Calphad XXXI

Stockholm May 5-10, 2002

Program and abstracts
Monday 6/5

08.00 Registration of late arrivals and day visitors
08.30 Welcome

NEW EXPERIMENTAL METHODS AND RESULTS

Chairpersons: John Ågren, Nathalie Dupin
Experimental determination of site occupancies for non-stoichiometric phases from diffraction data using the Rietveld method: valuable information for Calphad modeling. Jean-Marc Joubert and Yves Feutelais
08.40
09.10 Thermodynamics of Platinum-Barium Alloys. Rashed Alsaeed
09.30 Solubility of cubic carbide formers in liquid Cobalt. G. Andersson, C. Föjer, and B. Jansson
09.50 Comparative thermodynamic analysis of ternary system Pb-Bi-In. D. Zivkovic and D. Manasijevic

10.10 coffee

10.50 Formation Enthalpies of Compounds from Al-Ti System: Solution Calorimetry vs. Direct Reaction Calorimetry. K. Rzyman and Z. Moser
11.40 End of session

12.00 LUNCH

13.00 Poster session and software demonstration

NEW AB INITIO TECHNIQUES AND RESULTS

Chairpersons: Gerhard Inden, Karin Frisk
14.30
15.00 Sigma-phase Stability from First principles in Co-Cr System Phase Diagram Calculation. Jana Houserov and Jan Vrestal
15.20 Molecular Dynamics Simulation on Closing Mechanism of Single-Walled Carbon Nanotubes with Tersoff Potential. Sang Soo Han and Hyuck Mo Lee
15.40 An Atomistic study of phase equilibrium and solid-liquid interface dynamics. M Stan and M I Baskes

16.00 coffee

16.20 An ab initio study of monovacancies and divacancies in copper. D Andersson
16.40 Phase Stability of Al-Hf, Al-Nb, Hf-Pd and Nb-Pd Systems: From First-Principles to CALPHAD. G. Ghosh, M. Asta and G.B. Olson
17.00 Thermodynamic functions of dynamically stable and unstable lattices. G Grimvall
17.40 First-Principles calculation and CALPHAD modeling of Laves phases. Zi-Kui

18.00 DINNER
Chairpersons: Bo Sundman, Suzana Fries

Study of the mu-phase of Ni-Nb : Rietveld analysis, First Principles calculations and Calphad approach. Nathalie Dupin, Jean-Marc Joubert, Bo Sundman, Suzana G. Fries, Alain Pasturel and Marcel Sluiter

20.00 Ab-initio study of the precipitation of Al3Zr in Al-Zr, E Clouet, M Nastar, J M Sanchez, C Sigli

20.40 Invitation to workshops on selected topics Suzana G Fries and Bo Sundman

TUESDAY 7/5

MODEL DEVELOPMENT FOR THERMODYNAMIC PROPERTIES

Chairpersons: Andre Costa e Silva, Bengt Hallstedt

Effect of Interaction between Chemical and Magnetic Ordering on Phase Equilibria in Fe-Co-X (X=Al or Si) Ternary Systems. Ikuo Ohnuma, Osamu Ikeda, Tatsuro Sakai, Naohide Kamiya, Ryosuke Kainuma and Kiyohito Ishida

08.30 A Predictive Thermodynamic Model for the Al-NaF-AlF3-CaF2-Al2O3 System. Patrice Chartrand

08.50 The improved model for the Mo-rich Laves phase and its application for modern high-Cr steels, Ales Kroupa, Leona Korcakova, Jana Houserova, John Hald

09.10 Recent Developments in the Molten Chlorides Database of the Factsage Thermochemical Software, Christian Robelin, Patrice Chartrand and Arthur D. Pelton

09.30 Combining ab-initio calculation with Calphad method at finite temperatures, Xiaogang Lu

10.10 coffee

10.30 Hume-Rothery and Calphad Thermodynamics, Larry Kaufman

11.00 Surface Properties of the Ni-Co-Al System, R. Novakovic and E. Ricci

11.20 Modelling Hume-Rothery Phases in the Ag-Cu-Zn Ternary System, Victor Vitusevych, Suzana G. Fries, Anne Drevermann, Ulrike Hecht and Bo Sundman

11.40 Al3TM based phases in binary and ternary alloy systems, M. Yurechko, B. Grushko, T.Ya. Velikanova and K. Urban

12.00 LUNCH

13.00 Poster session and software demonstration

COMBINATION OF KINETICS AND CALPHAD METHODS

Chairpersons: Arthur Pelton, Malin Selleby

Kinetic Simulation of Carbide/Nitride Precipitation in Steel Weldment with Cr-Mo-V-N-C Redistribution below 700 C. J. Sopousek, Jan Vrestal,

Assessment of the Diffusional Mobility of f.c.c. solution in the Al-Zn Binary System, Yuwen Cui, R. Kainuma, P. Wollants, K. Ishida

A Diffusion Mobility Database for Ni-Base Superalloys, C. E. Campbell, W. J. Boettinger, U. R. Kattner

Modeling of intermetallic formation in hot dip galvanizing, Jinichiro Nakano, Gary R. Purdy, Dmitri V. Malakhov

http://www.met.kth.se/calphad/program5.html
16.20 coffee
16.40 A Semi-Empirical Atomistic Approach in Materials Research, Byeong-Joo Lee
A quantification of the kinetic character of mixed-mode solid-state phase transformations, Jilt Sietsma and Sybrand van der Zwaag
Application of Continuous Displacement Treatment of Cluster Variation Method to Phase Transformation of Metals and Alloys, R. Kikuchi and K. Masuda-Jindo
17.40 End of session
18.00 DINNER
Chairpersons: Fred Hayes, Ursula Kattner
20.00 Computational Investigations on the Phase Transformation in Fe-Base Ternary Alloys based on the Phase Field Method, Toru Miyazaki
20.20 The Computation of the Evolution of Morphology Using a Phase-Field Model Coupled to MTDATA, R. S. Qin, E. R. Wallach, R. H. Davies, A. T. Dinsdale, and R. C. Thomson
20.40 Phase-field modeling of the thermo-mechanical properties of carbon steels. Dong Jin Seol, Kyu Hwan Oh, Jung Wook Cho, Jung-Eui Lee and U-Sok Yoon

WEDNESDAY 8/5

INDUSTRIAL APPLICATIONS
Chairpersons: Philip Spencer, Patrice Chartrand
Investigation of the effect of different thermodynamic models used for the slag phase on the overall results from CFD simulations of vacuum degassers. Johan Björkvall and Lage Jonsson
08.30 Carbides and intermetallic phases in ferritic steels, A. Schneider, G. Inden
09.10 Recent Applications of Calphad Thermodynamics, Larry Kaufman
09.40 Prediction of carbon content of austenite in TRIP steels Lars Höglund
10.00 coffee
10.20 A Thermodynamic Database for Solder Alloys, Ursula Kattner
10.40 Thermodynamic Databases for Industrial Applications - Steel and Cemented Carbides Karin Frisk
11.20 Materials optimization using the Calphad approach, R Sandström
12.00 LUNCH
13.00 Poster session and software demonstration
Chairpersons: Mats Hillert, Victor Vinograd
15.00 Thermo-Calc Software: Tools for material and process development. Thomas Helander
15.30 A thermodynamic evaluation of the C-Co-W-Hf-Zr system for cemented carbide applications. Johan Bratberg and Bo Jansson
15.50 A preliminary evaluation of the Fe rich region of the Fe-Ti-P system and its implications on the processing of IF (interstitial free) steels, Roberto Avillez, Andre Costa e Silva
16.10 Application of Calphad to diffusional reactions between coating and substrate John Ågren
16.40 coffee
19.00 CONFERENCE DINNER
THURSDAY 9/5

ASSESSMENT AND ASSESSMENT METHODS

Chairpersons: Bo Jansson, Byeong-Joo Lee

08.30 Indium-nitrogen: Small System = Big Surprise Experimental, Thermodynamic and Phase Stability Analysis, R. Schmid-Fetzer, B. Onderka and J. Unland

09.00 A preliminary thermodynamic assessment of BaO-SrO-TiO2-ZrO2 system. Weiping Gong and Zhanpeng Jin

09.20 Thermodynamic Assessment of the Al2O3-CaO-SiO2 System. Huahai Mao, Malin Selleby and Bo Sundman

09.40 Thermodynamic Modeling of the Zr-O System. Raymundo Arroyave, Larry Kaufman and Thomas W. Eagar

10.00 coffee

10.30 Remarks on crystallochemical aspects in thermodynamic modeling, R. Ferro and G. Cacciamani

11.00 Thermodynamic assessment of the Ga-O binary system, M. Zinkevich and F. Aldinger

11.20 Thermodynamic Assessment of the Co-O System, Ming Chen, Bengt Hallstedt, and Ludwig J. Gauckler

11.40 End of session

12.00 LUNCH

13.00 Poster session and software demonstration

Chairpersons: Tim Andersson, Olga Fabrichnaya

15.00 A New Strategy for Optimizing Systems with Multiple Non-stoichiometric Compounds: Application to the Cu-In-Se system. Jianyun Shen, Xinquan Wang, and Tim Anderson

15.30 Glass-Forming Alloys: Search for Deep Multicomponent Eutectics, Didier de Fontaine

15.50 Phase Equilibria Calculations in the Ni-Al-Cr-Co and Ni-Al-Cr-W Systems with Respect to New Experimental Information on the gamma and gamma' Phase Region, P. Broz, R. Picha, J. Bursik

16.10 coffee

16.30 A reassessment of the Al-Pt binary system, S. Prins, L.A. Cornish, W. Stumpf, B. Sundman

16.50 Thermodynamic Evaluation of the ternary system Ag-Au-Cu including a short range order description, Alexandra Kusoffsky

17.10 A new version of the Fe-Co phase diagram, B.Pushkarev and Y.Ustinovshikov

17.30 End of session

18.00 DINNER

FRIDAY 10/5

Chairpersons: Alan Dinsdale, Marius Stan

08.30 The assessment of thermodynamic parameters of the MgO-Al2O3-SiO2 system. O. Fabrichnaya, L. Lukas, H. Seifert, F. Aldinger

09.00 Tentative description of the Cu-Cu2O subsystem by the associated model M.T. Clavaguera-Mora, N. Clavaguera, J.L. Touron

09.20 The Cu-O System Revisited. Bengt Hallstedt and Ludwig J. Gauckler

http://www.met.kth.se/calphad/program5.html 2002-04-28
09.40  Assessment of CaMgSi2O6 - NaAlSi2O6 - CaFeSi2O6 pyroxenes: CVM modelling and a polynomial fit to the CVM results. Victor Vinograd

10.00 coffee
10.30  Presentation of results from workgroups
11.50  Final words

12.00 LUNCH

Bus transportation to central Stockholm will be arranged both before and after lunch

POSTERS

All posters can be mounted on Monday and stay mounted until Friday

1 Thermocalc+Zircobase calculations applied to Zircaloy's alloys - Influence of oxygen and hydrogen concentration on the equilibrium alpha/beta phases at high temperature. J.C. Brachet, C.Toffolon-Masclet, T.Guilbert, D.Hamon, C.Grandjean, P. Jacques, R.Cauvin
2 A Thermodynamic Assessment of the Neodymium-Oxygen System, P. Franke
3 High temperature vaporizations in assessment of gaseous molecule thermodynamic data. Matthias Heyrman and Christian Chatillon
4 Ordered Ground States in Multicomponent Ni-based Alloys Studied by Monte Carlo Simulation. J. Bursik
5 Thermodynamic Assessment of the Mn-O System, A. Nicholas Grundy, Bengt Hallstedt, Ludwig J. Gauckler
6 A Study of the Thermodynamics of Aluminum Nitride Precipitation in Steels and Ferrous Alloys, Andre Costa e Silva, Fernando Rizzo and John G. Speer
8 Thermodynamic assessment of the ternary uranium-oxygen-zirconium system. C. Gueneau, M. Baichi, S. Chatain, C.Chatillon, B.Sundman
9 Ab-initio calculated energetics of sigma-phase in Cr-Fe and Cr-Co systems based on equilibrium volume, Jana Houserova, Jan Vrestal and M Sob
11 Recommendations for notations, symbols etc, Mats Hillert.
12 Thermodynamic Assessment of the Mo-Zr Binary system, Rosa Jerlerud-Perez and Bo Sundman
13 Phase equilibria of the Al-Cu-Fe system in the vicinity of quasicrystal phase, Liming Zhang and Reinhard Luck
14 Phase equilibria in low Ta-containing martensitic steels, A Danon, C Servant.
15 A new version of the Fe-Cr phase diagram, B.Pushkarev and Y.Ustinovshikov
16 Comparisons between experimental and calculated solidification paths for Fe-Cr-C alloys, A Antoni-Zdziobek, C Tassin, J Ägren.
17 Calculation of thermodynamic quantities using artifical neural networks, H Strandlund
18 Using the gas constant as an adjustable parameter, Dmitri V. Malakhov

http://www.met.kth.se/calphad/program5.html
21 Application of Statistical Moment Method to Phase Transformation of HCP (Ti, Zr, Hf) Metals, K. Masuda-Jindo, S. R. Nishitani and Vu Van Hung

22 Thermal analysis of copper-based special bronzes, A. Kostov, D. Zivkovic, S. Jakovljevic:
Calphad XXXI

Abstracts

Djurönäset Conference Center

Stockholm

Sweden
New Experimental Methods and Results

Monday May 5  8.40-12.00

Session chairman: John Ågren
Experimental determination of site occupancies for non-stoichiometric phases from diffraction data using the Rietveld method: valuable information for Calphad modelling.

Jean-Marc Joubert and Yves Feutelais

**Keywords:** non-stoichiometric phases, Rietveld method, sublattice model, X-ray diffraction

Analysis of powder diffraction data may yield valuable information to people interested in phase diagrams. The Rietveld method provides most accurate analysis of powder diffraction patterns for evidencing an additional phase, for refining lattice parameters and performing quantitative phase analysis.

In addition, structural refinement of a given phase may be performed, including the determination of atomic positions and occupancy factors, if sufficient scattering contrast is available between the elements sharing the same sites.

Basic principles of the method will be given as well as possibilities and limits concerning the determination of site occupancies. Two examples will be detailed. Tl₅Te₃ has been investigated within its whole homogeneity domain in order to determine the mechanism for non-stoichiometry.

This mechanism will be discussed in relation with the description chosen in a recent optimization of Tl-Te system. The mu phase in Nb-Ni system has also been investigated by X-ray diffraction over its whole homogeneity domain. Compositional phase limits have been determined by electron probe micro-analysis. Determination of the mutual occupancies on the 5 sites of the structure has been performed for each sample. Mechanism for the accommodation of the non-stoichiometry will be described as a function of niobium composition. Comparison with thermodynamical models previously used to describe mu phases in the Calphad approach will be made.

From these two examples, conclusions will be drawn concerning the high ability of the Rietveld method to be used in conjunction with the sublattice model. Not only, the choice of a model to account for the non-stoichiometry can be made upon experimental basis, but it is also suggested that experimental site occupancies should be used as experimental data in the frame of an optimisation with the Calphad method.
Thermodynamics of Platinum-Barium Alloys

Rashed Alsaed

Keywords: Platinum-Barium system, Gibbs free energy, thermodynamic data

Galvanic cells with Barium Flouride as solid electrolyte were used to obtain the thermodynamic properties of Platinum-Barium system at 1073 K. A complete set of thermodynamic data was obtained for intermetallic compounds Pt5Ba and Pt2Ba. The range of homogeneity of Pt2Ba was determined by coulometric titration.
Solubility of cubic carbide formers in liquid Cobalt

G. Andersson, C. Föjer and B. Jansson

AB Sandvik Coromant, SE-126 80 Stockholm, Sweden

ABSTRACT

Coated cemented carbide is today the dominant tool material for metal cutting. The development of new coating processes has lead to new requirements on the supporting cemented carbide substrates. Cracks will unavoidably form in the hard coatings and might during machining propagate into the substrate and cause failure. Increased resistance to crack propagation can be obtained by creating a binder phase enriched zone near the surface. The main technique used today to generate such a functional gradient is to sinter a substrate containing a cubic carbonitride phase under denitriding conditions. Outward diffusion of nitrogen will, due to a strong thermodynamic coupling, cause the cubic phase to dissolve and an inward diffusion of the cubic phase formers.

The formations of gradients during sintering of multi-component cemented carbides have been studied experimentally and by computer simulations in collaboration with several academic groups. The computer simulations have proven to be an important tool for detailed understanding of the growth of gradients.

