NISTIR 6927

Databases for Computational Thermodynamics and Diffusion Modeling

Workshop Report

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NIST
National Institute of Standards and Technology
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Donald L. Evans, Secretary
TECHNOLOGY ADMINISTRATION
Phillip J. Bond, Under Secretary of Commerce for Technology
NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY
Arden L. Bement, Jr., Director

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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

9:10 *Computer Simulations and Database Needs for Energy Savings, Zero Environmental Impact and Quality Improvements For the Heat Treating Industry*
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

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 mulicomponent 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 7×10^{15} J (7×10^{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.

<u>Action Items</u>

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).
7. Encourage links to CALPHAD web site (http://www.calphad.org).
   – 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

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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 *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, *e.g.*:
        - von Barth & Hedin
        - Vosko
        - Ceperley & Alder (Perdew & Zunger)
The selection of an exchange potential will impact the results, *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, *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)
Pseudo-potentials and plane-wave basis set
Siesta (http://www.uam.es/depatamentos/ciencias/fismateriac/siesta)
Pseudo-potentials and LCAO basis set
ABINIT (http://www.abinit.org)
Pseudo-potentials and plane-wave basis set

Full-potential Methods:

Wien97(http://www.tuwien.ac.at/theochem/wien97), replaced now by:
Wien2k (http://www.wien2k.at)
Linear Augmented Plane Wave (LAPW) and local orbital method
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.

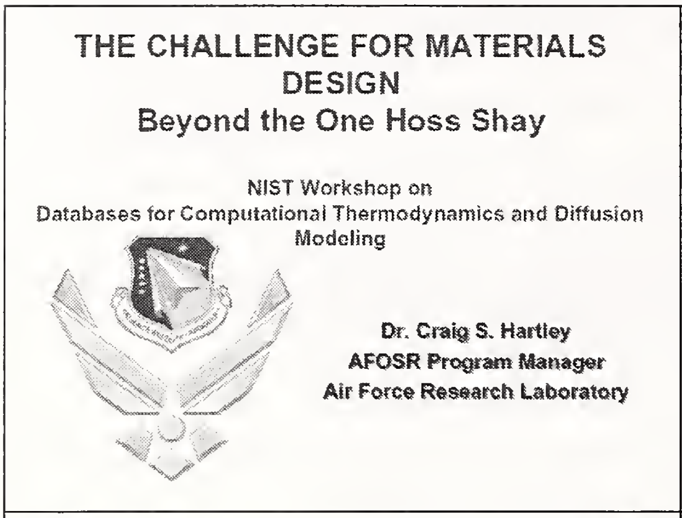
The objectives of Workshop were identified as:

- 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

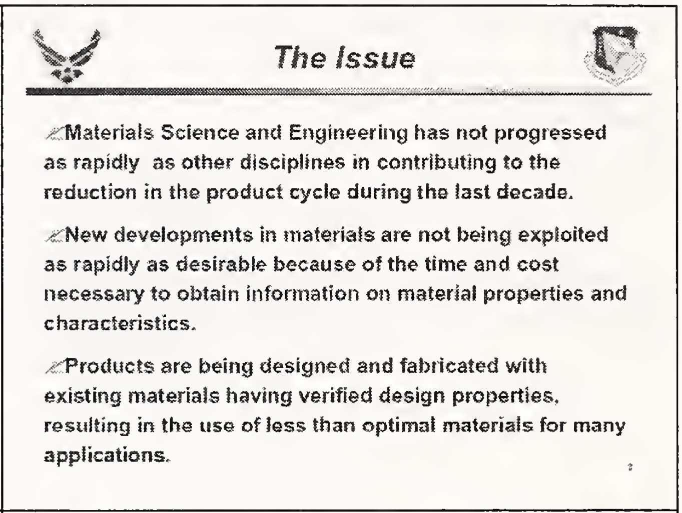
Craig S. Hartley, AFOSR (Air Force Office of Scientific Research), Arlington, VA



THE CHALLENGE FOR MATERIALS DESIGN
Beyond the One Hoss Shay

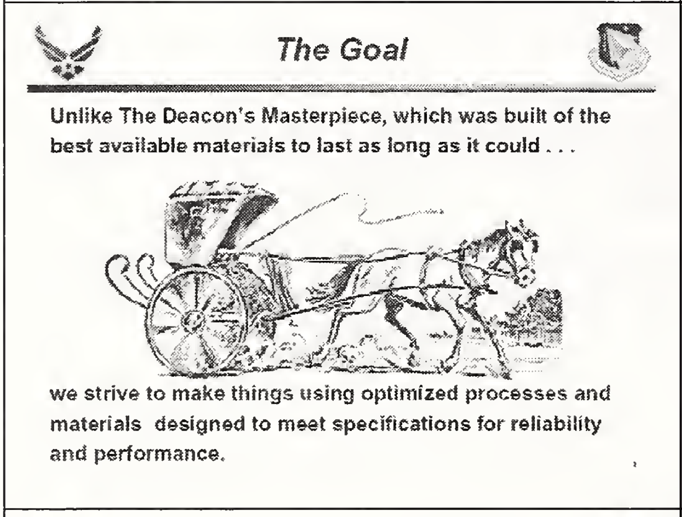
NIST Workshop on
Databases for Computational Thermodynamics and Diffusion Modeling

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



The Issue

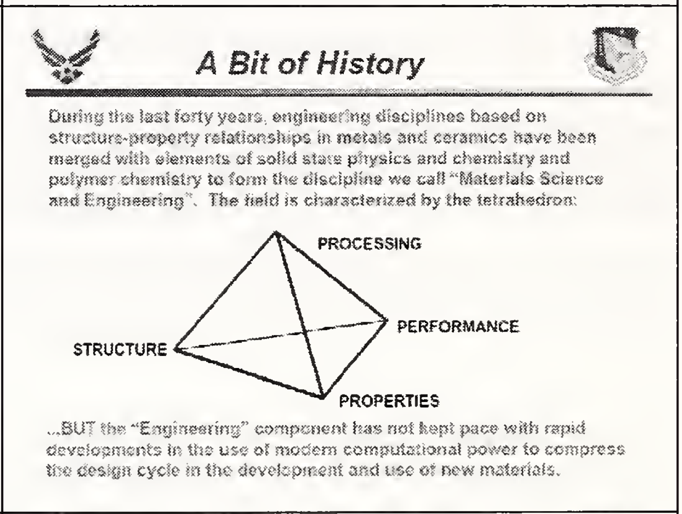
- Materials Science and Engineering has not progressed as rapidly as other disciplines in contributing to the reduction in the product cycle during the last decade.
- New developments in materials are not being exploited as rapidly as desirable because of the time and cost necessary to obtain information 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.



The Goal

Unlike The Deacon's Masterpiece, which was built of the best available materials to last as long as it could . . .

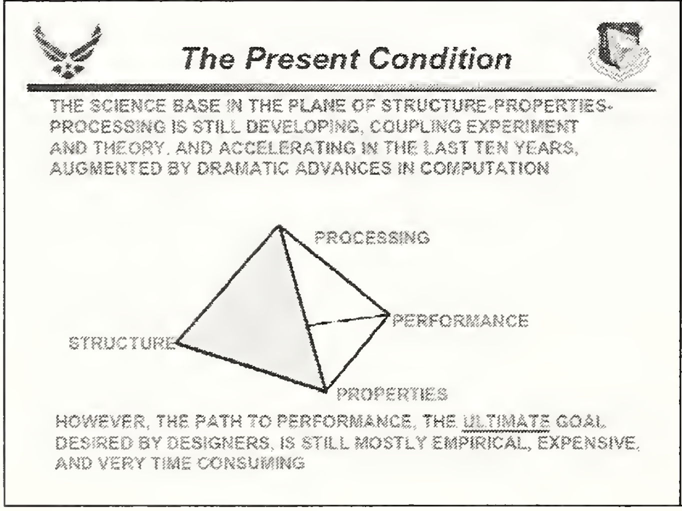
we strive to make things using optimized processes and materials designed to meet specifications for reliability and performance.



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". The field is characterized by the tetrahedron:

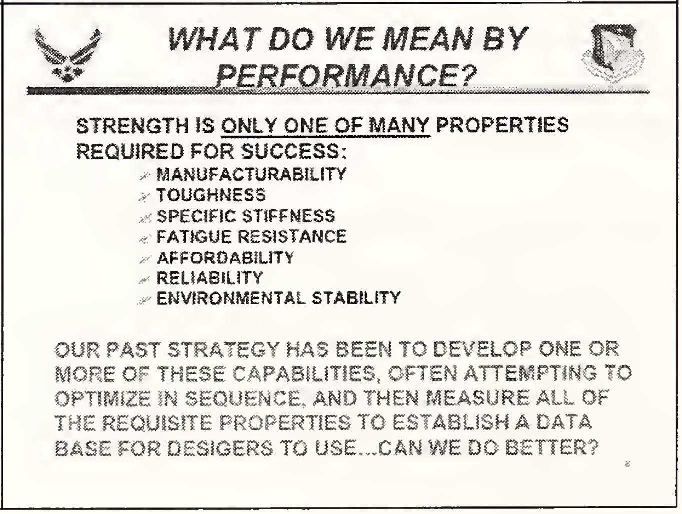
...BUT the "Engineering" component has not kept pace with rapid developments in the use of modern computational power to compress the design cycle in the development and use of new materials.



