-component RE-Fe-B alloy systems.

References

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Biographical Note
Dr. Jiang Wang completed his studies as a PhD student in Central South University in 2008 and then joined as postdoctoral researcher in Swiss Federal Laboratories of Materials Science and Technology, Switzerland in October 2008. Since October 2011, he works as a research scientist in Guilin University of Electronic Technology, China. His research work focuses on phase equilibria, phase structure and physic properties of metal materials (e.g. Mn/Fe-based alloys) through both experiments and calculations.
Experimental Determination of Phase Diagrams in the Al-Fe-Si Ternary System

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Key words: Phase equilibria, Al-Fe-Si phase diagram, hot-dip aluminizing

Hot-dip Aluminizing process (HDA) is an effective way to improve the corrosion resistance of steel sheets. This method is performed by dipping the steel sheet into molten Al bath maintained at 670 ~ 730 °C \cite{1}, by which the steel sheet is coated with Al layer. Aluminized steel sheets are applied for building materials, exhaust equipments, surface-treated high-strength steel for hot-stamping deformation and so on. However, there is a fundamental defect in this method, i.e., the Al coated layer is easily delaminated due to the brittle η-phase rapidly grown at the interface between a steel substrate and Al layer. In these days, addition of Si into the molten Al bath is known to be efficient to suppress the growth of the η layer resulting from occupation of Si in the diffusion path of Al \cite{1}. Meanwhile, intermetallic compounds (IMCs) formed in HDA changed from binary phases of η and Si to ternary ones of η, τ\textsubscript{1}, τ\textsubscript{5} and τ\textsubscript{6} by the addition of Si. Among these ternary phases, τ\textsubscript{1} precipitated in the η layer, τ\textsubscript{5} formed as a major IMC layer and τ\textsubscript{6} mostly formed in the liquid Al. Formation behaviors of IMCs during the aluminizing reaction are generally interpreted on the basis of phase diagrams. However, phase equilibria on the Al-Fe-Si ternary system so far has not been precisely investigated. Especially, information of phase equilibria at high temperatures was limited to some single-phase regions and three-phase regions \cite{2}. In the present study, therefore, experimental determination of phase equilibria at Al-rich portion in the Al-Fe-Si ternary system was carried out by means of alloying method.

High-purity Al (99.999\%), Fe (99.99\%) and Si (99.999\%) were melted by high frequency induction furnace under Ar-atmosphere and ingots of Al-Fe-Si alloys were prepared. Then, samples cut from those ingots were encapsulated in silica quartz tube backfilled with Ar-gas, heat-treated at 900 ~ 600 °C for 7 ~ 30 days, and quenched into ice water subsequently by breaking quartz tube. Microstructures were observed and equilibrium compositions were determined by a field emission-electron probe micro analyzer (FE-EPMA) equipped with a wavelength dispersive X-ray spectrometer (WDS).

Isothermal phase diagrams of Al-rich portion in the Al-Fe-Si ternary system were precisely determined in the present study. Existence of single-phase regions was almost identical to phase diagrams in the literature \cite{3}. However, their solubility ranges and three-phase regions were considerably different from reported phase diagrams. On the other hand, the τ\textsubscript{5} phase, which was observed as the main IMC layer the HDA process, is confirmed to be a stable phase at 700 °C as shown in Figure 1. Phase transformation of τ\textsubscript{5} + η + Liq. → τ\textsubscript{6} is coincident with literature assessed by Y. Du et al. \cite{4}.

![Figure 1. Experimentally determined phase diagram of Al-rich portion in Al-Fe-Si ternary system.](image)

References


Biographical Note

Ryosuke Ishikawa is master course student in Materials Science from the Tohoku University (Japan). He obtained his bachelor’s degree in Materials Science.
P16

Thermodynamic Calculation of Ni-Al-RE (La, Nd) Ternary system

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Key words: CALPHAD, Ni-Al-RE, Superalloys, Thermodynamic optimization

Nickel-base superalloys become more attractive recently for its use in aerospace. As the most important constitutional ternary system the Ni-Al-La and Ni-Al-Nd ternary system has been studied in the present work.

In this study, the phase equilibrium of the Ni–Al–La ternary system in a nickel-rich region was observed at 800 °C and 1000 °C using scanning electron microscopy backscattered electron imaging, energy dispersive X-ray spectrometry and X-ray diffractometry. The solubility of Al in the Ni5La phase was re-measured at 800 °C and 1000 °C. Herein, we report a new ternary phase, termed as Ni2AlLa, confirmed at 800 °C. Its X-ray diffraction (XRD) pattern was indexed and space group determined using Total Pattern Solution (TOPAS), and the suitable lattice parameters were fitted using the Pawley method and selected-area electron diffraction. Ni2AlLa crystallizes in the trigonal system with a space group R3 (no. 146), a = 4.1985 Å and c = 13.6626 Å.

Thermodynamic optimization of the Ni-Al-RE (La, Nd) ternary systems has been conducted in the present work. Al-RE (La, Nd) binary systems were thermodynamically re-optimized while taken into consideration the solubility of RE in fcc (Al). A self-consistent set of thermodynamic parameters for the Al–RE (La, Nd) binary system and the Ni–Al–RE (La, Nd) ternary system includes ternary phase, which was optimized using the CALPHAD method. Isothermal sections at 800 and 1000 °C for Ni-Al-La ternary system, 600 and 700 °C for Ni-Al-Nd ternary system have been reproduced. Isopleths with 93 at.% Al, 9 at.% Ni and 3 at.% Nd for Ni-Al-Nd ternary system have been calculated also. The calculated thermodynamic and phase equilibria data for both the binary and the ternary systems agree fairly well with the experimental data. This work can be used as multi-component thermodynamic database for Ni-based superalloys.

Figure 1. The graphical abstract of this paper

Biographical Note

J.F. Liao: Graduate student of School of Materials Science and Engineering, Jiangxi University of Science and Technology, whose research field is calculation and determination of phase diagram.
Thermodynamic Assessment of the Te–X (As, Si, Co) Systems

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Key words: Te–X (As, Si, Co) systems, phase diagram, CALPHAD

Phase Change Random Access Memory (PCRAM) materials are recognized as the most promising candidates for the next non-volatile mainstream memory technology. The core of PCRAM is based on chalcogenides phase-change material, as they exhibit large variation of electrical resistances during phase change from amorphous to crystallization. In particular, chalcogenides containing tellurium are widely used in PCRAM. In order to improve the performance of PCRAM, doping modification is usually adopted, and this work focuses on arsenic, silicon and cobalt. Phase diagram plays a key role as a map guiding in industrial production. As a part of the thermodynamic database, thermodynamic assessments of the Te-As, Te-Si and Te-Co binary systems were carried out by using the CALCuletion of PHase Diagrams (CALPHAD) method.

The Te-As system was remodeled according to the new experimental data reported by Chen et al. [1]. The Te-Si system was reevaluated based on the evidences of the existence of SiTe2 crystalline phase and the invariant reactions reported by Mishra et al. [2]. The Te-Co system was assessed according to the available experimental data of Klepp, K. O et al. [3] and Geffken, R. M et al. [4].

The thermodynamic parameters were evaluated based on the experimental data available in the literature as described above in the present work. Thermodynamic models were constructed for all the phases of the three systems. The liquid phases were described by the substitutional solution model. The intermetallic compounds in the Te-X (Si, As) systems, were treated as stoichiometric phases. The compounds β-CoTe and γ-CoTe2 were the non-stoichiometric phase which has homogeneity range and were treated by sublattice model in the Te-Co system. A set of self-consistent thermodynamic parameters for Te-X (As, Si, Co) systems was constructed. The calculated results agree well with the experimental points from the literature.

References

Acknowledgements
The financial supports from the National Key Research and Development Program of China (Materials Genome Initiative: 2017YFB0701700) and the National Natural Science Foundation for Youth of China (Grant No. 51601228) are greatly acknowledged.
Due to the traditional floating door structure size is difficult to meet the needs of the period of big data. Resistive Random Access Memory (RRAM) has simple structure, small battery size, good miniaturization, fast operation speed, low power consumption, and compatible with the complementary metal oxide semiconductor (CMOS) technology. RRAM is regarded as one of the most promising non-volatile memory in the next generation [1]. At present, the widely used RRAM materials are mainly composed of Transition Metal (TM) and TM oxides. Considering that different combinations of TM oxides and TM oxides may cause changes in the performance of resistive memory [2-3]. Therefore, in this work, a series of studies are carried out on the resistive memory materials based on Mo-X (X = Hf, Zr) system. The Mo-Hf and Mo-Zr systems belong to interesting systems exhibiting the existence of a variety polytypes of Laves phases. However, the room temperature brittleness of Laves phase alloy is serious, and the fracture toughness is still very low, which cannot meet the actual requirements. Therefore, overcoming the brittleness of Laves phase alloys is the main research direction in the future. On the other hand, due to various factors, the material will be in a free energy state and a metastable state that is higher than the equilibrium state. In many cases, some properties of metastable materials are superior to those of equilibrium materials, and even some special properties have emerged. Therefore, the study of material metastable state is not only of theoretical significance, but also of practical value.

The Laves stable phase and metastable phase of Mo-Hf and Mo-Zr systems were studied in the present work. The relative stability of the Laves phase in these systems is revealed by comparing the energy calculated by the first-principles of these structures. The enthalpy of formation of HfMo2 Laves phase and enthalpy of mixing for the solid solution phases in dilute solution were predicted by first-principles calculations. This thermochemical information, which is unavailable from experiments, provides meaningful values for parameterization of the Gibbs energy functions. A set of self-consistent thermodynamic parameters for the Mo-Hf and Mo-Zr systems was constructed, which is compatible with our previous studies. This study confirms that the Gibbs energy of the currently re-evaluated Laves phase requires fewer fitting parameters, and the phase diagram is in good agreement with the experimental data in the literature, which greatly enriched the thermodynamic database of the systems.

References

Acknowledgements
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P19

Thermodynamic Assessment of the Al-C and Al-C-Mg Systems

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Key words: Al₄C₃, Al₂MgC₂, Synthesis, XRD, DFT, DSC, DTA

To reduce its environmental footprint by lightweight vehicles design, the transportation sector relies on an increased use of magnesium based materials. Commercial thermodynamic databases¹⁻³ regarding the Al-C-Mg are unreliable as the Al₂MgC₂ carbide is currently not described due to a lack of data. As a result, no guidance can be provided regarding the underlying mechanisms of the grain refinement of Mg-Al alloys by carbon inoculation which are debated in the literature. Therefore, the purpose of this study was to provide a reliable thermodynamic assessment of the Al-C-Mg system.

First of all, a literature review of the Al-C-Mg system and its subsystems highlighted disagreements and shortages regarding the data related to the Al₄C₃ and Al₂MgC₂ carbide phases. On one hand, the standard enthalpy of formation and the decomposition temperature of Al₄C₃ are still debated in the literature. On the other hand, the thermodynamic properties of Al₂MgC₂ and the nature and temperature of its invariant decomposition had yet to be investigated.

Regarding the Al-C system, the standard enthalpy of formation of Al₄C₃ was determined by DFT calculations and its decomposition temperature was re-investigated by thermal analysis. Plus, the heat capacity of the binary carbide was confirmed by DSC and DFT calculations.

Regarding the Al-C-Mg system, the lack of data mentioned earlier is a consequence of practical difficulties, including high vapour pressure of Mg and high affinity of Mg with oxygen, as well as a rapid hydrolysis of Al₂MgC₂ in contact of moisture. To deal with this challenging system an experimental procedure based on the use of sealed Ta crucibles was developed. This procedure is promising as it allowed working with magnesium up to 2094 K (1821°C) and 41 bars of pressure. As a result, Al₂MgC₂ was synthesized and its crystal structure was confirmed for the first time on the basis of single-crystal X-ray diffraction data. The standard enthalpy of formation of the ternary carbide was investigated by DFT, and its heat capacity was determined by DFT and DSC. In addition, the ternary peritectic decomposition of Al₂MgC₂ was characterized by DTA.

Lastly, CALPHAD assessments of the Al-C and Al-C-Mg systems were conducted on the basis of the critically assessed literature data as well as of those freshly obtained. Self-consistent thermodynamic descriptions of Al₂MgC₂, (Al,Mg)C₃ and of the Al-C-Mg liquid phase were obtained. Those descriptions will fuel the thermodynamic databases and will enable the development of Mg-Al alloys and Mg-Al matrix carbon materials reinforced composites. This study provides a convincing argument supporting the fact that Al₂MgC₂ is responsible for the grain refinement of Mg-Al alloys by carbon inoculation.

Figure 1. Section of the Al-C-Mg system calculated at 1000K and 1 bar without taking into account the gas phase

References


Biographical Note

This study was conducted during the Ph.D. thesis of G. Deffrennes at LMI, Univ. Claude Bernard Lyon 1. Currently, the author is a postdoctoral researcher at SIMaP, Univ. Grenoble Alpes, where he works on the assessment of the CaO – K₂O – SiO₂ ternary system.
P20

Thermodynamic Assessment of CaO-MgO System

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Key words: CaO, MgO, ab initio, CALPHAD

CaO and MgO are extensively utilized in steelmaking processes for reducing the acidic nature of the slag. They are also used as furnace linings owing to their excellent refractory properties. Recently, dolomite (mixture of CaO and MgO) is being used as a catalyst for biodiesel synthesis. Hence, it is imperative to understand the phase equilibria and thermochemistry of the CaO-MgO system.

There is an ambiguity in the thermochemical information pertaining to this system. Enthalpies of formation for CaO and MgO reported by Berman et al. [1] significantly differ from the values reported by Gourishankar et al. [2]. The melting point of CaO reported in the literature are in the range of 3178 to 3222 K. Similarly, the melting point of MgO recommended by SGTE significantly differs from the value reported by Ronchi et al. [3]. To resolve these uncertainties, a critical analysis of the experimental data was performed in this work.

Since, the thermochemical information pertaining to the CaO-MgO system is rather limited, ab initio calculations were performed. Enthalpies of formation for CaO, MgO were computed using density function theory (DFT). Quasi harmonic approximation (QHA) was used to compute the finite temperature thermodynamic properties for the same. Enthalpy of mixing of CaO and MgO was obtained by randomizing the Ca and Mg atoms in the solid solution using special quasirandom structures (SQS). Finally, thermodynamic optimization was performed using the thermochemical and constitutional data from literature along with the ab initio data generated from the present work as input. The calculated phase boundaries shown in Figure. 1 are in good agreement with the experimental data.

![Figure 1. Calculated phase diagram of the CaO-MgO system](chart.png)

References


Biographical Note

I am a final year dual degree student (Bachelor’s + Master’s) at the Department of Metallurgical and Materials Engineering in Indian Institute of Technology Madras. My research interests include computational materials thermodynamics and density functional theory.
P21

Thermal Conductivity of the Mg-based Alloy: Experimental Measurement and CALPHAD Modeling

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Key words: Mg alloy1: Thermal conductivity2: Microstructure3: CALPHAD4

Magnesium alloys are used as important lightweight structural materials in fields of automobiles, aircraft and electronics, due to their extremely low density, high specific strength, excellent damping property, good electromagnetic shielding and environmental friendly. Thermophysical properties, including heat capacity, thermal diffusivity, and thermal conductivity, are essential input for the prediction of the temperature-dependent microstructure and thermo-mechanical properties. Thermal conductivity controls the temperature gradients occurring in materials, which play an important role in the microstructure and the performance of alloys. High thermal conductivity can allow rapid heat transfer, which enables efficient cooling and suppresses the formation of mechanical harmful hot-spot defects. Besides, high thermal conductivity ensures a uniform temperature distribution which reduces thermally induced stresses and thus improves fatigue properties. However, there are relatively few studies on the thermophysical properties of Mg–based alloys and the constituent binary systems, especially the thermal conductivity, which seriously restricts the simulation and prediction of such alloys.

In this study, microstructure and thermal conductivity of Mg-Al, Mg-Zn and series binary Mg-RE (RE=Y, Gd, La, Ce, Nd, Sm) alloys in both as-cast and annealed states were studied. Microstructure and phase identification of the alloys were investigated by using electron probe microanalysis and X-ray diffraction techniques and thermal conductivity was measured on a Netzsch LFA457 using laser flash method. Based on the obtained results from the measurements, the possible mechanism of thermal conductivity variation was analyzed. Considering the available experimental data from literature and the present work, thermal conductivity of the these systems including pure elements, stoichiometric and solid solution phases was evaluated using the CALPHAD method (CALculation of PHase Diagram) and a set of self-consistent parameters for the description of thermal conductivity was obtained. Calculations using the obtained parameters and the available experiment data show reasonable comparison.

Figure 1. Calculated thermal conductivities of (Mg) with the experimental data

References

Biographical Note
Shuhong Liu is currently an associated professor at Powder Metallurgy Institute, Central South University, P.R China. Her research interesting includes phase diagram, thermodynamics and thermo-physical properties of Al-based and Mg-based alloys and their application in alloys design.
**P22**

**Phase Field Modelling of Diffusion Induced Grain Boundary Migration in Binary Alloys**

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**Key words:** DIGM, Phase field method.

A phase field model is developed to study Diffusion Induced Grain boundary Migration (DIGM) in binary alloys. DIGM has been suggested to be an important part of the discontinuous precipitation reaction observed in many alloy systems.

The source of driving force for DIGM is in the model assumed to come from the elastic strain energy, originating from the misfit strain just in front of the advancing grain boundary. A parametric study for a hypothetical binary system is first considered, and the model is then applied to DIGM in binary Fe-Zn. The simulation results are discussed and compared to the experimental work by Hillert and Purdy [1].

A schematic diagram of DIGM is presented in figure 1. Two grains of the same phase ‘α’ is separated by a slant boundary. A higher activity of component A of the hypothetical system (with A and B components) is applied on the top (surface) of the domain. The grain boundary happens to move faster at the intersection of the boundary and the surface shown in figure 1(b), which is faster than the grain coarsening due to gradient in the phase field variable shown in figure 1(a).

![Schematic of DIGM](image)

**Figure 1. Schematic of DIGM, (a) without driving force and (b) with driving force**

**References**


**Biographical Note**

The first author is a PhD student at Material Science and Engineering Department of KTH, Stockholm under the supervision of Henrik Larsson and Joakim Odqvist. He is working on the Phase Field modeling of microstructural evolution in different alloys.
The Third Generation of CALPHAD Databases: A Re-assessment of the Al-C System

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Key words: Einstein temperature, Einstein model, Neumann-Kopp, Al-C, CALPHAD

When developing the third generation of CALPHAD databases, it is critical to apply the unary descriptions to higher-order systems, i.e. binary, ternary etc. Modeling the compounds and metastable end-members of solution phases within the framework of compound energy formalism is then of great importance.

Since the third generation of CALPHAD databases are valid down to 0 K, the conventional Neumann-Kopp rule should not be directly applied to describe metastable end-members; otherwise it violates the third law of thermodynamics, i.e. zero entropy at 0 K. One alternative is to use a modified expression as suggested by Hillert and Selleby [1]. However, this method gives an excess contribution to the heat capacity at 0 K and therefore, new solutions or models are needed in developing the third generation data.

The Al-C binary system has been chosen to be assessed due to its simple non-magnetic elements. In this system, Al₄C₃ is the only stable carbide while Al₄C₇(fcc) and Al₃C₃(bcc) are metastable end-members for the solution phases. The heat capacity of compound can be modeled using the Einstein model if there is enough experimental data. Whereas if the available experimental data is limited, the “hybrid” Neumann-Kopp/Einstein model is suggested to be used. In this model, the Einstein model is used to describe the harmonic vibrations while the Neumann-Kopp relation describes other vibrational contributions to the heat capacity. The “hybrid” Neumann-Kopp/Einstein model can also be applied for modeling the stable or metastable end-members.

However, the Einstein model cannot well describe heat capacities at extremely low temperatures. When the temperature approaches 0 K, the Einstein model shows a faster decrease in heat capacity compared to experiments. Thus, one could only well describe heat capacities at certain low temperatures using the Einstein model. There are several methods suggested in this work for estimating the Einstein temperature. One can use DFT calculations or estimate compounds’ Einstein temperatures based on mass-effect model [2], i.e. the Einstein temperature of a compound can be estimated by the stoichiometric coefficients and Einstein temperatures of the components.

A re-assessment of the Al-C system was performed taking into account both experimental thermodynamic and phase diagram information. The descriptions of C [3] and Al [4] used in this work have been developed for the third generation of CALPHAD. Overall, a good fit to the experimental data was obtained. New methods have been tested to extrapolate liquids and solids of those binaries to the temperature ranges where they are not stable. This work is ongoing to examine and finalize the extrapolation methods.

Figure 1. Graphical abstract

Acknowledgement

The present work has been performed within the Hero-m²i Center. The authors gratefully acknowledge the participants of the Stockholm workshops sponsored by SGTE for valuable discussions.

References


Biographical Note

Zhangting He is a Ph.D student at Department of Materials Science and Engineering at KTH Royal Institute of Technology, where she works on Generic CALPHAD project within Hero-m²i Center to develop the third generation of CALPHAD databases.
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The Study of the Liquidus Projection of the Cu-Pd-Sn Ternary System

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Key words: liquidus projection, phase equilibria, Cu-Pd-Sn system, SEM-EPMA

The present research is devoted to the investigation of the phase equilibrium diagram of the Cu-Pd-Sn ternary system with the use of experimental and calculation methods.

Palladium, copper and tin are the main components of many dental alloys and solders for manufacturing of orthopedic constructions. When selecting compositions of such alloys and choosing conditions of their heat treatment, it is extremely necessary to have information about phase equilibria and components interactions at high temperatures. Besides of practical importance of the information about Cu-Pd-Sn alloys, obtained data could be important for developing of thermodynamic models of phases, existed in Cu-Pd-Sn ternary system.

Literature analysis showed reliable phase diagrams of Cu-Pd, Cu-Sn and Pd-Sn boundary binary systems, but data on Cu-Pd-Sn ternary system are scarce and describe only solid state equilibria [1-3]. The lack of information about high-temperature phase relations became the reason for providing the current research.

Preliminary calculation of liquidus surface projection of discussed system using ThermoCalc software predicted 14 invariant reactions, where liquid phase takes part (2 reactions of I type, 9 reactions of II type and 3 reactions of III type). The calculated liquidus projection is shown in Figure 1. The temperatures and equilibrium phases of these reactions should be defined experimentally.

About 80 samples within the ternary area were synthesized and examined using experimental methods such as differential thermal analysis, scanning electron microscopy, electron probe microanalysis and X-Ray diffraction analysis. The temperatures of nonvariant reactions have been defined. Also the positions of nonvariant points have been indicated accurately with the use of SEM-EPMA method.

Taking into account the topology of polythermal sections and well-known data about binary systems the liquidus surface projection of the Cu-Pd-Sn ternary system was constructed.

References


Biographical Note

Georgiy Khartsyzov is a Bachelor student in Department of Metallurgical and Casting Technologies at Peter the Great St. Petersburg Polytechnical University. His research interests focus on experimental research of phase equilibria in multicomponent metallic systems.
The Mo–Nb–Zr and Mo–Ti–Zr Systems: Phase Diagram, Thermodynamic Description and Solidified Microstructure

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Key words: Mo–Nb–Zr; Mo–Ti–Zr Phase diagram; Thermodynamic calculation

Zirconium-based alloys have been extensively used as core materials for nuclear reactors owing to their small thermal neutron absorption cross section, high corrosion resistance and sufficient mechanical performance [1].

To facilitate the research and development of relevant materials, knowledge of phase equilibria in the Mo–Nb–Zr and Mo–Ti–Zr systems is necessary. In the present work, the phase diagrams of the Mo–Nb–Zr and Mo–Ti–Zr systems were determined by means of X-ray diffraction (XRD), optical microscopy (OM) and electron probe microanalysis (EPMA). Based on a critical evaluation of the experimental data obtained from both the present work and literature, the Mo–Nb–Zr and Mo–Ti–Zr ternary systems were assessed by means of the CALPHAD (CALculation of PHAse Diagram) method. A set of self-consistent parameters was obtained to describe the Gibbs energy of individual phases. The Scheil simulation [2] for representative as-cast alloys was performed by using the present thermodynamic modeling. According to the calculated Scheil solidification curves of several key alloys, the solidified microstructure for the alloys was analysed. Comprehensive comparisons between the calculated and measured phase diagram information show that the reliable experimental data can be well accounted for by the present description.

Figure 1. The Mo–Nb–Zr system (a) Calculated liquidus projection in comparison with the present experimental data; (b) the presently performed Scheil-simulation for the representative samples

Figure 2. The experimental isothermal sections of the Mo–Ti–Zr system at (a) 900 °C and (b) 1100 °C

Acknowledgment:

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References:


Biographical Note

Huaqing Zhang, a PH.D student in Central South University, Changsha, Hunan province, PR China. Her supervisor is Professor Yong Du. She is interested in phase diagram determination, thermodynamic modeling on the grain boundary.
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The Mo-Ni-W: Three-dimensional Phase Diagram and Solidified Microstructure

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Key words: Mo-Ni-W, phase diagram, liquidus projection, thermodynamics modeling

Ti (C, N)-based cermets are recognised as promising cutting tool materials, which may replace the conventional WC-Co hardmetals, owing to their excellent wear resistance, high-temperature hardness, low friction coefficient to metals and superior thermal deformation resistance [1]. As an important sub-system of cermets, a good knowledge about phase diagrams and thermodynamic properties in the Mo-Ni-W system is essential to conduct new cermets design.