The growth is controlled by diffusion in the liquid binder and the kinetics depends on gradients in chemical potentials, diffusivities and solubilities in the liquid binder phase. In order to improve the diffusion simulations more accurate experimental information on thermodynamic properties and diffusivities are needed.

Therefore, an experimental technique to determine the solubility of cubic carbide formers in the liquid Co based binder phase has been developed. The method is based on heat treatment of a compound of a straight WC-Co grade and a grade also containing a cubic carbide phase. The carbide forming metal will diffuse into the liquid binder of the straight grade without forming any cubic carbide. A state close to the equilibrium can be reached by long time holding. Thus, after cooling the solubility in the liquid binder can be determined by standard methods. Making sure that graphite or M6C carbide is present in the compound during the heat treatment controls the carbon activity. The experimental method has been used to determine the solubility of Hf, Nb, Ta, Ti and Zr in the Co rich binder phase.

The experimental method can also be used to study the kinetics of diffusion and surface tension driven viscous flow of the liquid by interrupting the process before an equilibrium state is reached and analysing gradients in the WC-Co part of the compound.
Comparative thermodynamic analysis of ternary system Pb-Bi-In

D.Zivkovic, D.Manasijevic

Univ. of Belgrade, Technical Faculty Dept. of Metallurgy, VJ 12, Bor, Yugoslavia

Keywords: alloy thermodynamics, Pb-Bi-In system

Results of thermodynamic investigation of two sections in the ternary system Pb-Bi-In are presented in this paper. The sections Pb-BiIn2 and Pb-BiIn were investigated by calorimetric measurements, quantitative DTA and thermodynamic predicting, while the chosen alloys were characterized by X-ray analysis and optic microscopy in order to confirm their phase diagrams. Obtained results were compared with literature data.

References
Magnesium alloys are one of the most promising lightweight materials for automotive applications. The current use of magnesium in automotive applications is usually limited to non-critical parts because of their restricted creep properties. Technically used alloys are mainly consisting of aluminium and zinc. Rare earths additions improve creep resistance of these alloys by forming precipitates. Some attempts were made by the automotive industry in the last decades to replace the Rare earths metals by Calcium. But die-sticking and hot-cracking behavior caused problems. Newly developed Mg-Al-Ca-based alloys with microalloying additions of Si and Sr show significantly better tensile and compressive creep properties than the benchmark AE42 alloy [2001Luo]. This improved creep resistance is attributed to the thermal stability and the interfacial coherency of the (Mg,Al)2Ca phase in the microstructure of the alloys. Despite the high potential of Ca additions for the technical development of Mg-alloys, the phase diagram of the ternary Mg-Al-Ca system is not known. Only for the Mg-rich corner the phase relations are determined. The technically very important homogeneity range of precipitations Al2Ca and Mg2Ca expected in casted alloys was also unknown.

The ternary aluminum-calcium-magnesium phase equilibria were investigated using X-ray diffraction methods, metallography, scanning electron microscopy with energy or wave-length dispersive X-ray microanalysis and differential thermal analysis. The complete phase diagram was determined. During this study two new compounds were found in the binary Al-Ca system. A detailed experimental investigation and thermodynamic calculation of this binary system is already published [2001Kev1+2]. Large ternary solubilities were found for the binary phases CaMg2, Al2Ca and Al3Ca8. Microstructures of compositions near these phases show remarkable rod-like crystals that are identified as intergrowth between CaMg2 and Al2Ca. Thermodynamic parameters were optimised using the Calphad method incorporating all experimental data.

References
Formation enthalpies of compounds from Al-Ti system: solution calorimetry vs. direct reaction calorimetry.

K. Rzyman, Z. Moser

Institute of Metallurgy and Materials Science, Polish Academy of Sciences 30-059 Kraków, Reymonta Street 25, POLAND

The influence of applied calorimetric method on experimentally determined formation enthalpy values is analysed. Analysis is performed on compounds from Al-Ti system: Al₃Ti, AlTi and AlTi₃. Obtained results are shown on the background of the mechanism of formation of compounds. The role and sequence and kinetics of formation of compounds is emphasized. Discussion is based on our own new results of enthalpies of formation for Al₃Ti, while data for AlTi and AlTi₃ were previously published. In addition to comparison of the results obtained both by the solution method and the direct reaction technique, also the literature data are taken into consideration including those from ab initio. Comparison of the obtained results leads to the conclusion that the difference of the values of formation enthalpies by methods listed above, grows up with the increase of the titanium content in the compounds.
Pauling File, Binaries Edition, an Inorganic Materials Database and Design System

P. Villars 1, M. Berndt 2, K. Brandenburg 2, K. Cenzual 3, J. Daams 1, F. Hulliger 1, H. Okamoto 1, K. Osaki 4, A. Prince †, H. Putz 2, S. Iwata 5

1 Materials Phases Data System, Vitznau, Switzerland,
2 Crystal Impact, Bonn, Germany,
3 Dept. of Inorganic Analytical and Applied Chemistry, Univ. of Geneva, Switzerland,
4 Japan Science and Technology Corporation, Tokyo, Japan,
5 RACE, University of Tokyo, Japan

The PAULING FILE is a comprehensive database covering all families of non-organic compounds (no C-H bonds). It consists of four interconnected parts: Constitution, Structure, Diffraction, and Physical Properties. The linkage between the four different groups of data was considered as most important, therefore the PAULING FILE was designed as a phases-oriented materials database. The editors have for every chemical system evaluated which distinct phases exist, using all information available in the PAULING FILE, and each database entry has been linked to such a distinct phase.

Beside the classical applications in phase analysis and teaching, the PAULING FILE project was started in the optic to create a tool for materials design. The aim is to use modern computer technology to search for additional rules and correlation in published data and use them in the design of new materials.

The first off-line version of the PAULING FILE, Binaries Edition*, is limited to binary compounds. Nevertheless, the data equal over 30,000 printed pages, i.e. a 20 volume Handbook set:
- 8,000 phase diagrams (with updated phase assignment) covering 2,300 binary systems,
- 28,300 structural data sets (including atom coordinates and displacement parameters, when determined) for more than 10,000 different phases,
- roughly 3,000 experimental and 27,000 calculated diffraction patterns, and
- around 17,300 physical-property entries (with about 43,100 numerical values and about 10,000 figure descriptions) for some 5,000 phases.

To reach this result, the editors have critically analyzed and processed 21,000 original publications and over 15 full-time manpower years editor work was necessary to edit the data. Whereas the coverage for crystal structures, diffraction data and phase diagrams can be considered as satisfactory, it is just a beginning for property data.

The PAULING FILE is funded by Japan Science and Technology Corporation (JST) and Materials Phases Data System (MPDS) and jointly copyrighted by JST and MPDS. Editor-in-chief: P. Villars (MPDS), editors: K. Cenzual, J.L.C. Daams, F. Hulliger, H. Okamoto, A. Prince †, K. Osaki, project coordinator: S. Iwata, CD-ROM software: Crystal Impact.

* for further information see http://www.paulingfile.com
New Ab initio Techniques and Results

Monday May 6, 14.30-18.00

Session chairman: Gerhard Inden
A review of First-principles approaches to Alloy Thermodynamics

P. E. A. Turchi\(^1\), V. Drchal\(^2\), J. Kudrnovsky\(^2\), C. Colinet\(^3\), Z. K. Liu\(^4\), and L. Kaufman\(^5\)

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\(^5\)Dept. of Materials Science and Engineering, MIT, Cambridge, MA 02139, USA.

A fundamental understanding of alloy phase stability and ordering must be based on a proper description of the scattering properties of the electrons (1). In particular, the quantum mechanical Hamiltonian that pertains to the motion of electrons must be matched to an Ising-type Hamiltonian that describes states of configurational order. In the case of the generalized perturbation method (GPM) (1,2), or the embedded cluster method (ECM) (3), such a mapping is achieved by means of an expansion of the band energy in terms of site-occupation numbers at zero temperature. Consequently, the energetics of the Ising Hamiltonian is defined analytically from the scattering properties of the chemically random state of the alloy at any composition. In another approach, the so-called Connolly-Williams method (CWM) (4), the matching of the two Hamiltonians is assumed a priori. The energetic parameters that enter the Ising Hamiltonian are obtained by a fitting procedure from a set of total energies associated with a limited number of ordered alloy configurations, and after having made some assumption about the most relevant cluster interactions.

The two approaches will be contrasted, and it will be recalled that, despite the abundant literature on the subject, the GPM and the ECM still possess many attractive features that the CWM does not have (5), and are capable of predicting a wide range of alloy properties (2). In particular, ground states of order, thermodynamic functions, short-range order induced diffuse scattering intensities, and ultimately phase diagrams can be predicted. We will discuss the application of the first-principles tight-binding linear muffin-tin orbital (TB-LMTO) method, within the coherent potential approximation (CPA) and the local density approximation of density functional theory, to the study of phase stability properties of substitutional alloys based on periodic lattices with the prediction of equilibrium properties and phase diagrams of several binary and ternary alloys. The statistical mechanics part of the problem is solved with the cluster variation method (CVM). It will be shown that in some instances tendencies toward order are predicted although the assessed phase diagrams indicate complete miscibility or are not capable of confirming or identifying metastability. Consequences of both approaches to mapping of the energetics within the standard CALPHAD formalism will be discussed and illustrated.

Acknowledgments

Work of P.T. was performed under the auspices of the U. S. Department of Energy by the University of California Lawrence Livermore National Laboratory under Contract W-7405-ENG-48. Partial support for L.K. from the Yucca Mountain Site Characterization Project at LLNL is gratefully acknowledged. Partial supports for V.D. and J.K. from the Grant Agency of the Academy of Sciences of the Czech Republic, Project 1010829, and the U. S.-Czechoslovak Science and Technology Program, Project 95-018. are gratefully acknowledged.

References

Keywords: Ab initio, Chromium, Cobalt, Thermodynamics

Lattice stability difference of complex structures, such as sigma-phase, can be successfully calculated from the first principles. Calculated lattice stability differences can supplement existing values of lattice stability differences evaluated more or less reliably for simple structures on the base of experiments.

A part of systematic study of sigma-phase stability are equilibrium volume calculations of sigma-phase stability in Co-Cr system. The optimisation of structure parameters with respect to minimum energy was performed during calculations. Calculated lattice stability differences are successfully used for phase diagram construction. The model, presented in [1,2], was used for thermodynamic description of sigma-phase and thermodynamic description of remaining phases was taken from [3]. Entropy term of sigma-phase formation was adjusted to phase equilibrium data.

The mentioned results are validated by comparison of calculated Gibbs energy and enthalpy of formation of Co-Cr sigma-phase with results of calorimetric experiments and with results of calculations presented in [3].

References:
Molecular Dynamics Simulation on Closing Mechanism of Single-Walled Carbon Nanotubes with Tersoff Potential

Sang Soo Han and Hyuck Mo Lee

KAIST, South Korea

Keywords: Carbon nanotube, Closing mechanism, Molecular dynamics simulation, Tersoff potential

The research on growth kinetics of carbon nanotubes (CNT) has become very active recently, however it was not reported in detail about the growth mechanism. The formation and growth remain still controversial. The structure of CNT remain open-ended during growth and carbon atoms at the end of the tube have highly reactive dangling bonds, which results in a thermodynamically unstable state. Therefore, most tubes tend to have a close-ended structure. In this study, the molecular dynamics simulation with Tersoff potential on closing mechanism of various single-walled CNT is introduced because the Tersoff potential has been extensively used for modeling of group IV elements (C, Si, Ge) with covalent bonding. The growth mechanism was investigated with diameter and length of CNT. A heptagon-octagon pair and a nonagon newly formed in (10,0) single-walled CNT caused the closed structure of the CNT and it was confirmed that the longer is the length of CNT, the faster is the closing process. In the case of (18,0) single-walled CNT, the zipper-like closing mechanism was observed.
AN ATOMISTIC STUDY OF PHASE EQUILIBRIUM AND SOLID-LIQUID INTERFACE DYNAMICS

Marius Stan and Michael I. Baskes

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Keywords: dynamics, equilibrium, interface, potential

A semi-empirical Lennard-Jones/Embedded Atom Method model is used to capture real materials behavior through the introduction of many-body forces. By the means of molecular dynamics calculations, the free energies of the liquid, solid solutions, and non-stoichiometric compounds are determined. The chemical potential is used to calculate binary equilibrium phase diagrams. The calculations illustrate the consequences of differences in energy and size between the components on the phase diagrams. The model is used to study the dependence of the solid/liquid interface velocity on temperature and composition. An asymmetry in velocity between solidification and melting is found and the slowing of the interface velocity during solidification is demonstrated.

Fig. 1 MD simulation of melting

Fig. 2 Calculated phase diagram
An ab initio study of monovacancies and divacancies in copper

David Andersson

Ideal solids are perfect crystals, but in reality they always contain defects of some sort. These defects can give rise to both wanted and unwanted properties. Vacancies, being the simplest defect, influence physical properties like diffusion, electrical conductivity, heat capacity and thermal expansion. Monovacancies and divacancies in copper were studied from first-principles (ab initio) theory. The calculations were done with the VASP code, which is a plane-wave pseudopotential implementation of the density functional theory. The quantities that were calculated are the monovacancy and the divacancy formation, migration and binding enthalpies as well as the formation volumes. Further, the monovacancy and the divacancy formation entropies were estimated from a least-squares analysis of experimental data of the vacancy concentration. The calculated vacancy parameters are compared to previously published experimental and theoretical investigations. Possible explanations for the discrepancies between these results are also discussed. Under the assumption that the formation enthalpies and entropies are independent of temperature we are able to reproduce the experimental Arrhenius plot of both the total vacancy concentration (monovacancies plus divacancies) and the self-diffusion coefficient.
Phase Stability of Al-Hf, Al-Nb, Hf-Pd and Nb-Pd Systems: From First-Principles to CALPHAD

G. Ghosh, M. Asta and G.B. Olson

Northwestern University, United States of America

Keywords: First-principles, Nb-base alloys, Phase stability, Superalloys

To support quantitative design of Nb-base superalloys, we have undertaken a comprehensive study of phase stability of Nb-X and other binary systems of interest. Of particular interest is to design Nb-alloys, containing coherent precipitates that would be analogous to classical gamma systems, for operating at 1300°C and above. As a part of this research, we will present the results of phase stability calculations from first-principles. The results of these calculations are integrated with CALPHAD approach to model the relevant binary and ternary phase diagrams. Besides the stability of desired coherent phase(s), we will also present the results of phase stability of TCP phases, that may stable or metastable, obtained from first-principles calculations.
Thermodynamic functions
of dynamically stable and unstable lattices

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It is now well established that elements and alloys may be dynamically unstable in common lattice structures. For instance, in the Ag-Zn system a bcc phase is experimentally observed near 50 at.% Zn, but a Zn-rich alloy is unstable in the bcc lattice structure. This implies that the bcc Ag$_{c}$Zn$_{1-c}$ alloy becomes dynamically unstable above a certain critical concentration $c_{\text{crit}}$. Similarly, Mg is unstable in the bcc lattice structure at ambient pressure and temperature, but the bcc phase becomes dynamically stable at pressures above a critical pressure $P_{\text{crit}}$. This paper exemplifies, with graphs showing a characteristic behavior, how the enthalpy $H$, the entropy $S$, the Gibbs energy $G$, and the heat capacity $C_{p}$ vary in such systems, as one goes from a region that is dynamically stable, i.e. representing the thermodynamically stable or a metastable phase, to a region of lattice instabilities where $S$ is not defined. In particular, the behaviour in the vicinity of $c_{\text{crit}}$ or $P_{\text{crit}}$ is considered.
Ab initio study of vacancy ordering in TiC

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Keywords: defect interactions, ordering, titanium carbide, vacancies

The ordering of constitutional vacancies in substoichiometric TiC is studied theoretically on the basis of ab initio calculations. Both the Connolly-Williams method and the generalized perturbation method were applied and yielded similar results for the effective interaction energies of carbon vacancies. The calculated interaction energies (up to four-body terms) are used as input data for Monte Carlo simulations of the vacancy ordering as a function of temperature and composition. The phase diagram for the vacancy ordered structures has been established, see Fig. 1. Three ordered superstructures of vacancies (Ti2C, Ti3C2, and Ti6C5) are found to be ground state configurations. Their stability has been verified by full-potential total energy calculations of the fully relaxed structures, see Fig. 2.

