Program and Abstracts
Thermo-Calc Software

The output from thermodynamic and kinetic software strongly depend on databases of good quality; therefore, the developments and constructions of thermodynamic and kinetic databases have always been a highly-demanding and challenging task which requires expertise and experience.

The PARROT module in Thermo-Calc is an important, basic and integrated module of both the Thermo-Calc Classic and DICTRA software.

The PARROT module consists of a comprehensive subroutine package for data evaluation of thermodynamic and kinetic model parameters from experimental observations of quantities describing a set of equilibrium states or dynamic processes in various multicomponent heterogeneous interaction systems.

The module is interactively connected with all other basic modules in the Thermo-Calc and DICTRA software.

www.thermocalc.com
CALPHAD XXXIX

Program and Abstracts

Organizing Committee

Byeong-Joo Lee, Pohang University of Science and Technology (POSTECH)
Chang-Seok Oh, Korea Institute of Materials Science (KIMS)
Joonho Lee, Korea University
Jae-Hyeok Shim, Korea Institute of Science and Technology (KIST)
Hyuck Mo Lee, Korea Advanced Institute of Science and Technology (KAIST)

Co-organized by
The Korea Institute of Metals and Materials
Metals Bank, Korea Institute of Materials Science
## Table of Contents

- **Program at a Glance** ................................................................. 4
- **Venue** ..................................................................................... 5
- **General Information** ................................................................. 5
- **Student Fellowships Awardee** .................................................. 6
- **Map of Session Room** ............................................................... 7
- **Official and Social Programs** .................................................... 8
- **Session Program** ..................................................................... 9
- **List of Poster Presentations** ...................................................... 18
- **Abstracts (Oral Presentation)** .................................................. 22
- **Abstracts (Poster Presentation)** ............................................... 102
- **Authors Index** ....................................................................... 154
- **List of Participants** ................................................................. 159
## Program at a Glance

<table>
<thead>
<tr>
<th>May 23 (Sun)</th>
<th>Breakfast</th>
<th>Session 1 (09:30)</th>
<th>Coffee Break</th>
<th>Session 3</th>
<th>Coffee Break</th>
<th>Session 4</th>
<th>Lunch</th>
<th>Welcome Reception</th>
</tr>
</thead>
</table>

**Note:** Times are in 24-hour format.
Venue

Ramada Plaza Jeju Hotel
1255 Samdo2-dong, Jeju City, Jeju 690-032, Korea
Phone: +82 64 729 8100  FAX: +82 64 729 8554
http://www.ramadajeju.co.kr

Transportation
The most convenient public transportation to and from the Jeju International Airport is a taxi service. You may take a taxi at short-distance taxi stand at the front of passenger terminal.
Distance about 4km / taxi fare approx. 3,500 KRW / about 10min.’s ride

General Information

Poster Presentation
The poster will be on display from Monday morning to Wednesday morning in the Halla Hall (8F). Poster size should be less than 90 × 130 cm in either portrait or landscape format. Poster boards and Velcro will be provided. Posters should be mounted on the poster boards no later than 18:00 on Monday and authors are recommended to remove his/her poster before Wednesday noon.

Electricity
The standard voltage is 220 volts and the outlet has two round holes used in many countries.

Internet Service
The internet service will be available in secretary room (Ora Hall) as well as guest rooms.
Student Fellowships Awardee

The following is a list of recipients of student fellowship offered by CALPHAD, Inc.

Ji-Young Noh
Dept. Physics
Sookmyung Women’s University
52 Hyochangwon-gil, Yongsan-gu
Seoul 140-742
KOREA

Arkapol Saengdeejing
Dept. Materials Science & Engineering
The Pennsylvania State University
University Park, PA 16802
USA

Sulata Kumari Sahu
Liquid Metals & Structural Chemistry Division
Indira Gandhi Centre for Atomic Research
Kalpakkam - 603 102
INDIA

K. Santhy
Dept. Metallurgical & Materials Engineering
Indian Institute of Technology Madras
Chennai - 600 036
INDIA

Weihua Sun
State Key Laboratory of Powder Metallurgy
Central South University
Changsha, Hunan 410083
P. R. CHINA

Yinan Zhang
Dept. Mechanical Engineering
Concordia University
Montreal, Quebec, H3G 1M8
CANADA
Map of Session Room

8F
Ramada Plaza Jeju Hotel

- Session room: Tamna Hall
- Posters: Halla Hall
- Internet connections: Ora Hall
- Secretary: Ora Hall
Official and Social Programs

Registration (May 23, 2010)
14:00 to 18:00 Entrance Hall (1F)
After 18:00 (Sun) Lobby (8F)

Welcome Reception (May 23, 2010)
18:30 to 21:00 Banquet Lobby (8F)

Conference Dinner (May 26, 2010)
18:30 to 21:30 Tamna Hall (8F)

General Meal Times
Breakfast 07:00 to 08:00 at restaurant “The Blue” (2F)
Lunch 12:30 to 13:30 at Banquet Lobby (8F)
* 12:10 to 13:00 (Wednesday)
Dinner 18:30 to 20:00 at Banquet Lobby (8F)
Coffee Break 10:10 to 10:40 at Lobby (8F)
15:30 to 16:00 at Lobby (8F)

Conference Excursion
Wed 13:00 to 17:30 Jeju Forkvillage (at Pyoseon Area)

Accompanying Person Program
Mon 10:30 to 17:00 Seongsan Sunrise Park and Boat Trip to Udo
Tue 10:00 to 16:00 Jeju Botanical Garden and O’Sulloc Green Tea Museum
Thu 10:00 to 16:00 Seogwipo Area
Session Program

Day 1 : Monday, May 24
• Session 1 : First principles calculations and cluster variation method
• Session 2 : First principles and atomistic calculations
• Session 3 : CALPHAD approach related to alloy systems – I
• Session 4 : CALPHAD approach related to alloy systems – II

Day 2 : Tuesday, May 25
• Session 5 : Modeling of thermodynamic properties and liquid solutions
• Session 6 : CALPHAD approach related to alloy systems – III
• Session 7 : CALPHAD assessment of non-metallic systems – I
• Session 8 : CALPHAD assessment of non-metallic systems – II

Day 3 : Wednesday, May 26
• Session 9 : Lattice stability / Experiments that need thermodynamic analysis – I
• Session 10 : Experiments that need thermodynamic analysis – II

Day 4 : Thursday, May 27
• Session 11 : CALPHAD approach related to ferrous alloys – I
• Session 12 : CALPHAD approach related to ferrous alloys – II
• Session 13 : Database/Software and CALPHAD assessment of metal-hydrogen system
• Session 14 : CALPHAD approach related to thin films and phase field methods

Day 5 : Friday, May 28
• Session 15 : Phase stability of alloy systems – I
• Session 16 : Phase stability of alloy systems – II
## Monday (Morning), May 24

<table>
<thead>
<tr>
<th>Time</th>
<th>Session 1: First principles calculations and cluster variation method</th>
</tr>
</thead>
<tbody>
<tr>
<td>08:20</td>
<td>Opening and welcome address (Hyuck Mo Lee and Byeong-Joo Lee)</td>
</tr>
<tr>
<td></td>
<td><strong>Session 1</strong>: First principles calculations and cluster variation method</td>
</tr>
<tr>
<td>[O1]</td>
<td>08:30 \textit{Tetsuo Mohri}</td>
</tr>
<tr>
<td></td>
<td>Challenges in the theoretical calculations of phase equilibria and phase transformation by CVM</td>
</tr>
<tr>
<td></td>
<td>Alloying iron aluminides: fundamental investigation of the metastable b.c.c. phase equilibria in systems Fe-Al-M (M = Mo, Nb, Ti)</td>
</tr>
<tr>
<td>[O3]</td>
<td>09:10 \textit{Erwin Hueger, Tomas Kana and Mojmir Sob}</td>
</tr>
<tr>
<td></td>
<td>\textit{Ab-initio} study of blocking of hcp-fcc phase transformation in Pd thin films by domain boundaries</td>
</tr>
<tr>
<td></td>
<td>Stability of Laves phases in the Ta-V system</td>
</tr>
<tr>
<td>[O5]</td>
<td>09:50 \textit{Blazej Grabowski, Lars Ismer, Tilmann Hickel, and Jörg Neugebauer}</td>
</tr>
<tr>
<td></td>
<td>\textit{Ab-initio} concepts for an efficient and accurate determination of thermodynamic properties up to the melting point</td>
</tr>
<tr>
<td>10:10</td>
<td>Coffee Break (30min)</td>
</tr>
</tbody>
</table>

### Session 2: First principles and atomistic calculations

<table>
<thead>
<tr>
<th>Time</th>
<th>Session 2: First principles and atomistic calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td>[O6]</td>
<td>10:40 \textit{Marcel H.F. Sluiter and Emre S. Tasci}</td>
</tr>
<tr>
<td></td>
<td>Liquid structure as a guide for phase stability in the solid state: prediction of stable compounds in the Au-Si and Au-Ge alloy systems</td>
</tr>
<tr>
<td>[O7]</td>
<td>11:00 \textit{Yi Kong and Yong Du}</td>
</tr>
<tr>
<td></td>
<td>Phase stability of Pr-Pt binary system</td>
</tr>
<tr>
<td></td>
<td>First principles concepts to determine the heat capacity of Fe-based alloys</td>
</tr>
<tr>
<td>[O9]</td>
<td>11:40 \textit{George Kaptay}</td>
</tr>
<tr>
<td></td>
<td>Equilibrium in nano-materials with special emphasis to the Al-Ti-C system</td>
</tr>
<tr>
<td>[O10]</td>
<td>12:00 \textit{Byeong-Joo Lee}</td>
</tr>
<tr>
<td></td>
<td>Recent progress in atomistic simulations for nano or nano-structured materials</td>
</tr>
<tr>
<td>12:30</td>
<td>Lunch</td>
</tr>
</tbody>
</table>
### Session 3: CALPHAD approach related to alloy systems - I

**Chair:** Rainer Schmid-Fetzer / Yong Du

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker(s)</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>14:00</td>
<td>Zi-Kui Liu</td>
<td>Building the infrastructure for materials design based on computational thermodynamics</td>
</tr>
<tr>
<td>14:20</td>
<td>Libin Liu, Ligang Zhang, Haiying Qi, Guoxing Huang and Yong Du</td>
<td>Thermodinamic database for Mg based alloy systems</td>
</tr>
<tr>
<td>14:40</td>
<td>Liling Jin, Youn-Bae Kang and Patrice Chartrand</td>
<td>Modeling of thermodynamic properties and phase equilibria in Mg-Al-Mischmetal systems</td>
</tr>
<tr>
<td>15:00</td>
<td>Yinan Zhang, Dmytro Kevorkov, Mamoun Medraj, Jian Li and Elhachmi Essadiqi</td>
<td>Experimental investigation of the Mg-Zn-Ca system via diffusion couples and key experiments</td>
</tr>
<tr>
<td>15:20</td>
<td>M. Medraj, M.N. Khan, M. Aljarrah and J.T. Wood</td>
<td>Investigation of the solidification behavior of commercial Mg alloys through experiments and thermodynamic calculations</td>
</tr>
<tr>
<td>15:40</td>
<td></td>
<td>Coffee Break (30min)</td>
</tr>
</tbody>
</table>

### Session 4: CALPHAD approach related to alloy systems - II

**Chair:** Zi-Kui Liu / Liblin Liu

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker(s)</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>16:10</td>
<td>Artem Kozlov, Joachim Gröbner and Rainer Schmid-Fetzer</td>
<td>What can we learn about the Mg-Si-Sn-(Ca) system from solidification of aluminum alloy W319?</td>
</tr>
<tr>
<td>16:30</td>
<td>Pavel Broz and Jiri Bursik</td>
<td>Theoretical and experimental study of phase equilibria in the Al-Ni-Zn system</td>
</tr>
<tr>
<td>16:50</td>
<td>Erwin Povoden-Karadeniz, Piotr Warczok, P. Lang, A. Falahati and E. Kozeschnik</td>
<td>A thermodynamic model of Guinier-Preston-zones in the Al-Mg-Si system</td>
</tr>
<tr>
<td>17:10</td>
<td>Jean-Claude Crivello, Mauro Palumbo, Taichi Abe and Jean-Marc Joubert</td>
<td>First ab initio calculation of a σ-phase in a ternary system: Cr-Mo-Re</td>
</tr>
<tr>
<td>17:30</td>
<td>Yong Du, Lijun Zhang, Dandan Liu, Senlin Cui, Weibin Zhang, Dongdong Zhao, Honghui Xu and Shuhong Liu</td>
<td>Atomic mobility and diffusivity for fcc phase in Al alloys</td>
</tr>
<tr>
<td>18:30</td>
<td></td>
<td>Dinner</td>
</tr>
<tr>
<td>20:00</td>
<td></td>
<td>Poster Session</td>
</tr>
</tbody>
</table>
**Tuesday (Morning), May 25**

### Session 5: Modeling of thermodynamic properties and liquid solutions
Chair: Jean-Claude Tédnac / Nathalie Dupin

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker(s)</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>08:30</td>
<td>Bo Sundman, Malin Selleby and Mats Hillert</td>
<td>An attempt to correct the quasi-chemical model for liquids</td>
</tr>
<tr>
<td>08:50</td>
<td>Youn-Bae Kang and Arthur D. Pelton</td>
<td>Modeling short-range ordering and clustering in liquid solutions</td>
</tr>
<tr>
<td>09:10</td>
<td>In-Ho Jung and Pierre Hudon</td>
<td>Thermodynamic modeling of phosphate glass system</td>
</tr>
<tr>
<td>09:50</td>
<td>Xiao-Gang Lu</td>
<td>Modeling of thermodynamic and thermophysical properties</td>
</tr>
<tr>
<td>10:10</td>
<td></td>
<td>Coffee Break (30min)</td>
</tr>
</tbody>
</table>

### Session 6: CALPHAD approach related to alloy systems - III
Chair: Bo Sundman / Xiao-Gang Lu

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker(s)</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>10:40</td>
<td>Jean-Claude Tedenac and Catherine Colinet</td>
<td>Phase stability of titanium rich intermetallic phases in the Ti-X (X: Al, Ga, Si, Sn) systems</td>
</tr>
<tr>
<td>11:00</td>
<td>Johan Bratberg, Bo Sundman and Nathalie Dupin</td>
<td>Application of the combined CEF to the description of the σ phase in the Pd-Ta system</td>
</tr>
<tr>
<td>11:20</td>
<td>DongEung Kim, Venkateswara Rao Manga, Shun-Li Shang and Zi-Kui Liu</td>
<td>Thermodynamic modeling of Al-Ni-Pt system using a 4-sublattice model</td>
</tr>
<tr>
<td>11:40</td>
<td>V.M. Chad, F. Ferreira, P.B. Fernandes, G.C. Coelho and C.A. Nunes</td>
<td>Thermodynamic Modeling of the Ta–B System</td>
</tr>
<tr>
<td>12:00</td>
<td>Nathalie Dupin, Christine Guéneau, Chantal Martial, Jean-Christophe Dumas, Christian Chatillon and Bo Sundman</td>
<td>Reassessment of the thermodynamic description of the (U-Pu-C) system</td>
</tr>
<tr>
<td>12:30</td>
<td></td>
<td>Lunch</td>
</tr>
</tbody>
</table>
Tuesday (Afternoon), May 25

Session 7: CALPHAD assessment of non-metallic systems - I
Chair: Patrice Chartrand / In-Ho Jung

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>14:00</td>
<td>Bruno N. Stoco and André Costa e Silva</td>
<td>Estimating viscosities in steelmaking slags with basis on a thermodynamic model-Applications in the CaO-Al₂O₃-MgO-SiO₂ system</td>
</tr>
<tr>
<td>14:20</td>
<td>Hans J. Seifert, Zhu Pan, Olga Fabrichnaya, Roland Neher, Kristina Brandt and Mathias Herrmann</td>
<td>Thermodynamic evaluation of the Si-C-Al-Y-O system and applications for liquid phase sintering of silicon carbide ceramics</td>
</tr>
<tr>
<td>14:40</td>
<td>Sulata Kumari Sahu, C.V. Vishnu Vardhan, Rajesh Ganesan and T. Gnanasekaran</td>
<td>Phase diagram and thermo-chemical studies on Pb-Fe-O system</td>
</tr>
<tr>
<td>15:00</td>
<td>Ming Chen, Christodoulos Chatzichristodoulou, Jacob R. Bowen, and Yi-Lin Liu</td>
<td>Experimental investigations and re-modeling of the LaO₁.₅-MnOₓ-ZrO₂ system</td>
</tr>
<tr>
<td>15:20</td>
<td>Jeroen Heulens, Nele Moelans, Bart Blanpain and Patrick Wollants</td>
<td>Phase field modeling of isothermal crystallization of metallurgical slags using FACT thermodynamic databases for oxide systems</td>
</tr>
</tbody>
</table>

15:40 Coffee Break (30min)

Session 8: CALPHAD assessment of non-metallic systems - II
Chair: André Costa e Silva / Hans J. Seifert

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Title</th>
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</thead>
<tbody>
<tr>
<td>16:30</td>
<td>Wan-Yi Kim, Arthur D. Pelton and Sergei A. Decterov</td>
<td>Extended viscosity model for the glass region of oxides solutions</td>
</tr>
<tr>
<td>16:50</td>
<td>Guillaume Lambotte and Patrice Chartrand</td>
<td>Assessment of the quaternary reciprocal system Al, Na, Si // F, O: a thermodynamic approach to the corrosion of the refractory lining in aluminum electrolysis cell</td>
</tr>
<tr>
<td>17:10</td>
<td>Elizabeth Renaud, Christian Robelin and Patrice Chartrand</td>
<td>Thermodynamic evaluation and optimization of the Na⁺, Ca²⁺, Al³⁺, Fe²⁺, Fe³⁺ // F, O²⁻, Va system</td>
</tr>
<tr>
<td>17:30</td>
<td>Pertti Koukkari, Risto Pajarre and Klaus Hack</td>
<td>Ten years of using advanced Gibbs’ian methods through spreadsheets</td>
</tr>
</tbody>
</table>

18:30 Dinner
20:00 Poster Presentation
### Wednesday (Morning), May 26

<table>
<thead>
<tr>
<th>Time</th>
<th>Session 9: Lattice stability / experiments that need thermodynamic analysis - I</th>
</tr>
</thead>
<tbody>
<tr>
<td>08:30</td>
<td><strong>Larry Kaufman</strong>&lt;br&gt;Third generation of lattice stabilities for metals</td>
</tr>
<tr>
<td>08:50</td>
<td><strong>Mauro Palumbo, Malin Selleby, Bo Sundman, Tilman Hickel and Suzana G. Fries</strong>&lt;br&gt;On the lattice stabilities of pure Cr and pure Fe</td>
</tr>
<tr>
<td>09:10</td>
<td><strong>Kyung-Hun Kim, Jun Ho Bae, Byeong-Chan Suh, Myeong-Shik Shim and Nack J. Kim</strong>&lt;br&gt;Microstructure and texture evolution of twin-roll cast magnesium alloys during thermo-mechanical treatments</td>
</tr>
<tr>
<td>09:40</td>
<td><strong>Nong-Moon Hwang</strong>&lt;br&gt;Diamond deposition with simultaneous graphite etching: Thermodynamic paradox or indication of diamond deposition by gas phase nuclei?</td>
</tr>
<tr>
<td>10:10</td>
<td>Coffee Break (20min)</td>
</tr>
</tbody>
</table>

### Session 10: Experiments that need thermodynamic analysis - II

<table>
<thead>
<tr>
<th>Time</th>
<th>Session 10: Experiments that need thermodynamic analysis - II</th>
</tr>
</thead>
<tbody>
<tr>
<td>10:30</td>
<td><strong>Yong-Su Lee, Jae-Hyeok Shim and Young Whan Cho</strong>&lt;br&gt;Review on available thermodynamic database of complex metal hydrides</td>
</tr>
<tr>
<td>11:00</td>
<td><strong>Moon-Ho Jo</strong>&lt;br&gt;Vectorial growth of VLS semiconductor nanowires: Thermodynamics vs. kinetics</td>
</tr>
<tr>
<td>11:30</td>
<td><strong>Sang Ho Oh</strong>&lt;br&gt;Atomic-scale observations of phase transformations in nano-sized materials: Deviations from the bulk behaviors</td>
</tr>
<tr>
<td>12:10</td>
<td>Lunch</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Time</th>
<th>Conference excursion</th>
</tr>
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<tbody>
<tr>
<td>13:00</td>
<td>Conference excursion</td>
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<tr>
<td>17:30</td>
<td>Conference excursion</td>
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<table>
<thead>
<tr>
<th>Time</th>
<th>Conference excursion</th>
</tr>
</thead>
<tbody>
<tr>
<td>18:30</td>
<td>CALPHAD award ceremony&lt;br&gt;Presentation for the next CALPHAD meeting&lt;br&gt;Conference dinner&lt;br&gt;Korean traditional music performance</td>
</tr>
<tr>
<td>21:30</td>
<td>Conference excursion</td>
</tr>
</tbody>
</table>
### Session 11: CALPHAD approach related to ferrous alloys - I

**Chair:** Qing Chen / Andre Schneider

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker(s)</th>
<th>Topic</th>
</tr>
</thead>
<tbody>
<tr>
<td>08:30</td>
<td>K. Ishida</td>
<td>$\alpha/\gamma$ equilibria and martensitic transformation in Fe-Mn-X(X: $\alpha$ stabilizing element) system</td>
</tr>
<tr>
<td>09:10</td>
<td>Wei Xiong, Malin Selleby, Hualei Zhang and Levente Vitos</td>
<td>Remaining issues in the CALPHAD technique: Illustrations using the Fe-Cr and Fe-Ni binaries</td>
</tr>
<tr>
<td>09:30</td>
<td><em>Ikuo Ohnuma, Shinya Abe, Toshihiro Omori, Ryosuke Kainuma and Kiyohito Ishida</em></td>
<td>Experimental investigation and thermodynamic assessment of the Fe-Si binary system</td>
</tr>
<tr>
<td>09:50</td>
<td><em>Ales Kroupa, Dominik Legut, Jana Pavlu and A. Zemanova</em></td>
<td>The CALPHAD and \textit{ab-initio} modelling of Z-phase in ternary Cr-Nb-N system and advanced steels</td>
</tr>
<tr>
<td>10:10</td>
<td><strong>Coffee Break (30min)</strong></td>
<td></td>
</tr>
</tbody>
</table>

### Session 12: CALPHAD approach related to ferrous alloys - II

**Chair:** K. Ishida / Ales Kroupa

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker(s)</th>
<th>Topic</th>
</tr>
</thead>
<tbody>
<tr>
<td>10:40</td>
<td><em>Philippe Schaffnit, Charles Stallybrass, Joachim Konrad and Axel Kulgemeyer</em></td>
<td>The CALPHAD approach in the development of micro-alloyed steels for line pipe applications</td>
</tr>
<tr>
<td>11:00</td>
<td><em>Qing Chen, Xiao-Gang Lu, Henrik Strandlund and Anders Engström</em></td>
<td>Modeling of metastable phase equilibria and phase transformations in multicomponent steels</td>
</tr>
<tr>
<td>11:20</td>
<td><em>Dong-Kwon Lee, Kyung-Jun Ko, Byeong-Joo Lee, Hyung-Ki Park and Nong-Moon Hwang</em></td>
<td>Monte-Carlo and phase field simulations of abnormal grain growth in Fe-3%Si steel approached by sub-boundary enhanced solid-state wetting</td>
</tr>
<tr>
<td>11:40</td>
<td><em>Chengying Tang, Minmin Tong, Yong Du, Honghui Xu, Joonho Lee, Qingrong Yao and Yuehui He</em></td>
<td>Phase equilibria of the Fe–Ni–Ta system at 1100°C</td>
</tr>
<tr>
<td>12:00</td>
<td><em>Christian Leinenbach, Jiang Wang, Sebastian Buhl and Chunlei Liu</em></td>
<td>Interface reactions of Cu-Sn-Ti based active brazing filler metals with diamond and steel substrate</td>
</tr>
<tr>
<td>12:30</td>
<td><strong>Lunch</strong></td>
<td></td>
</tr>
</tbody>
</table>
### Thursday (Afternoon), May 27

#### Session 13: Database/software and CALPHAD approach related to metal-hydrogen system

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker/Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>14:00</td>
<td>Suzana G. Fries, Mauro Palumbo, Thomas Hammerschmidt and Bo Sundman</td>
</tr>
<tr>
<td></td>
<td>The Sapiens project: a call for creating sustainable thermodynamic databases</td>
</tr>
<tr>
<td>14:20</td>
<td>Aimen Gheribi and Arthur D. Pelton</td>
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<tr>
<td></td>
<td>Identifying optimal conditions for alloy and process design using thermodynamic and properties databases, the FactSage software and the mesh adaptive direct searches algorithm</td>
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<tr>
<td>14:40</td>
<td>Bai Kewu and Wu Ping</td>
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<td></td>
<td>Chemical potential phase diagrams and hydrogen storage thermodynamics</td>
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<tr>
<td>15:00</td>
<td>Ursula R. Kattner</td>
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<tr>
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<td>Thermodynamic databases for metal-hydrogen systems</td>
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<tr>
<td>15:20</td>
<td>Jean-Marc Joubert and Stéphanie Thiébaut</td>
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<td>Thermodynamic optimization of the system Pd-Rh-H-D-T</td>
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</table>

15:50 Coffee Break (30min)

#### Session 14: CALPHAD approach related to thin films and phase field methods

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker/Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>16:20</td>
<td>Bengt Hallstedt</td>
</tr>
<tr>
<td></td>
<td>Prediction of phase formation during thin film deposition by thermodynamic calculation</td>
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<tr>
<td>16:40</td>
<td>S.R. Nishitani, K. Togase, Y. Tokumoto and I. Yonenaga</td>
</tr>
<tr>
<td></td>
<td>Micropipes and surface energy of compound semiconductors</td>
</tr>
<tr>
<td>17:00</td>
<td>M. Kajihara and M. Hashiba</td>
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<tr>
<td></td>
<td>Solid-state reactive diffusion in the Sn/(Pd-Ni) system</td>
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<tr>
<td>17:20</td>
<td>N. Moelans</td>
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<td>Phase field simulations of growth and coarsening in the interdiffusion zone of leadfree solder joints</td>
</tr>
<tr>
<td>17:40</td>
<td>R.P. Shi, C.P. Wang, X.J. Liu and Y. Wang</td>
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<td></td>
<td>Simultaneous mechanisms in the formation of core/shell microstructure</td>
</tr>
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18:30 Dinner
## Friday (Morning), May 28