In this work, the isothermal section of the Mo-Ni-W ternary system at 900°C and liquid projections were experimentally established using X-ray diffraction and electron probe microanalysis. Based on the experimental phase diagram data from the present work and the literature, the Mo-Ni-W system was assessed by means of the CALPHAD method. The ternary liquid, fcc-(Ni), bcc-(Mo) and bcc-(W) phases were described with a regular solution model. The two-sublattice model was used to describe the intermediate phases of MoNi₃, MoNi, (Mo,W)Ni₅, WNi, and W₂Ni. The present modeling covers the entire composition and temperature ranges of the Mo-Ni-W system, and a set of self-consistent thermodynamic parameters were finally obtained. Comprehensive comparisons between the calculated and measured phase diagram data show that all experimental information is satisfactorily accounted for by the present thermodynamic description. The liquidus projection and the Scheil simulation for representative as-cast alloys were calculated by the presently obtained parameters.

Figure 1. The presently performed Scheil-simulation for the representative samples

Figure 2. Calculated isothermal sections of the Ni-Mo-W ternary system at 900°C together with the experimental data in the present work.

References

Biographical Note
Meifang Tang, Graduate student from Central South University, China
Supervisor: Prof. Dr Zikui Liu
Research field: CALPHAD approach; Phase diagram thermodynamics.
The High-throughput Way from 0K to High Temperatures: The aiMP (ab initio Materials Project) CALPHAD Database

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Key words: Ab-initio Predictions, Database Development, High-Throughput Calculations, Neumann-Kopp

Within the Materials Genome Initiative (MGI), several open databases containing ab initio calculated materials properties have been developed. Among them, the Materials Project (materialsproject.org) [1,2] is one of the most prominent one and today contains data on 133,691 compounds. However, there are several restrictions on using the data:

- Only enthalpy of formation at 0K is reported.
- There are known discrepancies in enthalpy of formation from ab initio calculations at 0K and CALPHAD assessed at 298K [3].
- No information on heat capacity available.
- No information on entropy at 298K $S^{298K}$ available.
- No information on solid or liquid solutions available.

In this talk, the approaches developed recently by GTT-Technologies to overcome these restrictions are introduced:

- The enthalpy of formation is semi-empirically extrapolated from 0K to 298K using element-specific corrections according to the approach by Kirklin et al. [3].
- The heat capacity is approximated using a modified Neumann-Kopp approach in the temperature range of 298K to 3000K.
- $S^{298K}$ is either approximated from phonon calculations reported by [2] or using another modified Neumann-Kopp approach.
- A selection of functional groups (e.g. NO$_3$, OH) are corrected separately according to the approach outlined in [4], and their contributions to heat capacity and $S^{298K}$ are treated separately from the elements.
- At the moment, solid solutions are generated as ideal solutions and for the description of the liquid phase the SGTE (Scientific Group Thermodata Europe) Solutions database is recommended.

These approaches have been used to generate the aiMP (ab initio Materials Project) CALPHAD database available in FactSage. The current version 2.2.1 contains data for 83,983 solid phases and is designed to be used for three major applications:

- Benchmarking the accuracy of ab initio calculations extrapolated to relevant temperatures.
- Using as starting point for a CALPHAD assessment.
- Combining standard FactSage databases with AIMP to estimate thermochemical properties in parts of chemical compound space where otherwise no data is available to describe the behavior of minor elements.

Finally, the accuracy and application are exemplified by discussing a few phase diagrams and future work is discussed.

Figure 1. Graphical abstract

References

Biographical Note
Moritz to Baben is Managing Director at GTT-Technologies since October 2017. He did his PhD on quantum-mechanically guided materials design of hard coatings at Materials Chemistry, RWTH Aachen University. After Post-Doc at RWTH Aachen, Uppsala University and Max Planck Institute for Iron Research Düsseldorf, he joined GTT-Technologies in 2016.
The Experimental and Theoretical Study of Bi-X (X = Sn, Ni) Nanoalloys
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Key words: Ag-Ni system, nanoalloy preparation, CALPHAD

The Bi-X (X = Sn, Ni) nanoalloys of various compositions were prepared by means of demanding synthesis, and basic properties from the point of view of the influence of particle radius on the melting temperature depression were studied.

The Bi-X nanoparticles (NPs) were synthesized by reduction of metal precursors in various ratios by NaBH₄. NPs were isolated by centrifugation and washed with methanol to remove impurities. One part of NPs was dispersed in methanol for transmission electron microscopy (TEM) analysis and the rest of NPs was left to dry under inert atmosphere at 60 °C and characterized by differential scanning calorimetry (DSC), X-ray powder diffraction (PXRD), and inductively coupled plasma optical emission spectroscopy (ICP-OES).

Melting properties obtained from DSC analysis were compared with theoretical calculations. Shape and composition of particles after annealing were characterized by scanning electron microscopy with energy X-ray dispersive spectroscopy and by ICP-OES again.

The influence of the particle size on the melting temperature and temperature of phase transformations will be modelled using the CALPHAD method extended towards the application for nanosized systems [1-3] in combination with ab initio calculations of the surface stress [4].

The results of the theoretical prediction will be compared with the information obtained from the DSC measurements.

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References

Figure 1. The structure and thermal properties of the Bi-Sn nanoalloy (35mol% of Sn)

Biographical Note
The Effect of Atomic Size Ratio on the Formation Enthalpy and Phase Stability of Laves Phase in Refractory-metal Based Phase Diagram

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Key words: refractory elements, phase stability, atomic size, first-principles calculation

For designing refractory-metal based alloys such as Nb-Cr alloys, the control of the stability of AB₂-type Laves phases appearing in the alloys is important. It has been pointed out that the atomic size ratio of constituent elements, Rₐ/Rₐ, is quite important to understand the stability of Laves phase [1]. Through the investigation of ternary phase diagrams including Al and transition elements with refractory elements, such as Al-Ni-Nb system, authors have found that the average size of elements forming B2 phase is important to explain the stability of Laves phases [2].

The stability of Laves phase has been investigated using ab initio calculations [1]. We have also performed ab initio calculations based on the density functional theory and obtained formation energies ∆H for various C15-type structures composed of refractory elements, such as NbCr₂. We have adopted the ultrasoft pseudo potential and the PBE-GGA potential for the calculations. Lattice constants have been optimized and the electronic energies have been obtained for each C15-phase. The package produced by the abinit project [3] was employed for the numerical computations. A part of result is shown in Fig.1. It is quite interesting that the formation enthalpy ∆H of various C15 Laves seemingly increases with decreasing Rₐ/Rₐ even in unstable range.

It is quite interesting that the formation enthalpy ∆H of various C15 Laves seemingly increases with decreasing Rₐ/Rₐ even in the unstable range with Rₐ/Rₐ lower than 1.06. It is also noteworthy that the stability of refractory-metal based Laves phases are quite low, while it appears in many refractory-metal based binary phase diagrams as compounds which is stable up to its melting point. By a comparison between the atomic size ratio of constituent elements, Rₐ/Rₐ, and types of refractory-metal based binary phase diagrams, it is found that BCC-BCC two-phase region appears in the BCC phase continuous solid solution with increasing Rₐ/Rₐ, and with higher Rₐ/Rₐ Laves phase appears. Such a trend is also confirmed in ternary phase diagrams such as Cr-Mo-Nb system [4]. By using a simple pair-interaction model and CALPHAD method we evaluate the composition dependence of the enthalpy of BCC solid solutions with different Rₐ/Rₐ to understand the effect of Rₐ/Rₐ on the phase stability of Laves phases with relatively small formation enthalpy in binary phase diagram.

This work was supported by the Advanced Low Carbon Technology R&D (ALCA) program of the Japan Science and Technology Agency (JST).

Fig. 1 Formation energy of C15 phase.

References

Biographical Note
Seiji Miura holds a PhD in Engineering by Tokyo Institute of Technology and is a Professor of Div. Mat. Sci. Eng., Faculty of Engineering, Hokkaido University.
P30

Temperature-dependent Hardness Model of Materials

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Key words: hot hardness, temperature, diffusion, slip system

In the present work, a new temperature dependent hardness model is proposed based on the thermally activated dislocation width in combination with our previous Vickers’ hardness model. The thermally activated dislocation width, a basic building block for the temperature dependent Peierls-Nabarro flow stress in the hardness model, captures dislocation-diffusion mechanisms during the materials’ deformation. In the proposed model, the material hardness is determined by (a) diffusion mechanisms, (b) slip systems, (c) diffusing species, and (d) phase transformations. The model has been calibrated for and agrees well with experimental hot hardness results of 16 materials, which were available from the public domain, including metals and ceramics. The new hardness model can be integrated and tabulated with diffusivity databases.

Biographical Note
Hongyeun Kim is a graduate student at the Materials Science and Engineering, Penn State University since 2014.08. Dr. Zi-Kui Liu is his advisor.
P31

Synthesis and Constitution of a Database for the Ta-W-C System

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Key words: Ta-W-C, thermodynamic database, carburizing, tantalum alloy

Our work deals with carburizing of some tantalum alloys. For a better prediction of the different phases that may appear after this kind of treatment, a thermodynamic database on the ternary system Ta-W-C is necessary.

In the early 2000’s the work of Frisk et al. [1] led to the development of a database for cemented carbides (Co-Nb-Ta-Ti-W-C-N) in order to improve metal cutting. This work presented an assessment of Ta-W-C system mainly based on experimental information from Rudy [2]. More recently, Cacciamani et al. [3], published results about the thermodynamic modeling of a six component (C-Co-Cr-Ni-Ta-W) system for Cobalt based alloys.

However, all descriptions of these multi-component systems require a perfect knowledge of each binary system. This is why the Ta-C, W-C and Ta-W systems have been fully re-exploited from the published data. The approach suggested by Gabriele Cacciamani et al. [3] with MC and M\textsubscript{2}C is used.

In this work, the thermodynamic models used are presented for each phase, the three binary systems and the corresponding ternary system obtained by combining them are described. They are also confronted with experimental data both from phase diagrams as well as energetic information. From these confrontations, the descriptions chosen for the Ta-W-C system are validated and can be used for calculations on our alloy of interest (Ta97.5%-W2.5%). This alloy is presented and the calculations made from the thermodynamic database are related to the experimental results obtained after sample carburizing (Figure 1). Thus, the use of the database made it possible to understand the formation and morphology of carbides.

References


Biographical Note

Laurent Carette, graduated in 2016 from ECAM Lyon School of engineering is actually working for CEA on the doctoral project dedicated to the study of low pressure carburizing of tantalum alloy. This project is in collaboration with ECAM Lyon, ICB and LaBoMaP.
P32

Symmetric Tilt Boundary Energy of Cu

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Key words: First principles calculation, dislocation theory

1 Introduction

Small angle boundary energy is easily predicted by Read–Shockley model[1], which is a typical example of the reliability of the dislocation theory. The angle θ dependency of the small angle boundary energy E is given by,

\[ E = \frac{1}{2} \tau_0 b \theta (A - \log \theta) \]

where \( b \) is the size of Burger’s vector, and \( \tau_0 \) is determined by the mechanical properties of the target material, and \( A \) is related to the core energy of dislocation and is expected constant.

The bottom panel of Fig.1 shows the experimental[2], and calculated θ dependency of symmetric tilt grain boundary energy of Cu <100> direction. The calculated curve using EAM[3] shows the different angles of the tangents at both ends of \( \theta = 0^\circ \) and \( \sim 90^\circ \) due to the size difference of Burger’s vectors, which are illustrated inside the plot. Those are so called geometrically necessary dislocations, whose sizes are \( a \) and \( a/\sqrt{2} \), respectively, where \( a \) is the lattice constant. The experimental curve, however, shows an identical angle. Figures on the top side panel are E/\( \theta \)-log \( \theta \) plots, which are derived from the previous equation

\[ E/\theta=1/2 \tau_0 b(A-\log \theta) \],

which tells that the ratio E/\( \theta \) is linear to log \( \theta \). When we plot it, this linear dependency of the curves is observed even in the middle range of the angle as shown in Fig.1. The EAM calculated result shows that the slope of the curve at near 90° is obviously smaller than that at near 0°, as expected from Burger’s vectors of Read-Shockley model. On the other hand, the experimental results show almost identical slope, which indicates obvious inconsistency against the calculated results or theoretical prediction.

For revealing this discrepancy, we are performing the first principles calculation.

2 Method

We used VASP(Vienna ab initio simulation package) for the first principles calculation[4]. The boundary models are constructed for \( \Sigma 3, 5, \) and 7 near 0° and 90° for Cu (100) symmetric tilt boundary. The ionic relaxations are performed by the routine provided in VASP under the hand-controlled outer shapes.

The pseudopotential for Cu is PAW PBE with the energy cutoff of 273.214 eV, which is the default value of POTCAR. The energy are obtained by tetrahedron method with Blöchl corrections. The energy convergences are checked by mainly k-point meshes and system sizes.

3 Results

The preliminary results are also plotted in Fig.1. The calculated time for Cu is much longer than Al, the calculated points are few. The models calculated angles are still high, however, shows similar values with the EAM results. We will report the E/\( \theta \)-log \( \theta \) plots with the lower angle results.

![Figure 1. Experimental and calculated θ dependency of symmetric tilt grain boundary energy of Cu. See text for details.](image)

References


Biographical Note

Ms. Yamada is a graduate student of Department of Quantum and Radiation Engineering, Osaka Prefecture University. She is now working on the experimental researches of point defects in glassy materials using positron annihilation method.

Prof. Nishitani is still struggling on VASP calculations.
Survey on Thermodynamic Models for Mg-based Alloys for the Development of CALPHAD-type Database for Thermoelectric Materials

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Key words: CALPHAD, thermoelectric materials, point defects, Mg-based alloys

Thermoelectric generators can be used to convert waste heat into electricity, thus reducing CO₂ emission and fossil fuel consumption. Their fabrication requires the development and optimization of thermoelectric materials as well as contacting electrodes. Therefore, to find the appropriate synthesis conditions and suitable contacts, measurements of thermoelectric properties, phase identification and kinetic experiments, are carried out in our group to understand fundamental material properties and, in the end, maximize the efficiency and the life time of a thermoelectric generator. We combine efforts on experiments and CALPHAD-modeling [1] to bring support in understanding observations on phase stability, as phase diagram knowledge provides a starting point and a roadmap for alloy and processing design.

Progress in the development of thermoelectric materials is usually obtained by an increased chemical-structural complexity, i.e. amount of alloying and number of dopant elements; therefore there is great interest to develop consistent thermodynamic descriptions for chemically complex systems accounting for small degrees of non-stoichiometry. Actual CALPHAD modeling has proved to be a powerful and versatile method dealing with consistent thermodynamic models which acknowledge crystallographic features of individual phases as well as point defects contribution to the Gibbs energy. In view of technological applications of semiconductors one of the most important thermodynamic properties is the electronic carrier concentration of a phase with semiconducting properties. Off-stoichiometry in a small degree can lead to variations by orders of magnitude in the carrier concentration, and small changes in stoichiometry are related to the chemical potentials of the components in a contacting phase [2]. However typical “defect-centered” approaches, stressing on small deviations from stoichiometry, need to be connected with a CALPHAD approach to adequately describe the Gibbs energy of phases over wide composition and temperature ranges.

We present in this work an evaluation of different thermodynamic models to account for several aspects of Mg-based alloys, such as: modeling of the gas phase for highly volatile constituents like Mg, valuable for the thermodynamic understanding of partial pressure effect on phase stability, modeling the strong chemical interaction in liquid solutions using associate and quasi-chemical models, and intrinsic defect modeling in the compound energy formalism combining own Hall effect measurements and calculated defect formation energies available in literature. We aim to obtain a thermodynamic description consistent with all available physical understanding of two systems, namely Mg-Ag-Sb for which, to the best of our knowledge, no CALPHAD assessment was done before, and Mg-Si-Sn featuring solid solutions of Mg₃Si-Mg₂Sn undergoing dephasing due to the presence of a miscibility gap. The starting point for the latter is the thermodynamic description retrieving parameters from the literature [3] successfully reproducing the published results. Figure 1 shows the calculated isotherm at 600 °C using Thermocalc software and the TDB file written for this work. The stable phase configuration for Mg₃Si-Mg₂Sn solid solutions is shown for one processing temperature. Controversial experimental and calculated information exist regarding this isopleth, in particular, concerning the limits of the miscibility gap. By optimizing interaction parameters using own experimental measurements we intend to bring conflicting data in agreement.

Figure 1. Calculated isotherm at 600 °C for Mg-Si-Sn.

References


Biographical Note

Silvana Tumminello is a postdoctoral researcher at the German Aerospace Center, Cologne-Germany in the group of Thermoelectric Materials and Systems, collaborating with the group of Computational Thermodynamics at ICAMS-RUB, Bochum-Germany. Her research interests are in application-oriented research for materials development, combining experimental techniques and modeling/simulation methods for an integrated approach.
P34

Study on the Phase Diagrams of Bi-Te Binary and Bi-Te-RE (Yb, La, Ce, Nd, Sm, Tb, Er) Ternary Systems

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Key words: Bi-Te, Bi-Te-RE, phase diagram, CALPHAD

Bi-Te based alloy is one of the most mature thermoelectric materials at present. Because of its special electronic structure, rare earth elements (RE) can be doped to effectively adjust the energy band structure of thermoelectric materials and reduce the thermal conductivity of the crystal lattice thus improve the thermoelectric properties. The solid solubility of rare earth elements in Bi-Te alloys, the formation of ternary compounds, phase stability, phase transition temperature and other phase diagram information can guide the design of thermoelectric materials via doping rare-earth elements. In this work, phase diagram and phase structures of Bi-Te system is carefully checked. The isothermal sections of Bi-Te-RE ternary systems were partly established by equilibrium alloy method. A ternary compound BiTeRE was found. It is found that the solid solubility of rare earth elements in Bi-Te matrix increases with the decrease of the atomic radius of rare earth elements.

Figure 1. Experimentally determined Bi-Te-Yb isothermal section at 573K
Study of Phase Equilibria in the Fe-As-S Ternary System

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Key words: Fe-As-S system, phase equilibria, SEM-EPMA, polythermal sections

Arse nict, sulphur and iron are the accompanying elements of many polymetallic ores, treated for exploration of non-ferrous and precious metals. It is very important to remove arsenic from metallurgical semiproducts and then neutralize it in a form of low toxic compounds, like arsenic sulphides or arsenides (FeAs, Fe₂As, Fe₃As₅). Therefore, information about phase equilibria in the Fe-As-S ternary system, especially at high temperature range, is relevant.

The Fe-As-S system is very difficult for experimental study due to high toxicity and high partial pressures of arsenic and its compounds. These difficulties determine serious lack of available information regarding phase diagram of the discussed system, as well as absence of liquidus surface projection scheme. Data about phase equilibria are published only at several original issues [1-2], but they all devoted to low-temperature equilibria. Following literature reviews of the discussed system [3, 4] refer to mentioned above original works. Consequently, the necessity of detailed experimental investigation of phase equilibria at Fe-As-S system is evident.

With the applying of special experimental technique with using of the high pressure furnace, developed by authors or the project, arsenic sulphides and arsenides were synthesized. The scheme of constructed experimental unit for synthesis of arsenic-contained compounds is given in Figure 1. The furnace comprises high-pressure internal camera that can reach up to 70 atm pressure and external heater element with maximum heating temperature up to 950°C. Initial sulphides and arsenides as well as high purity iron and arsenic were used for synthesis of ternary compositions. Obtained samples were investigated with the use of spectrum of experimental physico-chemical methods, namely, differential thermal analysis (DTA), scanning electron microscopy (SEM), energy-dispersive microanalysis (EPMA) and X-ray diffraction analysis (XRD). The study of phase equilibria in the Fe-As-S ternary system was started from construction of Fe₅S₇, molten iron Fe₃S₇, FeAs and FeS-Fe₃As quasibinary sections. Temperatures of phase transitions and nonvariant reactions also compositions of coexisting phases have been defined. Obtained information will be used for construction the liquidus surface projection of the Fe-As-S ternary system.

Figure 1. High-pressure furnace

1 – External reactor; 2 – Furnace with heating elements; 3 – Sealed ampoule with sample; 4 – Heat insulator; 5 – Furnace thermocouple; 6 – Sample thermocouple; 6a – Sample temperature controller; 7 – Pressure gauge; 8 – Precision valve; 9 – High purity argon; 10 – Power-supply circuit; 11 – Furnace temperature controller.

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References

Biographical Note
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Fields of interest: Copper and nickel metallurgy, phase equilibria, thermal Analysis, SEM/EPMA, thermal analysis.
P36

Study of Multicomponent Alloys Based on d-elements of the Periodic System

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Key words: high-entropy alloys, solid solution, segregation, entropy of mixing

The subject of obtaining new types of materials, characterized by outstanding properties, is of increasing interest to science. In the last decade one of the types of such materials, that attracts scientists, is high-entropy alloys (HEAs).

One of the main reasons why this type of alloys is of interest in material science is that such systems are characterized by the best combination of qualities and properties of classic conventional alloys. An example of correlation of the alloy’s properties (in particular elastic strength and hardness) is presented at the fig 1. [1]

For today, on the basis of the relevant literature on this topic, several main rules can be distinguished, which have to be followed for high-entropy alloys: these are multicomponent systems based on 5 or more elements, with content of each other from 5 to 35 at.% [2], alloys must also have high entropy of mixing (≥13.381 J/mol =1.61R) [3], which is quite obvious from their name. Additionally, there are some empirical parameters proposed in accordance with the Hume-Rothery rules, which alloys scientists to predict the single-phase solid solution structure formation in alloys (and, certainly, HEA) [3]. One of the main ones are: ΔSmix, ΔHmix, δ, Ω, Δγ. Our scientific team with the applying of physico-chemical approach has proposed one additional factor among HEAs criteria.

Scientific research is divided into two parts. First part of the research is devoted to the study of the structure and properties of HEAs based on Fe-Ni-Co-Cu-Cr system through a series of experiments. After obtaining required data the temperature and compositional ranges of solid solution are defined, types of crystal structures are determined and also important conclusions are made regarding appearance of second phase in the number of alloys.

On the second step of carrying out the present work we’ve come to suggestion about one more factor, which, we suppose, doesn’t less important than exciting ones. This factor is expressed in the occurrence of a severe exothermic effect in the process of synthesis of primary alloys from the initial mixture of powders of pure metals in their elementary form. Within the framework of this study for analyzing 7 multicomponent systems were chosen: the first is Ag-Cr-Mn-Ti-Co-Au-Cu-Fe-Ni-Rh-Pt-Pd, and the next six are formed by gradual removal of one of the constituent components from the system (it is respectively Ag, Cr, Mn, Ti, Co, Au). DTA, SEM-EPMA and measurements of microhardness by Vickers method were used as experimental methods of research.

It was found that for a number of compositions (where the number of components was more than eight) a high exothermic effect could be observed from the information connected with the initial heating of the powder mixture of pure metals. On the contrary, during the secondary heating of an already formed sample, the indicated exothermic effect is not observed. Moreover, microhardness measurements detected abrupt change of discussed property, proving formation of HEAs.

![Figure 1. Correlation between HV -hardness and elastic strength for composites, ceramics, glasses, metallic and high entropy alloys](image)

References


Biographical Note

Vasileva Anna: Master degree student at the St. Petersburg Mining University. Areas of interest: phase equilibria, HEAs, metallurgy of non-ferrous metals.
Site Preference and Occupation of H in Transition Metals
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Key words: Metal-H system, Hydrogen dissolution, Sublattice model

In the CALPHAD type thermodynamic optimization, the proper description of sub-lattice occupancy of atoms or molecules in a given crystal structure is one of the key components for the successful reproduction of its thermodynamic properties and phase diagram. Therefore, the site occupancy data from experiments and first-principle calculations are widely used in the CALPHAD optimization. While doing the optimization of Metal (M) – Hydrogen (H) system, we have found inconsistent descriptions of solid fcc, bcc and hcp M-H solutions in available literature. Therefore, we have studied the simple but proper method to evaluate the site occupancy of hydrogen atoms in metals and use this concept we could well reproduce the M-H systems with less number of model parameters.

Site preference between octahedral site (O-site) and tetrahedral site (T-site) of interstitial elements (C, N, O, H, etc.) in host metal can be determined by applying “ball-in-hole” concept. O-sites can provide bigger space than T-sites for interstitial atoms. Therefore, relatively large sized interstitial elements such as C, N and O are dominantly located in O-sites. However, hydrogen can be located at T-site due to its small atomic size. Based on the critical evaluation of the site preferences of hydrogens in metal, lattice parameters and atomic radii of metals, we concluded that the size of T-site should be bigger than 0.038 nm for H occupation. Although the crystallographic site ratio between substitutional sites and T-sites is 1:2, 1:6, 1:2 for HCP, BCC and FCC, respectively, the effective site ratios of the solid solution should be 1:2, 1:1.5, 1:2, respectively because of repulsion between hydrogen atoms in T sites. That is, the already existing hydrogen in a T-site hinders the occupation of a new hydrogen atom to the neighboring T-site, which can reduce possible T sites for hydrogen occupation.

Based on this structural information for site occupancy of hydrogen in T sites, the HCP, BCC and FCC solid solutions of M-H system can be better described by using a two-sublattice CEF model. It is found that the number of model parameters in particular temperature-dependent terms can be reduced by using proper sublattice site ratio selection. The thermodynamic optimization results of the Zr-H system will be presented as the example.