![Calculated phase diagram of the vacancy ordering.](image1)

![Heat of formation for vacancy ordered structures.](image2)
In CALPHAD modeling, laves phases are typically described with a two-sublattice model, i.e. \((A,B)_2(A,B)\). There are four end-members, \((A)_2(A)\), \((A)_2(B)\), \((B)_2(A)\), \((B)_2(B)\), with the lattice stability of non-existing end-members being typically assigned 5000J/mole of atoms.

In the present work, first-principles calculations are carried out to compute the total energy of laves phases in the Mg-Al-Ca system using the full-potential linearized augmented plane wave (FP-LAPW) method implemented in the WIEN2k package. As the benchmark, the total energies of pure Mg, Al and Ca in the fcc, bcc, and hcp structures are calculated and compared with the results in the literature and from the CALPHAD method with good agreements. Next, the total energies of the stable Laves C-14 (Mg2Ca) and Laves C-15 (Al2Ca) are calculated and compared with the data available in the literature, followed by the total energy calculations of the remaining three end-members.
New Ab initio Techniques and Results

Monday May 6, 20.00 – 21.00

Session chairman: Bo Sundman
Study of the \(\mu\) phase of Ni-Nb: Rietveld analysis, First Principles calculations and Calphad approach

Nathalie Dupin\(^1\), Jean-Marc Joubert\(^2\), Bo Sundman\(^3\), Suzana G. Fries\(^4\), Alain Pasturel\(^5\) and Marcel Sluiter\(^6\)

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The \(\mu\) phase, prototype \(\mathrm{Fe}_7\mathrm{W}_6\), has a complex crystal structure with five different sites. It appears in several systems (Co-Mo, Co-Nb, Co-Ta, Fe-Nb, Ni-Ta, \ldots) within a range of homogeneity that varies depending on the binary system considered. Several attempts were made to model this phase with the Calphad approach but the general model is still elusive [97Ans,98Kum]. The main problem in such kind of phase is how to model the site occupancy in the different sublattices as a function of composition as there usually are a lack of experimental crystallographic information and a lack of estimates for the several model parameters used as compound energies required by the Compound Energy Formalism (CEF)[81Sun].

In this work, powder X-ray diffraction data of five samples in the homogeneity range of stability of the \(\mu\) phase in the binary system Nb-Ni is reported. Rietveld analysis is performed and the crystal structure is refined for the five compositions at 1273 K, experimental site occupancies being obtained.

Simultaneously, first-principles total energies were calculated providing energies of formation at 0 K, \(H_i(T=0\text{K})\), for all the possible \(i\) configurations of the site occupancy in the \(\mu\) phase.

In order to describe the energetics of the system at higher temperatures two methods will be used: a) cluster expansion and cluster variation method (CE-CVM) and b) \(H_i(T=0\text{K})\) entered directly as compounds in the CEF and a Bragg-Williams approximation for the entropy, as normally used in the Calphad approach.

The comparison of the site occupancies, obtained by both approaches, to the experimentally obtained occupancies as function of composition will be shown.

A re-assessment of the \(\mu\) phase of this system is performed with the modified CEF [00Ans] using the new information for this phase.

This work can demonstrate whether the simple direct use of FP energetics together with the BW statistics is a good approximation for the \(\mu\) phase behaviour as has been shown for the A15 [98Tou] and for the \(\sigma\) phases [01Ber,02Fri] at high temperatures. This work shows how Calphad assessments can combine FP and crystal structure results in order to improve thermodynamic descriptions.

Ab-initio study of the precipitation of Al$_2$Zr in Al

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(Dated: April 28, 2002)

Zr precipitates in Al to form the phase Al$_2$Zr which can have the stable DO$_{23}$ structure or the metastable L1$_2$ structure. The aim of this study is to obtain these solubility limits and then to model kinetics of precipitation.

We use ab-initio calculations to obtain a thermodynamic model, similar in its expression to Calphad approach, which allows us to calculate the solubility limit of Zr in Al for the stable as well as the metastable phase diagrams [1]. The cohesive energies of ordered compounds is obtained from FP-LMTO (Full Potential Linear Muffin Tin Orbital) calculations, and we then use the cluster expansion theory to fit a generalized Ising model to this database. This allows us to calculate in the Bragg-Williams approximation the configurational free energy at finite temperature. Contribution of electronic excitations to the free energy is found to be insignificant, and the vibrational contribution is included by considering the harmonic approximation as well as the Debye model.

In order to study kinetics, we consider the diffusion through the jumps of a vacancy. In this purpose, we generalize our description of thermodynamics of the binary Al-Zr to the one of the ternary Al-Zr-Vacancy system by including interactions with vacancies. Saddle point energies for the migration of the vacancy are fitted using experimental diffusion coefficients. Doing the same mean-field approximation as for thermodynamics, we can deduce from this atomistic description of kinetics the phenomenological coefficients of the full Onsager matrix [2], and we will show how this leads to a more complete description of kinetics than the one usually used in diffusion database as Dictra.


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Model Development

for Thermodynamic Properties

Tuesday May 7, 08.30-12.00

Session chairman: Andre Costa e Silva
Effect of Interaction between Chemical and Magnetic Ordering on Phase Equilibria in Fe-Co-X (X=Al or Si) Ternary Systems.

Ikuo Ohnuma, Osamu Ikeda, Tatsuro Sakai, Naohide Kamiya, Ryosuke Kainuma and Kiyohito Ishida
Tohoku University, Japan

Keywords: magnetism, order-disorder phenomena, phase equilibria, thermodynamics

It is well known that the magnetic properties, such as the Curie temperature, Tc, and the mean magnetic moment, b, of the ordered compounds differ from those of the disordered state. For instance, both Tc and b of the Ni3Pt (L12) and NiPt (L10) and Tc of the CoPt (L10) and CoPt3 (L12) ordered compounds are strongly depressed due to the ordering compared with those of the metastable disordered Ni-Pt and Co-Pt alloys [1]. On the other hand, Tc of the Ni3Fe (L12) ordered compound is higher than that of the disordered phase [2]. In consequence, the stability of the ordered phase is depressed or enhanced due to the interaction between the chemical and magnetic ordering caused by the decrease or increase of Tc and b. The purpose of this study is to investigate the interaction effect on the phase equilibria in the Fe-Co-Al and Fe-Co-Si ternary systems and to evaluate the interaction of the FeCo (B2) ordering based on a phase diagram of the Fe50Co50-Fe70Al30 and Fe50Co50-Fe84Si16 (at.%) pseudo-binary systems.

The Curie temperature and A2/B2 transition temperature of Fe-Co-Al and Fe-Co-Si alloys were determined using a DSC. Figure 1 shows the result of the measurement. The fictitious Curie temperature of the B2 ordered Fe50Co50 alloy and the fictitious A2/B2 transition temperature without the interaction effect were estimated to be 1360°C and 270°C, respectively. Taking into account the interaction effect, i.e., the positive deviation of the Curie temperature, +240°C, and the positive deviation of the A2/B2 transition temperature, +460°C, of the stoichiometric FeCo alloy, the thermodynamic assessment of the Fe-Co binary system was carried out.

A Predictive Thermodynamic Model for the Al-NaF-AlF$_3$-CaF$_2$-$\text{Al}_2\text{O}_3$ System

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**Keywords:** Cryolite, Predictions, Quasichemical-Model, Thermodynamic

A large body of experimental thermodynamic and phase-equilibrium data exists for the Al-Na-Ca-F-O system. This system is of primary importance for Al$_2$O$_3$-reduction cells. All available data are critically evaluated to obtain optimized parameters of thermodynamic models of all phases. The bath model is the Quasichemical model in the quadruplet approximation that evaluates 1st- and 2nd-nearest-neighbor short-range-order. Other solution models are used for non-stoichiometric solid cryolite, the gas phase and molten Al. The models are then used to predict the thermodynamic properties and metal-bath-gas equilibria in the multicomponent heterogeneous system. All experimental data were reproduced within experimental error limits, and in most cases ternary and multicomponent data were predicted by the model, not fitted. The model parameters form a database that is part of the FactSage Thermochemical Software. This software can be used to predict/simulate metal-bath-gas equilibrium (phase amounts, compositions, activities/partial pressures, enthalpies, Tliquidus, etc) for 25°C $<$ T $<$ 1100°C, for P $<$ 4 atm, and for bath ratios (wt.%) from 3.0 to AlF$_3$ saturation.
The improved model for the Mo-rich Laves phase and its application for modern high-Cr steels

Ales Kroupa, Leona Korcakova, Jana Houserova, John Hald

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Keywords: High-Cr Steels, Laves Phase

Laves phase is important intermetallic phase, which have significant influence on the mechanical properties of modern high-Cr steels. The possibility to predict the temperature stability and amount of this phase for newly proposed materials is therefore very important and helpful because these materials are too complex for real systematic experimental study. The discrepancies were found between the predicted temperature stability and experimental results of the Laves phase in the Cr,Mo steels, where the theoretical stability of Laves phase is significantly lower than the experimental observation indicates. Such problem was not found in steels with higher W content, where the theoretical predictions and experimental results agree reasonable well. The modification of Laves phase model is carried out in two stages. At first, present two-sublattice model (Fe,Cr)2(Mo,Xi) was modified to stabilize the phase at temperatures around 600°C in high-Cr steels. At the same time existing low-temperature experimental data (under 900°C) for Fe-Cr-Mo subsytem were used to verify this assessment with relevant experiments. The modified description of the Laves phase will be presented and reasonable agreement of the prediction with the experimental results for lower order systems as well as for the multicomponent systems, corresponding to the modern steels will be shown. This Laves phase model allows to predict the behaviour of Laves phase in dependence on many important alloying elements as Mo, W etc. Second stage of the modification will comprise the broadening of the model by addition of further elements, which play important role in the Laves phase thermodynamics. Si is typical example of such element. It plays significant role in modern steels and its concentration in Laves phase is between 1-5 at% according to various experiments. Because of lack of any experimental data concerning the influence of Si on Laves phase in simpler subsystem, the assessment of the Si influence on the Laves phase stability can be accomplished by the help of first-principle calculation. This work was supported by the project 106/00/0855 of the Grant agency of Czech Republic and by the projects S2041105 of The Academy of Sciences of the Czech Republic.
Recent Developments in the Molten Chlorides Database of the Factsage Thermochemical Software

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Keywords: Factsage, Molten_chlorides, Quasichemical_model, Thermodynamic_database

Molten chlorides are involved in many industrial processes. An overview will be given concerning the recent progress in the molten chlorides database of the Factsage Thermochemical Software. At present, this database is mainly composed of LiCl, NaCl, KCl, MgCl₂, CaCl₂, SrCl₂, BaCl₂, MnCl₂, FeCl₂, FeCl₃, CoCl₂, NiCl₂ and AlCl₃. New additions mainly consist of FeCl₂-CoCl₂-MgCl₂-MnCl₂-NiCl₂, NaCl-KCl-ACl₂ (where A is Co²⁺, Mn²⁺ or Ni²⁺) and NaCl-KCl-AlCl₃. All available experimental data (enthalpy of mixing of the liquid, activities in the liquid, phase diagram) were critically evaluated to obtain optimized parameters of the thermodynamic models used for the liquid and the FeCl₂-CoCl₂-MgCl₂-MnCl₂-NiCl₂ solid solution, as well as the thermodynamic properties (H₂⁹⁸, S₂⁹⁸ and Cp) of the stoichiometric compounds involved in the NaCl-KCl-ACl₂ and NaCl-KCl-AlCl₃ systems. The liquid model is the Quasichemical Model taking into account cation-cation short-range order. The multicomponent solid solution was modeled using a cationic substitutional model with a Temkin entropy and a polynomial excess Gibbs energy. We also started to study the dissolution of water in the NaCl-KCl-MgCl₂-CaCl₂ electrolyte (used for magnesium production), which is reported to involve oxide species (MgO, CaO) and hydroxychloride species (MgOHCl, CaOHCl). The liquid was modeled by applying to the Na⁺, K⁺, Mg²⁺, Ca²⁺/Cl⁻, O₂⁻, OH⁻ system (diluted in O²⁻ and OH⁻) the Quasichemical Model in the Quadruplet Approximation, that evaluates coupled 1st- and 2nd-nearest-neighbor short-range order.
Combining ab-initio calculation with CALPHAD method at finite temperatures

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Ab-initio calculation methods at finite temperatures are briefly reviewed. A new method has recently been proposed to evaluate the vibrational contribution of the lattice ion to the total free energy. Several examples are presented, showing that the calculated thermodynamic properties are in good agreements with the experiments. However, more future works should be done on this method to check the validity and generality. Some discussions will also be made on the usage of the results from ab-initio calculation together with the CALPHAD method.
Hume-Rothery and CALPHAD Thermodynamics

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Hume-Rothery’s “Atomic Theory for Students of Metallurgy” was an advanced text that introduced modern quantum mechanics to us as undergraduates in the early 50’s. In 1966 I had the opportunity to spend a week in Geneva at the Battelle Conference on “Phase Stability in Metals and Alloys” with H-R, Brewer, Zener, Friedel and Kubaschewski. Hume-Rothery invited me to review the subject for Volume 14(1969) of Progress in Materials Science which he edited and we had an 30-month discussion by mail covering many aspects of the Geneva Conference and my PMS paper until his death in September 1968. Kubaschewski’s Brunel and Sheffield Conferences in July 1971 and the Munster Conference in 1972 set the stage for the birth of the “CALPHAD Method”, Journal and annual conferences which continue today. At the 2001 TMS Annual meeting in New Orleans the Symposium on “Computational Thermodynamics and Materials Design” illustrated many cases where “CALPHAD THERMODYNAMICS” affording the broadest description of the stable, metastable and unstable phases over wide ranges of composition, temperature and pressure could be used in the description of commercially useful materials and processes. The present discussion will make the connection between H-R’s seminal work, the basis adopted for the predictive CALPHAD method and practical application of the science of “Alloy Thermodynamics”.

Surface Properties of the Ni-Co-Al System

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Keywords: LIQUID ALLOYS, MICROSCOPIC FUNCTIONS, SURFACE SEGREGATION, SURFACE TENSION

The energetics and its effect on alloying behaviour of Ni-Co, Ni-Al and Al-Co as well as of Ni-Co-Al liquid alloys has been analysed through the study of surface properties (surface tension and surface composition) and microscopic functions (concentration fluctuations in the long-wavelength limit and chemical short-range order parameter) in the frame of statistical mechanical theory in conjunction with the quasi-lattice theory (QLT). An attempt has been made to link surface phenomena of ternary Ni-Co-Al system and its subsystems with the bulk through the study of the concentration dependence of various thermodynamic, structural and surface properties.

References:
Modelling Hume-Rothery Phases in the Ag-Cu-Zn Ternary System

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Ag-Cu, Ag-Zn and Cu-Zn are experimentally well determined binary systems and for each one there are thermodynamic descriptions available. The solution A1 (α brass), A2 (β brass) and D82 (γ brass) phases are stable in these systems. The disordered A2 phase presents a second order transformation to the B2 superlattice at low temperature in the Cu-Zn system. Experimental results seems to indicate that the A2 phase does not present the same transformation in the Ag-Zn system, another ordered phase appears as stable one at low temperature.

The experimental Ag-Cu-Zn ternary phase diagram is well determined. All the brass phases stable in the binaries form large ternary solutions and the ranges of solubility are experimentally determined. There are also measurements of partial and integral enthalpies of the liquid ternary phase.

A strategy for modelling the ternary solution from the binary solutions phases is presented.

The lack of information when modelling multicomponent phases with many sublattices, as in the case of γ brasses, is pointed out.

Experimental and theoretical informations that can help in the modelling of multicomponent ordered and disordered solution phases are discussed.
Orthorhombic ε-phases in binary Al-Pd(Rh) and ternary Al-Pd-Mn(Fe,Co) and Al-Rh-Cu

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Complicated orthorhombic structures closely related to decagonal quasicrystals were observed in the Al-Pd and Al-Rh alloy systems. In Al-Pd two structures with the same lattice parameters $a=2.35$ and $b=1.68$ nm and $c=1.23$ and 5.74 nm are formed between 74.6 to 71.9 at.% Al. They are designated $ε_6$ and $ε_{28}$ respectively (the index is the number $l$ of the strong $(00l)$ reflection corresponding to the interplanar spacing of about 2 nm). In Al-Rh the $ε_6$ structure with the lattice parameters $a=2.34$, $b=1.65$ and $c=1.23$ is also formed at 75 at.% Al while another structure designated $ε_{16}$ ($a=2.34$, $b=1.65$ and $c=3.28$nm) is formed at 76 at.% Al. Additionally, two other related structures designated $ε_{22}$, and $ε_{34}$ were observed in ternary Al-Pd-Mn (Fe, Co) alloys. They can be reliably identified by electron diffraction. The $c$ lattice parameters of the $ε$ phases form a row: $c_{16}=c_6(τ+1)$; $c_{22}=c_6(τ+2)$; $c_{28}=c_6(τ+3)$; $c_{34}=c_6(τ+4)$, where $τ=(1+5^{1/2})/2$ is the golden mean.