### Session 15: Phase stability of alloy systems - I

Chair: Hanchul Kim / Ursula R. Kattner

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker(s)</th>
<th>Title</th>
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<tbody>
<tr>
<td>08:30</td>
<td>Marcel H.F. Sluiter</td>
<td>Lattice stability in the presence of interstitial solutes</td>
</tr>
<tr>
<td>08:50</td>
<td>Tilmann Hickel, Ali Al-Zubi, Blazej Grabowski and Jörg Neugebauer</td>
<td>First principles determination of phase transitions in magnetic shape memory alloys</td>
</tr>
<tr>
<td>09:10</td>
<td>K. Santhy and K.C. Hari Kumar</td>
<td>Thermodynamic assessment of Nb-Ni-Ti ternary system by combining first-principles method and CALPHAD approach</td>
</tr>
<tr>
<td>09:30</td>
<td>Arkapol Saengdeejing, James E. Saal and Zi-Kui Liu</td>
<td>First-principles calculations and thermodynamic modeling of the B-C system</td>
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<td>09:50</td>
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<td>Coffee Break (30min)</td>
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</tbody>
</table>

### Session 16: Phase stability of alloy systems - II

Chair: K. Santhy / Arkapol Saengdeejing

(Awardees of the CALPHAD student fellowship)

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker(s)</th>
<th>Title</th>
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<tbody>
<tr>
<td>10:20</td>
<td>Ji-Young Noh and Hanchul Kim</td>
<td>Electronic and elastic properties of (Fe,Mn)\textsubscript{3}AlC studied by density functional theory calculations</td>
</tr>
<tr>
<td>10:40</td>
<td>Jae Hoon Jang, In Gee Kim and H.K.D.H. Bhadeshia</td>
<td>Crystal structure and formation energy of epsilon-carbide</td>
</tr>
<tr>
<td>11:00</td>
<td>X. Tao, P. Jund, C. Colinet and J.C. Tédénac</td>
<td>Phase stability and physical properties of Cr\textsubscript{5}B\textsubscript{3}-type intermetallic compounds from first principles calculations</td>
</tr>
<tr>
<td>11:20</td>
<td>S. Ranganathan</td>
<td>Thermodynamic modelling of the non-equilibrium phase transformation during spontaneous vitrification in Ti-Cr alloys</td>
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<tr>
<td>11:40</td>
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<td>Closing</td>
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<tr>
<td>12:00</td>
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<td>Lunch</td>
</tr>
</tbody>
</table>

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List of Poster Presentations (May 24 and 25)

[P1] Honghui Xu, Biao Hu, Yong Du and Zhanpeng Jin
Phase equilibria of the Ni-Si-Zn system at 600°C

[P2] Li Chen, She Q. Wang, Yong Du, Shu Z. Zhou, Tie Gang, Ji C. Fen, Ke K. Chang, Yi W. Li and Xiang Xiong
Machining performance of Ti-Al-Si-N coated inserts

[P3] Lijun Zhang, Yong Du and Ingo Steinbach
Phase-field simulations of the Ni-Al diffusion couples

[P4] Jianchuan Wang, Yong Du, Honghui Xu, Lixian Sun, Yi Kong, Chao Jiang and Yifang Ouyang
The effect of Ti atom on hydrogenation of Al(111) surface

[P5] Jingrui Zhao, Peisheng Wang, Hailin Chen, Yong Du, Lijun Zhang, Honghui Xu and Shuhong Liu
Experimental investigation and thermodynamic modeling of the Cu-Fe-Mg and Cu-Mg-Si systems

[P6] Weihua Sun, Yong Du, Honghui Xu and Zhaohui Yuan
Experimental investigation and thermodynamic modeling on the Cu-Ni-Si system

Development of the thermodynamic and atomic mobility database for active brazing of diamond to steel substrate

[P8] Adela Zemanova and Ales Kroupa
The experimental and theoretical study of the In-Ni-Sn system

[P9] Luiz T.F. Eleno, Jacques Lacaze and Bo Sundman
Thermodynamic assessment of the aluminum corner of the Al-Fe-M-Si system

[P10] Luiz T.F. Eleno and Cláudio G. Schön
The volume as a new variable in the cluster variation method (CVM)

[P11] Nara M. Guimarães, Danieli A.P. Reis, Carlos de Moura Neto, Gilberto C. Coelho, Daniel S. de Almeida, Francisco Piorino and João M. Kruszy
Experimental investigation of the ZrO$_2$-Y$_2$O$_3$-Nb$_2$O$_5$ system at 1550°C

[P12] Satoshi Iikubo, Keisuke Tomiyasu, Kazumasa Horigane, Kazuyoshi Yamada, Hiroshi Ohtani and Mitsuhiro Hasebe
Neutron diffraction study of FeCr$_2$O$_4$ spinel
[P13] Leszek A. Zabdyr and Grzegorz Garzeł
Assessment of the lead-free solder Bi-Cu-Sn alloy system.

[P14] Nikolai M. Barbin, Dmitry I. Terentiev and Sergei G. Alekseev
Thermodynamic simulation of oxidation of metal powders

First-principles study on Fe substituted Cr23C6

Packing structure and the permeation properties of hydrogen separable membrane in Ni-Al metallic glass

[P17] Jaewon Chang, Sun-kyoung Seo and Hyuck Mo Lee
Experimental investigation of phase equilibria in the Sn-Ni-Zn system

[P18] Hoon-Hwe Cho, Dong-Woo Suh, Jae Kon Lee and Heung Nam Han
Numerical analysis of dilatational anisotropy of layered steel in dilatometry

Experimental investigation and thermodynamic modeling of the Au-Ge-X (X=Cu, Ni) ternary systems

A model and database for the viscosity of molten oxides

[P21] Pertti Koukkari and Risto Pajarre
Use of virtual invariant phases in rate-controlled Gibbs’ian calculations

Stacking fault energy and structure energy difference of semiconductor compounds

[P23] Reza Naraghi and Malin Selleby
Thermodynamic re-assessment of the Iron-Carbon system

[P24] Risto Pajarre, Pertti Koukkari and Toshihiro Tanaka
Modeling the surface tension of reciprocal molten salt mixtures

[P25] Joo Hyun Park
Applications of computational thermodynamics on the phase equilibria of complex oxide systems for slags and inclusions in metallurgical industries

[P26] Ji Hoon Ryu, Hyun You Kim, Da Hye Kim and Hyuck Mo Lee
Amine induced structural change of cubo-octahedral platinum nanocluster and its properties
Prediction of long-term precipitate evolution in austenitic heat-resistant stainless steels

CaTCalc - An advanced software for calculating thermodynamic equilibria and phase diagrams of multicomponent systems

The melting of the silica–encapsulated silver nanoparticles

Local strains in SiGe alloys for the strained silicon

SiC polar surface energy by the first principles calculations

Thermodynamic analysis of phase equilibria in the Fe–Si–W ternary system

Experimental study and thermodynamic modeling of the Bi-Cu-Ni ternary system

Thermodynamic Modeling of the CoO-x-FeO-y system

A design method of Fe-based bulk metallic glass based on phase diagram calculation

Modeling the effect of oxygen adsorption on surface tensions of molten metal alloys

Predicting novel microstructures in polymer blends under two-step quench

Phase diagram calculation of epitaxial Pb(Zr1-xTi_x)O3 thin films at different thicknesses

Thermodynamic modeling of the Sn-U, Sn-Pu, Pb-U and Pb-Pu systems

Fcc-type miscibility gap in some Cu-Ni base alloys at high temperatures

Theoretical derivation of the equation for the exponential temperature dependence of excess Gibbs energy of solutions
[P42] Tran Thai Bao, Joonho Lee and Jung-Goo Lee  
Thermodynamic properties of Sn-Ag nanoparticles

[P43] Taeyoung Kim, Eunju Kim, Joonho Lee and Youn-Bae Kang  
Using CALPHAD thermodynamic data to understand the carbothermic reduction of steelmaking slag by microwave heating

[P44] Roberto R. de Avillez, André Costa e Silva and Raimundo A.F.O. Fortes  
Thermodynamic studies of steelmaking slags with respect to foaming in Electric Arc Furnace

[P45] Ricardo N. Carvalho, Marília M. Lima, Ricardo R. Silva, Cesar A.W. Olea, Marcelo A.C. Ferreira and André Costa e Silva  
Thermodynamic evaluation of the effects of segregation on phase transformations of 13Cr supermartensitic stainless steels

[P46] Heung-Soon Lee and Byeong-Joo Lee  
Formation of Si/Ge bilayer nano-tubes by a self-bending process: A molecular dynamics study

[P47] Daehoon Kang and In-Ho Jung  
Critical thermodynamic evaluation and optimization of the Ag-Zr, Cu-Zr and Ag-Cu-Zr systems and its applications to amorphous Cu-Zr-Ag Alloys

[P48] Je-Wook Jang, Ki-Hyun Kim, Junhyun Kwon and Byeong-Joo Lee  
Effect of stress on self-diffusion in bcc Fe: An atomistic simulation study

[P49] Hyun-Kyu Kim, Won-Seok Ko and Byeong-Joo Lee  
Atomistic modeling for NaCl-type MC carbides in steels

[P50] Tae-Ho Lee, Chang-Seok Oh, Sung-Joon Kim and Eun-Joo Shin  
Experimental determination of stacking fault energy of the 18Cr-10Mn high interstitially alloyed stainless steels

Thermodynamic assessments of the Cu–Ti–Zr system and boundary Cu–Ti, Cu–Zr, and Ti–Zr systems
Abstracts: Oral Presentations, May 24 (Monday)

- Session 1: First principles calculations and cluster variation method
- Session 2: First principles and atomistic calculations
- Session 3: CALPHAD approach related to alloy systems – I
- Session 4: CALPHAD approach related to alloy systems – II
Challenges in the theoretical calculations of phase equilibria and phase transformation by CVM

Tetsuo Mohri

Division of Materials Science and Engineering, Graduate School of Engineering
Hokkaido University, Sapporo 060-8628, Japan

Cluster Variation Method has been recognized as one of the most reliable theoretical tools to investigate alloy phase equilibria. This is due to the capability of incorporating wide range of atomic correlations which play a crucial role in determining phase transition temperature. Recently, the applicability of CVM calculations has been extended in various realms in alloy theory such as configurational kinetics, transformation dynamics and local relaxation phenomena due to atomic displacements.

One of the key tools which should be addressed in these developments is Continuous Displacement Cluster Variation Method (CDCVM). In CDCVM, around each Bravais point, additional points (quasi-lattice point) to which an atom can be displaced are introduced. And the atoms displaced to different quasi lattice points are regarded as different atomic species located at a Bravais lattice point. Then, additional entropy due to the atomic displacements is dealt with as the configurational entropy of a multi component alloy on a non-deformable lattice. In this way, local lattice relaxation effects on phase equilibria are successfully taken into account in the free energy formula. Some of the calculated results are demonstrated and the possible extension to phase equilibria at an interface is discussed.
Alloying iron aluminides: fundamental investigation of the metastable b.c.c. phase equilibria in systems Fe-Al-M (M = Mo, Nb, Ti)

Pablo G. Gonzales-Ormeño, Luiz T. F. Eleno and Cláudio G. Schön

1 Universidad Nacional Tecnológica del Cono Sur de Lima
Sector 3 Grupo 1A 03-Cercado-Villa El Salvador, Lima, Peru
Escola Politécnica da Universidade de São Paulo, v. Prof. Mello Moraes
2463- CEP 05508-900- São Paulo, Brazil

In a recent work by some of the present authors [1] it was speculated that the low Mo solubility in Fe₃Al matrices can be traced back from the interaction of a metastable miscibility gap in b.c.c. Mo-Fe and the first-order A2-B2 (FeAl) metastable equilibria in Mo concentrated compositions. This is in striking contrast with the large Ti solubility in Fe₃Al experimentally observed in the Fe-Al-Ti system, which is supposed to arise from the interaction of a stable B2 phases in the binary sistems Ti-Fe and Fe-Al, which induces a continuous B2 field in the b.c.c. metastable diagram with compositions close to Fe₃AlₓTi₁₋ₓ [2]. This issue is further investigated in the present work via ab-initio calculations in systems Fe-Al-M (M = Mo, Nb, Ti) using the FP-LAPW electronic structure calculations combined with cluster variation method calculations in the irregular tetrahedron approximation. It is shown that system Fe-Al-Nb corresponds to an intermediate case, since the metastable Nb-Fe system has phase separating characteristics at Nb-rich compositions and ordering characteristics at the Fe-rich compositions. The Fe-Al-Ti system is recalculated using ab-initio data for the sake of completion.

Ab-initio study of blocking of hcp-fcc phase transformation in Pd thin films by domain boundaries

Erwin Hueger¹, Tomas Kana²,³ and Mojmir Sob¹,⁴

¹ Institute of Metallurgy, Clausthal University of Technology
   D-38678 Clausthal-Zellerfeld, Germany
² Institute of Physics of Materials, Academy of Sciences of the Czech Republic
   CZ-616 62 Brno, Czech Republic
³ Faculty of Mechanical Engineering, Brno University of Technology
   CZ-616 69 Brno, Czech Republic
⁴ Department of Chemistry, Faculty of Science, Masaryk University
   CZ-611 37 Brno, Czech Republic

Analyzing experimental data and calculating corresponding energy barriers from first principles, we explain the persistence of hexagonal close-packed (hcp) structure in Pd thin films grown on W(001) and Nb(001) substrates. We present a mechanism of phase transformation from a higher-energy hcp Pd structure present in nanograins to the Pd ground-state face-centred cubic (fcc) structure. The behavior of ab initio calculated total energies along possible transformation paths predicts that the hcp Pd structure should already have transformed into the ground-state fcc structure at room temperature. We conclude that it is the orthogonal pattern of rectangular domains in the (11-20)-oriented hcp Pd film, induced by the four-fold symmetry of the substrate surface, which hinders the hcp film phase to convert back to the ground-state fcc phase. Thus, carefully introduced arrangements of structural defects may increase stability of manufactured non-equilibrium phases.
Stability of Laves phases in the Ta-V system

J. Pavlů¹,², J. Vřešťál¹,², X.-Q. Chen³,⁴ and P. Rogl³

¹ Department of Chemistry, Faculty of Science, Masaryk University, Brno, Czech Republic
² Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Brno, Czech Republic
³ Institute of Physical Chemistry, University of Vienna, Vienna, Austria
⁴ Shenyang National Laboratory for Materials Science, Institute of Metal Research Chinese Academy of Sciences, Shenyang, China

TaV₂ is one of the unexpected Laves phases formed by elements of the same group. The phase diagram of the Ta-V system exhibits two polytypes of Laves phases: TaV₂-C14 and C15. At high temperatures, the C14 phase is the equilibrium phase, whereas C15 is stable at lower temperatures, similar to many other systems. However, at zero Kelvin temperature ab initio calculations reveal a stability sequence with C14 as the most stable phase followed by the C36 structure and the C15 type.

In the present contribution, the phenomenon described above is explained on the basis of the differences in the temperature dependence of the heat capacity of the Laves phases at constant pressure and that of the standard element reference structures. The comparison with the published phenomenological assessment [1] and with the experimental data [2] reveals a good agreement between the ab initio calculation based results and the experimental findings.


Acknowledgement: Financial support of Czech Science Foundation by grant No. P108/10/1908, Ministry of Education of the Czech Republic Nos. MSM0021622410, AV0Z20410507 and MEB 060915 in combination with the WTZ CZ/11-2009 is gratefully acknowledged.
Ab initio concepts for an efficient and accurate determination of thermodynamic properties up to the melting point

Blazej Grabowski, Lars Ismer, Tilmann Hickel and Jörg Neugebauer

Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany

Phase diagrams play a crucial role in the thermodynamic evaluation and design of materials. In order to improve the existing description of phase diagrams, additional information on e.g. the volume/pressure dependence of thermodynamic properties, the detailed balance of the various physical excitation mechanisms, and the free energy of unstable phases is desirable. Since an experimental approach to this information is partly not even feasible, the interest in ab initio based methods, in particular density functional theory (DFT), has been recently re-intensified. While in principle ideally suited to tackle such basic questions, the actual application of DFT faces two key challenges: 1) Are the present days exchange-correlation functionals sufficient to guarantee the desired accuracy in the free energy? 2) Are the available statistical methods efficient enough to enable a DFT based calculation of all relevant free energy contributions up to the melting point?

To address these two questions, we have performed a systematic DFT study of thermodynamic properties for a wide range of metals up to the melting point [1,2]. Two popular exchange-correlation functionals (LDA and GGA-PBE) have been considered and the quasiharmonic approximation (full volume/pressure dependence), including the electronic contribution as well as the first-order electron-phonon coupling, has been used. Besides the comparison of the thermal expansion, heat capacity, or the temperature dependent bulk modulus with experimental data, we also compared directly the constant pressure DFT free energies. The results showed over a large temperature range a very good agreement with CALPHAD data.

For the specific case of aluminum, we extended the study beyond the quasiharmonic approximation including the explicitly anharmonic vibrations and the anharmonic vacancy contribution (both fully temperature and volume dependent). To master the challenge of calculating the computationally highly expensive anharmonic free energy, we have developed a hierarchical scheme to coarse grain the configurations space, which allows reducing the error in the ensemble average to < 1meV/atom [3]. Including all these excitation mechanisms, we were able to tackle the long standing debate about the dominating physical mechanisms determining the isobaric heat capacity of aluminum close to the melting point [3].

Liquid structure as a guide for phase stability in the solid state:  
Prediction of stable compounds in the Au-Si and Au-Ge alloy systems

Marcel H.F. Sluiter¹ and Emre S. Tasci²

¹ Department of Materials Science & Engineering, Delft University of Technology  
Mekelweg 2, 2628CD Delft, the Netherlands  
² Fisica de la Materia Condensada, Universidad del Pais Vasco  
Apartado 644, 48080 Bilbao, Spain

There is an ongoing challenge to truly predict the stable structure of a compound. Among the many approaches to this problem (for a recent comprehensive review see Woodley and Catlow [1]), we can mention the Data Mining Structure Predictor combining data-mining with first-principles calculations by Fischer et al. [2] and evolutionary or genetic algorithms coupled with first-principles calculations such as proposed by Oganov and Glass [3] and d’Avezac and Zunger [4]. For certain alloy systems, such as those that form Zintl phases [5] there is a well-documented relationship between local atomic structure in the solid crystalline state and in the liquid state. In the case of eutectic Au-Si and Au-Ge alloys there are no extreme changes in the density upon solidification, such as for example in the case of pure Si [6]. Therefore, one might suspect that atomic coordination in the liquid phase and in the crystal phase are similar. Thus, we use the known coordination number distribution in the liquid phase as a criterion for selecting prototype crystal structures. For Au₈₀Si₂₀ and Au₇₁Ge₂₉ we predict the existence of stable compounds.

Phase stability of Pr-Pt binary system

Yi Kong$^{1,2}$ and Yong Du$^{1,2}$

1 State Key Laboratory of Powder Metallurgy, Central South University
Changsha 410083, PR China
2 Science Center for Phase Diagrams & Materials Design and Manufacture, Central South University
Changsha 410083, PR China

We present first-principles calculations on the phase stability of the Pr-Pt binary system at finite temperatures. Firstly, crystal structures and enthalpy of formation at zero temperature of five compounds in the Pr-Pt system are calculated from first-principles calculations, and compared with available experimental data. Secondly, mechanical properties, such as elastic constants and bulk modulus, of these compounds are calculated within elastic theory. Finally, in order to study the phase stability at finite temperatures, frequencies of lattice vibration are calculated and then combined with thermal excited electrons to obtain free energy at different temperatures for Pr$_3$Pt$_4$, PrPt$_2$, and LT-PrPt compounds. The comparison of the free energies of these three compounds shows that about 6 kJ/mol heat of formation is released during the experimentally observed decomposition of Pr$_3$Pt$_4$ into PrPt$_2$ and LT-PrPt compounds.

Acknowledgement: The financial support from the National Natural Science Foundation of China (Grant Nos. 50801069 and 50721003) is greatly acknowledged.
First principles concepts to determine the heat capacity of Fe-based alloys

F. Körmann, A. Dick, T. Hickel and J. Neugebauer
Max-Planck-Institut für Eisenforschung GmbH, 40074 Düsseldorf, Germany

The iron-carbon phase diagram plays an important role in the thermodynamic evaluation of steels and other Fe-based alloys. Besides the ferrite and the austenite, in particular cementite (Fe₃C) is a decisive ingredient for a CALPHAD simulation of this system. Since the experimental data for the heat capacity $C_p$ of cementite are not conclusive, the temperature dependence of the heat capacity is approximated by a constant in traditional CALPHAD evaluations [1]. The huge progress in the field of first principles modeling of thermodynamic properties achieved over the last years opens nowadays new routes to determine heat capacities without experimental input. Such first principles approaches are based on density functional theory. Combining these approaches with statistical concepts allows to compute thermodynamic quantities such as e.g. free energies, thermal expansion coefficients, equilibrium point defect concentrations of crystalline bulk materials up to the melting temperature [2]. For Fe-based alloys the incorporation of magnetic excitations is a particular challenge in this context [3].

In this talk we discuss our recently developed concepts to capture the relevant physical mechanisms contributing to the heat capacity such as vibronic, electronic, and magnetic effects in iron and cementite. A particular focus will be on the magnetic entropy of these alloys. To capture these contributions an effective nearest-neighbor Heisenberg model is constructed. For the solution of this model the numerically exact Quantum Monte Carlo method is employed. Using the example of ferrite, we demonstrate the excellent performance of our theoretical approach below as well as above the Curie temperature. The subsequent application to the heat capacity of cementite [4] shows again a very good agreement with the experimental data and allows an evaluation of their temperature dependence. This example nicely shows how first principles concepts can contribute to a refinement of CALPHAD-derived phase diagrams of Fe-based alloys.

Equilibrium in nano-materials with special emphasis to the Al-Ti-C system

George Kaptay

BAY-NANO Institute for Nanotechnology, University of Miskolc
3515 Hungary, Miskolc, Egyetemvaros, E/7

Equilibrium in nano-materials is different from the equilibrium of microscopic or macroscopic materials. This is partly because a significant ratio of atoms/molecules is positioned at interfaces and partly due to the curvature of the nano-phases.

Formally, the molar Gibbs energy of a nano-phase differs from that of a macro-phase by a \( p_L \cdot V_m \)-term, with \( V_m \) = molar volume of the nano-phase and \( p_L \) = the Laplace pressure, being proportional to the surface energy and the curvature of the nano-phase. However, the problem of nano-materials equilibrium is much more complicated than just an additional term in the molar Gibbs energy. In this talk the following sub-problems will be discussed:

- the phase rule for nano-systems is different from that for the macro-systems,
- the total Gibbs energy of a nano-system depends on the relative arrangement and morphology of the phases, and thus the equilibrium state will also depend on arrangement and morphology of phases,
- the surface energy itself is size-dependent,
- the surface energies of two, close interfaces depend on their separation,
- segregation should be taken into account into material balance equations (i.e. segregation in nano-phases might be different from that of a macro-phase).

An example on the Al-Ti-C system will be presented.

Acknowledgement: The support of NAP-NANO and CK-OTKA-NKTH, Hungary, is truly acknowledged.
Recent progress in atomistic simulations for nano or nano-structured materials

Byeong-Joo Lee

Department of Materials Science and Engineering
Pohang University of Science and Technology (POSTECH), Pohang 790-784, Korea

Atomistic simulations such as molecular statics (MS), molecular dynamics (MD) and Monte Carlo (MC) simulations are used to understand the materials behaviour in more fundamental level, e.g. the atomic level. MD simulations have been performed to investigate dynamic behaviour of materials during structural evolution. However, their applicability has been limited only to pure elements or simple alloy systems. This was because the empirical interatomic potentials necessary for the simulations were available only for a limited range of materials systems. Further, the materials phenomena that could be investigated using the MD simulations were highly limited because of the short simulation time.

In the present talk, it will be emphasized that recent progresses in interatomic potential modelling extended the materials systems into a wider range including multicomponent carbide, nitride systems as well as various semiconducting systems. A MS+MC or MS+MC+MD hybrid simulation that overcomes the time limitation of MD simulations and enabled a correct examination of the effect of alloying elements on materials behaviour will be introduced. How the atomistic simulation techniques can be used for analysis of atomic structural evolution in nano or nano-scaled materials will also be introduced.
Building the infrastructure for materials design based on computational thermodynamics

Zi-Kui Liu

Department of Materials Science and Engineering, The Pennsylvania State University
University Park, PA, 16802, USA

The building blocks of engineering materials are individual phases. Their spatial distributions compose microstructures which dictate materials properties and performances. Therefore, the foundational information for materials design is the properties of individual phases as a function of temperature, pressure, composition, and other environmental conditions. The CALPHAD modeling provides such an approach in building those information databases from pure elements to multi-component engineering materials and acts as the foundation for the materials research paradigm driven by computation [1]. With the incorporation of data from first-principles calculations, the robustness and predictability of CALPHAD modeling have been significantly enhanced [2]. Furthermore, based on the tremendous amount of information from first-principles calculations, not only for stable phases, but more importantly also for metastable and in some cases unstable phases, we have further ventured into activities in creating an infrastructure in building information databases covering all experimental, first-principles, estimated, and evaluated data [3]. In this presentation, our approaches will be discussed.

Thermodynamic database for Mg based alloy systems

Libin Liu¹, Ligang Zhang¹, Haiying Qi¹, Guoxing Huang¹ and Yong Du²

¹ School of Materials Science and Engineering, Central South University
² Research Institute of Powder Metallurgy, Central South University
Changsha Hunan 410083, P.R.China

Magnesium alloys are potential candidates for the structural, automotive and aerospace applications due to their low density, high specific strength, and good castability, etc [1]. However, some shortcomings such as limited creep and corrosion resistance at elevated temperatures have prevented Mg-based alloys from gaining more applications. Alloying are found to be effective method capable of improving the mechanical properties and corrosion resistance for magnesium alloys [2-3], while accurate phase diagram and thermodynamic properties should be of helpful. A high precision thermodynamic description of the multi-component Mg systems has been creating via thermodynamic modeling and experiment. The database for Mg-based alloy systems contains at least the following 23 components: Mg-Ag-Al-Ca-Ce-Cu-Fe-Gd-K-La-Li-Mn-Na-Nd-Ni-Pr-Si-Sn-Sr-Th-Y-Zn-Zr. This database shall consist of a core database of 11 important elements, where all binary, all ternary Mg-X-Y, as well as selected quaternary and quinary systems will be accurately described. In the present report, the recent progress of this task has been summarized.

