Databases for Computational Thermodynamics and Diffusion Modeling

Workshop Report

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Disclaimer

This report is intended as a record of the presentations and discussions that took place at a NIST Metallurgy Division and NIST Center for Theoretical and Computational Materials Science sponsored workshop. The opinions, conclusions, or recommendations that are expressed herein are those of the organizers or individual presenters and do not necessarily reflect the views of NIST. All references to commercial products in this report are for identification purposes only and do not constitute any endorsement by NIST. The policy of NIST is to use the International System of Units (SI, metric units) in all its publications. In this document however, works of authors outside NIST are sited which describe properties in certain non-SI units.
Abstract

Databases for computational thermodynamics and diffusion modeling can be applied to predict phase diagrams for alloy design and alloy behavior during processing and service. Databases that are currently available to scientists, engineers and students need to be expanded and improved. The approach of the workshop was to first identify the database and information delivery tool needs of industry and education. Improved modeling capabilities result in decreased new alloy and process development time and ultimately in cost savings. A roadmap will be developed for how these needs can be met during the next decade in a cost effective way through expanded collaborative efforts in education, basic research and database development.

The workshop format was a series of invited talks given to the group as a whole followed by general discussions of needs and benefits to provide a roadmap of future activities.
Program

Thursday, March 21

8:00    Opening Remarks
Ursula R. Kattner, NIST, Gaithersburg, MD
John E. Morral, University of Connecticut, Storrs, CT

8:10    Air Force Programs in Materials Engineering and Design
Craig S. Hartley, Air Force Office of Scientific Research (AFOSR), Arlington, VA

8:40    Application and Needs Assessment of Thermodynamic Databases at Howmet Castings
Ty W. Hansen, Howmet Research Corporation, Whitehall, MI

Rick Sisson, Worcester Polytechnic Institute (WPI), Worcester, MA

9:40    Materials Programs at NSF
K.L. Murty, National Science Foundation (NSF), Arlington, VA

9:50    Break

10:00   Microstructure - Process - Property Models for the Aluminum Industry
Joanne L. Murray, Alcoa Technical Center, Alcoa Center, PA

10:30   Applications of Computational Thermodynamics to Virtual Aluminum Castings
Ravi Vijayaraghavan, Ford Motor Company, Dearborn, MI

11:00   Use of Quasi-Thermodynamical Models for Simulation of Epitaxy of III-V Compound Semiconductors in Electronic Industry
Yuri Makarov, Semiconductor Technology Research Inc., Richmond, VA

11:30   Lunch

12:30   NSF Supported Computational Education Program at Penn State
Zi-Kui Liu, Penn State University, University Park, PA

1:00    Thermodynamic Measurements
Philip Nash, Illinois Institute of Technology, Chicago, IL

1:30    Configurational Entropies in Real Alloy Phase Diagram Calculations
Fan Zhang, CompuTherm LLC, Madison, WI
2:00  
**Current Capabilities in First-Principles Modeling of Alloy Thermodynamics**
Patrice E.A. Turchi, LLNL, Livermore, CA

2:30  
Break

2:45  
**Database Development and Industrial Applications**
Arthur D. Pelton, Centre de Recherche en Calcul Thermochimique (CRTC), Montreal, Quebec

3:15  
**Development of Thermodynamic Databases**
Philip J. Spencer, The Spencer Group, Ithaca, NY

3:45  
**Application of Thermodynamics to Alloy Design and Development**
Charles J. Kuehmann, QuesTek Innovations LLC, Evanston, IL

4:15  
**Construction and Application of a Diffusion Mobility Database for Ni-Base Superalloys**
Carelyn E. Campbell, NIST, Gaithersburg, MD

4:45  
**Incorporation of CALPHAD Calculations into Phase Field Modeling**
William J. Boettinger, NIST, Gaithersburg, MD

6:00  
Dinner

7:00  
**Current and Future Applications of CALPHAD Technology**
Larry Kaufman, Brookline, MA

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**Friday, March 22**

8:00  
**Thoughts on the Acceleration of Phase Equilibria Research**
J.-C. Zhao, General Electric Company, Schenectady, NY

8:30  
Discussion and Roadmap Oversight

10:30  
Summary and Conclusion

11:30  
Lunch

12:30  
Adjourn
Presentation Summary

The workshop program consisted of three parts. The program on Thursday morning was devoted to the identification of national needs and benefits featuring speakers from industry, funding agencies and academia. The program on Thursday afternoon featured speakers from academia, national laboratories and consulting firms presenting current capabilities and software. The program on Friday morning was dedicated to roadmap plan development.

The workshop began with opening remarks by J.E. Morral (University of Connecticut) and U.R. Kattner (NIST Metallurgy Division) in which the objectives and the planned outcome for the workshop were presented. The first two presentations focused on the data need of the aerospace industry. C.S. Hartley (Air Force Office of Scientific Research (AFOSR)) emphasized the immediate need for improved performance of engineered materials. He presented the MEANS (Materials Engineering for Affordable New Systems) program at AFOSR that fosters the development of scientific principles and understanding which are the basis for computational materials engineering, data needs and necessary experimental validation. T.W. Hansen (Howmet Research Corporation) described the products and product requirements at Howmet. He discussed the application of current phase equilibria modeling capabilities and their limitations. He then presented future data and software needs to improve and expand the modeling efforts. The presentation of R.D. Sisson (Worcester Polytechnic Institute (WPI), Center for Heat Treating Excellence) showed how computer simulations can be employed for energy savings, environmental and quality improvements for the heat treating industry. He pointed out that heat-treating modeling is limited by the available databases, i.e., look-up tables and that computational thermodynamics could solve part of the data problem.

K.L. Murty (National Science Foundation (NSF)) gave an overview of funding provided by the Division of Materials, Metal Program. He stated that the majority of the 2001/2002 funding increase went to bio-, nano- and information technology programs.

The next two presentations focused on data needs for aluminum and other light metal alloys. J.L. Murray (Alcoa) gave an overview of commercial aluminum alloys and properties which are important for the manufacturing process. She pointed out that, although many of the binary phase diagrams with aluminum are known, not all phase boundaries are known with sufficient accuracy and identified the systems that need further refinement. R. Vijayaraghavan (Ford Motor Company) presented the modeling efforts in the design and processing of cast aluminum-alloy engine parts. For this modeling, a suite of software codes is employed. The codes include property calculations, as well as structural analysis. The data needs for the modeling tools were highlighted.

In last talk of the Thursday morning session, Yu.N. Makarov (Semiconductor Technology Research, Inc.) talked about the modeling requirements for the manufacturing of III–V compound semiconductors. He presented quasi-thermodynamical models that also take into account kinetic processes during the epitaxial growth of the semiconductors.

The presentations of the Thursday morning session clearly demonstrated the power of modeling approaches, but also underscored the urgent need for reliable databases, such as thermodynamic, kinetic and physical property data. Although the construction of databases has made significant progress in recent years, faster progress is needed.
In the afternoon the focus was on current capabilities and programs in data generation and assessment. Z.-K. Liu (Penn State University) gave an overview of the redesigned Materials Science and Engineering program at Penn State University. This program integrates traditional education in thermodynamics and kinetics of materials with new courses that employ computational models. The goal was not only to include modern material development tools into the curriculum, but also to stimulate student interest.

Although thermodynamic modeling can reduce the amount of experimental data needed, measured data are crucial for the development of databases and verification of the predictions obtained by these databases. P. Nash (Illinois Institute of Technology (IIT)) presented an overview of the experimental methods that are available for thermodynamic measurements at IIT. At the end of the presentation an overview of centers in the U.S.A. and worldwide carrying out experimental research activities in this field was given. There are so few such centers that a critical mass barely exists to ensure continued competence in the U.S.A. in the measurement of thermodynamic data in the future.

The following two presentations focussed on the contribution that ab initio modeling can make to the modeling of real materials. F. Zhang (Computherm, LLC) showed how results from first principles (ab initio) calculations can be used to improve the model descriptions that are used in phenomenological modeling approaches, such as the Calphad method. P.E.A. Turchi (Lawrence Livermore National Laboratory (LLNL)) gave an overview of the available ab initio methods, software packages and property data that can be obtained from these calculations. (See also “Some Notes on First-Principles Electronic Structure Methods and Calculations,” page 17.) He also gave examples on how the results from ab initio calculations can provide data for other computational modeling approaches, i.e., the Calphad method.

These presentations were followed by two talks on database development. A.D. Pelton (Centre de Recherche en Calcul Thermochimique (CRTC)) presented an overview of the steps in developing databases and a description of the decision-making process in selecting models. He presented the databases that were obtained from this strategy and gave examples of their application to industrial processes. P.J. Spencer (The Spencer Group) gave an overview of available thermodynamic databases for pure inorganic substances and alloy systems. He pointed out the needs and benefits of database construction and emphasized that self-consistent databases require careful construction.

The remaining presentations of Thursday afternoon were dedicated to the application and coupling of thermodynamic calculations with kinetic modeling. C.J. Kuehmann (QuesTek Innovations, LLC) gave examples for the incorporation of thermodynamic calculations into a larger scheme of materials design. Different software suites are used depending on the dimensionality of the material (atomic, nano, micro, ...). Results from the software package PrecipiCalc were demonstrated. C.E. Campbell (NIST Metallurgy Division) reported the results of the construction of a multicomponent diffusion database for superalloys. This database was constructed using the same principles as for CALPHAD type thermodynamic databases and it was shown that it has the same predictive power. W.J. Boettinger (NIST Metallurgy Division) discussed a few approaches to phase field modeling. Examples were shown for solidification and precipitation simulations. He showed how thermodynamic and mobility data fit naturally into the phase field modeling approach. Although phase field modeling is a powerful tool for the simulation of growth processes its application is still limited by computational power.
The final presentation of the first day was given by L. Kaufman. He presented a series of examples of analysis of multicomponent materials to illustrate the wide variety of applications for computational thermodynamics and diffusion modeling.

The discussions on Friday morning began with a short talk by J.-C. Zhao (General Electric Company) in which he presented his thoughts on the acceleration of phase equilibria research using concepts of high throughput or combinatorial methods. He discussed the use of samples constructed of diffusion multiples to accelerate experimental phase diagram investigations. He also showed how the results were used to verify the databases. The remaining time of Friday morning was dedicated to the discussion of what was learned from the presentations and to the development of a draft of a roadmap. The discussion was lead by W.J. Boettinger (NIST Metallurgy Division). The results of the discussion and roadmap oversight are summarized in the following chapter.
Computational Thermodynamics and Diffusion Modeling Roadmap

The roadmap is the result of the discussions following the presentations at the workshop and has been agreed on by the majority of the workshop participants.

Vision 2010

By the year 2010 all Materials Science and Engineering students will learn to solve real world materials problems using thermodynamic and diffusion modeling software, while materials engineers in industry will have the computational tools and the background needed to lead the world in the design and optimization of both materials and materials processing.

Benefits

The benefits of providing materials engineers with the knowledge, software and databases to model materials and processing are savings in costs, energy and natural resources via optimization studies. Also, properties can be improved, new materials can be discovered and development time can be reduced. Specific benefits are:

- Computational thermodynamics has already been successfully used in the development of new alloys and the understanding of microstructures.
- Reduced product cycle time via Federal programs, such as MEANS (Materials Engineering for Affordable New Systems) and AIM (Accelerated Insertion of Materials), will reduce costs sharply and make USA industry more competitive; e.g., savings to the auto industry on engine blocks and cylinder heads could top $100 M.
- Reduction in energy use by the heat treating industry alone is estimated as $7 \times 10^{15}$ J ($7 \times 10^{12}$ BTU) over a ten-year period due to improved efficiency.

Approach

- Organize a series of "work groups" consisting of representatives from Academia, Industry and Federal Agencies that will oversee and expand plans to create new teaching tools for Universities and Technical Colleges.
- Build an experimental infrastructure that can make ultra-high precision thermodynamic and diffusion measurements.
- Build an educational infrastructure for the teaching and application of computational thermodynamics and diffusion modeling.
- Prepare a comprehensive public library of thermodynamic and diffusion property databases that apply to common and emerging alloy systems.
- Increase processing-structure-property modeling efforts, i.e., improve application modeling.
Objectives, Strategies and Action Items

Coordinators are suggested for each of the action items.

I. Education

1. Interest faculty in teaching applied thermodynamics and kinetics with:
   a. New course materials (traditional and web based).
   b. Industrial contacts.
   c. Research opportunities (e.g., via joint projects).
2. Interest students in applied thermodynamics and kinetics with:
   a. Real world problems.
   b. Hands on experience doing computational thermodynamics and diffusion modeling.
   c. Job opportunities in computational materials design.
3. Increase the technical ability of students with more emphasis on:
   a. Better appreciation of the underlying physics as well as classical concepts.
   b. The understanding of the behavior of multicomponent alloys, not just binary alloys.
4. Encourage institutions to support teaching initiatives:
   a. Provide funding.
   b. Support outside funding initiatives.
5. Provide training for those already in industry.

Action Items

1. Prepare a collection of useful applied problems.
   - Karl Spear (Penn State)
2. Publish an article about the NSF program at Penn State on computational thermodynamics and kinetics.
   - Zi-Kiu Liu (Penn State)
3. Prepare a catalog of currently available course materials.
   - TBD
4. Explore the possibility of a course on computational methods.
   - Bill Scott (ASM)

II. Thermodynamic and Diffusion Data

1. Experimental data:
   a. Promote a national initiative to rebuild the thermodynamic and diffusivity measurement infrastructure.
b. Establish goals for improving the accuracy of phase diagram measurements by an order of magnitude.
c. Establish “best practice guide” for using assessed data.
d. Make assessment software more user friendly, more robust, and with less complexity (i.e., make it run faster).

2. Virtual data:
a. Encourage First Principles calculations of interaction energies and defect formation energies.
b. Encourage Molecular Dynamics calculations of atomic mobilities.
c. Develop estimation software for unknown thermodynamic parameters (empirical, semi-empirical, first principles), for example Miedema’s model for the estimation of enthalpies of formation.
d. Develop estimation methods/software for atomic mobilities/diffusion data.

**Action Items**

1. Review the status of estimating molar volume.
   - Phil Nash (IIT).
2. Expand the scope of the CALPHAD community to include diffusion modeling.
   - Bill Boettinger (NIST), Zi-Kiu Liu (Penn State).
3. Capture the diffusion data in NIST archives.
   - TBD
4. Organize diffusion assessments and modeling sessions at the 2003 CALPHAD meeting.
   - John Morral (UConn), Afina Lupulescu (RPI), Arthur Pelton (CRTC)
5. Organize diffusion modeling and assessment sessions at ASM meetings through the Atomic Transport Committee.
   - Rick Sisson (WPI), John Morral (UConn).
6. Prepare a “wish list” of needed thermodynamic and kinetic information for physicists to model.
   - TBD
7. Prepare a list of physicists doing First Principles and Molecular Dynamics studies and distribute the “wish list” to them.
   - Patrice Turchi (LLNL)
8. Develop standard problems for establishing “best practices”.
   - Ray Thompson (UAB), Charlie Kuehmann (QuesTek).

### III. Public Databases

1. Encourage the publishing of a full set of parameters used in phase diagram and diffusivity assessments that appear in the open literature.
2. Develop public databases that are comprehensive for common commercial alloys systems and emerging alloy systems.
3. Develop databases for other data: molar volume, viscosity, *etc.*
4. Encourage a standard format be used in public databases.
5. Develop methods of delivering public databases into macrocodes; encourage standardized interfaces.

**Action Items**

1. Write letters to journal editors encouraging policies that require authors to list parameters used in assessment articles.
   - Everyone
2. Encourage authors of proprietary databases to publish descriptions of constituent subsystems.
   - Everyone
3. Recommend and publish the SGTE format for data (CALPHAD web site and journal).
   - Zi-Kiu Liu (Penn State).
4. Encourage North American participation/membership in SGTE, which is now open to non-European members.
   - Phil Spencer (The Spencer Group).
5. Compile database and software needs for practical applications.
   - Charlie Kuehmann (QuesTek).
6. Devote an issue of the CALPHAD Journal to data delivery, coupling of micro and macro computer codes.
   - Zi-Kiu Liu (Penn State).
   - Everyone

**IV. Funding**

1. Make use of NSF undergraduate initiatives to obtain funding for education programs.
2. Obtain public funding for experimental measurement of data.
3. Promote the value of thermodynamic and diffusion modeling.

**Action Items**

1. Distribute present roadmap to contract monitors, industrial research laboratories, funding agencies.
   - Everyone
2. Create a list of materials that have been certified to meet specified criteria with the aid of computational thermodynamics and diffusion modeling.
   - TDB
3. Obtain a grant to study the effect of thermodynamic and diffusion modeling on the economy.
   - TDB
4. Approach researchers in industry to supply data on financial benefits of using computational thermodynamics.
   - Everyone
V. Work Groups

1. Educational Programs and Instructional Materials.
   - Zi-Kiu Liu (Penn State).
2. Experimental Measurement of Thermodynamic Data.
   - Phil Nash (IIT)
3. Diffusivity Assessments and Modeling.
   - Bill Boettinger (NIST), Carrie Campbell (NIST), John Morral (UConn)
4. Thermodynamic Assessments.
   - Ursula Kattner (NIST)
Acknowledgement

The authors wish to thank Carelyn Campbell, Raymond Thomson, Charles Kuehmann and Zi-Kui Liu for contributing their notes and the speakers for providing their view graphs for the preparation of this report.
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Complementary Contribution

The following section was contributed for the report after the workshop.

Some Notes on First-Principles Electronic Structure Methods and Calculations

by Patrice E. A. Turchi
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I. When performing so-called first-principles (or \textit{ab initio}) electronic structure calculations, it is always wise to keep in mind the following constraints:

A. Constraints within Density Functional Theory (DFT)

1. Local Density Approximation (LDA) (or LSDA: Local Spin Density Approximation)
   Exchange Potential, \textit{e.g.:}
   - von Barth & Hedin
   - Vosko
   - Ceperley & Alder (Perdew & Zunger)

   The selection of an exchange potential will impact the results, \textit{e.g.}, the total energy.

2. Beyond LDA
   - LDA+U
   - LDA++
   - GGA (Generalized Gradient Approximation)
   - SIC (Self-Interaction Correction)
   - GWM (Gutzwiller Wave Method)
   - DMFT (Dynamical Mean-Field Theory)

   Going beyond the LDA may be necessary in some instances when electron correlation play an important role, \textit{e.g.}, to reproduce the bandgap in semiconductors, the electronic behavior of oxides such as NiO or MnO or of strongly correlated systems such as those based on Ce and Pu, or when magnetism is involved.