The overall $ε$-phase range in Al-Pd-Mn extends to about 5 at.% Mn at 800 ºC, in Al-Pd-Fe to about 10 at.% Fe at 950 ºC and in Al-Pd-Co to about 16.5 at.% Co at 950 ºC. With the increase of the Mn, Fe and Co concentration the Al concentration of the $ε$-range increases. The Al-Rh $ε_6$ phase can dissolve up to 10 at.% Cu, with the increase of the Cu concentration the Al concentration of this phase decreases. The geometry of the “ε”- phase ranges in the ternary systems is discussed.
Combination of Kinetics and CALPHAD Methods

Tuesday May 7, 15.00-18.00

Session chairman: Arthur Pelton
Kinetic Simulation of Carbide/Nitride Precipitation in Steel Weldment with Cr-Mo-V-N-C Redistribution below 700 °C

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Keywords: Diffusion, Steel, Welded joints

The welded joints of dissimilar alloys usually represent the weakest point in many technical solution. In the case of weld applications at elevated temperatures, the mechanical properties can be related with chemical concentration and phase transformation processes in diffusion-affected zone. The kinetics of ÕSN 15 128 (low alloyed Cr-Mo-V steel) / P91 (8.5wt% Cr 1%Mo-V-N steel) weldment was simulated using combination of CALPHAD method [1] and the same method as can be found in DICTRA programme [2, 3, 4]. The thermodynamic database STEEL11.TDB [5] and mobility database DIF12.TDB [6] were applied in the simulation. The equilibrium calculations using CALPHAD method allowed us to predict phase diagrams for both ÕSN 15 128 and P91 steels. The diffusion and phase transformation processes occurred in ÕSN 15 128/P91 welded join were simulated using DICTRA programme. It enabled us to evaluate time-distance dependences for phase composition and element redistribution in diffusion-affected zone in temperature range 700-575°C. This simulation results at different temperatures were compared with experimental results.

The most interesting results concern carbonitride and high chromium carbide phase transformations.

The described method can be used for weldments design. Supported by GA CR (106/00/0855).

References
Assessment of the Diffusional Mobility of f.c.c. solution in the Al-Zn Binary System

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The diffusion mobility of the f.c.c. solid solution in the Al-Zn binary system was critically assessed using the DICTRA (Diffusion Controlled Transformation) software. The procedure got started from estimating the temperature dependence of self and tracer diffusion coefficients in hypothetical f.c.c. Zn upon the empirical equation, and optimized further parameters on the ground of applicable experimental kinetic information. The established mobility data were then applied to yield the tracer and interdiffusion coefficients, and their dependences on temperature and composition. Reasonable agreement was generally found between the predicted and the experimental values. It is also noted that, negative interdiffusion coefficients appear within the f.c.c. immiscibility gap, which give rise to the so-called uphill diffusion. Three simulation examples presented in the end of the article demonstrate the feasibility of the current assessment with nice reproductions of the accessible diffusion experiments.
A Diffusion Mobility Database for Ni-Base Superalloys

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National Inst. of Standards & Technology, United States of America

Keywords: diffusion couples, multicomponent diffusion, Ni-base superalloys

An eleven-component diffusion mobility database for the gamma (fcc) phase of Ni-base superalloys is evaluated and is employed for several processing applications. The quality of the mobility database is examined through the correlation of the diffusivity at the melting temperature, the comparison with measured quaternary diffusion coefficients, and the comparison with measured and simulated multicomponent diffusion couples between commercial superalloys. Diffusion coefficients calculated using the same diffusion mobility database with different thermodynamic databases are compared to determine the sensitivity of the mobilities to the thermodynamics. Using the predicted solidified structure of a model ternary alloy, linear and non-linear heating rates are optimized to produce a homogenized structure while avoiding incipient melting and minimizing time. The diffusion in a gamma matrix is modeled enabling prediction of the composition and particle size of gamma prime during cooling. The dissolution of B2-rich coating on a gamma + gamma prime substrate is predicted and confirmed experimentally.
Modeling of intermetallic formation in hot dip galvanizing

Jinichiro Nakano, Gary R. Purdy, Dmitri V. Malakhov

The formation of intermetallic compounds (including dross particles) during hot dip galvanizing is a complex process. In spite of serious attempts to understand the underlying reactions [1], it is still not possible to predict with confidence either the sequence with which various phases appear in the system or the amount of dross formed in a galvanizing bath. The Gibbs energies of the intermetallics in galvanizing systems are very close to each other in the temperature range of practical interest, 430-480°C. It should not then be surprising that the sequence is extremely sensitive to minor variations of such process parameters as: composition of steel; bath temperature and composition; and surface properties.

In this contribution, the concept of thermodynamic nucleation potential [2] is applied to the processes of phase formation in the Fe-Zn system. It is assumed that, in the beginning, a metastable equilibrium between α-Fe and liquid Zn is promptly (in several seconds) attained, leading to a supersaturated solution of Fe in molten Zn. Then the driving forces for the onset of precipitation of all intermetallic compounds are compared, and the phase possessing the maximal value is considered most likely to appear in the system. Precipitation from the supersaturated melt is associated with dross formation (unwanted from the ecological viewpoint); the amount of dross is estimated at various temperatures (Fig. 1).

To apply the approach outlined above, it is necessary to extrapolate the phase boundary BCC + L / L more than 300°C below the temperature of the peritectic reaction BCC + L ⊃ Γ. A metastable continuation of the liquidus, calculated using the most recent optimization of the Fe-Zn system [3], shows a sudden change of slope and two closely located inflection points (Fig. 2). It is probable that these artefacts (resulting in an underestimated metastable solubility of Fe!) are “approximation phantoms” caused not by a specific behavior of the Fe-Zn system itself, but by an excessively large number of adjustable parameters employed in [3]. To obtain a more consistent liquidus shape, a partial optimization was carried out. While the descriptions of FCC, Γ, Γ₁, δ, ζ and η phases suggested in [3] were retained, the thermodynamic properties of BCC and L have been reassessed. Although geometrical structures of phase boundaries cannot be directly taken into account during optimization, our new assessment does provide a metastable continuation of the liquidus free of inflection points.

A Semi-Empirical Atomistic Approach in Materials Research

Byjong-Joo Lee

POSTECH, South-Korea

Keywords: Atomistic Simulation, Modified EAM, Semi-Empirical

Atomistic Simulation can be a useful tool to analyze and predict phase transformations, surface/interface atomic structures and mechanical properties of metals. In order to obtain reliable results within reasonable computing time, it is important to use a well-assessed semi-empirical atomic potential for elements and alloy systems. In the present presentation, a recently developed atomic potential model, the second nearest-neighbor modified embedded atom method (2NN MEAM), will be introduced. Various physical properties of elements (mainly bcc transition metals), including elastic constants, structural properties, point defect properties, surface properties and thermal properties will be calculated and compared with experiments or high level calculations. Some examples for description of alloy systems and atomistic approaches in materials research will also be presented.
A quantification of the kinetic character of mixed-mode solid-state phase transformations

Jilt Sietsma and Sybrand van der Zwaag

Delft University of Technology, The Netherlands

Keywords: diffusion control, interface control, mixed mode, solid-state transformation

A large part of the solid-state phase transformations in metals comprises of the formation of a new phase that is different in composition from the parent phase. Important examples of such transformations are the austenite-to-ferrite transformation in steel and the precipitation of intermetallic phases in aluminium. In transformations of this kind, two processes are jointly governing the kinetics, viz. diffusion of at least one component and the intrinsic velocity of the interface. Depending on the relative rates of these two processes, the kinetic character of the transformation is situated between the two extremes of diffusion control, in the case of fast interface kinetics and/or slow diffusion, and interface control, in the opposite case. In general, such a transformation is said to occur under mixed-mode conditions. The classical descriptions of the two limiting processes have been given by Zener (1949) for diffusion control and by Christian (1981) for interface control.

In the present paper the character of the kinetics of a mixed-mode transformation is quantified, on a scale between full diffusion control and full interface control, as a function of a single parameter that accounts for the diffusivity, the interface mobility, the magnitude of the driving force and the surface-to-volume ratio of the growing phase. This quantification enables an adequate assessment of the applicability of different transformations models in which additional assumptions are used to circumvent complicated mixed-mode calculations. The quantification is shown to be consistent with mixed-mode calculations performed on a 2D system. Moreover, it is found that in the course of the transformation its character shifts between diffusion control and interface control.
Application of Continuous Displacement Treatment of Cluster Variation Method to Phase Transformation of Metals and Alloys

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\textbf{Keywords}: cluster variation method, phase transformation, continuous displacement treatment, metals and alloys

Cluster Variation Method (CVM) has been very successful in the computations of alloy phase diagrams as well as in many problems of the materials science related to the phase transitions. Originally, CVM was developed in the framework of the so-called rigid lattice approximation, but it has recently been extended to include continuous atomic displacements due to thermal lattice vibration and local atomic distortion due to size mismatch of the constituent atoms. In the present study, we focus our attention on the latter continuous displacement treatment of CVM. The continuous displacement (CD) formulation of the CVM is applied to study the phase stability of the binary alloys. The basic idea is to treat an atom which is displaced by $r$ from its reference lattice point as a species designated by $r$. The effects of continuous atomic displacement on the thermodynamic quantities of binary alloy systems are investigated in detail using the well established cluster approximations, i.e., pair, quasi-chemical tetrahedron and tetrahedron cluster approximations.
Combination of Kinetics and CALPHAD Methods

Tuesday May 7, 20.00-21.00

Session chairman: Fred Hayes
Computational Investigations on the Phase Transformation in Fe-Base Ternary Alloys based on the Phase Field Method

Toru Miyazaki

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The kinetic simulation based on the phase field method with Calphad data-base becomes very powerful in fundamental understanding of the phase transformation in real alloy systems. In the present study, we calculate the dynamics of microstructure changes due to the phase decomposition and microstructure development in Fe-Al-Co and Fe-Cr-Co ternary alloy systems based on the phase field method. The thermodynamic parameters for these alloys were introduced from the Calphad data-base where the composition and temperature dependencies of atomic interchange energy are taken into account so as to be applicable for the phase diagram of the real alloy systems. The elasticity and mobility of atoms are assumed to depend on the local order parameters such as composition, degree of order and so on. Time dependent morphological changes of the microstructure such as formation of modulated structure by spinodal decomposition, strain induced morphological changes of precipitates, the order-disorder transition with phase decomposition and discontinuous precipitation will be demonstrated. The results simulated are quantitatively in good agreement with the experimental facts in the real alloy systems.

By utilizing this method, it is expected to open a new field of materials science such as phase transformations due to the multi-component diffusion, multi-structural transformation and complex pattern formation, which are the most important and interesting phenomena but difficult in the materials science.
The Computation of the Evolution of Morphology Using a Phase-Field Model Coupled to MTDATA

R. S. Qin\textsuperscript{1}, E. R. Wallach\textsuperscript{1}, R. H. Davies\textsuperscript{2}, A. T. Dinsdale\textsuperscript{2}, and R. C. Thomson\textsuperscript{3}

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Keywords: Morphology, MTDATA, Phase-field model

This paper describes a program which has been developed to enable the computation of morphological evolution, for example on solidification, based on a new phase-field model and a theory for propagation rates of planar interfaces. The model incorporates solute diffusion theory with a statistical description for the interfacial geometry. A direct link to MTDATA through the use of a user application interface has been utilised to provide thermodynamic input. Comparisons between kinetic and thermodynamic driving forces, chemical potentials and partial Gibbs energies will be presented. The new phase-field model removes the restriction on the interface thickness in earlier work, such as the Wheeler-Boettinger-McFadden model. This enables computation in systems with large dimensions and also for phases with very limited solubility. The phase-field mobility is obtained via quantitative calculation of the propagation rate of a planar interface. All the thermodynamic and conservation laws are maintained after introducing the solute diffusion theory with a statistical description for phase distribution. The use of the model will be described and illustrated with simulations of the solidification of Al-Si and Cu-Ni alloys.
Phase-field modeling of the thermo-mechanical properties of carbon steels

Dong Jin Seol, Kyu Hwan Oh, Jung Wook Cho, Jung-Eui Lee and U-Sok Yoon

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Keywords: continuous casting, mechanical property, phase-field model, steel

The high temperature stress model for continuously cast steels has been developed. The effect of dendritic morphology on the mechanical strength of carbon steels has been investigated for the first time with a thermodynamically based calculation of dendritic morphology by a phase-field model. The characteristic solid fraction at the liquid impenetrable temperature (LIT) was evaluated as 0.9 by investigating the contact behavior of secondary arms during unidirectional solidification of d and g phases. Geometrical hardening of the mushy zone due to the contact and combining of dendrite arms has been evaluated using a geometrical hardening parameter defined as the contact ratio between adjacent secondary arms in the transverse cross section of primary arms. The critical solid fraction at zero strength temperature (ZST) was evaluated as 0.65 from the minimum non-zero contact ratio. The calculated critical fracture strength with the stress model for steels in a mushy zone describes the measured tensile strength well.
Industrial Applications

Wednesday May 8, 8.30-12.00

Session chairman: Philip Spencer
Investigation of the effect of different thermodynamic models used for the slag phase on the overall results from CFD simulations of vacuum degassers.

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In the present work sulphur removal and reoxidation during vacuum degassing treatment is studied with the macro kinetics derived by a three phase computational fluid dynamic, CFD, model that was earlier developed at Mefos. The developed model describes the stirring effect of argon bubbling through porous plugs combined with steel slag reactions. The modelling approach divides the overall model into separate parts describing the thermodynamics, the thermophysics and the transport descriptions and combines these parts into different reaction models outlining the reoxidation reactions and the desulphurisation. The overall result depends on the quality of each of the different parts. In this work the emphasis is on thermodynamics. An extensive description of the heat and fluid-flow equations may be found in earlier publications [1,2].

In order to use a coupled thermodynamic, thermophysic and kinetic description the concept of local thermodynamic equilibrium has been used. This means that the equilibrium conditions are solved for each calculation node along every calculation sweep during the CFD simulation. Solving for a time step in the range of 0.1 to 1 second, $10^8$ calculations may be needed for a calculation grid 100x100x100. Furthermore, the total simulated time is normally at least 14 minutes. Thus a great number of calculations are done during these CFD simulations, meaning that the calculation speed of computers normally available today prohibits a complex description of the thermodynamic conditions in such a model. Wagners model for diluted solution has been used to calculate the activities in the steel phase and the KTH model by Björkvall et al [3] has been used to calculate the activities in the slag phase. An empirical expression suggested by Ohita and Suito [4] has also been used to calculate the alumina activity in the slag phase. There is a disparity between the calculated alumina activity using the KTH model [3] and the expression suggested by Ohita and Suito [4].

In order to investigate the effect of the different ways to calculate the alumina activity on the overall model, a number of CFD simulations have been done using industrial data from two different degassers. The most important difference between the use of the different expressions concerns the oxygen activity in the steel melt. The oxygen activity has a predominate effect on the sulphur removal as well as on the final aluminium content in the steel. The effect of modifying the initial data used in the simulations has also been investigated with respect to the initial sulphur content in the slag. Reasonable agreement regarding the final sulphur content between calculated and measured has been observed. The discrepancy noticed regaining the final aluminium content between reported and calculated values is discussed.

References
Carbides and intermetallic phases in ferritic steels

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This paper presents results on phase transformations in new ferritic steels for application in power plants at 650 °C. The initially martensitic structure is strengthened by carbides (M_{23}C_6, M(C,N)) and Laves phase particles.

Thermodynamic calculations using Thermo-Calc are performed for 12%Cr steels with alloying additions of Si, C, N, W, V, Nb, Ta, Co, and/or B. Phase equilibria are calculated at constant temperatures and compared with predictions from Schaeffler diagrams. The calculations show that in many cases the effect of alloying elements differs from the simple Schaeffler-type description. The calculation of phase fractions of ferrite, carbides and Laves phase allows an optimization of heat treatments.