Modeling of thermodynamic properties and phase equilibria in Mg-Al-Mischmetal systems

Liling Jin, Youn-Bae Kang and Patrice Chartrand

1 Center for Research in Computational Thermochemistry (CRCT), Dept. of Chemical Engineering
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Mg–based alloys and Al-based alloys with rare earth metals show several interesting applications in the automotive and aeronautical industries because of their low density and potentially high strength/weight ratios. The aim of current study is to optimize thermodynamic properties and phase diagrams of Al-RE (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu), Mg-Al-RE (La, Ce, Pr and Nd) systems and Al-RE’-RE” (Al-La-Ce, Al-La-Pr, Al-La-Nd, Al-Ce-Pr, Al-Ce-Nd, and Al-Nd-Pr) and to build a thermodynamic database concerning Mg, Al and RE, which will guide the magnesium and aluminum alloys design. Optimized model parameters of the Gibbs energies for all phases in these systems have been obtained. The optimization procedure are bias by putting a strong emphasis on the observed trends in the thermodynamic properties of Al–RE, Al-Mg-RE, Al-RE’-RE” systems, like enthalpy of formation, enthalpy of mixing. The Modified Quasichemical Model [1], which takes short–range ordering into account, is used for the liquid and the Compound Energy Formalism is used for the solid solutions in the binary systems. Diffusion couple experiments are carried out for Mg-Al-(Ce, La, Nd) systems in order to validate the modeling parameters. Furthermore, first-principles calculations using VASP and ABINIT software are performed for the partial enthalpies of mixing in the Al-(Ce, La, Pr, Nd) binary systems and the Al-Mg-(Ce, La, Pr, Nd) ternary systems (Supercell method) and enthalpies of formation for the metastable intermetallic compounds.

Experimental investigation of the Mg-Zn-Ca system via diffusion couples and key experiments

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Mg alloys have attracted significant attention as the lightest commonly used structural alloys for aerospace and automotive industries. In the present study, nine diffusion couples and thirty-six key samples were prepared to map the phase diagram of the Mg-Zn-Ca ternary system. The isothermal section at 335°C has been constructed. Four ternary phases and their complete homogeneity ranges have been studied. The microstructure, layer thickness, phase compositions and homogeneity ranges have been analyzed using EPMA. X-ray diffraction has been used for the phase analysis and solubility limit determination. FIB-TEM has been used to lift out the ternary single phase and to identify the crystal structure. The crystallographic information of the new ternary phases and the interdiffusion coefficients at the interfaces for this ternary system are still underway. The details of these studies will be discussed during this conference.
Investigation of the solidification behavior of commercial Mg alloys through experiments and thermodynamic calculations

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Solidification behavior of three commercial magnesium alloys (AZ91D, AM60B, and AE44) has been studied using experimental analysis and thermodynamic calculations. Solidification curves at different cooling rates have been drawn from the experimental data using heat transfer model (HTM). Using mutlicomponent thermodynamic database, solidification curves have been calculated at equilibrium and Scheil conditions. Further, phase distributions, volume fraction of the phases and phase formation sequences have been calculated and analyzed. Differential Scanning Calorimetry (DSC) has been used to obtain the thermo-physical properties such as transition temperatures and solidification enthalpies at different cooling rates. For all the studied alloys, it is apparent that cooling rate has very little effect on liquidus temperature. However, solidus temperature somewhat decreases with increasing cooling rate. The latent heat of solidification increases significantly with increasing cooling rate. Based on the experimental data obtained in this work, analytical models relating transition temperatures and latent heat of solidification with cooling rate have been developed.
What can we learn about the Mg-Si-Sn-(Ca) system from solidification of aluminum alloy W319?

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Tin is inevitable as a tramp element in recycled aluminum alloys. This is of commercial importance since low Sn levels are more costly. Recent studies reveal a significant impact of Sn content on solidification characteristics and mechanical properties of as-cast and heat treated aluminum alloy W319 [1]. It was found that modeling the role of Sn during solidification is essentially limited by the modeling depth of current thermodynamic databases. This emanates from a combination of two factors: (i) Most major databases focus on the composition range close to the base element, such as Al in this case, generally sufficient for equilibrium calculations limited to that range. (ii) Strongly segregating components, such as Sn, may accumulate in the residual liquid from an initial 0.1% to more than 50%. Local equilibrium calculations, crucial for the Scheil model, are prone to complete failure in that range [2]. These studies indicated the key role of a quantitative modeling of the Mg-Si-Sn system to understand the final stage of solidification in a typical W319 alloy, Al-7.5Si-3.5Cu-0.3Mg-0.1Sn (wt.%). The results of combined experimental work and thermodynamic modeling are presented here for Mg-Si-Sn and also for the quaternary Mg-Ca-Si-Sn system, which is also relevant for advanced magnesium alloys.

Theoretical and experimental study of phase equilibria in the Al-Ni-Zn system

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The knowledge on the thermodynamic behavior of the Al–Ni–Zn system is useful from the point of view of lead-free soldering. Preliminary thermodynamic prediction of phase equilibria for this system may be performed on the base of existing assessments for binary subsystems [1-3]. Only limited knowledge on liquidus surface for zinc-rich part of the system [4] and phase equilibria at 850°C for nickel-rich part [5] can be found in the literature. This work is focused on microstructure and phase transformation study of the Al–Ni–Zn system as the base for thermodynamic description of phase equilibria, which has not been performed yet. Differential scanning calorimetry was used for specification of temperature regions for long term annealing of prepared samples and for determination of temperatures of phase transformations. The microstructure was studied and quantified mostly by means of scanning electron microscopy. Thermodynamic modeling and phase diagram calculations were performed using software package ThermoCalc.


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A thermodynamic model of Guinier-Preston-zones in the Al-Mg-Si system

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Precipitation hardening in Al-Mg-Si alloys is of great importance for the development of heat-treatable materials with outstanding mechanical properties. In particular metastable low-temperature precipitates govern the mechanical properties of these materials. Thermodynamic modeling of these metastable phases is demanding due to lack of experimental equilibrium data.

General agreement exists that the sequence of metastable precipitates in 6016 Al-Mg-Si alloy during continuous heating after previous solution treatment and quenching can be simplified as solute clusters $\rightarrow$ GP(Guinier-Preston)-zones $\rightarrow$ $\beta''$ $\rightarrow$ $\beta'$. A thermodynamic description of metastable GP-zones is presented that is based on a critical assessment of available first-principles data, as well as estimations of the thermodynamic solvus that were based on experimental information on the dissolution temperature of GP-zones.

Up to now the generally accepted model for early GP-zones is adopted from [1] proposing Mg-Si layers in Al-matrix with Mg:Si=1:1. On the contrary, the new model is based on an ordered Al\textsubscript{3}Mg, L\textsubscript{1}\textsubscript{2} structure as evident from experiments [2]. Employing a four substitutional sublattice description for ordering, this model allows a simultaneous reproduction of microstructural, thermodynamic and chemical findings. The new thermodynamic model of GP-zones is successfully applied to kinetic simulations of precipitation sequences in 6016 Al-alloys.

Stacking of L\textsubscript{1}\textsubscript{2}-substructures has also been proposed as a reliable mechanism of GP-zones formation in other systems, for instance Al-Cu [3], and the application of the presented approach in other systems is thus promising.

First *ab initio* calculation of a $\sigma$-phase in a ternary system: Cr-Mo-Re

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For the first time, the enthalpies of formation at 0 K of all the ordered configurations in a ternary $\sigma$-phase, i.e. $3^5=243$ configurations, have been calculated using the electronic first principles methodology. The Density Functional Theory (DFT) method has been used in the Generalized Gradient Approximation (GGA), with Projector Augmented Wave (PAW) pseudo-potentials, as implemented in Vienna ab initio Simulation Package (VASP).

The Cr-Mo-Re system has been judiciously chosen to be investigated since the two binary Cr-Re and Mo-Re $\sigma$-phase are known for showing inverse Re sites preference: high coordination number (CN) sites in Cr-Re [1] and low CN in Mo-Re [2]. Occupancies of the inequivalent sites have been computed as a function of composition and temperature using the only configurational entropy, in the Bragg-Williams approximation.

The results show that the Cr-Mo-Re $\sigma$-phase presents a miscibility gap at low temperature and that the Gibbs energy surface is convex above $\sim$750K. Re site preference is shown to change progressively in the ternary field when passing from Mo-Re to Cr-Re binary borders. The relative stability of this ternary phase will be discussed by analyzing the crystallographic parameters and the electronic properties features.

Atomic mobility and diffusivity for fcc phase in Al alloys

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A hybrid approach of first-principles calculation, semi-empirical correlation, DICTRA modeling, supplemented with experiment is employed to simulate the atomic mobility of fcc phase in Al alloys. First-principles calculations are utilized to compute the self- and impurity diffusivities corresponding to the metastable states, such as self-diffusivity of fcc-Mg and impurity diffusivity of Cu in it. Analyzing the assessed atomic mobilities for fcc phase in 42 binary systems, we find a simple semi-empirical relation that correlates the four mobility end-members. For a general binary system denoted by A-B, the relation can be expressed as follows:

\[ Q_A^A + Q_B^B = Q_A^B + Q_B^A \]

and

\[ \ln(D_A^{0A} * D_B^{0B}) = \ln(D_B^{0A} * D_A^{0B}) \]

where \( Q_i^j \) is the activation energy for element i diffusing in pure j, and \( D_i^{0j} \) is the corresponding pre-exponential factor. i and j denote A or B. When evaluating the atomic mobility for ordered L1\textsubscript{2} (\( \gamma' \)) fcc phase, we developed an effective strategy, which takes the homogeneity range and defect concentration into account. Such a strategy results in a dramatic decrease for the number of atomic mobility parameters to be evaluated for \( \gamma' \) phase.

Based on various kinds of experimental diffusivities and thermodynamic parameters available in the literature, the first-principles computed diffusivities in metastable states, and the semi-empirical correlation, atomic mobilities of the elements in binary fcc phases of the Al-Fe, Al-Ni, Fe-Ni, Al-Cu, Al-Si, Cu-Si, Al-Mg, Cu-Mg, Al-Zn, and Cu-Zn systems are assessed as a function of temperature and composition by means of DICTRA software. The obtained atomic mobilities in the binary systems are then synthesized to compute diffusivities of fcc phases in the Al-Fe-Ni, Al-Cu-Si, Al-Cu-Mg and Al-Cu-Zn ternary systems.

Comprehensive comparisons between the calculated and measured diffusivities show that most of the experimental data can be well reproduced by the presently obtained atomic mobilities. The mobility descriptions are further validated by comparing calculated and measured concentration profiles for various diffusion couples including those prepared in the present work.

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Abstracts: Oral Presentations, May 25 (Tuesday)

- Session 5: Modeling of thermodynamic properties and liquid solutions
- Session 6: CALPHAD approach related to alloy systems – III
- Session 7: CALPHAD assessment of non-metallic systems – I
- Session 8: CALPHAD assessment of non-metallic systems – II
An attempt to correct the quasichemical model for liquids

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There are many liquids where the configurational entropy shows strong deviation from ideal mixing at certain compositions. Several different models have been proposed to handle this like the associated model, the two-sublattice liquid model and the quasichemical model.

In this presentation the quasichemical model will be reviewed and how its behaviour depends on the number of nearest neighbors and the bond energy, both for ordering and phase separation. In particular a correction of the extrapolation of the Gibbs energy of the model to low temperatures when long range ordering is excluded will be discussed.

Modeling short-range ordering and clustering in liquid solutions

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Short-range ordering (SRO) (preferential formation of A-B nearest-neighbors) and clustering (preferential formation of A-A and B-B nearest-neighbors) in various liquid solutions have been modeled using the Modified Quasichemical Model (MQM) in the pair approximation. In ternary solutions A-B-C, positive deviations from ideal solution behavior along the AB-C join are observed when there is strong SRO in the A-B binary sub-system. This effect is predicted by the MQM from the binary model parameters with no additional ternary terms, or with only small ternary terms; this is not the case when the associate model is used to model the SRO. In binary liquid solutions which exhibit clustering, the observed typical “flattened” form of the resultant miscibility gaps is accounted for naturally by the MQM; this is not the case when the Bragg-Williams random mixing model is used.
Thermodynamic modeling of phosphate glass system

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The oxide systems containing P$_2$O$_5$ are important for pyrometallurgical processes, glass-making and new calcium phosphate bio-glasses. In spite of their importance, the thermodynamic modeling of P$_2$O$_5$ containing systems has not been performed properly yet. Even the thermodynamic data and phase diagram of pure P$_2$O$_5$ are not well-known. In the present study, the preliminary thermodynamic modeling results of pure P$_2$O$_5$ and several binary P$_2$O$_5$ oxide systems will be presented. In particular, the network structure of P$_2$O$_5$ in molten oxide was carefully examined and simulated using the Modified Quasichemical Model to accurately describe the thermodynamic properties of molten phosphate slag.
Mixing enthalpies of liquid alloys and thermodynamic assessments of the Cu–Fe–TM (TM = V, Cr, Co, Ni) systems

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Effective development of the copper–iron based materials requires the thermodynamic database. The construction of such database suggests the conducting thermodynamic assessments of the ternary systems using the available experimental information. The main problem for the development of the thermodynamic descriptions is the general lack of the reliable data on the thermodynamic properties for these systems.

The mixing enthalpies of liquid Cu-Fe-TM (TM = V, Cr, Co, Ni) alloys have been investigated at 1873 K along the sections $x_{Cu}/x_{Fe} = 3, 1, 1/3$ in the composition range $x_{TM} = 0$-0.55. The experimental study has been undertaken using the high-temperature isoperibolic calorimeter. The concentration dependence of integral mixing enthalpies of the ternary liquid alloys has been described with Muggianu-Redlich-Kister equation. The mixing enthalpies of liquid alloys are sigh-changing. The composition dependence of these functions denotes the key role of binary interactions during the formation of ternary liquid alloys. The contribution from the ternary interactions to integral mixing enthalpy of liquid alloys is mainly negative in Cu-Fe-V, Cu-Fe-Cr system and is mainly positive in the Cu-Fe-Co, Cu-Fe-Ni.

The thermodynamic assessments of these systems have been conducted on the basis of our own data and experimental information on the phase equilibria using the CALPHAD method. The isothermal and polythermal sections of the phase diagram, liquidus, solidus, stable and metastable miscibility gaps surfaces have been calculated. The undercooling degrees for the metastable liquid phase separation in the Cu-Fe-Co and Cu-Fe-Ni have been assessed.
Modelling of thermodynamic and thermophysical properties

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In this presentation, two categories of physical properties are considered. One is the thermodynamic properties, i.e. the properties considered in the traditional CALPHAD approach, such as heat capacity, enthalpy, entropy and Gibbs energy. The other is thermophysical properties, including volume/density, thermal expansivity, bulk modulus, shear modulus, Young’s modulus and Poisson’s ratio.

Typically, the CALPHAD approach describes the thermodynamic properties at atmospheric pressure, then adds high-pressure contributions separately by adopting appropriate equations of state, in which volume, bulk modulus and pressure are usually involved. However, these thermodynamic and thermophysical properties are intrinsically correlated at all temperatures and pressures. Individual modeling requires unnecessarily large amounts of model parameters, and more seriously results in inconsistency.

This issue is discussed in detail, and methods are proposed in order to develop consistent databases for stable and metastable alloy systems.

Phase stability of titanium rich intermetallic phases in the Ti-X (X: Al, Ga, Si, Sn) systems

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In multicomponent titanium systems the $\alpha/\beta$ solid solutions are in equilibrium with D\textsubscript{0}$_{19}$, B\textsubscript{8$_2$}, D\textsubscript{8}$_8$ or D\textsubscript{8m}$_{2}$ intermetallic compounds. Understanding the phase stabilities lead to understand the behaviour of alloys and systems. The total energies of intermetallic compounds in the binaries system have been calculated using the Vienna Ab Initio package \cite{1,2} making use of the projector augmented waves technique \cite{3,4} in the generalized gradient approximation \cite{5}. In the PAW potentials, the 3d and 4s orbitals as well as the semicore 3p orbitals are treated as valence orbitals for Ti while 4d, 5s and 5p orbitals are used as valence orbitals for Sn. The calculations have been performed for the experimentally observed compounds \cite{6, 8} at their ideal stoichiometry \cite{9}.

In this paper we will present the results of calculations of phase stabilities of Ti rich intermetallic phases in relation with the Calphad assessments of binaries known at present. Vacancy and antisite defect formation energies have been calculated. Based on statistical thermodynamic models \cite{10-13}, the defect concentrations have been calculated as function of temperature and deviation from stoichiometry in each of the phases \cite{11-13}.

\begin{thebibliography}{99}

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\end{thebibliography}
Application of the combined CEF to the description of the $\sigma$ phase in the Pd-Ta system

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The combined, also referred as partitioned, CEF [1-3] allows to separate the Gibbs energy of an ordered phase in two contributions. The classical CEF is added to a non-configurational contribution.

$$G_m = G(y_i^s) + G(x_i)$$

where $y_i^s$, the site occupation of species $i$ in sublattice $s$, is used to express the configurational term and $x_i$, the composition of species $i$ in the phase under consideration, to express the non-configurational part. $x_i = \Sigma a_i^s y_i^s / \Sigma a_i^s$ as with $a_i^s$ as the fraction of the total number of sites corresponding to site $s$.

The configurational contribution is expressed with the classical CEF while the non configurational contribution is only expressed as the sum of a reference term, weighted sum of the Gibbs energy of the pure elements in the structure under consideration, and an excess term expressed with Redlich-Kister polynomials. Ideal entropy contribution is thus only introduced in the configurational term.

In the present work, this formalism is applied to the description of the $\sigma$ phase in the binary Pd-Ta system for which only few experimental data is available. Using some ab initio results for the metastable pure elements in this complex structure [4] and experimental data on site occupation for stable compositions [5], it allows to keep a description close to the general crystallographic knowledge on this phase keeping a reduced number of variables.

Thermodynamic modeling of Al-Ni-Pt system using a 4-sublattice model

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The Al-Ni-Pt ternary alloys are being studied as a new bond coat in the thermal barrier coating system for jet engine and gas turbine. A thermodynamic modeling of the Al-Ni-Pt ternary system together with a partial remodeling of the binary subsystems, especially Al-Pt binary system is carried out in the present work by combining first-principles calculations with the CALPHAD method. A four sublattice model is used to model the fcc phase in order to describe the order-disorder transformation, not only in the binary subsystem, but also in the Al-Ni-Pt ternary system. In order to obtain the mixing enthalpies of solid solution phases, the first-principles calculations of special quasirandom structures (SQS) are performed. The enthalpy of formation of binary compounds and end-members in sublattice models are also predicted. The obtained model parameters, phase equilibria and thermodynamic properties are presented and discussed.
Thermodynamic modeling of the Ta-B system

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The development of new high-temperature materials is essential for future generations of aircraft engines and land-based gas turbines. RM-Boron Silicide-based (RM: refractory metal) composites are potential alloy candidates because they may present a good balance of properties required for high-temperature applications [1,2]. Among the information for alloy design and potential evaluation for use as structural material, the phase equilibrium is one of the most important. The aim of the present work is the thermodynamic modeling of the Ta-B system, as part of a research project, which investigates the phase relations in the Ta-rich corner of the Ta-Si-B system. New experimental information on the binary were recently reported by [3], including the possible stability of a new phase PHI. The phases PHI, Ta₃B₂, TaB, Ta₃B₄ and B were modeled as stoichiometric compounds. The phases L (liquid), BCC, Ta₂B and TaB₂ were modeled as solutions, using the sublattices model, with their excess terms described by the Redlich-Kister polynomials. The optimization procedure was based on experimental data of liquidus temperatures, data of invariant transformations and enthalpy of formation. The calculated Ta-B diagram reproduces well the experimental values from the literature.

Reassessment of the thermodynamic description of the (U-Pu-C) system

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The mixed carbide (U,Pu)C is a reference material for Generation IV nuclear fuels. The analysis of the physico-chemical behaviour of fuels for Gas-cooled Fast Reactor or Sodium Fast Reactor systems in nominal and accidental conditions requires the assessment of phase diagrams and associated thermodynamic properties in order to (i) predict the possible chemical interactions between fuel components, (ii) study the fuel chemistry (fission product location) as a function of temperature and burnup, (iii) optimize the fuel fabrication. For that purpose, a thermodynamic database named FUELBASE [1] using the CALPHAD method is developed by CEA since 2005 in the framework of the ACTINET European network [2,3]. The list of the elements included in the FUELBASE is: U-Pu-O-C-N-Si-Zr-Ti-Mo-W-Re-Nb-Am-Np. The available thermodynamic description of the ternary system U-Pu-C [6] based on the binary descriptions of U-C [4] and Pu-C [5] systems having shown some important disagreement with experimental data in the range of composition of application interest, a deep reassessment of this ternary as well as of the constituting binary systems U-C and Pu-C was performed. Special attention was paid to the carbon potential experimental measurements of Anthonysamy and al. [7] in order to find good agreement between elemental composition, phase structure and carbon potential measurements. The present description should give valuable information to optimise the fabrication process of the fuel and predict its behaviour under operating or accidental conditions.

Estimating viscosities in steelmaking slags with basis on a thermodynamic model-Applications in the CaO-Al₂O₃-MgO-SiO₂ system

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Slags are critical components in several iron and steelmaking processes. In steelmaking, in special, several different slags with various optimum properties are used in the different processing steps from melting and refining to continuous casting. Besides thermodynamic properties, viscosity and surface tension are among the most important properties considered in the design of slag compositions for steel processing. A brief review of the approaches at modeling viscosities indicate that viscosity correlations with chemical composition, basicity (both chemical and optical) and more recently with slag constitution have been attempted with different degrees of success. In this work, a model to describe slag viscosity based on the Riboud [1] viscosity model combined with the thermodynamic Kappor-Frohberg-Gaye [2] cell model is described and presented as a potential alternative to obtaining slag viscosity estimates directly from computational thermodynamics software, a need of several users in the steelmaking area. The first results of the adjustment and application of the model to the CaO-Al₂O₃-MgO-SiO₂ are presented and the quality of the adjustment is discussed as well as its current limitations. The next steps of the project involve the extension of the model to include FeO e CaF₂.

Thermodynamic evaluation of the Si-C-Al-Y-O system and applications for liquid phase sintering of silicon carbide ceramics

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A thermodynamic dataset for the Si-C-Al-Y-O system was developed for calculations of heterogeneous phase equilibria and reactions in SiC-base engineering ceramics. The quinary system is of major interest for the understanding of the liquid phase sintering of silicon carbide ceramics using additives like alumina (Al₂O₃) and yttria (Y₂O₃). The thermodynamic dataset was developed by the CALPHAD method of thermodynamic optimization. Analytical descriptions for the Gibbs free energy functions of phases in the Si-C-Al-Y-O system were re-assessed in comparison to earlier descriptions [1-3]. The sublattice model was described in the compound energy formalism for the treatment of the solid solution phases. The liquid phase was described by using the partially ionic liquid model presented as (Al⁺³, Si⁺⁴, Y⁺³)₉(O⁻², SiO₄⁻⁴, Va, AlO₃/2, SiO₂, C)₉ covering metallic liquid and oxide liquid as a single phase. During liquid phase sintering SiO₂, Y₂O₃ and Al₂O₃ react with SiC resulting in gaseous species CO, SiO, Al₂O and Al. These interactions cause weight losses, porosity and the formation of sintering skins or even instabilities of the materials during the liquid phase sintering process at temperatures higher than 1800°C. The thermodynamic calculations were used to understand such heterogeneous reactions and find out suitable sintering conditions.

Phase diagram and thermochemical studies on Pb-Fe-O system

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Liquid lead and lead bismuth eutectic (LBE) alloy are considered as candidate coolant for fourth generation nuclear reactors and as spallation neutron target as well as coolant in accelerator driven transmutation systems because of their favorable thermal, physical and chemical properties [1]. Though these coolants are corrosive towards structural steels, a protective oxide layer that prevents this corrosion can be formed over the steel by controlling the oxygen concentration in the coolant [2]. In this context, study of the interaction of components of structural steels with lead and bismuth in the presence of oxygen is of technological importance. Although many of the ternary compounds involved in Pb-M-O systems (M = Cr, Fe) have been reported, their equilibrium phase diagrams and thermochemical data of the ternary systems are not available. In this experimental work, results on ternary phase diagram and thermochemical studies on Pb-Fe-O system are reported.

Equilibrium phase fields of the ternary Pb-Fe-O system were established by long-term equilibriations for the temperature range: 1048-1133 K. The obtained phase fields are: (1) Pb-Fe-FeO (2) Pb-FeO-Fe$_2$O$_4$ (3) Pb-Fe$_3$O$_4$-PbFe$_5$O$_{8.5}$ (4) Pb-PbFe$_5$O$_{8.5}$-PbFe$_2$O$_5$, (5) Pb-PbO-Pb$_2$Fe$_2$O$_5$, (6) Fe$_3$O$_4$-PbFe$_3$O$_{8.5}$-PbFe$_{12}$O$_{19}$, and (7) Fe$_3$O$_4$-Fe$_2$O$_3$-PbFe$_{12}$O$_{19}$. Using these results partial phase diagram of the Pb-Fe-O ternary system has been constructed over a temperature range of 1048 ≤ T/K ≤ 1133. Standard molar Gibbs energy of formation of ternary oxides PbFe$_5$O$_{8.5}$(s) and PbFe$_2$O$_5$(s) were determined by measuring equilibrium oxygen partial pressures over the relevant phase fields using solid oxide electrolyte based emf methods and are given by:

\[
\Delta_f G^o_m \text{PbFe}_5\text{O}_{8.5}(s) \pm 1.0/(\text{kJ.mol}^{-1}) = -2189.3 + 0.6470 T \ (\text{K}) \ (1048 \leq T/K \leq 1133) \\
\Delta_f G^o_m \text{Pb}_2\text{Fe}_2\text{O}_5(s) \pm 0.3/(\text{kJ.mol}^{-1}) = -1170.7 + 0.3640 T \ (\text{K}) \ (1048 \leq T/K \leq 1130)
\]

Experimental investigations and re-modeling of the LaO$_{1.5}$-MnO$_x$-ZrO$_2$ system

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Oxygen ion conducting yttria stabilized ZrO$_2$ (YSZ) and perovskite type Sr-doped LaMnO$_3$ (LSM) are widely used as electrolyte and cathode materials in solid oxide fuel cells (SOFCs). Establishing the phase diagram of the LaO$_{1.5}$-MnO$_x$-ZrO$_2$ system as a function of temperature and $P$(O$_2$) is a prerequisite for successful modeling of the LSM-YSZ reactions under varying current load. There is only one experimental study of the subsolidus phase equilibria of the LaO$_{1.5}$-MnO$_x$-ZrO$_2$ system [1], but it is not considered adequate as it is based on a small number of investigated compositions and it lacks crucial experimental information (annealing temperature and $P$(O$_2$), annealing time, etc.). Two thermodynamic modeling attempts of the phase equilibria in LaO$_{1.5}$-MnO$_x$-ZrO$_2$ [2, 3] resulted in different geometries for the phase diagram at 1000°C in air. We therefore find that there is a need for further experimental work in the LaO$_{1.5}$-MnO$_x$-ZrO$_2$ system.