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

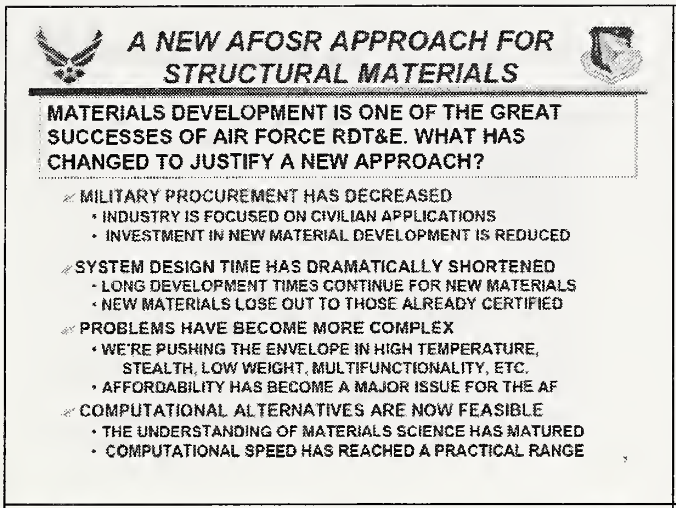


WHAT DO WE MEAN BY PERFORMANCE?

STRENGTH IS ONLY ONE OF MANY PROPERTIES REQUIRED FOR SUCCESS:

- MANUFACTURABILITY
- TOUGHNESS
- SPECIFIC STIFFNESS
- FATIGUE RESISTANCE
- AFFORDABILITY
- RELIABILITY
- ENVIRONMENTAL STABILITY

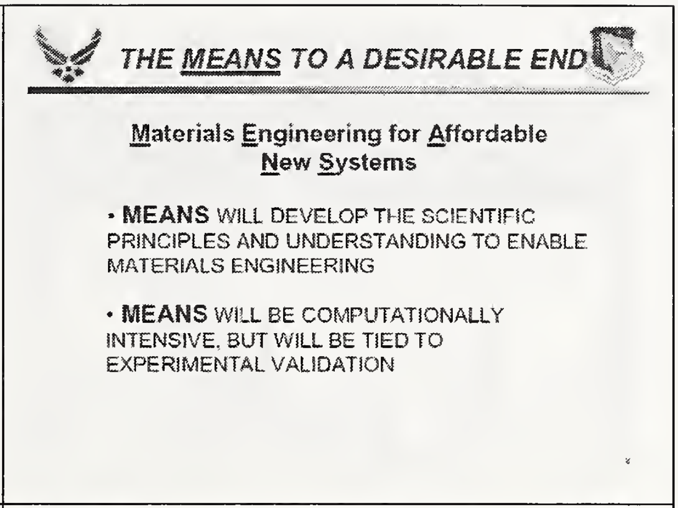
OUR PAST STRATEGY HAS BEEN TO DEVELOP ONE OR MORE OF THESE CAPABILITIES, OFTEN ATTEMPTING TO OPTIMIZE IN SEQUENCE, AND THEN MEASURE ALL OF THE REQUISITE PROPERTIES TO ESTABLISH A DATA BASE FOR DESIGERS TO USE...CAN WE DO BETTER?



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?

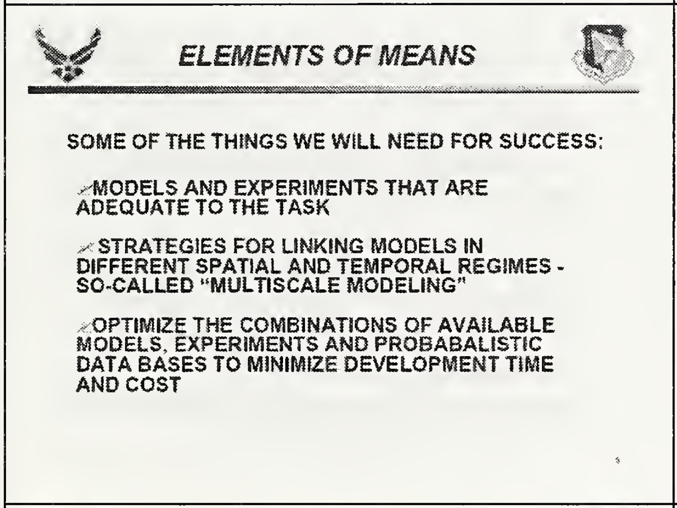
- MILITARY PROCUREMENT HAS DECREASED
  - INDUSTRY IS FOCUSED ON CIVILIAN APPLICATIONS
  - INVESTMENT IN NEW MATERIAL DEVELOPMENT IS REDUCED
- SYSTEM DESIGN TIME HAS DRAMATICALLY SHORTENED
  - LONG DEVELOPMENT TIMES CONTINUE FOR NEW MATERIALS
  - NEW MATERIALS LOSE OUT TO THOSE ALREADY CERTIFIED
- PROBLEMS 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

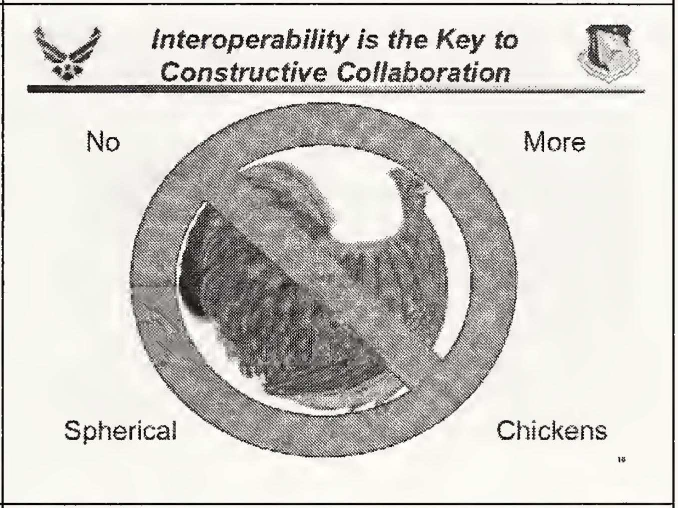
- **MEANS** WILL DEVELOP THE SCIENTIFIC PRINCIPLES AND UNDERSTANDING TO ENABLE MATERIALS ENGINEERING
- **MEANS** WILL BE COMPUTATIONALLY INTENSIVE, BUT WILL BE TIED TO EXPERIMENTAL VALIDATION



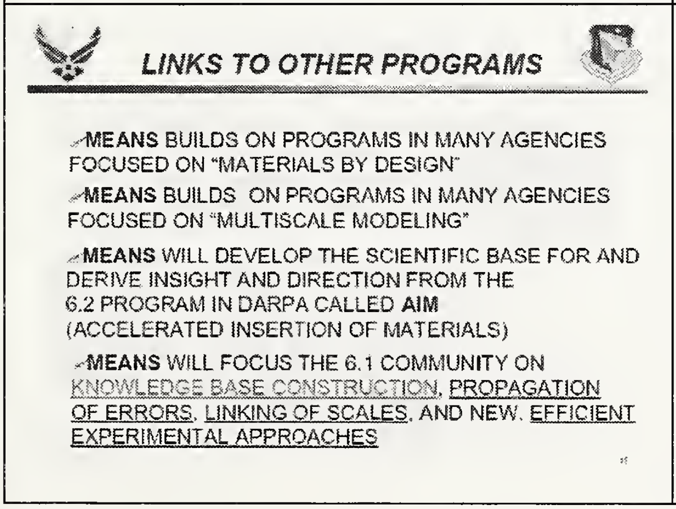
ELEMENTS OF MEANS

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 PROBABALISTIC DATA BASES TO MINIMIZE DEVELOPMENT TIME AND COST

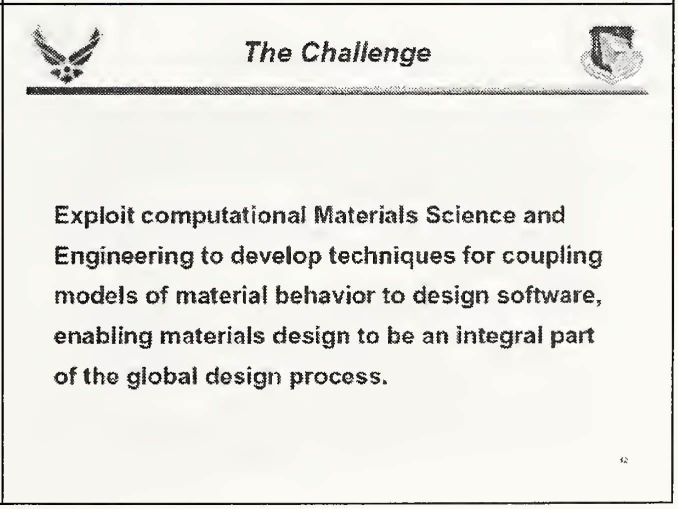


Interoperability is the Key to Constructive Collaboration



LINKS TO OTHER PROGRAMS

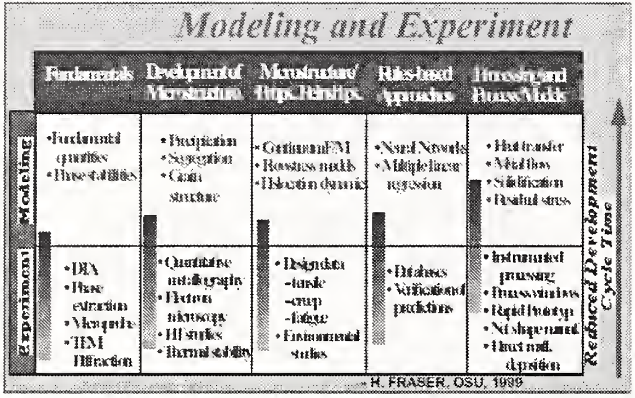
- **MEANS** BUILDS ON PROGRAMS IN MANY AGENCIES FOCUSED ON "MATERIALS BY DESIGN"
- **MEANS** BUILDS ON PROGRAMS IN MANY AGENCIES FOCUSED ON "MULTISCALE MODELING"
- **MEANS** WILL DEVELOP THE SCIENTIFIC BASE FOR AND DERIVE INSIGHT AND DIRECTION FROM THE 6.2 PROGRAM IN DARPA CALLED **AIM** (ACCELERATED 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



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.