The growth kinetics of M_{23}C_6 carbides and Laves phase particles in W containing steels is calculated for the conditions during heat treatment at 780 °C and service at 650 °C using the cell model of DICTRA.
At the recent TMS Meeting in Seattle recognizing the contribution of William Hume-Rothery to the development of CALPHAD Thermodynamics(1) the author contrasted the status of the Calculation of Phase Diagrams at the Battelle-Geneva meeting in 1966 and the Symposium on Computational Thermodynamics and Materials Design held at the 2001 annual meeting of TMS in New Orleans. Many cases were cited where “CALPHAD THERMODYNAMICS” affording the broadest description of the stable, metastable and unstable phases over wide ranges of composition, temperature and pressure described commercially useful materials and processes(1,2). These discussions provided recent examples of the design of metallic glasses, bulk ceramic superconductors, high strength weldable low carbon steels, thin films of solar cell and magnetic alloys for computer disk drives. Combined thermodynamic and kinetic analyses were applied to synthesize tough Ultra High Strength steels and predict microstructural changes in boilers and turbines used in fossil fuel plants to raise the operating temperatures above 650°C. Recent studies directed toward the design and characterization of the waste package contemplated for the Yucca Mountain Repository(2) will be discussed which deal with the kinetics of phase transformation of the sigma and P-Phase in Ni-Cr-Mo alloys providing an idealized model of C-22. In addition Pourbaix diagrams have been calculated for similar alloys in a series of well water compositions simulating the environment of the repository. Finally examples extending the application of such methods to description of phase stability of niobium-base alloys(3) and anode materials for advanced Li-batteries will be presented.

REFERENCES


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Prediction of carbon content of austenite in TRIP steels

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The mechanical properties of TRIP steels are controlled by the final fraction, size and morphology of retained austenite as well as its composition after annealing at low temperatures.

In this work a method to predict the final fraction and composition of retained austenite has been developed. The method is based on the assumption that the ferrite grows at low temperatures as Widmanstätten ferrite under para-equilibrium conditions.
A Thermodynamic Database for Solder Alloys

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Keywords: database, multicomponent, solder

New solder alloys for electronic assemblies are being developed as replacement for traditional Pb-containing solder materials as a result of international pressure to remove Pb from the waste stream. Phase equilibria information is needed for the evaluation of candidate solder alloys in terms of their melting behavior and the effects of possible effects of contamination by other elements, such as Pb, on manufacturing and reliability. Parameterization of phase equilibria data through thermodynamic modeling and phase equilibria calculations allows compact storage and retrieval of this information for any composition or temperature of interest.

A database for solder alloys has been assembled for 7 components: Sn, Ag, Bi, Cu, In, Pb, Sb. Since the number of constituent binary and ternary subsystems for such a database is large, it is desirable to utilize assessments published in the literature. These assessments must be reviewed for consistency of the phase description and, in some cases, it may be necessary to remodel individual phases. The reliability of the phase equilibrium calculation, however, depends on the quality of the descriptions of the individual phases. One important criterion for the evaluation of these descriptions for solder alloys is the requirement that calculated reaction temperatures need to be known with a relatively high accuracy. A summary of the evaluation of available thermodynamic descriptions and results from assembling this database are being discussed.
Thermodynamic Databases for Industrial Applications
– Steel and Cemented Carbides

Karin Frisk, Alexandra Kusoffsky, Johan Bratberg and Bo Sundman

Within the frame of the Centre of Computational Thermodynamics [1], improved thermodynamic databases for industrial applications in steel and cemented carbides are developed. The work involves a combination of experimental studies and thermodynamic modelling. The main objective is to increase the accuracy of predictions made through calculations of multi-component phase equilibria in selected ranges. The calculations are focused on specific applications. Examples of results from calculations on cemented carbides, high-speed steel, sintered steels and stainless steel are given as well as an outline of future work which is planned.

References
Solid State Thermal Energy Storage
in Binary “Plastic Crystals” - Calculation of Binary Phase Diagrams

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Keywords: High Temperature Guinier X-ray diffraction, DSC, Solid State Phase Change, Thermal Energy Storage Materials, Thermodynamic Modeling

Organic molecular “Plastic Crystals” undergo solid-state phase transitions with reversible absorption or release of large amount of heat. These solid-state heat storage materials have great potential for practical devices and are candidate materials for passive solar buildings and drywalls. These materials are superior to ordinary sensible heat storage materials like concrete or brick, for example: the energy stored in concrete is 0.01 cal/gm, as compared to these materials, which can store about 20-80 cal/gm. We have investigated organic crystals such as Pentaerythritol\([C-(CH2OH)4](PE)\), Pentaglycerine\([CH3C-(CH2OH)3](PG)\), Neopentylglycol\([CH3]2-C-(CH2OH)2](NPG)\), Neopentylalcohol\([CH3]3-C-(CH2OH)1](NPA)\), and amines such as 2-Amino-2-Methyl-1, 3-Propanediol \([CH3(NH2)C-(CH2OH)2](AMPL)\) and tris(hydroxymethyl)aminomethane\([H2NC(CH2OH)3](TRIS)\). The solid-state phase transition temperatures for the individual compounds lie in the range from –31°C\((NPA)\) to 188°C\((PE)\). There is a need to vary the solid-state phase transition temperature \((T_{str})\) for various applications, and phase diagram reveals the compositional dependence in binaries on the \(T_{str}\). Phase diagrams, such as Tris-NPG, PE-AMPL, NPG-AMPL, and NPG-PG have been experimentally developed, as well as modeled.

Experimental determination of the binary phase diagrams was carried out using Guinier X-ray diffraction and Differential Scanning Calorimetry (DSC). For example, in Tris-NPG binary the low temperature phases are designated \(a\) or \(b\) and the high temperature phases as \(g\) or \(g'\). It was found that below ~43°C, there is virtually no solubility of Tris in NPG or visa-versa. The NPG rich \(b\) phase transforms to a NPG rich \(g'\) plastic phase at ~43°C. Between ~43°C to 105°C a wide \(a+g'\) phase region is observed. A two-phase region with \(g+g'\) plastic phases rich in NPG and TRIS, storing different amounts of energy, is also observed between 127.5°C to 150°C.

Thermo-Calc and FACT software are being used for theoretical modeling to simulate the binary phase diagrams providing a basis for analysis of the experimental results. Agreement between the simulations and our experimental results with the data available in the literature is a strong motivation for developing a thermodynamic database for such organic compounds undergoing solid-state phase transitions. Thermodynamic and crystal structure database for the above mentioned binaries will be presented for use in thermal energy storage application.
Material optimisation using the Calphad approach

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Royal Institute of Technology, Sweden

Keywords: aluminium, materials optimisation, stainless

In materials selection, mathematical optimisation has successfully been used for a long time to maximise a target function with a range of boundary conditions on different properties. The result is a ranking of the suitability of materials for a given application. This approach, which is referred to as materials optimisation, has now been realised for adaptation of the alloy composition. The basis of the system is a large number of composition - microstructure - property relations for physical, mechanical, technological and environmental properties. With the help of Thermo-Calc, the phase fractions and compositions are determined. The property relations and Thermo-Calc have been integrated into an optimisation system. The system has been used to analyse and simultaneously optimise mechanical and corrosion properties of duplex stainless steel. In the same way mechanical and various technological properties have been studied for aluminium alloys.
Industrial Applications

Wednesday May 8, 15.00-16.40

Session chairman: Mats Hillert
Thermo-Calc Software - Tools for material and process development

Thomas Helander
Thermo-Calc Software AB

Software for calculation of phase diagrams and thermodynamic properties have been developed since the 1970’s. By now software and computers have developed to a level where it is possible to do calculations for “real” multicomponent materials. This provides material scientists with powerful tools, supporting material and process development such as:

- Thermodynamic software for calculation of phase diagrams and thermodynamic properties e.g. Thermo-Calc
- Programming interfaces, which enables access to the thermodynamic software from a user-written software. Accurate data for thermodynamic properties and phase equilibria can then easily be incorporated into software written in e.g. C++, Matlab and FORTRAN.
- Software for simulating the rate of diffusion controlled phase transformations such as DICTRA. These can give important and complimentary information on rates of phase transformations and diffusion processes.

The aim of the current presentation is to show how these tools can be applied in different areas of material and process development.
A thermodynamic evaluation of the C-Co-W-Hf-Zr system
For cemented carbide applications.

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Keywords: DTA, HfC, ZrC

Cemented carbides consist of hard carbide particles of hexagonal WC and often cubic carbides cemented together in a binder consisting of mainly Co. A thermodynamic evaluation with the cubic carbide formers Hf and Zr in cemented carbide has been done. Both thermodynamic evaluations of lower order systems and experimental investigations have been performed. The experimental information was necessary for a satisfactory thermodynamic description due to lack of earlier experiment of this alloy system.

The assessment work with the C-Co-W-Hf-Zr system has resulted in a satisfactory description of the thermodynamic properties compared to the experimental values. This work has been done by combining new assessment of the Co-Hf and Co-Zr systems with already assessed investigations of the Hf-C and Zr-C systems. New experimental information in higher order systems has been used to improve the thermodynamic descriptions and to verify the reliability of the assessments.

The main results of the experimental work are,
- measurements of the composition of the cubic carbide in selected equilibria.
- measurements of the temperatures of the liq+fcc+WC+grafit and liq+fcc+WC+M6C equilibria in the C-Co-Hf, C-Co-Zr and C-Co-W-X (X=Hf and Zr) systems.
- measurements of the solubility of Hf and Zr in liquid cobalt.

Detailed comparisons between calculated and experimental data are presented.
Modern IF (interstitial free) steels rely on a two fold strategy to achieve good formability and non-aging properties: extensive removal of interstitial (nitrogen and carbon) during steelmaking and gettering of these elements through precipitation in the solid state. Niobium and titanium are the preferred elements for the removal of carbon and nitrogen from solid solution in the steel. In order to achieve better mechanical properties, phosphorus can be intentionally added to these steels. The possibility of precipitation of Fe-Ti-P compounds during the processing of IF steels has recently been identified. The formation of these compounds can reduce the amount of titanium available for gettering carbon and nitrogen as well as interfere with the desired effect of phosphorous additions. In this work, the thermodynamic data for the Fe-Ti-P system currently available is extended through a preliminary assessment of the thermodynamic data of the relevant Fe-Ti-P ternary compound. This database is then used to evaluate the temperature and composition conditions that might lead to ternary compound precipitation during steel processing. The eventual impact on alloy design and steel processing is highlighted.
Application of Calphad to diffusional reactions between coating and substrate

John Ågren

Materials Science and Engineering, KTH, Sweden

The combination of a multicomponent coating on a multicomponent substrate alloy is a very complex system involving not only multicomponent thermodynamics and diffusion effects, e.g. up-hill diffusion, but also difficult questions on the shape and stability of the diffusion path in a multi-component multi phase system. A satisfactory understanding serving as a basis for coating engineering can be achieved by a combined thermodynamic and diffusion kinetic approach. The long-term research within the field in our and other groups will be briefly reviewed and some scientific challenges will be discussed in more detail.
Assessment and Assessment Methods

Thursday May 9, 8.30-12.00

Session chairman: Bo Jansson
Indium-nitrogen: Small System – Big Surprise
Experimental, Thermodynamic and Phase Stability Analysis

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Results of a CVD crystal growth method intended to produce large amounts of InN needed for thermodynamic experiments are presented. Polycrystalline films of InN were grown by reaction of InCl₃ and NH₃ in a hot-wall silica reactor under nearly atmospheric pressure. Samples were analyzed using X-ray diffraction and chemical analysis. The decomposition of InN was studied both in thin film and powder form. InN films have been investigated by isothermal heating under nitrogen and subsequent microscopic inspection. The removal of the nucleation barrier of forming the first liquid phase is emphasized. InN powder decomposition experiments involved two different customized thermogravimetric methods, dynamic oscillation TGA, and isothermal stepping TGA for a higher resolution of the decomposition start. That decomposition start was found consistently at (773 ± 5) K under 1 bar of nitrogen.

Nevertheless, it is suggested that InN may be metastable even below room temperature based on a CALPHAD type thermodynamic analysis of all available phase equilibrium and thermodynamic data. This included the determination of the absolute entropy of InN, 31.6 ± 3 J/mol·K, based on a Debye- and Einstein-analysis of the experimental data on the heat capacity. All calculations of pressure are corrected for the fugacity of nitrogen which becomes crucial above 1000 bar. The contradictory literature data in the In-N system are discussed based on three different internally consistent thermodynamic analyses of the system which highlight the consequences resulting from different choices made on the decomposition temperature of InN. Widely reproduced data in the literature are shown to produce thermodynamically impossible negative absolute entropy of InN. Complete P-T-x phase diagrams are given which strongly suggest that solid InN is metastable under ambient conditions.

To find out that InN crystals could be reproducibly superheated more than 500 K before they actually decompose comes as a surprise – in a small system composed of only four “simple” phases: gas, liquid, stoichiometric InN, and the unimportant solid In.

This study was supported by the German Research Council (DFG) under Grant No. Schm 588/23.
A preliminary thermodynamic assessment of BaO-SrO-TiO₂-ZrO₂ system

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Keywords: BaO-SrO-TiO₂-ZrO₂, CALPHAD method, default structure, thermodynamic assessment

The TiO₂-based systems have attracted more and more attention owing to the surprisingly large number of compounds with peculiar dielectric properties. Among them, BaTiO₃, Ba₂Ti₉O₂₀ and BaTi₄O₉ are of most importance, but the sintered temperature of BaTiO₃ is rather high, the temperature coefficient of BaTi₄O₉ is not ideal, and it is rather difficult to form single Ba₂Ti₉O₂₀. Similarly, the investigations on ZrO₂-containing systems have progressed rapidly due to many peculiar physical properties. For example, the magnesia, calcia, and ceria stabilized zirconia have a high degree of corrosion resistance, cracking or disintegration resistance if exposed to thermal changes. Moreover, the partial replacements of Ti by Zr or Ba by Sr are in favour of refining the grain sizes and broadening the Curie transition of BaTiO₃, adjusting the temperature coefficient of BaTi₄O₉ and promoting the formation of Ba₂Ti₉O₂₀. Knowledge of the phase diagram and thermodynamic properties is of fundamental importance for understanding materials properties. By means of CALPHAD method, this work assesses all reasonable thermodynamic data first to obtain the Gibbs free energies of compounds included in BaO-SrO-TiO₂-ZrO₂. The fit to the experimental data is satisfactory. The lattice stabilities for BaO, SrO and TiO₂ in ZrO₂-based structures are also obtained by combined with thermodynamic and phase diagram information. To assure certain solubility, defect structures are established, BaTiO₃, ZrTiO₄ and SrZrO₃ are described using compound energy model with the formula (Ba²⁺,Va)₁(Ti⁴⁺)₁(O₂⁻,Va)₃, (Zr⁴⁺,Ti⁴⁺)₁(O₂⁻)₂ and (Sr²⁺,Va)₁(Zr⁴⁺)₁(O₂⁻,Va)₃, respectively. Binary phase diagrams calculated in this work can account for most of experimental data by a set of self-consistent thermodynamic functions for ZrO₂-BaO, ZrO₂-SrO, SrO-TiO₂ and ZrO₂-TiO₂. On the basis of thermodynamic description of binary systems, the corresponding pseudo-ternary phase diagrams, including several key isothermal and vertical sections as well as the reaction scheme for BaO-TiO₂-ZrO₂, SrO-TiO₂-ZrO₂, BaO-SrO-TiO₂ and BaO-SrO-ZrO₂ are calculated and predicted, which make out the material properties understanding.
The Al2O3-SiO2 System has been reassessed using CALPHAD technique. To describe mullite solid solution phase property, the compound energy model, which extends from sillimanite to a hypothetical state of alumia was applied. It is possible to represent the information on the range of stability of mullite, including some showing that mullite extends to higher SiO2 contents than represented by the composition of 3:2 mullite. For liquid phase, the associate model with the formula as (AlO1.5, SiO2) was used. It is compatible with the ionic two-sublattice model as (Al+3)(O-2, SiO4-4, AlO1.5, SiO2) and therefore readily to extend to ternary or higher order systems. The calculation was done by software package Thermo-Calc. The comparisons between calculated properties and experimental data are given.
Thermodynamic Modeling of the Zr-O System

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Keywords: Assessement, Modeling, Thermo-Calc, Zr-O

In this study, the complete zirconium-oxygen system has been critically assessed at 1 atm. from 300 C to liquidus temperatures. Thermochemical measurements and phase diagram data were used to model the Gibbs free energies of seven phases. Additionally, the ordered interstitial HCP-based solutions were included and considered as simple line compounds. By using the PARROT module in Thermo-Calc, it was possible to optimise the parameters of the models used to describe the Gibbs free energies of the HCP, BCC, Liquid, gamma ZrO_{2-x}, beta ZrO_{2-x} and alpha ZrO_{2-x} phases. The Gas phase was considered to behave ideally. Although phase diagrams including the stoichiometric zirconia phases have been assessed, this is the first time, to the best of our knowledge that a complete assessment of this system is published.
Remarks on crystallochemical aspects in thermodynamic modeling

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In a paper published by a group of scientists coordinated by I. Ansara [1], general problems and difficulties arising in thermodynamic modeling of intermetallic phases were discussed. From a crystallochemical point of view two groups of questions are worthwhile to be mentioned:

a) The subdivision of the atoms pertaining, in a certain space group, to a set of equipoints (or Wyckoff position, WP) into two or more groups of equipoints of lower multiplicity, when some ordering takes place, i.e. on passing from a structure to its derivative ordered variants (cF4-Cu \( \rightarrow \) cP4-AuC\(\text{u}_3\), for inst.). It may be remarked that a coherent crystallographic approach is very useful in modeling thermodynamic properties of the involved phases.

b) The crystallographically sound thermodynamic description of a complex phase, having a structure corresponding to several sets of Wyckoff positions.