In the present work, the phase relation in the LaO$_{1.5}$-MnO$_x$-ZrO$_2$ system has been experimentally determined at 1200°C and 1400°C in air and at 1200°C in N$_2$ ($P$(O$_2$) ~ 100 Pa). Tie lines between LaMnO$_3$ and t-ZrO$_2$ and between LaMnO$_3$ and La$_2$Zr$_2$O$_7$ are confirmed at 1200°C in air. The geometry of the phase diagram changes at 1400°C in air due to the appearance of a stabilized ZrO$_2$ phase, found to be of cubic symmetry by backscattered electron diffraction. Tie lines of LaMnO$_3$-c-ZrO$_2$, LaMnO$_3$-La$_2$Zr$_2$O$_7$ and c-ZrO$_2$-La$_2$Zr$_2$O$_7$ are observed. At 1200°C in N$_2$ ($P$(O$_2$)~100 Pa) the LaMnO$_3$-t-ZrO$_2$ tie line observed at 1200°C in air is replaced by the La$_2$Zr$_2$O$_7$-MnO tie line. Stabilization of c-ZrO$_2$ is observed and a new compound forms, which is being reported for the first time. The proposed composition of the new compound is La$_2$Zr$_5$MnO$_{14+\delta}$. The LaO$_{1.5}$-MnO$_x$-ZrO$_2$ system was therefore re-modeled, based on both literature data and the phase diagram data from the present work. A thermodynamic description of the LaO$_{1.5}$-MnO$_x$-ZrO$_2$ system is presented, which includes modeling of the new phase (La$_2$Zr$_5$MnO$_{14+\delta}$) found in the present work. The current description of the LaO$_{1.5}$-MnO$_x$-ZrO$_2$ system gives a better agreement with most of the experimental data.

Phase field modeling of isothermal crystallization of metallurgical slags using FACT thermodynamic databases for oxide systems

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In this work, we present the use of FACT databases [1] for oxide systems in phase field simulations of isothermal crystallization of metallurgical slags. The considered systems are CaO-Al₂O₃-SiO₂ and FeO-Fe₂O₃-SiO₂. Both systems have a wide spread of applications in both ferrous and non-ferrous pyrometallurgical industries. In the phase field model, the oxides molecules (CaO, FeO, Fe₂O₃, …) are assumed to be the diffusing species and the components. The phase field model is constructed using the multiphase field approach from [2] and the multicomponent approach from [3]. The Gibbs energies of all phases and the chemical potentials of all components in all phases are retrieved from the thermodynamic database using ChemApp [4]. Stoichiometric phases are often present in slag systems and cannot be readily treated by the phase field method. An artificial parabolic Gibbs energy is constructed for such phases, based on the method used in [5]. The simulation results provide unique insight in the crystallization of minerals in a liquid slag. In the CaO-Al₂O₃-SiO₂ system, elementary diffusion path simulations show the influence of the diffusion kinetics in the liquid on the selection of the tie-line in a two phase region (between liquid and stoichiometric solid). In the FeO-Fe₂O₃-SiO₂ system, simulations illustrate how the diffusion of O₂ (due to an open boundary with the atmosphere) influences the growth of spinel (FeO·Fe₂O₃) particles in the liquid.

Linking thermodynamics, structure and viscosity of oxide melts

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The ability to predict slag viscosities accurately is of interest in many industrial areas such as iron, steel and non-ferrous metal production, glassmaking, enamels, coal combustion and gasification, waste disposal, geological magmas, etc. A new model for the viscosity of liquid slags has been developed. It is distinct from other viscosity models in that it directly relates the viscosity to the structure of the melt, and the structure in turn is calculated from the thermodynamic description of the melt given by the Modified Quasichemical Model.

The model takes into account the following structural features which have the most pronounced effect on the viscosity:

- formation of a three-dimensional network by network formers such as SiO$_2$ and B$_2$O$_3$
- the so-called “Charge Compensation Effect” when Al$^{3+}$ cations assume tetrahedral coordination and enter the silica network, while the additional negative charge resulting from the fourth oxygen is compensated by the presence of a second cation, such as Na$^+$, in the vicinity of Al$^{3+}$
- formation of large clusters in solutions of alkali oxides with SiO$_2$ or B$_2$O$_3$.

For the binary systems SiO$_2$-MO$_x$ and B$_2$O$_3$-MO$_x$, where MO$_x$ is a basic oxide, the model requires very few optimized parameters. This is all the more remarkable as the viscosity of silicate slags spans over 20 orders of magnitude as a function of composition. Each ternary system which exhibits the “Charge Compensation Effect” requires 2 temperature-independent ternary parameters. The viscosities of all other subsystems and higher-order systems are predicted from these parameters within experimental uncertainty without additional model parameters. All available experimental data have been considered. So far the model has successfully been applied to multicomponent oxide melts containing Si, B, Al, Ca, Mg, Li, Na, K, Mn, Ni, Fe$^{2+}$, Fe$^{3+}$, Pb, Zn, Ti and F.
Extended viscosity model for the glass region of oxides solutions

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The ability to predict slag viscosities accurately from the liquid to the glass region of oxide solutions is of interest in many industrial areas such as iron, steel and non-ferrous metal production, glassmaking, enamels, coal combustion and gasification, waste disposal, geological magmas, etc.

It is well-known that the viscosities in the liquid and the glass region exhibit Arrhenius and Non-Arrhenius behavior respectively. Our recently developed viscosity model, which is the subject of the preceding presentation, reproduces viscosities in the liquid melt region. The model is extended to describe and predict viscosities in the glass region. In order to take into account the Non-Arrhenius behavior, the model requires two additional binary parameters for each $\text{MO}_x\text{SiO}_2$ and $\text{MO}_x\text{B}_2\text{O}_3$ system, where M is any basic oxide. Two additional ternary parameters are required for each system $\text{MO}_x\text{Al}_2\text{O}_3\text{SiO}_2$ in order to describe the viscosity maxima due to the Charge Compensation Effect. The model reproduces the viscosities of multi-component solutions in the $\text{Al}_2\text{O}_3\text{CaO}\text{MgO}\text{Na}_2\text{O}\text{K}_2\text{O}\text{SiO}_2\text{B}_2\text{O}_3\text{PbO}$ system from the liquid to the glass region within experimental error limits.
Assessment of the quaternary reciprocal system Al, Na, Si // F, O: 
A thermodynamic approach to the corrosion of the refractory lining 
in aluminum electrolysis cell

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In Hall-Héroult cells, the corrosion of the refractory cathode lining (Al2O3-SiO2 with CaO, MgO, Fe2O3), which is mainly due to the penetration of cryolithic bath (Na3AlF6-CaF2-Al2O3) below the carbon cathode blocks, can considerably shorten the life span of the cell. In order to study the resistance of refractory materials, corrosion tests and post-mortem analyses of shut-down cells have been conducted. These studies provide useful information but might not correspond to the chemical reactions taking place in service at high temperature. In the present study, the corrosion problem (simplified to Al2O3-SiO2 refractory materials exposed to a simple NaF-AlF3 cryolithic bath) has been treated as thermodynamic equilibrium occurring between the different phases and solutions present in the refractory lining. In order to perform thermodynamic calculations, the quaternary reciprocal system Al, Na, Si // F, O has been assessed using the Modified Quasi-Chemical Model (MQM) [1] for the oxyfluoride liquid solution. The thermodynamic modeling is rather complex as a result of the charge compensation effect in molten silicate, the strong short range ordering and the immiscibility in reciprocal system. However the MQM, which takes into account both first nearest and second nearest neighbor short range order, has permitted to reproduce the thermodynamic properties of the strongly ordered oxyfluoride melt. All available thermodynamic data for unary, binary, ternary and reciprocal systems have been critically reviewed. The results of the thermodynamic optimization are presented along with experimental data and represent the first thermodynamic modeling over the complete composition range and for all temperatures of the ternary and quaternary reciprocal system.

Thermodynamic evaluation and optimization of the \( \text{Na}^+, \text{Ca}^{2+}, \text{Al}^{3+}, \text{Fe}^{2+}, \text{Fe}^{3+} // \text{F}^-, \text{O}^{2-}, \text{Va}^- \) system

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Nickel ferrite (\( \text{NiFe}_2\text{O}_4 \)) is a promising material for the replacement of the traditional carbon anodes in the Hall-Héroult process for the reduction of alumina. The dissolution rate of inert anodes in the electrolyte has to be minimized; hence the importance of modeling the thermodynamic properties and phase equilibria in cryolitic baths.

The global system considered is \( \text{NaF-AlF}_3-\text{Al}_2\text{O}_3-\text{CaF}_2-\text{FeO-Fe}_2\text{O}_3 \). The thermodynamic study has to take into account the following ions: \( \text{Na}^+, \text{Ca}^{2+}, \text{Al}^{3+}, \text{Fe}^{2+}, \text{Fe}^{3+} // \text{F}^-, \text{O}^{2-} \) with the dissolved metal. \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) have been added to the existing model for the \( \text{Na}^+, \text{Ca}^{2+}, \text{Al}^{3+} // \text{F}^-, \text{O}^{2-} \) system optimized by Chartrand and Pelton [1]. Thermodynamic properties of new pure compounds have been evaluated. The Quasichemical Model in the Quadruplet Approximation [2] has been used in order to describe the cryolitic bath (liquid) behavior. New solid solutions have been modeled using the Compound Energy Formalism [3]. Among the newly evaluated solid solutions for the fluoride systems, the major ones are: high-temperature cubic cryolite \( \text{Na}^+,\text{Ca}^{2+},\text{Va}_8(\text{Na}^+)_4(\text{AlF}_6^{3-},\text{FeF}_6^{3-})_1(\text{AlF}_6^{3-},\text{FeF}_6^{3-},\text{FeF}_4^{3-})_3 \) and chiolite \( \text{Na}_8(\text{Al}^{3+},\text{Fe}^{3+})_3\text{F}_{14} \). For the oxide systems, the wustite solid solution \( \text{FeO-}[\text{Na}_2\text{O},\text{Fe}_2\text{O}_3] \) from the FToxid FactSage™ database has been modified to take into account \( \text{Na}^+ \) solubility.

The distinctive feature of this work is the consideration of two oxidation states for iron (\( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \)) within a reciprocal oxide/fluoride system. The distribution between the two possible oxidation states mainly depends on the reducing or oxidizing conditions \( (P(\text{O}_2) \) and \( P(\text{F}_2)) \).

Ten years of using advanced Gibbs’ian methods through spreadsheets

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ChemSheet is software that combines a spreadsheet interface and Calphad thermochemical calculations. When published by VTT of Finland and GTT-Technologies of Germany some 10 years ago, ChemSheet was the pioneering multi-phase thermodynamic program, which was made accessible to non-experts through its commonplace interface.

During the last decade, ChemSheet and its sister products have been adopted by both industrial users and active scientists worldwide. Due to the generic modelling principles based on Gibbs free energy minimization, the applications range from high temperature systems even to biochemical analysis, covering materials chemistry, corrosion, chemical reactor scale-up and industrial process simulation. Practical models and expert systems have been developed e.g. in chemical technology, pulp and paper, cement and lime manufacturing, metallurgy, steelmaking, power production and environmental processing.

Within ChemSheet, the new Constrained Gibbs Energy method allows the use of immaterial constraints in the conservation matrix of the minimization problem, thereby enabling the association of constraint matrix properties with structural, physical, chemical or energetic attributes. Thus, the scope of free energy calculations can be extended beyond global chemical equilibria and phase diagrams. The most notable applications include surface and interfacial energies, electrochemical Donnan equilibria, calculation of paraequilibria and the reaction-rate controlled constrained systems. Selected ChemSheet approaches representing both phase equilibrium studies and applications of constrained Gibbs energies will be presented.

Abstracts: Oral Presentations, May 26 (Wednesday)

- Session 9: Lattice stability / Experiments that need thermodynamic analysis – I
- Session 10: Experiments that need thermodynamic analysis – II
Third generation of lattice stabilities for metals

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At the 14th National Conference, November 2008 [1] in Changsha, China, Sundman, Dupin and Chen observed that it was time for a 3rd generation of thermodynamic databases referring to “assessment of metastable extensions of ab initio calculations. The development of such techniques has been rapid but without the CALPHAD type assessments the ab initio values are as scattered and incomplete as the experimental values are”. This is even more true when the lattice stabilities of the principal structures of the pure elements, which are used as the endpoints in many systems are assessed. Recent ion beam mixing (IBM) experiments [2-4] have provided more examples [5-7] of such metastable metallic structures that can be retained and characterized so that the gap between ab-initio and CALPHAD results can be reduced. Unfortunately the widely used VASP(ab-initio) values [8] for the Fe, Ru, Os group and Mo differ substantially [9-15] from recent ab-initio results [10,11] as well as CALPHAD assessments [13-15].

[7] Palatnik and Izvestia, ANSSSR Metally, No.2 (1972)
On the lattice stabilities of pure Cr and pure Fe

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The development of thermodynamic databases has been going for a long time using the present set of available lattice stabilities, as presented in SGTE database [1,2]. It is well known, however, that these lattice stabilities present some drawbacks and can be improved. For example, there are experimental evidences that the melting temperature of pure Cr is significantly lower than the assessed value used by SGTE (2180 K). Furthermore, till present, lattice stabilities are modeled above room temperature by polynomial expressions with limited physical meaning. In the framework of the Sapiens project, new lattice stabilities are being developing starting from zero K, incorporating available physical models as well as first principles data and trends. Iron and Chromium are the first elements for which this approach is applied.

In this work, experimental data on thermophysical properties for these elements have been collected from the literature. By critically evaluating these experimental data, including the most recent ones, and adopting thermodynamic models as proposed for example in Ringberg workshops and later [3], new lattice stabilities for Cr and Fe are evaluated. The “inverse pyramid effect” [4] has been evaluated for these new lattice stabilities in higher order systems.

[3] See i.e. the issue of CALPHAD, B. Sundman and F. Aldinger (Eds.), CALPHAD, 19 (1995)
Microstructure and texture evolution of twin-roll cast magnesium alloys during thermo-mechanical treatments

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Mg alloys have the great potential as lightweight structural materials especially in transportation systems due to their low density and high specific strength. Recent development of twin-roll casting technology has shown that it can efficiently produce low cost, high performance Mg alloy sheet products. They are usually subjected to thermo-mechanical treatment (TMT) such as warm rolling to modify the microstructure so that optimum combination of mechanical properties can be obtained. Critical requirements for the Mg alloy sheets are not only high strength, but also high formability. However during thermo-mechanically treatment, the strong basal texture is developed and it is of common knowledge that the poor ductility of wrought Mg alloys is due to the strong basal texture. Therefore it is important to modify the texture of Mg alloys by various TMTs. However, the detailed mechanism of texture evolution during thermo-mechanical treatment is not yet clear.

In the present study, the effect of TMT on the evolution of texture by recrystallization has been investigated. To analyze the exact microstructural and textural evolution in particular, the static recrystallization behavior has been analyzed at the same area before and after re-heating. It shows that basal texture becomes stronger with an increase in the rolling reduction as expected. However, re-heating between rolling passes results in the reduction of basal texture. The deformation bands consisting of twins act as nucleation sites for static recrystallization. Static recrystallization induced by re-heating between rolling passes results in a weakening of basal texture, which becomes more evident with an increase in re-heating time. It also shows that the rolling temperature and reduction ratio can affect the texture evolution. More importantly, recrystallization behavior of Mg alloys is quite different depending on the alloy system. This is mainly due to the difference in nature of deformation twins formed during rolling. In the case of Mg alloys containing rare-earth (RE) elements, deformation twins are all tension twins, while other alloy systems contain either compression or double twins. Tension twins present in RE containing alloys promote the formation of recrystallized grains with random texture, resulting in improved formability of Mg-RE alloys.
Diamond deposition with simultaneous graphite etching:
Thermodynamic paradox or
indication of diamond deposition by gas phase nuclei?

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Films, nanowires and nanotubes prepared by chemical vapor deposition (CVD) have been believed to grow from individual atoms or molecules. A drastically different growth mechanism in some CVD systems, based on a building block of charged gas phase nuclei has been suggested with convincing evidences [1]. In this mechanism, growth occurs by two steps: first, charged nanoparticles are formed in the gas phase, and second, they are incorporated into a crystal as a building block. The two-step process seems to be a general mechanism in the growth of nanowires, nanotubes and films by CVD processes [2,3]. The generation of such hypothetical charged gas phase nuclei has been confirmed in many CVD systems. However, it becomes important whether these charged gas phase nuclei are the building-block of the growing films, nanowires and nanotubes or not. Although many experimental results imply that these charged gas phase nuclei should be the major growth source, it is difficult to prove this experimentally. On the other hand, it is experimentally well established that less stable diamond films grow with simultaneous etching of more stable graphite. This phenomenon would violate the second law of thermodynamics if the diamond deposition occurs by an individual carbon atom. In order to avoid the violation of the second law, the charged gas phase nuclei, which was confirmed experimentally, should be the building unit of growing diamond films.

Review on available thermodynamic database of complex metal hydrides

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Some complex metal hydrides, group I and II metal borohydrides in particular, have very high hydrogen content even up to 18.5 wt% in the case of LiBH$_4$ and some of them are quite reversible with or without catalytic additives. However, both the thermodynamics and sorption kinetics of these metal borohydrides are not favorable yet for the mobile applications where the operation temperatures of typical fuel cells are normally below 373K and rather fast charging time in the order of a few minutes are required at present. In addition, the full reversibility and reasonable sorption cycle performance have yet to be realized in order to consider these materials seriously as reliable hydrogen storage media for the development of practical storage systems. For that, we must have more information on basic thermodynamic properties of these rather “complicated” complex metal hydrides. However, it is not straightforward to measure even basic thermodynamic parameters of these compounds as they are extremely air-sensitive. Moreover, the dehydrogenation reactions are complicated including multiple polymorphic transitions with or without evolution of hydrogen, abrupt change in morphology such as foaming, multiple reactions often occurring almost at the same time, and even chemical reaction with the container material. All of these do contribute to the uncertainties in the reaction enthalpy and entropy of the dehydrogenation reactions of these complex metal hydrides. Therefore, thermodynamic calculations, based on DFT calculations in particular, of these complex metal hydrides would be quite useful to critically evaluate the reliability of the thermodynamic parameters obtained by experiments. Some critical issues on the reliability of those calculated enthalpy and entropy values will also be raised in the hope that we might be able to build up much more accurate and reliable thermodynamic data on complex metal hydrides, which will eventually lead us to find better hydrogen storage materials with more favorable thermodynamic properties for practical applications.
Vectorial growth of VLS semiconductor nanowires: Thermodynamics vs. Kinetics

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Self-organized ensemble formation in nature is often found during the crystal growth at the various length scales, as in the prominent examples of block-copolymers, colloidal crystals, and solidification of alloys. The integrated nanowire (NW) ensemble, which can serve as a common ground for the various applications into electronic circuits, biological probes and energy conversion vehicles, require such spontaneous ordering over a large anisotropic energy barrier set at the different length scales in the NW axial and radial directions. Thereby manipulating NW growth directions by a self-organized manner can provide momentous advantages for such integrated NW systems. In vapor-liquid-solid (VLS) NW growth, however, the nucleation at the eutectic liquid catalyst is isotropically random, thus the NW growth direction is arbitrarily different from NW to NW, lacking in massive parallelism. Here, we demonstrate a simple and robust growth to coherently command the growth direction of VLS NWs with a local kinetic control over the V-L-S interfaces at the nanometer scale. Specifically, it is shown that the presence of the temperature gradient spontaneously reorganizes the NW growth direction in parallel to its local gradient at an increased growth rate. We provide a phenomenological model for the directional NW growth within the framework of the interfacial thermodynamic stability. In particular, we discuss the role of the temperature gradient on the redistribution of a local kinetic variable, i.e. local interfacial supersaturation, on the thermodynamic stability at the fluctuating V-L and L-S interfaces. Our growth scheme is universally applicable regardless of the growth substrates, thereby provides practical implication for integrated NW growth.
Atomic-scale observations of phase transformations in nano-sized materials: Deviations from the bulk behaviors

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As the size of a material decreases towards nanometer levels, surface (free surface or interface with a dissimilar material) plays an increasing role in governing the material’s phase stability. In thermodynamic aspects, the total energy calculation of nano-sized materials often needs to be rephrased by including extra energy contributions related to the surfaces. Many thermal experiments already showed that the phase transformations of nano-sized materials occur at temperatures way different from those expected for the bulk counterparts. The atomic-scale dynamics of phase transformations are challenging to observe but can be captured in real-time through in-situ heating experiments in transmission electron microscope (TEM). Here I present in-situ TEM observations of the phase transformations of nano-sized materials, which, we hope, can be understood better with aid of thermodynamic calculations. Firstly, the premelting of (compressively) strained Cu (110) thin films is presented, which proceeded by discontinuous growth of quasi-liquid layers from the surfaces at temperatures much lower than the melting point of Cu ($T_m = 1083 \, ^\circ$C). In order to account for the observed melting behavior, we propose a strain effect on surface premelting. Secondly, an oscillatory mass transport mechanism is presented, which was observed during the vapor-liquid-solid growth of sapphire nanowires in TEM. The oscillatory mass transport and layer-by-layer growth mechanisms will be discussed in the light of the dynamic interface free energies that change with mass transport. The last subject deals with the decomposition of single crystal ZnO in the TEM atmosphere, which occurred, unexpectedly, with the formation of a few nanometer-thick liquid-like layer at the moving interface.
Abstracts: Oral Presentations, May 27 (Thursday)

• Session 11: CALPHAD approach related to ferrous alloys – I
• Session 12: CALPHAD approach related to ferrous alloys – II
• Session 13: Database/Software and CALPHAD assessment of metal-hydrogen system
• Session 14: CALPHAD approach related to thin films and phase field methods
$\alpha/\gamma$ equilibria and martensitic transformation in Fe-Mn-X
(X: $\alpha$ stabilizing element) system

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The $\gamma$-loop of the Fe-Cr system shows a peculiar shape where Cr stabilizes the $\alpha$(bcc) phase near the A4 temperature while it stabilizes the $\gamma$(fcc) phase near the A3 temperature. Zener [1] pointed out that magnetic contribution plays a significant role in the $\alpha/\gamma$ equilibria in iron alloys. In 1973, the present author reported that the $\alpha/\gamma$ equilibria of Fe-Mn-X (X: $\alpha$ stabilizing element) show various shapes and that a peculiar $\gamma$-loop similar to that of the Fe-Cr system is formed [2], which is due to the large temperature dependence of the partial molar free energy change of Mn between the $\gamma$ and $\alpha$ phases by the magnetic effect [3,4].

Recently, we found that martensitic transformation from the bcc($\alpha$) to the fcc($\gamma'$) phase occurs in the Fe-Mn-Ga [5] and Fe-Mn-Al [6] systems. The origin of this unique phase change is caused by the peculiar $\gamma$-loop of $\alpha/\gamma$ equilibria formed in the Fe-Mn-X (X: ferrite stabilizing element) system. The characteristic magnetic properties of Fe-Mn-Ga and Fe-Mn-Al systems are also shown.

Boron in steels. The Fe-Cr-B ternary phase diagram: Application to liquid phase sintering of Boron-containing stainless steels


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Thermodynamic calculations for the Fe-Cr-B and Fe-Mo-B ternary systems are presented. The ternary diagrams are obtained by extrapolation from the binary systems, available in the literature. Four phases have been considered in the extrapolation: Liquid, α-bcc, γ-fcc and M₂B [1]. The tetragonal borides were described as a two-sublattice phase (Fe, Cr)₀.₆₆₇(B)₀.₃₃₃ since Cr₂B, Fe₂B and Mo₂B have identical crystal structure. Also the liquid formation by a eutectic reaction between these mixed borides and the host matrix was studied as a function of temperature and the initial concentration of Cr in the matrix. The isothermal sections corresponding to the Fe-Cr-B were calculated by means of THERMOCALC software package. These calculations have been used to study the time and temperature evolution of the liquid phase sintering of Boron-containing stainless steels.

Remaining issues in the CALPHAD technique: Illustrations using the Fe-Cr and Fe-Ni binaries

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The CALPHAD technique has been developed for more than 30 years and earned its reputation due to its success in assisting the materials design. Plenty of thermodynamic databases generated by CALPHAD method are available. There is no doubt that they are reliable to some extent for applications in engineering. However, some remaining issues in the CALPHAD approach itself still exist. Some of them are related to the magnetic models, and the problems will be enlarged in the low temperature range. In this work, the Fe-Cr and Fe-Ni systems are chosen as the studying subject due to its importance in stainless steels, constructional materials in nuclear reactor, and magnetic materials.

The magnetic properties of the Fe-Cr and Fe-Ni alloys, including Curie/Néel temperature and mean magnetic moment, have been studied in detail by ab initio calculations, CALPHAD modeling and DSC measurements in addition to a comprehensive literature review. The study on solubility limits of Cr in (α-Fe) indicates that the magnetic effects play a key role in thermodynamic description at low temperatures. Inconsistence is found unexpectedly between CALPHAD model and atomistic predictions. The mean magnetic moment of the Fe-Ni alloys have been calculated via the exact muffin-tin orbitals method in the frame of the density functional theory. It is found that none of the reported thermodynamic descriptions can represent the magnetic properties of this system correctly. The present study shows that the prediction of T₀ line for studying martensitic transformation relies on the description of the magnetic properties.

The related problems call for a new magnetic model (at least modification) of the CALPHAD approach. In this work it is illustrated that a single Redlich-Kister polynomial by introducing the weiss factors is not suitable for describing the magnetic properties of the Fe-Ni alloys. More extensive work on the other magnetic alloy systems is of high interest before introducing a new magnetic model. Meanwhile, the inputs from atomistic modeling, e.g. the ab initio calculations, are indispensable.
Experimental investigation and thermodynamic assessment of the Fe-Si binary system

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Fe-Si base alloys are one of important practical materials, which are widely used in electromagnetic applications and high-strength steels, and are recently studied as spin-electronics devices, etc. Despite its remarkable significance, thermodynamic assessment of the Fe-Si binary system has not been carried out completely because the bcc phase in this system exhibits two-fold ordering from the disordered A2 to the intermediately ordered B2 and further to the ordered D0₃ structures. To describe thermo-dynamic properties of the bcc phases appropriately, at least four sub-lattices are necessary, which prevents former researchers from trying to evaluate the basic binary system thoroughly.

In this paper, phase separation between bcc phases as well as the two-fold ordering reactions was experimentally investigated in detail. After that, thermodynamic assessment of the Fe-Si binary system was completed with taking the two-fold ordering reactions into account.

Fe-Si alloys were prepared by induction melting. Diffusion couples, whose compositions were chosen to sandwich the A2/B2/D0₃ boundaries, were prepared by a Thermec-Master (thermo-mechanical process simulator) and heat-treated at temperatures between 700°C and 1000°C in evacuated quartz capsules. Composition profiles across the phase boundaries were measured by an FE-EPMA (JEOL JXA-8500F) and two-phase separation between B2 and D0₃ phases were determined. Two-phase alloys were also prepared and heat-treated at 600°C and 650°C for long hours. Equilibrium compositions were determined by the FE-EPMA, whose spatial resolution of X-ray analysis is as small as 0.5μm with 6.0kV accelerating voltage.