Figure 1 Zr-H binary phase diagram

Figure 2 Zr-H system PCT-isotherms

Reference

Biographical Note
Taehyoung Kim and Minkyu Paek is a graduate student and Post Doctoral Fellow in Seoul National University (SNU). In-Ho Jung is an associate professor at SNU.
Relative Stability of Stacking Faults in Fe-Nb Alloys in Comparison with the Convex Hull for Bulk Phases

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Keywords: stability, defects, convex hull, ab initio

Properties of materials are to a wide extent determined by the presence of defects. The stability and concentration of these defects is closely related to their atomic structure. Using HR-TEM for samples made of phase-pure Nb-rich NbFe₂ Laves phase (35 at.% Nb), we observed different types of planar defects [1]. This is a surprising finding, since the Fe-Nb binary bulk phase diagram for this composition predicts precipitation of µ Fe₂Nb₆ phase upon cooling from elevated temperatures.

Employing density functional theory we have therefore studied the relative stability of the experimentally observed planar defects against a decomposition into Laves Fe₂Nb and µ Fe₂Nb₆ phases. Based on these results we introduce a new framework that is based on the concept of a convex hull [2]. One of the challenges we had to address in this context is the dependence of the formation energy of defect-containing structures on the supercell size used in the ab initio calculations. The resulting diagram reveals that Nb-rich crystal structures next to basal and pyramidal stacking faults can become energetically more favorable than the nucleation of an epitaxially constrained µ phase. Excess Nb, therefore, results into an enhanced formation of 2D stacking faults rather than forming 3D Nb-rich precipitates of µ phase. The concepts suggested here, should be applicable to the energetic assessment of defect phases in many intermetallic systems.

References

Biographical Note
Ali Zendegani obtained his Master degree in Materials Science and Simulation from the Interdisciplinary Centre for Advanced Materials Simulation (ICAMS) at Ruhr-University Bochum. He is now a PhD student at Max-Planck-Institut für Eisenforschung GmbH. He investigates the energetics of Laves phases in Fe-Nb alloys taking into account the vibronic and magnetic contributions by performing ab initio calculations.
Automated CALPHAD Modeling and Uncertainty Quantification of a Ternary System Using ESPEI

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Key words: machine learning, high-throughput, software tools, uncertainty quantification

References


Biographical Note

Brandon Bocklund is a doctoral candidate at the Pennsylvania State University. His research is focused on connecting experimental data and first-principles calculations based on density functional theory to high-throughput, machine learning-assisted CALPHAD modeling techniques for the development and maintenance of thermodynamic databases.
P40

Reassessment of Ti-Cr-C

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Key words: Ti-Cr-C, TiC, assessment, titanium, chromium, carbon

The thermodynamic description of the Ti-Cr-C ternary system has been reassessed. The previous description for the Ti-Cr-C system was assessed by Schuster et al. [1]. Their thermodynamic description contains three ternary interaction parameters, \( \delta_{L_{C,C,Ti}} \) and \( \delta_{L_{C,C,Ti}} \), for the liquid phase and \( \delta_{MC,Ti,C} \) for the fcc phase.

With these three parameters their description is able to reproduce the experimentally determined solidification sequence found in literature rather well, both regarding composition and temperature. The only discrepancy is the temperature for the invariant reaction \( L \leftrightarrow TiC + Cr_{2}C_{2} + Cr_{2}C_{3} \) which is about 63 K too high compared to their own experiments. Their description also reproduces the solubility range for the fcc phase (MC, where \( M=Ti,Cr \)), which was experimentally determined by Booker et al. [2] and Kerans et al. [3].

However, recent experiments by Haglöf et al. [4] show that the solubility of Cr in MC was overestimated by Booker et al. [2] at 1773 K and that the solubility is even more overestimated by the thermodynamic description by Schuster et al. [1] at 1673 K (see Fig. 1). The experiments by Haglöf et al. [4], which were performed in the equilibria MC-MC-MC and MC-MC-MC-graphite, also show that there is a solubility of Ti both in \( M_{1}C_{2} \) and in \( M_{2}C_{3} \) (\( M=Ti,Cr \)). These Ti solubilities were not accounted for in the thermodynamic description by Schuster et al. [1] (see Fig. 1).

The reassessment of the Ti-Cr-C system in this work has been made in order to enable the thermodynamic description to:

1. Reproduce the solubility of Cr in MC, as determined by Haglöf et al. [4].
2. Include the solubility of Ti both in \( M_{1}C_{2} \) and in \( M_{2}C_{3} \), as determined by Haglöf et al. [4].
3. Better reproduce the invariant reaction temperature for \( L \leftrightarrow TiC + Cr_{2}C_{2} + Cr_{2}C_{3} \).

Figure 1. Ti-Cr-C isothermal section at 1673 K calculated using the Thermo-Calc Software [5] together with the thermodynamic description by Schuster et al. [1]. Markers show phase compositions determined by Haglöf et al. [4].

References


Biographical Note

Fredrik Haglöf has worked 12 years with process development (hot rolling of steel and sintering of cemented carbides). Since three years, he is an industrial Ph.D. student, for Sandvik Coromant R&D, at the department of Materials Science and Engineering, KTH. Topic: Ti-Cr-C-N

Main supervisor: Prof. Malin Selleby.
Predicative Strategy of Matching the Band Structures with Reduction Potentials for the Purpose of More Efficient Catalyst Design and Light-assisted Degradation

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Currently it is crucially important to predict the efficiency of water splitting and water pollutants (dyes) degradation under visible light irradiation before designing and synthesizing metal oxides with desired properties [1]. Such predictive theory would help to 1) minimize the development costs and 2) reduce the timespan between idea and final product. Thus, we present a novel approach based on matching the band structures with the reduction potentials of metal oxides (photocatalysts), reactive oxygen species (ROS) and organic dyes. This strategy takes into account the universal ability of chemical species to acquire electrons and, consequently, be reduced. All the redox potentials are mapped based on conduction band (CB) and valence band (VB) values of metal oxides and highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) values of dyes. Furthermore, this concept helps to explain the mechanism of either photocatalytic degradation or water splitting, emphasizing on the role of light-generated carriers (electrons, holes and ROS) and their interaction with HOMO/LUMO of the dye. The strategy was tested and verified on two independent photocatalysts towards degradation of water pollutants under visible light exposure. For example, by using the matching approach, we were able to predict and further confirm during our hands-on experiments the ability of BiNbO$_4$ and Ag-doped BiNbO$_4$ materials to degrade cationic methylene blue (MB), rhodamine B (RhB) and anionic acid red 1 (AR1) dyes [2]. The strategy was successfully extended to Bi$_2$O$_3$ and Pd-doped Bi$_2$O$_3$ materials towards degradation of MB, AR and brilliant green (BG) dyes [3]. By using this approach, a possible dye degradation mechanism was proposed. This method can be further extended into antimicrobial field to predict the disinfection efficiency of metal oxides against bacteria [4].

References

Biographical note
Andrei Lebedev is a PhD student in Engineering Product Development (EPD) pillar at the Singapore University of Technology and Design. His research focuses on the development of new photocatalytic materials sensitive to visible and UV light with specific emphasis on the ability to predict their properties for water treatment purposes.
A Thermodynamic Database for Advanced Lightweight Steels

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Key words: CALPHAD, thermodynamic database, lightweight steels

Traditionally, automakers have regarded steels as the main material for autobody panels, having given ideal mechanical properties and safety at a low cost. However, the increasingly stringent regulations of energy consumption and CO₂ emission have compelled automotive manufacturers to look for effective methods to reduce vehicle weight in order to increase fuel efficiency. Therefore, lightweight steels are attracting considerable interest for automobile applications due to the weight reduction without loss of high strength and with retained excellent plasticity. Frommeyer and Brüx [1] developed the Fe-28Mn-12Al-1C (wt.%) steel with the yield strength of 730 MPa, ultimate tensile strength of 1000 MPa and total elongation of around 55% at room temperature. Moreover, the addition of 12 wt.% Al reduces the density of the steel to about 6.5 g/cm³.

Recently, many researchers have attempted to further improve the specific mechanical properties by adding some other alloying elements such as Cr, Cu, Mo, Ni, Si and Ti. Due to the alloying elements as well as many processing variants such as hot and cold rolling, solution and annealing treatment, and coiling, lightweight steels can form a variety of microstructures. The phases in lightweight steels include bcc, fcc, κ-carbide, ordered B2 and D0₃, β-Mn, M₆C and M₃C₅, which makes the physical metallurgy complex. Therefore, a detailed understanding of thermodynamic properties and phase equilibria of the lightweight steel system is fundamental in order to optimize their microstructure, such as catalysing the nano-precipitation of the coherent κ-carbide and ordered B2 phase and avoiding the formation of the brittle β-Mn phase.

To be able to accelerate the design and development of advanced lightweight steels, our group currently focuses on the establishment of the thermodynamic database for lightweight steels, containing the elements, Al, C, Cr, Cu, Fe, Mn, Mo, Nb, Ni, Si, Ti and V. In this presentation, the study of several key systems will be described, including the experimental phase equilibria and thermodynamic modelling.

Figure 1. Microstructure of the Fe-9Mn-9Ti (wt.%) alloy annealed at 1373 K for 10 days.

References

Biographical Note
Weisen Zheng obtained the PhD from KTH Royal Institute of Technology, and the Doctor of Engineering from Shanghai University. He currently works as a lecturer at Shanghai University. His research focuses on thermodynamic and kinetic modelling of metallic systems using both computational and experimental techniques, including CALPHAD, ab initio calculations and diffusion-couple.
Precipitate Softening Induced by Reorientation during Copper Precipitate-dislocation Interaction in Alpha-iron
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Key words: Molecular dynamics, Dislocations, Precipitates, Softening, Orientation adjustment

Understanding the mechanism involved in neutron irradiation embrittlement in nuclear reactor pressure vessel (RPV) materials is necessary to ensure the structural integrity of RPVs in aging nuclear power plants. In RPV materials, the nanoscale defects induced by radiation are the critical factors that inhibit dislocation motion and lead to stress concentration, which in turn results in the formation and propagation of cracks. Small Cu-rich precipitates are formed during neutron irradiation in ferritic pressure- vessel steels containing a low concentration of Cu. These Cu precipitates act as hardening sources that can induce loss of ductility and an increase in the ductile-to-brittle transition temperature of RPV steel, as the other irradiation-induced defects do.

With regard to the crystal structure of Cu precipitates, experimental investigations suggest that the small sized Cu precipitates keep BCC coherent structure in the beginning of the nucleation. However, when a Cu precipitate grows larger, its structure will change with different sizes as BCC→9R→3R→FCC with the orientation relationships of \(
\langle 110 \rangle_{\text{BCC}} / / \langle 111 \rangle_{\text{BCC}}\) and \(\{114\}_{\text{BCC}} / / \{110\}_{\text{BCC}}\) determined from TEM observations. These types of structure will contribute to different pinning effects on the dislocation and therefore introduce considerable influence on the mechanical properties of RPVs and Fe-Cu alloys. Therefore, understanding the atomic-scale mechanisms between dislocations and precipitates is necessary for developing predictive models to estimate the lifetimes of nuclear power plant components. However, detailed knowledge about the interaction mechanisms between a dislocation and Cu precipitate is difficult to obtain even when employing in situ methods of transmission electron microscopy.

Simulations using molecular dynamics (MD) can be primary complementation tools to investigate and understand microscopic phenomena in dislocation-precipitate interactions. In our study, we focus on the dislocation’s pinning strength in a relaxed copper precipitate and the atomic mechanism that controls the unpinning of edge dislocations. As a result, we found out that the softening happens in precipitates with critical size where the BCC-FCC phase transformation happens, which can be reflected in the decrease of the critical shear stress in stress and strain curves. A new two-stage atomistic mechanism including processes of orientation adjustment and atomic collective migration is discovered. Although the result for Cu precipitate’s size-only dependent pinning effects have been reported in the previous studies, the atomic mechanism for this softening were never clarified. This atomistic mechanism provides a good explanation for previous simulation results concerning the dislocation-Cu precipitate pinning effect and offers a new perspective for researches of dislocation-obstacle pinning interaction.

References

Biographical Note
Xiaoyu Wu, born in Beijing, China on August 25th, 1994, graduated with Bachelor’s degree from Beihang University in Material Science, Master candidate from Tsinghua University in Material Science.
The Zinc-Rich Corner of the Zn-Fe-Si-Sn Quaternary System at 450 °C

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Key words: Zn-Fe-Si-Sn quaternary system, phase diagram, scanning electron microscopy

Hot-dip galvanizing is one of the most versatile techniques to protect steel against corrosion [1], for which Zn and its alloys are mainly used from amongst various materials. In addition, Si has been introduced to steels as either de-oxidant or strengthening alloying element [2]. The addition of alloy elements, such as Sn, has proven to be effective for Si-reactivity control. Some scholars have investigated the effect of Sn and its alloys in Zn bath [3, 4] but few provided a solid mechanism. In fact, galvanizing Si-containing steels in a Sn-containing bath involves the Zn-Fe-Si-Sn quaternary system. The phase relationship of the Zn-rich corner isothermal sections at 450 °C, which is the conventional galvanizing temperature, can provide important information to understand the effect of Sn in a Zn bath during the hot-dip galvanizing of Si-containing steels.

450 °C isothermal sections of Zn-Fe-Si-Sn quaternary system with Zn fixed at 70 and 93 at.% were studied using optical microscopy, scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDS), and X-ray diffractometry (XRD). In this work, twenty-two alloys were designed to determine the phase relations of Zn-Fe-Si-Sn Quaternary system at 450 °C. The main results are listed below:

(1) Five four-phase regions exist in the isothermal section of the Zn-Fe-Si-Sn quaternary system at 450 °C with 70 at.% Zn. In contrast, no four-phase region was experimentally identified in the isothermal section with 93 at.% Zn.

(2) The δ phase can coexist with the Liq. and FeSi phases.

(3) The maximum solubility of Sn and Zn in the FeSi phase are 0.4 and 1.2 at.%, respectively. The Sn in ζ, δ, Γ₁, and Γ phases are 0.3, 1.1, 4.3, and 3.9 at.%, respectively. The Si in δ, Γ₁, Γ, and FeSn phases are limited to 0.6, 0.3, 0.2, and 0.3 at.%, respectively.

(4) No quaternary compound was found in the two sections.

Figure 1. Isothermal sections of the Zn-Fe-Si-Sn quaternary system at 450 °C with Zn being fixed 70 (a) and 93 at.% (b).

References

Biographical Note
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Optimization of Surface Energy of Pt – An Atomistic Study

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Key words: Surface energy, Surface segregation, 2NN MEAM, Monte Carlo

Platinum is widely used as catalysts for various reactions: oxygen reduction, hydrogen oxidation, hydrogen evolution [1]. Often, catalytic reactions occur on the surface of Pt or Pt bimetallic nanoparticles. Therefore, knowing which faces and which atoms are exposed on the surface of Pt bimetallic nanoparticles is a key factor for predicting catalyst performance. Since surface energy is one of the factors that have significant effects on the shape and atomic configuration of nanoparticles, accurate information on the surface energy of the various surfaces of platinum is an important predictor of catalyst performance.

Despite the fact that surface energy is a fundamental quantity in understanding surface structure of nanoparticle, the results of experimental measurements and theoretical calculations for the surface energy of pure Pt show a wide range of scattering. It is necessary to further ensure the surface energy of Pt to find the equilibrium shape and atomic configuration in Pt bimetallic nanoparticles accurately. In this article, we critically assess and optimize the Pt surface energy using a semi-empirical atomistic approach based on the second nearest-neighbor modified embedded-atom method interatomic potential [2,3]. That is, the interatomic potential of pure Pt was adjusted in a way that the surface segregation tendency in a wide range of Pt binary alloys is reproduced in accordance with experimental information. The final optimized Pt surface energy (mJ/m²) is 2036 for (100) surface, 2106 for (110) surface, and 1502 for (111) surface [4].

We believe the finally optimized Pt surface energy is one of the most accurate ones among the experimental and calculated values reported during the last 40 years. We propose the present procedure as a means of evaluating the accuracy of surface energy also for other elements. The refined interatomic potentials can be utilized to find the equilibrium shape and atomic configurations of various Pt bimetallic nanoparticles more accurately.

Figure 1. Surface energy of Pt obtained since 1977 for the (100), (110), and (111) surfaces by experiments, thermodynamics calculation, for molecular-mechanical calculation and quantum mechanical calculation. The red (dark gray) and green (light gray)-colored data represent surface energy calculated by our group in 2003 and present work, respectively.

References

Biographical Note
Jin-Soo Kim is a graduate student in the Computational Materials Science and Engineering Lab. (lead by Prof. Byeong-Joo Lee) at POSTECH, Korea.
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New Thermodynamic Modeling of the Co-Cr system based on a New Approach of the CEF (NACEF)

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Key words: Co-Cr system, CALPHAD, NACEF

The Cobalt-Chromium system is of outstanding importance as a base for many alloys, especially high-temperature steels, and it’s known for its specific magnetic properties, for which it is used in many industrial applications thanks to its stiffness. It is used in hard disks as a magnetic recording medium and in other applications, for high-speed cutting tools for example.

The phase equilibrium diagram Co-Cr has been studied by various authors. The system presents four solid solutions: The liquid, Fcc_A1, Hcp_A3 and Bcc_B2 with a Sigma phase which is considered to be an intermetallic having a solubility range of 56.5 to 61% Cr and presents a congruent transition with the bcc phase.

Several authors are interested in studying the σ phase because of its weakness (especially in steels) in order to control its presence in multi-constituent systems based on calculations by the CALPHAD method. The most recent modeling in the literature for this system is that of Li et al. which was supported by first-principles calculations.

In the present work, the liquid, bcc, fcc and hcp phases are described using substitutional solution models and the sigma phase is modelled on a 5-sublattices model using a new approach of the Compound Energy Formalism (NACEF). The evaluation of the thermodynamic parameters was carried out using the PARROT module included in the Thermo-Calc software. The data for the pure elements was extracted from the SGTE unary database. Energies of the end-members were taken directly from the work of Li et al.

The present work show that the use of the NACEF approach for the sigma phase modelling allows to take into account at the same time all the phase diagram data (see Fig. 1), structural data such as the site occupancies obtained by Kabliman et al as well as the energies of the totally ordered configurations.

Figure 1. Co-Cr calculated phase diagram [this work] with all experimental data

References

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Nonlinear Size-dependent Melting and Melting Enthalpy of Bi Nanocrystals


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Bi nanocrystal is of considerable interest because it can be used as the phase-change inclusions providing the desired melting temperature and high volumetric energy density for phase-change thermal storage materials\(^\text{[1]}\). Bi Nano-flowers can also be used as a highly selective catalyst for electrochemical reduction of CO\(_2\) to formate. It is well known that the melting point of nanoparticles is lower than that of their bulk counterparts because of significant size effects. It is indicated that the size dependence of the melting temperatures for Ag and Ag–Cu alloy NPs shows a nonlinear function with respect to the inverse of the particle size and satisfactory agreement with experimental observations\(^\text{[2,3]}\).

We report on the nonlinear size-dependent melting temperature and melting enthalpy of the Bi nanoparticles. Considering the surface effects on the chemical potential of the Bi nanoparticles, the correction factor, considering the effects from the shape, the surface strain due to non-uniformity and the uncertainty of the surface tension measurement, was determined by fitting the experimental melting temperatures of Bi nanoparticles with various sizes\(^\text{[1]}\). The chemical potential of Bi nanoparticles was obtained by thermodynamic assessment. On the basis of the obtained thermodynamic parameters, the size dependent melting temperature and melting enthalpy of Bi nanoparticles with sizes of 8.1nm, 9.8nm, 13.2nm and 14.9nm, have been calculated, respectively. It is shown that thermodynamically calculated size dependence of the melting temperatures for Bi NPs shows a nonlinear function (Figure 1) respect to the inverse of the particle size, which is good agreement with the experimental results performed by Wang\(^\text{[1]}\). It is also indicated that the nonlinear size dependent melting enthalpy function respect to the inverse of the particle sizes of Bi nanoparticles, which agree well with Wang’s experimental results. In this work, the chemical potential of the Bi nanoparticles were assessed by introducing the surface effect, the calculated nonlinear size dependence of the melting temperature and melting enthalpy for the Bi nanoparticles agreed very well with the reported experimental values.

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![Figure 1. The size-dependent melting temperature of Bi nanocrystals (solid curve) with the measured melting temperatures of Bi nanocrystals with the sizes of 8.1, 9.8, 13.2, and 14.9 nm, respectively.](image)

References


Biographical Note

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Nano-phase Diagram of Ag-based System with Key Experiments and Thermodynamic Modelling

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We report on the nano phase diagram of Ag-based Ag-Cu and Ag-Au systems by means of key experiments and thermodynamic modelling. For the Ag-Cu system, four key Ag-Cu alloy nanoparticles samples with compositions ranges from Ag$_2$Cu$_3$ to Ag$_5$Cu$_6$ have been first prepared by NaBH$_4$ reduction, silica-coated, UV–visible absorption spectra and transmission electron microscopy characterization, and then melted by differential scanning calorimetry. Based on the measured melting temperatures of the Ag-Cu nano-alloys as well as the thermodynamic properties of the pure Ag and Cu nanoparticles and Ag–Cu systems in literature, considering the surface effect on the chemical potential of nanoparticles, thermodynamic optimization for the Ag-Cu nano-system was then conducted by fitting the experimental data. A set of self-consistent thermodynamic parameters for the Ag-Cu nano-system is finally obtained. The obtained thermodynamic properties can be used to predict the phase transition temperatures of Ag-Cu nano-system with any size large than ~5 nm, and to calculate the phase diagram of Ag-Cu nano-system. The comprehensive comparisons show that the calculated melting temperatures agree well with the experimental ones, the calculated phase diagram agree well with the experimental observations.

For the Ag-Au system, Ag-Au nanoparticles with compositions ranges from Ag$_5$Au$_2$ to Ag$_5$Au$_8$ and sizes range from 17.3 nm to 55.0 nm were first prepared, silica-coated, and transmission electron microscopy examined. The phase transition temperatures (i.e., melting temperatures) of the silica–coated Ag–Au nanoparticles were determined by means of differential scanning calorimetry. Based on the obtained experimental nano–phase diagram of the Ag–Au system and the thermodynamic properties of the pure Ag and Au, thermodynamic optimization of the Ag–Au system were then performed by using the assessed literature data and the present experimental data, considering the surface effect of the shape, the surface strain because of the uniformity, and the uncertainty of the surface tension for nanoparticles on the chemical potential of nanoparticles. A consistent thermodynamic data set for the Ag–Au nanosystem is obtained by optimization of the experimental data. The obtained thermodynamic parameters can be used to calculate the nano-phase diagram of Ag-Au system. It is indicated that the calculated phase diagram agrees well with the experimental values.

This work establishes a methodology for predicting/determining the melting behavior, thermodynamic properties and nanophase diagram as a function of size for different nano-alloy systems.

![Figure 1. The nano-phase diagram of Ag-Cu system with various sizes.](image)

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References


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Modelling Density of Ironmaking Slag

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Key words: Molten slag, density, Al₂O₃-CaO-MgO-SiO₂

Density is one of the most important thermophysical properties of industrial slags. The experimentally determined density, especially at high-temperatures, for high melting point substances are scarce. Due to the experimental difficulties, unavailability of high-temperature density measuring instruments and high costs involved, it is worthwhile to have a model, which can reliably estimate the density of industrial slags.

A density model for Al₂O₃-CaO-MgO-SiO₂ system and its subsystems is established in this work. Excess volume of the slag is modelled using a Redlich-Kister [1] type of polynomial for the binary and extrapolated to higher order systems using Muggianu [2] scheme. Approximately 650 experimental data points for density are collected from various sources for the Al₂O₃-CaO-MgO-SiO₂ system and its subsystems, for optimizing the model parameters of the density model. The optimization was done using the PARROT [3] module of the Thermo-Calc software [4]. All data (unary, binary and ternary) were used simultaneously for the optimization.

Model parameters are optimized and refined iteratively until the sums of squares of error did not show any appreciable change. In the final run of the optimization, all data together with all model parameters (except unary) were used.

The experimental data are plotted against the calculated data for unary, binary, ternary and quaternary systems. Figure 1 shows the parity plot for the density of Al₂O₃-MgO-SiO₂ system.

Figure 1. Al₂O₃-MgO-SiO₂ ternary system

References


Biographical Note

I am a graduate student at the Department of Metallurgical & Materials Engineering in Indian Institute of Technology Madras. My research interests include computational materials thermodynamics and process metallurgy.
Magnetic Transition in Ordered BCC Phases of Fe-Al Alloys
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Key words: Fe-Al system, antiphase boundaries, Order-Disorder transition, Curie Temperature

Curie temperature is one of the key data in phase diagrams and magnetic properties of materials. Phase diagram in the Fe-Al system including Curie temperatures have been well investigated for many years due to the high potential as structural applications [1]. The magnetism is influenced by the atomic ordering, however, only few experimental results have been reported about the Curie temperature of the BCC phase in Fe$_{1-x}$Al$_x$ alloys of x $\geq$ 25 due to the several effects related to the B2 and D0$_3$-ordered phases. It is known that thermally induced antiphase boundaries (APBs) are introduced during heat treatment (via growth of individual ordered regions) and that thermal robustness of a ferromagnetic spin order within the APBs is different from that in the matrix domains [2]. Thus, the present work focuses on the relationship between magnetic properties and structure in the ordered BCC phase in Fe-Al alloys with different antiphase domain (APD) structures in order to estimate the magnetic properties of the A2, B2 and D0$_3$ structures.