In the mentioned paper [1], various important structure types (\(\sigma\), \(\mu\), \(\chi\), Laves) have been analysed and suggestions given for a convenient thermodynamic modeling, coherent with a correct crystallographic description. It is well known, on the other hand, that detailed decriptions of the different structure types are available. Daams et al. [2], for instance, systematically presented a critically revised description of the structure types giving for each prototype not only the Pearson symbol, space group, lattice parameters and occupied WP, but also a description of the coordination (coordination polyhedra and next neighbour histograms). These data have been summarized also in a few papers [3-6] in which the role of the coordination, described in terms of “atomic environment types” (AET) has been discussed and used for a systematic presentation of the different prototypes, their possible classification and grouping in inter-related families. These aspects are certainly relevant while discussing phase (and alloy system) properties and possibly while looking for general criteria for their thermodynamic “sub-lattice” modeling. The modeling of typical complex phases is here considered on this basis and a number of examples are presented of “sub-lattice” descriptions. The \(\sigma\) phase is briefly presented as an example.

In the \(\sigma\) phase (tP30-CrFe) Cr and Fe atoms are distributed in the P4\(_2\)/mmn space group according to 5 WP: 2a, 4f, 8i’, 8i’’ and 8j. However only 3 different AET are present, respectively coded as 12\(^{5.0}\) (CN12, pertaining to the atoms in 2a and 8i’’); 12\(^{5.0\cdot3.6.0}\) (CN15, pertaining to the atoms in 4f) and 12\(^{5.0\cdot2.6.0}\) (CN14, pertaining to the atoms in 8i’ and 8j). A crystallographically sound description could therefore correspond to the identification of three sublattices with site formula 10:4:16 (in full agreement with the suggestions given in [1]).

References

Thermodynamic assessment of the Ga-O binary system

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Keywords: assessment, gallium, oxygen, thermodynamics

Thermodynamic and phase diagram experimental data relevant to the Ga-O binary system have been critically assessed. A self-consistent set of Gibbs energy functions describing the phases in this system is presented for the first time. The adjustable parameters of the models are obtained by least-squares fit to the experimental data. The liquid phase is described by Hillerts partially ionic liquid model. The gallium oxides are modelled as stoichiometric phases. The gas phase is treated as an ideal solution of the species Ga, Ga₂, Ga₂O, GaO, O, O₂, and O₃. The calculated phase diagram and thermodynamic properties are compared with the experimental measurements.
Until now, the phase diagram of the Co-O system has not been well established. The purpose of the present work is to perform an assessment on both the solid and the liquid phases in the Co-O system. A tentative calculated phase diagram is also presented. The thermodynamic properties of CoO, Co3O4 and the liquid phase were assessed and an optimized set of parameters of Gibbs energy functions is proposed. The two stable solid oxides, CoO and Co3O4, were both treated as stoichiometric compounds. The paramagnetic-antiferromagnetic transition of CoO is well represented by a magnetic ordering model. The Co3O4 spinel phase was described as a normal spinel at room temperature and with cation redistribution at high temperatures. A high temperature anomaly of Co3O4 was interpreted as a normal-inverse spinel transition. An ionic two-sublattice model was used to model the liquid phase. A calculated phase diagram is presented and values for the thermodynamic properties are compared with experimental data.

The present optimization agrees very well with most experimental data and offers a consistent description of the binary Co-O system. However, there are a few weak points in the present optimization. There is a large uncertainty among the experimental and the presently calculated Gibbs energies of the reaction 3CoO(s)+0.5O2(gas,1bar)=Co3O4(s). Due to the lack of experimental data, the properties of the liquid phase are uncertain. There is a very large uncertainty on the oxygen solubility in solid Co. Further experimental investigations are necessary to verify these points.
Assessment and Assessment Methods

Thursday May 9, 15.00 – 18.00

Session chairman: Tim Andersson
A New Strategy for Optimizing Systems with Multiple Non-Stoichiometric Compounds: Application to the Cu-In-Se System.

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Keywords: assessment, sublattice, ternary

A new strategy is presented to treat difficulties encountered in the optimization of complex systems that include multiple non-stoichiometric compounds described by the sub-lattice model. Successful optimization of such systems often relies on the identification of starting values of the model parameters, including the reference Gibbs energies and the interaction coefficients of the end-members defined in the sub-lattice model. Complicating the process to specify initial parameter values is that some cannot be directly derived from the experimental data. In addition, the procedures to estimate values are limited. As a result the optimization often fails or results in an arbitrary solution. In the proposed method, the structure of the sub-lattice is initially simplified by requiring a one-to-one correspondence relationship between the site fraction (y) and the phase composition (x) based on the assumption of minimal defects for each non-stoichiometric compound. A linear relationship between the chemical potential and the model parameters is then derived. The coefficient of each parameter in this linear relationship represents the contribution of this parameter to the chemical potential.

Combining the available information, a set of reasonable starting values of the parameters can be evaluated from the regression results using the simplified linear relationships where the chemical potentials are estimated from the neighboring phases. This optimization strategy is tested in the assessment of the Cu-In-Se system. The a-CuInSe2 phase in this system is the absorber material in 20% efficient thin-film solar cells. Thermodynamic optimization of this system using conventional approaches repeatedly failed. The optimisation process, however, was successful when the starting values were obtained by the proposed method. For example, each of the 18 calculated invariant three-phase equilibria in the 500°C isothermal section was in agreement with recent experimental results [1], although the calculated homogeneity regions of some phases are somewhat narrower than the experimental values.

References
Glass-Forming Alloys:
Search for Deep Multicomponent Eutectics

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Keywords: CALPHAD, CVM, Eutectics, Multicomponent

It is shown that several familiar glass-forming criteria can be combined in a single one: that of promoting the existence of deep eutectics. Examples of applications of this rule will be given for various model multicomponent systems treated by both CVM and CALPHAD methods.
Phase Equilibria Calculations in the Ni-Al-Cr-Co and Ni-Al-Cr-W Systems with Respect to New Experimental Information on the gamma and gamma’ Phase Region

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Keywords: gamma and gamma’, Ni-based superalloys, Phase diagram, Thermodynamics

Ni-based alloys play a significant role in the group of new prospective materials mainly in the field of high temperature engineering applications. The most important microstructural feature of these so-called superalloys is characterised by the coexistence of gamma-gamma’ and positional geometry of ordered intermetallic phase gamma’ (Ni3Al type) in disordered terminal Ni-rich solid solution gamma. Therefore, the good knowledge of the phase diagrams in such systems is of great importance. In recent three years, the attention has been paid to the study of quaternary systems Ni-Al-Cr-Co and Ni-Al-Cr-W involving iso-concentration sections at 70 and/or 75 at. % Ni for the temperature 900 and 1000 oC and new experimental phase data have been obtained [1,2,3]. The coexistence of gamma and gamma phases, their compositions and phase ratios were compared with theoretical data obtained by means of the software Thermo-Calc using model description according to Ansara, e.g. [4]. The thermodynamic database constructed on the base of available information for lower order systems taking into the account the logical concept of the model description, as described e.g. in [1], and updated later by interaction parameters for tungsten exploiting the commercial database designed for Ni-based superalloys [5], was successfully applied. The results confirmed the applicability of the created database for the phase equilibria calculations in studied systems comparing them with our experiments and those published previously for the system with tungsten [6]. Grateful acknowledgement goes to the Grant Agency of the Czech Republic for the financial support under project No. 106/02/0876.

References:
A reassessment of the Al-Pt binary system

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The Al-Pt system is important as it is similar to the Al-Ni system and also shows a $\gamma'/\gamma$ (Pt)/Pt₃Al phase relationship. This phase relationship in the Al-Pt system has been identified as the basis of potential high temperature alloys, replacing the Ni-based superalloys in applications where the Ni-based superalloys have reached their upper temperature limits [01Hil1].

A current study investigating the Al-Cr-Pt-Ru alloy system has lead to this reassessment of the Al-Pt binary system as in the CALPHAD assessment by Wu and Jin [00Wu], modelling of the L1₂ Pt₃Al phase did not accommodate the ordering of the L1₂ phase, as reported by Mishma et al. [86Mis] and Bronger et al. [97Bro]. A low temperature martensitic transformation for the Pt₃Al has also been reported [86Mis] and experimental observations of ternary Al-Pt-X alloys indicated that the ternary additions either stabilise the high temperature or the low temperature form of Pt₃Al (L₁₂ and DO₂¹ respectively) [01Hil2]. The previous assessment [00Wu] also did not include the $\beta$ phase since there are some discrepancies about its existence [90Mas]. Experimental analysis of some ternary alloys indicated a phase which is considered to possibly be the $\beta$ phase.

The current reassessment allows for the introduction of the effects of ordering of the Pt₃Al phase and the Pt₂Al and $\beta$ phases have also been included. The phase diagram is in good agreement with experimental observations.

The assistance of the PDI and DACST is gratefully acknowledged.

References
Thermodynamic Evaluation of the ternary system Ag-Au-Cu
- including a short range order description

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The disordered and ordered phases of FCC-type in Ag-Au-Cu are described thermodynamically with a Gibbs energy expression for 4 sublattices. Using the compound energy formalism and an expression for the the nearest neighbour bond energies it is possible to obtain a thermodynamic description including both short and long range order. The short range order contribution to the Gibbs energy is connected to the bond energies through some reciprocal parameters allowing mixing on two sublattices simultaneously. It is shown that the use of nearest neighbour bond energies in connection with the compound energy formalism will reduce the number of optimised parameters and allow for better extrapolations.

* former employer: the Royal Institute of Technology, dept. of Materials Science and Engineering. The work has been done at the Royal Institute of Technology.
A new version of the Fe-Co phase diagram

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X-ray diffraction, transmission electron microscopy, photoelectron spectroscopy and magnetic studies of the Fe_{65}Co_{35}, Fe_{50}Co_{50} and Fe_{35}Co_{65} alloys were been performed after different isothermal heat treatments from 500°C up to 1200°C at 50-100°C. It has been shown that the very thin continuous layer of fcc Co is formed at the surface of the specimen during heat treatment at 600-1000°C. If a surface layer 40 mµ thick is removed the mixture of fcc Co and bcc Fe strips is observed. After removing a 70 mµ thick layer the bcc Fe(Co) solid solution is identified. The conclusion is made that at 1000°C and below the tendency toward separation is responsible for the separation microstructure at the surface and in the bulk (globular particles occupy about 5-10% of the bulk). B2 type ordering is absent at all. So-called A2→B2 transition is really a result of increase of the 3d-electrons localization on the Fe atoms in the Fe_{50}Co_{50} alloy. So-called “550°C anomaly” is the result of a phase transformation occurred by a martensite mechanism and resulted in a small increase of the lattice parameter. On the basis of these data a new version of the Fe-Co phase diagram is submitted. The phase diagram has not the B2 ordering region but has two lines mining the changes in the electron structure (1) and in the lattice parameter (2). The conclusion is made that the magnetic properties of Fe-Co alloys only slightly depend on the temperature of the heat treatment because all the region of the diagram below 1000°C is the one of existence of the solid solution and separation microstructures.
Assessment and Assessment Methods

Friday May 10, 08.30-12.00

Session chairman: Alan Dinsdale
The assessment of thermodynamic parameters of the MgO-Al2O3-SiO2 system.

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Max-Planck-Institut fuer Metallforschung, Stuttgart, Germany

The thermodynamic parameters for the system MgO-Al2O3-SiO2 were not optimized before, in spite of phase diagram was experimentally studied in several works [60Mua, 76Sma]. Partially ionic liquid model was successfully applied to many oxide systems. According to [94Hal] the Al2O3 should be introduced in form of neutral species AlO3/2 in anion sublattice. In this study data for binary systems are taken from previous assessment: MgO-Al2O3 [92Hal], MgO-SiO2 [95Hua], Al2O3-SiO2 [95Dum].

Thermodynamic data for ternary compounds cordierite and sapphirine are assessed in this study using experimental data on subsolidus phase relations [76Sma]. The attempt to use partially ionic liquid model (Mg2+)p(O2-,SiO44-,AlO3/2,SiO2)q (model 1) to describe liquidus surface shows several inconsistencies. According to experimental data of [27Gre] miscibility gap in ternary system exists only at concentrations of Al2O3 less than ~5 weight %. According to our calculations a miscibility gap is very wide and continues to the direction of the Al2O3-SiO2 binary until it intersects SiO2(Cr)+Mullite+Liquid univariant line. The shape of Cordierite+SiO2(Tr)+Liquid and SiO2(Tr)+SiO2(Cr)+Liquid univariant curves is inconsistent with experimental data [60Mua]. Experimental data indicated that the SiO2 content in liquid increases with increasing of Al2O3 content, but the calculations shows opposite tendency. Changing of ternary mixing parameters allows us to reduce the size of miscibility gap, but then the other parts of liquidus surface become inconsistent with experimental data [60Mua]. The modifications of the ionic liquid model is considered in this work. An idea of Degterov [99Deg] that Al-O-Si and Si-O-Si second-nearest-neighbor pairs are predominant is interpreted here by adding of a mixed anion AlSiO4-1 to the anion sublattice (Mg2+)p(AlSiO4-1, O2-, SiO4-4, AlO3/2, SiO2)q assuming interaction between Al and Si in SiO4 tetrahedra. This description (model 2) reproduces liquidus surface and above mentioned univariant reactions better than calculations based on model 1. The miscibility gap is smaller than for the model 1, but it is still wider than obtained by [27Gre]. The liquidus surface, isoplethes and isothermal sections of phase diagram calculated for both models are presented.

References
Tentative description of the Cu-Cu$_2$O subsystem by the associated model

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There are several experimental data on the equilibrium properties of the rich Cu part (Cu-Cu$_2$O) of the Cu-O system due to its important role in many materials and processes. Consequently, the thermodynamic properties of the system have been modeled and the phase diagram has been critically assessed either with the associated model [1] or the sublattice model [2].

Our interest is to study the thermodynamic properties of the rich part of the Cu-O-Pb-H system. Therefore, we are interested in a simplified description of the Cu-Cu$_2$O subsystem. We already modeled liquids of this subsystem with a totally associated model where the associates are Cu and Cu$_{1/2}$O [3]. That approach, with only one interaction parameter between the two associates, gives a good qualitative description of the phase diagram but a poor description of the oxygen activities.

Our purpose was to apply the strongly associated regular (SAR) model [4] as a first step to improve the description of the liquid phase with the partially associated subregular model. We present here the methodology used, the results obtained and the tentative thermodynamic description proposed of the Cu-Cu$_2$O system.

The main features are: a partially associated liquid with Cu$_2$, Cu$_2$O and O species with interaction only between the Cu$_2$ and Cu$_2$O species; a stoichiometric Cu$_2$O compound; and an ideal Cu solid solution.