B. Other Constraints

1. Shape of the Potential Function:
   - Muffin-Tin
   - ASA (Atomic Sphere Approximation; with equal or non equal sphere radii)
   - Full Potential
2. **Core versus Valence Electrons** (This selection is usually not talked much about but may be important if calculations are carried out as functions of pressure).

3. **Scalar Relativistic versus Fully Relativistic** (For magnetic systems and heavy elements, including the 5d transition metals and beyond, a fully relativistic treatment of the electrons is recommended).

4. **Magnetism: Co-linear (Ising-like), Non Co-linear (Heisenberg-like)** (In the case of magnetic systems, it may be necessary in some instances to carry out large supercell calculations to predict the proper type of magnetism, such as in the case of chromium).

5. **Atomic Positions and Site Occupancy** (A calculation for an ordered compound requires the knowledge of the atomic positions; in the case of an off-stoichiometric or chemically random alloys, additional approximations are necessary).

6. **Born-Oppenheimer approximation (electron-phonon coupling)** (This approximation may be severe when performing molecular dynamics-type calculations).

II. Two main categories of methodologies are defined depending on the desired type of calculations:

A. **Methods Limited to Ordered Structures (Wave Methods)**

- **Pseudo-Potential**
- **LAPW or FP-LAPW** (Full Potential Linear Augmented Plane-Wave)
- **LMTO or FP-LMTO** (Full Potential Linear Muffin-Tin Orbital)
- **ASW** (Augmented Spherical Wave)
- **LASTO** (Linearized Augmented Slater-Type Orbital)

B. **Methods that can also handle Disordered Structures (Green's function Methods)**

- **KKR** (Korringa-Kohn-Rostoker)
- **TB-LMTO** (Tight-Binding Linear Muffin-Tin Orbital)
These two methods can be used within the mean-field CPA (Coherent Potential Approximation), or beyond, to treat in an approximate way chemical disorder.

III. Based on electronic structure calculations the following properties can be obtained:

- **Equilibrium Properties**
  - lattice parameter(s)
  - structural energy differences
  - crystal structure minimization
- Elastic Properties
  - bulk modulus
  - elastic constants
  - phonon spectrum
- Electronic Properties
  - densities of states (γ of heat capacity data)
  - spectroscopic data (ARPES, UPS, XPS, PAS)
- Transport
  - conductivity (DC and AC)
  - reflectivity
- Magnetic Properties
  - magnetic moments and magnetic ordering

and Alloying Effects on Properties, in particular:
- Heat of formation (heat of mixing)
- Heat of transformation
- Ordering energy

IV. A series of software is now available to perform electronic structure-based calculations of materials properties, e.g.:

Pseudo-potential-based Methods:
- VASP (http://cms.mpi.univie.ac.at/vasp)
- Siesta (http://www.uam.es/departamentos/ciencias/fismateriac/siesta)
- ABINIT (http://www.abinit.org)

Full-potential Methods:
- Wien97 (http://www.tuwien.ac.at/theochem/wien97), replaced now by:
- Wien2k (http://www.wien2k.at)
- LmtART (http://www.mpi-stuttgart.mpg.de/andersen/LMTOMAN/lmtman.pdf)
  Full-Potential Linear Muffin-Tin Orbital (PLMTO)
- TB-LMTO-ASA (http://www.mpi-stuttgart.mpg.de/andersen/LMTODOC/LMTODOC.html)
V. Limitations and Challenges for Ab Initio Approaches:

There is still a number of challenges that *ab initio* approaches have to face. Notable examples include a full *ab initio* description of:

- The liquid phase of multi-component alloys and the amorphous state of matter for which the interaction between the fluctuations of alloy composition with topological disorder has to be properly accounted for.
- Some systems such as hydrides, carbides and nitrides for which large lattice distortions have to be accounted for.
- Charge transfer effect in alloys and compounds (e.g., oxides).
- The un-bias description of magnetic order in alloys.
- Correlated electron systems for which the current approximations based on the local-density approximation (LDA) and beyond are not applicable. Recent progress made in this field based on the dynamical mean-field theory (DMFT) is worth noting although the implementation has not been carried out in "user friendly" codes.
Presentations

View graphs, additional remarks from the speakers and comments/questions of the workshop attendees are given.

Opening Remarks

Ursula R. Kattner, NIST, Gaithersburg, MD
John E. Morral, University of Connecticut, Storrs, CT

Excerpts from a recent editorial by J. Ågren, Physical Metallurgy, Department of Materials Science and Engineering, Royal Institute of Technology, Stockholm, Sweden (J. Phase Equilibria 22 (2002) 2-3) where he describes his views of the CALPHAD future were shown:

“... Today, Calphad assessments usually come as spin-offs from other projects.

Nevertheless, calculation of phase equilibria and phase diagrams by means of the Calphad technique has been tremendously successful from all points of view over the last two decades. ...

... But, what are the future needs? What are the challenges?

All experts in the field realize that good databases are needed, but it does not seem likely that the funding agencies will change their mind about databases ... Of course some databases, covering limited subsystems, are of industrial interest and can be developed on a commercial basis. In general these databases will not be available to the general public.

The only way to demonstrate the importance of thermodynamic databases is to apply thermodynamic calculations to other areas of science and technology. And perhaps, that is the best way to get the inspiration and stimulus to develop the field further and avoid getting old-fashioned.

...

Thus the challenge of the next decade is to demonstrate that Calphad has the strength to solve various problems, problems that would be very difficult to solve otherwise. The existence of new software interfaces that allow the user to include advanced thermodynamic calculations in her or his software will make this possible.”

Ågren also emphasized the future of applied thermodynamics in such as Scheil solidification, paraequilibrium calculations, and DICTRA simulations.

The objectives of Workshop were identified as:

• Needs (most important)
• Benefits (savings in cost, energy, environment)
• Abilities (current abilities)

with the goal to develop a roadmap for obtaining databases with improved accuracy for practical applications.
Air Force Programs in Materials Engineering and Design
Craig S. Hartley, AFOSR (Air Force Office of Scientific Research), Arlington, VA

THE CHALLENGE FOR MATERIALS DESIGN
Beyond the One Hoss Shay
NIST Workshop on Databases for Computational Thermodynamics and Diffusion Modeling

Dr. Craig S. Hartley
AFOSR Program Manager
Air Force Research Laboratory

The Goal
Unlike The Deacon’s Masterpiece, which was built of the best available materials to last as long as it could... we strive to make things using optimized processes and materials designed to meet specifications for reliability and performance.

The Present Condition
THE SCIENCE BASE IN THE PLANE OF STRUCTURE-PROPERTIES-PROCESSING IS STILL DEVELOPING, COUPLING EXPERIMENT AND THEORY. AND ACCELERATING IN THE LAST TEN YEARS, AUGMENTED BY DRAMATIC ADVANCES IN COMPUTATION.

However, the path to performance, the ultimate goal desired by designers, is still mostly empirical, expensive, and very time consuming.

The Issue
Materials Science and Engineering has not progressed as rapidly as other disciplines in contributing to the reduction in the product cycle during the last decade.

New developments in materials are not being exploited as rapidly as desirable because of the time and cost necessary to obtain information on material properties and characteristics.

Products are being designed and fabricated with existing materials having verified design properties, resulting in the use of less than optimal materials for many applications.

A Bit of History
During the last forty years, engineering disciplines based on structure-property relationships in metals and ceramics have been merged with elements of solid state physics and chemistry and polymer chemistry to form the discipline we call “Materials Science and Engineering”. This field is characterized by the tetrahedron:

...BUT the “Engineering” component has not kept pace with rapid developments in the use of modern computational power to compress the design cycle in the development and use of new materials.

WHAT DO WE MEAN BY PERFORMANCE?

STRENGTH IS ONLY ONE OF MANY PROPERTIES REQUIRED FOR SUCCESS:
- MANUFACTURABILITY
- TOUGHNESS
- SPECIFIC STIFFNESS
- FATIGUE RESISTANCE
- AFFORDABILITY
- RELIABILITY
- ENVIRONMENTAL STABILITY

OUR PAST STRATEGY HAS BEEN TO DEVELOP ONE OR MORE OF THESE CAPABILITIES, OFTEN ATTEMPTING TO OPTIMIZE IN SEQUENCE, AND THEN MEASURE ALL OF THE REQUISITE PROPERTIES TO ESTABLISH A DATA BASE FOR DESIGNERS TO USE...CAN WE DO BETTER?
### A NEW AFOSR APPROACH FOR STRUCTURAL MATERIALS

Materials development is one of the great successes of Air Force RDT&E. What has changed to justify a new approach?

- Military procurement has decreased
- Industry is focused on civilian applications
- Investment in new material development is reduced
- System design time has dramatically shortened
- Long development times continue for new materials
- New materials lose out to those already certified
- Problems have become more complex
- We're pushing the envelope in high temperature, stealth, low weight, multifunctionality, etc.
- Affordability has become a major issue for the AF
- Computational alternatives are now feasible
- The understanding of materials science has matured
- Computational speed has reached a practical range

### THE MEANS TO A DESIRABLE END

**Materials Engineering for Affordable New Systems**

- **Means** will develop the scientific principles and understanding to enable materials engineering
- **Means** will be computationally intensive, but will be tied to experimental validation

### ELEMENTS OF MEANS

Some of the things we will need for success:

- Models and experiments that are adequate to the task
- Strategies for linking models in different spatial and temporal regimes - so-called "multiscale modeling"
- Optimize the combinations of available models, experiments and probabilistic data bases to minimize development time and cost

### LINKS TO OTHER PROGRAMS

- **Means** builds on programs in many agencies focused on "materials by design"
- **Means** builds on programs in many agencies focused on "multiscale modeling"
- **Means** will develop the scientific base for and derive insight and direction from the 6.2 program in DARPA called AIM (Accelerated Insertion of Materials)
- **Means** will focus the 6.1 community on knowledge base construction, propagation of errors, linking of scales, and new, efficient experimental approaches

### Interoperability is the Key to Constructive Collaboration

No More

Spherical Chickens

### The Challenge

Exploit computational Materials Science and Engineering to develop techniques for coupling models of material behavior to design software, enabling materials design to be an integral part of the global design process.
A hierarchy of computational models will be integrated through computational thermodynamics to design a metal/ceramic system that addresses control of oxygen behavior both in a BCC Nb-based matrix as well as in stable oxide films with controlled expansion and adherence.

**ATOMIC SCALE**

1) The friction stress for irreversible slip during fatigue will be modeled at the atomistic scale using the Peierls-Nabarro model and the thermally activated flow approach.

**DISLOCATION SCALE**

2) The formation of dislocation cell substructure will be modeled by considering interactions of dislocation pile-ups and cell walls at the dislocation cell size level using results from irreversible slip modeling.

**MEANS Projects in Metallic Materials**

- **COMPUTATIONAL DESIGN OF ADVANCED AEROTURBINE MATERIALS**: PI – G. Olson, Northwestern U.
- **DEVELOPMENT OF A PHYSICALLY BASED METHODOLOGY FOR PREDICTING MATERIAL VARIABILITY IN FATIGUE CRACK INITIATION AND GROWTH**: PI – K. Chan, Southwest Research Institute
- **MICROSTRUCTURE-BASED MODELING FOR LIFE-LIMITED COMPONENTS**: PI – H. Fraser, Ohio State U.
- **DEVELOPMENT OF AN ACCELERATED METHODOLOGY FOR THE EVALUATION OF CRITICAL MECHANICAL PROPERTIES OF POLYPHASE ALLOYS**: PI – P. Dawson & M. Miller, Cornell U.
- **MURI on Design of Multifunctional Materials**: TBA

**Objectives:**

- To develop physics-based fatigue crack initiation and growth models
- To develop a probabilistic approach for linking physically based models into a continuum framework
- To demonstrate the utilities of the methodology in a probabilistic design setting
**MICROSTRUCTURE SCALE**

3) Microstructure-based fatigue crack initiation and growth models will be developed at the grain level using results from dislocation structure modeling:

- **Dislocation-Based Fatigue Crack Initiation Model**
- **Dislocation-Based Fatigue Crack Growth Model**

\[(S: \text{Stress Range}; N: \text{Fatigue Life}; \frac{d}{dN}: \text{Crack Growth Rate}; K: \text{Stress Intensity Factor Range})\]

**APPLICATIONS**

Potential applications of the probabilistic fatigue models include component design and life-prediction analyses that include material variability and confidence limits for the fatigue properties.

**APPROACH**

- **Microstructure-based Databases**
  - Quantitative characterization used to describe microstructure
  - Neural networks used to reveal functional dependencies of properties on microstructural features
  - Prediction of variations of microscale bar together with property measurement provides necessary distribution

This information will be used to develop physically-based models for prediction of fatigue properties.

**APPROACH (CONT'D)**

- **Prediction of Microstructure Evolution**
  - Phase Field model will be used as the primary computational method to calculate the microstructural evolution
  - Modeling will include the coupling of growth in the diffusion fields of minority alloying elements, accommodation of coherency strain, and anisotropy in interlaminar & interfacial strength, energy & mobility
  - Development of constitutive equations & finite element based models for grain growth and overall transformation kinetics including nucleation and growth

**CONTINUUM SCALE**

4) The microstructure-based fatigue crack initiation and growth models will be integrated into a probabilistic framework at the continuum level.

**Microstructure-based Modeling for Life-Limited Components**

- **Aims**
  - The development of microstructure-based databases for the alloys Ti-6Al-4V and Ti-6242-V
  - A determination of the property-controlling microstructural features influencing fatigue and crack growth in Ti-6Al-4V and Ti-6242-V
  - A robust methodology for quantitatively determining the microstructural features and their representation in modeling and simulation
  - Quantitative validation methodologies for the prediction of the development of microstructural features, which are key to influencing LCF and da/dN, as a function of load-mission
  - The development of a set of microstructure-based models for the prediction of LCF and da/dN in Ti-6Al-4V and Ti-6242-V
  - The development of a set of FEM-based tools for the analysis of fatigue life and crack growth in turbine rotors
Accelerated Methodology for Evaluation Of Critical Properties In Polyphase Alloys  
(P. Dawson & M. Miller, Cornell U.)

- Objectives:
  - Rapid evaluation of stiffness and strength of polyphase metallic systems
  - Reduced time for insertion of alternative materials in mechanical design

- Methodology:
  - Develop protocols for a suite of simulations and experiments to assess elastic moduli and anisotropic yield surfaces
  - Deploy around the Digital Material framework
  - Interface required diagnostic tools via the Digital Material

- Diagnostic Tools:
  - Simulation: grain-by-grain finite element models of polycrystals
  - Experiments: mechanical tests and in situ diffraction measurements
  - Visualization: advanced graphics as interpretation aids

Digital Material – Collaboration Environment

Experiments and Simulations

The Vision

- The periodic table is the ultimate database
- Imagine a design space that extends from the periodic table to input into current design software.
- What do we need to do to fill the gaps in this space?

Following the Vision

Steering by the North Star

doesn't mean that you're trying to go there.

The Payoff

Optimal utilization of materials and processes to produce affordable, reliable and durable products for military and civilian applications.
Additional points made by speaker:

- To include computational materials as a design component the ability to compute design properties is needed
- Materials computational power is not up to speed to use to replace existing materials
- Engineering part of materials science has fallen behind; need to make connection to performance (strength, toughness, fatigue resistance, etc.)
- MEANS: Materials Engineering for Affordable New Systems
  - Tied to experimental validation
  - Need models (robust)
  - Need methods to link models
  - Need methods to optimize models
  - Interoperability is key
  - Focus on basic science on knowledge base
  - Make materials science an integral part of global design process

Questions/comments from workshop attendees:

- Is OOF related to the OSU program? — No, not formally, yes philosophically.
- Performance - structure relationship not well correlated yet
- Need to get manufacturers involved in model development or they will not trust design process and use the new materials.
Application and Needs Assessment of Thermodynamic Databases at Howmet Castings
Ty W. Hansen, Howmet Research Corporation, Whitehall, MI

Introduction
- Howmet Castings Background
- Current Capabilities
- Howmet Applications
- Howmet Thermodynamic Needs

Overview
- World Market Leader in 2 Very Attractive Markets
- Leadership Positions
  - Differentiated & Defendable
  - Technology Leader
  - Operational Excellence
  - Excellent Customer Relationships
- 29 Manufacturing Facilities in 5 Countries
- Over 11,000 Employees

Alcoa Industrial Components Group
- Howmet Part Alcoa Industrial Components Group
- Based in Salt Lake City, Former Cordant Headquarters
- Group Also Includes:
  - Huck Fasteners
  - Alcoa Forgings
  - Alcoa Automotive
- Total Revenues ~ $3.4B
- 42 Locations
- 17,000 Employees

Airframe Market
- Aircraft Components: Al & Ti
  - Doors, Nacelle, Seat, Flight Control, APU and Environmental Systems
- Missile Components: Al & Ti
  - Missile Bodies, Fins, Optical Seeker and Fuel Components, Electronic Environments
- Rocket Components: S/A
  - High Pressure Furl and LOX Pump and Turbine Housings

Major Customers
- Aero Engine
  - Pratt & Whitney Aircraft
  - Pratt & Whitney Canada
  - Rolls Royce
  - General Electric Aircraft Engine
  - Honeywell
- Industrial Gas Turbine
  - Siemens Westinghouse
  - Alstom
  - General Electric Power Generation
  - Solar

Alcoa Industrial Components Group Based in Salt Lake City, Former Cordant Headquarters Group Also Includes:
- Huck Fasteners
- Alcoa Forgings
- Alcoa Automotive

Total Revenues ~ $3.4B
42 Locations
17,000 Employees

Airframe Market Aircraft Components: Al & Ti
- Doors, Nacelle, Seat, Flight Control, APU and Environmental Systems
- Missile Components: Al & Ti
- Missile Bodies, Fins, Optical Seeker and Fuel Components, Electronic Environments
- Rocket Components: S/A
- High Pressure Furl and LOX Pump and Turbine Housings

Major Customers Aero Engine
- Pratt & Whitney Aircraft
- Pratt & Whitney Canada
- Rolls Royce
- General Electric Aircraft Engine
- Honeywell

Industrial Gas Turbine
- Siemens Westinghouse
- Alstom
- General Electric Power Generation
- Solar
## Application and Needs Assessment of Thermodynamic Databases at Howmet Castings

### Current Capabilities

- Howmet utilizes three solvers:
  - ProCAST - Ni, Ti, Fe, Al
  - JMatPro - Ni
  - Pandat - Ni

### Application and Needs Assessment of Thermodynamic Databases at Howmet Castings

#### IN718

![IN718 Graph](image)

- ProCAST: 2 minutes
- JMatPro: 15 seconds
- Pandat: 3 minutes

### Howmet Applications

- Heat Treat Optimization
- \(\gamma\) solvus, solidus
- Alloy Development
  - \(\gamma\) solvus, \(\gamma\) volume, liquidus/solidus, phase evolution and stability
  - Alloy Targeting for Castability
    - \(\gamma\) solvus, liquidus/solidus, phase evolution and stability

### Benchmark SX Alloy

![Benchmark SX Alloy Graph](image)
Summary from workshop organizers:

Products:
- Turbine blades and vanes (IGT): directionally solidified, single crystal, equi-axed
- Airframes (Al, Ti)
- 88% of the production are turbine parts, 35% are spare parts

Success measures: Price, quality, delivery

Current modeling capabilities:
- ProCast: finite element software package for simulation of casting processes, includes lever rule and Scheil solidification calculations: Ni, Ti, Fe, Al databases from Thermotech
- JMatPro: software package for the calculation of physical and mechanical properties, includes lever rule calculations: Ni database (Thermotech)
- Pandat: phase equilibria calculations: Ni (not using, too difficult, long calculation time)
- Test phase equilibria calculations for IN718 had different run times and gave different results

- Heat Treatment Optimization
  - Calculation of $\gamma'$ solvus, solidus (motivation: sell reduced heat cycle to customers, need more experimental verification)
- Alloy Development
  - Calculation of $\gamma'$ solvus, $\gamma'$ volume, liquidus/solidus, phase evolution, stability
  - Objective: improve castability (customers - small base; non-patented alloys)
  - Use lever calculations, trend analysis (not accuracy)
  - Patent conflicts
  - Stress-rupture calculations
- Concerns/ Needs
  - Are we using the tools correctly
  - How do we make the tools better
- Database needs
  - Improved accuracy
  - Density model (liquid) porosity
  - Add Pt, Si, Pd to database for coatings
  - Model diffusion in solid state

Questions/comments from workshop attendees:
UES: Si added in latest version of Ni database
Alloy development restricted by composition limits on thermodynamic database

Richard D. Sisson, Worcester Polytechnic Institute, Center for Heat Treating Excellence (WPI, CHTE) Worcester, MA


Rick Sisson
Mohammad Maniruzzaman
Materials Science & Engineering Program
Mechanical Engineering Department
Worcester Polytechnic Institute
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Research Needs identified in the Heat Treating Technology Roadmap Workshop - 6-7 February 1997

Quenching Technology
Models for heat transfer behavior in quench baths that will ensure uniform cooling of a range of blanks.