Fe-30Al (at. %) alloy was prepared by induction melting under an Ar atmosphere. Small specimens cut from the ingots were sealed in quartz tubes. They were homogenized at 1050°C for 1day treatment and subsequently additional aging heat treatment in either of B2-ordered regions or D0$_3$-ordered regions were performed in order to prepare several specimens with different APD structures. The crystal structure and microstructures of the specimens were examined by transmission electron microscopic (TEM) observations. The thermomagnetization curves were measured by vibrating sample magnetometer (VSM).

As shown in Figure 1, three kind of specimens with different degree of ordering were obtained; (a) B2-single phase without APBs, (b) B2-single phase with APBs related to B2/A2 phase transition and (c) D0$_3$-single phase with APBs related to D0$_3$/B2 phase transition. The magnetic measurements for these specimens showed different Curie temperatures. It is interesting that the specimen (b) has two Curie temperatures which is attributed to the A2-type disordering in the B2/A2-APB region in addition to the B2 matrix. It is suggested from these experiments that A2-phase has the highest Curie temperature, followed in order by D0$_3$ and B2-phase about curie temperature in Fe-Al alloys.

Figure 1 | The TEM images (dark-field images) and selected area electron diffraction pattern of three specimens prepared by different annealing, (a) B2-phase without B2/A2-APBs, (b) B2-phase with B2/A2-APBs and (c) D0$_3$-phase with D0$_3$/B2-APBs.

References

Biographical Note
The author is a graduate student in the department of materials science and engineering in Tohoku University. He is investigating the properties in the Fe-Al system and microstructure in Fe-based shape memory alloys.
Thermodynamic Evaluation of the Ga-Mn System
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Key words: Ga-Mn, phase diagram, thermodynamic modeling, CALPHAD

The Ga-Mn alloys are important with a wide range of applications as the functional materials. For example, the alloys with the Ni$_2$MnGa phase are promising functional alloys with shape memory and magnetocaloric effects. However, the phase equilibria in the Ga-Mn system are still uncertain and require more efforts to understand the difference between existing experimental phase diagrams as shown in Fig. 1. In addition, thermodynamic modeling of the Ga-Mn system is not yet available. Therefore, it is critical to establish a reliable Ga-Mn phase diagram providing fundamental information for engineering applications.

Because of the four allotropes of Mn, the phase equilibria in the Ga-Mn system are complex. Experiments are challenging due to the significant difference in melting point between Ga and Mn. Meanwhile, there are more than 12 intermetallic phases in this system, and the crystal structure of some phases is still not well defined. Among these phases, GaMn$_2$ and GaMn phases are ferromagnetic, and phases like GaMn$_5$, Ga$_4$Mn$_5$, Ga$_3$Mn$_5$, Ga$_2$Mn$_3$ are reported to be decagonal quasicrystal approximants.

In this work, the Ga-Mn phase diagram is evaluated thermodynamically by considering both experimental information and ab initio calculations. Reported experimental information is critically reviewed. To further settle the discrepancy between current four versions of Ga-Mn phase diagrams, some experiments and theoretical calculations are conducted to understand the crystal structure of possible phases and phase reactions.

This work is supported by the NSF DMR-MMN program (award No. 1808082).

References

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Isothermal Sections of the Co-Cr-Ti System at 800 and 900°C

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Key words: Co-Cr-Ti, phase equilibria, L12 phase, Chi phase

The Co-Cr-Ti alloys are promising candidates for high temperature Co-superalloy manufacturing. Compared with conventional Co superalloys, L12 strengthened Co-Cr-Ti alloys especially show distinct potential of high mechanical properties, even have lower density [1]. Besides, Co-Cr-Ti alloys are considered as ideal materials for biomedical applications with their good performance of biocompatibility, hardness, wear and corrosion resistance [2]. However, the partial isothermal sections are investigated only by one research group [3] so far. And the results of are inconsistent with other reported data with L12 and (εCo) involved.

In this work, The Co-rich corner of the isothermal sections at 800 and 900°C have been determined by scanning electron microscopy, energy-dispersive X-ray spectroscopy and X-ray diffraction.

The solubility limit of Cr in the fcc_L12 Co3Ti phase is up to c.a. 14 at.% at 800 and 900°C, and thus much larger than the model-prediction using the reported databases.

The Chi phase (Co2Cr3Ti) was not found at both temperatures. This is different with the work performed by Livshits and Khorin, who considers the Chi phase as a stable phase from 750 to 1150°C [3]. The appearance of the Chi phase [3] was possibly resulted from the insufficient annealing time (5-80 hours). The high impurity (0.10-0.24 wt.% Fe) in the raw materials may also stabilize the Chi phase.

The three-phase regions changes suggest there is an invariant reaction near 800°C, which is (εCo) + Co2Ti = σ + fcc_L12.

References

Figure 1. Partial isothermal sections of Co-Cr-Ti at (a) 800°C and (b) 900°C

Biographical Note
Shiyu Fu is a Ph.D. student of Dr. Xiaogang Lu at Shanghai University and Dr. Wei Xiong at University of Pittsburgh (http://www.pitt.edu/~weixiong). Mr. Fu focuses on the study of thermodynamic modeling of the Co alloy systems.
Isothermal Section at 1200 °C of the Al-Nb-V System
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Key words: Al-Nb-V system, experimental phase diagrams, refractory metals, high-entropy alloys.

A new concept for development of metallic alloys has been studied by the scientific community in recent years, these are multi-principal element alloys, also known as High Entropy Alloys (HEAs) [1]. HEAs with refractory metals and aluminium as constituents are possible alloys for use in aerospace industry, since they have high specific resistance [2]. In this way, an investigation of phase equilibrium relations involving refractory metals and aluminium is required. For this work, the Al-Nb-V system was chosen, since only one complete experimental isothermal section of this system [3] and three partial isothermal sections - on the Nb-rich corner [4] - are available in the literature. For this work, 23 samples were produced by arc melting alloys under Ti-gettered argon. The alloys were treated at 1200 °C for 10 days to determine the isothermal section of the system at this temperature. The microstructural characterization was performed via X-rays diffraction (XRD) scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Comparing the isothermal section available in the literature with that proposed in this work, some differences were observed. The isothermal section found in the literature proposes the stability of the ternary compound NbVAI₂, which was not found in the present work. Besides that, higher values of V solubility in Nb aluminides were measured in agreement with Jiao et al. [4]. The results allowed to propose an isothermal section at 1200 °C of the Al-Nb-V system. This proposal is found in Figure 1 with all experimental results (tie-lines and tie-triangles) obtained.

Figure 1. Isothermal section at 1200°C of the Al-Nb-V system indicating all experimental results of this work

References

Biographical Note
Júlio C.P. Santos is a Ph.D. student in materials science in the Department of Materials Engineering at University of São Paulo (EEL-USP) under supervision of Dr. G.C. Coelho. He holds a Master’s Degree in materials science at same institution. His research interests focus on experimental phase equilibria, CALPHAD modeling and thermodynamics.
Investigation and Modeling of Molar Volume of the Binary Sigma Phase

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Key words: sigma phase, molar volume, compound energy formalism, first-principles calculations

The sigma phase is a non-stoichiometric intermetallic compound, crystallizes in a tetragonal structure with 30 atoms distributed on five nonequivalent sites denoted as 2a, 4f, 8i₁, 8i₂ and 8j [1-2] (see Fig. 1). It mostly forms between transition element systems, and only two systems contain a main-group element, i.e., A-Al (A=Nb, Ta). The sigma phase, in general, is detrimental precipitation in many technologically important materials, such as duplex stainless steels and Ni-based superalloys [1-2]. On the other hand, the sigma phase is also reported to enhance the properties (such as creep strength, ductility and superplasticity etc.) of duplex stainless steels when the distribution, morphology and quantity of the sigma phase are properly controlled through pre-treatment [3]. The precipitation of the sigma phase should be carefully avoided or controlled.

The present work systematically clarifies the influence of the atomic mixing and the atomic order (i.e. atomic constituent distribution or site occupancy preference on inequivalent sites of a crystal) on the molar volume of the binary sigma phase. Additionally, a new integrated thermodynamic and molar volume model to consider physically both atomic mixing and order factors was developed.

First, we calculated the molar volumes, atomic charges, density of states and electron localization functions of the binary sigma phase with different atomic order by using EMTO-CPA (Exact Muffin-Tin Orbitals - Coherent Potential Approximation), VASP and Bader’s AIM approaches. The calculation results indicate that the effect of the atomic mixing on the molar volume of the sigma phase depends on the tendency of electron loss or gain of the two constituent elements; the effect of the atomic order on the molar volume of the sigma phase depends on the atomic bonding of the two constituent elements.

Then, the integrated thermodynamic and molar volume model was built within the compound energy formalism (CEF), enabling the thermodynamic calculations to determine equilibrium site occupancies for the subsequent volume calculations. The developed model physically considers the influencing factors of both atomic mixing and atomic order on molar volume. The model parameters of the CEF were assigned by using the first-principles calculated energies and molar volumes of the complete sets of ordered configurations of the sigma phase, as well as the extrapolated molar volumes of the pure elements in the hypothetic sigma phase structure. Such extrapolation for pure elements is based on the experimental data from the literature and the first-principles calculations. We applied the integrated model to study the binary compounds, e.g., Cr-Co, Cr-Fe, Cr-Mn, Mo-Fe, Mo-Mn, Mo-Re, Re-Cr, Re-Fe, Re-Mn, Nb-Al, Ta-Al, V-Fe, V-Ni, and ternary compounds Cr-Fe-X (X=Co and Ni). The integrated thermodynamic and molar volume databases can predict successfully the molar volume of the binary and ternary sigma compounds.

Figure 1. Crystal structure of the sigma phase. Atoms occupying on different Wyckoff positions, namely 2a, 4f, 8i₁, 8i₂ and 8j, are indicated by different colors.

References

Biographical Note
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Interactive Industrial Application to Represent Isothermal Sections of Multi-component Phase Diagrams.

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**Key words:** Steelmaking, BOF, Industrial application

“Make the slag and the steel will make itself” is an old phrase in steelmaking. The converter or basic oxygen furnace (BOF) process is a necessary step in the steel production during which carbon, phosphorus and other impurities present in the hot metal, coming from the blast furnace, are removed and steel is produced. This steel is tapped from the converter and further refined, next cast, rolled and finished.

The BOF process is complex due to many reasons: high temperatures, multiple phases present, interactions of kinetics and thermodynamics, etc. Emphasis in this work is put upon the BOF steelmaking slag. Yet, even though this has been topic of many research projects no full understanding of all the slag related phenomena has been far from achieved. One of the difficulties is the multi-component nature of the slag. In its most simplified form, the slag is a three component system consisting of CaO, SiO₂ and FeO. However, in practical applications this slag contains more than three components, making graphical representations of equilibria complex and difficult.

This work shows the potential to apply CALPHAD based data for industrial applications via an interactive visual tool. Isothermal sections of multi-components phase diagrams were constructed with Factsage 7.1 software. Addition of extra components to the calculated isothermal sections, gives a graphical representation which can be used to gain insight in certain observed phenomena in the BOF process. To illustrate that the interactive visualisation yields an interesting tool to integrate CALPHAD based calculations in industry two case studies from steelmaking are discussed: the effect of MgO upon the refractory wear and the effect of MgO upon dephosphorization.

![Figure 1. Isothermal section of CaO-SiO₂-FeO-MgO-Al₂O₃ system at 1650°C. Calculated with Fartage 7.1.](image)

**Biographical Note**

Lotte De Vos is a PhD student at the University of Ghent (Department of Materials, Textiles and chemical Engineering). Her research topic is related to the properties and behavior of slags systems in steel refining process, more specifically the slag in the Basic Oxygen Furnace in the steel production process.
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High-throughput CALPHAD-type Calculation in Screening Coherent Precipitate-strengthening AlCuFeNiTi Multi-principal Element Alloys

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Key words: multi-principal element alloys, high entropy alloys, high-throughput calculation, coherent precipitate strengthening

Multi-principal element alloys (MPEAs) is the term used to describe an alloy system composed of several kind of elements in equal or nearly equal atomic composition, which is very different from conventional alloy systems and bearing outstanding mechanical properties. The origin can be traced back to 2004, Cantor et al. published a literature with the topic about equiatomic multicomponent alloys. While Yeh et al. firstly proposed the concept of High Entropy Alloys (HEAs). Their works opened a vast unexplored composition range for alloy design and has been attracting large amount of research all over the world. Due to the multi-dimensional composition space of MPEAs, studying with traditional trial-and-error experiments are costly and time-consuming. On the other hand, most of the study has conformed to the concept of HEAs; however, phase stability is determined by Gibbs energy, which containing contributions from both enthalpy and entropy. Configurational entropy is just the one of the factor to affect the stability. In this research, high-throughput CALPHAD-type calculation is employed to study MPEAs. Combining the computational thermodynamics and the grid search in the composition space, which can improve the efficiency significantly. Using the high-throughput calculation (HTC) function in Pandat software and PanHEA database developed by CompuTherm LLC, we screened the whole composition and temperature space of all the quinary systems in PanHEA database. By performing multiple points of CALPHAD-type calculations a big dataset can be obtained, then set the criterions, e.g., fcc and L12 (ordered fcc) 2 phases co-exist, to sort out the desired points. The coherent precipitate-strengthening mechanism of Ni-based superalloys is employed here with contrast to the single solution phase HEAs. Basing on the calculation results we have found that: The AlCuFeNiTi quinary system with Ni less than 0.6 retains fcc and L12 co-existing without any topological close-packed (tcp) phase formation. Moreover, fcc and L12 are stable above 1100°C and there is a temperature window of fcc single phase at around 1200°C for solution heat treatment. A high-throughput CALPHAD-type calculation for screening coherent precipitate-

Figure 1. Phase fraction versus temperature plot of the Al61.1Cu8.1Fe0.09Ni58.2Ti0.7 MPEA screened out by high-throughput CALPHAD-type calculation. Fcc and L12 phases are stable above 1100°C without tcp phase formation.

References


Biographical Note

Shao-yu Yen is a PhD student in Department of Material Science and Engineering at National Cheng Kung University (NCKU) in Taiwan. His researches focus on computational thermodynamics-assisted design of multi-principal element alloys and Al alloys, as well as phase equilibria and ab initio-aided CALPHAD modeling.
High-Throughput Measurements for the Micro-mechanical Plastic Deformation in Mg-Al Alloys

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Key words: High throughput method, Micro-mechanical technique, Magnesium alloys, Materials design

In recent years, magnesium alloys, as lightweight commercial materials, have received considerable attention for wide and attractive applications in the aircraft, automotive, aerospace and communication due to their low density, earth abundance, good castability as well as high specific stiffness [1,2]. However, there is a strong limitation for the application of Mg alloys, mainly resulting from the reduced ductility and poor formability especially at room temperature. Thus, it is essential to develop and design Mg alloys to improve the mechanical performance.

High throughput methodologies have boosted constitute a promising strategy for accelerated materials design, research and discovery, which provides rapid screening the composition-microstructure-properties relationships of materials by a diffusion multiple approach [3,4]. By taking advantage of compositional variations obtained from the diffusion couples and diffusion multiples, the phase diagrams, diffusion coefficients, precipitation kinetics, solution-strengthening effects, and precipitation-strengthening effect could be investigated in an efficient and systematic approach combined with the micro-mechanical technique for example nanoindentation and micropillar compression test.

In this investigation, micro-mechanical technique combined with high-throughput method were used to ascertain the influence of solute atoms on the strength of deformation modes, such as basal slip, twinning process and pyramidal slip systems and plastic deformation behavior in Mg alloys. The solid solution strengthening is well described for each deformation mode. This high throughput process could provide an efficient way to predict and improve mechanical properties of Mg alloys.

![Composition profile](image)

Figure 1. (a) The microstructure and composition profile in the diffusion region analysed by EBSD and EPMA; (b) CRSS values of individual deformation modes varies with Al content.

References


Biographical Note

Jingya Wang is currently a research assistant in the Mechanics of Materials Group and Computational Alloy Design Group at the IMDEA Materials Institute in Madrid. Her research mainly focuses on the kinetics behavior of hcp Mg alloys and the micromechanical property study of Mg alloys.
High Throughput Modeling of Cr-Fe-Ni Sigma Phase

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Key words: sigma phase, high throughput, 5 sublattice model

The Fe-Cr-Ni system is of great technological importance and is a fundamental part of many key alloys. The sigma phase, much like other topologically close-packed phases, is a brittle phase that is detrimental to the properties of the alloys in which it forms. The most prevalent descriptions of the phase use 3 sublattices on which only a single sublattice contains mixing. While some work has been done to consider the solubility on multiple sublattices current descriptions of the phase fail to properly capture the site occupancies.

In this work we reassess the phase using first-principles calculations based on density functional theory (DFT) to develop a description for the sigma phase using a 5 sublattice model based on the Wyckoff positions of the unit cell. In addition magnetic configurations will be considered. A high-throughput DFT workflow for efficient, robust relaxation of structures and calculation of finite temperature properties was written and implemented using the Atomate software package. A CALPHAD model for the sigma phase was developed automatically using the ESPEI software package. The energy of the electronic structure was then assessed to determine the stability. From this the interaction parameters will be determined using ESPEI in order to work toward a more complete description of the Cr-Fe-Ni system. These parameters were optimized from phase equilibria using ESEI’s multi chain Monte Carlo feature. The thermodynamic properties were then compared with existing literature.

Figure 1. Site occupancies compared to literature\textsuperscript{4,5}

References

Biographical Note
Matthew’s research is focused on designing new Ni-base alloy compositions specifically for additive manufacturing processes. He is using a joint experimental/computational approach. Data from experiments and first principles calculations are used to build CALPHAD models, which are then used for designing the new alloys, which will then be fabricated and further characterized.
Thermodynamic Re-assessment of the Zr-Mn System and Experimental Investigation of the Zr-Fe-Mn System

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Key words: phase relations, phase diagrams, heat capacity, CALPHAD

Composite materials based on high-alloyed steels e.g. high-alloyed austenitic stainless TRIP-steel (Transformation Induced Plasticity) reinforced by Mg-PSZ (MgO-stabilized zirconia) are of particular interest due to the wide range of their possible technological applications especially in automotive production. Development of such composite materials requires the knowledge of thermodynamic properties and phase relations. The Zr–Fe–Mn system is one of the important sub-systems. Additionally this system presents interest for nuclear materials.

The aims of the present work are measurements of thermodynamic properties of the C14-ZrMn₂ Laves phase, thermodynamic re-assessment of the Zr-Mn system and experimental study of the phase relations in the Zr-Fe-Mn system.

Samples have been prepared using Arc-melting method in the Ar-atmosphere. For the heat treatment, samples were encapsulated in quartz ampules with the Ar-atmosphere. Ar pressure in the ampules has been chosen corresponding to 1 atm pressure at annealing temperatures. After long time annealing, samples were quenched into ice-cold water. The phase assemblage in the samples has been identified using the X-ray powder diffraction (XRD) and scanning electron microscopy combined with dispersive X-ray spectrometry (SEM/EDX). Temperatures of invariant reactions were determined by differential thermal analysis (DTA). For heat capacity measurements, differential scanning calorimetry (DSC) method was used by the classical three-step continuous method with a constant heating rate.

The phase diagram of Zr–Mn was investigated. Presence of high temperature compound of ZrMn was revealed. According to DTA investigations, high temperature stability limit of 1680 K was established for this compound. Heat capacity of the C14-ZrMn₂ Laves phase was measured for the first time in the temperature range between 220 K and 1023 K. Based on the obtained experimental results and calorimetric data [1] thermodynamic parameters of the Zr–Mn system were re-assessed. Current thermodynamic description of Zr–Mn in combining with available thermodynamic descriptions of Zr–Fe [2] and Fe–Mn [3], was used for interpolation into the ternary area of the Zr–Fe–Mn system.

Based on the preliminary calculations of the Zr–Fe–Mn phase diagrams, samples for investigations of phase relations in the ternary system were chosen. Obtained specimens after long time annealing were analyzed by XRD and SEM/EDX. Using these results, isothermal sections of the Zr-Fe-Mn system were constructed at temperatures 1073 and 1193 K. Wide extension of phase with C14-Laves structure into ternary system was found. Very limited solubility of Mn was revealed in C15-Laves phase, while more substantial solubility of Mn was found in the intermediate Zr₂Fe compound.

Current experimental results on phase relations in the Zr-Fe-Mn systems could be used for further optimizing of thermodynamic description using CALPHAD approach.

Figure 1. Heat capacities of C14-ZrMn₂

References

Biographical Note
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Fundamental Investigation of High Entropy Alloys in Relation to High Demanding Industrial Applications

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Key words: CALPHAD, high entropy alloys, Thermo-Calc, thermodynamics

High Entropy Alloys (HEAs) have gained an extensive popularity in the past years. Taking into account that they usually contain at least 5 elements, it is very difficult to investigate them experimentally. In order to accelerate the research, a multicomponent database for thermodynamic calculations is being developed following the CALPHAD method. The database contains Al,Co,Cr,Fe,Ni,Ta and W. It will be used to design novel HEAs in order to meet targeted industrial needs, for instance the request for new high-temperature alloys.

The principal elements, such as Al, Co, Cr, Fe and Ni have already been fully assessed (parameters describing phase stabilities in all binary and ternary systems containing these elements have already been added to the database). It covers the whole temperature and composition range, which is fundamental in case of HEAs, composition of which is placed in the centre of phase diagrams. The ternary systems containing Ta and W are being systematically added.

During creation of the multicomponent database, the Al-Co-Fe had to be fully modelled due to the lack of any thermodynamic description available in the literature. The system is present in the vast majority of HEAs and it was essential to include it in the database. It was very challenging because of the complex interaction between magnetic and structural ordering transformations influencing the phase stabilities. Most of the available experimental data was reproduced in a satisfactory way. The paper from the assessment will be submitted soon.

The reliability of the multicomponent database is being verified with the available experimental data. Due to the sluggish diffusion in HEAs it takes a lot of time to bring an alloy into equilibrium state, hence, many published results do not show the actual equilibrium compositions. Some discrepancies were observed regarding the stability of fcc phase after extrapolating into the multicomponent system, therefore, metastable ternary parameters were added. Figure 1 presents the calculated phase diagram for quinary AlxCoCrFeNi, with x ranging from 0 to 2 mole together with experimental data regarding equilibria between fcc and bcc phases. Filled and empty squares denote one- and two-phase fields respectively. The green colour stands for a good agreement with our calculations, whereas the red colour indicates some inconsistencies.

In the next step, a selection of key compositions will be synthesised and they will undergo experimental validation.

Biographical Note
PhD. student at the Department of Chemistry and Industrial Chemistry, University of Genoa, Italy. M.Eng. degree in Materials Engineering from AGH University of Science and Technology in Cracow, Poland.
Research interest is designing new materials for industrial applications through thermodynamic modelling.
Four Decades of CALPHAD: Statistical Trends in Published Thermodynamic Models

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Key words: TDB, databases, statistics, machine learning

A quantitative statistical analysis of over 700 published CALPHAD-based thermodynamic models, spanning nearly four decades of scientific inquiry, is performed using the Thermodynamic DataBase DataBase (TDBDB) dataset [1] and the pycalphad software [2]. With this approach, the published model parameters for each published assessment are automatically extracted, aggregated and analyzed, providing a cohesive view of the scientific progress made by the CALPHAD community since its inception.

We introduce a taxonomy for binary systems, based on the chemical grouping of elements on the periodic table, to explain the clustering of thermodynamic excess mixing parameters in the liquid, solid solution and stoichiometric phases, and also to predict the models of binary systems in unexplored regions of the chemical space. We show that this taxonomy is highly predictive for choices of sublattice model and mixing parameters in both liquid and solid phases, potentially reducing the complexity of model selection.

References

Biographical Note
Richard Otis is a materials and manufacturing technologist at NASA’s Jet Propulsion Laboratory, a division of Caltech. He is also the creator and lead developer of the open-source pycalphad software package.

Figure 1. The aggregated excess mixing entropies of 50:50 binary liquids show a typically small excess entropy in transition metal (TM) liquid systems, while the negative average excess entropy in TM-Metalloid binaries reflects an ordering tendency for those liquids.
First-principles Calculation of Hydrogen Dissolution and Diffusion Properties in V-Mo-W Alloy Membranes
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Key words: Hydrogen, dissolution, diffusion, V-Mo-W, the first-principles method

Vanadium-based alloys have been identified as one of the most promising hydrogen separation membrane materials due to their high hydrogen permeability and cost less. In this paper, we systematically studied the effect of W doping on the structure, mechanics, H-dissolution and H-diffusion properties of V-Mo alloy by using the first-principles method. Our calculation results show that V8Mo4W4 alloy is a body-centered cubic structure with high symmetry and stability. The absorption of a single H atom at the tetrahedral interstitial site (TIS) is the most thermodynamically stable with the minimum enthalpy of solution one among all the tetrahedral interstitial site (TIS), the diagonal interstitial site (DIS), and octahedral interstitial site (OIS); and H solution enthalpy at TIS are -32.23 kJ/mol, -20.55 kJ/mol and -0.97 kJ/mol for V16H, V12Mo2H and V6Mo4W4H, respectively. The optimal way of H-diffusion is TIS-to-TIS instead of TIS-to-OIS. As shown in Fig 1, H-diffusion energy from TIS to TIS in V16H, V12Mo2H and V6Mo4W4H are 0.138 eV, 0.188 eV and 0.132 eV, respectively. The values of H-diffusion coefficient (D) are 1.68×10^-8 m²/s, 8.31×10^-9 m²/s, and 1.87×10^-8 m²/s for V, V-Mo, and V-Mo-W, respectively, at the typical 673K temperature. The calculation results also show that V-Mo-W alloy also has good elastic properties. All these results indicate that the addition of W element not only further reduces the solubility of hydrogen and inhibits hydrogen embrittlement, but also enhances hydrogen diffusivity and improves the mechanical properties of V-Mo alloy. This provides a theoretical reference for the design of the ternary alloy and further obtains a better hydrogen permeable membrane.