References
The thermodynamic description of the liquid phase of the Cu-O system by Hallstedt et al. (J. Phase Equilib., 15[5], 483(1994)) shows an (unwanted) instability in the form of a miscibility gap at high temperature. This is a very narrow miscibility gap close to $x_O=1/3$ with a (minimum) critical point at about 1900K and $x_O=0.32$. There is also a normal miscibility gap in this system. The liquid was modelled using a two-sublattice ionic liquid with the formula $(Cu^{+1},Cu^{+2})p(O_2,Vaq)q$. The major cause of the instability was found to be the parameter. Below $x_O=1/3$ there should be essentially no $Cu^{+2}$ present, so this parameter was given a large positive value relative to, which describes normal liquid Cu. It was not possible to get rid of the instability by simply changing this value. However, by using the reciprocal reaction:

$$3Cu(I)+Cu(II)2O_2=Cu(I)+2Cu(I)2O$$

and setting $DG=0$ the instability could be removed. The liquid phase was thus reoptimised and a slightly better fit to experimental data could be obtained compared to the published version. This approach has also been used in recent assessments of the CoO and MnO systems. The liquid in these systems seems less prone to instabilities than in the CuO system, though. The CuO liquidus at oxygen pressures larger than 1bar was recently measured by Kosenko and Emelchenko (J. Phase Equilib., 22[1], 12(2001)) essentially confirming the old measurements by Roberts and Smyth (J. Am. Chem. Soc., 43, 1061(1921)). We could improve the fit to these data somewhat, but it is still not perfect, possibly because of other conflicting data in the oxygen rich region of the liquid. The instability in the liquid also affects extrapolations to higher order systems such as the AgCuO system. In this work we will compare the CuO system before and after reoptimisation and we will show the effect on the AgCuO system.
Assessment of CaMgSi$_2$O$_6$ - NaAlSi$_2$O$_6$ - CaFeSi$_2$O$_6$ pyroxenes: CVM modelling and a polynomial fit to the CVM results

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Pyroxenes of composition within the diopside – jadeite – hedenbergite ternary, CaMgSi$_2$O$_6$ – NaAlSi$_2$O$_6$ – CaMgSi$_2$O$_6$, typically occur in natural metamorphic rocks that have experienced high-pressures and moderately high temperatures. Reconstruction of exact values of the crystallisation pressures and temperatures requires knowledge of the activity-composition relationship in this ternary solid solution. This relationship is complicated due to the effects of long-range and short-range ordering within M2 (Ca,Na) and M1 (Mg,Fe,Al) sublattices coupled through cross-site interactions. The ordering effects in the binaries have been successfully modelled using the cluster variation method (CVM). However, the CVM formalism becomes cumbersome when it is applied to ternary solid solutions. To overcome this difficulty, the excess free energies of the binaries, resulting from the CVM-assessment, have been refitted using the polynomial functions of the form

$$G_{\text{mix}}^{\text{ex}} = x_i x_j \sum_n A_n (x_i - x_j)^n$$

and

$$G_{\text{ord}}^{\text{ex}} = x_i x_j \sum_m B_m \exp\left(-C_m (x_i - x_j)^2\right).$$

The first equation is the familiar Redlich-Kister expansion, while the second one is a combination of Gaussians. The Gaussians permit to accurately fit bell-shaped depressions in the excess free energies of the binaries caused by long-range ordering. Both the Redlich-Kister polynomials and the Gaussians permit an easy extrapolation to the ternary composition using the method of Muggianu.
POSTERS
Thermocalc Zircobase calculations applied to Zircaloy’s alloys
- Influence of oxygen and hydrogen concentration on the equilibrium alpha/beta phases at high temperature


CEA, France

Keywords: phase transformation, thermodynamic calculation, zirconium alloys

During the oxidation of zirconium base alloys at high temperature, drastic evolution of the microstructure arises because of the partition of the main alloying elements due to the oxygen diffusion under the (ZrO2) oxide layer formed. The chemical composition and the fraction of the equilibrium alpha and beta phases are strongly affected by the local oxygen content and a good knowledge of this quite complex thermodynamic equilibrium is necessary to understand the microstructural evolution during the oxidation process. Moreover, in some cases, pick-up of hydrogen has to be taken into account and then, the additional hydrogen concentration influence has to be considered.

So, the aim of this poster presentation is to illustrate the comparison between some experimental data and thermodynamic calculations using “Thermocalc” software associated to the “Zircobase” database recently developed on multi-component Zr base systems [1].

The alloys considered are of the “Zircaloy’s” type (i.e.: Zr-Sn-Fe-Cr-(Ni)) with typical oxygen content ranging from ~100 ppm up to 3 % (in weight). The influence of a typical addition of ~1000 ppm of hydrogen has been also studied.

Neodymium and its oxide are encountered in various applications ranging from pigments in glasses and ceramics, constituents in certain high-Tc superconducting oxides to Nd-Fe-B permanent magnets. In special cases Nd, can be used as an agent for de-oxidation and de-sulfurisation of steels. Despite of the application of Nd in these special but important fields, little is known about the phase diagram and the thermodynamics of the Nd-O system. The phase diagram of the system which is quoted in present standard reference books is very uncertain; it is based on one of two estimated diagrams proposed by B. Love in 1961.
In the present work, the literature has been evaluated for thermodynamic data on the Nd-O system, including information on the phase diagram and data from calorimetric and electrochemical experiments. Using these data and the SGTE recommendations for pure Nd, a thermodynamic description of the binary system Nd-O is obtained. The assessment includes the liquid, the sesquioxide and its high-temperature polymorphs, the monoxide and the oxygen solubility in solid neodymium.
High temperature vaporizations in assessment of gaseous molecule thermodynamic data.

C. CHATILLON, M. HEYRMAN

C.N.R.S. - I.N.P.G., France

Keywords: Al2O3, assessment, congruent vaporization, Y2O3

In a first part, definitions of congruent and azeotropic vaporizations are given. The difference between these two ways of vaporization is underlined. Then, we show how to calculate these vaporization states by using thermodynamic softwares. In a third part, experimental aspects of the congruent vaporization are emphasized. For example, alumina in W effusion cells has a congruent vaporization (there is no change in the chemical nature of alumina) but in Mo effusion cells, the presence of gaseous species such as MoO or MoO2 will change the vaporization of alumina. In another way, when you vaporize alumina in vacuum at high temperature, you must take care of the furnace flow which is opposite to the vaporised flow. After experimental measurements, three points must be check: the partial vapour pressures ratios must be constant whatever is the temperature, the chemical nature of the sample must be unchanged and thermodynamic data issued from the experiments must permit to re-find the congruent vaporization. The notion of congruent vaporization can finally be used to test the value of thermodynamic data. For example, Y2O3 vaporizes at high temperature according to the reaction: Y2O3 -> 2YO+O. In the SGTE data, the obtained reaction was Y2O3 -> YO+YO2 so the thermodynamic data for the species YO2 are erroneous.
Ordered Ground States in Multicomponent Ni-based Alloys
Studied by Monte Carlo Simulation

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Keywords: Monte Carlo, nickel, ordering

Step-by-step improvement of Ni-based superalloys in last decades resulted in a rather complex alloying. Advanced superalloys contain typically over six alloying elements; on the other hand the present assessments of thermodynamic parameters for phase diagram calculations are usually dealing with quaternary, ternary or even binary subsystems. Another class of promising methods of prediction of phase constitution of alloys is based on the computer modelling at the atomic level. Among them, the Monte Carlo simulation (MCS) technique is particularly suitable for modelling the details of order/disorder phase transitions. This applies also to the case of Ni-based superalloys where the superior mechanical properties at high temperature can be attributed to the dispersion of coherent precipitates of an ordered phase (gamma prime, L12 type) distributed in a disordered ductile matrix (gamma, face centered cubic lattice).

The aim of this work was to study ordering processes in complex Ni-based systems with up to six alloying elements using a MCS technique. This method is well established and used in many branches of solid state physics including this particular problem [1,2]. To simulate the ordering processes in our systems the Ising Hamiltonian was used to express the configurational energy of the system. Pair interactions were introduced by means of phenomenological Lennard-Jones potentials [3]. Pair interactions up to the third coordination sphere were taken into account. The ordering process itself was realised by direct atomic pair exchanges (Kawasaki dynamics). The value of an average lattice parameter was readjusted periodically during the calculation. The crystal structure of low-energy ordered states was studied on real-space snapshots of the atomic arrangement of simulated crystal block after reaching the equilibrium.

Grateful acknowledgement goes to the Grant Agency of the Czech Republic for the financial support under project No. 202/01/0383.

References:
Thermodynamic Assessment of the Mn-O System

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Keywords: Assessment, Manganese-Oxygen

This work is part of a project to model the thermodynamic properties of the quaternary La-Sr-Me-O system (Me=Mn, Co, Fe, Ni) using the CALPHAD method. Particular emphasis will be placed on the La1-xSrxMeO3+- d perovskites, that are used as cathode material for solid oxide fuel cells (SOFC). The binary systems La-O [1], Sr-O [2] and Co-O [3] and the ternary system La-Sr-O [4] have already been optimized by us. Here we present the Mn-O system [5].

An optimization of the Mn-O system has been published by Wang and Sundman [6]. This optimization is, however, seriously flawed: the liquid phase becomes stable at low temperatures, the phase Mn2O3 never melts and the phase Mn1-xO becomes more stable then Mn2O3 at xO=0.6 between 1500K and 3000K.

We have assessed the thermodynamic properties of the phases Mn1-xO, Mn3O4, Mn2O3 and MnO2 and the liquid phase and propose an optimized set of parameters for the Gibbs energy functions. The oxides Mn3O4, Mn2O3 and MnO2 are treated as stoichiometric compounds, the phase Mn1-xO is modeled using the compound energy model, the liquid phase using the ionic two-sublattice model. All the shortcomings of Wang and Sundman’s assessment could be resolved and a good representation of most experimental data is accomplished.

In previous work, the importance of the formation of aluminum nitrides for the processing and application of steels other ferrous alloys was highlighted. Examples in industrial practice include grain size control through nitride or carbonitride precipitation, elimination of solute nitrogen and texture control in flat steel products, and formation of internal oxides and nitrides during service at high temperature. As the precipitation of these compounds is largely controlled by their solubilities the knowledge of the thermodynamic conditions of the system is important. The present availability of data bases and the use of the CALPHAD approach make it possible to improve the understanding and prediction of the occurrence of these phenomena. In this work, the possibilities and limitations of the application of calculations in the Al-Fe-N system will be presented and some applications to steel and other ferrous alloys will be discussed. As the data more readily available for industrial applications is in the form of “solubility products”, these will be will be compared with the currently available data bases and experimental data, for the more relevant temperature and composition ranges. The applicability and limitations of the expressions for solubility products will also be discussed.
Experimental Study and Modeling of Phase Equilibria in the Ni-Ga-N System.


NIST, USA

Keywords: assessment, GaN, metallization, Phase Diagram

GaN semiconductor is of interest for application in optoelectronic devices. Fabrication of reliable electrical contacts to GaN is one of the limiting factors hindering commercialization of the devices. The characteristics of metal contacts to GaN are affected by the reactions occurring at a Metal/GaN interface. Selection of a contact metal that is thermally stable and provides desirable electrical characteristics is extremely difficult due to lack of fundamental studies for the multicomponent reactions. Therefore, information on phase equilibria and diffusion in Metal-Ga-N systems is highly desirable to control the mechanism of contact formation. Since nickel is one of the promising elements in the industrial electrical contacts to GaN, the Ni-Ga-N phase diagram can serve as a roadmap for processing Ni-based electrical contacts to GaN semiconductor.

This paper describes experimental evaluation and thermodynamic modeling of phase equilibria in the Ni-Ga-N system. Ternary GaN(x)Ni(1-x) compositions along the GaN-Ni tie-line were prepared from GaN and Ni powders and annealed at 973K for 650 hrs at two different conditions: i) in open system under the flowing nitrogen at 1 atm and ii) in sealed quartz ampoules. XRD analysis has shown that the resulting phase equilibria for the samples with x>0.3 are different for the (i) vs (ii) annealing conditions. This can be explained by different effective nitrogen pressures in the open (i) vs closed (ii) systems, which in turn can cause change in stability of equilibrium tie-lines on the Ni-Ga-N phase diagram.

Experimental results were compared to the calculated ternary phase equilibria. Using published data for the Ni-Ga and Ni-N systems, and our own assessment for the Ga-N system, we have calculated isothermal (T=973 K) sections of the ternary Ni-Ga-N system at various nitrogen pressures. As expected with increasing nitrogen pressure, the GaN phase becomes more stable thus making the equilibria along the GaN-Ga(y)Ni(1-y) tie-lines more stable compared to those for the N-Ga(y)Ni(1-y) tie-lines. Important technological conclusion, deduced from the experimental and computational analyses, was that Ni and GaN do not form a stable couple and react forming nickel gallides. This fact should be taken into consideration when processing nickel metallization for the GaN devices.
Thermodynamic assessment of the ternary uranium-oxygen-zirconium system

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Keywords: assessment, phase diagram, thermodynamic, uranium-oxygen-zirconium

To predict the material behavior in severe nuclear reactor accidents, a quantitative description of the chemical interactions between the UO2 fuel and zircaloy cladding as a function of temperature and composition is needed. The phase relations and thermodynamic properties of the important ternary (U-Zr-O) system have to be determined. In the present study, a thermodynamic assessment of the ternary (U,Zr,O) system is presented. The thermodynamic parameters of the zirconium-oxygen and uranium-zirconium systems have been taken from previous assessments [1,2]. The uranium-oxygen binary has been recently modelled on the basis of a critical analysis of all available experimental data [3,4,5]. The wide composition range of the uranium dioxide is represented by using a three sublattice model, one for the cations, one for the normal site of oxygen ions and one for the interstitial oxygen ions. This model has been extended by adding zirconium to represent the (U,Zr)O2-x mixed oxide.

The UO2-ZrO2 system has been assessed by taking into account the recent measurements of UO2 activity by high temperature mass spectrometry [4,6]. Finally, some ternary interaction parameters in the liquid phase described by an ionic two sublattice model have been optimized to represent the liquidus experimental data.

Ab-Initio Calculated Energetics of Sigma-Phase in Cr-Fe and Cr-Co Systems Based on Equilibrium Volum

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The first-principles electronic structure calculations of the total energy differences of sigma phase and SER (Standard Element Reference) state in Cr-Fe and Cr-Co systems based on equilibrium volumes will be presented.

The total energy of formation of sigma-phase related to the weighted ratio of total energies of pure SER structures in binary system is calculated in two steps. The first one is the calculation of total energies of formation of all 32 possible configurations occurring in the sigma-phase related to the weighted ratio of total energy of sigma-phase of pure elements. These calculations were performed by LMTO-ASA method (Linear Muffin-Tin Orbital method in the Atomic Sphere Approximation) [1,2]. The next step is evaluating the total energy difference of sigma-phase and SER structure of pure elements. It was done using the FLAPW method incorporated in the WIEN97 code [3]. Both mentioned types of calculations were provided within the GGA (General Gradient Approximation) [4] for the exchange-correlation term.

The total energy of formation of sigma-phase of composition similar to the experimental ones related to the weighted ratio of total energy of SER of pure elements is calculated from previous two steps at the end. All calculations were performed at the equilibrium volume (corresponding to the minimum on the energy-volume curve) to overcome the uncertainty connected with the use of experimental volume of binary sigma-phases for total energy calculation of hypothetical (i.e. unstable) sigma-phase structure of pure components. These total energies of formation can be compared with experimental enthalpies of formation of sigma-phase measured by calorimetry under the assumption that energy of formation does not depend on temperature. Both, measurements and calculations, provide the positive values of enthalpy of formation with respect to the SER state of pure components whilst the negative one can be obtained provided that the total energy of sigma-phase is related to the weighted ratio of total energy of sigma-phase of pure elements.

Total energy differences calculated at equilibrium volume of sigma-phase does not differ substantially from that calculated at experimental volume [5]. Our treatment gives us better insight to the formation and stability of sigma-phase in Cr-Fe and Cr-Co system.

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Energetic and electronic properties of platinum alloys Pt$_3$Al-X.


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In the current study we report ab initio calculations on the energetic and electronic properties of the platinum group minerals carried out using density functional theory with the local density approximation. Total energy calculations have been performed and predict equilibrium lattice that is on average 1\% smaller than experiment. Heats of formation have been calculated to predict the relative stability of cubic Vs tetragonal binary and ternary phase of Pt$_3$Al-X. The study aims at developing a thermodynamic data base for platinum group minerals (PGMs) alloys for input into CALPHAD/Thermocalc.
Recommendations for notations, symbols etc.