Process Modeling
Microstructure response models based on alloy composition, atmosphere, temperature, and time models to predict distortion and residual stress profiles database of thermal and mechanical properties of quenched components
models for continuous cooling transformations (CCT) of heat treatable alloys models for continuous heating transformations (CHT) of heat treatable alloys

Software Packages
predictive software that heat treaters can use to compare and select furnace equipment from different suppliers (a standard method of predicting furnace variability is incorporated)

General Needs for Roadmap
Heat Treating Processes that allow a shorter cycle time and require lower cost equipment.
Alternative quenching media that are more environmentally friendly and that transfer heat more efficiently.
Improved process sensors, including those for carbon content, residual stress, and cleanliness. Also, more advanced controls that fully exploit there and other sensors.
Enhanced computer modeling of processes, which include composition, distortion, residual microstructures, and final properties.
More effective dissemination of solutions to specific problems.

Proposed Research from Roadmap

Goal A: Integrated process models
Quenching Models
Electromagnetic models
Mechanical Models
Transformation Databases
Predict Heat-up parameters
Predict carburization, nitriding, and sintering behavior
Predict cooling behavior
Materials Databases and process inputs
heat transfer coefficients (heating & cooling)
physical property data (thermal expansion, specific heat, thermal conductivity, density)
Electrical and Magnetic property data

Modeling Heat Treating Processes

Finite Difference Models (FDM)
Finite Element Models (FEM)
Computational Fluid Dynamics Models (CFD)
Data Needs -
thermal properties - k, c_p, ρ
diffusion coefficients - D_i
phase transformation rates - λ(T, composition)
elastic and plastic properties - E(T, composition)

An Energy Savings Model for the Heat Treatment of Castings

DOE - funded, 4 year project, WPI & U. Conn & U. Mass.

Develop, verify and market an integrated system of software, databases, and design rules to enable quantitative prediction and optimization of heat treatment of aluminum castings to increase quality, increase productivity, reduce heat treatment cycle time and reduce energy consumption.
Reduce cycle times for solutionizing cast aluminum alloys from 12 to 2 hours, increase energy consumption by more than 50%

Emulated energy savings of 1 billion BTUs in 10 years

Computer Modules
HTFURNACE - predict local temperature cycle in a part
PTLOAD - optimizes part loading
STCOVCON - optimizes temperature control in furnaces
GURMACHCC - predicts cooling rates and microstructures as a function of quenching process parameters and position on the part
An Energy Savings Model for the Heat Treatment of Castings
DOE-funded, 4-year project, WPI & U. Conn & U. Mass.

Solutionizing Prediction
- PHASECALC: phase diagram for industrial alloys
- DIFFCALC: diffusivities
- CASTSIM: predicts local segregation as a function of alloy composition and thermal cycle
- CASTDYN: predicts local segregation after solutionizing treatment

Property Prediction
- PROPERTIES: predicts local values of strength
- POSTPROCESS: presents results to facilitate decision making

Databases for heat treating

Databases
- Heat Transfer and Quenching performance database:
  - heat capacity
  - thermal conductivity
  - emissivities
  - heat transfer coefficients
- Phase diagrams for selected alloys
- Diffusivities versus composition and temperature
- Properties versus microstructure
  (i.e. porosity, Si particle size, undissolved Ti and grain size)

4140 Steel IT diagram showing two quench path
Source: Atlas of IT diagrams, United States Steel, 1963

Characterization of Quenching Fluid
- Specific Heat vs. Temperature for 304 Stainless Steel
Source: Handbook of Stainless Steel and TPRC

Specific Heat vs. Temperature for 304 Stainless Steel

Heat transfer coefficients of SS304 probe quenched in mineral oil

Heat transfer coefficients vs. temperature
SS304 probe quenched in different quenchants

Cooling rate 4140 steel probe as a function of temperature quenched in mineral oil (HR88A)

Heat transfer coefficients vs. temperature
quenched in mineral oil (HR88A)

QUENCHPAD - CHTE Quench Database

Quenching Database - Flowchart
Additional points made by speaker:

- Heat treating modeling limited by available databases
- Software uses look-up tables as databases, source of potential problems: data such as $c_p$ are sparse and differences between different sources have a trickle down effect on derived properties

Questions/comments from workshop attendees:

- Calculation of phase equilibria could solve part of the database problem
- Quenching modeling will be geometry/equipment specific
Materials Programs at NSF

K.L. Murty, NSF (National Science Foundation), Arlington, VA
Types of Individual Investigator Grants

- Regular grants
- Focused Research Group (FRG)
- Grant Opportunities for Academic Liaison with Industry (GOAL)
- Small Grant for Exploratory Research (SGER)
- Technical Conference Support

DMR/Metals Program

Emphasis on creating a framework for the development of advanced metallic materials

- New Metallic Systems
- Bulk, thin films, wires and particles
- Characterization
- Processing
- Environmental Effects

DMR METALS RESEARCH PROGRAM FUNDING

FY 2001 METALS RESEARCH PROGRAM

Funding Actions (budget $11.1M)
- 29 research grants ($3.3M)
- 70 continuations ($7.4M)
- 4 conferences ($25K)
- 30 REU students ($163K)
- 8 other supplements (equip., etc.) ($102K)

Success rates for proposals
- 28% regular IIA proposals
- 41% CAREER proposals

Materials Research and Education *Our “road map”*

- Prepare the future
  - young investigators, diversity, education, dissemination of knowledge, public understanding
  - rich mix of disciplines

- Stimulate, support and sustain the best research and education
  - merit review, partnerships, international cooperation

- Provide the tools
  - instrumentation and instrument development, shared facilities
K. Linga (KL) Murty
< research experience – central theme >

Defects
Characterization
Kinetics &
Microstructure

IIA Programs
Grant Opportunities for Academic Liaison with Industry (GOALI)
- Typically $90 - $125K/yr for 3 or 4 years
- 2 PI's (one from the industrial company)
- Strong industrial interaction is a must
- Mail reviewed
- Deadline: none, but August - October preferred for reserch funds

Small Grant for Exploratory Research (SGER)
- Limited to $100K max. for 1 year
- Usually high risk, innovative ideas
- PD reviewed
- Target date: November

NSF Coordinated Programs: Individual Investigator Grants
Coordinated NSF Programs:
- Faculty Early CAREER Development
- ADVANCE
- NSF-EC Cooperative Program

Faculty Early CAREER Development
- Typically $75 - $100K/yr for 5 years
- Usually panel reviewed
- FY 2002 deadline: July 26, 2001
- Several eligibility requirements

IIA Programs
Regular Investigator Grants
- Typically $75 - $150K/yr for 3 years with 1 or 2 PI's
- Peer reviewed by mail
- Deadline: none, but August to November is best time to submit the proposal based on budget availability

Focussed Research Group (FRG)
Typically $180 - $250K/yr for 3 years and 3 to 4 PI's
- The whole is greater than the parts
- Mail reviewed (co-review with other programs/divisions desirable)
- Deadline: none, but August - October preferred for accessible funds

Conference Grants
- Typical support level $5 - $10K for one year
- The GPG describes the necessary information for a conference proposal
- PD reviewed

NSF-EC Cooperative Int. Program
- Supports the US portion of collaborative research with the European Commission
- A broad funding range exists
- Mail and panel reviewed
- FY 2002 deadline: July 17, 2001
- See Dear Colleague letter (NSF 01-105)

FY 2002 Education Proposals IGERT (NSF 00-78)
- Integrative Graduate Education and Research Traineeship (IGERT) Program
- Fall proposal deadline date: Jan. 18, 2002 (proposals in June)
- Looking for new models of graduate training with multidisciplinary research themes
- Proposals are panel reviewed

FY 2002 DMR Education Grants
- DMR supports innovative education approaches to materials-related education
- 20 grants listed on DMR WEB page
- Target date: November 1, 2001
Additional points made by speaker:

Division of Materials Research (DMR)/Metals Program at NSF:
- 01-02 funding increased by 8% (majority of increase to bio-, nano-, and information technology)
- Mission: People - Ideas - Tools
- Types of Grants:
  - Regular
  - FRG (Focused Research Group)
  - GOALI (Grant Opportunities for Academic Liaison with Industry)
  - SGER (Small Grants for Exploratory Research)
- Metals funding stays at the same level at around 11 million dollars
Microstructure - Process - Property Models for the Aluminum Industry
Joanne L. Murray, Alcoa Technical Center, Alcoa Center, PA

Microstructure - Process - Property Models for the Aluminum Industry

Joanne Murray
Alcoa Technical Center
2002 March 21

Production of Body Stock Alloys
courtesy of Tom Rouns, Alcoa Technical Center

Scalping removes the as-cast surface of the ingot

Preheating heats the metal for hot rolling and produces the correct microstructure for hot rolling and subsequent operations

Microstructural Changes During Preheating

Many complex simultaneous reactions:
• Dissolution of Mg₂Si
• Precipitation of Al₁₂Mn₃Si dispersoids
• Transformation of Al₆[Fe,Mn] to Al₁₂[Fe,Mn]₃Si insoluble constituents
• Partial dissolution of Al₁₂Mn₃Si dispersoids
• Growth of insoluble constituents by Mn diffusion
• Growth of Al₁₂Mn₃Si dispersoids

Aluminum alloys & products

<table>
<thead>
<tr>
<th>Non-heat treatable - Work-hardened</th>
<th>Heat treatable - Precipitation hardened</th>
<th>Other</th>
</tr>
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<tbody>
<tr>
<td>1xxx Al-Fe-Si</td>
<td>6xxx Al-Mg-Si</td>
<td>Casting alloys</td>
</tr>
<tr>
<td>• Commercial purity Al</td>
<td>• 6061 - Medium strength structural alloys</td>
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<td>• 6063 - soft alloy extrusions, architectural applications</td>
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<td>• 6262 - free machining</td>
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<td>2xxx Al-Cu-X</td>
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<td>5xxx Al-Mn-Mg</td>
<td>7xxx Al-Mg-Zn-X</td>
<td></td>
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<td>• 5182 - end stock</td>
<td>• 7x75 high strength, corrosion resistant</td>
<td></td>
</tr>
<tr>
<td>• Lighting sheet</td>
<td>• 7x50 high strength, better corrosion resistance, less quench sensitivity</td>
<td></td>
</tr>
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</table>
Hot Reversing Mill

- Single stand/multiple pass
- Ingot thickness reduced to ~4'' in multiple passes
- Both head and tail sheared at final slab thickness

5 Stand Hot Continuous Mill

- Multistand/single pass rolling
- Slab thickness reduced to hot mill gauge of ~0.1''
- Coiled at exit temperatures that allow recrystallization

Hot Continuous Mill: exit – cooling – coil storage

Continuous Cold Rolling

- Two unwind stations
- Coils ends are butt welded together
- Sheet unwound into accumulator
- Accumulator pays-off into cold mill while next coil is welded
Continuous Cold Rolling

- Multistand/single pass rolling
- Hmg thickness reduced to finish gauge of <0.01"
- Coiled at exit temperatures that allow stabilization

Oiler and Slitter

- Oil applied to sheet
- Slit to width, cut to length

Example research goals

- Preheat and solution treatment practice improvement and simplification
- Reduce end-to-end variability
- Continuous casting
- Grain structure control
- Development of aging practices
- Reduce through thickness variability

Alloying additions and/or impurities
No element is completely soluble in aluminum, most solubilities are quite limited

- Major: Ag, Cu, Li, Mg, Mn, Si, Zn
- Minor: Cr, Zr, V, Mn, Fe, Si
Almost all systems have eutectic reactions

Melting reaction data:

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<tr>
<th>eutectic</th>
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<td>No</td>
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Peritectic systems that need work

Ternary+ systems

Al-Mg-Si-Sn
Al-Mg-Si-Pb
Al-Mg-Si-Bi

for free machining alloys

Al-Cu-Mg-Ag

-Si-Zn...

to follow up on Polmear's work

• Al-Cu-Li solvus along polythermal sections
• Al-Cu-Mg-Li
• Al-Li-Zn
• Al-Li-Si ...

for preheat of Li bearing alloys
Elements of very low solubility

- Na
- Ca
- S
- P

- Represent interactions in the Hall bath
- Important in quest for inert anode
- Na, Ca, Li removed by gas fluxing (furnace or in-line) or salt fluxing
- Low levels may affect alloy properties

Phase diagrams to support modeling of continuous casting

Metallurgical characteristics of interest are through thickness variation of -

- Grain structure
- Cell structure
- Dendrite arm spacing
- Constituent particle size, number
- Solute distribution

**Modeling requires (in addition to the usual suspects) the phase diagram under pressure**

Thermodynamic properties to support modeling of aging processes (esp. nucleation)

- Free energies of the non-equilibrium crystal structures
- Interfacial strain and energies for 2nd phase particles
- Bulk modulus(T)

- (Also - heats of formation of phases for which we have no measurements)

*Via VASP or other first principles techniques*

Impurity diffusion data

*Graph showing diffusion coefficients for various impurities in aluminum*
Diffusion: needs

- Grain boundary diffusivities
- Effect of non-equilibrium vacancy distributions

Example: surface quality and bending of autobody sheet as a function of hot mill lay-on temperature

- If Mg$_2$Si growth occurs while the sheet is on the hot mill,
- then it sees a non-equilibrium vacancy distribution that varies through-thickness,
- because most of the deformation occurs at the surface of the sheet,
- Variation of diffusivity gives rise to variation of Mg$_2$Si particles,
- which in turn gives rise to through-thickness variation of properties.

Additional data to support modeling

- Liquid Al – oxide/nitride/carbide interface energies
- Average grain size distribution and average grain boundary mobility in a real commercial material

Additional points made by speaker:

Elements of interest can be grouped in:
- Major elements; Ag, Cu, Li, Mg, Si, Mn, Sn
- Minor elements; Cr, Zr, V, Mn, Fe, Si

Aluminum industry has two basic alloy groups:
- Non-heat treatable alloys - e.g., 1xxx, 3xxx, 5xxx series
- Heat treatable alloys – high-strength 2xxx, 7xxx series

An example of a modeling opportunity in the area of non-heat treatable alloys is prediction of metastable phases formed during solidification. Different phases form depending on, for example, solidification rate. The distribution of these phases affects the (important) surface finish properties.

Modeling opportunities abound in the area of heat treatable alloys. To optimize homogenization heat treats, one needs standard phase diagrams and relatively simple diffusion models, but the solvus and melting temperatures are needed with very good precision (i.e., < 2.5 °C (5 °F)). More sophisticated precipitation models are needed to design new alloys with optimized combinations of strength, fracture toughness and corrosion resistance.

Some other microstructure modeling needs are associated with grain structure, texture, pressure dependence of solidification microstructure.

In summary, the success of computational materials science in the steel industry demonstrates the feasibility of using a computational approach to design industrial processes. It remains to develop the corresponding databases for aluminum alloys and to codify our practical expertise in terms of quantitative microstructure models.
Applications of Computational Thermodynamics to Virtual Aluminum Castings
Ravi Vijayaraghavan, Ford Motor Company, Dearborn, MI

Contributors
- John Allison
- Chris Wolverton
- Xinyan Yan - ALCOA
- Mei Li
- Jacob Zindel
- Shannon Weakley (University of Michigan)
- Larry Godlewski
**Initial Validation**

- R. Vijayaraghavan, J.W. Zienel and J.E. Allison

*Data from ASM Specialty Handbook, Aluminums and Alloys, 1993*

<table>
<thead>
<tr>
<th>Element</th>
<th>Si</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
<th>Mg</th>
<th>Zn</th>
<th>Ti</th>
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<td>Compo.</td>
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<td>3.6</td>
<td>0.03</td>
<td>0.11</td>
<td>0.1</td>
<td>0.90</td>
<td>0.14</td>
<td>379</td>
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</table>

**Quench Experiments**

*Influence of Quenching Temperature on Quench Experiments*

**Effect of Iron in 319**

- Increase in Fe causes
  - Decrease in ductility
  - Increase in tendency for microvoids
  - Decrease in fatigue strength

**Iron Intermetallies**

**Modified Chemistry**

- Al (FeSi), Aluminium-rich solid solution
- Eutectic Silicon
- Al + Fe phase
- Script - Al(FeSi)3
- β phase or AlFeSi phase (AlFeSi)
- Q phase (Al2C6)2Si3

*Ford Motor Company*
Prediction of Microstructure and Micromegregation in 319 Aluminum Alloys

X. Yan, R. Vijayaraghavan, S.-I. Chen and Y. A. Chang

- Directly coupled to multicomponent phase diagram calculation engine
- Undercooling
- Convection
- Back diffusion in primary aluminum
- Thermal history as input

Predictions
- Solidification path
- Phase evaluation
- Concentration profiles of alloying elements
- Secondary dendrite arm spacing

First-Principles + Computational Thermodynamics

Providing inputs to materials properties models

Chris Wolverton*, John Allison, Ravi Vijayaraghavan (Ford)
V. Ozolins (Sandia National Laboratories)
Xin-Yan Yan (Univ. of Wisconsin/Alcoa)

(*cwolverton@ford.com)

Microstructure Prediction

Yield Strength - Wedge Casting

Solidification Time (minutes) vs. 0.2% Yield Strength

Phase Fraction of Intermetallics

Phase Fraction of Strengthening Precipitates in 319

First-principles free energies for Al_2Cu 0 phase
Existing commercial empirical thermodynamics code

Modeling Properties - Thermal Growth

First-principles results + Computational thermodynamics + Experiments

Measured (symbols) vs. model (curves) thermal growth during aging of W319.