CURRENT STATUS OF COMPUTATIONAL METHODS



Modeling and Experiment

	Fundamentals	Development of Microstructure	Microstructure/ Prop. Relationships	Rules-based Approaches	Processing and Process Models
Modeling	•Fundamental quantities •Phase stabilities	•Precipitation •Segregation •Grain structure	•Continuum FEM •Robustness models •Dislocation dynamics	•Neural Networks •Multiple linear regression	•Heat transfer •Metal flow •Solidification •Residual stress
Experiment	•DTA •Phase extraction •Microprobe •TEM Diffraction	•Quantitative metallography •Electron microscopy •HT studies •Thermal stability	•Design data -tensile -creep -fatigue •Environmental studies	•Databases •Verification of predictions	•Instrumented processing •Process windows •Rapid Prototyp •Net shape manuf. •Direct matl. deposition

Reduced Development Cycle Time

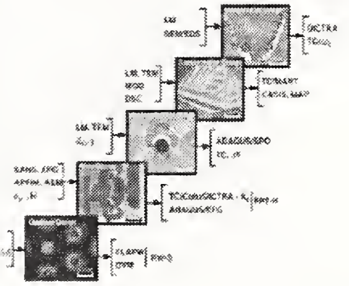
– H. FRASER, OSU, 1999

MEANS Projects in Metallic Materials

- COMPUTATONAL 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

Computational Design of Advanced Aeroturbine Materials (Olson, NWU)

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.



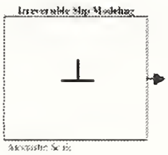
DEVELOPMENT OF A PHYSICS-BASED METHODOLOGY FOR PREDICTING MATERIAL VARIABILITY IN FATIGUE CRACK INITIATION AND GROWTH (Chan, SWRI)

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

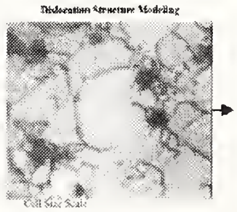
ATOMIC SCALE

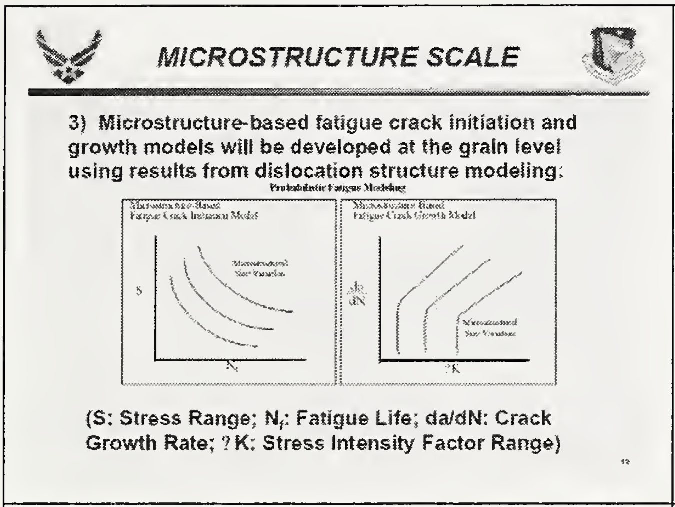
1) The friction stress for irreversible slip during fatigue will be modeled at the atomistic scale using the Peierls-Nabarro model and the thermally activated flow approach.



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.

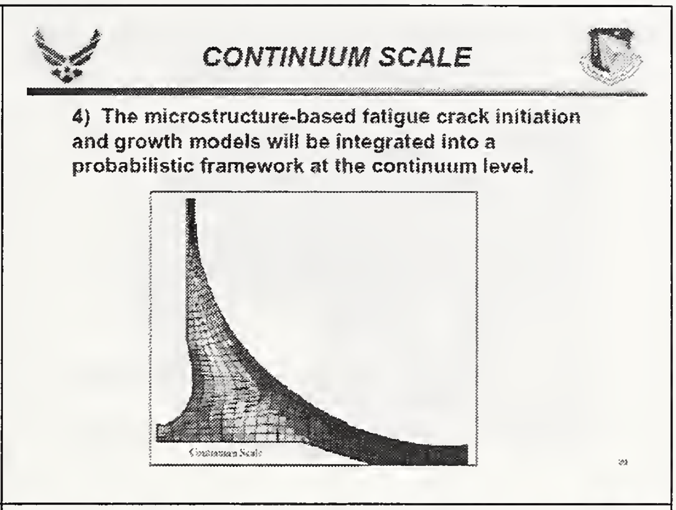




MICROSTRUCTURE SCALE

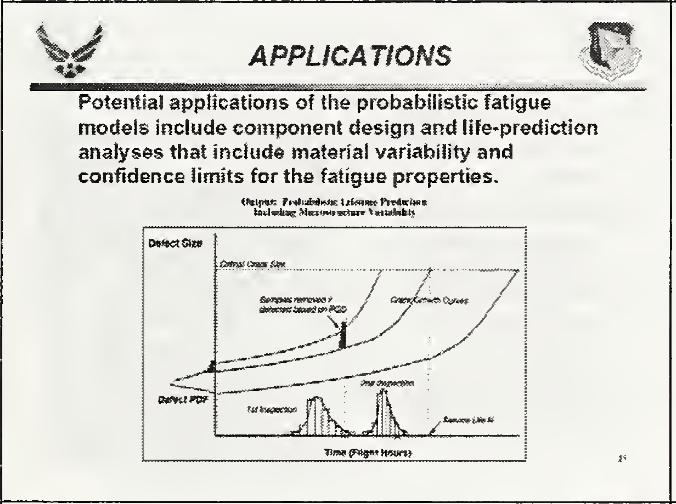
3) Microstructure-based fatigue crack initiation and growth models will be developed at the grain level using results from dislocation structure modeling:

(S: Stress Range; N_f: Fatigue Life; da/dN: Crack Growth Rate; ? K: Stress Intensity Factor Range)



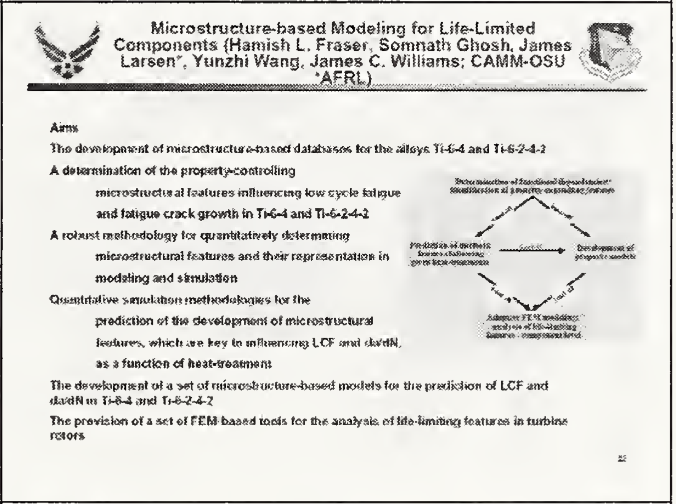
CONTINUUM SCALE

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



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.



Microstructure-based Modeling for Life-Limited Components (Hamish L. Fraser, Somnath Ghosh, James Larsen*, Yunzhi Wang, James C. Williams; CAMM-OSU *AFRL)

Aims

The development of microstructure-based databases for the alloys Ti-6-4 and Ti-6-2-4-2

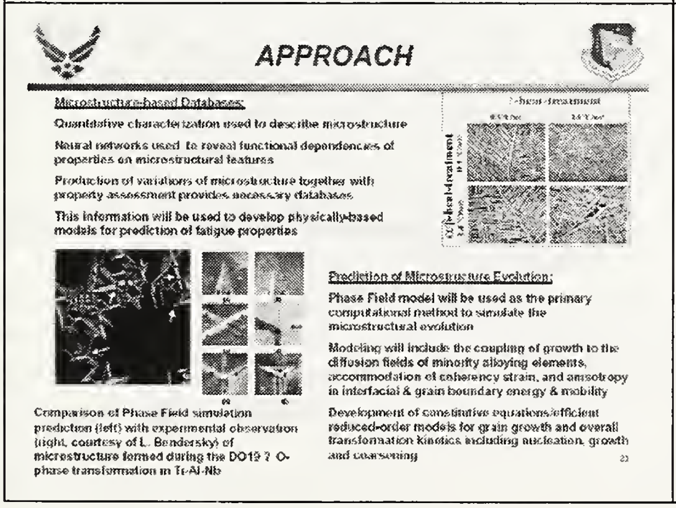
A determination of the property-controlling microstructural features influencing low cycle fatigue and fatigue crack growth in Ti-6-4 and Ti-6-2-4-2

A robust methodology for quantitatively determining microstructural features and their representation in modeling and simulation

Quantitative simulation methodologies for the prediction of the development of microstructural features, which are key to influencing LCF and da/dN, as a function of heat-treatment

The development of a set of microstructure-based models for the prediction of LCF and da/dN in Ti-6-4 and Ti-6-2-4-2

The provision of a set of FEM-based tools for the analysis of life-limiting features in turbine rotors



APPROACH

Microstructure-based Databases:

Quantitative characterization used to describe microstructure

Neural networks used to reveal functional dependencies of properties on microstructural features

Production of variations of microstructure together with property assessment provides necessary databases