Fig 1. The diffusion energy barriers of the H atom in V, V-Mo and V-Mo-W.

References

Biographical Note
Zhongmin Wang is a professor at Guilin University of Electronic Technology and has been engaged in new energy materials, hydrogen energy technology, material chemistry, functional film materials and other research work in recent years.
Experimental Phase Diagram of the Fe-rich Region in the Fe-Zr, Fe-Nb-Zr and Fe-Sn-Zr Systems.

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Key words: Zr alloys, Phase diagrams, Fe23Zr6, Nuclear materials.

Zirconium-based alloys are widely used as fuel cladding in nuclear pressurized water reactors for their excellent mechanical properties, irradiation stability and resistance to corrosion. Alloys with Fe, Nb and Sn, Zr is the main element in the Zirlo-type alloys, currently used as structural elements and as burnable components in nuclear reactors. Although Zr is a major component in this type of alloys, it is most important to know the phase diagrams of their components as well as possible. Further knowledge on the effect of the alloying elements will allow advancing in the understanding of the microstructure of these alloys, on which mechanical properties and corrosion strongly depend. Besides, the experimental data of the phase diagrams is a prerequisite before modelling by techniques such as the CALPHAD method and inclusion of the binary and ternary systems in thermodynamic databases such as the Zircobase.

The information on the binary and ternary phase diagrams of the main components of the Zirlo type alloys (Fe-Sn-Zr, Fe-Nb-Zr) is still incomplete and, according to many authors, some uncertainties persist. A systematic study should include the study of all binary, ternary and even quaternary metallurgical systems at different temperatures.

The binary phase diagram of the Fe-Zr system has been studied for some time now by several authors. However, in the Fe-rich region the existence of the Fe23Zr6 compound, which was first described in 1962, remains controversial [1-3]. To clarify the origin of this phase, the present work deals with the manufacture and prolonged heat treatments at different temperatures of alloys located in the Fe-rich region of the Fe-Nb-Zr, Fe-Sn-Zr and Fe-Zr phase diagrams. The experiments have been performed with raw materials whose degree of purity was varying. The present phases were identified by using X-ray diffraction (XRD), semi-quantitative microanalysis by using scanning electron microscopy analysis with energy dispersive spectrometry (SEM-EDS) and quantitative microanalysis by using electron microprobe with wavelength dispersive spectrometry (SEM-WDS).

Particularly, in the Fe-rich corner of the Fe-Nb-Zr ternary system the experimental information is scarce. Recently, Liang et al. [3] and Arreguez et al. [4] have studied this region without differentiating the lattice parameters of the (Zr1-xNbx)Fe2, Zr(NbFe)2, and (ZnNb)Fe phases. In the present work SEM-WDS, XRD, synchrotron radiation light source and neutron diffraction techniques were used to find the boundaries of the phases (Zr1-xNbx)Fe2, Zr(NbFe)2 and (ZnNb)Fe with their lattice parameters.

Finally, by using the results of characterization of heat-treated alloys for long annealing times at 800°-900°-1000°-1100°-1200°-1300°C, it is suggested that the presence of the Fe23Zr6 compound is an equilibrium phase of the Fe-Zr binary system, as shown in Fig. 1. Also, by using the results of characterization of heat-treated alloys for long annealing times at different high temperatures and the preliminary results published in previous works [2-4], the phase diagrams sections at 800°-900°-1000°-1200°C and 800°-900°-1100°-1200°C in the Fe rich corner of the Fe-Nb-Zr and Fe-Sn-Zr systems respectively has been constructed.

Figure 1. Proposed phase diagram for the Fe-rich region of the Fe-Zr system.

References

Biographical Note
M.R. Tolosa is a PhD student at Universidad Nacional de Tucumán working on binary and ternary Zr-based alloys with a scholarship from CONICET, Argentina. He has published on the Fe-Nb-Zr and Fe-Sn-Zr phase diagrams. Recently, an investigation on stability of the Fe23Zr6 phase in Zr alloys was sent for publication.
Experimental Investigation and CALPHAD Assessment of the Ti-Al-Mo-V-Cr System Including Metastable Phase \( \omega \)

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**Key words:** Phase diagram thermodynamics; Metastable phase; Crystal structure; Ti-Al-Mo-V-Cr

In view of the lack of the thermodynamic data about the stable and metastable phases of multi-component Ti alloys, the following research work have been carried out by means of experiment-simulation complementary method, coupled key experiments, first-principles calculations and CALPHAD (CALculation of PHase Diagram) approach. (1) The Ti-Mo-V, Ti-Mo-Cr, Ti-V-Cr and Al-Mo-V systems have been optimized and the thermodynamic parameters of the Ti-Al-Cr system have been revised based on the experimental phase equilibria data available in the literature. (2) The isothermal sections of the Ti-Al-Mo-V, Ti-Al-Mo-Cr and Ti-Al-Cr ternary systems at 700 and 800 °C with the composition of 20 at.% Al have been studied by means of X-ray diffraction (XRD), scanning electron microscope (SEM) and electron probe microanalysis (EPMA). (3) Based on the thermodynamic descriptions of constitutive ternary systems as well as the experimental phase equilibria data of the quaternary systems available in the present work, the Ti-Al-Mo-V, Ti-Al-Mo-Cr, Ti-Al-V-Cr and Ti-Mo-V-Cr systems have been evaluated and the Al-Mo-V-Cr system has been extrapolated. The thermodynamic database of the Ti-Al-Mo-V-Cr system has been constructed. The established database was used to describe the solidification behaviors of Ti alloys Ti-5553 (Ti-5Al-5Mo-5V-3Cr, in wt.% ) and B120VCA (Ti-13V-11Cr-3Mo, in wt.%) under Gulliver-Scheil non-equilibrium condition. (4) The energy difference Gm(\(\omega\))−Gm(\(\beta\)) at 0 K has been computed by first-principles calculations. The crystal structure of the metastable \(\omega\) phase has been studied. The \(\beta\)-\(\alpha\)'/\(\alpha\)' martensitic transformation and athermal \(\omega\) formation of the Ti–M (M = Mo, V, Nb, Cr, Al) binary systems at low temperature are thermodynamically described. The metastable phase diagrams of the Ti–M (M = Mo, V, Nb, Cr, Al) systems with \(T_0(\beta/\alpha)\) and \(T_\omega(\beta/\omega)\) curves are calculated by means of the CALPHAD.

The completion of the work provides the key thermodynamic data for the quantitative description of multi-component Ti alloys microstructure evolution and enlarges the application of the CALPHAHD approach.

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**References**


**Biographical Note**

Biao Hu, Ph.D., Associate Professor, Master’s supervisor, graduated from Central South University, China, majored in Materials Physics and Chemistry, now works in Anhui University of Science and Technology, China, main research: phase diagram thermodynamics and dynamics calculations and determination of the nonferrous alloys, such as Ti, Cu, Al alloys.
Experimental Investigation of the NbAl₃-VAl₃ Isopleth

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Key words: Phase diagram, Al-Nb-V system, NbAl₃-VAl₃ isopleth, High-entropy alloys

Since the beginning of the 21st century, a new concept of alloy development has attracted the interest of the scientific community. These are alloys with multi-principal elements, which are known as high-entropy alloys. Considering their potential application at high temperature, refractory metals have been used as constituents of such alloys, known as refractory high entropy alloys. Further development of these alloys considers the addition of aluminum to refractory high-entropy alloys with the objective of reducing their density, a critical point for the aerospace industry. Their application at high temperature requires the knowledge of the equilibrium relations in the binary and ternary subsystems.

In this context, one of the systems of interest is the ternary Al-Nb-V, which has received little attention so far, with only one complete isothermal section published by Raman [1] at 1000 °C. Raman suggested a phase separation between NbAl₃-VAl₃ in spite of their identical crystal structure (TiAl₃-prototype). The investigation of this system was also initiated in the master project of J.C.P. Santos [2], who studied the isothermal section at 1200 °C and conducted a preliminary thermodynamic modeling of the system based on results of microstructural characterization of as-cast and heat treated samples.

The present study aims at the determination of the isopleth NbAl₃-VAl₃ to verify the possibility of complete solid solubility or phase separation in different temperatures. Arc-melted alloys were produced and heat treated at 1200 °C for 10 days, and characterized via X-ray diffractometry (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

The as-cast microstructures suggest complete solubility of Nb and V in the TiAl₃-prototype structure. There are also evidences of this solubility after annealing, as indicated by the tie-lines in Figure 1. However, phase separation at lower temperatures cannot be ruled out. Further experiments are still necessary to evaluate this possibility.

References

Biographical Note
Karoline Elerbrock Borowski is an undergraduate student in Materials Engineering at University of São Paulo - Campus Lorena (EEL-USP). Currently she is working in a research internship project “Experimental investigation of the NbAl₃-VAl₃ isopleth” with financial support from FAPESP (São Paulo State Grand Agency) under supervision of Prof. G.C. Coelho.
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Experimental Investigation and Thermodynamic Description of the Fe–Nd–Pr System

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Key words: Fe–Nd–Pr system, phase relations, differential thermal analysis, CALPHAD method

The high performance Nd–Fe–B based rare-earth permanent magnets have been used more and more with the development of renewable energy industry such as wind-power and electric vehicles [1]. The light rare-earth elements Ce and Pr can be used as the partial substitution of Nd to reduce the cost. The ratio of light rare-earth elements to Nd needs to be controlled to achieve a good magnetic performance [2]. The phase relations of the corresponding system including the Fe–Nd–Pr ternary system are very important to better understand the effect of light rare-earth elements on the magnetic performance of the Nd–Fe–B-based magnets.

So far, no systematic experimental investigation of the Fe–Nd–Pr ternary system was reported. In the present work, the liquidus surface projection was constructed with 53 as-cast alloys by scanning electron microscopy (SEM) equipped with energy dispersion spectroscopy (EDS), X-ray diffraction (XRD) and differential thermal analysis (DTA) methods. The primary solidification regions of bcc(Fe), fcc(Fe), Fe17RE2, (RE=Nd, Pr here after) dhcp(RE) and bcc(RE) were experimental determined. The as-cast alloys with primary phases were illustrated in Figure 1.

The phase relations in the Fe–Nd–Pr system at 973, 873 and 673 K were investigated with 10, 12 and 16 alloys heat-treated at the corresponding constant temperatures, and the corresponding isothermal sections were constructed. At 873 and 673 K, four stable phases, bcc(Fe), Fe17RE2, Fe17Nd2 and dhcp(RE) were found. There is one three-phase region and four two-phase regions at both 673 and 873 K. The solid solubility of Fe in dhcp(RE) and RE in bcc(Fe) are limited, and Fe17Pr2 and Fe17Nd2 form a continuous solution as Fe17RE2. The solid solubility of Pr in Fe17Nd2 is determined as 6.75 at.% at 673 K and 7.96 at.% at 873 K. The two phase region of Fe17Nd2+dhcp(RE) at 933 K was determined.

Based on the experimental results determined in the present work and the thermodynamic description of the Fe–Nd and Fe–Pr system, Gibbs free energies of the phases in the Nd–Pr and Fe–Nd–Pr system were optimized with CALPHAD method. The optimization process was carried out with the software Thermo-Calc. The obtained thermodynamic parameters can well reproduce the experimental data. The calculated liquidus surface projection in comparison with the tested results in the present work are shown in Figure 1.

The primary solidification region of Fe17Nd5 in Figure 1 was optimized based on the thermal analysis of four samples prepared by annealing at 873 K and the isothermal phase relations at different temperature. With the DTA test of the four alloys annealing at 873 K, the isopleth at Fe57.5Nd42.5–Fe72Pr28 were determined. The eutectic reaction liq. → Fe17RE2+Fe17Nd2+dhcp(RE) was also determined to be 953 K by DTA. Within the isopleth, the melting temperature of Fe17Nd5 decreased with the increasing of Pr-content of the alloys. The calculated isopleth of Fe57.5Nd42.5–Fe72Pr28 can well reproduce this tendency.

References


Acknowledgements

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Experimental Determination and Thermodynamic Modeling of the Fe–Mo–Zr System

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Key words: Fe–Zr system, Fe–Mo–Zr system, Phase, CALPHAD

Zirconium alloys are widely used in nuclear industry for their low neutron absorption cross sections, excellent mechanic properties and corrosion resistance [1]. The stainless steel-zirconium alloys are used to dispose the high-level nuclear metallic waste [2]. Thus, it is meaningful to investigate the Fe–Mo–Zr system.

The stability of the Fe<sub>2</sub>Zr<sub>6</sub> phase in Fe–Zr system was controversial in literature. In the present work, the stability of the Fe<sub>2</sub>Zr<sub>6</sub> phase is confirmed and the partial Fe–Zr phase diagram was revised by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), electron probe micro-analyzer (EPMA) and differential thermal analysis (DTA) methods. The Fe<sub>2</sub>Zr<sub>6</sub> phase is measured to be a stoichiometric compound. On the basis of the experimental results in the present work and literature, the Fe–Zr system is reassessed using CALPHAD (CALculation of PHAse Diagram) method. The calculated Fe–Zr phase diagram is shown in Figure 1(a). A satisfactory agreement is obtained between the calculated results and experimental data.

The liquidus surface projection and isothermal section at 1273 K of the Fe–Mo–Zr system were established by experiments in the present work. Eleven primary solidification regions were deduced in the liquidus surface projection, and eight three-phase regions were derived in the isothermal section at 1273 K. No ternary compound was observed. According to the experimental results in the present work, the Fe–Mo–Zr system is modeled. The solution phases, liquid, bcc and fcc, are treated as the substitutional solution. By the sublattice model, and the C14 and C15 phases are treated as (Fe, Mo, Zr)<sub>2</sub>(Fe, Mo, Zr). The models of μ and FeZr<sub>2</sub> phases are (Fe, Mo, Zr)<sub>3</sub>(Mo, Zr)<sub>2</sub>(Fe, Mo, Zr) and (Fe, Mo, Zr)<sub>3</sub>(Mo, Zr) respectively.

The optimization is carried out by means of the module PARROT in the software Thermo-Calc [3], which can handle various kinds of experimental data. The program works by minimizing an error sum where each of the selected data values is given a certain weight. In the assessment procedure, the weight is chosen by personal judgment and changed by trial and error during the work until most of the selected experimental information is reproduced within the expected uncertainty limits. Finally, a set of self-consistent thermodynamic parameters is obtained.

Figure 1(b) shows the calculated isothermal section at 1273 K of the Fe–Mo–Zr system using the present thermodynamic description, which reproduced the experimental results.

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Experimental Phase Equilibria and Thermodynamic Modeling of the Fe-Ni-Ta System

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Key words: Fe-Ni-Ta system, Phase equilibria, CALPHAD

The phase equilibria at 1473 and 1273 K in the Fe–Ni–Ta system were investigated by means of Scanning Electron Microscopy (SEM) with Energy Dispersive Spectrometer (EDS) and X-ray Diffraction (XRD). The experimental results indicated that Fe7Ta6 and Ni7Ta6 formed the continuous solid solution phases (Fe,Ni)7Ta6. The isothermal sections of the Fe–Ta–Ni system at 1473 and 1273 K include the same four three-phase regions, fcc(Fe,Ni) + Ni3Ta + Fe2Ta, Ni3Ta + Ni2Ta + Fe2Ta, (Fe,Ni)7Ta6 + Fe2Ta + Ni2Ta and bcc(Ta) + (Fe,Ni)7Ta6 + NiTa2. In the present work, the three-phase regions Fe2Ta + Ni2Ta + Ni3Ta at 1473 and 1273 K are inferred on basis of the present experimental phase relations. The solubility of Ni in Fe2Ta was about 40.9 at.% at 1473 K and 35.5 at.% at 1273 K, respectively. The solubilities of Fe in Ni3Ta, Ni2Ta and NiTa2 were about 9.6, 4.3 and 11.2 at.% at 1473, respectively. The solubilities of Fe in Ni3Ta, Ni2Ta and NiTa2 were about 7.4, 2.6 and 9.8 at.% at 1273 K, respectively. Based on the experimental results in the present work, the Fe–Ni–Ta system was optimized using CALPHAD technique. A set of self-consistent thermodynamic parameters for the Fe–Ni–Ta system was obtained. As shown in Fig. 1, the experimental isothermal sections at 1473 and 1273 K were reproduced well.

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This work was supported by the National Key R&D Program of China (Grant No. 2017YFB0703001) and National Natural Science Foundation of China (NSFC) (Grant No. 51671025).

Figure 1. Calculated isothermal sections at (a) 1473 K and (b) 1273 K in comparison with the present experimental data.
Estimation of the Solid-liquid Interface Energy of a Multi-component Metallic Alloy Using a Solid/liquid Interface Sublattice Model

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Key words: High entropy alloys, pseudo binary diagram, CALPHAD, Gibbs model

The solid-liquid interface energy is one of the most important material parameters controlling nucleation and growth in the solidifications process of a multi-component alloy. Yet, it is also one of the least known physical properties of the alloys due to the experimental difficulties and the limitations of existing models for the solid-liquid interface energy. In this paper, we proposed a solid/liquid interface sublattice model to consider the rough nature of the solid-liquid interface layer and to quantitatively estimate the coexisting chemical ordering in the solid-liquid interface. By coupling with readily available solution model parameters from CALPHAD technique and the interface sublattice model, we estimated the bond energies between like or dislike atoms occupying the solid and liquid interface sublattices, and formulated the configuration entropy of these atoms in the interface sublattices. The composition- and temperature-dependent solid-liquid interfacial energies of the metallic alloy systems were predicted via a method of a constraint minimization of the interface layer energy. The calculation results validated by the experimental data indicated the proposed solid/liquid interface model not only presents a robust method to estimate the solid-liquid interface energy from a pure to a multicomponent metallic alloy but also sheds light on the intricate interface chemistry in metallic alloy systems.

References

Biographical Note
Dr. Bai Kewu, as a senior research scientist of Institute of High Performance Computing Singapore, have been concentrated on the research of the thermodynamic and kinetic properties of materials using CALPHAD technique and first principles molecular dynamics method.

Figure 1 The predicted and experimental solid-liquid interface energy in Al-based and Ag-based metallic system.
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Experimental and Theoretical Study of the Al–Cu–Zn phase diagram
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Key words: Al-Cu-Zn, phase diagram, experimental investigation, CALPHAD reassessment

The Al–Cu–Zn ternary system has been investigated intensively in the past because of its technical importance for developing of the light-weight alloys. Our work is focused on doubtful regions of the phase diagram which have not yet been satisfactorily resolved in the scientific literature and on the divergent results from the experimental and theoretical publications [1,2]. Our experimental study of the Al–Cu-Zn binary system was mainly focused on a description of the solubility between γ_alCu and γ_CuZn binary brass phases and mutual relation between ternary intermetallic phase τ and τ’. The theoretical part was focused on the CALPHAD reassessment, which includes newly described phases and improvement of the sublattice models of some phases with respect to their crystal structure and solubility.

Samples were prepared from the pure elements (5N) encapsulated in evacuated quartz ampoules and melted in conventional tube furnace. Samples were remelted several times for homogenization. Long term annealing was performed in evacuated quartz glass ampoule. Annealed samples were quenched in water to the room temperature.

A combination of dynamic and static methods was used for the phase diagram investigation. Overall and phase composition of metallographically prepared samples were analyzed by scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM-EDX). X-ray diffraction (XRD) was applied to the structure determination of the intermetallic phases found in studied system. HT-XRD was used for the evaluation of the high temperature phases. Temperatures of phase transitions were measured on high-temperature DTA in evacuated quartz glass DTA ampoules with heating and cooling rate 5 K min⁻¹. Fig. 1 shows the obtained isothermal section at 400°C of the experimental ternary phase diagram.

The ternary phase diagram Al-Cu-Zn was reassessed by CALPHAD-type approach by the ThermoCalc software. The assessment was based mainly on published experimental data [1] and on our new experimental results. With respect to the new experimental results the assessment has slightly changed in comparison with recent work published by Liang [2]. The liquid phase was modeled to obtain better agreement with the experimental results [2]. We used four-sublattice models for γ_alCu and γ_CuZn phases which are based on their structure. The τ’ phase was implemented into the phase diagram with respect to the experimental [2] and our structural results. For the final reassessment, we used the Parrot module of the ThermoCalc software.

Figure 1. Vertical section of Al-Cu-Zn experimental phase diagram at 400 °C

This work was supported by FWF under the Lise-Meitner fellowship M 2293-N34

References

Biographical Note
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The research topics: alloys, experimental description of phase diagrams, CALPHAD modelling.
P71

Experimental and Theoretical Investigation and Critical Assessment of Thermodynamic Data for Pure Tin and Indium from 0K.

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Key words: two state liquid model, extended Einstein model, heat capacity, ab-initio calculations.

Thermodynamic data for crystalline white and grey tin and for indium were assessed using an extended Einstein model from 0K. The liquid phase was described using a two state model. During the assessments careful analysis of the experimental data was carried out. It appeared that, in addition to various contradictions in the data for the liquid phase, which is common for most of the elements, there is also a lack of experimental data for the heat capacity for the white and especially the grey phases of tin. In addition due to a very sluggish transformation between grey and white tin, the data for the enthalpies of transformation had been evaluated through various approximations. For these reasons additional theoretical (ab initio) and experimental investigations were needed for crystalline tin. In case of indium the experimental data appeared to be more complete.

In order to obtain a precise evaluation of $S^\circ_{298}$ it was necessary to make use of a technique involving multiple Einstein functions, which allows the experimental heat capacity and enthalpy data for the solid phase to be approximated accurately from 0K up to the melting point. In the case of the grey-white tin transition this method was also applied to evaluate the enthalpy of transformation and the heat capacity of grey tin at temperatures above 200K. The resulting values are in a good agreement with ab initio data.

Acknowledgement:
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References

Biographical Note
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Figure 1. Calculated heat capacity curve for pure tin [1].
Experimental and Theoretical Study of Ag-Pb-Sn System

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Key words: Ag-Pb-Sn system, CALPHAD assessment, DSC

The Ag-Pb-Sn system was studied in the scope of this work. The detailed knowledge of this system is important for several practical applications. The electronic industry, where the transfer towards the materials for lead-free soldering calls for the knowledge of this system, is one of them. The results of these calculations are of particular interest where lead-free solders replace or are used for repair of conventional Pb-Sn solders. There is a possibility of the newer solders being contaminated by relatively significant amount of lead from existing solder joints and component terminations.

The thermoelectric materials are the other field for practical applications of this system. E.g. PbTe, SnTe, Ag-Pb-Te, are all promising thermoelectric alloys. For further improvement of their properties and understanding of materials microstructural evolution, phase diagrams are very important. Therefore this system will be part of multicomponent thermodynamic database for the multicomponent system Ag-Pb-Sn-Te.

In the scope of the experimental program, the phase equilibria were studied after long term annealing at the temperatures 200-500 °C. The annealing times are selected to be close enough to the thermodynamic equilibrium.

A combination of dynamic and static methods was used for the phase diagram investigation. The morphology, overall and phase compositions of samples were analyzed by scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM-EDX). The diffraction analysis was carried out using X-Ray powder diffraction (XRD) (Scintac, XRD-2000V/H, USA) with Cu- Kα as the lighting source. Temperatures of phase transitions were measured using DSC equipment Netzsch 404 C.

The thermodynamic assessment of the system is based on the binary systems Ag-Pb [1], Ag-Sn [2,3] and Pb-Sn [4] from the database created in the scope of the COST MP0602 Action.

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![Figure 1. The predictions of liquidus projection of the Ag-Pb-Sn system](image)

References


Biographical Note

Adela Zemanova is researcher at Structure of Phases and Thermodynamics Group, Institute of Physics of Materials, The Czech Academy, Brno, working in experimental thermodynamics and CALPHAD calculations of metal systems.
Evaluation of Accurate Interdiffusion Coefficients with Uncertainty Using Home-made Code Diff-calc
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Key words: Interdiffusivity, Uncertainty, Matano method, Distribution function, Diff-calc

Accurate interdiffusivity is the key to fully understand in different materials processes. Boltzmann-Matano and Matano-Kirkaldy methods together with the diffusion couple/multiple technique are commonly used to determine the interdiffusivity in binary and ternary alloys. However, there are still two problems to be solved for accurate interdiffusivities in the target systems. One is the reasonable fitting of the experimental composition-distance profiles, while the other is the quantification of uncertainty for the obtained interdiffusivities.