Application of DICTRA

Mai Li, Ravi Vijayaraghavan and John Allison

Yield strength model

Intrinsic, precipitation, solid-solution, unknown

With and without a chilled bulkhead

4.6 l Truck Block (Yield Strength in MPa)

Without chilled bulkhead

With chilled bulkhead

Modeling the aging behavior of Al-Si-Cu alloys

S.C. Weakley, W. Donkin, C. Wolverton, J.W. Jones, J.L. Allison

\[ \sigma_i(U,C) = \sigma_i(U) = \sigma(C) = \sigma(U,C) \]

Yield Strength

Precipitation strength

Solid solution strength

Intrinsic strength

"Unknown" strength

Predicted Yield Strength

Yield Strength

Specimen Location: Hot Base 602 Hot Base 602 Hot Base 909

YS Experimental 416 407 411

Prediction 400 400 400

Virtual Aluminum Castings

Initial Geometry Filling Thermal Analysis

Mechanical Prop. Yield Strength Microstructure (MMC)

Without chilled bulkhead

With chilled bulkhead
Additional points made by speaker:

The design of alloy and process for a cast aluminum-alloy engine parts (blocks, heads) by a coupled thermodynamic-kinetic-property-service model is maturing in a program at Ford. A suite of codes has been developed and is being tested. These codes include a thermodynamic calculator and database to predict thermodynamic properties, effect of process variables, solidification microstructure, material properties (residual stresses) and service behavior. Structural analysis is carried out with the software package Abacus.

A major effort in alloy improvement is also underway as part of the modeling effort. Alloy 319 is being examined for potential 5% to 10% cost saving through increase in Fe content. Work is well underway to model and predict various properties as a function of Fe content and Fe plus second-element effects. The modeling program is closely matched with an experimental verification program on these alloys.

Solution and aging heat treatment is an area of great opportunity in the cast aluminum systems. Work is beginning with kinetic modeling of phase transformation using the DICTRA software program. Although empirical modeling of properties such as hardness exists for these processes, it is hoped that more robust models, based on phenomenological descriptions, will lead to new alloy and process developments.

Future needs:
- Mg and expanded Al diffusion mobility databases
- Automated optimizer for multicomponent data descriptions
- Comparison of results from first principles with thermodynamics databases
- Extension of first principles and phase field modeling for multicomponent systems
- First principle modeling of the liquid phase
Use of Quasi-Thermodynamical Models for Simulation of Epitaxy of III-V Compound Semiconductors in Electronic Industry

Yuri N. Makarov, Semiconductor Technology Research Inc., Richmond, VA

Outline
- Introduction
- Modeling of epitaxial growth
- Chemical processes in MOVPE
  - Gas-phase chemistry
  - Surface chemistry
- Quasi-thermodynamic model of surface chemistry
- Application example: growth of group III-nitrides
  - Evaporation of group III-nitrides
  - GaN MOVPE
  - InGaN and AlGaN MOVPE
- Conclusions

Activities:
Research projects in USA and Europe
Consulting in the area of crystal growth and epitaxy
EUROPE: AIXTRON, Wacker, Osram, Nukem, SiCrystal, Forschungszentrum Jülich, FBH, etc.
USA: Emcore, Fox Group, CFD Res. Corp., Cornell University, Cree, TDI, Kyma, Crystal IS, NCSU, etc.

Supply of software for modeling of crystal growth and epitaxy:
- “Virtual Reactor” software for modeling of sublimation growth of SiC, AlN;
- CVD-Module for modeling of MOVPE/CVD processes on the basis of commercial code CFD-ACE
- Simple 1D code for modeling of MOVPE of III-V’s and nitrides in vertical and horizontal reactors

What is Semiconductor Technology Research, Inc.?
Pre-history:
1993-1996 Group for modeling of crystal growth and epitaxy at University of Erlangen-Nürnberg, Germany
1996- establishing CompuSoft International Ltd. in Savonlinna, Finland

Today: Consortium for modeling of crystal growth and epitaxy:
STR Inc., Richmond, USA
STR GmbH, Erlangen, Germany;
CompuSoft Int., Savonlinna, Finland;

Metal organic vapor phase epitaxy (MOVPE) of compound semiconductors - why?
High Efficiency Solar Cells
High Brightness LEDs

InP, InGaP
GaAs, InGaP, AlGaAs
GaN, InGaN, AlGaN
GaAs, AlGaAs, InGaAs
Metal organic vapor phase epitaxy (MOVPE) of compound semiconductors – how?

General scheme of deposition process

Gas flow (III and V group precursors and carrier gas)

Gas-phase reaction mechanism: unimolecular decomposition of TMGa

This reaction mechanism is typical for all group III precursors: Trimethylgallium (TMGa), trimethylaluminum (TMAI), trimethylindium (TMIn).

Gas-phase chemistry in AlGaN growth

Possible ways of aluminum losses:
1. Condensation of adduct TMAI:NH3 on reactor inlet and cold walls
2. Formation of oligomers and AlN particles
Chemistry in MOVPE

- Gas phase chemical reactions may affect the deposition rate and uniformity by several reasons: a) different diffusion rates of precursors and reaction products; b) parasitic reaction leading to formation of particles and losses of material;
- Rate constants of reactions are usually taken from experiments on precursor pyrolysis in flow tube reactors. The estimation of molecular structure and bond energies of precursors using quantum chemistry methods may be very useful to evaluate the validity of commonly accepted rate parameters.
- The main “bottleneck” in MOVPE modeling is the description of surface chemical processes.

Key features of the quasi-thermodynamic model of chemical processes at the growing surface

Basic assumptions:
1. The rates of atomic incorporation into the crystal and of the crystal decomposition are much higher than their net difference (quasi-equilibrium between the adsorption layer and the crystal bulk).
2. Kinetic effects at the stage of adsorption/desorption are accounted for by the sticking/gas desorption coefficients of individual species.
3. Kinetic effects at the stage of species transport are accounted for by solving transport equations (Navier-Stokes equations)

Capabilities important for modeling of semiconductor growth:
- the model allows the calculation of species desorption rates from thermo-chemical properties of gaseous and solid substances;
- the accounts of the elastic strain effect via a contribution to the Gibbs energy of solid phase

Group III-nitrides – metastable materials with unusual properties

- Nitrides do not react chemically with nitrogen; nitrogen activation is required for growth.
- GaN evaporates congruently under vacuum conditions; higher pressures change evaporation mechanism.
- Nitrides are stable at temperatures > 300°C, whereas the thermodynamic estimations predict crystal decomposition
- Liquid phase has catalytic effect on crystal decomposition

Formation of kinetic barrier in adsorption and desorption of nitrogen

Full kinetic model for surface processes

Drawback:
- lack of necessary information on mechanisms and reaction rate constants requires to fit parameters

Advantages of quasi-thermodynamic model for surface processes

- Works in a wide temperature range
- Works in a wide range of pressure including vacuum
- Allows one to take into account kinetic effects
- Requires to build up kinetic model only for a limiting stage
- Can be ease extended to alternative set of species and chemical reactions

<table>
<thead>
<tr>
<th>Reaction</th>
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<tr>
<td>AsH₂(a) + H(a)</td>
<td>AsH₃ + V</td>
</tr>
<tr>
<td>AsH₂(a) + H(a)</td>
<td>AsH₃(a) + V</td>
</tr>
</tbody>
</table>
Kinetics of nitrogen evaporation and condensation – reason for the metastability

Surface chemical processes during GaN growth

Rate-limiting processes
- Low temperatures: sites for Ga adsorption are blocked by methyl radicals
- Intermediate temperatures: transport of Ga containing species to the growing surface
- High temperatures: Ga desorption

There is the strong experimental trend to move towards the high GaN growth temperatures because of the better quality of the material. Accurate description of gallium desorption from the growing surface is necessary for predictive modeling.

Surface chemical processes during InGaN growth

Primary reaction pathways
- Adsorption of gaseous species
- Ammonia cracking on the surface giving rise to N\textsubscript{2} and H\textsubscript{2}
- Indium, gallium, and nitrogen incorporation into the crystal
- Desorption of indium: the limiting process for indium incorporation at elevated temperatures.

2D modeling of InGaN MOVPE in AIX 200 RF reactor: comparison to experimental data

The model provides a good quantitative reproduction of the experimental data without any parameter fitting. Account of the strain effect is very important.
Effects of strain and T:

- In content decreases gradually with temperature due to indium desorption.
- Elastic strain enhances indium desorption

![Diagram of In content vs. temperature for different strain conditions](image1)

Composition fluctuations in InGaN/GaN heterostructures

- Double PL peaks are observed in the temperature range 700-800°C where the strain effect on InGaN composition is mostly pronounced.

The appearance of In-rich and In-depleted zones is related to coexistence of strained and unstrained InGaN islands rather than to phase separation.

Effects of surface chemistry in AlGaN MOVPE: effect of growth temperature

- At high temperatures, desorption of gallium becomes significant and results in depletion of the growing layer with gallium

![Diagram of X_M vs. growth temperature](image2)

Effects of surface chemistry in AlGaN MOVPE: effect of the growth rate

Intensive gallium desorption may be suppressed by increasing total group-III flow (growth rate).

![Diagram of X_M vs. total group-III flow](image3)

Particle formation during chemical vapor deposition of SiC

- Irradiant layer observed over substrate in experiment at Siemens (Erlangen, Germany)

![Particles on the substrate](image4)

Particle formation during chemical vapor deposition of Si (cooperation with NIST - R. Davis, J. Maslar)


Summary

- The main difficulties in MOVPE modeling are related to development of predictive surface chemistry models.
- Quasi-thermodynamic approach allowing description of the surface chemical processes and growth on basis of thermochemical data of gaseous and solid species, represents the good alternative to detailed multistep kinetic models.
- Quasi-thermodynamic models of nitride crystal growth and epitaxy require reliable thermodynamic properties of solid phases and vapor species.

What we need?

- Reliable thermodynamic properties of GaN, AlN, InN, AlGaN, InGaN, AlGaN, AInN
- Thermodynamic properties of vapor species and products of decomposition
- Thermodynamic properties of different adducts between metalorganic species and ammonia
- Kinetic parameters of rate-limiting processes (diffusion coefficients, rates of gas phase chemical reactions, sticking probabilities, etc.)
- Experiments and models of adduct and particles formation in the gas phase during CVD

Use of Valence Force Field (VFF) modeling for estimating thermodynamic properties of multi-component compounds

Enthalpy of mixing for ternary compounds

Comparison with experimental data

Interaction parameter \( W \) is defined by the expression

\[
H_{\text{mix}} = W \cdot x(1-x)
\]

<table>
<thead>
<tr>
<th>Compound</th>
<th>VFF-modeling (kJ/mole)</th>
<th>Experiment (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>InGaAs</td>
<td>12.985</td>
<td>11.76–12.56</td>
</tr>
<tr>
<td>InGaP</td>
<td>16.112</td>
<td>13.36–18.45</td>
</tr>
<tr>
<td>InGaN</td>
<td>30.464</td>
<td></td>
</tr>
<tr>
<td>GaAsP</td>
<td>4.283</td>
<td>4.19</td>
</tr>
</tbody>
</table>
Contributors:


Additional points made by speaker:

Group III nitrides offer the opportunity to develop super-bright LED lights with a potential market in the $20 B range.

Metal organic vapor phase epitaxy (MOVPE) is the preferred method of fabrication for these semiconductors. Current drawbacks to development are associated with a lack of good process models and empirical data. The quasi-thermodynamic model presented here offers a way to overcome this lack of data.

The semiconductor nitrides of greatest interest are GaN, AlGaN, and InGaN. Progress has been made using a quasi-thermodynamic approach to model the epitaxial growth process at the growing surface. The ability to accurately model the growth process is complicated by the process variables of strain, temperature, pressure, surface chemistry, and kinetics. The quasi-thermodynamic model takes the host of process variables into account and has been applied to group III nitrides. Results are encouraging to date. Opportunities exist in the need for accurate surface chemistry models, data on thermodynamic properties of III-nitrides, and kinetic parameters for various reactions.
**NSF Supported Computational Education Program at Penn State**
Zi-Kui Liu, Penn State University, University Park, PA

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**An Integrated Education Program on Thermodynamics, Kinetics, and Materials Design**

Supported by NSF DMR-0073836

Zi-Kui Liu (liu@matse.psu.edu)
Long-Qing Chen, Karl Spear and Carlee Allison

Department of Materials Science and Engineering
The Pennsylvania State University

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**Objective**

- Improve the student learning experience and educator teaching experience on two of the core components in the curriculum of materials science and engineering, i.e. Thermodynamics and Kinetics, emphasizing on graduate study.

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**Conventional Situation**

- Common stereotype: Thermodynamics and kinetics are problematical to learn and difficult if not impossible to apply in the real world.
- Traditionally, the fields of materials science and engineering have been predominantly on processing of materials, establishing structure-property relations, and measuring properties.

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**Current Graduate Curriculum**

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**Materials Science and Engineering**

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**Materials Science and Engineering**

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**Performance**

**Property**

**Structure**

**Processing**

**Chemistry**

**Thermodynamics**

---

**Crystallography**

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**Kinetics**

---
**An Integrated Education Program on Thermodynamics, Kinetics, and Materials Design**

**Development in Recent Years**

- **Computational Thermodynamics**
  - Coupling of phase equilibrium and thermochemistry (CALPHAD)
  - First-principles calculations
- **Phase transformation simulation**
  - Sharp interface
  - Diffuse interface (phase-field)
- **System materials design based on the above**
  - Northwestern University and Questek Innovation

**Faculty Expertise at Penn State**

- **NSF**: 34 faculty members, 150 graduate students.
- **Karl Spear**
  - Thermodynamic modeling of ceramics
  - Teach graduate thermodynamics
- **Long-Qing Chen**
  - Phase-field simulation
  - Teach undergraduate thermodynamics, graduate kinetics
- **Zi-Kai Liu**
  - Thermodynamic modeling of alloys
  - Teach undergraduate phase transformation
  - Knowledge of system materials design

**The Project**

- **Time Period**: 09/01/00-08/31/03.
- **Financial support**: NSF, University matching and in-kind.
- **Build a new PC lab in the department**
- **Web site**: http://nsfedu.metsce.psu.edu

**Modified Undergraduate Courses**

- **MatSE 401**: Thermodynamics of Materials
  - Introduction of computational thermodynamics: P-T diagrams of pure elements.
- **Mat 405**: Phase Transformations in Alloys
  - Calculation of phase diagrams and equilibrium phase fractions
- **Mat 435**: Metallurgy Lab II
  - Experimental and calculated phase diagrams
- **Mat 436**: Metallurgy Lab III
  - A computational lab on avoiding clogging in a continuous casting process

**The Computer Lab with 20 PCs for students**
### Modified Graduate Courses

- MatSC501: Thermodynamics of Materials
  - Addition of one session every week on computational thermodynamics
  - Homework on computational activities
  - Exams based on the output of calculations
- MatSC503: Kinetics of Materials
  - Introduction of mobility database
  - Homework on diffusion simulation (Dictra)
  - Introduction of Monte-Carlo, microscopic diffusion and phase-field simulation tools.

### New Courses

- MatSC597C: Introduction of Computational Thermodynamics
  - Thermodynamic modeling. Database development
- MatSC597K: Computational Materials Science II: Continuum, Meso-scale Simulations
  - Dictra, Monte-Carlo, Phase-field
- MatSC598A: System Materials Design
  - Engineering design principles. Materials design procedure. Design projects.

### Example of MatSE401

![Pure Fe](image)

**Reference State?**

### Example of Metal405

![Graphs](image)

### Metal 436: Computational Lab

- A manufacturer wanted to increase the Cr content of a material from 18 to 25 weight per cent. However, clogging starts to occur during the continuous casting of this material because solid Cr₂O₃ is formed. By calculating the equilibria in the steel/slag system, a simple correction could be found through the adjustment of the steel melt composition or temperature.

### Homework of MatSC501

- Answer the following questions using FactSage.
  - Can a Ni(s) crucible be used to contain Fe₃O₄ with no reaction at 1000K? Answer the question here. If a reaction occurs, what are the solid products?
  - Can a Ni(s) crucible be used to contain Fe₂O₃ with no reaction at 1300K? If a reaction occurs, what are the solid products?
  - Can a Na(s) crucible be used to contain Li₂O with no reaction at 1300K? If a reaction occurs, what are the solid products?
Homework of MatSC501

- A flowing H₂O₂ gas mixture is equilibrated with a large quantity of a Ti(s) + TiO(s) mixture at 1000K before it passes over small separated samples of Sc, V, Mn, Cr, Zr, Cu, Co, and Ni heated at 1000K. The gas is passed over these samples until they finally equilibrate with the H₂O₂ gas mixture.
  - What will the chemical state of the above metals be when the above described equilibrium is reached in the system?
  - What will the final oxygen potential be at equilibrium in the 1000K furnace?