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

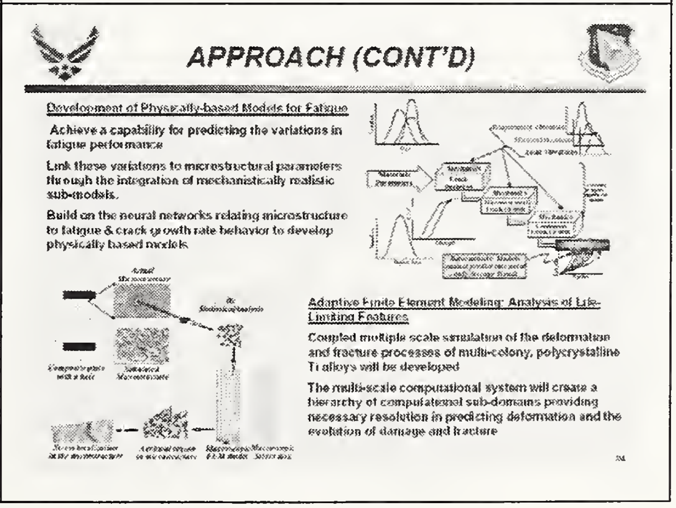
Comparison of Phase Field simulation prediction (left) with experimental observation (right, courtesy of L. Bendersky) of microstructure formed during the DO19 ? O-phase transformation in Ti-Al-Nb

Prediction of Microstructure Evolution:

Phase Field model will be used as the primary computational method to simulate the microstructural evolution

Modeling will include the coupling of growth to the diffusion fields of minority alloying elements, accommodation of coherency strain, and anisotropy in interfacial & grain boundary energy & mobility

Development of constitutive equations/efficient reduced-order models for grain growth and overall transformation kinetics including nucleation, growth and coarsening



APPROACH (CONT'D)

Development of Physically-based Models for Fatigue

Achieve a capability for predicting the variations in fatigue performance

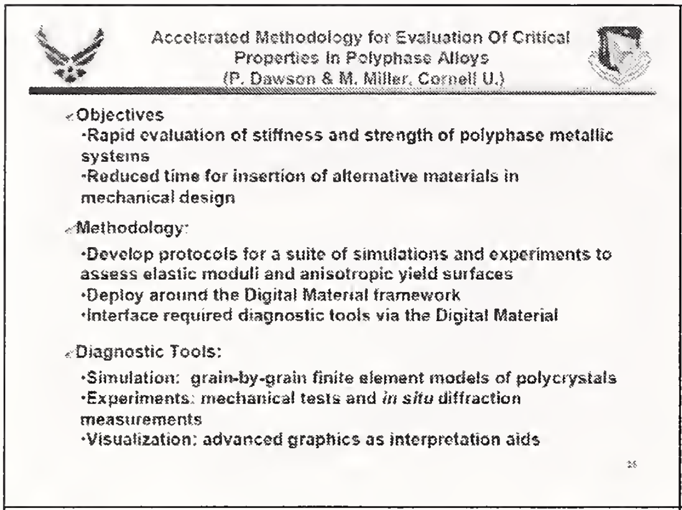
Link these variations to microstructural parameters through the integration of mechanistically realistic sub-models.

Build on the neural networks relating microstructure to fatigue & crack growth rate behavior to develop physically based models

Adaptive Finite Element Modeling: Analysis of Life-Limiting Features

Coupled multiple scale simulation of the deformation and fracture processes of multi-colony, polycrystalline Ti alloys will be developed

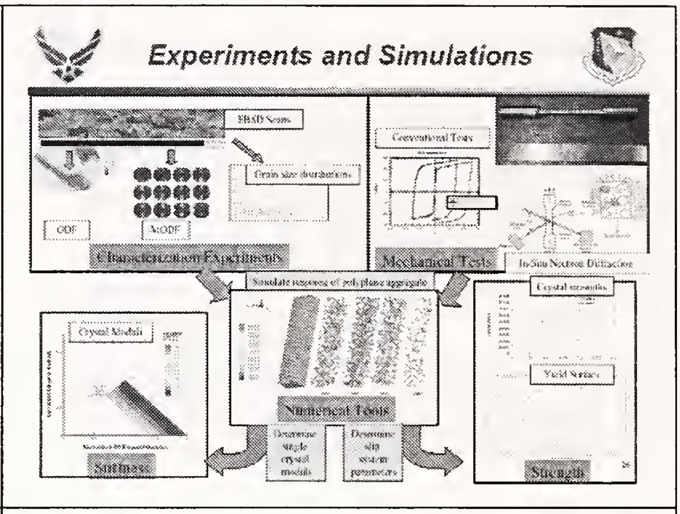
The multi-scale computational system will create a hierarchy of computational sub-domains providing necessary resolution in predicting deformation and the evolution of damage and fracture



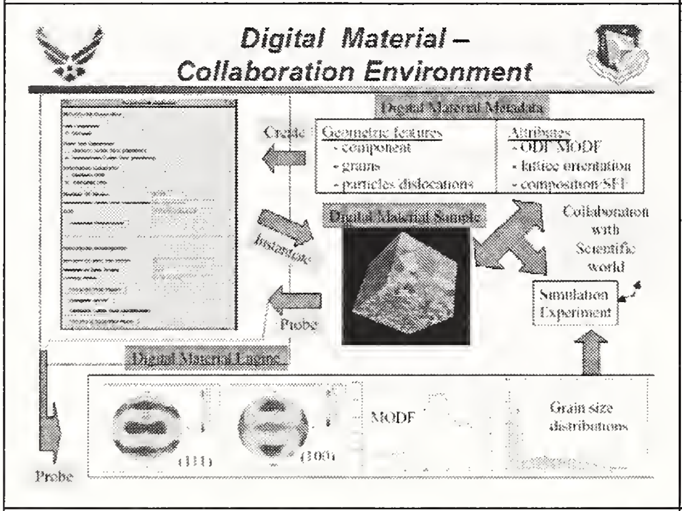
Accelerated Methodology for Evaluation Of Critical Properties In Polyphase Alloys

(P. Dawson & M. Miller, Cornell U.)

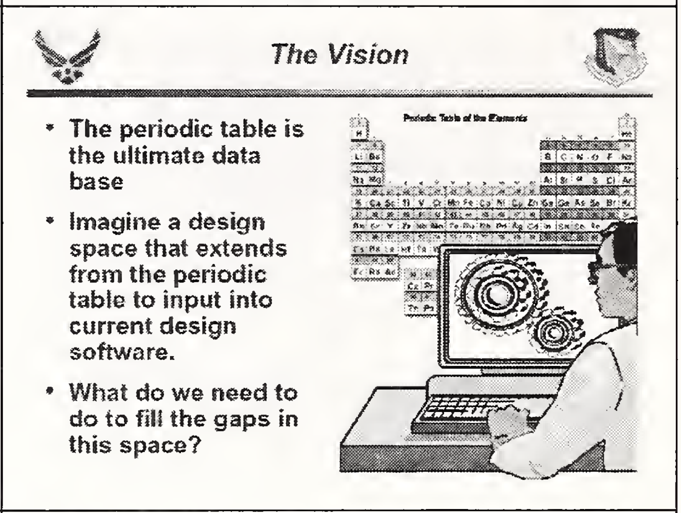
- Objectives
  - Rapid evaluation of stiffness and strength of polyphase metallic systems
  - Reduced time for insertion of alternative materials in mechanical design
- Methodology:
  - Develop protocols for a suite of simulations and experiments to assess elastic moduli and anisotropic yield surfaces
  - 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



Experiments and Simulations

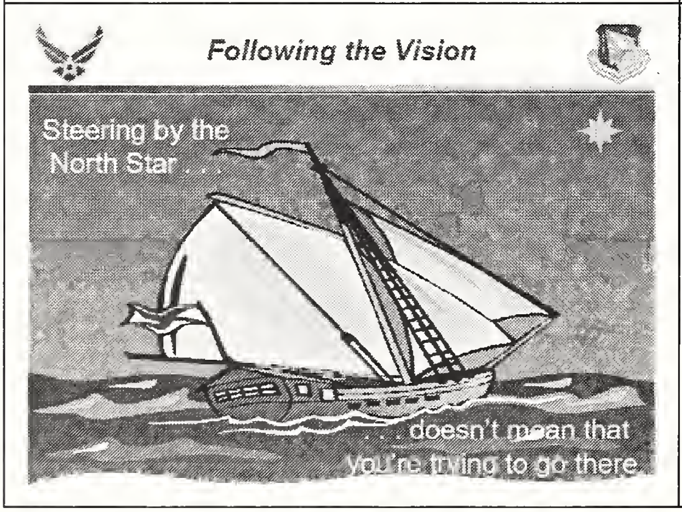


Digital Material – Collaboration Environment

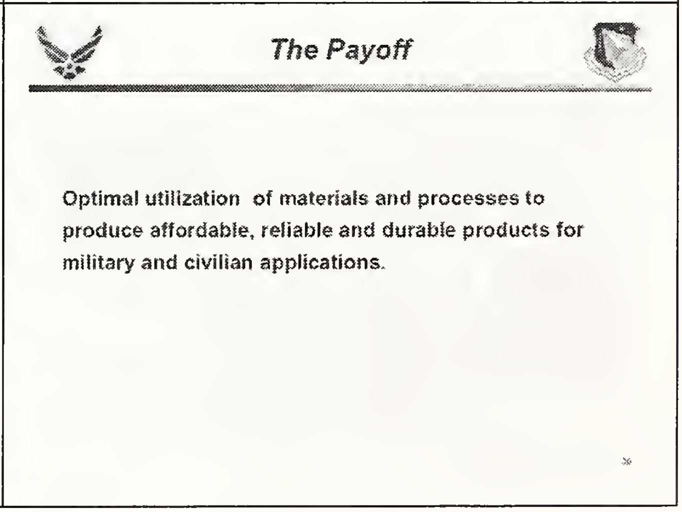


The Vision

- The periodic table is the ultimate data base
- 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?