For the first problem, two of the present authors proposed that the distribution functions can serve as the best fitting function for composition-distance profiles. In this work, based on the distribution functions and the essence of Matano methods, a home-made code named as Diff-calc was developed. In the Diff-calc code, the entire process for calculation of interdiffusivity is automatic if the experimental composition profiles are available.

For the second problem, a general approach for evaluation of uncertainty of interdiffusivity was developed. All the sources of errors, including the experimental measurement by i.e., EPMA, the numerical fitting and the calculation procedure, were considered, and propagated to the final interdiffusivities. Such approach for uncertainty quantification was also incorporated in Diff-calc code.

Finally, the developed Diff-calc code was applied in different true alloys to evaluate their accurate interdiffusivities with uncertainty quantification.

Fig.1. Framewrok of home-made code Diff-calc

References

Biographical Note
Xiaoke Wu is now a Ph.D. candidate at Central South University in China. He is interested in the evaluation of accurate diffusion coefficients in alloys as well as their uncertainty quantification.
Experimental and Computational Study of Phase Equilibria and Diffusion in Fe-Cr-Al-Ni System

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\textbf{Key words}: diffusion couple, steels, phase diagram, thermodynamic modeling

Fabrication of engineering components suitable for high-temperature applications usually involves welding of alloys that differ considerably in composition. At high temperatures, diffusion of alloying elements across the dissimilar welds can occur and result in the formation of deleterious phases. One can investigate the propensity of phase formation in dissimilar welds as a function of time using simulation tools such as DICTRA [1,2], which can help in determining the lifetime of such components. This, however, requires reliable thermodynamic and mobility databases.

Over the decades, increasing demands on high-temperature properties have led to the development of many steel grades with higher Ni content. This means that the thermodynamic and mobility databases traditionally used for doing calculations in iron-base alloys should be augmented to deal with higher Ni content than normal. In the present work, diffusion couple experiments were carried out between several Fe-Cr-Al alloys and Fe-Ni alloys at 800°C to 1000°C, to validate the reliability of appropriate databases from Thermo-Calc Software AB. The Cr and Al contents of terminal Fe-Cr-Al alloys were varied from 16-30 wt% and 2-5 wt%, respectively. The Ni content of Fe-Ni terminal alloys was varied from 15% to 35 wt%.

The phase formation and diffusion profiles of elements across the interface were characterized using Electron Probe Micro Analyser. The results were compared with calculations performed using homogenization model in DICTRA [2]. The microstructure of the diffusion zone for the diffusion couple between Fe-25Cr-9.6Al and Fe-29Ni (mol%) at 950°C/144 h is shown in Figure 1. Experimentally measured and calculated Al diffusion profiles are shown in Figure 2.

\begin{figure}[h]
  \centering
  \includegraphics[width=\textwidth]{figure1.png}
  \caption{Microstructure in the diffusion zone of couple between Fe-25Cr-9.6Al and Fe-29Ni (mol%) at 950°C/144 h}
\end{figure}

\begin{figure}[h]
  \centering
  \includegraphics[width=\textwidth]{figure2.png}
  \caption{Comparison between experimentally measured and calculated Al diffusion profiles corresponding to the couple shown in Figure 1}
\end{figure}

Additionally, phase equilibria studies were performed on three alloys Fe-18Cr-9Ni-3Al, Fe-16Cr-18Ni-5Al and Fe-20Cr-20Ni-5Al (wt%) at 600-1100°C. Differential Scanning Calorimetry was used to determine the dissolution temperatures of B2-NiAl phase in the alloys.

\textbf{References}


\textbf{Biographical Note}

Rohit Ojha is a Metallurgical and Materials Engineer working at Sandvik Materials Technology for 10 years in the field of material characterization and computational thermodynamics. He is currently pursuing Doctoral degree at Indian Institute of Technology Madras, India.
Diffusivities and Atomic Mobilities in FCC Ag–Cu–Mg–Mn Alloys
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Key words: Atomic mobility; fcc Ag–Cu–Mg–Mn alloys; Diffusion couples; Interdiffusion coefficients.

Ag-based alloys with existence of face-centered cubic (fcc) phase have been found to possess high electrical and thermal conductivity, low light absorption. It was reported that addition of Cu, Mg and Mn in Ag-based alloys can increase the strength and resistivity and improve charge mobility of the alloys but decrease its electrical and thermal conductivity [1]. From both practical and scientific points of view, diffusion has attracted much interest in recent years for their applications in multi-component alloy designs. Recently, the diffusion controlled transformation (DICTRA) software program [2], which is operated under the CALPHAD framework has been wildly utilized to study the diffusion behavior in material and predict microstructural evolution. Such a method is focusing on the development of atomic mobilities of target alloys which are then combined with corresponding thermodynamic database to obtain diffusivities that are indispensable for computational kinetic studies.

On the basis of Ag/Ag–Mg and Ag/Ag–Mn semi-infinite diffusion couples, the interdiffusion coefficients in fcc phase of the Ag–Mg, and Ag–Mn alloys were measured at the temperature ranges between 873 and 1173 K by using the Sauer-Freise method [3]. Furthermore, by employing groups of bulk diffusion couples together with electron probe microanalysis technique, the composition dependence of ternary interdiffusion coefficients in Ag-rich fcc Ag–Mg–Mn, Ag–Cu–Mn and Ag–Mg–Cu alloys at 873, 973 and 1073 K were determined via the Whittle and Green method. The experimental interdiffusion coefficients were critically assessed to obtain the atomic mobilities of Ag, Cu and Mg and Mn in fcc Ag–Mg, Ag–Mn, Ag–Mg–Mn, Ag–Cu–Mn and Ag–Mg–Cu alloys by using the DICTRA (Diffusion Controlled TRAnsformations) software package. Finally, the experimental concentration profile in Ag–Cu–Mg–Mn quaternary alloys can be simulated based on available thermodynamic information and obtained mobilities for the fcc Ag–Mg, Ag–Mn, Ag–Mg–Mn, Ag–Cu–Mn and Ag–Mg–Cu systems. Moreover, the simulated results agree in general with experimental data. This work contributes to the establishment of a Ag-based kinetic database for computational design of high thermal and high electrical conductivity silver alloys.

Figure 1. Graphical abstract

Acknowledgment:
The financial supports from the National Key Research and Development Plan (Grant No. 2017YFB0306105) is greatly acknowledged.

References

Biographical Note
Qianhui Min currently a postgraduate in Central South University, Changsha, Hunan province, PR China. main research: Diffusion kinetic on Cu alloys.
P76

**Diffusion Studies of Molten Cu-X (X = Ni, Si) Alloys by \textit{ab initio} Molecular Dynamics Simulation**

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**Key words:** AIMD, diffusion

In this study, \textit{ab initio} molecular dynamics simulation is employed to calculate the self and impurity atomic diffusion coefficients in molten copper alloys. For efficient designing of copper alloys, reliable copper based diffusion database is inevitable. The prime aim of this work is to improve the efficiency of the copper rich alloy diffusion database.

Several studies [1–2] perform an AIMD simulation to calculate the self and impurity atomic diffusion coefficients. The AIMD simulation in this study calculates the self and impurity atomic diffusion coefficients for Cu-X (X=Ni, Si) molten alloys at four different temperatures. VASP 4.6 performs the AIMD simulation and the input is a cubic super-cell of 216 atoms. This cubic super-cell of 216-Cu, 216-Ni and 216-Si atoms represents the pure Cu, Ni and Si in a cubic crystal structure. In a binary alloy, randomly substituting the 216-Cu atoms, with appropriate numbers of Ni and Si atoms results in the Cu-X (X = Ni, Si) alloys of different compositions. This study uses eight different alloy compositions for a particular binary system at a specific temperature. LAMMPS generates the cubic lattice and basis for Cu, Ni, Si and Cu-X (X = Ni, Si) alloys. The set_atom command in LAMMPS generates the binary alloy of different compositions. The ATOMSK converts the LAMMPS (*.cfg) output to VESTA (*.xsf) readable file. The VESTA writes the POSCAR input file for the VASP calculations. The ultra-soft pseudo potentials of Cu, Si and Ni describe the interaction between frozen core (nucleus+ core e−) and the valence e−. The generalized gradient approximation (GGA-PW91) describes the exchange-correlation energy. The energy cutoff used for the plane wave basis set for this simulation is 260 eV. A very fast RMM-DIIS electronic minimization algorithm is used. The Fermi smearing scheme defines the partial occupancy for each orbital and the width of smearing is 0.2 eV. The projection operators are evaluated in the real space. The VASP performs 10,000 (2 fs/step) ionic steps. Within each ionic step it perform 4 electronic-SC loops at four different temperatures. The temperature is controlled by a Nosé-Hoover thermostat. The algorithm of Nosé perform a canonical NVT ensemble simulation.

The simulation temperatures for Cu-Ni system are 1750, 1873, 2073 and 2273 K. For Cu-Si system the simulation temperatures are 1723, 1900, 2100 and 2300 K. These simulation allows to extract activation energies and frequency factors for the temperature dependent diffusion coefficient assuming an Arrhenius type behavior in the liquid. In addition to the temperature dependence, the concentration-dependent impurity diffusion is also analyzed. The experimental measurement of molar volume for the Cu-Ni [3] and Cu-Si [4] system is the input to fix the super-cell volume. The density information for Cu-Ni and Cu-Si alloys from the literature is shown in Figure 1.

![Figure 1. Density of Cu-Ni [3] and Cu-Si [4] system](image)

**References**


**Biographical Note**

Dr. V. B. Rajkumar’s research interest are in computational thermodynamics. This include the experimental and theoretical investigation of phase diagram of the metallic systems, CALPHAD, physics based techniques (\textit{ab initio} calculation, MD and AIMD simulation) assisting CALPHAD modeling, diffusional studies and Phase field simulation.
Diffusion Research on the HCP Mg-Al-Sn Ternary Alloys
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**Key words**: Mg-Al-Sn, diffusion-couple technique, interdiffusion, impurity diffusion

Diffusion behavior in HCP Mg-Al-Sn ternary alloys was investigated at 673K and 723K by the experimental solid-state diffusion couple technique. The extraction of inter- and impurity diffusion coefficients, by the Whittle-Green and generalized Hall methods respectively, enables the diffusion properties of BCC Ti-Al-Nb alloys to be established. The results show that the average values of main interdiffusion coefficient $D_{\text{SnSn}}^{Mg}$ over the compositions is 1.28 times larger than $D_{\text{AlAl}}^{Mg}$ at 673K and 1.47 times at 723K, respectively, suggesting Sn diffuses slightly faster than Al in hcp Mg-Al-Sn alloys. The main interdiffusion coefficients $D_{\text{AlAl}}^{Mg}$ and $D_{\text{SnSn}}^{Mg}$, and the impurity diffusion coefficients $D_{\text{Al(Mg-Sn)}}$ and $D_{\text{Sn(Mg-Al)}}$ all increase with increasing the Al or/and Sn contents. More specific, the Al interdiffusion has strong dependence on the Sn content, however Al has minor effect on the Sn diffusion. The temperature dependence, from 673 K to 723 K, was noticed to be significant.

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**References**


**Biographical Note**

Mr. Zhengfei Zhou is a PhD Candidate enrolled in the College of Materials Science and Engineering, Nanjing Tech University, Nanjing, China. Currently, Mr. Zhou has been working as a research assistant in the Physical Division at The Aragon Materials Science Institute. Mr. Zhou demonstrates in lightweight metallic materials research.

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![Figure 1. The comparison of main interdiffusion coefficients of Al and Sn at 673K and 723K](image-url)
P78

Derivation of the Butler Equation from the Requirement of the Minimum Gibbs Energy and from the Hillert-equation, Taking into Account its Molar Surface Area Dependence by Surficial Concentrations

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Key words: surface tension; surface adsorption; solutions; Gibbs thermodynamics, Butler equation

The need for the new derivation.

The Butler equation (on the equality of the partial surface tensions of the components of a solution) is derived in this poster from the general requirement that in equilibrium the Gibbs energy of the solution phase (taking into account also its surface area) must have a minimum value. This new result was used our already in a previous paper for binary systems. This new derivation can we use for multicomponent solutions.

The Butler-equation in the literature.

Surface tension and surface adsorption are the basic concepts of colloid and surface sciences. The Butler equation is routinely used by many researchers to calculate surface segregation, surface adsorption and surface tension of liquid solutions. The Butler equation was extended to calculate surface phase transition at liquid surfaces and to calculate interfacial composition and interfacial energy of other interfaces, such as liquid/liquid, coherent solid/solid, solid/liquid and grain boundaries. Although the 628 citations received since 1932 is a considerable number (www.google.scholar, March 2018), the acceptance rate of the Butler equation is much below compared to the Gibbs adsorption equation. It is partly due to its cumbersome derivation and partly to the usage of ill-defined partial surface tensions. In our previous article we used the total minimize of the Gibbs-energy by the concentrations in the surface, but it is a difficult way in the following. In this poster the Butler equation will be derived from the requirement of the minimum total Gibbs energy also, but the starting equation come from Hillert, and it is quite simple method for a multicomponent system. On the other hand we don’t have to neglect the concentration dependence of the molar surface. Thus, it will be proven that the Butler equation is in full agreement with thermodynamics of Gibbs for any multicomponent system.

This work was financed by the GINOP 2.3.2 – 15 – 2016 – 00027 project.

References
Development of an Atomic Mobility Database for hcp in the Mg-X (X=Al, Zn, Ca, Sn, Y, Gd) Alloys

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Key words: magnesium alloys, mobility2, diffusion3, CALPHAD4

Magnesium is the lightest structural metal and its alloys have widely potential applications in aerospace, industry and transportation areas [1]. However, these applications are limited due to their poor mechanical properties of Mg and its alloys. A series studies have shown that the addition of rare-earth (RE) elements, such as Yttrium (Y), Gadolinium (Gd), but also some non-RE elements like Al, Sn into Mg and their alloys can help in removing the limitations [2]. The addition of RE elements in magnesium alloys play an important role in texture weakening. The formation of thermally stable precipitates could improve the strength and creep resistance of alloys [3]. Knowledge of both the thermodynamics and diffusion is of vital importance to understand and optimize the precipitation behavior in magnesium alloys. However, there are scarce information on the diffusion of the magnesium alloys.

This work aims to present partial diffusion kinetic database for Mg-X (X=Al, Zn, Ca, Sn, Y, Gd) based on the recently experimental results. On the basis of various critically reviewed experimental diffusivities as well as thermodynamic descriptions, atomic mobilities in hcp Mg-X (X=Al, Zn, Ca, Sn, Y, Gd) alloys were assessed by means of Diffusion Controlled TRAnsformation (DICTRA) software package. The reliability of the obtained atomic mobilities in the present work were verified by the comparisons between the model-predicted interdiffusivities and the measured ones.

Fig. 1 The model predicted (a) impurity diffusion coefficients of Al in hcp Mg as a function of inverse of the absolute temperature, (b) interdiffusion coefficients in the Mg rich solid solution of Mg-Al system at different temperatures as a function of compositions. The solid lines stand for the predictions of this work, which are compared with experimental results.

References

Biographical Note
I am a second-year PhD student from Central South University in China. What I used to do were some work on thermodynamic calculation and the development of diffusion mobility database. Besides, I am eager to do more work on microstructural simulation on precipitation of magnesium alloys in the further study.
Development of an Engineering-type Thermodynamic Database of the Al-Si-Mn-Fe-(Ni-V-Cr) System

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Key words: CALPHAD, Aluminum alloys, DFT calculations, Quasichemical model

Metals used in technological applications are rarely pure; they typically contain 1) alloying elements to tune their thermo-mechanical behavior as well as 2) impurities that can have detrimental effects on the material. For aluminum alloys, the presence of impurities may originate from various sources: from the raw material (such as bauxite which contains iron oxides and silica [1]), from the Bayer’s process (Na₂O), from the consumable carbon anodes of the conventional Hall-Héroult smelting process and even from the inert anodes [2] in future smelting technologies. It is thus of prime importance to understand the specific effect of impurities such as iron, chromium, nickel [3] and vanadium [4] on the energetic behavior of stable and metastable phases that form in conventional Al alloys. We focus our attention here on Al-Mn (3XXX) and Al-Si (4XXX) alloys.

This work aims at improving the actual thermodynamic database of the Al-Si-Mn-(Fe-Cr-Ni-V) system using the CALPHAD approach with a particular attention on the fine-tuning of the energetic behavior of the following solid solution phases: Al₁₃Mn, Al₅Mn, Al₁₃Fe₄, Al₁₃Fe₅, Al₁₃Fe₂Si, Al₁₃Fe₃Si, Al₅Mn₃Si, Al₁₃Mn₄Si₂, Al₁₃Mn₄(Al,Si)₂. To do so the following methodology was applied. Firstly, all Al-based binary, ternary and quaternary subsystems of interest have been critically assessed (i.e. identification of stable and metastable solutions and compounds, extraction of all the experimental data found in the literature and identification of high order composition range for which data are missing). As a result, 8 metallic samples were synthesized with the help of our industrial partner to overcome the lack of thermodynamic data. These samples were used to generate new phase diagram data. The compound energy formalism (CEF) [5] was used to describe the energetic behaviour of all the solid solutions defined previously. Density functional theory (DFT) calculations were also used to parameterize the standard Gibbs energy of some end-members used to define the Gibbs energy of these solid solutions. Finally, the quasichemical model modified in pair approximation (MQMPA) [6] was used for the description of the thermodynamic behavior of the metallic liquid phase. The MQMPA was chosen on the assumption that it would improve the predictive ability in high order system as it considers the potential presence of short-range ordering which will favor (A-A), (B-B) and/or (A-B) pairs.

References

Biographical Note
Myriam Mahfoud completed her bachelor's degree in physical engineering and is currently a research master's student in the chemical engineering department at the École Polytechnique de Montréal (CRCT).
Description of Ordered BCC-B2 Phase in Al-Pd System

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Key words: phase diagram, ordered phase, thermodynamic modelling, aluminum system

The AlPd phase with a wide homogeneity range in Al-Pd system has ordered BCC-B2 (CsCl prototype) structure. Previously the AlPd phase was described with the asymmetrical model (Al%, Pd) (Pd%, Va) in the Al-Pd system [1]. Va represents a vacancy and the symbol % marks the major component in the sublattice.

Extrapolation of the Al-Pd binary system to Al-Pd-Ni and also Al-Pd-Co ternary systems requires compatibility of models in corresponding binary subsystems. Therefore, comparison of the BCC-B2 model in Al-Pd system with model of the phase in Al-Ni [2] and Al-Co [3] systems was done and differences were found.

To ensure the consistency with the descriptions of other binary systems with BCC_B2 phase, the model for order-disorder transition was used and the (Al,Pd, Va) (Al,Pd, Va) symmetrical description for the BCC-B2 phase in Al-Pd system was created. The disordered BCC_A2 phase is not stable in the Al-Pd system, and therefore the BCC_A2 phase cannot be directly assessed. The approach presented by Dupin and Ansara [4] was used as a basis for the assessment. The phase diagram of the system calculated with symmetrical model is shown on Fig.1a.

Figure 1 (a) Al-Pd phase diagram calculated with the symmetrical model of BCC-B2 phase, (b) comparison of Gibbs energy of the symmetrical and asymmetrical model

Preliminary results of extrapolation of the binary system Al-Pd system to the ternary systems are discussed.

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References

Biographical Note
Viera Homolová is a scientist at Institute of Materials Research of Slovak Academy of Sciences since 2000. Her research work is focused on experimental and theoretical study of phase equilibria and phase transformations in various systems and thermodynamic modeling by CALPHAD method.
**P82**

**Design and Discovery of Ceramic Matrix Composites by Assessment of Inverse Phase Stability and Microstructural Evolution**

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**Key words:** phase field, materials design, optimization, CMC, ceramic matrix composites

Advancing the cutting edge of aerospace technology requires the development of more powerful propulsion systems and by extension, structural materials that can reliably perform at the correspondingly more extreme operating conditions. SiC/SiC ceramic matrix composites (CMCs) present an attractive option but maximum operating conditions are plagued by the existence of the relatively low melting point of residual silicon. In this area of research, there is a lack of information at high temperatures for CMCs whether it be in thermodynamic studies, first principles studies or experimental studies.

In order to improve CMCs, we must begin to alloy the systems with metals that can form carbides and silicides. The alloying elements of interest in this study are Hf and Zr. The reason for these materials is that Hf and Zr have low eutectic temperatures that are below the melting temperature of Si and thus through alloying of SiC, will allow us to react with residual Si and form Silicides that allow for higher operating temperatures. The goal of the project is to use thermodynamic information from high throughput CALPHAD assessments in order to help create microstructure evolution simulations of CMCs. Obtaining these assessments will allow us to examine free energies of the systems that will lend itself to a multi-phase field approach that will ultimately result in microstructure evolutions. We are hopeful that these assessments will help to prioritize possible experimental conditions and alloy concentrations that will lead to exciting new materials discoveries.

Utilization of thermodynamic information databases and phase-field methodology will help develop materials that are outside of conventional systems as we look to optimize properties of CMC materials.

When the simulations are complete, we will be verifying or rejecting these results experimentally. We will model the microstructure evolution during reactive phase formation of melt infiltrated SiC/SiC composites in which this information. Thermodynamic characteristics of the Si-C system are going to be explored first in order to lay the ground work for the binary system and allow us to explore the design space of Si-C-X ternary systems. This will allow us to look forward and begin developing a system of Si-C-X ternary systems that can identify promising candidates for new material candidates for use in aerospace.

**Figure 1.** Phase diagrams of Si-C (upper left), Si-Hf (upper right), Si-Zr (bottom left) and optical image of uninfiltrated preform (L) and BSE image of infiltrated sample (R)

**References**


**Biographical Note**

Elias is a third-year materials science engineering student at Texas A&M University. He received his bachelor’s degree in chemistry from The University of Texas-El Paso and received his master’s degree in analytical chemistry from the University of Florida. He is interested in phase field, materials design and optimization and nano-engineering.
Dendritic Growth of Pure and Binary Alloy Using the Phase Field Simulation Associating CALPHAD

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Key words: Phase field simulation, finite difference method, fortran 90

In this work, we present the dendritic solidification microstructure in two dimension for pure Ni, Cu-Ni, and Mo-Ta binary alloys using the phase-field model associating CALPHAD method. The governing equations for the phase field simulation are discretized with the finite difference numerical method. Simple explicit Euler time marching scheme is used for the time evolution of the phase field simulation variables. The governing equations are solved with the fortran 90 code and the representative microstructures are shown in the Figure 1.

The dendritic microstructure simulation of Ni [1] is presented here as a benchmark simulation. The governing equations for the binary alloy are from [2] and these equations were adopted by several researchers [3-4] in their studies. This work also discuss the extension of the methodology to Mo-Ta binary system and the effective usage of CALPHAD method to simulate the microstructure.

References

Biographical Note
Dr. V. B. Rajkumar’s research interest are in computational thermodynamics. This include the experimental and theoretical investigation of phase diagram of the metallic systems, CALPHAD, physics based techniques (ab initio calculation, MD and AIMD simulation) assisting CALPHAD modeling, diffusional studies and Phase field simulation.

Figure 1. Dendritic microstructure of Ni and Cu-Ni alloy
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Constructions of the Database on the Atomic Mobility and Young's Modulus for bcc Ti-rich Ti-Nb-Zr-Cr System

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Key words: Atomic mobility, Young's modulus, Ti–Nb–Zr–Cr system, diffusion couple, CALPHAD

Accurate diffusivities and Young's moduli are essential for the design and production of biomedical alloys with excellent properties. In the present work, ternary and quaternary interdiffusion behaviors in Ti-rich Ti–Nb–Zr, Ti–Nb–Cr, Ti–Zr–Cr and Ti–Nb–Zr–Cr systems at 1273 K were experimentally investigated via the diffusion couple technique. Ternary interdiffusivities of bcc Ti–Nb–Zr and Ti–Nb–Cr alloys were then determined using the Matano–Kirkaldy method while composition-dependent Young's moduli and hardness in bcc Ti-rich Ti–Nb–Zr–Cr system were determined via the nanoindentation technique. Subsequently, on the basis of the presently obtained interdiffusivities together with the diffusivity and mobility parameters of Ti–Nb–Zr–Cr sub-binary and sub-ternary systems and the thermodynamic descriptions for bcc Ti–Nb–Zr–Cr system, the atomic mobilities of Ti, Nb, Zr and Cr in bcc Ti–Nb–Zr–Cr alloys were assessed by means of CALPHAD (CALculation of PHase Diagrams) method [1, 2]. Moreover, the comprehensive comparisons between the experimental diffusion properties of bcc Ti–Nb–Zr, Ti–Nb–Cr, Ti–Zr–Cr and Ti–Nb–Zr–Cr systems (i.e., interdiffusivities, composition profiles, interdiffusion fluxes and diffusion paths) and the calculated/model-predicted data due to the present atomic mobilities were conducted to verify the reliability of the mobilities. In order for the convenience in further analysis, generalized transformation relations among interdiffusivities with different dependent components in multicomponent systems were derived [3]. Finally, the database of Young's modulus in bcc Ti–Nb–Zr–Cr system were established by means of CALPHAD approach, which was mainly based on the presently obtained experimental data. The present database on the atomic mobility and Young's modulus for bcc Ti–Nb–Zr–Cr system can provide the accurate interdiffusivity matrix and variations of Young's modulus over a wide composition range, which can accelerate the design/development of novel bio-Ti alloys.