Software in MatSC503

MatSC507C: Computational Thermodynamics

- Introduction
  - Review thermodynamic principles
  - Relate chemical reactions and phase diagrams to thermodynamic principles
- Thermodynamic Modeling of Pure Substances, Binary and Multicomponent Systems
  - Method of modeling
  - Modeling of random solution phases and multicomponent solution phases
- Computational Techniques and Applications
  - Database of pure substances
  - Database of binary systems
  - Database of ternary and multicomponent systems
  - Case studies of real problems
- Mini-project of the course

MatSC507K: Continuum, Mesoscale Simulations

- Dr. Liu
  - Review thermodynamic and kinetic principles
  - Modeling of kinetic stability
  - Simulation of diffusion and phase transformations
- Dr. DaNey
  - Monte Carlo simulation of grain growth
  - Finite-temperature transformation simulation for inclusion
- Dr. Chen
  - Kinetic Monte Carlo simulations, ordering and phase separation
  - Phase-field simulations and twin formation
  - Dislocation loop dynamics
  - Phase-field simulations and twin formation
  - Phase-field simulations and twin formation
  - Phase-field simulations and twin formation

Thermodynamic Modeling

**Thermochemical data:**
- enthalpy, entropy, heat capacity, activity

**Phase equilibrium data:**
- liquids, solids, phase boundary

Gibbs Energy of Individual Phases

Applications

Special Issue of CALPHAD on Computational Tools:
- EThERM, FACT, MTDATA, PANDAT, THERMOCALC, THERMOSUITE
MatSC59A: System Materials Design

- Principles of Design
  - Materials selection
  - Materials as a system
  - System approach to design
  - Cost and time management
- Design Tools
  - Thermodynamic design of microstructure
  - Computational thermodynamics (Thermo-Calc)
  - Computational Kinetics (Dictra)
- In-Class Example
- Team Project

MatSC598A: Project One:

Research data demonstrate that 80 to 96% of air pollutant due to exhaust gas of a vehicle is generated within 200 seconds between a vehicle start and the time the catalyst reaches its optimal operating temperature (around 340°C). This is particularly a problem for vehicles used for delivery as they are switched on and off often every day. You are asked to make a material-related design to develop an optimal solution for this case using the system materials design approach.

MatSC598A: Project Two:

Today's commercial high strength low alloys (HSLA) have typical yield strength of 80ksi (about 5664 MPa or 550 MPa). The figure below shows the development of HSLA in the past half century. With the ocean exploration of gas and petroleum going to deeper and deeper water and the increase of pipeline pressure, a yield strength as high as 120ksi is desirable. Design such an alloy using the System Materials Design approach with other properties balanced based on your application.

Evaluation Procedures

- Focus groups to gather student feedback
- Surveys of attitudes and knowledge
- Classroom observations
- Analysis of student presentations and reports through use of rubrics

Survey Results

- The majority of students indicated that course packets containing notes, problems, and guides for using the technology would aid their learning.

2002 Summer Workshop

- May 20-21 Computational Thermodynamics
- May 22-23 Processing Simulation and Dictra, and Introduction of Phase-Field Simulation
- May 24-25 Thermodynamic and Kinetic database development
- http://nsfedu.metsee.psu.edu
Additional points made by speaker:

Examples of course problems and materials:
- Clogging in continuous casting
- Phase diagram and free energy curves
- Thermodynamic modeling

Materials design projects:
- Catalyst design
- 830 MPa (120 ksi) HSLA (high-strength low-alloy) steel

Questions/comments from workshop attendees:

Are course materials available?
- Workshops are free to participants from education
- Materials can be distributes by CD or e-mail
- Web site

How many students are involved?
- 30, mostly PhD students
# Thermodynamic Measurements

Philip Nash, Illinois Institute of Technology, Chicago, IL

## Introduction

- Alloy and process development requires a thorough knowledge of phase equilibria and thermodynamics.
- Microstructural development, non-isothermal processing, distortion, quenching.
- Available experimental data is limited particularly for ternary and higher order systems.
- Calphad technique offers a method of determining phase equilibria and thermodynamics in an alloy system in much shorter time than by experimental methods.

## Data Needed for Modeling

- Gibbs energies of individual phases as a function of composition and temperature.
- Heat capacities.
- Activities.
- Enthalpies of formation, mixing, transformation.
- Entropies of formation, mixing, transformation.
- Phase equilibria (temperatures, compositions).
- Physical properties (density, thermal expansion, etc.).

---

**Outline**

- Introduction
- Experimental Methods
- Experimental Thermodynamic Activities
- Summary
Experimental Methods

- Calorimetry
  - Direct reaction
  - Solution
  - Solute-solvent drop
  - Differential scanning
- Vapor pressure
  - Gas phase equilibria
  - Rate of evaporation
- EMF
- Other methods

Experimental

The heats of formation are determined using a high temperature reaction calorimeter with a typical accuracy of ±1 kJ/mole.

The measurements are generally made with the calorimeter set at 1473K, using an argon atmosphere.

The calorimeter is calibrated using pure copper.

Samples are produced by mixing elemental powders in a mortar in the required molar ratio and pressing them into a small pellet.

Typical sample weight is about 100 mg.

![Kleppa Calorimeter](image)

![Al-Ni-Y Isothermal section](image)

![Heat of Formation of NiAl](image)

![Fig. 1: Assessed Al-Ni Phase Diagram](image)
Results

By using direct synthesis, the standard enthalpy of formation, $\Delta H_f^{298K}$, is calculated from:

$$nAl(s, 298K) + bNi(s, 298K) = cY(s, 298K) = AlNi_y Y (1473 K) \quad \Delta H_{f,\text{reaction}}$$ (1)

$$AlNi_y Y (s, 298 K) = AlNi_y Y (1473 K) \quad \Delta H_{f,\text{solid}}$$ (2)

From reaction (1) and (2) we get

$$nAl(s, 298K) + bNi(s, 298K) + cY(s, 298K) = AlNi_y Y (s, 298 K)$$

The standard enthalpy of formation is thus obtained.

$$\Delta H_f^{298K} = \Delta H_{f,\text{reaction}} - \Delta H_{f,\text{solid}}$$

$\Delta H_{f,\text{reaction}}$ and $\Delta H_{f,\text{solid}}$ are molar enthalpy changes for reaction (1) and (2).

Enthalpies of Formation of Al-Ni-Y Intermetallics

Advantages and Limitations of Direct Synthesis Calorimetry

- Advantages
  - Only two heat effects need be measured
  - Absolute temperature measurement not needed
  - High accuracy (typically ±1kJ/mol)
  - Experiment directly yields enthalpy of formation at 298K

- Limitations
  - Some systems give incomplete reactions, particularly very high melting point compounds
  - Temperature drift
  - Reduction in sensitivity over time

Table 2: Summary of high temperature reaction calorimetry results and Modak's semi-empirical model results. Calorimeter temperature set at 1473K unless noted.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H_{f,\text{calorimetry}}^{298K}$</th>
<th>$\Delta H_{f,\text{calorimetry}}^{298K}$</th>
<th>$\Delta H_{f,\text{calorimetry}}^{298K}$</th>
<th>$\Delta H_{f,\text{model}}^{298K}$</th>
<th>Melting point</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Al_{2}Ni_{3}Y$</td>
<td>-296.1 ± 0.5</td>
<td>323.2 ± 0.5</td>
<td>-92.9 ± 0.5</td>
<td>-117.3 ± 0.5</td>
<td>1270K</td>
</tr>
<tr>
<td>$Al_{2}Ni_{3}Y_{2}$</td>
<td>-416.0 ± 0.5</td>
<td>313.2 ± 0.5</td>
<td>-62.8 ± 0.5</td>
<td>-141.3 ± 0.5</td>
<td>1310K</td>
</tr>
<tr>
<td>$Al_{2}Ni_{3}Y_{3}$</td>
<td>0.00 ± 0.5</td>
<td>464.0 ± 0.5</td>
<td>-48.5 ± 0.5</td>
<td>-66.5 ± 0.5</td>
<td>1270K</td>
</tr>
<tr>
<td>$Al_{2}Ni_{3}Y_{4}$</td>
<td>0.00 ± 0.5</td>
<td>297.1 ± 0.5</td>
<td>-9.9 ± 0.5</td>
<td>-89.9 ± 0.5</td>
<td>1270K</td>
</tr>
<tr>
<td>$Al_{2}Ni_{3}Y_{5}$</td>
<td>0.00 ± 0.5</td>
<td>297.1 ± 0.5</td>
<td>-9.9 ± 0.5</td>
<td>-89.9 ± 0.5</td>
<td>1270K</td>
</tr>
<tr>
<td>$Al_{2}Ni_{3}Y_{6}$</td>
<td>0.00 ± 0.5</td>
<td>297.1 ± 0.5</td>
<td>-9.9 ± 0.5</td>
<td>-89.9 ± 0.5</td>
<td>1270K</td>
</tr>
<tr>
<td>$Al_{2}Ni_{3}Y_{7}$</td>
<td>0.00 ± 0.5</td>
<td>297.1 ± 0.5</td>
<td>-9.9 ± 0.5</td>
<td>-89.9 ± 0.5</td>
<td>1270K</td>
</tr>
<tr>
<td>$Al_{2}Ni_{3}Y_{8}$</td>
<td>0.00 ± 0.5</td>
<td>297.1 ± 0.5</td>
<td>-9.9 ± 0.5</td>
<td>-89.9 ± 0.5</td>
<td>1270K</td>
</tr>
<tr>
<td>$Al_{2}Ni_{3}Y_{9}$</td>
<td>0.00 ± 0.5</td>
<td>297.1 ± 0.5</td>
<td>-9.9 ± 0.5</td>
<td>-89.9 ± 0.5</td>
<td>1270K</td>
</tr>
</tbody>
</table>

*Calorimeter set at 1473K

Heat of Mixing

Schematic of calorimeter set-up for mixing measurements. Solute reaches thermal equilibrium with solvent before being dropped
Differential Scanning Calorimetry

- The temperature difference controls the electrical power to the sample and reference in order to maintain the same temperature. The peak area directly corresponds to the heat consumed or produced by the sample.

- Temperatures are measured in thin plates in contact with crucibles, thereby measuring the difference in heat flow from them. Signal proportional to the difference in heat capacities between the sample and reference and thus the instrument works as DSC.

Applications of Calorimetry and Sources of Error

- Integral and partial enthalpies of formation, mixing and transformation,
- Heat capacity-error for scanning DSC ~3%, for step DSC ~2%, for drop calorimetry ~5%
- Errors can arise from
  - mass and temperature measurements
  - incomplete reactions
  - reactions with crucible or atmosphere
  - impurities
  - calibration errors
  - heat effect errors

EMF Measurements

\[ \Delta G = - n F E \]

EMF measured as a function of temperature for fixed composition

\[ E = a + bT \]

\[ \Delta G_i = RT \ln a_i = \Delta H_i - T \Delta S_i \]

\[ = -nF(a + bT) \]

Application of Gibbs-Duhem permits calculation of the activity of the second component and hence integral Gibbs energy

Experimental Setup


Measured EMF of Ti-Al intermetallic vs. T

Applications and Sources of Error

- Activities, partial and integral Gibbs energies, enthalpies and entropies
- Major limitation is in maximum temperature

Errors can arise from:
- mass and temperature measurements
- reactions with atmosphere
- impurities
- multiple valence states
- thermal gradients in cell

Facilities for Experimental Studies of Alloy Thermodynamics—Inputs to Calphad, Phase Models

- Evan Copland, Nathan Jacobson—Materials Division, NASA Glenn Research Center, Cleveland, OH
- High Temperature Knudsen Cell Mass Spectrometer for thermodynamic activity measurements
- High Temperature Vacuum Furnace for Liquidus lines
- DTA
- Standard metallographic preparation + optical, electron microscopes

Measurement of Thermodynamic Activities

Measure vapor pressure of element in alloy—compare to pure material—$a(Al) = P_{v}(Alloy)/P_{v}(Pure\ Al)$

Knudsen Cell Technique

- Equilibrate alloy/vapor in small cell
- Sample vapor with mass spectrometer.
- Pressure = IT
- Best accuracy—$\text{mass}$ and $\text{vapor}$ content
- Double or Tropic cell system
- Modified commercial magnetic sector instrument
- Windows based Data acquisition system

Fe-Al System at 1573 K

Ion Current Ratio Technique

Activity coefficient vs. $X_{Al}$ at 850 K

Al Activities in $\alpha_2$ Ti$_2$Al + $\gamma$ TiAl
(Double Cell Technique)

| Ti Activities in $\alpha_2$ Ti$_2$Al + $\gamma$ TiAl
(Double Cell Technique) |
|-----------------------------------------------------|
| $\begin{array}{c}
\text{Ti}\text{Al} \\
\text{Ti}\text{Al}
\end{array}$ |

High Temperature Vacuum Furnace—
Liquidus Data for Refractory Containing Systems

Other Methods
- Equilibrium phase composition by WDS or EDS analysis
- Metallography-phase amounts by lever rule
- XRD-phase boundaries, site occupancy
- DTA-phase boundaries
- Dilatometry-phase boundaries, CTE's
- Diffusion couples-phase boundaries

Experimental Thermodynamics Research Activities in USA
- Ole Kleppa-Direct Synthesis Calorimetry, XRD
  binary alloys
- Philip Nash-Direct Synthesis Calorimetry, DSC, XRD
  binary, ternary alloys, higher-order systems
- Ramana Reddy-EMF
  binary alloys
- A. Navrotsky-Direct Synthesis Calorimetry
  oxides, nitrides
- N. Jacobson, E. Copland-Knudsen Effusion, High T
  liquidus
  binary, ternary alloys

Experimental Thermodynamics Research Activities
- France
  Gachon & Hertz-U. Nancy, Colinet-U. J. Fourier,
  Castanet & Bros-U. Marseille, Legendre-U. Paris
- Germany
  Sommer-Max-Planck-Stuttgart, Schaller-U. Kiel, Hilpert-IMES
- Poland
  Fitzer & Moser-IMM3-Krakow
- Japan
  Yamaguchi-Iwato U., Jacob-Tohoku U., Shoji-Nagoya U.,
  Yamana-Kyoto U., Sheng-ONRI
- Austria
  A. Mikula & H. Ipsen-U. Vienna
- Italy
  Borzone-U. Rome, Ferro-U. Genoa
Summary

- Thermodynamic and phase equilibria can be measured by a variety of techniques and with varying accuracies
- All techniques have inherent limitations
- Calorimetry is the most versatile technique but requires different types of calorimeter to obtain all of the data
- Most data results from studies of individual systems as part of some broader project objectives
- Systematic investigations are needed to yield consistent data that can be used for understanding alloy behavior and as benchmarks for first principles calculations
- Very few research groups in US involved in experimental thermodynamic or phase equilibria studies of alloys

Additional points made by speaker:

Concern was expressed that the number of centers not only in North America but also world wide with expertise in experimental determination of thermodynamic quantities is very small and that abolishment of one of these centers jeopardizes the availability of quality experimental data for thermodynamic quantities.

Improved accuracy for measured data is an important goal.
**Configurational Entropies in Real Alloy Phase Diagram Calculations**

Fan Zhang, CompuTherm LLC, Madison, WI

---

**Why Phase Diagram Calculations? (1)**

- New alloys with desired properties are constantly needed in today's world.
- Phase diagrams are road maps for alloy design — they are the starting point to understanding any phenomenon or process.
- Multicomponent Phase diagrams are needed since commercial alloys usually contain more than four components.
- It is impossible to determine such information purely by experiments.

**Computational Approaches**

- 'First Principles'
- Phenomenological (Calphad)

Successful aspects of Calphad approach:

- Many self consistent thermodynamic descriptions have been published for binaries, ternaries, even quaternaries.
- Thermodynamic databases for multicomponent systems have been developed.

---

**Objective of Calphad Approach**

**Idea:**
- Describe the Gibbs energy of each phase in a system using a simple empirical model equation.
- Optimize the model parameters using the available experimental information.
- Extrapolate the use of the model parameters to temperatures and compositions where the experimental data are not available.

**Objective:**
- To "predict" unknown properties (multicomponent alloys) by known information (binaries & ternaries).
**Workshop Presentations**

**Improve the Calphad Assessments**

- Improve Assessors' Skill
- Improve Models' Reliability

**The Ni-Al System**

**The Ti-Al System**

**Fcc Coherent Diagram by MC, BW, and CVM (Prototype diagram)**

**Configurational Entropy Obtained by the CVM Method**

\[ S^{CVM} = \gamma_4 S_4 + \gamma_3 S_{3p} + \gamma_2 S_p + \gamma_1 S_s \]

\[ S = -R \sum P_{\omega} \ln P_{\omega} \]
\[ S_p = -R \sum P_p \ln P_p \]
\[ S_{\omega} = -R \sum P_{\omega} \ln P_{\omega} \]

\[ G = G(\Omega) + G(\text{ordering} : \Omega \rightarrow \Omega') \]

Entropy of mixing: ideal mixing (Bragg-Williams)

\[ G = E(\beta K) + CTM \]

CompuTherm LLC
A Realistic Approach for Phase Diagram Calculation at the Present Time

1. Modeling equation should include a dash more of physics so that model parameters are more reliable in the "prediction".
2. Modeling equation should be simple so that it is readily applied to multicomponent systems.

Improve the Description of Configurational Entropy Currently Used by Calphad Approach (BW)

The Original CSA presented by Yang and Li[1947]

Basic assumption: energetically non-interfering clusters

Two-term entropy of mixing:

\[ S = \frac{Z}{2p} S_n - \frac{nZ}{2p} \]

Generalized Quasi-Chemical Method

\[ \frac{F}{kT} = \frac{Z}{2p} \sum \phi_i \phi_j \left( \ln \phi_i - 1 \right) \]

The Modified CSA [99Oat]

Original CSA:

\[ S = \frac{Z}{2p} S_n - \frac{nZ}{2p} \]

Modified CSA:

\[ S = \eta \cdot S_n - (\eta - 1)S \]

By using \( \eta \) as an adjustable parameter, more flexibility is obtained in describing the Gibbs energy-composition curves.

By introducing \( \eta \), the cluster interference is approximately taken into account by a two-term expression in the modified CSA. (multi-term expression is used in the CVM)
Application of the CSA to Binary Systems

- Au-Cu system
- Au-Ni system
- Cd-Mg system
- Al-Ni system

Cd-Mg Phase Diagram by FP and CSA

Apply the CSA Model to the Ni-Al System

Summaries

- We are NOT looking for the most accurate calculation of configurational entropies (MC or large cluster CVM) as in PROTOTYPE phase diagram calculations.
- We are looking for a calculation method suitable for REAL alloy phase diagram calculations which gives correct topologies (Bragg-Williams doesn't for no SRO).

The CSA model is very promising for this purpose.

Thank you for your attention!
Additional points made by speaker:

Improved models are needed to avoid physically unreasonable Gibbs energy functions in regimes where the phase is not stable.

Example metastable $\gamma/\gamma'$ in Ni-Al:
- Description of both phases as two independent phases with no order/disorder transition resulted in an unreasonable diagram in regimes of the phase diagram where these phases are metastable.
- Treatment of $\gamma$ and $\gamma'$ as one phases and the use of Bragg-Williams approximations for the calculation of the entropy of mixing do not generate the correct fcc metastable phase diagram due to the neglect of short range order.
  - Diagrams obtained from first principles and CVM (cluster variation method) or MC (Monte Carlo) give the physically most probable metastable diagram (work from Pasturel and Colinet).

Example metastable fcc diagram in Ti-Al:
- Results from different model treatments show diagrams with similar features to Ni-Al.