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There are many differences between notations, symbols etc. among the various groups working in the CALPHAD field. Even though this is not a very important issue and many differences are really quite trivial, it is now proposed that such differences should be eliminated. In a few instances a general agreement may improve communication.
Thermodynamic Assessment of the Mo-Zr Binary System

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The Mo-Zr binary system has been optimised using the available phase diagram experimental data, the estimated enthalpy of formation of the Laves phase_c15 and enthalpy of mixing of the liquid phase. During the optimising procedure all the experimental data were optimised simultaneously.

The excess Gibbs energy of the stable phases liquid, bcc, hcp and laves_c15 has been obtained. The solution phases: liquid, bcc and hcp, have been treated as substitutional solutions and the intermetallic phase Laves_c15 has been modelled using the sublattice model. A set of model parameters are given.
Centre of Computational Thermodynamics

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New technology is largely depending on the availability of high performance materials for functional as well as mechanical applications. The development of these materials can now be made on the computer with the aid of computational thermodynamics. To create the best conditions for long-term \textit{fundamental research} and short-term industry-related \textit{applied research} within the field of computational thermodynamics, the Centre of Computational Thermodynamics, CCT, was created in 2001. CCT is a joint research programme between the Royal Institute of Technology (KTH) and the Swedish Institute for Metals Research (IM), financed by the Swedish Research Council for Strategic Research (SSF), Jernkontoret and Swedish industry.

The objective of the fundamental research is to develop new methods and models, and to make use of first principle calculations to be used in parallel with the classical CALPHAD technique of evaluation. There is a focus on metal-metalloid systems such as oxides, sulphides, carbides and nitrides, and the descriptions will be compatible with the existing alloy databases. Models for diffusion in complex systems, e.g. ionic, are being developed and implemented in available software. Experiments are used to produce lacking information and to validate data and databases. Material production processes are modelled using general thermodynamic information. The objective of the applied research is to develop and update thermodynamic databases. The applied research takes advantage of the findings within the fundamental research. In this way, the methods and models are directly tested in real industrial materials and applications.

For more information: \url{www.met.kth.se/projects/cct/cct.html}
Phase equilibria of the Al-Cu-Fe system
in the vicinity of quasicrystal phase

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Key words: Phase equilibria, quasicrystal, Al-Cu-Fe.

Phase equilibria of the ternary Al-Cu-Fe alloy system were investigated for compositions in the vicinity of the icosahedral quasicrystal phase, which are described precisely as isopleths and isothermal sections obtained by the techniques of Differential Thermal Analysis (DTA), magnetothermal analysis (MTA), Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS) and optical microscopy. The formation of the icosahedral phase by a ternary peritectic reaction was reconfirmed. The reaction temperature was determined to be 882 °C. The shrinkage of the phase field with decreasing temperature gives indication of the compositional influence on the stability of icosahedral phase. It is re-confirmed that the Phi-Al10Cu10Fe1 phase exists in Al-Cu-Fe system; it forms from beta phase through a solid-state polymorphous reaction at 650 °C, and it is stable below the formation temperature. On the other hand, an ordered phase with B2 structure is found in as-cast and moderately cooled alloys, this metastability is characterized by a suppressed formation of the phi-phase during cooling.
Phase equilibria in low activation Ta-containing martensitic steels

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7-12 Cr martensitic steels have been extensively studied as structural materials for different applications in thermal power plants, pipe lines, etc., due to their high strength and ductility at normal service temperatures. In the past decade, CrWVTa martensitic steels were developed for specific applications to internal components of fusion reactors, owing to an attractive combination of properties such as good stability and lower induced activity under neutron irradiation \cite{1, 2}.

The first heat of a low activation martensitic steel manufactured at the industrial scale in Europe corresponds to the alloy Eurofer97 (9CrWVTa). Remarkable variations in the austenitic grain size distribution were previously observed in varying the heating rate to reach the $\gamma$-phase field for $T_\gamma = 1050$ °C and fixed holding time, meaning that “abnormally” grown grains developed in a fine grained austenitic matrix. “Dynamic” pinning effects due to the presence of Ta-rich particles (carbides, nitrides or carbonitrides) are probably responsible for the instability of the $\gamma$ matrix with respect to grain growth. In the framework of a broader study, phase equilibria were investigated for the Eurofer97 alloy. The SGTE steel database was updated to take into account the following thermodynamic optimizations for Ta-containing systems: Fe-Ta \cite{3}, C-Ta \cite{4}, N-Ta and C-N-Ta \cite{5}, Cr-Ta \cite{6}, Cr-Ni-Ta \cite{7} and Si-Ta \cite{8}. Results on equilibrium phases, transition temperatures and solubility of Ta carbonitrides were obtained and compared with experimental data (see Fig 1).

\begin{itemize}
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  \item \cite{6} N. Dupin, I. Ansara, J. Phase Eq. 14 (1993) 451.
  \item \cite{7} N. Dupin, I. Ansara, Z. Metallkd. 87 (1996) 555.
  \item \cite{8} C. Vahlas, P. Y. Chevalier, E. Blanquet, Calphad 13 (1989) 273.
\end{itemize}

Fig. 1 : Experimental data on solubility in austenite of:

\begin{itemize}
  \item \textbullet{} Stoichiometric TaC from Tamura et al., J. Nucl. Mater., 258-263 (1998) 1158
  \item \texttriangle{} TaC\textsubscript{0.87} from Narita, Trans. Iron Steel Inst. Japan 15 (1975) 147
  \item \textsquare{} TaN\textsubscript{0.85} from Narita, Trans. Iron Steel Inst. Japan 15 (1975) 147
\end{itemize}

compared to Thermocalc predictions for the (Ta, V)(C, N) carbonitride at $T = 1200$°C
Fe-rich portion of the Fe-Cr phase diagram.

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Transmission electron microscopy and the corresponding selected-area electron diffraction patterns of Fe-(10;20;30;40;47) wt. pct. Cr alloys heat treated isothermally from 500°C up to 1500°C at 100°C have been employed to construct the equilibrium Fe-rich portion of the Fe-Cr phase diagram. The high-temperature separation of Fe-Cr alloys occurs in a rather wide range of temperatures and compositions and reveals itself in different morphologies depending on temperature and composition: a tweed microstructure for the Fe-(20,30)%Cr at 1100-1300°C; $\alpha_1 + \alpha_2$ mixture, particles of the intermediate J-phase forming as a result of separation and particles of pure Cr for the Fe-(40,47)%Cr at 1100-1450°C. The structures of high-temperature separation do not change their morphology during subsequent prolonged heat treatment in the region of low-temperature separation. This implies that the difference in morphology between the high- and low-temperature separation arises as a result of kinetic causes. The electron domains are a visual confirmation of the second-order ordering-separation phase transition happening upon the change of the tendency from separation to ordering, and vice versa. The $\sigma$-phase region in the diagram is considered as a region containing two phases, namely, the $\sigma$-phase surface layer and the solid solution bulk. On the basis of the electron microscopy data obtained in this work, the Fe-rich portion of the Fe-Cr phase diagram has been constructed, which turns out to be substantially different from the generally accepted one. These differences include: two regions of the high- and low-temperature phase separation; two lines of the second-order ordering-separation phase transition; the region of coexistence of the surface $\sigma$-phase layer and the bulk $\alpha$ solid solution.

1,2 – second order phase transitions
"ordering-separation"
Comparison between experimental and calculated solidification paths for Fe-Cr-C alloys

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Keywords: Fe-Cr-C steels, solidification paths, experimental and calculated approaches, Dictra software.

In the as-cast state of rolling steels such as 100Cr6 alloy, some carbides may be observed as a result of microsegregation behavior during solidification. The nature and amount of these carbides depend on the redistribution between the liquid and solid phases of the two solute elements Cr and C which diffuse at very different rates. There are several approaches to predict microsegregation in a multicomponent alloy. The simplest method of equilibrium solidification assumes a complete diffusion inducing that liquid and solid phases are homogeneous. The Scheil-Gulliver analysis presumes no diffusion in the solid phases and infinite diffusion in the liquid. This solution has been improved by Brody and Flemings and later slightly modified by Clyne and Kurz to allow a more realistic treatment of diffusion, taking into account the diffusion in the solid with some solute redistribution. A more general numerical method for diffusion-controlled transformations, implemented in the Dictra software, assumes that equilibrium is only maintained at the liquid/solid interface and allows diffusion to be treated in the solid and in the liquid phases. In this program, thermodynamic data used to calculate the solid/liquid equilibria are combined with kinetic data. In this contribution, phase diagram and solidification path calculations are used to predict phase distributions for Fe-Cr-C alloys by the construction of the interfacial liquid path in the composition plane. Depending on the solidification model being used, either the phase boundary between gamma and M3C or that between gamma and M7C3 is reached, providing quite different microstructures. The results of the calculations have been compared to experimental measurements. High purity alloys have been elaborated and directionally solidified then quenched. SEM, TEM and microprobe experiments have been then carried out on the sample. The relations between experimental and calculated results are discussed and limitations of the different approaches are pointed out. In this case of practical interest, numerical simulation with the Dictra software is a very helpful tool to understand the solidification behavior of Fe-Cr-C steels and to predict the microstructure of this kind of alloys in the as-cast state.
Calculation of thermodynamic quantities
using artificial neural networks

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To predict the behavior of a set of functions for different combinations of dependent variables, a general approach based on artificial neural networks has been developed. This approach can be used for efficient calculation of thermodynamics quantities, and thus achieves high computational speed in simulations where evaluation of thermodynamic quantities are necessary. Examples how this method can be used in process simulations and simulations of phase transformations will be given.
Using the gas constant as an adjustable parameter

Dmitri V. Malakhov

At first glance, the title of this contribution seems absurd: the molar gas constant, \( R \), is a physical constant whose numerical value, \( 8.314472(15) \) J/(K mol) \( \cdot \), is well known. When necessary, \( R \) is directly used in thermodynamic calculations. Certainly, it is not intended to alter the gas constant! Quite the reverse, it is intended to make use of its firmly established value for checking whether a thermodynamic model is consistent or not. To clarify the matter, let us suppose that a thermodynamic model of a phase is being constructed using the CALPHAD method. Firstly, terms representing various contributions are distinguished: \( G(x, T, C) = G^{\text{ref}}(x, T) + G^{\text{id}}(x, T) + G^{\text{ex}}(x, T, C) + \cdots \). Then, adjustable coefficients \( C \) are evaluated by solving a corresponding least-squares problem [1]. A satisfactory accuracy of the solution itself does not guarantee that the function \( G^{\text{ex}}(x, T, C) \) chosen is physically reasonable. What if in addition to \( C \), the gas constant (forever engraved in the combinatorial term \( G^{\text{id}} \)) is also considered as an adjustable parameter evaluated in the course of assessment? A “significant difference” between the estimation of \( R \) and \( R \) itself gives would warn of a possible problem with the excess term.

In this contribution, this suggestion is explored in detail and exemplified on three scenarios.
1. Concentration dependencies of the chemical potentials and the enthalpy of mixing of a binary solution have been measured at several temperatures. Although \( \Delta_{\text{mix}} H(x) \) are pronouncedly asymmetric, it is nevertheless decided in favor of the Redlich-Kister formalism with a large number of coefficients for describing the solution properties. Is the usage of the polynomial model justified?
2. Heat capacity of a crystal has been measured at moderately low temperatures. One attempts to fit the experimental data using the function \( C_p = 3R(\theta_E / T)^3 \exp(\theta_E / T)/\left(\exp(\theta_E / T) - 1\right)^2 + aT + bT^2 \) suggested in [2] for this purpose. Are \( a \) and \( b \) physically meaningful as they are claimed to be?
3. A temperature dependence of equilibrium vapor pressure over a pure liquid \( A \) has been measured. In addition to \( \Delta_{\text{evap}} H_{\text{ref}} \) and \( \Delta_{\text{evap}} S_{\text{ref}} \), usually derived from such a tensimetric experiment, one also tries to estimate the difference between heat capacities of \( A(\text{gas}) \) and \( A(\text{liquid}) \). Is there a clue as to how many terms can be used in \( \Delta_{\text{evap}} C_p(T) \) for the given experimental data set?

The heuristic method proposed can be used as a simple and quick “negative” test for detecting possible inconsistencies of a thermodynamic model in hand including the cases of data “overfitting.”

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Influence of water activity on stability of cement phases in the system CaO - SiO2 - H2O - Al2O3 - SO3: a phase diagram study in space (H2O - CO2)

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Keywords: activity of water, cement phases, chemical potential diagram, stability

In relation with an experimental study of the weathering of concrete by meteoric waters, a thermodynamic study of cement phases has been undertaken in the system CaO - SiO2 - H2O - Al2O3 - SO3. Following phases have been taken into account: portlandite, amorphous alumina, calcite, monosulfoaluminate, ettringite, gypsum, monocarboaluminate, hydrogarnet, amorphous silica and several types of CSH phases. Experimental data indicate that the system is open to CaO, CO2 and SO3: these elements are exchanged between the cement matrix and the external aqueous fluid medium. By contrast, such element such as SiO2 and Al2O3 are immobile or "inert". Other hypotheses may be tested. Phase diagrams drawn with pairs of variables taken in the set \( \mu \text{CaO}, \mu \text{CO2} \) and \( \mu \text{SO3} \) allow to predict the mineralogical zonings that may be observed when submitting the cement matrix to the action of the aqueous fluid. The conspicuous features observed from core to rim of matrix are: disappearance of portlandite and its breakdown to ettringite and hydrogarnet, decrease of the Ca content of the CSH phases, appearance of amorphous silica and of calcite. Specific attention was given to the role of water activity upon the stability of phases; this can be discussed with \( \mu \text{H2O} \) as an axis of phase diagram. The metastability of monosulfoaluminate has been observed by many authors and several explanations have been given. We propose that water activity must be taken into account: chemical potential of water lower than water Gibbs free energy may prevail inside the cement matrix due to high ionic content of water. The stability limit of monosulfoaluminate with respect to ettringite is just below the water saturation of water. Phase diagrams have been computed with the help of "Zen+k" software presented in recent Calphad meetings which is appropriate to discuss stability / metastability properties of phase assemblages.
Application of Statistical Moment Method to Phase Transformation of HCP (Ti, Zr, Hf) Metals

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Keywords: structural phase transformation hcp metal Ti Zr and Hf, thermal lattice vibration, statistical moment method

The structural phase transformation of hcp metals Ti, Zr and Hf are studied using the moments method in the statistical physics. So far, the effects of thermal lattice vibration on the phase stability have been treated within the framework of harmonic or quasi-harmonic approximations. However, it is known that such harmonic theories are insufficient in many respects, e.g., for treating correctly the thermal lattice expansion and vibrational entropy for higher temperature region. The present method allows us to take fully into account the anharmonicity of thermal lattice vibration in the phase stabilities of metals and alloys. It is based on the fourth order moment approximation and gives us explicit mathematical expressions of the various thermodynamic quantities. The effective interatomic potentials of the HCP metals are derived by using the embedded atom method (EAM) as well as by non-orthogonal TB parametrization by Papacon stoupoulos et al.. The thermodynamic quantities, thermal lattice expansion, specific heats and compressibilities are calculated successfully using the non-orthogonal basis TB scheme. It is shown that the inclusion of anharmonic contribution of vibrational entropy by the statistical moments method gives rise to strong reduction of the transition temperature $T_c$ of hcp/bcc transition of Ti, $T_c$ being more than ~3000K when the vibrational entropy contributions are neglected (while experimental $T_c = 1155K$). We also discuss the effects of solute atoms (bcc and hcp stabilizing elements) on the transition temperature.
Thermal analysis of copper-based special bronzes

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The existence of fire and explosion is dangerous at places such as mines, oil refineries, petrol-filling stations, the plants for production of explosives etc. This causes the need of usage of tools which possess good combination of strength and thermal conductivity, which stroke into hard object is without sparks. Copper-based special bronze CuAlNiSiCr is used for non-sparking tools as a substitution for beryllium bronzes, because of its toxic and cancer influence.

In this paper, thermal analysis of copper-based special bronze CuAlNiSiCr is done by differential thermal analysis method. Results of characteristic temperatures and kinetic parameters of so-called martensite transformation are presented.

Investigated alloy (77.4-80.0 \%Cu, 11.7-12.1 \%Al, 7.5-9.2 \%Ni, 0.55-0.95 \%Si and 0.25-0.35 \%Cr) has following characteristics: good physical and mechanical characteristics, high strength due to the present martensite structure, high temperature interval of use without structural changes, non-toxic behaviour during the hot deformation, absence of sparking, simpler working technology and lower price then beryllium-bronzes (because only two operations are needed -- quenching and ageing).
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