Figure 1. Interdiffusivity for bcc Ti-rich Ti–Nb–Zr–Cr alloys at 1273 K.

References

Biographical Note
Dr. Weimin Chen is a assistant professor of Jinan University. The current research fields include the diffusion kinetics and the materials design.
ConvTDB: A Tool to Convert TDB Files for Use with FactSage

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Key words: Database Development, Data Management,

In this work, the conversion program ConvTDB is presented that allows for Thermo-Calc, Pandat or OpenCalphad TDB (Thermodynamic DataBase) files to be read and converted into a FactSage Database. Typically, the development of new, multi-component databases for thermodynamic calculations is based on previous assessments.

The major computational software packages for computational thermodynamics have different thermodynamic database concepts. While the advantage of the Thermo-Calc/Pandat/OpenCalphad TDB files lies in the ability to easily manipulate human- and computer-readable text files, the GUI-based FactSage Database concept supplies a more streamlined user interaction, making e.g. the distinction between enthalpy of formation, entropy at 298K and heat capacity easily accessible and allowing the generation of a solution phase description based on stoichiometric compounds using drag and drop, Figure 1.

To facilitate scientific proliferation of information, in recent years e.g. the CALPHAD journal requires each assessment to be accompanied with a digital version of the database to reduce the error-prone and unnecessary step of manual adjustment and copying of the thermodynamic parameters. The global need for a more streamlined and accessible inventory of digital thermodynamic databases has also been behind the foundation of the TDBDB, a repository of TDB databases, that is now usable by FactSage users as well due to ConvTDB.

Furthermore, the converter enables an easier way to compare modeling work across different software frameworks and thus provides a previously unavailable framework of testing.

This work tries to elucidate the differences and similarities in the database structures. Special care is taken to highlight incompatibilities and scientifically relevant assumptions as well as implicit definitions and requirements found in both database formats as a helpful guidance to database developers for both worlds.

The authors believe that its availability is a significant step towards a more coherent world of thermodynamic databases within the scientific CALPHAD community, and beneficial to the joint goal of clear and well-defined datasets.

ConvTDB is available as of now in FactSage7.3 and feedback is greatly appreciated.

Figure 1. Graphical Abstract.

Biographical Note
Florian Tang is a Software Developer with GTT-Technologies, Germany since 2018. Previously he acquired his PhD at RWTH Aachen University under the direct guidance from Bengt Hallstedt about ab-initio guided modeling of high-manganese steels with aluminium, having worked with Thermo-Calc Software.
Defect Structure of the $\alpha$Cr$_5$(Si,B)$_3$ and Cr$_5$(B,Si)$_3$ (T1 and T2) Compounds Using X-ray Synchrotron Diffraction and ab initio Calculations


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Key words: Phase Diagram; Ab-Initio; Density Functional Theory (DFT); X-ray synchrotron diffraction; Cr-Si-B, $\alpha$Cr$_5$Si$_3$ and Cr$_5$B$_3$ compounds

One of the most promising alloy classes for high temperature applications that may complement Ni-based superalloys is that based on binary and ternary systems of refractory metals such as Nb and Mo, often modified with Si and B [1]. These multiphase and multicomponent materials do not have a satisfactory oxidation resistance, but to ensure its structural stability at high temperatures during long service times, coating layers are necessary. Usually, an anti-oxidation layer is applied between the substrate (Nb or Mo alloy) and the Thermal Barrier Coating (TBC). Knowledge of the equilibria involved in these systems is fundamental, since the reactivity between the layers is very sensitive to temperature.

In particular, the Cr-Si-B system is very interesting as a case study for coatings in high temperatures, and a thermodynamic database for this system was already developed by T. F. Villela [2] using the experimental information by V. M. Chad [3]. However, as stated by Villela in his work, the thermodynamic description of the ternary system strongly depends on the thermodynamic model of the T1 and T2 compounds. Since there is a lack of information regarding the enthalpy of formation and defect structure of these two compounds, the objective of the present work was to determine these informations using X-ray synchrotron diffraction and ab-initio calculations, and, ultimately, apply the information using the CALPHAD method in order to obtain a more precise thermodynamic description of the Cr-Si-B ternary system.

A value of -30 kJ/mol and -41 kJ/mol was obtained as enthalpies of formation for the T1 and T2 phases, respectively. As for the defect structure, Villela [2] determined using WDS that the solubility of B and Si in both T1 and T2 phase happen with constant Cr. Moreover, X-ray synchrotron diffraction showed that Si dissolves preferentially in the 4a rather than in the 8h sublattice of the T2 phase, with a difference in the $\chi^2$ of 3.85 to 4.31, while there was no significant difference for the T1 phase.

The same results were confirmed using ab-initio calculations, where the simulated T2 structures with Si in the 4a sublattice in different proportions presented a difference of approximately 20 kJ/mol in the value of the $\Delta_f H$ compared to the 8h position. On the other hand, there was a small difference of 2 kJ/mol using the same methodology dissolving B at different proportions in the 4a and 8h positions in the T1 structure, indicating that B may randomly occupy the 4a and 8h sublattices.

These informations will be incorporated in the thermodynamic description of the Cr-Si-B ternary system, increasing the reliability of the extrapolation for higher-order systems.

Figure 1: X-ray synchrotron diffraction of the Cr20Si17.5B as-cast and heat-treated (1673K for 96h) samples, indicating in the inset the T2 structure, which was analyzed in this sample using the Rietveld method with the Fullprof package.

References


Biographical Note

Thiago Trevizam Dorini is a graduate student in Materials Engineering at University of São Paulo (EEL-USP), with an undergraduate degree at the same university. In 2018, Mr. Dorini was awarded with the Larry Kaufman Scholarship to present orally his latest work in the CALPHAD conference in Mexico.

In addition, Mr. Dorini worked in two articles, the first called "Thermodynamic reassessment of the Ni–In system using ab-initio data for end-member compound energies", published in 2017 in the CALPHAD journal and the second called "Elastic anisotropy and thermal properties of extended linear chain compounds MV$_2$Ga$_4$ (M = Sc, Zr, Hf) from ab-initio calculations" in 2018 in Materialia, alongside his supervisor Prof. Dr. Luiz T. F. Eleno and other co-workers.
Ceramic Filters: Thermodynamic Modelling of Al₂O₃ Based Systems

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Key words: spinel, pseudobrookite, assessment, inversion degree

Presence of non-metallic inclusion is harmful to mechanical properties and long lifetime safety of metallic components. One way to reduce the amount of non-metallic inclusions is melt filtration using ceramic filters. Alumina-based foams with functional coatings are suggested for molten metal filtration.

De-oxidation of molten steel results in formation of nonmetallic inclusions. Aluminum is one of the most common deoxidizers resulting formation of Al₂O₃ inclusions. The source of MgO can be slag or MgO-graphite bricks used as lining refractory. Titanium is an important alloy component in some high-grade steels. The carbon bonded materials based on Al₂O₃ are suggested as foam ceramic filters with functionalized surface. The filter surface can be functionalized by active coating based on the same chemical composition or crystal structure as non-metallic inclusions. The TiO₂ is one of possible inclusions and therefore reactions between TiO₂ and MgAl₂O₄ filter coatings as well as with other inclusions like MgAl₂O₄ or Al₂O₃ are important to understand filtration process. Rutile (TiO₂) coatings deposited on corundum substrates are supposed to filter actively MgAl₂O₄ and Al₂O₃, which are major type of inclusions in aluminum alloy melt. The phase relations in the Al₂O₃-MgO-TiO₂ system are important for modelling filtration of molten steel and Al alloy.

The review of previous investigations of the system was published [1] along with own experimental results. The isothermal sections of the MgO-TiO₂-Al₂O₃ system at 1273-1737 K were constructed based on obtained results [1] which are mainly in agreement with literature data [2-3]. Formation of continuous solid solutions Mg₂TiO₄-MgAl₂O₄ (Spinel, Sp) and Mg₃Ti₂O₆-Al₂TiO₅ (Pseudobrookite, Psbk) at temperature above 1673 K was confirmed. Phase diagram of the Mg₂TiO₄-Al₂TiO₅ join in the temperature range from 1273 to 1553 K appeared to be consistent with data of [3-4] but not with [2]. The solid-state reaction, Psbk s.s. ↔ Al₂O₃ + TiO₂ + Sp s.s., was found at about 1433 K. The eutectic invariant reaction L ↔ MgTiO₃ + Psbk s.s. + Sp. s.s. was detected at 1875 K. Invariant reaction of transitional type L + Al₂O₃ ↔ Sp s.s. + Psbk s.s was observed at 2006 K. Experimental data obtained for the Al₂O₃-MgO-TiO₂ systems were used to derive thermodynamic database. The compound energy formalism was applied to describe solid solutions and two sub-lattice partially ionic liquid model for liquid phase. Special emphasis was to reproduce the degree of inversion in spinel phase changing from inverse Mg₂TiO₄ to normal MgAl₂O₄ and in pseudobrookite phase from normal MgTiO₂ to completely disordered Al₂TiO₅. Correspondently, in accordance with crystal structure data spinel and pseudobrookite solid solutions were described by following formulae, respectively

(Mg²⁺,Ti⁴⁺,Al³⁺)₉(Mg²⁺,Al³⁺,Ti⁴⁺,Va)ₙ(Mg²⁺,Va)ₙ(O²⁻)ₙ
(Mg²⁺,Al³⁺,Ti⁴⁺,Mg²⁺)(O²⁻)ₙ

Calculated isothermal section is presented in Fig. 1.

Figure 1. Calculated isothermal section of the Al₂O₃-MgO-TiO₂ system at 1473 K

References


Biographical Note

Olga Fabrichnaya is a leader of Materials Thermodynamics group in Institute of Materials science at TU Bergakademie Freiberg, Freiberg Germany.
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Updating the Continuous Displacement CVM Free Energy: Proper Handling of the Mechanical Work Term

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Key words: cluster variation method, pressure - volume, stress - strain, unary systems

The pressure – volume term in CD - CVM.

The development of the continuous displacement cluster variation method (CD-CVM) was the last, and more important, contribution of Prof. Ryoichi Kikuchi to Materials Science. The simple idea of allowing the position of the center-of-mass of the atoms to become a variable in the thermodynamic model, by discretizing space close to the position prescribed by the reference lattice, is an elegant way to solve the partition function for a model system in equilibrium with a pressure reservoir, overcoming the limitations of the rigid lattice and/or of the harmonic approximations. By analyzing the original formulation [1], however, we observe that the pressure volume term in the free energy is described as:

\[ PV = PN \left( \frac{2a}{3} \right) \tag{1} \]

where \( a \) is the nearest neighbor distance of a reference FCC cell in the pair approximation (used in this original work). The value of \( a \) is set as a parameter for a given simulation and this could lead to the wrong assumption that the simulation is performed in a constant volume environment. This inconsistency is solved by reminding that in Kikuchi’s original formulation there was a separate minimization step of the free energy with respect of \( a \).

The actual nearest neighbor distance, however, can be easily calculated as a simple positional average of the pair probability distributions, and, more than this, there is nothing to prevent the distribution to drift with respect of the centers of the reference lattice, which sets the discretized regions corresponding to the integration domains (the point distributions are no longer “centered” in the integration domains). This shows that the mechanical work term can be evaluated directly as a function of the pair probability distributions, allowing to perform the minimization of the volume simultaneously with the free energy.

The present work describes how to evaluate the mechanical work term, in a way consistent with the Natural Iteration Method (NIM) [1]. The algorithm is tested by simulating the unary systems Nb, Ti and Zr in the BCC lattice using the pair approximation. As energy model the present work uses the (universal) equation of state suggested by Rose et al. [2].

Figure 1 shows a result obtained in a simulation of the equilibrium lattice parameter of BCC Nb using the new algorithm. Two simulations were performed, in the first the reference lattice parameter is considered constant, corresponding to the equilibrium value for \( T = 1200 \) K, and the temperature is varied either by increasing it or by decreasing it. In the second simulation the reference lattice parameter is also updated as a linear function of temperature (obtained in the first simulation), so that the distributions are kept approximately centered with reference to the integration domains at all temperatures. As observed, the simulations provide identical results (except at very low temperatures, since in these cases the distribution starts to get truncated at the boundaries of the integration domains for the first simulation).

References

Biographical Note
C. G. Schö̈n is professor at the Escola Politécnica da Universidade de São Paulo (Brazil). Obtained his PhD working at the Max-Planck-Institut für Eisenforschung (Düsseldorf, Germany) under supervision of Gerhard Inden. Member of the Brazilian Committee on Materials Phase Diagrams (Brazilian Section of APDIC). The present work was funded by FAPESP under project 2016/25248-3.
CALPHAD in the Cloud with Uncertainty Quantification

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Key words: CALPHAD, Uncertainty Quantification, Bayesian Inference, Thermo-Calc, Web Interface

Chemical thermodynamics form the cornerstone of materials science and engineering, and chemical thermodynamics play a key role throughout the materials design process. Designing new materials using an ICME approach begins with the use of chemical thermodynamics in the form of phase diagrams used to identify material concepts for further exploration. Designing new materials using an ICME approach ends with the use of chemical thermodynamics in the form of numerical process—structure models that enable optimization and sensitivity analysis of a material’s properties with respect to process conditions. Because the ICME design approach is so dependent on chemical thermodynamics, a design is only as good as the thermodynamic data and models upon which the design is based.

QuesTek has proposed to build out an uncertainty quantification/propagation framework to apply to CALPHAD thermodynamic databases with turnkey-ready user interfaces. In this framework, CALPHAD calculations will be performed in the cloud with a web interface. Development and maintenance of the uncertainty information are performed by the cloud host, so that users always have the latest version. Uncertainty quantification is based on the Bayesian theory via Markov Chain Monte Carlo simulations. This procedure is greatly generalized through the usage of Thermo-Calc as the back engine which performs all the CALPHAD calculations. Because of the high speed of Thermo-Calc’s core minimizer functions, the Markov Chain Monte Carlo calculations can be performed on many thermodynamic data for complicated systems.

In this presentation, QuesTek will introduce its technical endeavors ranging from the development of a cloud-based CALPHAD platform to run Thermo-Calc calculations to the establishment of uncertainty quantification algorithms. A quick overview of the workflow of these algorithms is shown in Figure 1. The input data for this model are experimental and/or computational results, which are of the same types for the construction of a thermodynamic database. The input data will be fed into a Markov Chain Monte Carlo algorithm for Bayesian analysis. Distributions of the thermodynamic database parameters will be collected. Eventually, the distribution of these parameters will be propagated to thermodynamic properties of interest, which can be conveniently obtained via the web-based user interface.

Figure 1. General workflow of QuesTek’s Bayesian-based uncertainty quantification framework

Biographical Note
Changning Niu is a Materials Design Engineer at QuesTek Innovations LLC, where he performs modeling and software development for materials design and engineering. He holds a Ph.D. degree in Materials Science and Engineering from North Carolina State University, USA.
**P90**

*Ab initio* Electrochemical Surface Diagrams for Complex Multicomponent Oxides

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**Key words:** electrochemical surface diagram, density-functional theory, complex multicomponent oxides

Feldspars are the most common rock forming minerals in the Earth’s crust. Understanding the properties of the surface of these minerals in an aqueous environment is critical for many natural processes, such as chemical weathering, and thus crucial in the context of geochemistry or climate science.

Focusing on the Ca-rich feldspar anorthite we combine density functional theory calculations with thermodynamic concepts to study the stability of the low index (001) surface of CaAl$_2$Si$_2$O$_8$. Considering relevant oxygen chemical potentials we first construct ternary phase diagrams for this complex four component oxide phase. Utilizing concepts from semiconductor defect chemistry [1] and our recent developments in the area of ab initio electrochemical phase diagrams [2, 3] we discuss the effect an aqueous environment has on the electrochemical stability of anorthite surfaces. Examining how changing Ca-concentrations and environmental pH-values affect the surface stability of anorthite, provides us with direct insights into the weathering behavior and rate of this mineral.

![Figure 1. Ternary surface phase diagram for the anorthite (001) surface, showing that there are 6 stable surface phases (colored areas) in the considered potential energy range. The boundaries for the competing oxide phases are marked by dot-dashed lines.](image)

**References**


**Biographical Note**

Mira Todorova is group leader at the Max-Planck-Institut für Eisenforschung in Düsseldorf/Germany, heading the group “Electrochemistry and Corrosion” in the Computational materials design department of Prof. Jörg Neugebauer.
Assessment of Thermodynamic Properties of CuCrO$_2$ from Calorimetric Measurements

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**Key words:** Delafossite CuCrO$_2$, drop calorimetry, DSC, thermodynamic properties

This work, carried out in cooperation with five laboratories, members of the French Research group TherMatHT (Thermodynamics of Materials at High temperature), reports a collective effort to describe the thermodynamic functions of the Delafossite phase CuCrO$_2$ by experimental methods. Indeed, to the best of our knowledge, this phase is poorly described in the literature, since the heat capacity ($C_p$) is only available in a limited temperature range, close to $T_{Nel} = 24$ K and below 150 K [1]. The other published data concern Gibbs energy of reaction ($\Delta G^\circ$) obtained by solid oxide electrolyte electromotive force method (emf) between 950 and 1350 K [2,3].

CuCrO$_2$ samples were synthesized by solid reaction in a furnace at 1273 K in Ar atmosphere [6] and their purity was checked by XRD, XRF, and EPMA. Heat capacity was measured by Differential Scanning Calorimetry between 298 and 850 K in a stainless steel crucible, and Drop Calorimetry was carried out to measure $H(T)$-$H(298)$ at higher temperature (from 823 to 1123 K).

Based on our measurements and existing data, we propose a full assessment of the thermodynamic functions of CuCrO$_2$: $\Delta H^\circ_{298.15}$, $S^\circ_{298}$ and heat capacity between 298 and 1300 K.

**Acknowledgments**
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Juliano Schorne Pinto is a Ph.D. student at Université de Toulouse and research associate at the CIRIMAT and Laboratoire de Génie Chimique.
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Automated Weighting of Data in CALPHAD – A Comparison between Frequentist and Bayesian Approaches

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Key words: data weighting, frequentist statistics, Bayesian statistics, assessment

The weighting of experimental datasets in the CALculation of PHAses Diagrams (CALPHAD) approach is a critical step in assigning appropriate error budgets and obtaining reasonable predictions. Currently, the assessor assigns weights based on a number of criteria, including the apparent quality of the measurements, thermodynamic consistency, the behavior of similar systems, and expert intuition [1]. This represents a significant effort and is a barrier to the accelerated development of CALPHAD models for new systems. While with current technology these manual procedures are irreplaceable, the burden may be significantly reduced through the introduction of automated weighting schemes. Within the past year, at least two such statistical methods have been independently developed, one frequentist [2] and the other Bayesian [3]. In this work, we describe both techniques and compare their strengths and weaknesses. We then use extensive sets of measurements of the low temperature specific heat and enthalpy of Hf and Al to compare the weights and models resulting from the dual methodologies. Finally, we examine the correlations between the automatically determined weights of both methods and metrics commonly employed by CALPHAD experts to weight datasets.

The frequentist approach to dataset weighting utilizes the prediction error of each dataset as measured via modified K-Fold Cross Validation (KFCV). The weight of each dataset is scaled by the datasets with the highest and lowest prediction errors, respectively. In the Bayesian approach, the dataset weights are included as hyperparameters in the inference. These hyperparameters rescale the assumed errors of each dataset in the likelihood definition. Normalization is then performed to compare these weights to those obtained through the frequentist approach. Figure 1 demonstrates the results of the two methods in the selection of weights and in the prediction of models for the specific heat of the low temperature phase of Hf. Notice that the ranking of measurements by their weights are similar between the two methods. The resulting model predictions are similar as well.

<table>
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<th>Frequentist statistics (low to high)</th>
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</tr>
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</tr>
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<td>63NE 1.000000</td>
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</tbody>
</table>

Figure 1. Schematic illustrating the dataset weights obtained by frequentist and Bayesian statistical methods and the resulting specific heat models.

References


Biographical Note

Noah Paulson is a postdoctoral researcher at Argonne National Laboratory developing reduced-order models and uncertainty quantification approaches for thermodynamic and mechanical properties of industrially relevant materials. Noah received his Ph.D. in Mechanical Engineering from Georgia Tech in 2017.
An Efficient and Versatile Method for Determining Mobility Data

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Key words: mobility, directional solidification, diffusion calculation

We are elaborating a method that drastically reduces the experimental effort for determining concentration and temperature dependent kinetic data of ternary and higher alloys. The method comprises a non-standard directional solidification routine, a diffusion experiment in a temperature gradient and the calculation of mobility parameters by comparing experimental and simulation results by an optimization algorithm. We called this method TEGDI referring to TEtemperature Gradient Diffusion.

Directional solidification and annealing techniques offer the opportunity to generate tunable varying concentration gradients along rod shaped samples. The samples feature a sequence of steep concentration gradients [1] evolving to characteristic concentration profiles during the heat treatment in a temperature gradient (Fig. 1) that are suitable for assessing different atomic mobility parameters in a single experimental run. A special TEGDI furnace was designed and built in which the temperature gradient during the diffusion heat treatment is accurately adjustable and stable over a long time.

For the accompanying calculations of the diffusion processes in the samples, the TEGDI code, a numerical simulation program, was developed that is used to compare theoretical and experimental results. The TEGDI code is applicable to arbitrary initial concentration profiles and temperature distributions. An optimization algorithm adjusts the mobility parameters of the respective alloying elements such that the deviations between experimentally measured and calculated concentration profiles after the diffusion become minimal.

The method has been verified for binary Al-Cu alloys [2] and is currently extended to the determination of individual mobilities during interdiffusion in Al-Cu-Zn alloys (with both Cu and Al as major component).

References

Biographical Note
Hannes Engelhardt studied materials science and engineering at Friedrich-Schiller-Universität Jena (Germany). He worked on the development of novel methods for the determination of thermodynamic and kinetic data of alloys during his PhD time and is currently working in the field of multicomponent diffusion and solidification phenomena.
P94

Alloying Effects on Mechanical and Electronic Properties of Multi-doped TiAl₃: A DFT Study

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Key words: Multi-doped TiAl₃, Ductility, Elastic properties, First-principles calculations, Electronic structure

Titanium aluminide TiAl₃, in stable D₀₂₂ phase, possesses good mechanical properties to be regarded as good candidates for high-strength structural materials. While properties such as high specific strength, corrosion resistance, high melting temperature (1400°C), large Young’s modulus (~220 GPa), low density (3.4 g/cm³) and Vickers microhardness of 4.65-6.70 GPa had been reported, its development and applications had been limited due to its intrinsic brittleness at ambient conditions. In order to improve its ductility to be comparable to its metastable counterpart, L₁₂ phase, several methodologies such as off-stoichiometry composition, doping, vacancy formation, size effect of feature design or extra-electron induced covalent strengthening were investigated in many works. However, the ductility achieved is still not satisfaction. Based on one of our earlier works [1], using DFT calculation and Pugh’s ratio qualitative analysis, we established an improvement in ductility better than L₁₂ phase by introducing group-IV elements as defects into TiAl₃-W alloy system. In fact, we were able to identify TiAl₃-WC with vacancy in a specific location to have a Pugh’s ratio lower than 0.571 [2] (determined empirically between ductile and brittle materials), and qualitatively be regarded as ductile.

In this work, using DFT, group IV dopants are regarded as alloying components instead of defects and their influences on the alloys’ mechanical properties are evaluated. As alloying components, the group IV doped TiAl₃-W systems generally became more brittle than L₁₂ phase. Additionally, ductility is observed to increase with increasing atomic size of group IV dopants, except for element C. Further analysis on the geometrical differences and electronic structure between the two different systems of dopants treatments revealed close correlation of lattice parameters ratio a/b with Pugh’s ratio, and the influences toward the distribution of localized electron charges among the systems.

The theoretical findings from this work will further the advancement of material design in the area of high-strength structural materials such as TiAl₃.

References

Biographical Note
Boon Teoh Tan is currently a PhD candidate in Singapore University of Technology and Design, under the pillar of Engineering Product Development. His work focuses specifically on mechanochemistry effects in metallic/non-metallic interfaces for industrial applications.
Applied CALPHAD Modeling of MX phases in Thermokinetic Simulations towards Predictive Microstructural Modeling of Microalloyed Steels

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Key words: Microalloyed, CALPHAD, Kinetic

Optimization of process development of high strength steels can be supported by thermokinetic simulation of strengthening MX carbonitrides, M being typically represented by Nb, Ti, and V, and X standing for C and N. Accurate thermodynamic description of MX, and associated phase compositions in agreement with experimental results in a multi-component steel setup are crucial for simulative precipitate evolutions during technological heat treatments. Composition-dependent parameters of a thermokinetic precipitation simulation setup and in particular interfacial energies and chemical driving forces are essential as they control nucleation and growth rates of strengthening particles in the steel matrix. Povoden-Karadeniz et al. [1] have presented the sensitivity of applicability of different thermodynamic assessments in a case study of kinetic simulation of NbC-containing microalloyed steels. In the present work, in extension of their study, the thermodynamic MX models involving microalloying elements Nb, V and Ti were re-evaluated in binary and ternary carbonitride systems, and their applicability in thermokinetic precipitation simulation was tested.

Results of this analysis, and our progress of applications of the refined CALPHAD database to grain growth and recrystallization simulations is presented and discussed.