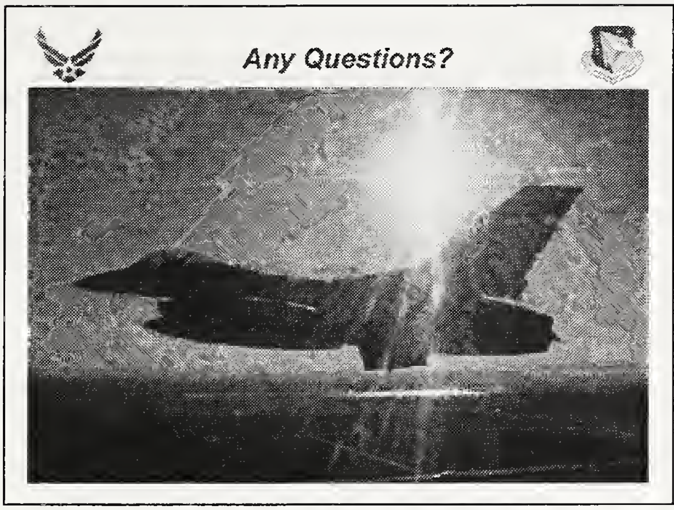


Following the Vision

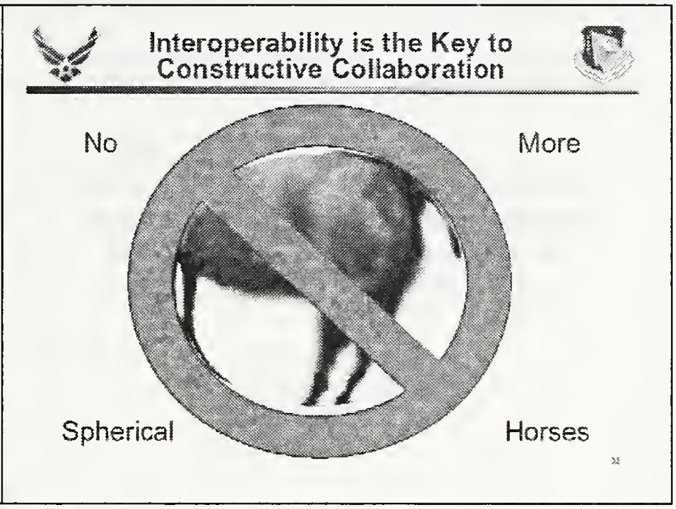


The Payoff

Optimal utilization of materials and processes to produce affordable, reliable and durable products for military and civilian applications.



Any Questions?



Interoperability is the Key to Constructive Collaboration

No More

Spherical Horses

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

Application and Needs Assessment of Thermodynamic Databases at Howmet Castings

Tyrus W. Hansen
Howmet Research Corporation
3/21/02

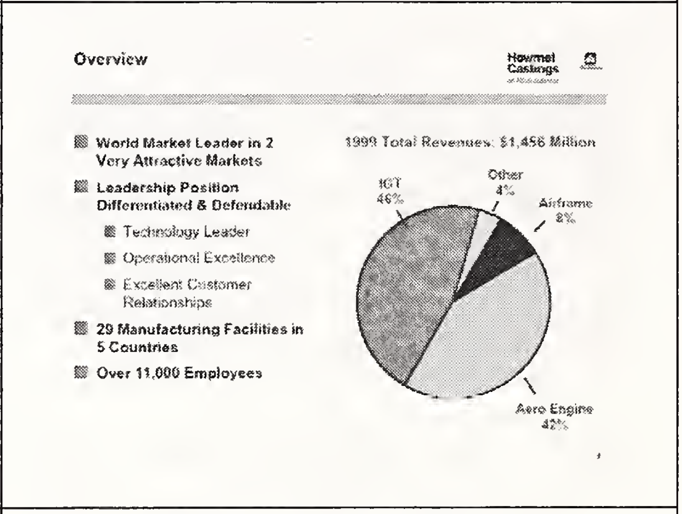
Application and Needs Assessment of Thermodynamic Databases at Howmet Castings

Introduction

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

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



Overview

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

1999 Total Revenues: $1,456 Million

Airframe Market

- Aircraft Components: Al & Ti
  Doors, Nacelle, Strut, Flight Control, APU and Environmental Systems.
- Missile Components: Al & Ti
  Missile Bodies, Fins, Optical Seeker and Fuel Components, Electronic Boxes/frames.
- Rocket Components: S/A
  High Pressure Fuel and LOX Pump and Turbine Housings.