Questions/comments on various models:
- Bragg-Williams as a point approximation method cannot describe all order/disorder transformations correctly.
- The expression for the entropy in CVM is a too complex for practical purposes. Although these phase diagrams are topologically correct, the accuracy of results is insufficient for practical applications.
- Cluster/site approximation (CSA) in its pure form has the problem that the disordered phase is stable at 0 K. This problem is overcome by the modified CSA with an adjustable parameter. This model gives results that are in good agreement with results obtained from MC.

Questions & Answers:

What about the vibrational entropy? - The model includes additional parameters for the entropy to account for this.
**Current Capabilities in First-Principles Modeling of Alloy Thermodynamics**

Patrice E.A. Turchi, Lawrence Livermore National Laboratory (LLNL), Livermore, CA

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### Objectives

- **Understand Trends in Ordering Phenomena.**
- **Predict Phenomena:**
  - Transient Ordering (with L. Reinhard)
  - Ordering in Complex Phases (with A. Finel)
- **Provide** Thermodynamic Data for Ab Initio Phase Diagram Construction
- **Provide** Estimates of Heats of Formation (from total energy vs. volume results)
- **Provide** Input for Phenomenological Approaches such as CALPHAD
- **Challenge** the validity of some assessed phase diagrams, and the validity of ab initio results

### Methods Limited to Ordered Structures:

- Pseudo-Potential
- LAPW or FP-LAPW
- LMTO or FP-LMTO
- ASW
- FP-LASTO

Methods that can also handle Disordered Structures (via, e.g., the CPA):
- KKR
- TB-LMTO

Properties:
- Equilibrium Properties
  - lattice parameter(s)
  - Structural energy differences
- Elastic Properties
  - bulk modulus
  - elastic constants
  - phonon spectrum
- Electronic Properties
  - densities of states (γ of heat capacity data)
  - spectroscopic data (ARPES, UPS, KPS, PAS)
- Transport
  - conductivity (DC and AC)
  - reflectivity
- Magnetic Properties
  - magnetic moments and magnetic ordering
  - and alloying effects on properties

---

### Background and Motivation

#### Phase Diagrams are:

- The basic road maps for alloy designers
- The graphical results of battles for survival between competing phases.

#### Orders of Magnitude:

- Total Energy $10^8$ Ry/atom
- Formation Energy $10^2 - 10^3$ Ry/atom
- Ordering Energy $10^4 - 10^5$ Ry/atom

#### Units:

- $1\text{mRy}$ ~ 13.6 meV
- $1\text{mRy}$ ~ 157 K
- $1\text{mRy}$ ~ 1312.76 J/mol (or J/g.at)

---

### Ab initio Electronic Structure Methods

Constraints within Density Functional Theory (DFT):

- Local Density Approximation (LDA)
- Exchange Potential, e.g.:
  - von Barth & Hedin
  - Vosko
  - Ceperley & Alder (Perdew & Zunger)
- Beyond LDA
  - LDA+U
  - GGA
  - SCT
  - GW

Other Constraints:

- Shape of the Potential Function:
  - Muffin-Tin
  - ASA (equal or non equal sphere radii)
- Full Potential
- Core versus Valence Electrons
- Scalar Relativistic versus Fully Relativistic
- Magnetism: Co-linear (Ising-like), Non Co-linear (Heisenberg-like)
- Atomic Positions and Site Occupancy
- Born-Oppenheimer approximation (electron-phonon coupling)

---

### Software Packages

Pseudopotential-based Methods:

- VASP
- SIESTA
- ABINIT

Full-potential Methods:

- Wund77/Wien2000 (FP-LAPW)
- FP-LMTO

---

**Acknowledgment**

Work 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.
CALPHAD Thermodynamics

Multi-component Phases:

\[
G^c_{\text{ref}}(\gamma, T) = \sum_{i} G^c_i(\gamma_i, T) + \sum_{i,j} G^c_{ij}(\gamma_i, \gamma_j, T)
\]

\[
G^c_i(\gamma_i, T) = \sum_{c} a^c_i G^c_{i}(c, T)
\]

Two-sublattice Model of a Binary Alloy:

\[
G^c_{\text{ref}}(\gamma', T) = \sum_{c} G^c_{\text{ref}}(c, T)
\]

Ordering:

\[
G^c_{\text{ord}}(\gamma, T) = G^c_{\text{ref}}(\gamma, T) + \Delta G^c_{\text{ord}}(\gamma, T)
\]

\[
\Delta G^c_{\text{ord}}(\gamma, T) = \sum_{c} \Delta G^c_{\text{ord}}(\gamma, T)
\]

Ab Initio to CALPHAD

**Methodology**

- **Ab Initio**
  - Tight-Binding Linear Muffin-Tin Orbital (TB-LMTO) method for the description of the electronic structure
    - Atomic Sphere Approximation (ASA)
    - Unequal sphere radii, zero-charge transfer (i.e., local charge neutrality)
    - von Barth-Hedin exchange potential
    - Fully relativistic treatment of the (core and valence) electrons
  - Coherent Potential Approximation (CPA) for the treatment of the chemically random state of the alloy
  - Generalized Perturbation Method (GPM) to determine the Effective Pair Interactions (EPIs)
  - Cluster Variation Method and the Newton-Raphson technique for the determination of the equilibrium free energy

**CALPHAD**

- Phase Diagrams
- Thermodynamic Database
- Kinetic Database

**Ab Initio**

- Heats of Formation
- Heats of Transformation
- Thermodynamic Functions

**CALPHAD**

- Statics
- Kinetics

**Unified Approach to Alloy Stability?**

Can the physical of the chemically disordered state and of any ordered configuration of an alloy be described within a unique framework?
Input from *Ab initio*: Heats of Formation

*Ab initio* Results: Formation Energy of the Chemically Random Solid Solution

\[ \Delta H_{\text{form}} = \Delta H_{\text{Ab initio}} + \Delta H_{\text{CALPHAD}} \]

\[ \Delta H_{\text{form}}(\text{OP6}) = \Delta H_{\text{LMTO-ASA}} \]

Comparison between *Ab initio* + CVM and *Ab initio* + CALPHAD Results for Ta-W and Ta-Mo Alloys

Molar Gibbs Energy versus alloy composition at various temperatures
Additional points made by speaker:

Background: Phase diagrams are graphical results of the survival battles of competing phases.

**Ab initio**, CALPHAD and experimental phase diagrams:
- Comparison of *ab initio* and experimental: Ni-V, Pd-V, Cu-Zn
- Coupling of *ab initio* and CALPHAD: Ni-Cr
- Comparison of *ab initio* and CALPHAD: Mo-Ta, Ta-W (very good), Mo-Ta-W

*Ab initio* can provide good information for
- Ground state properties
- Stability and ordering in alloys
- Short range order
- Supplement thermodynamic databases
Limitations and challenges for \textit{ab initio}:

- Liquid phase
- \textit{X-H} systems
- Transition element carbides, -nitrides, etc.
- Magnetic properties

See also “Some Notes on First-Principles Electronic Structure Methods and Calculations,” page 17.
Database Development and Industrial Applications
Arthur D. Pelton, Centre de Recherche en Calcul Thermochimique (CRTC), Montreal, Quebec

Thermodynamic Database Development and Industrial Applications

Arthur Pelton
CRTC
(Centre de Recherche en Calcul Thermochimique)
Ecole Polytechnique de Montreal,
Montreal, Canada

Steps in Developing Multicomponent Solution Databases

- Search literature for all available thermodynamic and phase equilibrium data.
- Select appropriate model for each phase (Gibbs energy as a function of T and composition).
- Critically evaluate and optimize each binary subsystem to obtain model parameters.
- Use model to estimate properties of ternary phases. Add ternary model parameters where necessary.
- Use model with binary and ternary parameters to predict Gibbs energy of multicomponent solutions.
- Calculate multicomponent equilibria by Gibbs energy minimization using databases.

Evaluated/Optimized F*A*C*T Solution Databases

- Alloys-Carbonitrides:
  - SGTE Solution Databases (ferrous and non-ferrous)
- Molten Oxide Slag/Glass:
  - Oxides of Al, As, B, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Pb, Si, Ti, Zn, Zr
  - Slags: S, SO₂, PO₃, CO₂, F, Cl, H₂O, OH
- Solid Oxides (carnegie):
  - Ilmenite: Fe₂O₃
  - Pseudobrookite: Fe₃O₄
  - Monoxide: Ca₂CuFe₂O₅
  - Garnet: Ca₃₂₇₃₇₃₃Fe₃O₁₂
  - Spinels: Fe₂ZnAl₂O₄
  - Forsterite: Mg₂SiO₄
  - Olivine: (Ca, Mg)Fe₂O₄
  - Corundum: Al₂O₃

Choice of models

- Single sublattice, random mixing:
  - Simple alloys
  - Simple common-ion systems
- Sublattice models, random mixing
  - Compound Energy Formalism:
    - Interstitial solutions
    - Complex solid solutions
    - Long-range ordering
    - Ceramic solutions
    - Simple molten ionic solutions
- Sublattice models, short-range-ordering:
  - Molten slags and glasses
  - Molten sulfides
  - Reciprocal salt solutions

The predictions are only as good as the models. The proper choice of a model which correctly reflects the structure, ordering and speciation of a given solution is essential.

Evaluated/Optimized F*A*C*T Solution Databases (continued)

- Solid Oxides (carnegie, continued):
  - Melilite: (Ca, Pb)²⁺Zn²⁺Fe⁴⁺Al³⁺Si₃O₁₂
  - Pyroxenes: (Ca, Mg, Fe)²⁺Mg₂SiO₄ (ortho, clin, proto)
  - Spinel: Fe₃⁺Mg⁺(Mn⁺, Ti⁺)O₄
  - Perovskites
  - ZrO₂-based solutions
  - Felspars
  - Wollastonite
  - Pseudowollastonite
  - Etc...
- Solids (liquid and solid):
  - Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba²⁺Al²⁺Fe²⁺³⁺K²⁺Nd²⁺F⁻Cl⁻Br⁻I⁻OH
  - Cr₂O₃, Al₂O₃, Al₂O₃
  - FeCl₃, FeCl₂, Cr₂O₃, NaCl, MnCl₂, MgCl₂, AICl₃...
Evaluated/Optimized F*A*C*T Solution Databases (continued)

- Sulfide Mattes:
  Cu+Fe-Ni-Co-Pb-Zn-S-As-

- Molten Alloys:
  - Fe + 32 solutes
  - Pb + 12 solutes
  - Sn + 18 solutes
  - Zn + 4 solutes
  - Al, Mg + 7 solutes

- Aqueous Solutions:
  Concentrated (non-ideal)

- Semiconductors (solid and liquid):
  Hg-Cd-Te-Sb-Se-Zn-(Na+Pb-Ti+Ca-O)

MgO-FeO-Fe₂O₃-Al₂O₃ system

- Accuracy: good
- Optimized region: Sub-Solidus region

Main Solutions

- Slag: (MgO-Al₂O₃-FeO-Fe₂O₃)
- Monoxide: (MgO, Al₂O₃, Fe₂O₃, Fe₃O₄)
  (Magnetite) (MW)
- Corundum: (Al₂O₃, Fe₂O₃)
- Spinel: (Mg, Fe⁺², Fe⁺³, Al⁺³) [Mg, Fe⁺², Fe⁺³, Al⁺³, V⁺], O₆
  (Magnetite, Fe₂O₃), Magnesoferrite(MW, MgFe₂O₄),
  Hematite(Fe₂O₃), Spinel(MgAl₂O₄))

Enthalpy of Mixing of the Metastable MgAl₂O₄-FeAl₂O₄ Spinel

T = 973 K

O Norcisky, 1966

F*A*C*T Consortium

Oxygen Partial Pressure over the MgAl₂O₄-FeAl₂O₄ Spinel Saturated with Al₂O₃ and Fe

The Miscibility Gap in the Fe₂O₃-MgFe₂O₄-
MgAl₂O₄-FeAl₂O₄ Spinel at 800°C
CaO-MgO-FeO-Fe₂O₃-SiO₂ System

- Accuracy: good
- Optimized region: Whole system except Ca₂SiO₄ region

Main Solutions
- Slag: (CaO-MgO-FeO-Fe₂O₃-SiO₂)
- Monoxide: (CaO-MgO-FeO-Fe₂O₃) (Lambe, Wustite)
- Spinel: (Fe²⁺, Fe³⁺, Mg)[Fe²⁺, Fe³⁺, Mg, V₃] O₆
- Magnesioferrite (MF, MgF₀⁷O₄)
- Olivine: (Ca, Mg, Fe³⁺)[Ca, Mg, Fe³⁺] SiO₄
- Fayalite (Fe₂SiO₄)
- Willemite (CaMgSiO₄)
- Pyroxene: (Ca, Mg, Fe²⁺)[Ca, Mg, Fe²⁺] (Si⁸) O₆
- Pyrope: pyrope, almandine, grossular
- Woollastonite: (Ca₂MgSiO₄)
- Clinopyroxene: (Ca₂MgSiO₄)
- Orthopyroxene: (Ca₂Fe₂SiO₆)
- Ca₂SiO₄
- Fe₂SiO₄

The CaSiO₃-FeSiO₃-MgSiO₃
Phase Diagram at 900°C

The CaSiO₃-FeSiO₃-MgSiO₃
Phase Diagram at 1200°C
### Some Applications of Oxide Databases

- Metallurgical Processing (slags)
- Inclusion Engineering
- Refractories
- Ceramics
- Glass Technology
- Geology
- Combustion, Gasification
- Hot Corrosion

### ASSET Project

(Shell Development, D' Randy John)


- Thermodynamic databases (alloys, carbonitrides, oxides, sulfides) are used to predict the corrosion products for a given atmosphere and alloy composition. Extensive experimental databases are then used to predict corrosion rates.

### Phase Diagram of the Fe-Ni-O System at 1279 K
The Application of FactSage™ Software to Steelmaking Processes

Feb., 2002
In-Ho Jung, Youn-Bae Kang and Arthur D. Pelton
CRCT, Ecole Polytechnique de Montréal, Canada

1. Inclusion modification:

Al₂O₃ modification by Ca treatment
- Al₂O₃ inclusion is formed after Al deoxidation process and very harmful to steel quality and nozzle clogging
- So Ca treatment is performed in the secondary steelmaking process to modified Al₂O₃ to low melting temperature composition
- To understand Ca treatment, the inclusion diagram of Ca and Al is necessary
- The effect of S to the Ca treatment is calculated
- Real Ca treatment process is simulated

Simulation of Ca treatment (CaSi wire injection)

2. Minimizing the losses of Ti in low carbon steel

- Ti is added in the low carbon steel as alloying element in the RH process after Al deoxidation
- But because Ti is strong oxidizing element, Ti can be consumed to formation of TiO₂ inclusion
- To minimize the losses of expensive Ti, the inclusion diagram of Ti and Al is necessary

Inclusion Diagram of Fe-Al-Ca-O System
3. Inclusions in stainless steel: [N], [Ti] and [C]

- Stainless steel contains a lot of nitrogen
- With addition of Ti alloying element, Ti can be consumed as TiN inclusion
- To minimize the losses of expensive Ti and reduce the inclusion, the inclusion diagram of Ti and N is necessary
- The effect of carbon to the TiN(TiN-TiC) formation is also calculated

![Inclusion Diagram of Fe-Al-Ti-O System at 1600°C](image)

![Inclusion Diagram in Fe-18 wt%Cr-8 wt% Ni-Ti-N-O at 1600°C](image)

![Inclusion Diagram in Fe-18 wt%Cr-8wt% Ni-Ti-N-O-C at 1600°C](image)

Databases and Software for Thermodynamic Simulation of Copper Smelting and Converting

Sergei A. Degterov and Arthur D. Pelton
École Polytechnique de Montréal
Centre for Research in Computational Thermochemistry
Manuel Zamalloa
Noranda Technology Centre

Flowsheet for copper extraction from sulfide concentrates

- 1250°C
  \[ P(O_2) = 10^{-11} \text{ atm} \]
  \[ P(S) = 10^{-1} \text{ atm} \]

Copper Sulfide Concentrate

<table>
<thead>
<tr>
<th>SMELTING</th>
<th>CONVERTING</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blast Furnace</td>
<td>Matte</td>
</tr>
<tr>
<td>Reverbatory Flash</td>
<td></td>
</tr>
<tr>
<td>Mitsubishi Noranda</td>
<td></td>
</tr>
</tbody>
</table>

| | Slaa Discard or Treatment |
| Slag |
| 25-30% Cu |
| 28-34% Fe |
| 9%-14% S |
| 2-9% SiO |
| Small amount of Pb, Zn, N, C, etc... |

| | 0.2-2% Cu |
| 0.2-1.3% S |
| 25% SiO |

| | 45-73% Cu |
| 30-60% Fe |
| 30-20% S |

| | 25% Cu |
| 20% SiO |

| | 0.3% Cu |
| 0.2% S |
| 2.5% Cu |

| | 25% SiO |

| | 0.5% Cu |
| 0.2% S |
| 2.5% Cu |

| | 20% SiO |

| | 0.5% Cu |
| 0.2% S |
| 2.5% Cu |

| | 20% SiO |
Solubility of copper in fayalite slag. The Cu-Fe-Si-O-S system.

Solubility of copper in the fayalite slag as a function of the Fe/Si ratio in the slag.

Sulfur content of silica-saturated slag in equilibrium with matte and liquid Cu or γ-Fe.

Experimental and calculated tie-lines in the Cu-Zn-S system at 1200°C and 1550°C.

Copper content of slag in equilibrium with matte at 1250°C and P(O₂) = 10⁻⁶ atm.

Calculated distribution of Pb between matte and slag at 1250°C, P(O₂) = 10⁻⁶ atm and at infinite dilution of Pb.

Dashed lines show SO₂ isobars.
Additional points made by speaker:

Choice of models - although model choices may be identical in subsystems, the use of different extrapolation methods is likely to result in different extrapolation behavior.

Cluster pair approximation and quasichemical models are used in the slag/glass and sulfide mattes databases.

FACT consortium includes 15 sponsors for database development.

FACT-app (Chem-app) software interface for inclusion into other software programs.
Development of Thermodynamic Databases
Philip J. Spencer, The Spencer Group, Ithaca, NY

Background
Thermodynamic calculations and simulations based on critically evaluated data are widely used as a basic tool in the development and optimization of materials and processes of many different types.
Such calculations can result in considerable savings in cost and time associated with experimental development work.
For these reasons thermodynamic database development is an important and increasing scientific activity.