Gibbs energy of the bcc phases, A2, B2 and D0₃ was described by the 4-sublattice split compound energy formalism (4SLs-CEF). Thermodynamic evaluation of whole phase diagram of the Fe-Si system was carried out. Figure 1 shows a result of calculation.
The CALPHAD and ab-initio modelling of Z-Phase in ternary Cr-Nb-N system and advanced steels

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The presence and morphology of intermetallic phases are crucial instruments allowing to influence the materials properties of many modern alloys. Therefore, good thermodynamic description of such phases is very important for complete thermodynamic assessment of multicomponent systems and reliable prediction of properties of complex advanced materials. The intermetallic phases and the Z-phase in particular play crucial role in the development of modern steels and current thermodynamic description is very difficult as the data about crucial ternary systems does not exist. Therefore combined CALPHAD and ab-initio approach was used for the description of above mentioned phases in Cr-Nb-N system, which is crucial for Z-phase and plays important role in modeling of phase equilibria in advanced steels. Namely the ab-initio approach was used for the calculation of Gibbs energies of pure constituents and intermetallic compounds in the crystallographic structures corresponding to the Z-phase at 0 K and phonon spectra. In combination with the CALPHAD method, the attempt to describe completely the ternary systems was made. The attention was paid to the Fe-Nb-V and Cr-Nb-V systems and their influence on the more complex systems.

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The CALPHAD approach in the development of micro-alloyed steels for line pipe applications

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Thermomechanically treated microalloyed steels are widely used for line pipe applications because of their high strength, high toughness at low temperature and good weldability. In the applied industrial development of new grades in combination with the definition of the suitable thermomechanical process (TMP), numerical approaches are more and more used. The behavior of microalloying elements and the grain size have to be controlled carefully over the whole process chain in order to maintain the excellent mechanical properties.

In the design process of a microalloyed steel, calculations of phase equilibria in order to determine the limits of Nb solubility were performed. In order to predict the formation of primary carbonitrides, the calculation of solidification using the Scheil-Gulliver model was applied. For the optimization of the cooling concept during the TMP, the prediction of the martensite start temperature based on $T_0$-temperature calculations was used. Furthermore the austenite grain growth was investigated by annealing experiments with a Gleeble thermomechanical simulator and phase-field simulations using the Micress code as well as mean-field modelling.

The technique described in a previous work [1] was applied to a NbTi microalloyed line pipe steel for the case of isothermal heat treatment between 1050°C and 1200°C. The input parameters for the phase-field simulations were deduced from physical models based on the results of isothermal holding experiments. The coarsening of the pinning particle was taken into account implicitly (assumed to undergo an Ostwald ripening process) as well as explicitly simulated by a numerical Kampann-Wagner model with the software package MatCalc. These simulations were compared with the mean-field concept proposed by Hillert [2]

Modeling of metastable phase equilibria and phase transformations in multicomponent steels

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Microstructure evolution in materials involves not only stable phases but also metastable ones. Thermodynamically unfavorable phases may appear transiently and compete with favorable phases, and thus change the kinetics of phase transformation remarkably [1]. In order to model such simultaneous and competitive phase transformations, appropriate descriptions of metastable phase equilibria and atomic mobilities are necessary in addition to that of stable ones. In this presentation, we study the kinetics of ferrite decomposition and precipitate evolution in several Fe-Cr-C steels by considering the concomitant nucleation, growth, and coarsening of both stable and metastable carbides. Existing thermodynamic and kinetic descriptions have been examined critically for metastable extrapolations. Possible improvements and general implications have been suggested. Our kinetic simulation was based on the generalized KWN [2] approach, and performed by using a new computational tool that is fully integrated with Thermo-Calc. Recently proposed models [3,4] for multicomponent nucleation and growth have been employed. The calculated temporal evolutions of the particle size, number density, volume fraction have been presented. The results show that competitive nucleation plays a very important role in the kinetics of ferrite decomposition.

Monte-carlo and phase field simulations of abnormal grain growth in Fe-3%Si steel approached by sub-boundary enhanced solid-state wetting

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Abnormal grain growth (AGG), which is also called the secondary recrystallization, often takes place after primary recrystallization of deformed polycrystalline materials. A famous example is the evolution of the Goss texture after secondary recrystallization of Fe-3%Si steel. A selective AGG of Goss grains has remained a puzzle over 70 years in the metallurgy community since its first discovery by Goss in 1935. We suggested the sub-boundary enhanced solid-state wetting as a mechanism of selective AGG of Goss grains. According to this mechanism, if Goss grains have sub-boundaries of low energy, they have an exclusively high probability to grow by solid-state wetting along a triple junction compared with other grains without sub-boundaries. This aspect has been confirmed by Monte-Carlo and Phase Field Model simulations. The simulations showed that if the abnormally-growing grain has a high fraction of low energy boundaries with the matrix grains, it favors the sub-boundary enhanced solid-state wetting and produces many island and peninsular grains frequently observed near the growth front of abnormally-growing Goss grains. The existence of sub-boundaries exclusively in abnormally-growing Goss grains has been experimentally confirmed. In order to understand why only Goss grains have sub-boundaries, the cold rolling process of the hot-rolled Fe-3%Si steel was analyzed by finite element method (FEM). The analysis showed that a small portion of Goss grains formed during hot rolling survives after cold rolling; the survived Goss grains have the lowest stored energy and are expected to undergo only recovery without recrystallization, producing sub-boundaries.
Phase equilibria of the Fe–Ni–Ta system at 1100 °C

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The phase equilibria of the Fe–Ni–Ta system at 1100 °C were investigated using 6 diffusion couples and 10 alloys, the compositions of which were selected on the basis of the experimental results of the (Fe-Ni alloy)/Ta diffusion couples. The samples were examined by means of optical microscopy, scanning electron microscopy, and electron probe microanalysis. Experimental results showed no existence of ternary compounds at 1100°C. The following five three–phase equilibria were observed: (1) (Ta)+Ta₂Ni+Ta(Fe,Ni), (2) Fe₂Ta+Ta(Fe,Ni)+TaNi₂, (3) Fe₂Ta+TaNi₂+TaNi₃, (4) Fe₂Ta+TaNi₃+(Fe,Ni), (5) TaNi₃+TaNi₈+(Fe,Ni). The compounds FeTa and NiTa form continuous solid solutions. The solubility of Fe in TaNi₂ and TaNi₃ was determined to be 18 and 7.8 at.%, respectively, while the solubility of Ni in Fe₂Ta was 40 at.%.

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Interface reactions of Cu-Sn-Ti based active brazing filler metals with diamond and steel substrate

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Super-abrasive tools with a diamond component are of great technical importance for the machining of metals, ceramics and stone. Cu-Sn-Ti filler metals have been widely used to braze diamond to e.g. steel substrates due to their relatively high strength and erosion resistance when compared to Ag-Cu alloys, and their lower melting point when compared to Ni-based alloys. The microstructural evolution in the vicinity of the involved interfaces during the brazing process is essential to achieve excellent performance and high service life times of the brazed components. Interface reactions between filler metals and diamond/steel substrate involve the formation and subsequent growth of many reaction products whose layering and morphology are the result of the interplay of the thermodynamics and kinetics of the whole system.

In this work, the application of the CALPHAD approach as an important tool for understanding and optimizing active brazing processes as well as brazing alloy compositions will be demonstrated. Based on our recently developed database thermodynamic and kinetic simulations using the Thermo-Calc® and DICTRA® software package were performed with the aim to predict interface reactions between Cu-Sn-Ti based filler metals and diamond as well as steel substrate, respectively. The simulation results were compared with experimental information on the interfacial microstructures obtained by scanning electron and transmission electron microscopy.
The Sapiens project:
A call for creating sustainable thermodynamic databases

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Probably CALPHAD databases users most frequent questions are: What is the origin of the information? Which data is inside? Can they be updated using my new experimental data? Can I change the model? How to connect them to 0 K first-principles calculated quantities? How to extract stable and metastable information to use in my own code for microstructure simulations?

Some of these questions are difficult to be answered even by CALPHAD databases creators. Changes, for example, in the melting temperature of a single pure element have an impact in the multicomponent database that is not easy to be evaluated if the model parameters and their relationship are not well documented. Proposals for changes to more physical models are available in literature since long time (see by instance the Ringberg series of recommendations sponsored by SGTE and Max-Plank Society), however, they have not been implemented even by SGTE due to the immense work it would require.

Motivate by these questions, the Sapiens project is created proposing well documented, flexible, cooperative and open work for the construction of knowledge-based and sustainable thermodynamic databases. Steels are selected as starting materials due to their challenging complexity which motivates several theoretical fronts in materials science like magnetism and metastability.

Sapiens project collects experimental data and uses physical based models at their best providing a forum for discussions and tests of new models and different applications. Iron and Chromium are the first elements studied in the project and first results are presented in this conference. Sapiens has industrial support and is purely academic. A call for international cooperation is done.
Identifying optimal conditions for alloy and process design using thermodynamic and properties databases, the FactSage software and the Mesh Adaptive Direct Searches algorithm

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With the FactSage software and database one can calculate phase diagrams and conditions of chemical equilibria in multicomponent systems; follow the course of equilibrium or Scheil-Gulliver cooling, predicting freezing ranges, volume changes and enthalpy changes; calculate the amounts of precipitates during subsequent annealing; calculate viscosities; etc. In principle, one could use the software to screen potential multicomponent alloys to find compositions having combinations of desired properties and phase assemblages (for example, minimum liquidus temperature, desired freezing range, desired density range and shrinkage ratio, type and amount of precipitates, etc.) by performing calculations in some systematic manner at a very large number of composition points. However, in order to screen a potential multicomponent alloy for compositions having optimal properties under a given set of constraints by such a brute force approach would require calculations at (at least) thousands of compositions, requiring several days of computation.

In the present work we apply optimization tools to automatically explore the possible compositions. To this end, we apply the Mesh Adaptive Direct Search (MADS) algorithm for constrained multi-objective optimization and combine it with the FactSage software. Direct search methods are designed to solve black-box optimization problems under very general sets of constraints, without computing derivatives, and require no information about the topology of the functions. This is essential if one is to optimize extremely complex and non-smooth functions with many local minima such as liquidus temperatures or discontinuous functions with many singularities such as the mass of precipitate in a phase after annealing at a given temperature.

Results for several examples will be presented.
Chemical potential phase diagrams and hydrogen storage thermodynamics

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Understanding of hydrogen storage thermodynamics is a key step toward design of new reaction paths and catalysts of the complex hydride systems. The method of Gibbs energy minimization often fails due to lack of Gibbs energy modeling parameters and difficulties in linking the bulk and surface defect stabilities. Use of chemical potential phase diagram by DFT calculations allows us to trace the hydrogen storage reaction paths and probe the different defects energetics in the material systems. The hydrogenation/dehydrogenation reaction paths and catalyst roles in the lithium boron hydrides and sodium alanate material systems are discussed using the chemical potential phase diagrams.

Thermodynamic databases for metal-hydrogen systems

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Thermodynamics determines the equilibrium temperature and pressure of the hydrogenation/dehydrogenation reactions in metallic hydrogen storage systems. The specific weight goal for hydrogen storage capacity of the US Department of Energy has limited the choice of candidate materials to light weight elements. The form in which hydrogen is stored in these systems is quite different from that in traditional, mainly transition group, storage materials. In light metal alloy systems hydrogen is stored in form of a hydride phase that is structurally different from the hydrogen-free metallic phases, while in the transition group metal alloys hydrogen is stored as an interstitial solution that has the same crystal structure as the parent phase. As a result, the transition group metal alloys have many advantages compared to the light metal hydride materials, for example, the reaction is not controlled by nucleation. Of the transition group materials, Zr,Ti-based Laves phases and bcc solid solutions are attractive because of their larger hydrogen storage capacity compared to the traditional AB5 compounds. Knowledge of the phase equilibria in these systems is the basis for optimizing alloy compositions and analysis of the of the reaction paths for the hydrogenation/dehydrogenation of these materials. Results from calculations with databases developed for light metal hydrides and transition metal-hydrogen systems with Laves phase will be presented.
Thermodynamic optimization of the system Pd-Rh-H-D-T

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Pd and Pd-Rh alloys are key materials for hydrogen and isotope storage. The Calphad method has been used to model the quinary system Pd-Rh-H-D-T. The constituting binary systems have been first described \cite{1}. Not only experimental phase diagrams but also thermodynamic properties such as calorimetric measurements and pressure-composition curves are well reproduced by adjusting parameters describing the Gibbs energy of the fcc phase according to the Calphad procedure. In order to describe Rh-H systems, a new equation of state of hydrogen has been obtained allowing to describe analytically the Gibbs energy and molar volume as a function of pressure \cite{2}. The binary systems can be combined and used to predict any kind of parameters in the quinary system e.g. isotope separation factor or plateau pressure as a function of Rh or isotope concentration. To achieve this, the Toop model should be used in the frame of the compound energy formalism. Paraequilibrium conditions (equilibrium as regards the fast diffusing elements) have been maintained by using calculations in pseudo-binary systems.

\begin{thebibliography}{9}
\end{thebibliography}
Prediction of phase formation during thin film deposition by thermodynamic calculation

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By physical vapour deposition (such as magnetron sputtering) extremely high cooling rates from the gas/plasma state are realised. The phases formed during deposition are often not those expected from the phase diagram. The phase formation depends on many factors, one of the most important being the substrate temperature, which determines the amount of diffusion during deposition. Typically a sequence from amorphous to single phase crystalline to multiphase is found on increasing substrate temperature. At relatively low substrate temperature only a single crystalline phase can form, since the diffusion is too slow to allow for phase separation. Then the phase with the lowest Gibbs energy at the deposited composition is expected to form. When depositing V$_2$AlC below about 600°C, V$_2$C is formed rather than V$_2$AlC. The figure below shows the Gibbs energies in the Al-V$_2$C section in the Al-V-C system. In this work we will investigate a few cases to see to how Gibbs energy curves can be used to predict phase formation.
Micropipes and surface energy of compound semiconductors

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In the compound semiconductors, large micropipes are produced in the grown single crystals or the epitaxially grown thin films. The origin of these micropipes have been proposed by Frank’s prediction, where the equilibrium radius ($r$) of the hollow core is determined by the force ($F$) balance between surface energy ($\gamma$) and the strained energy around dislocation core,

$$dF = 2\pi \gamma dr - \frac{\mu b^2}{8\pi^2 r^2} 2\pi r dr$$

If Burger’s vector ($b$) exceeds the order of magnitude 10Å, such a dislocation is only in equilibrium with an empty tube at its core.

Using physical properties of SiC, the radius of micropipe is predicted to be less than 10 Å, which is too small than expected from the experimental observations. Furthermore, the solvent process for SiC crystal growth, the generation of micropipes is highly depressed. For the liquid-solid interface applying the 1/10 of the vacuum-solid surface energy, the predicted radius becomes 10 times larger than that of vacuum-solid interface. This disagreement between the experimental result and the prediction suggests the another origin of the micropipe occurrence.

One possibility is the environmental dependency of the chemical potentials. In this study, ab-initio calculations of surface energy of 4H-SiC have been performed using VASP(Vienna Ab-initio Simulation Package). For the polar surface of (0001) shows 7.6J/m2 for C-rich side, and 2.8J/m2 for Si-rich side. The perpendicular surfaces against the polar surface show 3.5-4.5J/m2. This calculated results consistently explain the experimental results of the flat (0001) surface and the closeness of the micropipes of the grown crystals during the solvent processes.

Table 1. Micropipe radius predicted by Frank’s equation.

<table>
<thead>
<tr>
<th></th>
<th>Rigidity modulus $\mu$ [10¹¹ erg/cm³]</th>
<th>Surface energy $\gamma$ [erg/cm²]</th>
<th>$\mu/\gamma$ [cm²]</th>
<th>Dislocation radius For $b=10$Å [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>4.4</td>
<td>1400</td>
<td>0.32</td>
<td>4</td>
</tr>
<tr>
<td>NaCl</td>
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<td>155</td>
<td>0.10</td>
<td>12</td>
</tr>
<tr>
<td>SiC</td>
<td>25.0</td>
<td>5000 (vacuum)</td>
<td>0.20</td>
<td>6</td>
</tr>
<tr>
<td>SiC</td>
<td>25.0</td>
<td>500 (liquid)</td>
<td>0.02</td>
<td>63</td>
</tr>
</tbody>
</table>

Solid-state reactive diffusion in the Sn/(Pd-Ni) system

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Copper-base alloys are widely used as conductor materials in the electronics industry due to high electrical conductivity. If the Cu-base conductor is interconnected with a Sn-base solder, Cu-Sn compounds are produced at the interconnection between the conductor and the solder during soldering and then grow during energization heating at solid-state temperatures. The Cu-Sn compounds are brittle and possess high electrical resistivities. Hence, the growth of the compounds deteriorates the mechanical and electrical properties of the interconnection. To inhibit the formation of the compounds, the Cu-base conductor is usually plated with a Ni layer. However, Ni is not sufficiently corrosion resistant. Thus, the Ni layer is plated with a Au or Pd layer to improve corrosion resistance. In order to examine the influence of Ni on the growth behavior of compounds at the interconnection between the Sn-base solder and the multilayer Pd/Ni/Cu conductor during energization heating, the kinetics of the solid-state reactive diffusion in the Sn/(Pd-Ni) system was experimentally observed. In the experiment, Sn/(Pd-Ni)/Sn diffusion couples with Ni concentrations of 25.7, 50.5 and 74.6 at.% were isothermally annealed in the temperature range of 433-473 K for various times up to 545 h. For 25.7 at.% Ni, compound layers of (Pd, Ni)Sn₄, (Pd, Ni)Sn₃ and (Pd, Ni)Sn₂ are formed at the interface in the diffusion couple during annealing. On the other hand, (Pd, Ni)Sn₃ and (Pd, Ni)Sn₂ are not clearly recognized for 50.5 and 74.6 at.% Ni. For 74.6 at.% Ni, however, Ni₃Sn₄ is produced as a thin layer at the interface between (Pd, Ni)Sn₄ and the Pd-Ni alloy. The total thickness of the compound layers is proportional to a power function of the annealing time, and the exponent of the power function is smaller than 0.5. Thus, the growth of the compound layers is controlled by boundary and volume diffusion. At the experimental annealing times, the overall growth rate of the compound layers decreases with increasing Ni concentration of the Pd-Ni alloy. Consequently, the growth of compounds at the interconnection is decelerated by the addition of Ni into Pd in multilayer Pd/Ni/Cu conductor.
Phase field simulations of growth and coarsening in the interdiffusion zone of lead free solder joints

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Solute transport and the growth of intermetallic layers, precipitates and voids in the interdiffusion zone of solder joints is highly affected by temperature and solder and substrate compositions, but also by the initial size, shape and arrangement of the grains and precipitates. A phase-field model for multi-component alloys is developed that distinguishes different phases and grain orientations and considers the effect of bulk and grain boundary diffusion. Thereto, a recently developed phase-field model for grain growth in anisotropic systems [1] is combined with the phase-field approach of [2] and [3] for diffusion and phase transitions in alloys. Relations between the model parameters and an alloy’s interface and bulk properties are derived with high accuracy. Furthermore, the model formulation and parameter choice guarantee a constant diffuse interface width, even for large variations in interface properties. This is most efficient for the computations and gives a high controllability over the overall accuracy of the simulations.

The presented work fits within the activities of COST MP0602 “Advanced Solder Materials for High Temperature Application”. Simulation results will be discussed mainly for Ag-Cu-Sn solders in contact with Cu and Cu(Ni) substrates. For the bulk thermodynamic properties, the CALPHAD descriptions of the COST 531 database [4] are taken. As far as possible, information on diffusion and interface properties is taken from literature or provided by other participants of the Action.

Simultaneous mechanisms in the formation of core/shell microstructure

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Quantitative phase field model, employing CALPHAD thermodynamic and mobility databases as inputs, has been formulated to study the formation mechanisms simultaneously involved in the formation of the core/shell microstructures [1] from the liquid immiscible alloy during gas atomization process. The respective role of spinodal decomposition, fluid flow and Marangoni motion of second-phase droplets and their coupling at different stage of formation are analyzed. Several interesting mechanisms dominating the microstructure evolution, including "collision-induced-collision" (Figure 1), attractive actions between the droplets, were identified. This work sheds lights on improve control level on the design and development of the core/shell composite materials.

![Collision-induced-collision of droplets during coarsening](image)

Figure 1 Collision-induced-collision of droplets during coarsening

Abstract: Oral Presentations, May 28 (Friday)

- Session 15: Phase stability of alloy systems – I
- Session 16: Phase stability of alloy systems – II
Lattice stability in the presence of interstitial solutes

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It has long been known that impurities can affect the crystalline structure of elements such as Cr, Ta, and W. Here, *ab initio* calculations are applied to clarify the role of C, N, O, and F on the stability of tetrahedrally close packed structures such as A15 and sigma structures relative to the bcc crystal structure. It is shown that very small weight fractions of these impurities can drastically change the relative stabilities for the heavier transition metals. In lighter transition metals, or their alloys, such as FeCr, these impurities play a much less significant role.
First principles determination of phase transitions in magnetic shape memory alloys

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Martensitic phase transformations are of key importance for many modern material systems. They are responsible for high work-hardening rates and tensile strength in advanced steels as well as for the shape memory effect in various metallic alloys. A first principles determination of such first order structural transitions is often challenging, if different excitation mechanisms or a softening of vibrational modes needs to be considered. This applies also to Ni$_2$MnGa, being a typical Heusler alloy that shows a shape memory effect. In the high-temperature austenitic phase it has a cubic L2$_1$ structure, whereas below a critical temperature the symmetry is reduced by an orthorhombic distortion with lattice deformations of up to 10%. Due to the ferromagnetic order, the transition between several orthorhombic variants can also be triggered by a magnetic field. The material system is therefore a very promising candidate for applications, but its operation temperatures and ductility still need to be improved. For this purpose an extension of the currently very limited knowledge on the phase diagram and the nature of the transitions is decisive.

In order to identify the stable structures and their transitions we performed ab initio calculations of free energies for the austenite, the (modulated) pre-martensite and the unmodulated martensite. Quasiharmonic phonons and fixed-spin magnons are considered, employing density functional theory. Particular care has been taken to determine the shuffling structures related to soft phonons. Using this approach we were able to successfully describe the phase transition in detail, to reveal the involved delicate interplay of vibrational and magnetic excitations and to accurately determine the transition temperature [1]. The methods developed for the Heusler systems can now be applied to predict structural phase transitions also in other materials.

Thermodynamic assessment of Nb-Ni-Ti ternary system by combining first-principles method and CALPHAD approach

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The Nb-Ni-Ti ternary system is thermodynamically assessed by the CALPHAD approach with the help of first-principles calculations. To enable the thermodynamics description of the binary systems, the results from a previous evaluation are adopted for the Nb-Ni, Nb-Ti and Ni-Ti systems. First-Principle calculations have been performed to determine the energies of formation of the end-members of intermediate phases NiTi, Ni$_3$Ti and NbNi$_3$ phases due to solubility of third element and used as input data in evaluating the Gibbs energy functions of those phases. The optimization of the Nb-Ni-Ti system is performed by PARROT module using available experimental data from literature. Isothermal sections at 973 K, 1073 K and 1173 K and vertical sections at 28 and 60 at.% of Ni of the ternary system are calculated, showing good agreement with the experimental data. In addition, the liquidus projection of the Nb-Ni-Ti ternary system is calculated.
First-principles calculations and thermodynamic modeling of the B-C system

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The thermodynamic property of the B-C binary system is modeled through the CALPHAD approach using both experimental data in the literature and data from current first-principles calculations. First-principles calculations based on density functional theory (DFT) are performed using the Vienna Ab-initio Simulation Package (VASP). The projector augmented-wave (PAW) method is used and the exchange and correlation energy are described with the supplied generalized gradient approximation (GGA) pseudopotentials. The finite temperature thermodynamic properties are obtained from the first-principles calculations coupled with Debye model. After the assessment of the available experimental data and first-principles results, B11(B,C)(B,C,Va)(B,Va)(B,C,Va) sublattice model is selected [1] to describe the solubility of carbon in B4C phase.

Electronic and elastic properties of (Fe,Mn)$_3$AlC studied by density functional theory calculations

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Mn-Al-C steels have been extensively studied due to their technological applicability. These alloys are known that nano-sized kappa-carbide particles are dispersed in an austenic solid solution matrix [1], and are known to be ferromagnetic [2]. Kappa-carbide is expected to enhance the ductility and the stability of alloys. We have studied structural, electronic, and elastic properties of (Fe,Mn)$_3$AlC, kappa-carbides, focusing on the change in physical properties accompanied by the varying contents of Mn. We employed the density functional theory calculations in conjunction with the projector augmented wave potentials and the generalized gradient approximation. In the perovskite-type structure ($E2_1$) of (Fe,Mn)$_3$AlC, iron (or manganese) atoms are located at the face centers, aluminium atoms are at the corner of the cube, and the carbon atoms take the body-center site of the cube. We obtained the equilibrium crystal structure, and examined the change in formation energy for different concentrations of Mn. We have calculated elastic coefficients, such as bulk modulus and shear moduli, of the alloys. Finally, the electronic and magnetic properties were investigated by looking at charge density, electronic density of states, and band structure.

Crystal structure and formation energy of epsilon-carbide

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The thermodynamic properties of epsilon carbide are not established and its crystal structure has uncertainties because the iron to carbon ratio is not stoichiometric. The formation energy and equilibrium lattice parameters for the epsilon carbide structure with $\text{Fe}_3\text{C}$ and $\text{Fe}_2\text{C}$ formula units have been estimated using first-principles calculations based on the total energy all-electron full-potential linearized augmented plane-wave method within the generalized gradient approximation to density functional theory. The results show that formation enthalpy is about 5.13 kJ and 7.00 kJ for one mole of atoms in $\text{Fe}_3\text{C}$ and $\text{Fe}_2\text{C}$ respectively, which corresponds to about 0.25 kJ reduction and 1.62 kJ increments in the formation energies when compared with pure cementite [1]. The results are now being implemented in the CALPHAD type database for use with programs such as MTDATA or ThermoCalc.

Phase stability and physical properties of Cr$_5$B$_3$-type intermetallic compounds from first principles calculations

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We present a study of the thermodynamic and physical properties of Cr$_5$B$_3$-type intermetallic compounds (Ta$_5$Si$_3$ and W$_5$Si$_3$) by means of density functional theory based calculations [1-2]. The lattice constants, formation enthalpies, elastic constants and elastic moduli of these compounds have been calculated and compared to the available experimental values: the calculated lattice constants and formation enthalpy are in good agreement with the experimental data. The electronic density of states (DOS) and the bonding charge density have also been calculated to elucidate the bonding mechanism in these compounds and the results indicate that bonding is mostly of covalent nature. Concerning the mechanical behavior, the high B/G ratio indicates that these Cr$_5$B$_3$-type compounds are prone to ductile behavior.

Finally, by using a quasiharmonic Debye model, the Debye temperature, the heat capacity, the coefficient of thermal expansion and the Grüneisen parameter have also been obtained and are in good agreement with the available experimental results.