References

Biographical Note
Dr. Aurélie Jacob obtained her PhD in the development of thermodynamic database for high Cr steel in Germany after she finished her studies in France. She is now working as is research assistant at TU Wien since 2016 and as thermodynamic database developer for Matcalc Engineering GmbH. Her research topic is focusing on the thermodynamic modeling for technological applications where CALPHAD in used in kinetic simulation for prediction of precipitation.
P96

Acceleration of Binary and Ternary Complex Equilibrium Calculations for Integration in High Temperature Models

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Key words: Acceleration of equilibrium calculations, High temperature models, High-dimensional phase diagrams, Clifford Algebra, Cayley-Menger determinant

The inclusion of high-temperature multiphase, multicomponent equilibrium (MME) calculations into multiphysics and process models can provide significant insight into a system. Direct integration of MME calculations is in many cases, however, infeasible due extreme computational expense. Acceleration methods have been developed to address this problem. Existing methods only cater for a small number of system components. The extractive metallurgy systems that we work with involve in the range of 10 to 16 system components, which presents us with a 10 to 16-dimensional phase diagram.

Our acceleration method takes advantage of the fact that a phase diagram is a geometrical representation of a thermochemical system. The problem is that for complex systems the phase diagram is composed of hyper-volume phase regions and hyper-surface zero-phase fraction boundaries. In this article, we describe the use of Clifford Algebra to describe high-dimensional phase regions and boundaries and using the Cayley-Menger determinant as a high-dimensional lever rule to determine properties within phase regions.
Additional Constraints and Work Terms in Free Energy Minimisation

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Key words: Free energy minimisation, constraints, reaction rates

The use of Gibbs energy minimising programmes has been extended to novel systems by using additional constraints and by adjusting the data input to include the effects of various kinds of thermodynamic work[1], [2]. The adjustments have been applied via additional components where the component amount and related chemical potential correspond to work co-ordinate and work coefficient pair and in interfacial systems by modified standard state and excess energy expressions. Extending the application of equilibrium solvers enables the examination of new kinds of systems, using existing thermodynamic software and, as far as possible, established data. Requirement here is that the system stoichiometry, and possibly thermodynamic functions, can be defined by the user.

The new energy terms added to computational thermodynamic systems can be associated with e.g. surface energy, membrane equilibrium, or external electric and magnetic fields. The same technique can be used to model the development of systems over time, while observing the stages reached in internal reactions. The method has been shown to be applicable to reactive chemical systems, aqueous pulp suspensions, liquid surface properties and nanoparticle phase transformations.

Reference


Biographical Note

Dr. Risto Pajarre is a Senior Research Scientist at VTT Technical Research Centre of Finland Ltd and specialist in advanced free energy models and their industrial applications.
**P98**

**Ab initio Study of Native Defects in LiTi$_2$O$_4**

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**Key words:** Li ion battery, defect, first-principles calculation, spinel

Lattice defects are commonly in electrode materials and may affect their structural stability and electrochemical behavior. Here we use ab initio calculations based on density functional theory to investigate native cation defects in spinel LiTi$_2$O$_4$, an alternative negative electrode material for lithium ion batteries. We consider vacancies (V$_{Li}$ and V$_{Ti}$), interstitials (I$_{Ti}$ and I$_{Li}$), anti-site defects (Li$_{Ti}$ and Ti$_{Li}$), Frenkel defects and defect pairs of V$_{Li}$-I$_{Ti}$, V$_{Ti}$-I$_{Li}$, V$_{Li}$-V$_{Li}$, and Li$_{Ti}$-Ti$_{Li}$. Our calculations show that Li interstitial, Ti interstitial and Li Frenkel defects are dominant in LiTi$_2$O$_4$ with formation energies are less than 0.5 eV, while cation vacancies and Ti-Frenkel defect are hardly to form due to their high formation energies (larger than 2.0 eV). Surprisingly, the formation energy of Li interstitial (-0.54 eV) is negative, hinting that the initial lithiation process of LiTi$_2$O$_4$ is thermodynamically spontaneous. The much lower formation energy for Li-Frenkel (0.03 eV) suggests that lattice Li are much sensitive to environment and would be unstable when temperature or chemical environment is changed. This can account for the experimental finding that intercalation of additional Li into LiTi$_2$O$_4$ results in migration of lattice Li from 8a to the void 16c sites. Binding energies of defect pairs are calculated to shed light on the clustering of defects. We find V$_{Li}$ prefer to cluster with I$_{Ti}$, V$_{Ti}$ prefer to cluster with I$_{Li}$, and Li$_{Ti}$ prefer to combine with Ti$_{Li}$, but Li vacancies are prone to distribute in the lattice randomly. In addition, we find Li antisite can reduce the migration barrier of Li interstitial significantly. Thus the Li ion diffusion kinetics in LiTi$_2$O$_4$ could be improved by creating small amount of Li$_{Ti}$ antisite.

**Figure 1. The aims of the present research work.**

**Biographical Note**

Jianchuan Wang is now an associated professor of Central South University. He received his PhD degree in 2012 from Central South University. From Jan. 13, 2011 to Jan. 13, 2012, he was a visiting PhD student in the Max Planck Institut für Eisenforschung GmbH, Germany. In 2010, He received Scholarship Award for Excellent Doctoral Student, awarded by the Ministry of Education of China. He focuses research on first-principles calculation, especially on defect properties in energy storage/conversion materials.
Accelerated Design of $\gamma$-TiAl Alloys by High Throughput Calculation

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Key words: $\gamma$-TiAl, High Throughput Calculation (HTC), Alloy Design

The outstanding thermo-physical properties of the $\gamma$-TiAl-based alloys have attracted considerable interest among aerospace, automotive and other applications. The multiphase TiAl-based alloys exhibit low density, promising high temperature strength, and good resistance against oxidation and corrosion when compared to conventional titanium alloys. These alloys consisting of $\gamma$-TiAl (L1$_0$ structure), $\alpha_2$-Ti$_3$Al (D0$_1$9 structure) and $\beta_0$-TiAl (B2 structure), can be used well at temperatures below 750 °C. At higher temperature, $\alpha_2$ phase transforms into disordered $\alpha$-Ti(Al) (A3 structure), $\beta_0$ phase transforms into disordered $\beta$-Ti(Al) (A2 structure) and only the $\gamma$ phase keeps its ordered state until dissolution. Such phase transformations limit their applications as turbine engines used at high temperature and severe environments. For the successful aerospace applications, their temperature capability and property balance need further improvements.

Fig 1. Color map for the fraction of $\gamma$-TiAl phase at 950°C with the variations of Al and Zr content

Comprehensive understanding of the composition-processing-microstructure-property correlation is essential in aiding the selection of suitable alloy compositions and the control of processing conditions. We will demonstrate how to utilize a thermodynamic database developed by the CALPHAD method to aid alloy composition optimization. With the help of high-throughput calculations (HTC), the composition-phase stability relationship can be easily mapped for technically important alloys with variations of different alloy elements as shown in Fig 1. The TNM alloy will be used as an example to demonstrate the alloy design concept and the effect of alloy composition on the hypothetical design requirements will be understood through high throughput calculation (HTC) at numerous alloy compositions.

Biographical Note
Jun Zhu is a principal materials scientist of CompuTherm, LLC focusing on database development.
P100

Interdiffusivities and Atomic Mobilities in FCC Co–Cu–Mn Alloys

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Key words: Atomic mobility; fcc Co-Cu-Mn alloys; Diffusion couples; Interdiffusion coefficients.

The Cu–Mn system is an important basis for the development of the Cu-based high strength and conduction alloys and Mn-based high damping capacity alloys. Co is an important alloy element to improve the properties of the high damping and work ability in the Cu–Mn base alloys [1]. In addition, the Cu–Mn–Co systems is of importance for the development of the Cu–Co base magnetic alloys [2, 3]. From both practical and scientific points of view, diffusion has attracted much interest in recent years for their applications in multi-component alloy designs. Computer simulation gains its importance and effectiveness by casting insight into the complex materials processes. Recently, one software for simulating diffusion-controlled phase transformation in multicomponent systems was developed and named as DICTRA (Diffusion Controlled TRAnsf ormation) [4]. Based on the sharp interface and the local equilibrium hypothesis, DICTRA has been successfully utilized to simulate various phase transformation processes with the so-called atomic mobility database.

The interdiffusion coefficients and atomic mobilities of Co, Cu and Mn in the Co–Cu–Mn ternary system are of both practical and scientific importance.

By employing twelve groups of bulk diffusion couples together with electron probe microanalysis technique, the composition dependence of ternary interdiffusion coefficients in Co-rich fcc Co–Cu–Mn alloys at 1373, 1423 and 1473 K were determined via the Whittle and Green method. The experimental interdiffusion coefficients were critically assessed to obtain the atomic mobilities of Co, Cu and Mn in fcc Co–Cu–Mn alloys by using the DICTRA (Diffusion Controlled TRAnsf ormations) software package. Comprehensive comparisons between the calculated and experimental data show that a good agreement is obtained for diffusivities in ternary Co–Cu–Mn system. In addition, a further verification of the obtained atomic mobilities was carried out through comparing the model-predicted concentration profiles/diffusion paths of all the diffusion couples with the corresponding experimental data. The results indicate that the atomic mobilities can reproduce the experiment data reasonably well. This work contributes to the establishment of a Cu-based kinetic database for computational design of high strength and high electrical conductivity copper alloys.

Figure 1. Graphical abstract

Acknowledgment:
The financial support from National Natural Science Foundation of China (Grant No. 51671219) is greatly acknowledged.

References

Biographical Note
Huixin Liu currently a PH.D student in Central South University, Changsha, Hunan province, PR China. main research: Diffusion kinetic on Cu alloys.
A Novel Strategy to Optimize Atomic Mobility: Application to fcc Cu-Ni-Sn and Ag-Mg-Mn Phases

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Key words: Optimization, Atomic mobility, Sensitivity analysis, Thermal-physical property

The atomic mobility is of fundamental importance in material science, which is the basis of the material diffusion process simulation and kinetic database research. In this work, we analyze the sensitivity of the general model of atomic mobility and diffusivity\cite{1}, and we propose a novel method to optimize the atomic mobility according to the sensitivity characteristics of different parameters. In the mathematical sense, the optimization of the atomic mobility can be attributed to multivariate nonlinear optimization problem. The solution algorithms include the deterministic algorithms and heuristic algorithms. Generally speaking, deterministic algorithms are able to locate the local minimum more efficiently than the heuristic algorithms, i.e., simulated annealing algorithm, because they are able to use more information about the gradient vector and the Hessian matrix. In the process of optimization, the Levenberg-Marquardt method is used firstly, in order to obtain reliable parameter values in the sense of physically meaning, the multi-initial value method and the simulated annealing algorithm are adopted to check again, which can reduce the risk of falling into local extremum and over-fitting. It should be emphasized that the initial values of the parameters to be optimized and the iteration stop criteria are automatically selected. A home-made code is written to implement the algorithm.

This method is suitable for both binary and ternary systems. The atomic mobilities of Cu-Ni-Sn and Ag-Mg-Mn ternary systems are optimized by using the code, and the obtained atomic mobilities and the diffusion behavior based on parameter calculation verify the efficiency of the algorithm by comparing with the experimental data. It is expected that the presently developed algorithm can be generalized to efficiently optimize multi-component atomic mobility and other thermal physical properties such as molar volume, viscosity, etc.

References


Biographical Note

Changfa Du
Ph.D from Central South University in China
Supervisor: Professor Dr. Zhoushun Zheng
Research field:
\begin{itemize}
\item Mathematical modeling and application
\item Numerical method for partial differential equation
\end{itemize}
P102

Predictive Tool on the Equilibrium Combustion Ashes for Adapting Biomass Mixtures to Processes

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**Key words:** K-O, CaO-K2O, biomass, ash

This work is to implement a tool for predicting the behavior of any new used biomass (agricultural waste) or mixture of biomass, during combustion / gasification in a thermochemical process for the production of energy or biofuel. This tool will be based on a thermodynamic equilibrium simulation with a reliable and quality thermodynamic database. In the specific case of biomass burning, this base you can hold up to 20 chemical elements, but the predominant system is the ternary system K\textsubscript{2}O-CaO-\textsubscript{Si}O\textsubscript{2} (> 90% mass of biomass ash). The balance of the ternary system as well as the phases and related compounds are very well known, especially in the field of alkali-rich composition K\textsubscript{2}O for which no experimental data exist. Indeed, it is very difficult to develop and characterize samples in this area because of the high reactivity of alkali oxides with respect to moisture and CO\textsubscript{2} (g) in the ambient air. In addition, K\textsubscript{2}O(s) does not exist commercially and must be synthesized beforehand. The classical approaches encountered in the literature for such a prediction use empirical tools based on the chemical composition of biomass (K: Si ratio for example) by analogy with the criteria of coal [1,2]. These criteria may give some trends, but they fail as soon as the raw material is outside the composition range of the model.

The thermochemical conversion of biomass is a thermal process where it can be reasonable to consider that the thermodynamic equilibrium can be reached because of the high temperatures (800-1000 °C, 1300-1500 °C) and the long dwell times put involved in the processes. This project proposes to predict the behavior of biomass ash using thermodynamic equilibrium calculations. A database of stoichiometric compounds (8-20 elements) is already used in the literature to study the volatilization of inorganic species for coal [3] or biomass [4]. On the other hand, a database comprising the liquid and solid solutions is necessary for the predictions of agglomeration and condensation because they involve liquid phases. Such bases have already been used in the literature for coal but not for biomass [3,4]. Indeed, the major elements of the coal ash (Al, Ca, Fe, Si, Mg) are not the same as for the biomasses (Ca, K, Si, P, Mg) in particular the presence of alkalis (K, Na) significantly increases the amount of liquid phase. This work would propose:

- Synthesis of pure K\textsubscript{2}O + data revision thermodynamic of the K-O system
- Experimental thermodynamic study of the theoretical of the binary phase diagram CaO-K\textsubscript{2}O
- Experimental thermodynamic study of the theoretical of the phase diagram of the CaO-K\textsubscript{2}O-Si\textsubscript{2}O\textsubscript{2} ternary system
- Insertion of thermodynamic data of ternary CaO-K\textsubscript{2}O-Si\textsubscript{2}O\textsubscript{2} in the complete database + application calculations.

In our contribution, we will present first results on the K-O system and selected results in the binary and ternary systems.

**References**

**Biographical Note**
I.Nuta, chemical engineer, is research scientist on thermodynamics of the gaseous phase using Knudsen effusion method coupled with mass spectrometry and calorimetry. Her research activity is about the study of the thermochemical properties of compounds mainly for energy production and storage.
Investigation of Two-dimensional Diffusion and Kirkendall Effect in Single-phase Diffusion Triples

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\textbf{Key words:} Local discontinuous Galerkin (LDG) methods, Two-dimensional homogenization simulations, Diffusion triple, Kirkendall plane, Co-Fe-Ni

A fully discrete local discontinuous Galerkin (LDG) method has been successfully adopted to simulate two-dimensional (2D) homogenization in single-phase diffusion triples controlled by Fick’s laws. Binary Co-Ni and ternary Co-Fe-Ni diffusion triples were fabricated to verify the simulation results at 1473 K. There exists composition gradient on only one direction in areas far away from the triple conjunction of a diffusion triple, which can be efficiently calculated by one-dimensional (1D) sharp-interface diffusion simulations (for example, DICTRA: Diffusion-Controlled TRAnsformation simulation software). However, in the vicinity of triple conjunction (i.e. triple diffusion zone), there are composition gradients in two independent directions, which cannot be handled on this platform. In the present work, the LDG method combining with alloy thermodynamics and diffusion kinetics was demonstrated to tackle this 2D homogenization problem very well and the effectiveness of this method has been proved from a numerical example by realizing it with a standalone C++ code. In addition to the composition and flux evolutions during 2D homogenization processes, one can track the shift of the Kirkendall plane in the 2D single-phase diffusion zone effectively, while the traditional graphic method fails. This standalone code serves as a solid basis to further consider 2D diffusional multi-phase transformations assuming sharp interfaces in between.

![Figure 1. Schematic diagram of diffusion triples A2 and C2. The annealed A1 was made to diffusion triple A2 with another block (Co). The fabrication of C2 was similar to A2.](image)

![Figure 2. (a) Simulated mole fraction (the surface) of Co compared with the EPMA results (the green dots) for Co-Ni triple A2 (homogenized at 1473 K for 121 h for Co-Ni couple A1 and then 3 days for A2). The black dots at the boundary of the surface are the results calculated by 1D simulation software DICTRA. (b) The interdiffusion flux of triple A2. The arrows point to the direction of flux and the lengths of arrows represent the magnitude of the flux. It is a 2D diffusion process in the dashed-line box.](image)

![Figure 3. (a) Moving path of points on the Kirkendall planes of C2 (4 h for Co-Ni couple C1 and then 3 days for C2). Pink points are located on K1 and black points on K2. The blue lines are the moving path of some selected points on K1 and K2.](image)

**References**


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1. Thermodynamic assessment of the Co-Fe-Ni system and atomic mobility of its fcc phase;
2. Adopting a fully discrete local discontinuous Galerkin (LDG) method to simulate two-dimensional (2D) homogenization and Kirkendall effect in single-phase diffusion triples controlled by diffusion process.
Thermodynamic Assessment of Al-Sc-N Ternary System
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Key words: Nitride, First-principles calculation, Piezoelectric material

Aluminum nitride (AlN) is a piezoelectric material which is used in thin film bulk acoustic wave resonators (FBARs) for wireless telecommunication devices. Improvement in the piezoelectric property of AlN is highly desired for future evolution of communication systems. So far, the higher piezoelectric response is reported for Sc-doped AlN solid solutions [1], which is planned to be put into practical use as a frequency filter for the fifth-generation mobile communication systems. The phase equilibria regarding wurtzite phase that correlates with the piezoelectricity, are important to design high performance piezoelectric materials in Al-Sc-N ternary system. However, there are few systematic experimental reports, and thermodynamic database for this system has not been developed yet. In the present study, thermodynamic properties of various nitrides were estimated by first-principles calculations, and results were incorporated into the CALPHAD modelling of the Al-Sc-N ternary system.

We attempted to calculate the Gibbs energy of various nitrides using first-principles calculations and the Debye-Grüneisen model. For wurtzite and rock salt phases, the formation enthalpies in off-stoichiometric compositions were calculated by using supercells constructed by Special Quasi-random Structure (SQS) model. The lattice relaxation and total energy calculations were performed with DFT which is implemented in the Vienna Ab initio Simulation Package (VASP) code [2, 3].

The heat capacities of AlN (wurtzite) and ScN (rock salt) were calculated by the Debye-Grüneisen model and they were relatively in good agreement with experimental results. Figure 1 shows the calculated isothermal section diagram of the Al-Sc-N ternary system at 1273K. The calculated phase diagram is consistent with the experimental phase diagram reported by Schuster et al [4]. Furthermore, phase separation regarding the wurtzite phase was confirmed as a metastable state. Therefore, though the high concentration of Sc dissolved in AlN has been reported in thin film samples, the dissolution behavior of Sc is considered to be different in bulk sample.

Figure 1. The calculated isothermal section diagram of the Al-Sc-N ternary system at 1273K.

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Research topics: CALPHAD, First-principles calculation, Nitrides, Piezoelectric materials.
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Phase Transformations in Inconel 718 Superalloys during Additive Manufacturing

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Key words: Mean-field simulation, Additive manufacturing, Phase transformation, Inconel 718

The mechanical properties of additive manufacturing (AM) components are determined by microstructure evolution during and after the building processes. Ideally, one wants to minimize the efforts of post-heat treatment after the AM building process to achieve the best performance of the AM components, or at least, understand and control microstructure for an effective design during the post-processing steps.

Therefore, phase transformation modeling for the AM melting process becomes essential to a sustainable AM design with reduced costs and development cycles. In this work, a mean-field type of ICME simulation framework is established by coupling the finite element analysis (FEA) and the CALPHAD approach with experimental calibration. The modeling is applied to the phase transformations in Inconel 718 alloys during the powder-bed laser melting process. For the sake of improving modeling accuracy, the experimental continuous cooling transformation (CCT) diagram is directly coupled into the phase transformation modeling. The CCT diagram is determined by employing electron microscopy and quenching dilatometry. The experimental results indicate that the δ phase is the main precipitate phase during the cooling, and the precipitation kinetics are influenced by homogenization steps. The precipitation kinetics of the δ phase determined by experiments support the Johnson-Mehl-Avrami-Kolmogorov (JMAK) model analysis.

In addition, phase transformations at constant cooling rates are simulated using the TC-Prisma module in the Thermo-Calc software package aided by critical phase transformation experiments. The interfacial energies of precipitates are calibrated by fitting the simulations with experimental data and agree with the JMAK model analysis.

This work demonstrates the application of CALPHAD approach in AM modeling, and can assist in process optimization of AM Inconel alloys. The integration of finite element modeling and CALPHAD-based phase transformation provides a guidance to the future simulation of the in-situ laser melting in AM.

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Figure 1. Experimental CCT diagram and simulated phase transformations of Delta phase in additively manufactured Inconel 718 superalloys.

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Phase Equilibria of the Co-Sn-Bi Ternary System

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Key words: Co–Sn–Bi, phase equilibria, Sn–Bi based alloys, x-ray diffraction

The Sn–Bi based systems have been acknowledged as potential candidates for Pb-free solders, owing to their low melting point, relatively high strength and good solderability[1-4]. Co has been acknowledged as a promising alloying element or substrate material for Sn–Bi solders, a more detailed study on the phase equilibrium of the Co–Sn–Bi ternary system is important to gain a better understanding on the interfacial reactions and for developing Sn–Bi based solders. For this purpose, the present work is intended to experimentally determine the isothermal sections of the Co–Sn–Bi ternary system at 250 and 450 °C.

Phase relations of the Co–Sn–Bi ternary system have been studied experimentally for the whole composition range at 250 and 450 °C by means of scanning electron microscopy (SEM) coupled with energy-dispersive spectroscopy (EDS) and x-ray diffraction (XRD). In this work, nine alloys were designed to determine the phase relations of Co–Sn–Bi ternary system at 250 °C, and five alloys were prepared and thermally equilibrated to illustrate the phase relations of the Co–Sn–Bi system at 450°C. The main results are listed below:

1. Two isothermal sections at 250 and 450 °C of the Co–Sn–Bi system are constructed. Five three-phase regions, i.e., (Bi) + (Co) + CoSn₂, (Bi) + CoSn₂ + CoSn, L + CoSn + CoSn₂, L + CoSn + CoSn₃, and L + (Bi) + CoSn have been identified in the Co–Sn–Bi ternary system at 250 °C, while three three-phase regions L + (Co) + CoSn₂, L + CoSn₂ + CoSn, and L + CoSn + CoSn₃ have been determined in the 450 °C isothermal section.

2. The SEM-EDS analysis show that there is almost no solubility of Bi in the (Co) phase, and the maximum solubility of Bi in CoSn₂, CoSn₃ and CoSn₃ are all less than 1 at.%. Meanwhile, the solubility of Bi in CoSn is determined to be 2.7 and 0.4 at.% at 250 and 450 °C, respectively. The maximum solubility of Co in the L phase reaches 1.8 and 1.6 at.% at 250 and 450 °C, respectively.

3. No ternary compound was found in these two temperatures.

Figure 1. Experimentally determined isothermal sections of the Co–Sn–Bi system at 250 °C and 450 °C.

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Phase Transformations in TLPB Process for Inconel-718/Al and Ni/Al

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Key words: Transient Liquid Phase Bonding, INCONEL, SEM/EDS-EBSD, phase transformation

High temperature welds are a complex research field that requires the optimization of bonding process and investigation of phase transformation during its fabrication. Ni based superalloys and AI-Ni intermetallics, belong to those materials which still represent some challenges related to joining process. Inconel 718 is one of the most used superalloy in high temperature environment such as aerospace and power generation industry, due to the combination of solid solution and precipitation strengthening mechanisms. Because of its microstructural complexity, some difficulties arise when they are subject to brazing, fusion welding and diffusion welding techniques. In this context, the transient liquid phase bonding, TLPB, or diffusion brazing is an attractive alternative. TLPB was developed by Paulonis et al. and emerged from those problems during conventional welding processes. TLPB involves four main stages: melting of filler metal, substrate dissolution, isothermal solidification and homogenization if the connexion zone [1]. Although there are several publications on TLPB, fundamental mechanisms of diffusion-reaction processes for commercial alloys, microstructure evolution and the effects of the joining process on technological properties are still unclear. Knowledge of equilibrium phase diagrams, kinetics and diffusion are required to understand phase transformations, thermal stability and phase formation sequence during this process. Recent investigations show that it is feasible to use TLPB to obtain defects-free and reduced thickness joints in superalloys and AI-Ni intermetallics [2-4].

The aim of this work is to study the interconnection zone of Inc718 / Al / Inc718 couples bonded by TLPB at 800-1100°C, focus in the phase stability by means of SEM-EDS/EBSD and in-situ analysis using synchrotron X-ray source. Composition and nano and micro-hardness profiles were obtained. Additionally, phase evolution in the interconnection zone was monitored by changes in layers width and grain size. Cr,Nb,Fe-rich phases were identified next to the base material due to nickel outward diffusion from base metal and a thick AlNi layer and secondary phases in grain boundary towards joint centreline. Spheroidal nano-precipitates were found inside the large AlNi grains.

References

Figure 1. TLPB microstructure of Inc718/Al at 1000°C.

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