Outline of presentation
Available databases and their content
Importance of awareness of experimental problems in carrying out data assessment
Importance of mode choice/compatibility in progressing from binary to higher-order systems
Funding problems associated with database development
Practical applications of thermodynamic calculations

Available thermodynamic databases
Pure inorganic substances
- JANAF (U.S.A)
- IVTAN (Russia)
- SGTE (Europe)
- F*A*C*T (Canada)
- MALT (Japan)

Available thermodynamic databases

Useful References to Computational Thermodynamics
- ThermoTech - range of systems, comprehensive for steels
- COST 507 - light metal (Al, Mg, Ti) alloys
- ThermoTech - Nb-base, Al-base, Ti-base alloys
- NIST, Metallurgy Div. - Ni-base superalloys, solders
- F*A*C*T - Fe-, Al-, Cu-, Pb-, Zn-rich alloys
- Tohoku University - solders, Cu-base alloys, sulphides in steels

Useful References to Computational Thermodynamics
- CALPHAD 19 (1995) 433
- CALPHAD 21 (1997) 155
- CALPHAD 24 (2003) 55
- Zeitschrift fur Metallkunde 82 (2001) 513
Need for awareness of experimental problems in data assessment

The critical assessment of thermodynamic data is a skilled task which, preferably, requires experimental experience as well as experience in the use of the sophisticated software available.

Because of the very regrettable decrease in the number of laboratories carrying out thermodynamic measurements, there is a real danger of assessment work being carried out by talented scientists with sound theoretical skills, but an inadequate first-hand knowledge of the experimental difficulties associated with the numbers they are assessing.
Important considerations in thermodynamic database development for alloys

Many commercial alloys contain several constituent elements, e.g., steels, superalloys, Al-base alloys. The provision of a reliable, self-consistent database for calculations over a wide range of compositions requires careful preliminary preparations with regard to data and model compatibility. An example of such work is the COST 507 database for light metal alloys.

COST Action 507: Light alloy systems of potential interest

<table>
<thead>
<tr>
<th>Key system</th>
<th>Additional elements</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-Mg-Mn-Fe-Si</td>
<td>Cu, Cr, Ti, C</td>
<td>Cans</td>
</tr>
<tr>
<td>Al-Mg-Si-Cu</td>
<td>Fe</td>
<td>Extrusions</td>
</tr>
<tr>
<td>Al-Zn-Cu-Mg</td>
<td>Zr, Cr, Si</td>
<td>Aerospace</td>
</tr>
<tr>
<td>Al-Li-Cu-MgZr</td>
<td>H</td>
<td>Airframes</td>
</tr>
<tr>
<td>Ti-Al-Mo-Zr-Si-Nb</td>
<td>O, N, C</td>
<td>Gas turbines</td>
</tr>
<tr>
<td>Ti-Al-V-O-N-C</td>
<td></td>
<td>Gas turbines</td>
</tr>
</tbody>
</table>

COST 507: Matrix of binary systems representing building blocks for alloys of potential commercial interest
COST 507: Application of evaluated thermodynamic data for light metal alloy systems to casting and heat treatment processes

Key system for investigations
Al-Cu-Mg-Si (AlMe)

Partners in measurement and evaluation work:
- Inst. f. Anorganische Chemie, Univ. Vienna, Austria (activity & ph. discussions)
- Dept. of Met. and Materials, Univ. Leuven, Belgium (phase diagram validation)
- MPI f. Metallforschung, Inst. f. Werkstoff., Stuttgart, Germany (description)
- Lehrstuhl f. Theoret. Hoitt. und Lkunde, RWTH Aachen, Germany (calculation)
- MPI f. Metallforschung, PNL, Stuttgart, Germany (assessment)
- Centre de Thermochimie et Mechanique, Marseille, France (activity data)
- Universidade do Minho, Guimarães, Portugal (activity data)
Development of a database for Al-Cu-Mg-Si-Zn alloys

Data compatibility

Consider the example of a hypothetical database for Al-Cu-Mg-Si-Zn alloys.

A full thermodynamic description for this system requires self-consistent assessed data for:

- Elements (9): Al, Cu, Mg, Si, Zn
- Binary alloys: Al-Cu, Al-Mg, Al-Si, Al-Zn, Cu-Mg, Cu-Si, Cu-Zn, Mg-Si, Mg-Zn, Si-Zn
- Ternary alloys: Al-Cu-Mg, Al-Cu-Si, Al-Cu-Zn, Al-Mg-Si, Al-Mg-Zn
- Quaternary alloys: Al-Cu-Mg-Si, Al-Cu-Mg-Zn, Al-Cu-Si-Zn, Al-Cu-Zn-Si, Al-Mg-Si-Zn, Mg-Si-Zn

The work of SGTE in database development

SGTE in a consortium of partners engaged in the development of thermodynamic databases to complement the assessed and evaluated databases and their application to practical problems.

Our aims are:

- To develop, distribute and maintain open thermodynamic databases that can be used to solve complex problems in energy, industry, university, and industry
- Utilization of existing databases to form a new database and its application to practical problems
- SGTE database and user standard development

SGTE Member Organizations

<table>
<thead>
<tr>
<th>France</th>
<th>Germany</th>
</tr>
</thead>
<tbody>
<tr>
<td>INPG - LPCM (Grenoble)</td>
<td>LTH - RWTH (Aachen)</td>
</tr>
<tr>
<td>ThermoData (Grenoble)</td>
<td>Max-PlanckInstitut (Mülheim)</td>
</tr>
<tr>
<td>IRSID (Matisse-les-Metz)</td>
<td>GTT (Herzogenrath)</td>
</tr>
<tr>
<td>Univ. de Paris Sud (Chateauneuf)</td>
<td></td>
</tr>
<tr>
<td>Sweden</td>
<td>United Kingdom</td>
</tr>
<tr>
<td>Royal Inst. Technol. (Stockholm)</td>
<td>AEA Technology (Savoy)</td>
</tr>
<tr>
<td>ThermoCalc AB (Stockholm)</td>
<td>Natl. Physical Lab. (Teddington)</td>
</tr>
</tbody>
</table>

In process:

- Canada: ThermFact (Montreal)
- Japan: Tohoku Univ. - Mat. Sci. & Eng. (Sendai)
- Taiwan: NSC, Metall. Div. (Nantou)
Difficulties encountered in obtaining funding for database development

- Assessment work requires costly expertise and can be very time-consuming.
- Database development requires assessment of systems other than those of obvious direct relevance to a practical problem.
- With increased industrial funding for a project being a requirement of government agencies, the resulting confidentiality restrictions are increasingly limiting general availability of assessed data.
- Database development is greatly assisted by use of already available assessed data for relevant sub-systems. However, the confidentiality requirements resulting from industrial funding are leading to costly duplication of assessment work with resulting danger of incompatibility.

Applications in materials design and development

**Steels**
- Design and development of new stainless steel grades including prediction of amounts and formation temperatures of carbide and nitride phases.
- Design and development of new steels replacing nickel by manganese and/or nitrogen.

**Light metal alloys**
- Prediction of solidification ranges and phase formation in casting processes.
- Prediction of composition and temperature ranges for formation of metastable coating phases in PVD processes.

Design and development of new stainless steel grades

- Stainless steel production continues to grow by about 3 to 5% per annum.
- As a result of customer demand for specialized properties, and the need to reduce costs associated with expensive alloying elements, new stainless steel grades are being developed.

One development direction involves combining the properties of ferritic and austenitic steels in an optimum way in the well-known duplex stainless steels. Another direction aims to replace nickel by manganese and/or nitrogen.

If such new steel grades can be produced and marketed, their microstructural properties must be optimized. This allows definition of suitable conditions for casting, hot-rolling, heat treatment, cold rolling, etc.

The desired properties of the steels can thereby be produced.
Design and development of new stainless steel grades

Existing grades:
- Ferritic: X2 Cr 11
- Austenitic: X5 CrNi 18 10

Under development:
- Duplex: X2 CrNiMoN 22 5 3
- Austenitic: X5 CrNiMo 17 12 2

Proposed:
- Austenitic: X5 CrMnN 17 12

Design and development of new stainless steel grades

Conclusions

Calculations of phase constitution using assessed thermo-dynamic data provide reliable guidelines for selecting suitable compositions for new stainless steel grades.

Calculated liquidus and solidus temperatures, formation temperatures for precipitated phases, and composition and temperature ranges of stability of deleterious phases, enable time and expense to be saved in establishing suitable conditions for casting, hot-rolling, heat treatment, and other operations for the alloys.

Casting of light metal alloys

Thermodynamic calculations have been carried out to provide the following information as basis for controlled casting operations:
- temperature range of solidification
- crystallization paths for equilibrium and non-equilibrium conditions
- nature and amounts of phases formed during solidification
- heat capacities and enthalpy effects associated with phase transitions

Calculations have been carried out using the following models:
- Equilibrium cooling
- Scheil Model (no diffusion in solid phases formed)
- Diffusion in the solid phases
Casting of light metal alloys

The Scheil model applied to alloy AA2024

The Scheil model has been applied to simulation of the solidification of the commercial Al-Cu-Mg-base alloy AA2024. This alloy contains the additional alloying elements Fe, Mn and Si.

Important missing data, e.g. for the system Al-Cu-Mn, were evaluated as part of the work.

Scheil simulation for Alloy AA2024

Comparison of Scheil simulations with experimental results

<table>
<thead>
<tr>
<th>Experiment (ESS2c) (Cooling rate: 0.2-1.0 K/s)</th>
<th>Simulation (Subsystem Al-Cu-Mn-Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ( L_2 \rightarrow (\alpha) )  ( L_3 \rightarrow (\alpha) + Al_2Fe ) ( L_4 \rightarrow (\alpha) + Al_2Fe )</td>
<td>( L_2 \rightarrow (\alpha) )  ( L_3 \rightarrow (\alpha) + Al_2Fe ) ( L_4 \rightarrow (\alpha) + Al_2Fe )</td>
</tr>
<tr>
<td>2 ( L_2 \rightarrow (\alpha) + Al_2CuFe ) ( L_3 \rightarrow (\alpha) + Al_2Fe ) ( L_4 \rightarrow (\alpha) + Al_2Fe )</td>
<td>( L_2 \rightarrow (\alpha) + Al_2CuFe ) ( L_3 \rightarrow (\alpha) + Al_2Fe ) ( L_4 \rightarrow (\alpha) + Al_2Fe )</td>
</tr>
<tr>
<td>3 ( L_2 \rightarrow (\alpha) + Al_2CuFe ) ( L_3 \rightarrow (\alpha) + Al_2Fe )</td>
<td>( L_2 \rightarrow (\alpha) + Al_2CuFe ) ( L_3 \rightarrow (\alpha) + Al_2Fe )</td>
</tr>
<tr>
<td>4 ( L_2 \rightarrow (\alpha) + Al_2CuFe ) ( L_3 \rightarrow (\alpha) + Al_2CuFe )</td>
<td>( L_2 \rightarrow (\alpha) + Al_2CuFe ) ( L_3 \rightarrow (\alpha) + Al_2CuFe )</td>
</tr>
</tbody>
</table>
Prediction of composition ranges for metastable coating structures produced in PVD processes

Certain coatings produced by PVD techniques display superior properties for wear and corrosion resistance applications. This is leading to the systematic development of new high-performance coating materials.

PVD techniques allow required coating compositions to be achieved relatively easily. Variation of the substrate temperature may also allow the coating structure, and hence its properties, to be changed.

Thermodynamic calculations allow prediction of conditions for the appearance of possible metastable phases during PVD coating processes and thereby assist in the selection of optimum coating parameters to produce coatings with desired properties.

Prediction of composition ranges for metastable coating structures in the (Ti,Al)N system

Metastable (Ti,Al)N coatings with the cubic NaCl structure are superior to TiN for cutting tool applications due to their superior oxidation resistance and hardness at elevated temperatures. However, the deposition of (Ti,Al)N films with Ti/Al ratios below about 30/70 leads to a hexagonal coating structure which is not suitable for tribological coatings.

Prediction of energies of transformation between the cubic NaCl and hexagonal structures for transition metal nitrides

A thermodynamic analysis of the (Ti,Al)N system was made, which combined calorimetric measurements of the metastable to stable phase transition for 3 compositions in the section AlN-TiN with estimated values for Gibbs energy differences between the NaCl and ZnS wurtzite structural forms of pure TiN and AlN. This allowed Gibbs energy curves to be calculated for the hexagonal and cubic phases for various temperatures in the AlN-TiN system.

The point of intersection of these curves at each temperature defines the composition at which there is a transition from one structure to the other. This composition was found to be nearly temperature independent with a calculated value around 0.7 mole fraction AlN.
Gibbs energy of formation of the cubic and hexagonal phases in the AlN-TiN system at different temperatures

Experimental measurements for (Ti,Al)N coatings

Experimental measurements for Al2O3-AlN coatings

Metastable Al-O-N layers have been produced by reactive magnetron sputtering ion plating using an Al target and an Al-O-N gas mixture.

- For a substrate temperature of 198 °C and variable partial pressures of O2 and N2, a variety of coatings with different O and N contents were prepared and analysed by means of X-ray photoelectron spectroscopy, Auger electron spectroscopy, high-resolution transmission electron microscopy and high-resolution scanning electron microscopy.

Oxygen-rich Al-O-N phases were found to be nanocrystalline with a cubic gamma-Al2O3 (cubic structure). Nanocrystalline phases displayed a hexagonal AlN (wurtzite) structure. For O:N ratios around 2:3, the deposited phase was a TEM amorphous.

Thermodynamic calculations for Al2O3-AlN coatings

- An available thermodynamic assessment of the Al2O3-AlN system was amended to incorporate descriptions for the wurtzite and amorphous phases for the entire composition range. Using these data, Gibbs energy curves were calculated for the different metastable phases for temperatures between room temperature and 600 K. The experimentally observed composition ranges for the phases at 453K were used to help define the location of the Gibbs energy curve for the amorphous phase.

The metastable phase diagram was calculated and comparison made with experimental results.

Gibbs energy of formation of the spinel, amorphous and wurtzite phases in the Al₂O₃-AlN system at 463K

Calculated metastable phase ranges in the Al₂O₃-AlN system

Calculated metastable phase ranges in the TiB₂-TiC system

Conclusions

- Thermodynamic calculations are able to provide information of significant practical importance on the composition and temperature ranges of metastable coating phases.
- Estimation or calculation techniques are required to provide transformation energies for metastable structures of potential coating compounds (carbides, nitrides, borides, oxides, etc.), but the present work shows that with limited experimental support, satisfactory predictions of metastable phase ranges can be made.

Summary

- There have been rapid advances in software packages for simulation of the thermodynamics and kinetics of materials development and processing.
- These advances must now be matched through increased support for the measurement and critical assessment of "missing data" required for the simulations.
- Database development is essential for full implementation of thermodynamic calculation potential in many areas of materials technology.
Additional points made by speaker:

Needs for database construction:
Experimental experience: independent, first hand knowledge of experimental difficulties:
- Mn-Ti phase diagram used to illustrate some of the difficulties that may be encountered in experimental work and their effects on the thermodynamic assessment.
- Zr-B shows temperature differences up to 500 K between data sources.

Self-consistent databases require careful preparation: Example COST 507
- Number of components very large
  ♦ Need to break down into smaller tasks focusing on important subsystems: Example Al-Cu-Mg-Si-Zn
- Modeling of the intermediate phases and the subsystems must be compatible

SGTE and its aims:
- Identifies focus areas for database development
- Landolt-Börnstein publications: unary and binary systems
  ♦ Funding problem: experts are required, time consuming.

Predictions for PVD (physical vapor deposition) processes:
Metastable phases are important, since phase which has lowest Gibbs energy at any composition will form first.
Application of Thermodynamics to Alloy Design and Development
Charles J. Kuehmann, QuesTek Innovations LLC, Evanston, IL

February 21, 2002

Application of Thermodynamics to Alloy Design and Development
Charles J. Kuehmann
QuesTek Innovations LLC
Evanston, Illinois
March 21, 2002

- Hierarchy of Design Models
- How CMD Programs are Used?
- Available Multicomponent CMD Models for Ferrous Alloys

Materials by Design

Materials by Design

Materials by Design

Materials by Design

Materials by Design

Materials by Design
More About TCIPC

As CMD programs currently use TCIPC to incorporate Thermo-Calc/DICTRA, this implies:
- Program can run without Thermo-Calc and DICTRA
- User need to have proper privilege and setup for running Thermo-Calc and DICTRA in order to run CMD programs

CMD User Interface — Pre-Processor

PrecipiCalc™ Input/Output

Basic Multicomponent PrecipiCalc™ Equations

Materials by Design®

Materials by Design®

Materials by Design®

Materials by Design®

Materials by Design®

Materials by Design®

Materials by Design®
Additional points made by speaker:

Performance ↔ properties ↔ structure ↔ processing
Modeling employs thermodynamic quantities.

Computational materials design:
Entire suite of software is used depending on dimension level (atomic, nano, micro, ...) to model properties ⇒ "faster science" & "better engineering"
Software includes a series of process-structure and structure-properties models.
Software has no direct interface to Thermo-Calc - runs as independent process.

PrecipiCalc: uses nucleation conditions, growth law, full diffusivity matrix and fitting parameters of the precipitate surface energy to predict particle size distribution and composition of precipitates.
Construction and Application of a Diffusion Mobility Database for Ni-Base Superalloys
Carelyn E. Campbell, NIST, Gaithersburg, MD

The Construction and Application of a Diffusion Mobility Database for Ni-Base Superalloys

C. E. Campbell
National Institute of Standards and Technology
Metallurgy Division
Gaithersburg, Maryland 20859-8555

March 21, 2002
Partially funded by DARPA under GE AIM program

Diffusion in a Binary Alloy

Fick's first law for Flux, J
\[ J = -D \frac{dc}{dx} \]

Fick's second law (conservation of mass)
\[ \frac{dc}{dt} = D \frac{d^2c}{dx^2} \]

If D is independent of composition
\[ \frac{dc}{dt} = D \frac{d^2c}{dx^2} \]

If semi-infinite sample, error function solution.
\[ c(x,t) = A + Be^{-\left(\frac{x}{4Dt}\right)} \]

Temperature dependence
\[ D = D_0 \exp\left(-\frac{Q}{RT}\right) \]

Multicomponent Thermodynamics: Calphad Approach

Experimental phase diagram, Thermochemical data

Determine Gibbs Energy, \[ G = f(x,T,P) \]

Calculated phase diagram

\[ G^0 = G^0 + G^{ideal} + G^{excess} \]

Binaries \rightarrow\text{Ternaries} \rightarrow\text{Quaternaries} \rightarrow n\text{th order systems}

Need for Multicomponent Diffusion Data

\(\gamma\) precipitation during non-isothermal cooling
Heat treatment optimization
Protective coating applications

Diffusion Database Development

\(\gamma\) precipitate during non-isothermal cooling
Heat treatment optimization
Protective coating applications

\(\gamma\) precipitate during non-isothermal cooling
Heat treatment optimization
Protective coating applications

\[ \Delta G = \Delta G + \Delta G^{chem} \]

Concentration Dependence

\[ c = \frac{1}{2} \]
Databases used:
- Thermodynamics: Thermotech
- Diffusion mobilities: NIST Ni-mob

Double geometric grid: 200 points.