Thermodynamic modelling of the non-equilibrium phase transformation during spontaneous vitrification in Ti-Cr alloys

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Spontaneous vitrification is a phenomenon where a crystalline phase transforms to the amorphous phase on annealing at low temperatures. It is known to occur in several binary alloy systems. The models reported in literature to elucidate this phenomenon suffer from several drawbacks. These models treat this non-equilibrium process as an equilibrium process involving two metastable phases. The thermodynamics of the “spontaneous vitrification” process has been modelled using the concept of Transformation Diagrams. This method considers the thermodynamics of non-equilibrium phase transformation and does not involve assumptions of equilibrium at any stage. A significant conclusion derived from the present model is that it is the close-packed h.c.p. structure that transforms to the amorphous phase whereas the transformation of the relatively open b.c.c structure to the amorphous phase is forbidden, thermodynamically. These conclusions are in contrast with the predictions of the earlier models.
Abstracts: Poster Presentations (May 24 and 25)
Phase equilibria of the Ni-Si-Zn system at 600ºC

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The phase equilibria at 600ºC of the Ni-Si-Zn system were investigated by using a combination of reaction diffusion couples with equilibrated alloys. The alloys were prepared by melting the elemental ingredients in the alumina crucibles sealed in quartz tubes. The samples were examined by means of optical microscopy, X-ray diffraction, scanning electron microscopy with energy dispersive X-ray spectroscopy, and electron probe microanalysis. The γ phase region in the Ni-Zn system, which is controversial in the literature, is composed of two subdivisions, viz. γ-NiZn$_3$ and γ-Ni$_2$Zn$_{11}$. The ternary phase β’, which is isomorphous to the binary β phase (HT) and adjacent to β$_1$-ZnNi in the Ni-Zn system, is assumed to be the β phase stabilized by the third element Si. The existence of two ternary compounds, Ni$_2$SiZn$_3$ ($\tau_3$) and Ni$_3$Si$_2$Zn ($\tau_4$), reported in literature was confirmed. The solubility of Zn in NiSi$_2$ and Ni$_2$Si were determined to be 8.7 at. % Zn and 8.4 at.% Zn, respectively. The solubility of Zn in Ni$_2$Si was measured to be about 9.1 at.% Zn. The solubility of Zn in Ni$_3$Si$_2$, Ni$_3$Si$_2$ and NiSi, and that of Si in γ-NiZn$_3$, γ-Ni$_2$Zn$_{11}$ and Liquid are negligibly little. The following ten three-phase equilibria were well established: (1) $\tau_3$ + L + γ-Ni$_2$Zn$_{11}$, (2) $\tau_3$ + γ-NiZn$_3$ + $\tau_1$, (3) NiSi$_2$ + $\tau_3$ + L, (4) NiSi$_2$ + NiSi + $\tau_3$, (5) NiSi + $\tau_3$ + $\tau_4$, (6) NiSi + Ni$_3$Si$_2$ + $\tau_4$, (7) $\tau_4$ + Ni$_3$Si$_2$ + Ni$_2$Si, (8) $\tau_3$ + $\tau_4$ + Ni$_2$Si, (9) Ni$_2$Si + $\tau_3$ + $\tau_1$, and (10) Ni$_3$Si$_2$ + Ni$_3$Si + β$_1$-ZnNi.

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Machining performance of Ti-Al-Si-N coated inserts

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Ti-Al-Si-N quaternary coating has recently been developed for industrial applications due to its excellent machining performance. Here, we present a comparative research on Ti-Al-N single layer, Ti-Al-Si-N single layer, TiAlN-TiAlSiN bilayer and TiAlN/TiAlSiN multilayer coatings deposited onto cemented carbide substrates by cathodic arc evaporation. The incorporation of Si into Ti-Al-N coating results in an increase in hardness and thermal stability due to the formation of nanocomposite nc-TiAlN/a-Si\textsubscript{3}N\textsubscript{4} (nc means nanocrystalline and a means armorphous), and thereby causes an improved performance during continuous cutting. However, the lower toughness and adhesive strength with substrate reduce its cutting-life during milling. The tribological properties of Ti-Al-Si-N coated inserts during milling can be improved by a structure adjustment from the nanocomposite into TiAlN- TiAlSiN bilayer and TiAlN/TiAlSiN multilayer coatings, which cause an increase to 156% and 172% for the life-time of Ti-Al-Si-N coated inserts, respectively. Our results indicate that the machining performance of coatings containing Si in both continuous cutting and milling can be optimized by structure design of TiAlN/TiAlSiN multilayer, where the coating sustains a high hardness of Ti-Al-Si-N coating in addition to a good cohesive strength with the substrate similar to the Ti-Al-N coating.

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Phase-field simulations of the Ni-Al diffusion couples

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When two alloys are in intimate contact at elevated temperatures, interdiffusion occurs
and a unique microstructure develops in the vicinity of their contact interface. It is well
known that knowledge of this interdiffusion microstructure is of critical importance to
advanced alloy design. By linking to the real thermodynamic and atomic mobility databases,
2D phase-field simulation was employed to examine the evolution of interdiffusion
microstructures in various binary Ni-Al diffusion couples by means of MICRESS
(MICRostructure Evolution Simulation Software). A few representative diffusion couples
including the phases (Ni), L12 and B2 in the Al-Ni system were chosen as the target. Two
different strategies were employed to make up the diffusion couples involving two-phase
alloys. The simulated microstructures in various diffusion couples were classified into Type 0,
Type I, Type II and Mixed type according to the type of boundaries formed, and compared
with the corresponding experimental information. Moreover, the effect of coherent strain and
external stress on the interdiffusion microstructure was also taken into account.

Figure 1. Schematic diagram for the phase-field simulation procedure of
interdiffusion in the Al-Ni diffusion couples

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Rhine-Westphalia and the European community is highly acknowledged.
The effect of Ti atom on hydrogenation of Al(111) surface

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We presented first-principles calculations on dissociation of hydrogen molecule and subsequent diffusion of atomic hydrogen over both clean and Ti-doped Al(111) surfaces. Replacing one Al atom from surface or subsurface layer with Ti atom was considered. We find that such a substitutional doping is energetically favorable, although Ti atom prefers to substitute one of the Al atoms from the subsurface layer. The calculations show that the activation barrier for the dissociation of H₂ over clean Al(111) surface is quite high (1.28 eV). The energy barriers are reduced to 0.66 eV and 0.71 eV when Ti atom substitutes for one of Al atoms from the surface and subsurface, respectively. Thus Ti doping will decrease the hydrogen dissociation barrier by about 0.6 eV. However, H atoms are restricted by Ti strongly when Ti is in the surface layer, with the diffusion barrier being as high as 0.90 eV. Such a restriction hinders the diffusion of hydrogen atom away from the catalyst site. In the case of subsurface substitution, the diffusion barrier for H atom away from Ti atom is relative low (0.42 eV). The high dissociation barrier of H₂ over the clean Al surface is responsible for the slow kinetics of the hydrogenation on NaAlH₄. The present calculations can explain the experimentally observed improvement in absorption kinetics of H₂ through ball mill when Ti-based compounds were introduced into NaAlH₄.

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Experimental investigation and thermodynamic modeling of the Cu-Fe-Mg and Cu-Mg-Si systems

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The isothermal sections at 500 and 700°C of both the Cu-Fe-Mg and Cu-Mg-Si systems were measured by using a combination of X-ray analysis and scanning electron microscopy with energy dispersive X-ray analysis. For the Cu-Fe-Mg system, no experimental data are available in the literature and thus 10 alloys were prepared for each isothermal section. The phase equilibria in this system can be well described by a direct extrapolation from the relevant binary systems since no ternary compound was found. For the Cu-Mg-Si system, for which the literature data are mainly reported at 450°C isothermal section [1], 25 alloys for each isothermal section were prepared in order to establish the phase relationships between each binary phase and the 3 ternary phases. Based on the data both from the literature and the present work, a thermodynamic modeling for the Cu-Mg-Si system was then conducted. All of the phases, including the C15 MgCu₂-type ternary laves phase, have been modeled. The calculated phase equilibria and thermodynamic properties agree reasonably well with the experimental ones. Significant improvements have been made, compared with the previous assessments.

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Experimental investigation and thermodynamic modeling on the Cu-Ni-Si system

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The isothermal section of the ternary Cu-Ni-Si system at 700\textdegreeC was experimentally determined. Thirty Cu-Ni-Si alloys were prepared by arc melting the pure elements. The samples were annealed at 700\textdegreeC for 30 days, followed by examination with optical microscopy, DTA, X-ray diffraction, scanning electron microscopy with energy dispersive X-ray spectroscopy and electron probe microanalysis. Eleven ternary phase regions were determined. Two ternary compounds around the compositions of Cu\textsubscript{60}Ni\textsubscript{13}Si\textsubscript{27} and Cu\textsubscript{46}Ni\textsubscript{25}Si\textsubscript{29} were observed. The Cu\textsubscript{56}Si\textsubscript{11} phase can dissolve Ni up to 20 at.\%. A thermodynamic modeling for this system was performed by considering reliable literature data and incorporating the current experimental result. A self-consistent set of thermodynamic parameters was obtained, and the calculated results show a good agreement with the experimental date.

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Development of the thermodynamic and atomic mobility database for active brazing of diamond to steel substrate

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Cu-Sn-Ti filler metals have been used widely to braze superhard materials like diamond to steel substrate due to their relatively high strength and erosion resistance when compared to Ag-Cu alloys, and their lower melting point when compared to Ni-based alloys. The microstructural evolution of the interface area and filler metals during the brazing process is essential to achieve excellent performance of brazing joints. In order to better understand interface reactions between filler metals and diamond/substrate, thermodynamic and kinetic information related filler metals and diamond/substrate are necessary. In this work, thermodynamic and atomic mobility database of the multi-component systems related to Cu-Sn-Ti based filler metals and diamond as well as steel substrate have been developed using the CALPHAD method based on the available experimental information:

1. The Cu-Sn and Cu-Ti binary systems were improved, and the Sn-Ti binary system was also updated according to the new experimental data and recent theoretical calculation results. Thermodynamic modeling of the Cu-Sn-Ti ternary system was performed. Combined with previous assessments of binary or ternary systems, a thermodynamic database of the Cu-Sn-Ti-Fe-(Ni-C) systems has been obtained.

2. Based on the available thermodynamic information and diffusion coefficient data, the atomic mobilities of Cu, Fe, Ni, Ti and Sn in face-centered cubic (fcc) Cu-Sn, Cu-Ti, Cu-Fe and Ni-Sn alloys have been assessed as a function of temperature and composition in terms of the CALPHAD method using the DICTRA® software package.
The experimental and theoretical study of the In-Ni-Sn system

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The ternary In-Ni-Sn system was experimentally and theoretically studied in the scope of this work. The phase equilibria of the system In-Ni-Sn were investigated at 700 °C using X-ray diffraction (XRD), scanning electron microscopy (SEM) and the differential thermal analysis (DTA). This temperature was chosen because it allows obtaining reliable results in reasonable time that can be used as a starting point for CALPHAD modelling.

No theoretical assessment of the In-Ni-Sn system has existed up to now; hence this study is also focused on its thermodynamic assessment, using own experimental data and experimental data from [1]. The unary data were taken from new version of SGTE (4.4) database [2]. The thermodynamic data for In-Ni, Ni-Sn and In-Sn binary systems used in this assessment are taken from the SOLDERS thermodynamic database [3]. However, Ni3Sn2 phase existing in the Ni-Sn system and Ni3In phase in the In-Ni system, which are of the Ni3In type were remodeled to unify the thermodynamic models for phases with identical crystallographic structure within the thermodynamic database.


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Thermodynamic assessment of the aluminum corner of the Al-Fe-Mn-Si system

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A new assessment of the aluminium corner of the quaternary Al-Fe-Mn-Si system has been achieved that extends the COST507 database [1]. This assessment makes use of a recent improved description of the ternary Al-Fe-Si system [2]. In the present work, modelling of the Al-rich corner of the quaternary Al-Fe-Mn-Si system has been carried out by introducing Fe solubility into the so-called alpha-AlMnSi and beta-AlMnSi phases of the Al-Mn-Si system. A critical review of the data available on the quaternary system is presented and used for the extension of the description of these ternary phases into the quaternary Al-FeMn-Si.

The present work allowed to reproduce satisfactorily most of the experimental features available for the aluminum corner of the Al-Fe-Mn-Si system by accounting for significant substitution of Mn by Fe in the two relevant ternary compounds of the Al-Mn-Si system.

The volume as a new variable in the cluster variation method (CVM)

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The Cluster Variation Method (CVM), used in Thermodynamic calculations, is based on a mean-field approximation to the free energy. The CVM was originally devised to treat purely configurational cases. The scope of the present work is to enhance the method’s capabilities, introducing other contributions terms to the free energy. The volumetric contributions, either dilatacional or vibrational, are believed to be of great importance, and were therefore incorporated into the method in the present work.

Another aim is to verify whether this approach would solve the problem with the temperature range as calculated with the CVM using ab initio data. In this kind of calculation, the phase diagram temperature range is usually twice or three times as large as experimentally verified or, equivalently, as the ones obtained in CVM calculations using experimental data. Therefore, a new minimisation algorithm was proposed to handle the vibrational effects and the volume as a variable. The algorithm is based on the NIM (Natural Iteration Method), which is used for the minimisation in the configurational case.

The Debye-Grüneisen approximation has been adapted, with elastical considerations, for multicomponent systems (i.e., alloys). The method is based on the Anderson model, when ab initio elastic constants are available, or on Moruzzi-Janak-Schwarz model otherwise. In ab initio calculations it is possible to determine the elastic constants for each structure considered. Using these data, Debye temperature and bulk modulus at 0K are determined with greater accuracy. First-principles cohesion/formation energies in function of the volume for the b.c.c. Fe-Al (body-centered cubic iron-aluminum) system were used as an example to derive parameters to the model.
Experimental investigation of the ZrO$_2$-Y$_2$O$_3$-Nb$_2$O$_5$ system at 1550°C

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Ceramic materials based on the ZrO$_2$-Y$_2$O$_3$-Nb$_2$O$_5$ system are potential candidates for Thermal Barrier Coatings (TBC). The knowledge of phase equilibria is the key to develop the best compositions for processing these materials and optimize their properties. The Calphad method gives good predictions of phase equilibria when reliable databases are available. The aim of the present work is to contribute to the development of TBC databases through the experimental investigation of phase equilibria on the ZrO$_2$-Y$_2$O$_3$-Nb$_2$O$_5$ system. The binaries ZrO$_2$-Y$_2$O$_3$ and ZrO$_2$-Nb$_2$O$_5$ are well established [1,2], but experimental information is lacking on the Y$_2$O$_3$-Nb$_2$O$_5$, specially on the Nb$_2$O$_5$-rich side [3]. No information was found for the ternary so far. About 12 compositions on each binary and 3 on the ternary were chosen for this study. Pellets were cold pressed from mixtures of the pure oxides and sintered for one hour at 1500°C and subsequently annealed for 60, 120 and 180 hours at 1550°C. Their microstructures where characterized by X-ray diffractometry and scanning electron microscopy. Our results are in agreement with the literature data for the three binaries and give new information on the Y$_2$O$_3$-Nb$_2$O$_5$ and ZrO$_2$-Y$_2$O$_3$-Nb$_2$O$_5$ systems.

Neutron diffraction study of FeCr$_2$O$_4$ spinel

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Chromium spinels have attracted geological interest in trying to establish the thermodynamics that govern mineral formation. From the physics viewpoint they are challenging materials that have attracted much research interest in recent years due to complex magnetic ground states resulting from high geometrical frustration. The transition to an ordered state often takes place through a spin–lattice coupling that partially lifts the magnetic degeneracy. The study has been extended to tetragonal spinels, of which FeCr$_2$O$_4$ is one of interesting example. In the system, magnetic Fe$^{2+}$ and Cr$^{3+}$ ions occupy the tetrahedrally coordinated A sites and the B sites, respectively. This system undergoes a first order structural transition from the ideal cubic spinel structure to a tetragonally distorted phase in which magnetic interactions between Cr$^{3+}$ ions are no longer equivalent. Early magnetic studies by neutron diffraction were centered on solving the complex magnetic structure and showed characteristics typical of the cone spiral spin arrangement at low temperatures [1,2], although no analysis of intensities was considered. In order to clarify the magnetic ground state in FeCr$_2$O$_4$, we have carried out a detailed study using neutron powder diffraction. We will present a systematic analysis of obtained diffraction data. We will also discuss the phase stabilities based on free energies of competing states from the result of the first-principles calculations.

Assessment of the lead-free solder Bi-Cu-Sn alloy system

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Liquid phase of Bi-Cu-Su system was optimized basing on the available experimental data: tin activities from emf measurements, bismuth activities from vapour pressure experiments, integral enthalpy from calorimetry and phase boundaries from DSC/DTA.

Thermodynamic parameters for binary subsystems: Bi-Sn and Cu-Sn were taken from COST 531 database [1] and those for Bi-Cu alloys were from the most recent reassessment of this system made by Watson [2].

The existence of the extensive miscibility gap reported earlier by [3] was confirmed and good agreement of calculated phase boundaries and thermodynamic properties with experimental data was observed.


Thermodynamic simulation of oxidation of metal powders

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The dispersion of a melt in a gas flow is a common method for production of nanoparticle powders. The applicability of the thermodynamic simulation to the qualitative description of the processes, which take place in the surface layer of a metal droplet during its interaction with air, has been considered. The problem has been solved for a metal containing (wt %) 95 Fe, 0.5 V, 0.1 Cr, 0.2 Si, and 5 C.

The thermodynamic simulation was performed using an ACTPA program package based on the principle of maximizing the entropy of a thermodynamic system.

The following conditions and assumptions were used in the thermodynamic simulation:
1) The system is equilibrium and isolated;
2) The concentration of initial materials in the system corresponds to the metal-gas mass ratio under steady-state conditions of a real process;
3) The total pressure and the temperature variation range correspond to conditions of a real process;
4) The system can include two condensed phases of solutions (metallic and slag) and phases of individual substances;
5) The concentrations of the initial materials and the interaction products, the temperature, and the pressure are equal at any point in the volume of the system; that is, any distribution gradients are absent;
6) The solubility of gases in condensed phases and the interphase energy are disregarded;
7) The secondary oxidation does not change the temperature between the oxidized layer and the metal;
8) The external atmosphere is excluded from the interaction in the case of the internal oxidation;
9) The oxidation front moves from the surface to the bulk by layers; that is, the interaction of the first oxidized layer with the metal is simulated first.

According to the calculations, all oxygen is consumed for oxidation. The ratio between CO and CO\textsubscript{2}, which result from decarbonization of the surface layer, is close to four. The surface layer is fully decarbonized, and iron in this layer is partially oxidized to wustite. At temperatures of 1800-1850 K the thermal effect of the system in the equilibrium state changes its sign to positive.
First-principles study on Fe substituted Cr$_{23}$C$_6$

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Cr$_{23}$C$_6$ and its various solid solutions is a vital phase in the most modern of creep-resistant steels. Although there has been a great deal of work in understanding its significance with respect to elevated temperature properties, the detailed thermodynamic properties deserve further attention. In particular, there is a long-term need to establish the atom-distribution, energetic and structural implications of different atoms in the basic Cr$_{23}$C$_6$ crystal structure, including solutes such as iron and boron. The standard thermodynamic assessments which are based on macroscopic measurements do not reveal such information. To work towards this goal, we use the all-electron full potential linearized augmented plane-wave method (FLAPW) within the generalized gradient approximation [1], a scheme more accurate than a variety of other density functional methods. The calculated ground state equilibrium lattice parameter is 10.57 Å for nonmagnetic Cr$_{23}$C$_6$ and 10.56 Å for ferromagnetic FeCr$_{22}$C$_6$ where Fe atom prefers to substitute the 4a site. The formation enthalpy of Cr$_{23}$C$_6$ is calculated to be 1.82 kJ/atom-mol higher than the lowest formation enthalpy of FeCr$_{22}$C$_6$. In future work we hope to introduce boron and nitrogen into the lattice given its known influence on the coarsening behavior of the carbide, and indeed to incorporate the energies thus calculated into phase diagram calculation methods such as CALPHAD.

Packing structure and the permeation properties of hydrogen separable membrane in Ni-Al metallic glass

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Metallic glasses showing various functions have been newly at the center of attention in the field of hydrogen separable membrane. The main reason of this interest is due to the comparatively high permeability and resistance to hydrogen embrittlement of hydrogen separable amorphous membrane. Despite extensive study, the mechanism of hydrogen permeation and embrittlement has remained unclear. Therefore, in order to investigate the structural effect in amorphous membrane on the diffusivity of hydrogen and resistance to hydrogen embrittlement, we varied the atomic packing structure of Ni-Al amorphous membrane by changing cooling rate and examined its effect on two permeation properties. Finally, using Voronoi tessellation method, we analyzed the short-range ordering (SRO) structure of the simulated alloys and structural change by hydrogen charging which is related to the hydrogen embrittlement mechanism. We expect that this study in terms of structure could suggest the methodology to design hydrogen separable membrane of good quality, which can replace currently used high cost Pd-based membrane.
Experimental investigation of phase equilibria in the Sn-Ni-Zn system

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The ternary system Sn-Ni-Zn is of interest for the investigation of the interlayer formation of Sn-Zn high-temperature Pb-free solder and the Ni substrates. But up to now, only limited research has been reported on the Sn-Ni-Zn ternary system. In this study, the phase equilibria of the Sn-Ni-Zn ternary system, including three isothermal section in the Sn-Zn rich portion (less than 60 at.% Ni) at 200°C, 500°C, and 800°C, were investigated by means of the scanning electron microscopy (SEM), X-ray diffraction (XRD) and electron probe microanalysis (EPMA). The experimental results indicated that Zn solubility in \( \beta \)-Sn unary phase largely increases with Ni in the Sn-Ni-Zn ternary system. And there are larger ternary solubilities of Zn in the \( \text{Ni}_3\text{Sn}_2 \) and \( \text{Ni}_3\text{Sn}_4 \) phase in the Ni-Sn binary system and Sn in the \( \beta \), and \( \beta_1 \) phase in the Ni-Zn binary system. In addition, there are ternary phases \( \text{Sn}_4\text{Ni}_3\text{Zn}_4 \), and \( \text{Sn}_4\text{Ni}_4\text{Zn}_2 \) which are equilibrium state lower than about 500°C. Thermodynamic assessment of the Sn-Ni-Zn ternary system was carried out by means of CALPHAD method.
Numerical analysis of dilatational anisotropy of layered steel in dilatometry

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Dilatometry has been widely used as an experimental method to measure phase transformation behaviors in steels. One of important assumptions in the dilatometry is isotropic volume change of the dilatometric specimen. If the steel has micro-structural layers due to manganese inhomogeneity, however, the dilatation of the steel specimen shows an anisotropic behavior depending on direction of layers. In this study, numerical calculations on the dilatometry of layered steel were carried out to investigate the anisotropic behavior due to micro-structural layers. An implicit finite element code which was coupled with models for phase transformation and transformation plasticity was developed for thermo-elastic-plastic analyses. The calculated results indicate that the anisotropic behavior depending on direction of layers originates from the transformation plasticity. And the source of stress which causes this transformation plasticity is an induced stress to maintain continuum interface between the layers.
Experimental investigation and thermodynamic modelling of the Au-Ge-X (X=Cu, Ni) ternary systems

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The Au-Ge-Cu and Au-Ge-Ni alloys are potential candidates of the high temperature Pb-free solders. It is quite important to develop the comprehensive thermodynamic databases for these two ternary systems in order to design the novel solders as well as to understand the microstructure evolution at the interface between the solder and the substrate. The aim of the present work is to develop the thermodynamic descriptions of the Au-Ge-Ni and Au-Ge-Cu systems using the CALPHAD method.

As a very good support to the optimization work, some Ni-Ge alloy specimens (30-50at.%Ge) were arc melted, followed by DTA examination for the phase transformation. Additionally, the enthalpies of formation of β-Ni₃Ge (L1₂ ordered phase) and NiGe phases were determined with combination of calorimetric measurements and first principle calculations. Taking account of the experimental results of this work and the previous research, the Ni-Ge binary system was thermodynamically optimized. The Au-Ge-Ni ternary system was then extrapolated to calculate some isothermal sections, vertical sections and liquidus projection.

On the other hand, the Cu-Ge binary system was unavailable as only one constituent binary system in the Au-Ge-Cu ternary system. Thus it was assessed considering all the available experimental information from the literature, and then the extrapolation of the Au-Ge-Cu ternary system was carried out. Liquidus projection, some attractive vertical sections and isothermal sections were provided as well.
A model and database for the viscosity of molten oxides

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Over the past several years, through critical evaluation of all available thermodynamic and phase equilibrium data, we have developed a quantitative thermodynamic description of multicomponent oxide melts using the Modified Quasichemical Model for short-range ordering. From the resultant database the local structure of the liquid, in terms of the bridging behavior of oxygen as a function of composition and temperature, can be calculated. The structural description of the liquid can be refined by calculating the concentration of structural units, the so-called Q-species, based on the bridging behavior using some simplifying assumptions.

We have developed a model for the viscosity of silicate melts based on the concentration of Q-species in the liquid. In borosilicate melts, a unified network is formed which is built of Si-O-Si, B-O-B and Si-O-B oxygen bridges. In ternary systems containing Al$_2$O$_3$, a viscosity maximum arises due to the so-called “Charge Compensation Effect” when Al$^{3+}$ cations assume tetrahedral coordination and enter the silicate network, while the additional negative charge resulting from the fourth oxygen is compensated by the presence of a second cation, such as Na$^+$, in the vicinity of Al$^{3+}$. The viscosity of these systems is modeled by assuming that the charge compensated tetrahedral Al has the same effect on viscosity as Si. The model quantitatively predicts not only the viscosity maximum but also the complex shape of the curves of viscosity versus composition and temperature in ternary systems containing Al$_2$O$_3$ with only 2 temperature-independent ternary parameters. These are the only ternary parameters used by the model.

A database of unary, binary and ternary model parameters has been developed for oxide melts containing Si, B, Al, Ca, Mg, Li, Na, K, Mn, Ni, Fe$^{2+}$, Fe$^{3+}$, Pb, Zn, Ti and F. The viscosity of multicomponent melts is predicted from these parameters within experimental error limits for all available experimental data. The database will be part of FactSage thermochemical system.
Use of virtual invariant phases in rate-controlled Gibbs’ian calculations

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The constrained Gibbs energy minimization allows for the calculation of partial and constrained equilibria by introducing immaterial components into the conservation matrix of the thermodynamic system. When systems controlled by reaction rates are considered, it is of advantage to use additional virtual constituents as invariant phases to define the extent of the kinetically slow forward or reverse reactions for each intermediate state. The extent of reactions is deduced from experimentally known reaction rates, while the rest of the system may reach partial equilibrium through the minimization calculation.

The virtual constituents, which are used to set the constraints for either forward or reverse reactions will then serve as physically meaningful operators in the calculation, as they are directly connected with the inequality conditions of the minimization system. These conditions, being analogous with the Lagrange constraints are used to define the stability of a phase. Through this property the virtual invariants can be used to control the sequential progress of the rate-controlled minimization calculation and for pinpointing the gained equilibrium condition. As it is also possible to exceed the equilibrium point by using the dormancy condition for the virtual phase, the method also allows for the calculation of affinity diagrams through the whole range of the extent of reaction.