Aft Engine Mount

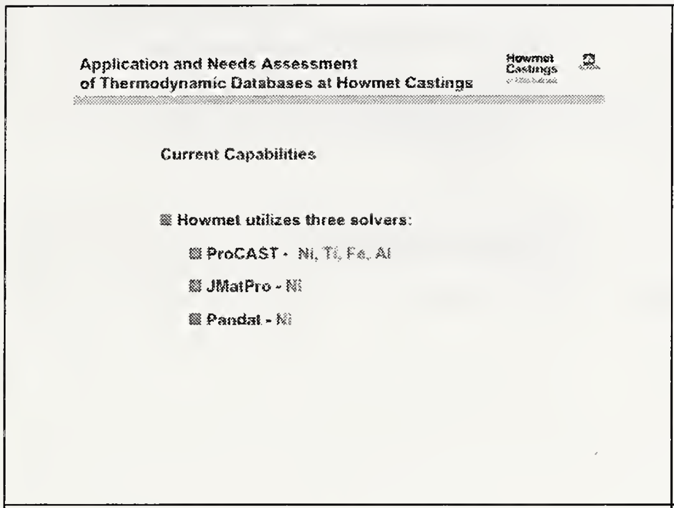
Major Customers

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

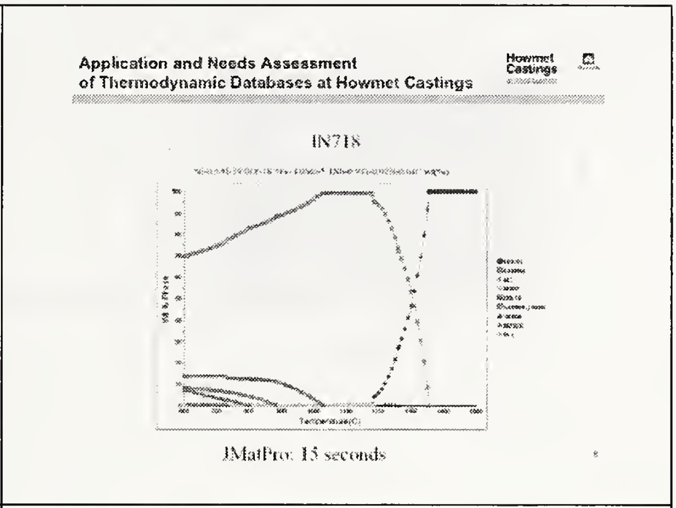


Application and Needs Assessment of Thermodynamic Databases at Howmet Castings

Howmet Castings

Current Capabilities

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

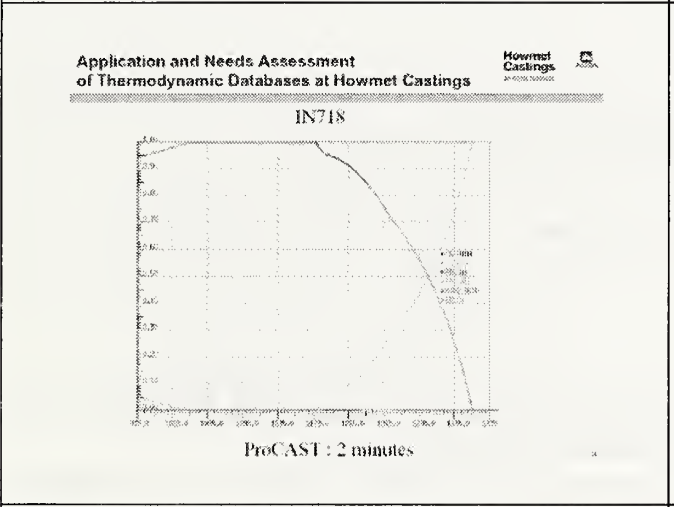


Application and Needs Assessment of Thermodynamic Databases at Howmet Castings

Howmet Castings

IN718

JMatPro: 15 seconds

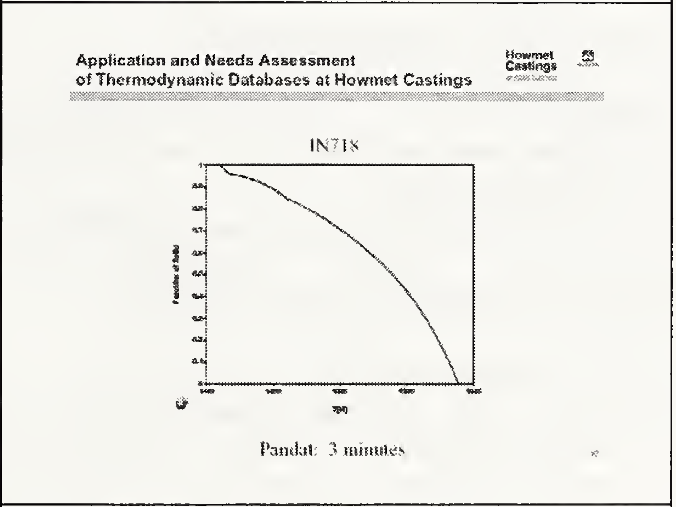


Application and Needs Assessment of Thermodynamic Databases at Howmet Castings

Howmet Castings

IN718

ProCAST : 2 minutes

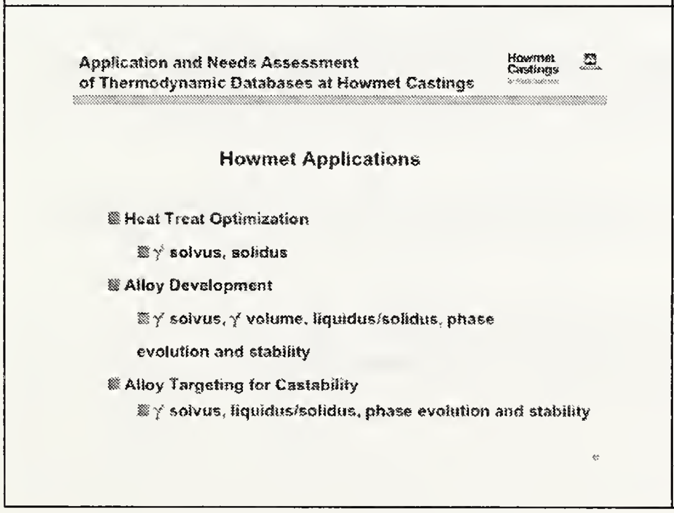


Application and Needs Assessment of Thermodynamic Databases at Howmet Castings

Howmet Castings

IN718

Pandat: 3 minutes

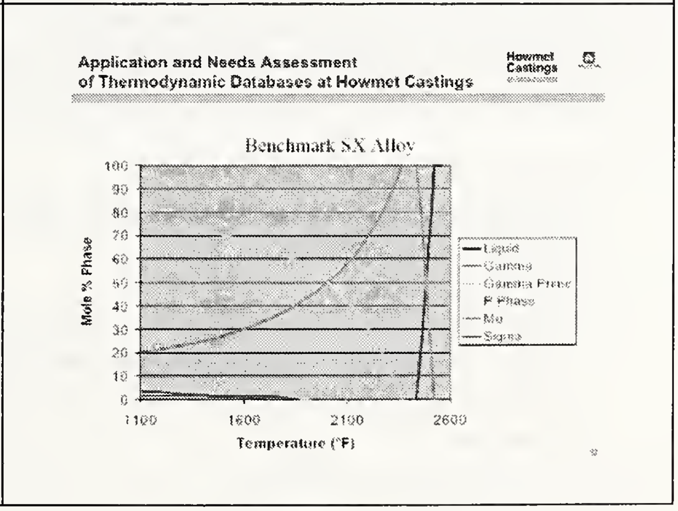


Application and Needs Assessment of Thermodynamic Databases at Howmet Castings

Howmet Castings

Howmet Applications

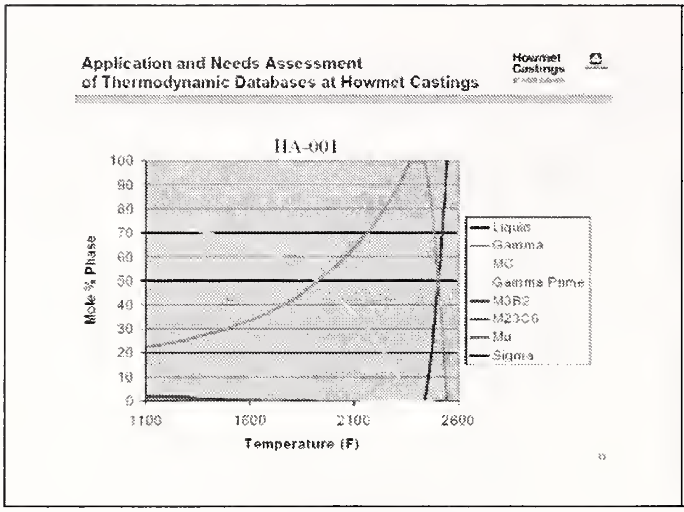
- Heat Treat Optimization
  - γ' solvus, solidus
- Alloy Development
  - γ' solvus, γ' volume, liquidus/solidus, phase evolution and stability
- Alloy Targeting for Castability
  - γ' solvus, liquidus/solidus, phase evolution and stability



Application and Needs Assessment of Thermodynamic Databases at Howmet Castings

Howmet Castings

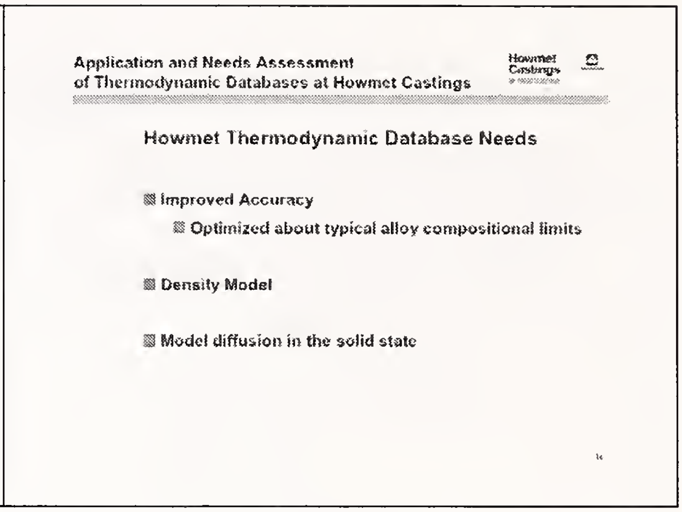
Benchmark SX Alloy



Application and Needs Assessment
of Thermodynamic Databases at Howmet Castings

Howmet Castings

HA-001



Application and Needs Assessment
of Thermodynamic Databases at Howmet Castings

Howmet Castings

Howmet Thermodynamic Database Needs

- ▨ Improved Accuracy
  - ▨ Optimized about typical alloy compositional limits
- ▨ Density Model
- ▨ Model diffusion in the solid state

<u>Summary from workshop organizers:</u>

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

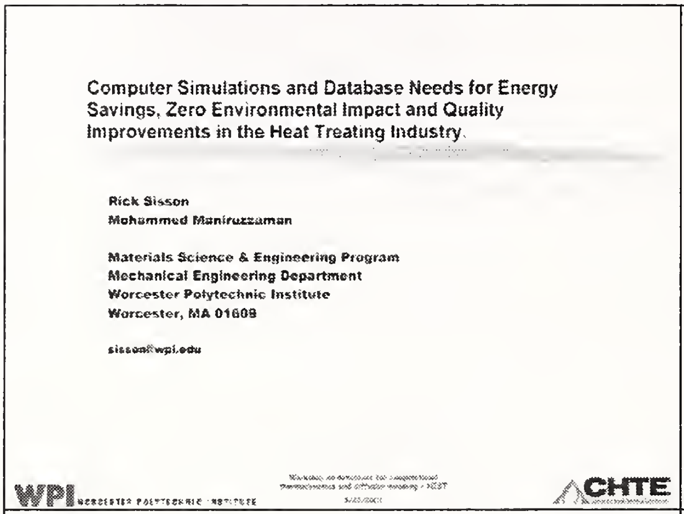
- Heat Treatment Optimization
  - Calculation of γ' solvus, solidus (motivation: sell reduced heat cycle to customers, need more experimental verification)
- Alloy Development
  - Calculation of γ' solvus, γ' volume, liquidus/solidus, phase evolution, stability
  - Objective: improve castability (customers – 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

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

Computer Simulations and Database Needs for Energy Savings, Zero Environmental Impact and Quality Improvements for the Heat Treating Industry

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



Computer Simulations and Database Needs for Energy Savings, Zero Environmental Impact and Quality Improvements in the Heat Treating Industry.

Rick Sisson
Mohammed Maniruzzaman

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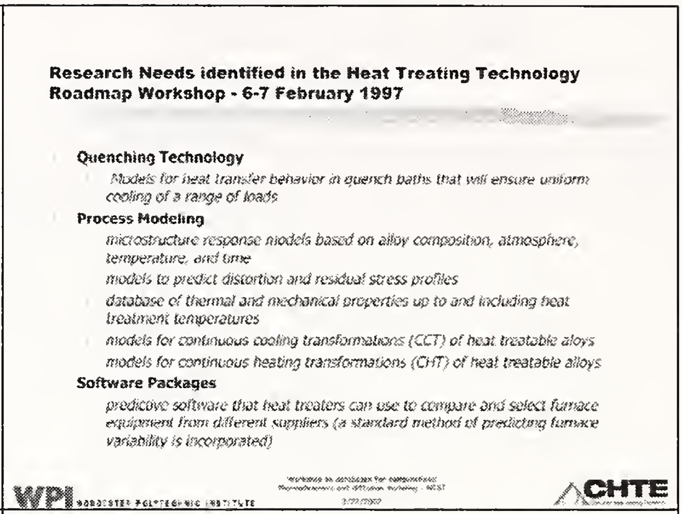
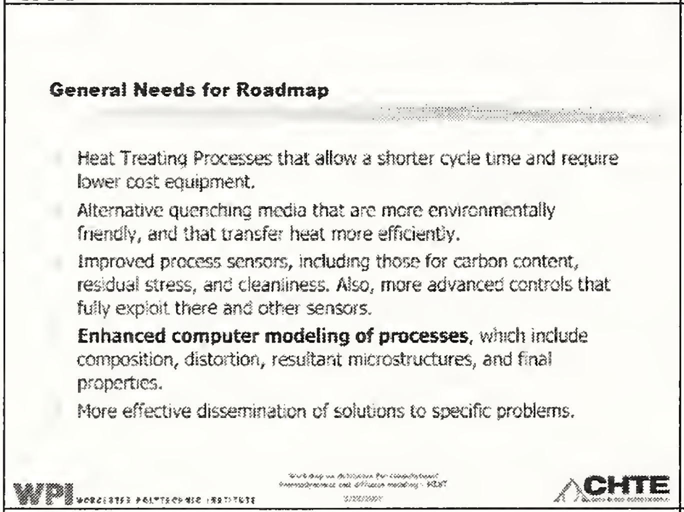