**Rene-N4/Rene-N5 at 1293°C for 100 h**

**Rene-N4/Rene-N5 Diffusion Couple at 1293°C**

Cr profile
Al profile

**René-N4/René-N5 Diffusion Couple at 1293°C**

Ti profile
Ta profile

**Porosity Prediction**

Back scatter image: 100 h

Maximum gives location of pore formation.

**René-88/IN-100, 1000 h at 1150°C**

At 1150°C equilibrium phase fractions:
- René-88: \( f = 1 \)
- IN-100: \( f = 0.636 \), \( f = 0.362 \)

Distance (m)

Experimental data from J. C. Zhao, GE-CRD, Schenectady, NY.
**René-88/IN-100: 1000 h at 1150°C**

Solidification of Ni-11Al-4.5Ta (at%)

**Phase Fraction Evolution**

- **Simulation Setup**
  - Used composition and phase fractions from solidification calculation.
  - Assume linear heating rates beginning at 800 K
  - Assume γ fraction is in equilibrium with γ matrix at each grid point.
  - Assume incipient melting occurs at the center between dendrites.

**Optimized Heat Treatment**

- For Ni-11Al-4.5Ta alloy solidified at 8 K/s
  - Heat from 800 K to 1655 K at 1 K/s
  - Hold at 1655 K until t = 1325 s (3x 470 s) Homogenous microstructure

**Summary**

- **Database Development**
  - Ni-base superalloys:
    - Ni-Al-Co-Fe-Mo-Nb-Re-Ta-Ti-W (Fe)
    - FCC γ phase, γ
  - Comparisons with
    - Diffusion correlations at melting temperature
    - Experimental quaternary diffusion coefficients
    - Multicomponent diffusion couples: (René-4/RE-100)
  - Experimental evaluation of selected ternary and quaternary systems

- **Applications**
  - Heat treatment optimization
  - γ precipitation during non-isothermal cooling
  - Coating deterioration
Additional points made by speaker:

Simple criterion for validation of mobility database is that the ratio of the diffusion activation energy of a pure component to the melting point of the pure component is roughly constant: \(-Q/RT_M = 17\).

Porosity prediction: Position of maximum in vacancy flux gives position for maximum pore formation.
Incorporation of CALPHAD Calculations into Phase Field Modeling
William J. Boettinger, NIST, Gaithersburg, MD

Phase Field Modeling using Thermodynamic and Mobility Databases
- Sharp vs. Diffuse Interface Modeling
- A few examples of Phase-Field Modeling
- Phase field variable: artificial or natural order parameter?
- Free energy functions
- Gradient Thermodynamics
  - Interface Energy
- Mobility Parameters
  - Phase field
  - Diffusion
- Addition of other fields
  - Elasticity
  - Electrostatic

Traditional Materials Science Approach:
Example: Solidification

Sharp vs. Diffuse Interface

<table>
<thead>
<tr>
<th>Solid</th>
<th>Liquid</th>
</tr>
</thead>
</table>

Sharp Interface Model

\[
\begin{align*}
C \to \text{Solid} & \text{ Liquid} \\
\end{align*}
\]

- Solve diffusion equations in solid and liquid
- Match solutions at interface; interface conditions
- Difficult 'moving boundary' problem

Diffuse Interface Model

\[
\begin{align*}
\delta \to \text{Solid} & \text{ Liquid} \\
\end{align*}
\]

- Add new variable and equation: \( \delta \) \( \times \) \( t \)
- Solve new eqn. and modified diffusion eqn.
  over entire domain
- No boundary conditions at interface
- Easy to program (new large computer)

Microsegregation (Warren and Boettinger, 1996)

\[
\begin{align*}
& D_S/D_L=10^{-5} \\
& D_D/D_L=10^{-1} \\
\end{align*}
\]

Binary Eutectic with Dilute Ternary Impurity
M. Plapp and A. Karma 1999

Simulation of \( \gamma' \) Precipitation w/Coherency Strains
Y. Wang, D. Banerjee, C.C. Su, (OSU) & A. Khachaturyan, (Rutgers)
Acta Mat. 46 (1998) 2983
Active researchers: Phase Field Modeling attempting "Calphad" Thermodynamic Databases

- I. Loginova, G, Amberg, J. Agren, Seattle 2001 TMS
- Miyazaki, Calphad 25(2001) 231. Discrete lattice Fe-Co-Al and InGaAsP, w/stress

Phase Field vs. Order Parameter(s)

- If thermodynamic database treats the phases together
  - e.g. chemical miscibility gap, order-disorder
  - Natural order parameter(s)
  - Thermo. between the phases is not artificial
  - Can get gradient energy coefficients from bulk thermo!
  - Need interatomic dimension / interface coordination #’s

- If thermodynamic database treats the phases independently:
  - e.g., liquid - solid,
  - Need to introduce artificial ‘phase field parameter, φ
  - Introduce energy hump (W) between the phases and gradient energy coefficients to get interface energy/adsorption consistent with experiments.

Gradient Thermodynamics

\[ F = \int \left[ f(c,φ,T) + \frac{φ^2}{2} \nabla φ \right] dV \]

Equilibrium

\[ \frac{∂F}{∂φ} = φ \nabla \cdot \left( \frac{φ^2}{2} \right) = 0 \]

\[ \frac{∂F}{∂c} = 0 \]

\[ c = \text{constant} \]

\[ \frac{∂φ}{∂t} = -Mφ \frac{∂f}{∂φ} - \nabla \cdot (φ \nabla φ) \]

\[ \text{Interface Kinetics} \quad \text{Diffusion Mobility} \]

\[ \frac{∂c}{∂t} = \nabla \left( M_c \nabla \left( \frac{∂f}{∂c} - \nabla Vc \right) \right) \]

\[ \text{Coupled Cahn-Hillard & Cahn-Alen Equations} \]

Alloy Free Energy Function

For equilibrium far from the interface

\[ \frac{∂f}{∂φ} = 0 \quad \text{and} \quad \frac{∂f}{∂c} = \text{constant} \]

Combined Alloy Free Energy Function for independent α & β phases

Wheeler, Boettinger, McFadden:

\[ f(φ, c, T) = (1 - p(φ))f^α(c, T) + p(φ)f^β(c, T) + W(c, T)g(φ) \]

Interpolating function

Double-Well function

\[ p(φ) = φ^1(6φ^2 - 15φ + 10) \]

\[ g(φ) = φ^1(1 - φ)^1 \]

Alternate method:

Interface Energies via Thermodynamic Functions: natural order parameters


Ternary Regular Solution Ag-Au-Cu with $\Omega_p$ heats of mixing

$$F = \int \left[ f(c_1, c_2, T) + k_{11}(\nabla c_1)^2 + k_{22}(\nabla c_2)^2 + k_{33}(\nabla c_3)^2 \right] dV$$

where

- $k_{ij} = 2Z_j d^2 \Omega_{ij}$
- $d = \text{interatomic distance}$
- $\Omega_j = \text{interface coordination number $= 3$ for [111]}
- $= 4 \text{ for [100]}$

Similarly, gradient energy coefficients can be obtained for order/disorder cases.

Elastic effects: Cubic $\rightarrow$ Tetragonal Transformation

- 3 field variables, $\eta_1, \eta_2, \eta_3$
- $\eta_1 = 1$
- $\eta_2 = 0$
- $\eta_3 = 0$
- $\eta_1 = 0$
- $\eta_2 = 0$
- $\eta_3 = 0$
- $\eta_1 = 0$
- $\eta_2 = 1$
- $\eta_3 = 0$
- $\eta_1 = 0$
- $\eta_2 = 0$
- $\eta_3 = 1$

Stress free strain, function of $\eta$; add elastic energy to free energy functional

Application to Electrochemistry, Jon Guyer at NIST

Diffusion Mobility Parameters for Phase-Field Calculations for Multicomponent Alloys

- Phase field models are usually derived in a volume fixed frame.
- A particular component, say 'n', is picked to be the solvent.
- One needs mobilities, $L_n(\phi)$, for the dynamic constitutive law:

$$J_i = \sum_{j=1}^{n-1} \frac{\delta F}{\delta X_i} = \sum_{j=1}^{n-1} \left( \frac{\partial F(X_1, \ldots, X_{n-1})}{\partial X_j} \right) = \sum_{j=1}^{n-1} \nabla \phi_j (\mu_j - \mu)$$

- Using the mobility matrix, $M$, obtained for each phase, the $L^*$ matrix for that phase is given by

$$L^* = \frac{\delta F}{\delta \phi_j} = \sum_{j=1}^{n-1} \left( \frac{\partial F(X_1, \ldots, X_{n-1})}{\partial X_j} \right)$$

where $M$ is the mobility matrix for each phase.

Electrochemistry

$$F(\phi, C_j, \psi) = \int \left[ f_v(\phi, C_j) + \frac{1}{2} \rho^2 + \frac{k}{\phi^2} \right] dV$$

- $F$ Helmholtz free energy
- $f_v$ Helmholtz free energy per unit volume
- $\phi$ phase field
- $C_j$ concentration of species $j$
- $\psi$ electrostatic potential
- $\rho = \sum N_j C_j F$ charge density
- $k_\phi$ phase field gradient energy coefficient

Conclusions

- Phase field calculations are based on thermodynamic functions and a few simple dynamic postulates.
- Calphad evaluations are ideal input data for phase field calculations.
- For thermodynamics involving natural order parameters, gradient energy coefficient and hence interface energies can be calculated.
- Otherwise, gradient energy coefficients and interpolation between individual free energies must be obtained by fit to measured surface energy
- Diffusion mobility assessments can be implemented in phase field calculations.
- Numerical difficulties still limit application.
Additional points made by speaker:

Diffuse interface model helps to overcome the moving boundary problem of the sharp interface model. Phase field method is ideal for modeling ordering processes since it naturally implements an order parameter.
Current and Future Applications of CALPHAD Technology
Larry Kaufman, Brookline, MA

Abstract

During the past year the author has had the opportunity of participating in two international symposia devoted to exploring recent examples of the development of methods for predicting multiphase equilibria in diverse materials. The first of these, held at the 130th TMS meeting in New Orleans was organized by Zi-Kui Liu and entitled “Computational Thermodynamics and Materials Design” (1). The second, organized by Patrice Turchi was entitled “CALPHAD and Alloy Thermodynamics” was held at the 131st TMS meeting held in Seattle (2). Most of the papers presented at these symposia are published and present a graphic record of the significant accomplishments made in this field in recent years. This workshop provides a fitting epilogue to those meetings in identifying those areas where development of data bases which are needed to foster future progress and reporting on techniques and advances in such efforts. The author has chosen several examples of recent work in the analyses of multicomponent systems used in lithium battery anodes (3,4), giant magneto resistance (5), zirconia ceramics (1,6), niobium alloys (7), metal-carbon systems (1,8), metallic glasses based on Al-Fe-Ni-Gd-Y alloys (9,10), transformation kinetics (1,11) and corrosion (11) to illustrate the variety of applications to which databases for multicomponent systems can be applied to describe equilibrium and kinetic behavior.

References

4. L. Kaufman, Research conducted under U.S. ATP Cooperative Agreement 70NANBOH3023.
11. Research in Progress under the Yucca Mountain Site Characterization Project at Lawrence Livermore National Laboratories, Livermore, CA.
Recent Developments in Anode Materials for Lithium Batteries

M.M. Thackeray, J.T. Vaughey, and L.M.L. Frasorson

Overview

Lithium-ion batteries, preferred for their high energy density and low temperature sensitivity, are widely employed for transportation, portable electronics, and large-scale stationary applications. However, the conversion of lithium to lithium ions at the negative electrode leads to volumetric dilatation of the electrode structure, which can result in severe loss of capacity and premature failure. One approach to overcome this problem is the use of intermetallic compounds (IMCs) as anode materials.

Metal Alloys and Intermetallic Compounds

With respect to negative-electrode materials, metal alloys or intermetallic compounds are attractive alternatives to graphite because they can be synthesized with high theoretical capacities, high power densities, and fast full-charging times. However, the choice of alloy depends on various factors such as cost, safety, and availability of raw materials.

The most important challenge is the cycling efficiency of lithium-ion batteries. The volume changes associated with the intercalation-deintercalation processes of the negative electrodes lead to a decrease in electrode efficiency and a decrease in the life cycle of lithium-ion batteries. The ideal negative material should be stable against lithiation and delithiation, reversible, have high power density, have high volumetric capacity, and be safe.

Introduction

Several ternary anode materials can pass a discharge, particularly for large-scale applications, such as electric vehicles and grid storage. These materials offer high volumetric capacities and, with anode structures that allow for low dimensional strain, can be expected for applications in rechargeable lithium-ion batteries. The choice of alloy or intermetallic compound depends on the application and the desired properties.

Specifically, the use of lithium alloys as anode materials for lithium-ion batteries has gained significant interest due to their high energy densities and fast charge/discharge rates.

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Specifically, the use of lithium alloys as anode materials for lithium-ion batteries has gained significant interest due to their high energy densities and fast charge/discharge rates.
Stable and metastable evaluation of the Cu-Co-Fe Phase diagrams

M. Bamberger, A. Mint¢*, L. Kaufman**, and R. Abbaschian***
Materials Science and Engineering, Technion, Technion City, Haifa, ISRAEL
**Nuclear Research Center-Negev P.O. Box 9201, Beer-Sheva, ISRAEL 5848
***140 Clark Road, Brookline, MA 02445-5848, USA

The Thermo-Calc SSOL database for the Cu-Co-Fe ternary system was modified according to experimental data obtained by electromagnetic levitation. Using the modified database, the solidus and the liquidus temperatures were calculated. Very good agreement was obtained between the calculated and the experimental data. The metastable two-melt separation and the compositions of the two melts were calculated as well, and compared with the experimental results.

1) INTRODUCTION

Recently, interest has been growing in extension of solid solubility of alloys exhibiting metastable miscibility gaps, such as Cu-Co alloys. Such materials are known to exhibit giant magneto resistance (GMR) (2, 3), namely a large drop in the electrical resistance under the influence of a magnetic field. For example, a supersaturated CuCo solid solution annealed at 440°C for different durations exhibits an increased GMR of up to 11% at room temperature. It is believed that the heat treatment caused solid-state spinodal decomposition, which is responsible for the enhanced GMR.

Previous studies showed that supercooling of Cu-Fe, Cu-Co or Cu-Fe-Co alloys beyond a certain limit results in metastable separation of the melt into two liquids, one Cu rich (called L2), the other Cu or Fe rich (called L1). Liquid phase separation and formation of metastable phases were observed during rapid cooling of these alloys.

However, there is only meager information on the stable ternary Cu-Co-Fe diagram.

Recently, some experimental data for the melting temperatures were published concerning the Cu-Co-Fe system (4). Based on the Fe-Cu/Al and Co-Cu/Al binary phase diagrams, approximate isothermal sections have been constructed (5).

The present work is aimed at obtaining a reliable database for the Cu-Co-Fe system, and to perform consistent calculations of the stable phase diagram.

Figure 1: Diagram of the ternary Cu-Co-Fe phase diagram.
Thermodynamic Modeling of the Zr-O System
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Abstract: In this study, the complete zirconium-oxygen system has been critically assessed at 1 atm from 300°C to liquidus temperatures. Thermocchemical measurements and phase diagram data were used to model the Gibbs free energies of seven phases. Additionally, the ordered, disordered HCP-based solutions were included and considered as simple line compounds. By using the PARROT module in Thermo-Calc, it was possible to optimize the parameters of the models used to describe the Gibbs free energies of the BCC, BCC, BCC, and HCP phases. The Gas phase was considered to behave ideally. Although phase diagrams including the stoichiometric amorphous phase have been assessed, this is the first time, to the best of our knowledge, that a complete assessment of this system is published.

Figure 1. Isothermal Sections in Nb-Ti-Cr at 1800°C, 1600°C, 1500°C and 1300°C. Two-Phase Regions are identified by Tie-Lines, Three-Phase Regions by Triangles and Single Phase Regions are Labeled.
Figure 3. Calculated Binary Phase Diagram Components of the Ti-Al-Cr System. The Liquid Phase is designated by L.

Figure 4. Calculated Isothermal Sections in Ti-Al-Cr at 1500°C, 1300°C, 1200°C, and 1000°C. Two-Phase Regions are identified by Tie-Lines, Three-Phase Regions by Triangles and Single Phase Regions are labeled.

Figure 13. Calculated Isopleth constrained by the Conditions that weight%Cr=4wt.%Al and wt%Ti=3wt%Cr.

Figure 17. Calculated Isothermal Section in the Nb-Cr-Mo System at 1200°C.
Validation of Thermo-Calc Database with Experiment
Experimental versus Calculated Ternary Phase Diagrams (Ni-Cr-Mo)

Equilibrium and Scheil Results for Solidification

Kinetics of Alloy Phase Transformation: TTT Diagrams
Preliminary results from DICTRA: application to temporal evolution of ordering in Ni-Cr

Ni-Cr Alloy: for Solid Solution \( \rightarrow \) Ni2Cr Ordered Phase: 50% transformation

Experimental input is required to validate thermodynamic quantities and diffusion coefficients that are used in the combined software Thermo-Calc- DICTRA to predict kinetics of phase formation as summarized in TTT diagrams.
Fig. 14 Experimental measurement of TCP phase formation in C-22 by Tammy Summers and Sharon G. Torres compared with calculation of $P_{\text{Phase}}$ formation in a Ni-21.1-13.5Cr Alloy.

DISCUSSION OF THE STABILITY OF THE FCC AND BCC PHASES IN THE Cr-Ni SYSTEM

As indicated in the INTRODUCTION the LS values used in current CT work have been criticized because ab initio values for some elements are substantially larger in magnitude than the LS values that are employed. Initially, it was suggested that these differences.
Additional points made by speaker:

For the assessment of the thermodynamic quantities of the TCP phases in Ni-X systems results from *ab initio* calculations were taken into account.

The thermodynamic description of the Ni-Cr-Mo system was used to generate Pourbaix diagrams for the prediction of the corrosion behavior under various conditions.
Thoughts on the Acceleration of Phase Equilibria Research
J.-C. Zhao, General Electric Company, Schenectady, NY
Additional points made by speaker:

Predictions of TCP phases for Ni-Base systems with currently available thermodynamic databases are not very reliable ⇒ lack of experimental data needs to be overcome to facilitate more accurate modeling of these phases. Accurate ternary phase diagram data are needed for the improvement of the model descriptions of these phases for multicomponent databases.