Stacking fault energy and structure energy difference of semiconductor compounds

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The stacking fault energies control the dissociation widths of the dislocations and thus important parameters of the mechanical or electronic properties of materials. These energies are precisely estimated by the direct observations of weak beam or high resolution images of transmission electron microscopy. The stacking fault region in zincblende or wurtzite crystals has the wurtzite or zincblende structure, respectively, and therefore, the stacking fault energy of a tetrahedrally coordinated crystal is closely related to the free energy difference between the zincblende and the wurtzite structure. The energy difference of these structures, however, are hardly determined experimentally.

In this paper, we have performed the ab-initio electronic structure calculations on the zincblende-wurtzite energy differences. The plane wave basis calculations have been performed using the Vienna Ab Initio Simulation Package (VASP) with the GGA Perdew-Wang 91 exchange-correlation functional, a projector augmented-wave (PAW) ion-core orbital description, 0.1[1/Å] of the k-point mesh, and a cut-off energy of 600 eV.

The relations between the experimentally determined stacking fault energies (γ’) [1] and the calculated structural energy differences (ΔE) are shown in Fig. 1. The calculated energy differences of GaN, BeO and ZnO shows wrong energies, where the zincblende structure is more stable than the wurtzite structure. Oxides and nitrides are constructed by the light elements, whose description of the core electronic orbitals are hardly reproduced. Ignoring these compounds, the stacking fault energy is well correlated with the energy difference of the zincblende and wurtzite structures.

Thermodynamic re-assessment of the Iron-Carbon system

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A re-assessment of the Fe-C system is presented following the recent analyses of pure iron and cementite with more physical validation from 0 K to very high temperatures. The Zener ordering contribution to the Gibbs free energy of the bcc phase associated with martensitic transformation has been reviewed and the possibility of having a relatively more accurate description of the bcc phase has been explored.

Keywords: Fe-C; Thermodynamic modelling; Zener ordering
Modeling the surface tension of reciprocal molten salt mixtures

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Surface tension of reciprocal binary salt mixtures has been modeled by a monolayer model where the activities of the salt constituents have been replaced by their cation/anion radii ratio weighted molar fractions. The model has previously been used to model the surface tensions of large number of simple common cation or anion mixtures with a good accuracy [1] and surface tensions of molten slags of varying composition with a fair accuracy [2,3]. When compared with published literature data, the extended model for reciprocal systems is found to work well for systems whose constituent common ion binaries were modeled successfully with the original model. Also in systems containing salts of Ag, Cd and Ba that were not included in the original work [1], the reciprocal mixtures are modeled satisfactorily in cases where the common ion constituent binaries follow the simple model. A satisfactory fit of the binaries in these cases requires the use of an adjusted value for ionic radius for the new cations.

Applications of computational thermodynamics on the phase equilibria of complex oxide systems for slags and inclusions in metallurgical industries

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The oxide systems for metallurgical slags and inclusions are at least ternary systems, in general. The phase equilibria including fully liquid phase and 'solid+liquid' coexisting area (mush zone), and thus the melting point and the solid fraction in a mush zone are of great importance not only in an understanding of the fundamental principles of metallurgical phenomena but also in an optimum design of industrial processes. However, there is still lack of reliable phase diagrams of complex oxide systems, e.g. metallurgical slags containing CaF$_2$, ZrO$_2$, and Cr$_2$O$_3$, etc., and inclusion systems containing TiO$_x$. Thus, the computational thermodynamic package, FactSage$^\text{TM}$, is widely used to expect the phase equilibria in metallurgical processes. Some examples of the applications of this methodology to the metallurgical reactions are as follows. The phase diagram, and mass fraction of liquid and solid compounds of the CaO-SiO$_2$-MgO-CaF$_2$-ZrO$_2$ quinary slags as well as the activity of components in a 'liquid' phase was calculated. Thus, a complex desulfurization behavior and a formation of intermediate compounds such as CaZrO$_3$ of this slag system are well explained. Second, the solidification path and thus a mass fraction of solid and liquid phases of the CaO-SiO$_2$-MgO-Al$_2$O$_3$-CaF$_2$ quinary inclusion systems frequently occurred in stainless steels were calculated. Hence, the crystallization behavior of MgAl$_2$O$_4$ spinel phase in oxide inclusions during steelmaking and continuous casting processes was clarified. Third, the stability diagram of the Al-Ti-O inclusion systems in the Fe-Cr-Si-Mn-Mg melts and the phase diagram of the MgO-Al$_2$O$_3$-TiO$_x$ ternary system at 1873 K was calculated under moderately reducing atmosphere, pO$_2$=10$^{-13}$ atm. The observed inclusion composition and morphology was in good correspondence to the calculated phase equilibria of this system, of which phase diagram has not been experimentally measured yet.

Amine induced structural change of cubo-octahedral platinum nanocluster and its properties

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Lots of ligands have been used to prevent cluster’s aggregation in chemical synthesis of nano cluster. Recently, many studies report that ligands can considerably change surface structure of nano clusters contrary to popular idea that they don’t affect the surface structure due to the weak interaction between nano cluster’s surface and ligands. These nano clusters have unique surface structures which lead to unique electronic and optical properties. For example, Au nano clusters have peculiar “staple” structure when they are covered with thiolate ligands [1]. These staple motifs are very different surface structure from what people have expected before. In this study, we investigate amine ligands induced structural change of cubo-octahedral Pt nano cluster and its properties. Similar to the thiolate covered Au nano clusters, Pt cluster also have “staple” structure on its surface when it interacts with amine ligands even it is a 4-fold symmetric staple structure different from staple structure on Au cluster. We reveal the electronic and structural properties of the 4-fold staple structure with atomic orbitals of amine molecule and Pt nano cluster.

Prediction of long-term precipitate evolution in austenitic heat-resistant stainless steels

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Numerical prediction of the long-term precipitate evolution in five different austenitic heat-resistant stainless steels, NF709, Super304H, Sanicro25, CF8C-PLUS and HTUPS has been carried out using a model based on the classical nucleation theory and evolution equations derived from the thermodynamic extremum principle that maximizes the dissipation rate of the total Gibbs energy of the system. The simulation of the precipitate evolution in the steels has been performed with the thermo-kinetic software package MatCalc developed by Kozeschnik et al. [1,2]. MX and M\textsubscript{23}C\textsubscript{6} are predicted to remain as major precipitates during long-term aging in these steels. The addition of 3wt.\% Cu produces very fine Cu-rich precipitates during aging in Super304H and Sanicro25. It is found that the amount of Z phase start to increase remarkably between 1,000 and 10,000 hours of aging at the expense of MX precipitates in the steels containing a high nitrogen content. However, the growth rate of Z phase is relatively slow and its average size reaches at most a few tens of nanometers after 100,000 hours of aging at 700°C, compared with 9-12\% Cr ferritic/martensitic heat-resistant steels. The predicted precipitation sequence and precipitate size during aging are in general agreement with experimental observations.

CaTCalc – An advanced software for calculating thermodynamic equilibria and phase diagrams of multicomponent systems

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CaTCalc [1] is a newly developed thermodynamic equilibrium program that features an advanced and robust algorithm that “automatically” calculates correct phase diagrams even of intermetallics or ceramics systems without initial selection of stable phases by the user. Almost full functionalities of thermodynamic software are incorporated in CaTCalc, so that complex chemical equilibrium analyses on multi-component system can be easily made. Some examples are given to illustrate its important computational capabilities and use interfaces.

The melting of the silica–encapsulated silver nanoparticles

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The size dependence of the melting temperature and the structure transformation of silica–encapsulated silver nanoparticles (NPs) were investigated by means of differential scanning calorimetry (DSC). The silver NPs, with sizes ranging about from 10 to 50 nm, were synthesized by reduction of metal precursor with a reducing agent and then coated with silica shell to isolate the particles from one another. The melting temperatures of resulting silica–coated NPs with different sizes were examined by DSC measurement.

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Local strains in SiGe alloys for the strained silicon

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Silicon germanium (SiGe) is one of the most important semiconductors, due to the starting materials or substrates of the strained silicon, whose transistors switch 35% faster than the normal Si. SiGe is a complete solid solution alloy with the cubic diamond structure. The electronic and thermodynamical properties are strongly affected by the 4.2% difference in the lattice constants of the constituents Ge and Si. Thus, the accurate knowledge of the atomistic bonding structure with the local strain relaxation is essential and crucial to clarify the origins of such properties and to utilize the device potential of SiGe.

In this paper, we have investigated the bond lengths for different types of neighbor atom pairs (Ge-Ge, Ge-Si and Si-Si bond) by the ab-initio electronic structure calculations for the comparison with the experimental investigations of extended X-ray absorption fine structure (XAFS) [1] in bulk SiGe alloy crystals in the entire composition range. Four different models of SiGe lattice structures [2] have been calculated under the full relaxation of the local coordinations with the constrained outer shapes. The energies, lattice and volume changes and bond length differences have been investigated in detail.

The most stable energies on the different Ge compositions show the dependency as shown in Fig.1. The energies of three models are located on the average of the constituent pure lattices. The local bond lengths for different types of neighbor atom pairs show the similar dependency. The model of 75% Ge, however, shows the large deviation from the linear dependency of energy. The origin of this deviation is investigated from the local coordination environment.

![Fig.1 Total energy dependency on Ge](image)

SiC polar surface energy by the first principles calculations

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SiC is receiving particular attention as the next generation materials for new power electronic devices. At the moment, the SiC crystal growth is mainly performed by the vapor deposition called 'improved Lely-method' [1]. In this method, it utilizes the phenomenon that vapor constituted by Si and C, sublimated from 'feed', deposits out of inert gas on the 'seed' whose temperature is lower than that of 'feed'. Authors have recently developed a new method which is 'Metastable Solvent Epitaxy'(MSE) [2]. In this method, carbon dissolved from 'feed'(3C-SiC) transports to 'seed'(4H-SiC) through thin Si solvent. Large micropipes are often observed at (0001)-face in the case of the vapor-method [3]. On the other hand, (0001)-face shows flat and wide surfaces in the case of MSE. We thought that the difference of the polar surface growth of SiC depends on the environment around 'seed'. Thus, we performed the first principles calculations of the surface energies as the controlling factor for growing crystal shape. In this calculation, we selected 3C, 4H and 6H-SiC in SiC polytypes, {0001}, {11-20} and {1-100}-faces hexagonal crystals. The {0001}-face is the polar surface and another faces are surfaces orthogonal to that. In the case of cubic crystal, we selected {111}, {1-10} and {11-2} because of the equivalence to those of hexagonal crystals. The first principles calculations are performed by VASP code. Bulk and slab-models of SiC are constructed by 'MedeA'. We calculated surface energies with the consideration of the chemical potential dependency [4]. As shown in the results of Figs.1, the polar surface is the most stable surface in (a) Si-rich, but is the most unstable surface in (b) C-rich. Thus, the results indicated that the polar surface grown in Si-rich environment should show larger area than those of another surfaces.

![Fig. 1 Surface energies in each environment](image-url)

Thermodynamic analysis of phase equilibria in the Fe-Si-W ternary system

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A thermodynamic analysis of phase equilibria in the Fe-Si-W ternary system has been carried out using the CALPHAD method with emphasis on the dissolution of Si in the MgZn₂-type (C14) Laves phase, Fe₂W. Among the three binary systems present in this ternary phase diagram, the thermodynamic parameters of the Fe-Si [1], Fe-W [2], and Si-W [3] binary systems were taken from reported results, however, some modification of the thermodynamic descriptions for Fe₂W and Fe₇W₆ was made in this study. The enthalpy of formation of the Laves phase along the Fe₂W-Si₂W pseudo-binary section was obtained from first-principles calculations. The ternary thermodynamic parameters were evaluated using the obtained formation enthalpy of the Laves phase, as well as the available experimental data on the phase boundaries. The calculated Fe-Si-W ternary phase diagrams have nicely reproduced the experimental results.

Experimental study and thermodynamic modeling of the Bi-Cu-Ni ternary system

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Phase equilibria in the Bi-Cu-Ni ternary system have been studied using DTA as well as by using the calculation of phase diagram (CALPHAD) method. Literature experimental phase equilibria data and DTA results from this study were used for thermodynamic modeling of the Bi-Cu-Ni ternary system. Isothermal sections at 300, 400, and 500°C and vertical sections from bismuth corner with molar ratio Cu:Ni=1/3, 1/1 and 3/1 were calculated and compared with new experimental results and with the data in literature [1]. Reasonable agreement between calculation and experimental data was observed in all cases.


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Thermodynamic modeling of the CoOₓ-FeOᵧ system

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The CoOₓ-FeOᵧ system has attracted a great deal of research efforts due to its importance in steel industry [1], soft magnetic material [2], oxygen separation membranes [3] and solid oxide fuel cell [4]. The knowledge of the accurate thermodynamic information on the CoOₓ-FeOᵧ system is indispensable.

The thermodynamic assessment of the CoOₓ-FeOᵧ system is performed by considering reliable literature data. The liquid phase is modeled using the ionic two-sublattice model. The solid oxide solution phases are described using the compound energy formalism. We model the cobaltowustite and spinel phases as (Co^{+2}, Fe^{+2}, Fe^{+3}, Va)(O^{2-})₁ and (Co^{+2}, Co^{+3}, Fe^{+2}, Fe^{+3}, Va)(O^{2-})₄, respectively. A set of self-consistent thermodynamic parameters describing the Gibbs energy of each phase is obtained eventually. The computed phase diagram and model-predicted thermodynamic properties are in good agreement with the experimental results.

The present thermodynamic modeling of the CoOₓ-FeOᵧ system will be adopted in the framework of material design for innovation fuel cell based on thermodynamic and kinetic databases.

A design method of Fe-based bulk metallic glass based on phase diagram calculation

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Glass formation is always a competitive process between the liquid phase and the resulting crystalline phases, which means that both the stability of liquid phase and the formation of competing crystalline phases should be considered for obtaining bulk metallic glass (BMG) with large glass-forming ability (GFA). In order to obtain the relationship between GFA and potential precipitated phases in the process of cooling down, the pseudo-binary diagram calculations with multi-component were employed to determine the preanalytic alloy for experiments using ThermoCalc software. The results reflect that the main phases precipitated from liquid phase near the eutectic point include alloying α-Fe, alloying γ-Fe, alloying ε-Fe, alloying MC, M7C3, M23C6, M6C, M12C, MoB and so on, which can be divided into two categories, namely, solid solution and compound. The experimental results indicated that the alloying γ-Fe with fcc structure would precipitate as long as it appears in the phase diagram corresponding to the component, whereas solid solution with hcp and bcc structures do not. The compounds such as M23C6, M6C, M7C3 and M8B6 (exclude MB2) with complex structures are favorable for keeping the amorphous state as potential precipitated phase. In particular, the MC phase which has simply fcc structure comparable to austenite should be suppressed absolutely in the phase diagram. The previously and recently experimental results confirm the validity of this design method. The successful application illustrates broad feasible utilizable prospect of phase diagram in material design.
Modeling the effect of oxygen adsorption on surface tensions of molten metal alloys

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Oxygen adsorption on a liquid metal alloy surface is modeled based on a modified Langmuir model. The metallic component composition of the surface layer is modeled using a monolayer constrained free energy model, where the bulk thermodynamic functions are scaled based on the effective coordination number \cite{1}. An oxygen adsorption layer, where the effect of blocked adsorption sites by nearby adsorbed gas molecules is approximated, is located over the metallic surface layer. Metallic composition of the surface layer, amount of adsorbed oxygen and the surface tension of are solved in one equilibrium calculation step by minimizing the total free energy of the system.

Model results have been compared with experimental surface tension values for Ag-Cu-O, Ag-Au-O and Ag-Sn-O systems as function of bulk composition and oxygen partial pressure. The enrichment of the more oxygen active metallic component on the surface and its influence on surface tension values are investigated.

Predicting novel microstructures in polymer blends under two-step quench

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Formation of nanostructures during two-step quench in binary systems having various types of miscibility gaps were investigated systematically via computer simulations using the phase field method. Schematic phase diagram for the two-step phase separation was presented in Fig. 1. Coupled spinodal decomposition and fluid flow processes were considered by solving simultaneously the Cahn-Hilliard and Navier-Stokes equations. Various interesting phenomena and novel morphological patterns were predicted (Fig. 2). It was found that the primary microstructures developed at the first quench temperature completely dominated the secondary microstructures formed during the second quench temperature. Depending on the morphology and scale of the primary microstructure, either multi-core/multi-shell or uni-core/uni-shell structures were predicted. The breakup of annuluses in two-dimension was analyzed. The growth and coarsening behaviors of bimodal droplets produced by the double-quench in systems with various viscosities were characterized.

![Fig. 1](image1.png)  ![Fig. 2](image2.png)
A thermodynamic analysis has been carried out to investigate the phase transformations at different thicknesses in epitaxial Pb(Zr$_{1-x}$Ti$_x$)O$_3$ films based on a Landau-Devonshire phenomenological model. The critical thickness of paraelectric phase ($|P_1|=|P_2|=|P_3|=0$), tetragonal phase ($|P_1|\neq 0$, $|P_2|=|P_3|=0$), orthorhombic phase ($|P_1|=|P_2|\neq 0$, $|P_3|=0$) and rhombohedral phase ($|P_1|=|P_2|=|P_3|\neq 0$) were calculated. The misfit strain and dislocation between film and substrate which were related to the composition of PbTiO$_3$ and film thickness were taken into account in the free energy calculation model. The phase diagrams of film/substrate systems were calculated below and over critical thickness. A change of the sequence of the phases and the appearance phases forbidden in the bulk crystal were predicted at different film thicknesses.
Thermodynamic modeling of the Sn-U, Sn-Pu, Pb-U and Pb-Pu systems

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The thermodynamic assessments of the Sn-U, Sn-Pu, Pb-U and Pb-Pu binary systems were carried out by using the CALPHAD (Calculation of Phase Diagrams) method based on experimental data on thermodynamic properties and phase equilibria. The Gibbs free energies of the liquid, bcc, fcc, (αSn), (βSn), (αU), (βU), (δ'Pu), (γPu), (βPu) and (αPu) phases were described by a sub-regular solution model with the Redlich–Kister equation, and those of the intermetallic compounds by a two-sublattice model. The thermodynamic parameters for the two binary systems were optimized to consistently reproduce the available experimental data with satisfactory agreement.
Fcc-type miscibility gap in some Cu-Ni base alloys at high temperatures

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The present work systemically deals with the direct observation and theoretic prediction of the fcc-type miscibility gap in some Cu-Ni base alloys at high temperatures, and thermodynamically explain the appearance of the fcc-type miscibility gap in the Cu-Ni-X (X=Mo, V, W, Nb, Ta, Cr, Fe, Co) alloy systems at high temperatures. The fcc-type miscibility gap existing at 900°C, 1000°C and 1100°C in both the Cu-Ni-Mo and Cu-Ni-V systems have been firstly found and experimentally determined, and typical separated microstructure (fcc1 + fcc2) (Here fcc1 and fcc2 phases stand for the fcc Cu-rich and fcc Ni-rich phases) of the Cu30.7Mo6.3Ni63 (at.%) alloy quenched from 1000°C was shown (Fig. 1) and substantiated by the XRD result (Fig. 2), where only the characteristic peaks of the fcc phase were found. In addition, the existence of fcc-type miscibility gap in the Cu-Ni-X (X= W, Nb, Ta) systems at 900°C, 1000°C and 1100°C also have been predicted by using the CALPHAD (CALculation of PHAse Diagrams) method. Finally, the appearance of the fcc-type miscibility gap in the Cu-Ni-X(X=Mo, V, W, Nb, Ta, Cr, Fe, Co)alloys at high temperatures have been thermodynamically discussed, and interpreted in relation to that Ni additions can stabilize the metastable fcc-type miscibility gap in the Cu-X(X=Mo, V, W, Nb, Ta, Cr, Fe, Co) binary alloys.

Fig. 1
Fig. 2
Theoretical derivation of the equation for the exponential temperature
dependence of excess Gibbs energy of solutions

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The exponential temperature (T, K) dependence of the interaction energies (L_i, J/mol) of
solution phases in the framework of the Redlich-Kister polynomials \( L_i = h_i \cdot \exp\left(-T / \tau_i\right) \) (h_i, J/mol and \( \tau_i \), K are semi-empirical parameters) is theoretically derived in this paper. In this
way this so far semi-empirical equation is given a more solid theoretical basis and thus it can
be used with more confidence. When this exponential equation is applied, artifacts such as
inverted miscibility gaps are automatically removed from the calculated phase diagrams.
Additionally, equations have been derived to estimate the parameters of the exponential
equation from the values of the previously assessed parameters of the corresponding linear
equation \( L_i = h_i \cdot \left(1 - T / \tau_i\right) \). Trial calculations showed that in the temperature interval of 650-
900 K the deviation between the results of the linear and exponential curves is less than 0.1 %.
Thus, this method provides an easy and fast approximated method to transform earlier
assessed data to the new formalism, still ensuring that artifacts are automatically removed
from the calculated phase diagrams.

Acknowledgement: The support of NAP-NANO and CK-OTKA-NKTH, Hungary, is truly acknowledged.
Thermodynamic properties of Sn-Ag nanoparticles

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Among many alternatives for Sn-Pb solders, Tin-Silver (Sn-Ag) is one of the most promising materials. The relative high melting point of Sn-Ag solders (approximately 30°C higher than the eutectic Sn-Pb solder) can be reduced if the size of the solder powder is lowered to a nanometer size. The high ratio of the surface area to volume is the driving force for depressing melting point of the nanoparticle powder.

In this study, different-size and different-composition Sn-Ag nanoparticle alloys were synthesized by the plasma-arc discharging method. The microstructures and thermodynamic property of Sn-Ag nanoparticles were analyzed by X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM) and differential scanning calorimetry (DSC). The aim of this work is to bring the experimental and theoretical information of the Sn-Ag nanoparticle alloys for the lead-free solder applications.


Acknowledgement: This work is supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD, Basic Research Promotion Fund) (331-2008-1-D00742).
Using CALPHAD thermodynamic data to understand the carbothermic reduction of steelmaking slag by microwave heating

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The carbothermic reduction of steelmaking slag by microwave heating is carried out at 1800~2000K. Thermodynamic equilibrium data for the carbothermic reduction of slag at these temperatures are difficult to obtain experimentally. Therefore, the CALPHAD thermodynamic data optimized at lower temperatures is anticipated to be extrapolated to the processing temperature for understanding the reaction mechanism.

The present study compared the experimental results with the calculated values based on the FactSage database. Experimental investigation was carried out in a microwave oven, with variety of the heating time, temperature, carbon addition and slag composition in order to understand chemical reaction during carbothermic reduction of slag. The chemical analysis results were compared with the calculated values according to the carbon consumption. It was concluded that the calculated results are reasonably accord with the experimental results.

Acknowledgement: This subject is supported by Ministry of Environments as “The Eco-technopia 21 project”.
Thermodynamic studies of steelmaking slags with respect to foaming in electric arc furnace

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Electric arc furnace (EAF) steelmaking relies heavily on slag foaming properties to operate efficiently with long arcs. Slag foaming allows for the use of a thick slag layer without increasing the slag weight. This improves thermal efficiency, decreases melting time and lowers both refractory and electrode consumption. Foaming is produced by the reduction of slag “FeO” with injected carbon. Electric furnaces slags are basic slags, highly oxidized and normally saturated or close to saturation with MgO, an important component of the slag refractories. It has been demonstrated that, besides having adequate viscosity and surface tension, slags with a small volume fraction of solid second phase particles, are the ones with the best foaming stability conditions.

In this work, the conditions for the precipitation of a small amount of magnesia-wustite in the relevant slag system are calculated. The effects of changes in slag composition and temperature on the amount of magnesia-wustite precipitated are discussed and the results are used to estimate the effective viscosity of the slag according to accepted empirical formulas. Control diagrams for use in the melt shop, based on isothermal cross-sections of the pseudo-ternary phase diagrams, MgO-SiO\textsubscript{2}-FeO, are also proposed.
Thermodynamic evaluation of the effects of segregation on phase transformations of 13Cr supermartensitic stainless steels

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Supermartensitic stainless steels are one of the materials considered for the corrosive environments found in the Brazilian pre-salt oil province. These steels are quenched and tempered to achieve uniform mechanical properties at high strength levels. The material is continuously cast and thermomechanically processed to produce high dimensional precision tubes. Even after this processing, some segregation remains. To guarantee uniform and reproducible properties, the understanding of the effects of this remaining segregation on phase equilibria -phases formed as well as transformation temperatures- is of paramount importance. This work presents results of ongoing work in which different computational thermodynamic and kinetic approaches are used to simulate the segregation as well as its effects on phase equilibria. The work aims at comparing the results of different methods of thermodynamic and kinetic simulation with experimental results to define the extent of the applicability of the modeling technique and to propose development avenues for the processing of this family of steels.
Formation of Si/Ge bilayer nano-tubes by a self-bending process:  
A molecular dynamics study

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Nano-materials, especially nanotubes, are expected to play important role in future material technologies, and many fabrication techniques (CNT or SiNT) are being developed. One of those fabrication processes is to use a self-bending behavior by the internal stresses of bilayer films [1-3]. However, there exists an ambiguous point in the governing mechanism of the self-bending behavior (bending direction). Here, we perform a molecular dynamics simulation study to clarify the role of two different internal stresses, one from the surface reconstruction and the other from the lattice mismatch between Si and Ge. We demonstrate that bending direction is primarily determined by the misfit stress and the reconstruction stress has a marginal effect only when the film thickness is small. We further propose that as the film thickness increases the elastic anisotropy affects the bending direction in addition to the lattice mismatch.