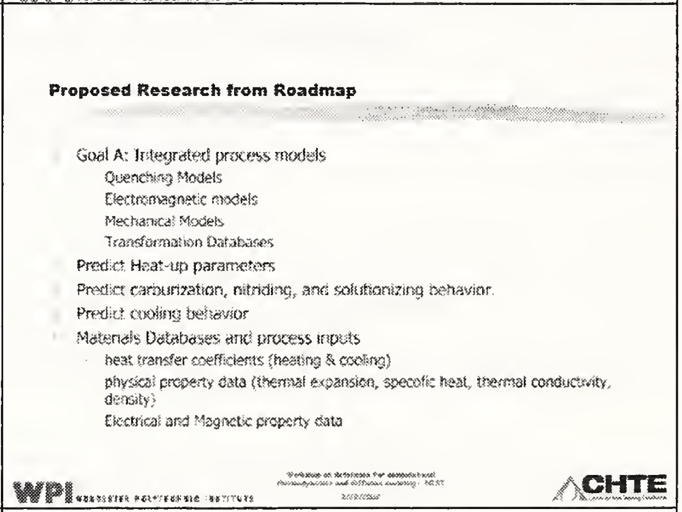
Research Needs identified in the Heat Treating Technology Roadmap Workshop - 6-7 February 1997

- **Quenching Technology**
  - *Models for heat transfer behavior in quench baths that will ensure uniform cooling of a range of loads*
- **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 up to and including heat treatment temperatures*
  - *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)*



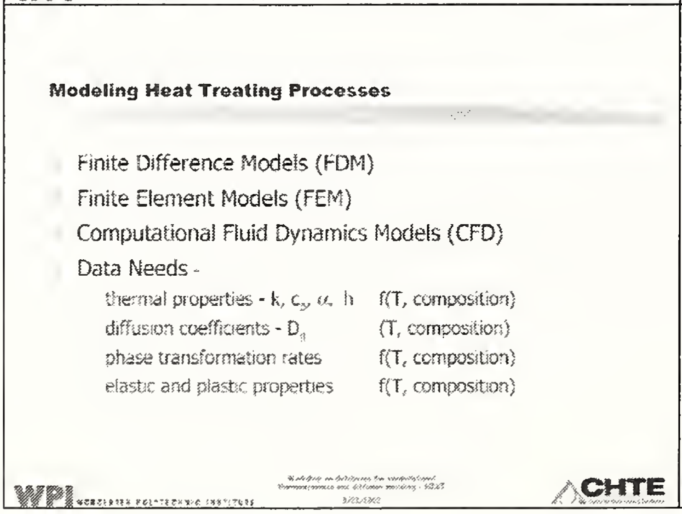
General Needs for Roadmap

- 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, resultant microstructures, and final properties.
- More effective dissemination of solutions to specific problems.



Proposed Research from Roadmap

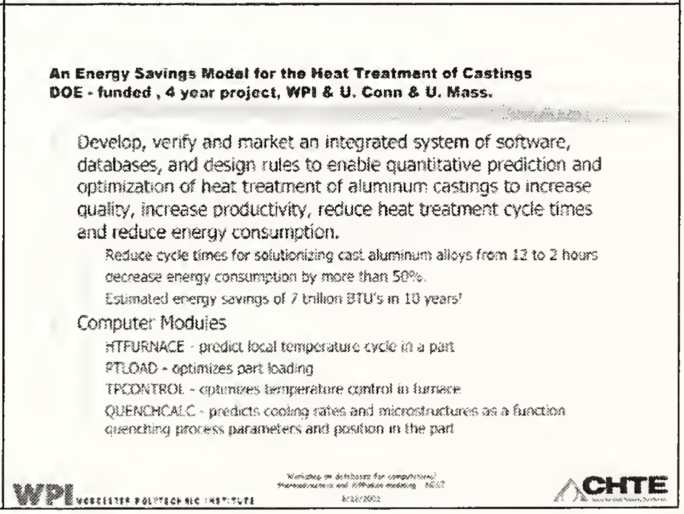
- Goal A: Integrated process models
  - Quenching Models
  - Electromagnetic models
  - Mechanical Models
  - Transformation Databases
- Predict Heat-up parameters
- Predict carburization, nitriding, and solutionizing behavior.
- Predict cooling behavior
- Materials Databases and process inputs
  - heat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



Modeling Heat Treating Processes

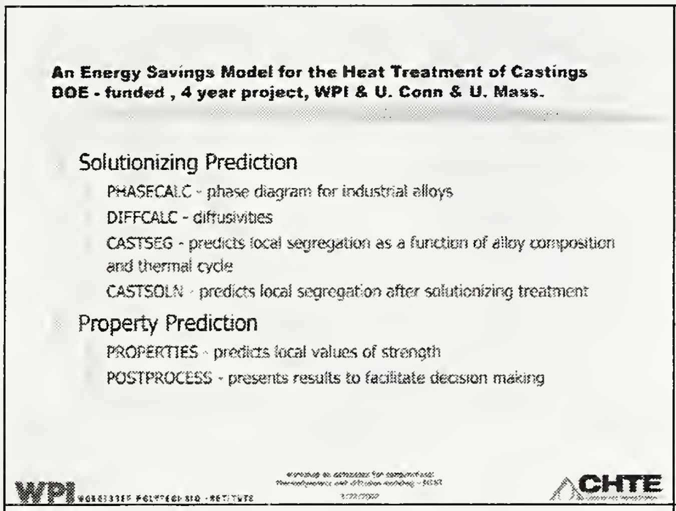
- Finite Difference Models (FDM)
- Finite Element Models (FEM)
- Computational Fluid Dynamics Models (CFD)
- Data Needs -

thermal properties - k, c_p, α, h	f(T, composition)
diffusion coefficients - D_i	(T, composition)
phase transformation rates	f(T, composition)
elastic and plastic properties	f(T, composition)



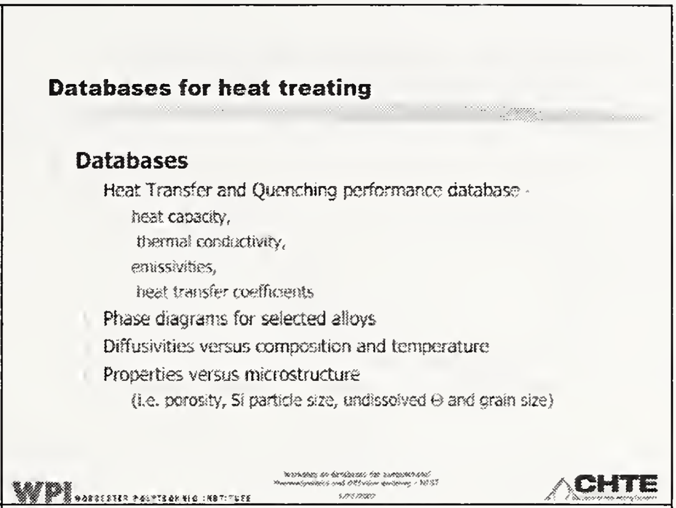
An Energy Savings Model for the Heat Treatment of Castings
DOE - funded , 4 year project, WPI & U. Conn & U. Mass.

- 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 times and reduce energy consumption.
  - Reduce cycle times for solutionizing cast aluminum alloys from 12 to 2 hours
  - decrease energy consumption by more than 50%.
  - Estimated energy savings of 7 trillion BTU's in 10 years'
- Computer Modules
  - HTFURNACE - predict local temperature cycle in a part
  - PTLOAD - optimizes part loading
  - TFCONTROL - optimizes temperature control in furnace
  - QUENCHCALC - predicts cooling rates and microstructures as a function quenching process parameters and position in the part



An Energy Savings Model for the Heat Treatment of Castings
DOE - funded , 4 year project, WPI & U. Conn & U. Mass.

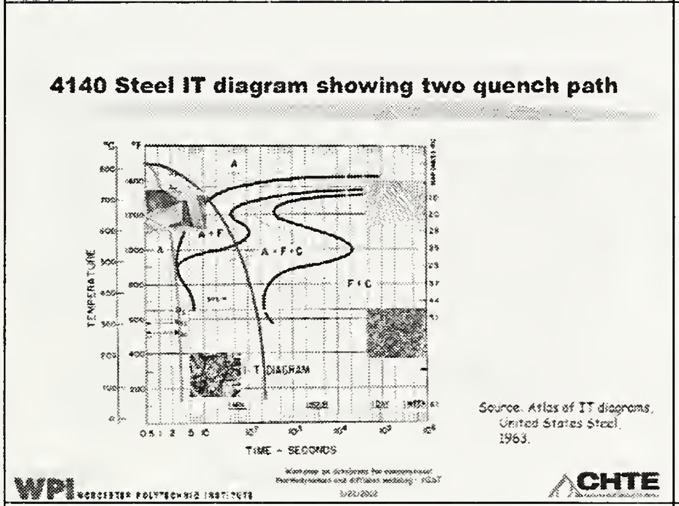
- Solutionizing Prediction
  - PHASECALC - phase diagram for industrial alloys
  - DIFFCALC - diffusivities
  - CASTSEG - predicts local segregation as a function of alloy composition and thermal cycle
  - CASTSOLN - predicts local segregation after solutionizing treatment
- Property Prediction
  - PROPERTIES - predicts local values of strength
  - POSTPROCESS - presents results to facilitate decision making



Databases for heat treating

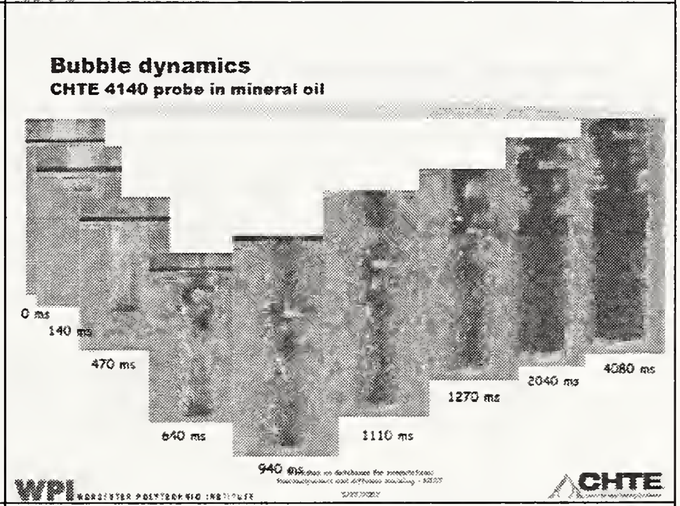
Databases

- 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 Θ and grain size)

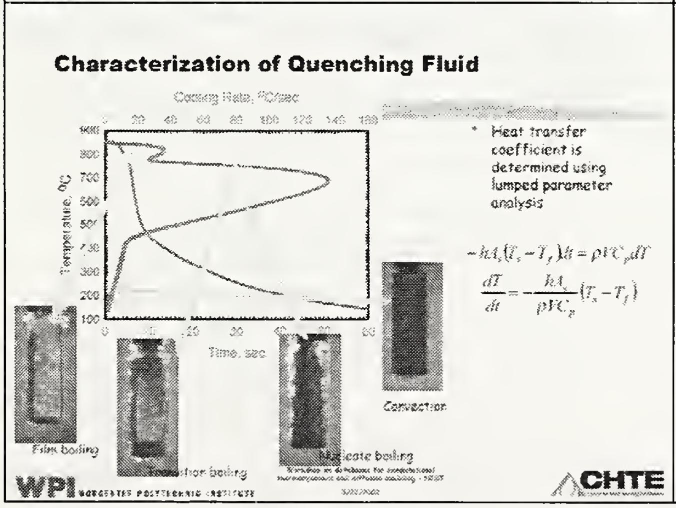


4140 Steel IT diagram showing two quench path

Source. Atlas of IT diagrams, United States Steel, 1963.