Critical thermodynamic evaluation and optimization of the Ag-Zr, Cu-Zr and Ag-Cu-Zr systems and its applications to amorphous Cu-Zr-Ag Alloys

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A complete literature review, critical evaluation and thermodynamic modeling of the phase diagrams and thermodynamic properties of all solid and liquid phases in the Ag-Zr, Cu-Zr and Ag-Cu-Zr systems at 1 bar total pressure are presented. Optimized model equations for the thermodynamic properties of all phases are obtained which reproduce all available thermodynamic and phase equilibrium data within experimental error limits from 25°C to above the liquidus temperatures at all compositions. Using the optimized model parameters, the phase diagram of the Ag-Cu-Zr system is predicted properly for the first time. In particular, the ternary liquid miscibility gap is predicted from model parameters, which is important for the applications to the Cu-Zr-Ag amorphous alloy design. The database of optimized model parameters was applied to the heat treatment calculations of the amorphous Cu-Zr-Ag alloys.
Effect of stress on self-diffusion in bcc Fe: An atomistic simulation study

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The effect of stress on the self-diffusion in bcc Fe has been investigated using a molecular dynamics simulation. The diffusivities under hydrostatic, uniaxial and shear stresses are calculated and analyzed to clarify the governing factor that affect the diffusion under stresses. The diffusivity is retarded by compressive pressures, while enhanced by shear stresses and shows an intermediate behavior under uniaxial stresses. The mechanism for those stress-dependencies is discussed through the effect of stresses on vacancy formation enthalpy and migration energy.
 Atomistic modeling for NaCl-type MC carbides in steels

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NaCl-type MC carbides are one of the most important precipitates for strengthening steels. To obtain desired materials properties, it is necessary to understand the precipitation behavior of carbides and the interaction between precipitates and various defects such as dislocations or grain boundaries. As a means to enable an atomic-level investigation on the behavior of MC carbides, in the present study, Modified embedded-atom method (MEAM) interatomic potentials for Fe-Metal-C (Metal: Ti, Nb, Mo, W) ternary systems and constituent binary Fe-Metal and Metal-C systems are developed. It will be shown that the potentials reproduce various fundamental physical properties (structural properties, elastic properties, thermal properties and surface property) of relevant systems reasonably well. The applicability of the potentials to atomistic studies for multi-component carbides, such as (Ti,Nb,Mo,W)C, and their effects on the deformation and mechanical properties of steels will also be discussed.
Experimental determination of stacking fault energy of the 18Cr-10Mn high interstitially alloyed stainless steels

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Nitrogen as an alloying element provides several beneficial effects on the properties of stainless steels, in particular those associated with good combination of mechanical properties and improved resistance to localized corrosion. Owing to progress in processing technologies, some commercial grades of high nitrogen steels (HNS) are now available, however, two factors have raised obstacles to wider application of HNS: the low solubility of nitrogen in ferrous alloy melts requires high-pressure metallurgy and the loss of ductility or toughness at high-nitrogen content above 0.7~0.8wt.%. Recently high interstitially alloyed (HIA) steels utilizing carbon as a major alloying element together with nitrogen has been proposed to overcome the preceding difficulties in a cost-effective way, where computational thermodynamics had a crucial role to optimize constitutions and processing parameters.

In the present study, the stacking fault energies of the high interstitially alloyed stainless steels of Fe-18Cr-10Mn-(C+N) alloys were evaluated by the Rietveld whole-profile fitting combined with the double-Voigt size-strain analysis for neutron diffraction profiles. At fixed N+C content, the ratio of mean-squared strain to stacking fault probability remained constant regardless of the accumulated strain, whereas the ratio gradually increased with increasing N+C content. Almost linear dependence of measured stacking fault energy on N+C content was established in contrast to result from empirical equation for stainless steel with low interstitial alloying elements.
Thermodynamic assessments of the Cu–Ti–Zr system and boundary Cu–Ti, Cu–Zr and Ti–Zr systems

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The liquid alloys of Cu-Ti, Cu-Zr and Cu-Ti-Zr are known by high glass forming ability. Rapidly quenched and bulk amorphous alloys were obtained on the base of binary and ternary melts of these systems. Therefore stable and metastable transformations with participation of the liquid phase are interesting object for thermodynamic modeling.

The thermodynamic assessments of the boundary binary Cu-Ti, Cu-Zr, Ti-Zr systems and ternary Cu-Ti-Zr system have been carried out in the frameworks of the CALPHAD-method. The set of self-consistent parameters of thermodynamic models of the phases has been obtained taking into account our experimental data on the mixing enthalpies of liquid alloys (besides Ti-Zr system) and the literature data on the phase equilibria. The excess Gibbs energy of Cu-Ti-Zr liquid alloys was described using the ideal associated solution model on the assumption that associates CuTi, CuTi$_2$, Cu$_2$Zr, CuZr and CuZr$_2$ formed in the melts. The composition dependence of thermodynamic properties of Ti-Zr liquid alloys and terminal solid solutions in all systems was modeled by Redlich-Kister polynomials. The Cu$_2$Ti, Cu$_3$Ti$_2$, Cu$_4$Ti$_3$, Cu$_5$Zr, Cu$_{51}$Zr$_{14}$, Cu$_8$Zr$_3$, Cu$_{10}$Zr$_7$, CuZr and CuZr$_2$ compounds were treated as stoichiometric compounds. Thermodynamic properties of the binary and ternary intermetallic compounds Cu$_4$Ti, CuTi, γ-phase (Cu(Ti,Zr)$_2$) and τ$_1$-phase (Cu$_2$TiZr) with homogeneous ranges were described using Compound Energy Formalism.

The calculated phase diagrams and thermodynamic properties of phases of Cu-Ti, Cu-Zr, Ti-Zr and Cu-Ti-Zr systems agree well with the experimental data. This fact allows us to use obtained thermodynamic models of phases to calculate metastable phase transformations between supercooled liquid and terminal solid solutions. The composition ranges of formation of rapidly-quenched and bulk amorphous alloys in the Cu-Ti-Zr system were estimated by relative position of metastable liquidus and $T_0$ lines.
## Authors Index

### A
- Abe, Shinya ........................................... 76
- Abe, Taichichi ......................................... 41
- Abdulov, Alexander R. ............................... 47, 153
- Agraval, Pavel G. ...................................... 47, 153
- Al-Zubi, Ali ............................................. 95
- Alekseev, Sergei G. .................................... 116
- Aljarrah, M. ............................................. 37
- de Almeida, Daniel S. .................................. 113
- de Avillez, Roberto R. .................................. 146
- Chen, Hailin ............................................ 107
- Chen, Li .................................................. 104
- Chen, Ming .............................................. 57, 136
- Chen, Qing .............................................. 79
- Chen, X.-Q. .............................................. 26
- Cho, Hoon-Hwe ......................................... 120
- Cho, Young Whan ...................................... 69, 129
- Cho, Yi-Gil ............................................. 120
- Coelho, Gilberto.C. ................................... 52, 113
- Colinet, Catherine .................................... 49, 100
- Costa e Silva, André ................................. 54, 146, 147
- Crivello, Jean-Claude ................................ 41
- Cui, Senlin ............................................. 42

### B
- Bae, Jun Ho ............................................. 67
- Bale, Christopher ...................................... 59, 122
- Bao, Tran Thai ......................................... 131, 144
- Barbin, Nikolai M. ..................................... 116
- Barford, Rasmus G. ..................................... 136
- Belisle, Eve .............................................. 59, 122
- Bhadeshia, H.K.D.H. .................................... 99, 117
- Blanpain, Bart .......................................... 58
- Borzone, G. .............................................. 121
- Bowen, Jacob R. ........................................ 57
- Bratberg, Johan .......................................... 50
- Brandt, Kristina ......................................... 55
- Brosh, Eli ............................................... 59, 122
- Broz, Pavel ............................................... 39
- Buhl, Sebastian .......................................... 82
- Bursik, Jiri ............................................... 39
- Bursik, Jiri ............................................... 39

### C
- Carvalho, Ricardo N. ................................... 147
- Castro, F. ................................................. 74
- Chad, V.M. ............................................... 52
- Chang, Jaewon .......................................... 119
- Chang, Ke K. ............................................. 104
- Chartrand, Patrice .......................... 35, 61, 62
- Chatillon, Christian .................................... 53
- Chatzichristodoulou, C. .............................. 57
- Cui, Senlin ............................................. 42

### D
- Deckerov, Sergei A. ................................... 59, 60, 122
- Delsante, S. ............................................. 121
- Dick, A. ................................................ 30
- Dreval’, Liya A. ......................................... 47, 153
- Du, Yong ................................................ 29, 34, 42, 81, 103, 104
- Dumas, Jean-Christophe ............................. 53
- Dupin, Nathalie ......................................... 50, 53
- Dumas, Jean-Christophe ............................. 53

### E
- Eleno, Luiz T.F. ......................................... 24, 111, 112
- Engström, Anders ...................................... 79
- Essadiqi, Elhachmi ..................................... 36

### F
- Fabrichnaya, Olga ...................................... 55
- Falahati, A. ............................................. 40
- Fen, Ji C. ................................................ 104
- Fernandes, P.B. ......................................... 52
- Ferreira, F. .............................................. 52
- Ferreira, Marcelo A.C. ................................. 147
- Fleury, Eric ............................................. 118
- Fortes, Raimundo A.F.O. .............................. 146
<table>
<thead>
<tr>
<th>Name</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fries, Suzana G</td>
<td>66, 83</td>
</tr>
<tr>
<td><strong>G</strong></td>
<td></td>
</tr>
<tr>
<td>Ganesan, Rajesh</td>
<td>56</td>
</tr>
<tr>
<td>Gang, Tie</td>
<td>104</td>
</tr>
<tr>
<td>Garzel, Grzegorz</td>
<td>115</td>
</tr>
<tr>
<td>Gheribi, Aimen</td>
<td>84</td>
</tr>
<tr>
<td>Gnanasekaran, T.</td>
<td>56</td>
</tr>
<tr>
<td>Gonzales-Ormeño, Pablo G</td>
<td>24</td>
</tr>
<tr>
<td>Grabowski, Blazej</td>
<td>27, 95</td>
</tr>
<tr>
<td>Gröbner, Joachim</td>
<td>38</td>
</tr>
<tr>
<td>Grundy, A. Nicholas</td>
<td>59, 122</td>
</tr>
<tr>
<td>Guéneau, Christine</td>
<td>53</td>
</tr>
<tr>
<td>Guimarães, Nara M.</td>
<td>113</td>
</tr>
<tr>
<td><strong>H</strong></td>
<td></td>
</tr>
<tr>
<td>Hack, Klaus</td>
<td>63</td>
</tr>
<tr>
<td>Hallstedt, Bengt</td>
<td>88</td>
</tr>
<tr>
<td>Hammerschmidt, Thomas</td>
<td>83</td>
</tr>
<tr>
<td>Han, Heung Nam</td>
<td>120</td>
</tr>
<tr>
<td>Han, J.J.</td>
<td>137</td>
</tr>
<tr>
<td>Hasebe, Mitsuhiro</td>
<td>114, 134</td>
</tr>
<tr>
<td>Hashiba, M.</td>
<td>90</td>
</tr>
<tr>
<td>He, Yuehui</td>
<td>81</td>
</tr>
<tr>
<td>Herrmann, Mathias</td>
<td>55</td>
</tr>
<tr>
<td>Heuger, Erwin</td>
<td>25</td>
</tr>
<tr>
<td>Heulens, Jeroen</td>
<td>58</td>
</tr>
<tr>
<td>Hickel, Tilmann</td>
<td>27, 30, 66, 95</td>
</tr>
<tr>
<td>Hillert, Mats</td>
<td>44</td>
</tr>
<tr>
<td>Horigane, Kazumasa</td>
<td>114</td>
</tr>
<tr>
<td>Hu, Biao</td>
<td>103</td>
</tr>
<tr>
<td>Huang, Guoxing</td>
<td>34</td>
</tr>
<tr>
<td>Hudon, Pierre</td>
<td>46</td>
</tr>
<tr>
<td>Hwang, Nong-Moon</td>
<td>68, 80</td>
</tr>
<tr>
<td><strong>I</strong></td>
<td></td>
</tr>
<tr>
<td>Ikubo, Satoshi</td>
<td>114, 134</td>
</tr>
<tr>
<td>Ishida, Kiyohito</td>
<td>73, 76, 142</td>
</tr>
<tr>
<td>Ismer, Lars</td>
<td>27</td>
</tr>
<tr>
<td><strong>J</strong></td>
<td></td>
</tr>
<tr>
<td>Jang, Jae Hoon</td>
<td>99</td>
</tr>
<tr>
<td>Jang, Je-Wook</td>
<td>150</td>
</tr>
<tr>
<td>Jiang, Chao</td>
<td>106</td>
</tr>
<tr>
<td>Jin, Liling</td>
<td>35</td>
</tr>
<tr>
<td>Jin, S.</td>
<td>121</td>
</tr>
<tr>
<td>Jin, Zhanpeng</td>
<td>103</td>
</tr>
<tr>
<td>Jo, Moon-Ho</td>
<td>70</td>
</tr>
<tr>
<td>Joubert, Jean-Marc</td>
<td>41, 87</td>
</tr>
<tr>
<td>Jund, P.</td>
<td>100</td>
</tr>
<tr>
<td>Jung, In-Ho</td>
<td>46, 149</td>
</tr>
<tr>
<td>Jung, Woo-Sang</td>
<td>129</td>
</tr>
<tr>
<td><strong>K</strong></td>
<td></td>
</tr>
<tr>
<td>Kainuma, Ryosuke</td>
<td>76, 142</td>
</tr>
<tr>
<td>Kajihara, M.</td>
<td>90</td>
</tr>
<tr>
<td>Kana, Tomas</td>
<td>25</td>
</tr>
<tr>
<td>Kang, Daehoon</td>
<td>149</td>
</tr>
<tr>
<td>Kaneko, T.</td>
<td>133</td>
</tr>
<tr>
<td>Kang, Youn-Bae</td>
<td>35, 45, 145</td>
</tr>
<tr>
<td>Kaptay, George</td>
<td>31, 143</td>
</tr>
<tr>
<td>Kattner, Ursula R.</td>
<td>86</td>
</tr>
<tr>
<td>Kaufman, Larry</td>
<td>65</td>
</tr>
<tr>
<td>Kevorkov, Dmytro</td>
<td>36</td>
</tr>
<tr>
<td>Kewu, Bai</td>
<td>85</td>
</tr>
<tr>
<td>Khan, M.N.</td>
<td>37</td>
</tr>
<tr>
<td>Kim, Da Hye</td>
<td>128</td>
</tr>
<tr>
<td>Kim, DongEung</td>
<td>51</td>
</tr>
<tr>
<td>Kim, Eunju</td>
<td>145</td>
</tr>
<tr>
<td>Kim, In Gee</td>
<td>99, 117</td>
</tr>
<tr>
<td>Kim, Ki-Hyun</td>
<td>151</td>
</tr>
<tr>
<td>Kim, Hyun You</td>
<td>128</td>
</tr>
<tr>
<td>Kim, Kyung-Hun</td>
<td>67</td>
</tr>
<tr>
<td>Kim, Nack J.</td>
<td>67</td>
</tr>
<tr>
<td>Kim, Sung-Joon</td>
<td>152</td>
</tr>
<tr>
<td>Kim, Taeyoung</td>
<td>145</td>
</tr>
<tr>
<td>Kim, Wan-Yi</td>
<td>59, 60, 122</td>
</tr>
<tr>
<td>Ko, Kyung-Jun</td>
<td>80</td>
</tr>
<tr>
<td>Ko, Won-Seok</td>
<td>151</td>
</tr>
<tr>
<td>Kong, Yi</td>
<td>29, 106</td>
</tr>
<tr>
<td>Name</td>
<td>Page(s)</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>M</td>
<td></td>
</tr>
<tr>
<td>Manasijević, Dragan</td>
<td>135</td>
</tr>
<tr>
<td>Manga, Venkateswara Rao</td>
<td>51</td>
</tr>
<tr>
<td>Marković, Branišlav</td>
<td>135</td>
</tr>
<tr>
<td>Martial, Chantal</td>
<td>53</td>
</tr>
<tr>
<td>Masaki, Y.</td>
<td>124</td>
</tr>
<tr>
<td>Medraj, Mamoun</td>
<td>36, 37</td>
</tr>
<tr>
<td>Minić, Duško</td>
<td>135</td>
</tr>
<tr>
<td>Moelans, Nele</td>
<td>58, 91</td>
</tr>
<tr>
<td>Mohri, Tetsuo</td>
<td>23</td>
</tr>
<tr>
<td>de Moura Neto, Carlos</td>
<td>113</td>
</tr>
<tr>
<td>N</td>
<td></td>
</tr>
<tr>
<td>Naraghi, Reza</td>
<td>125</td>
</tr>
<tr>
<td>Neher, Roland</td>
<td>55</td>
</tr>
<tr>
<td>Neugebauer, Jörg</td>
<td>27, 30, 95</td>
</tr>
<tr>
<td>Nishitani, S.R.</td>
<td>89, 124, 132, 133</td>
</tr>
<tr>
<td>Noh, Ji-Young</td>
<td>98</td>
</tr>
<tr>
<td>Nunes, C.A.</td>
<td>52</td>
</tr>
<tr>
<td>O</td>
<td></td>
</tr>
<tr>
<td>Oh, Chang-Seok</td>
<td>152</td>
</tr>
<tr>
<td>Oh, Sang Ho</td>
<td>71</td>
</tr>
<tr>
<td>Ohnuma, Ikuo</td>
<td>76</td>
</tr>
<tr>
<td>Ohshima, T.</td>
<td>124</td>
</tr>
<tr>
<td>Ohtani, Hiroshi</td>
<td>114, 134</td>
</tr>
<tr>
<td>Olea, Cesar A.W.</td>
<td>147</td>
</tr>
<tr>
<td>Omori, Toshihiro</td>
<td>76</td>
</tr>
<tr>
<td>Ouyang, Yifang</td>
<td>106</td>
</tr>
<tr>
<td>P</td>
<td></td>
</tr>
<tr>
<td>Pajarre, Risto</td>
<td>63, 123, 126, 138</td>
</tr>
<tr>
<td>Pan, Zhu</td>
<td>55</td>
</tr>
<tr>
<td>Palumbo, Mauro</td>
<td>41, 66, 83</td>
</tr>
<tr>
<td>Park, Hyung-Ki</td>
<td>80</td>
</tr>
<tr>
<td>Park, Joo Hyun</td>
<td>127</td>
</tr>
<tr>
<td>Park, Kyoungh-Won</td>
<td>118</td>
</tr>
<tr>
<td>Pavlů, Jana</td>
<td>26, 77</td>
</tr>
<tr>
<td>Pelton, Arthur D.</td>
<td>45, 59, 60, 84, 122</td>
</tr>
<tr>
<td>Ping, Wu</td>
<td>85</td>
</tr>
<tr>
<td>Author</td>
<td>Page</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>------</td>
</tr>
<tr>
<td>Piorino, Francisco</td>
<td>113</td>
</tr>
<tr>
<td>Povoden-Karadeniz, Erwin</td>
<td>40</td>
</tr>
<tr>
<td>Q</td>
<td></td>
</tr>
<tr>
<td>Qi, Haiying</td>
<td>34</td>
</tr>
<tr>
<td>R</td>
<td></td>
</tr>
<tr>
<td>Ranganathan, S.</td>
<td>101</td>
</tr>
<tr>
<td>Renaud, Elizabeth</td>
<td>62</td>
</tr>
<tr>
<td>Reis, Danieli A.P.</td>
<td>113</td>
</tr>
<tr>
<td>Robelin, Christian</td>
<td>62</td>
</tr>
<tr>
<td>Rodríguez, J.C.</td>
<td>74</td>
</tr>
<tr>
<td>Robelin, Christian</td>
<td>62</td>
</tr>
<tr>
<td>Rodríguez, J.C.</td>
<td>74</td>
</tr>
<tr>
<td>Rogl, P.</td>
<td>26</td>
</tr>
<tr>
<td>Ryu, Ji Hoon</td>
<td>128</td>
</tr>
<tr>
<td>S</td>
<td></td>
</tr>
<tr>
<td>Saal, James E.</td>
<td>97</td>
</tr>
<tr>
<td>Saengdeejing, Arkapol</td>
<td>97</td>
</tr>
<tr>
<td>Sahu, Sulata Kumari</td>
<td>56</td>
</tr>
<tr>
<td>Santhy, K.</td>
<td>96</td>
</tr>
<tr>
<td>Schaffnit, Philippe</td>
<td>78</td>
</tr>
<tr>
<td>Schmid-Fetzer, Rainer</td>
<td>38</td>
</tr>
<tr>
<td>Schön, Cláudio G.</td>
<td>24, 112</td>
</tr>
<tr>
<td>Scott, A.</td>
<td>121</td>
</tr>
<tr>
<td>Seifert, Hans J.</td>
<td>55</td>
</tr>
<tr>
<td>Selleby, Malin</td>
<td>44, 66, 75, 125</td>
</tr>
<tr>
<td>Seo, Seung-Woo</td>
<td>117</td>
</tr>
<tr>
<td>Seo, Sun-Kyung</td>
<td>119</td>
</tr>
<tr>
<td>Shang, Shun-Li</td>
<td>51</td>
</tr>
<tr>
<td>Shi, R.P.</td>
<td>92, 139</td>
</tr>
<tr>
<td>Shibutani, Yoji</td>
<td>118</td>
</tr>
<tr>
<td>Shim, Jae-Hyeok</td>
<td>69, 129</td>
</tr>
<tr>
<td>Shim, Myeong-Shik</td>
<td>67</td>
</tr>
<tr>
<td>Shin, Eun-Joo</td>
<td>152</td>
</tr>
<tr>
<td>Shou, Kazuhisa</td>
<td>130</td>
</tr>
<tr>
<td>Silva, Ricardo R.</td>
<td>147</td>
</tr>
<tr>
<td>Sluiter, Marcel H.F.</td>
<td>28, 94</td>
</tr>
<tr>
<td>Sob, Mojmir</td>
<td>25</td>
</tr>
<tr>
<td>Song, You Young</td>
<td>117</td>
</tr>
<tr>
<td>Stallybrass, Charles</td>
<td>78</td>
</tr>
<tr>
<td>Steinbach, Ingo</td>
<td>105</td>
</tr>
<tr>
<td>Stoco, Bruno N.</td>
<td>54</td>
</tr>
<tr>
<td>Strandlund, Henrik</td>
<td>79</td>
</tr>
<tr>
<td>Suh, Byeng-Chan</td>
<td>67</td>
</tr>
<tr>
<td>Suh, Dong-Woo</td>
<td>120</td>
</tr>
<tr>
<td>Sun, Lixian</td>
<td>106</td>
</tr>
<tr>
<td>Sun, Weihua</td>
<td>108</td>
</tr>
<tr>
<td>Sundman, Bo</td>
<td>44, 50, 53, 66, 83, 111</td>
</tr>
<tr>
<td>Sung, Yun-Mo</td>
<td>131</td>
</tr>
<tr>
<td>T</td>
<td></td>
</tr>
<tr>
<td>Talijan, Nadežda</td>
<td>135</td>
</tr>
<tr>
<td>Tanaka, Toshihiro</td>
<td>126, 138</td>
</tr>
<tr>
<td>Tang, Chengying</td>
<td>81, 131</td>
</tr>
<tr>
<td>Taniguchi, R.</td>
<td>132</td>
</tr>
<tr>
<td>Tao, X.</td>
<td>100</td>
</tr>
<tr>
<td>Tasci, Emre S.</td>
<td>28</td>
</tr>
<tr>
<td>Tédenac, Jean-Claude</td>
<td>49, 100</td>
</tr>
<tr>
<td>Terentiev, Dmitry I.</td>
<td>116</td>
</tr>
<tr>
<td>Thiebaut, Stéphanie</td>
<td>87</td>
</tr>
<tr>
<td>Todorović, Radiša</td>
<td>135</td>
</tr>
<tr>
<td>Tojal, C.</td>
<td>74</td>
</tr>
<tr>
<td>Togase, K.</td>
<td>89, 133</td>
</tr>
<tr>
<td>Tokumoto, Y.</td>
<td>89</td>
</tr>
<tr>
<td>Tokunaga, T.</td>
<td>134</td>
</tr>
<tr>
<td>Tomiyasu, Keisuke</td>
<td>114</td>
</tr>
<tr>
<td>Tong, Minmin</td>
<td>81</td>
</tr>
<tr>
<td>Turchanin, Mikhail A.</td>
<td>47, 153</td>
</tr>
<tr>
<td>V</td>
<td></td>
</tr>
<tr>
<td>Vardhan, C.V. Vishnu</td>
<td>56</td>
</tr>
<tr>
<td>Vitos, Levente</td>
<td>75</td>
</tr>
<tr>
<td>Vřeštál, Jan</td>
<td>26, 135</td>
</tr>
<tr>
<td>W</td>
<td></td>
</tr>
<tr>
<td>Wang, C.P.</td>
<td>92, 137, 139, 140, 141, 142</td>
</tr>
<tr>
<td>Wang, Jianchuan</td>
<td>106</td>
</tr>
<tr>
<td>Wang, Jiang</td>
<td>82, 109, 121</td>
</tr>
<tr>
<td>Wang, Peisheng</td>
<td>107</td>
</tr>
<tr>
<td>Wang, She Q.</td>
<td>104</td>
</tr>
<tr>
<td>Name</td>
<td>Pages</td>
</tr>
<tr>
<td>-----------------------</td>
<td>-------</td>
</tr>
<tr>
<td>Wang, Y.</td>
<td>92, 139</td>
</tr>
<tr>
<td>Warczok, Piotr</td>
<td>40</td>
</tr>
<tr>
<td>Watson, A.</td>
<td>121</td>
</tr>
<tr>
<td>Wollants, Patrick</td>
<td>58</td>
</tr>
<tr>
<td>Wood, J.T.</td>
<td>37</td>
</tr>
<tr>
<td>Xiong, Wei</td>
<td>75</td>
</tr>
<tr>
<td>Xiong, Xiang</td>
<td>104</td>
</tr>
<tr>
<td>Xu, Honghui</td>
<td>42, 81, 103, 106, 107, 108</td>
</tr>
<tr>
<td>Yamada, Kazuyoshi</td>
<td>114, 134</td>
</tr>
<tr>
<td>Yamamoto, Y.</td>
<td>124, 132</td>
</tr>
<tr>
<td>Yao, Qingrong</td>
<td>81</td>
</tr>
<tr>
<td>Yonenaga, I.</td>
<td>89, 124, 132</td>
</tr>
<tr>
<td>Yoshikawa, Takeshi</td>
<td>138</td>
</tr>
<tr>
<td>Yu, Y.</td>
<td>142</td>
</tr>
<tr>
<td>Yuan, Zhaohui</td>
<td>108</td>
</tr>
<tr>
<td>Zabdyr, Leszek A.</td>
<td>115</td>
</tr>
<tr>
<td>Zemanova, Adela</td>
<td>77, 110</td>
</tr>
<tr>
<td>Zhang, Hualei</td>
<td>75</td>
</tr>
<tr>
<td>Zhang, Ligang</td>
<td>34</td>
</tr>
<tr>
<td>Zhang, Lijun</td>
<td>42, 105, 107</td>
</tr>
<tr>
<td>Zhang, Yinan</td>
<td>36</td>
</tr>
<tr>
<td>Zhang, Weibin</td>
<td>42</td>
</tr>
<tr>
<td>Zhang, Wei-Wei</td>
<td>136</td>
</tr>
<tr>
<td>Zhou, Shu Z.</td>
<td>104</td>
</tr>
<tr>
<td>Živković, Dragana</td>
<td>135</td>
</tr>
<tr>
<td>Zhao, Dongdong</td>
<td>42</td>
</tr>
<tr>
<td>Zhao, Jingrui</td>
<td>107</td>
</tr>
</tbody>
</table>
## List of Participants

<table>
<thead>
<tr>
<th>Name</th>
<th>Country</th>
<th>Email/Contact Information</th>
</tr>
</thead>
<tbody>
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- *Solidification simulation*: solidification path and heat evolution using Scheil and Lever-rule model
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