Bubble dynamics
CHTE 4140 probe in mineral oil

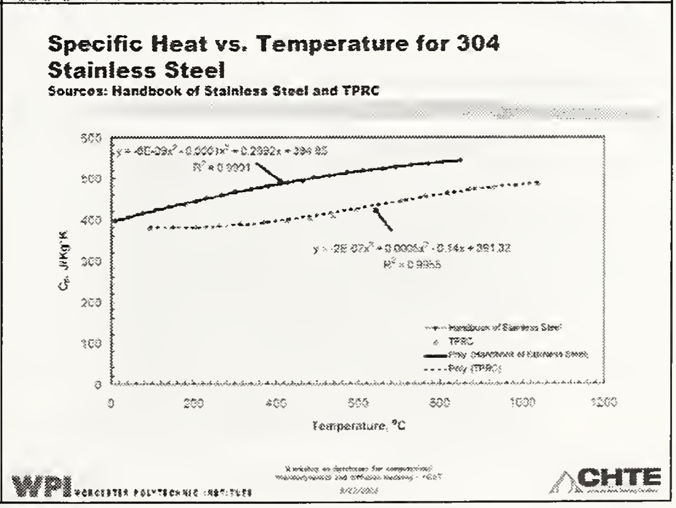


Characterization of Quenching Fluid

- Heat transfer coefficient is determined using lumped parameter analysis

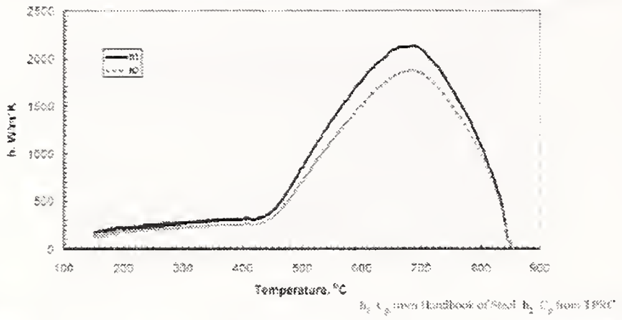
$$-hA_s(T_s - T_f)dt = \rho V C_p dT$$

$$\frac{dT}{dt} = -\frac{hA_s}{\rho V C_p}(T_s - T_f)$$



Specific Heat vs. Temperature for 304 Stainless Steel
Sources: Handbook of Stainless Steel and TPRC

Heat transfer coefficients of SS304 probe quenched in mineral oil



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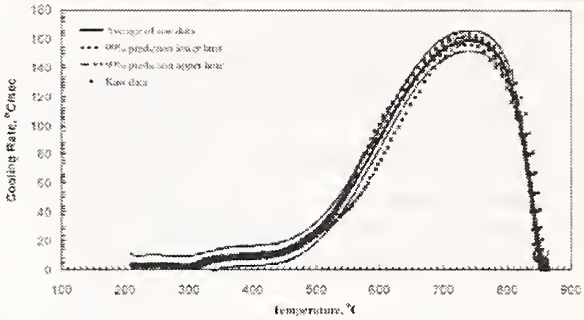
Workshop on databases for computational thermodynamics and diffusion modeling - NIST

CHTE

Cooling rate 4140 steel probe as a function of temperature

quenched in mineral oil (DHR88A)



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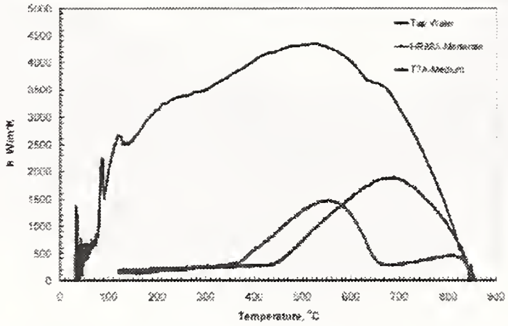
CHTE

Heat transfer coefficients vs. temperature

SS304 probe quenched in different quenchants



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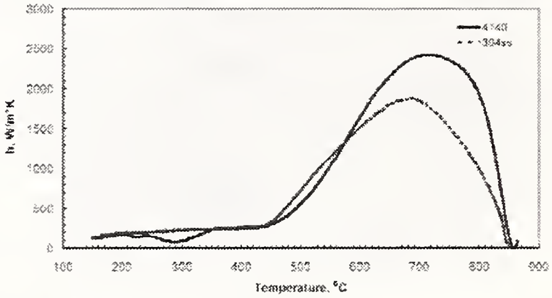
CHTE

Heat transfer coefficients vs. temperature

quenched in mineral oil (HR88A)



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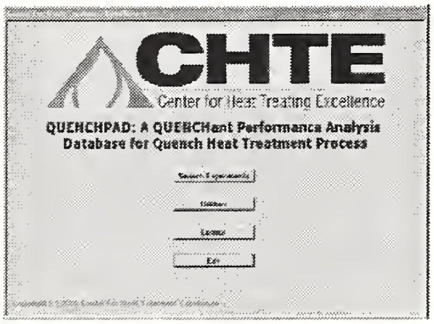
QUENCHPAD - CHTE Quench Database



CHTE

Center for Heat Treating Excellence

QUENCHPAD: A QUENCHant Performance Analysis Database for Quench Heat Treatment Process

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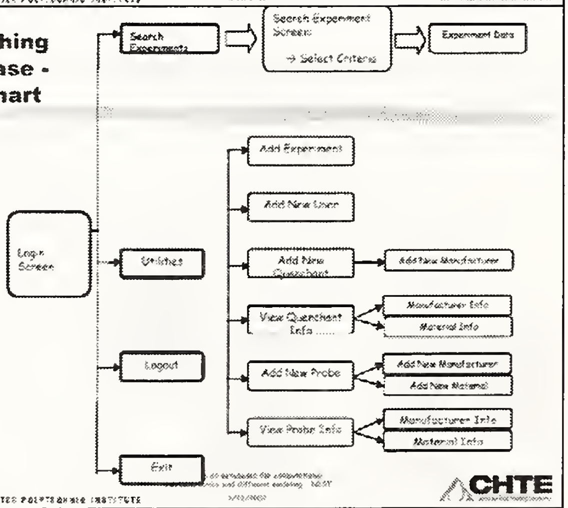
CHTE

Quenching Database - Flowchart



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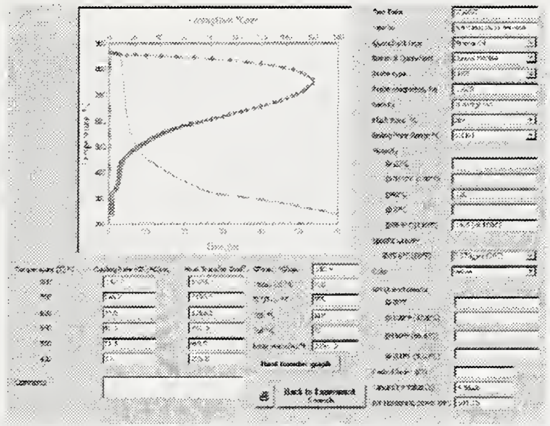
Typical QUENCHPAD Report sheet



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CHTE

Additional points made by speaker:

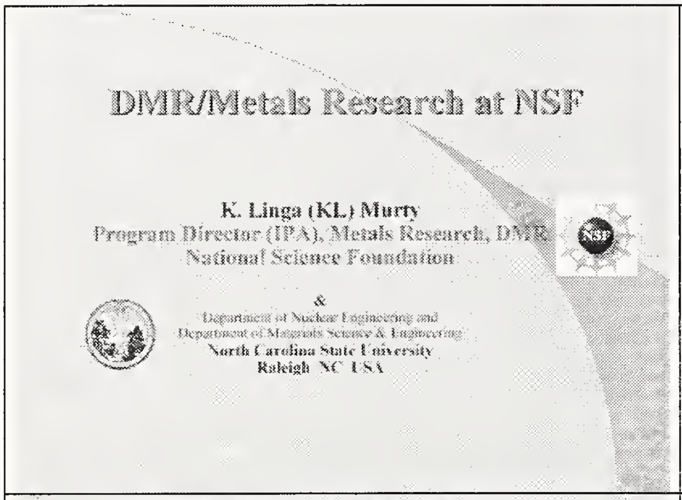
- Heat treating modeling limited by available databases
- Software uses look-up tables as databases, source of potential problems: data such as c_p are sparse and differences between different sources have a trickle down effect on derived properties

Questions/comments from workshop attendees:

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

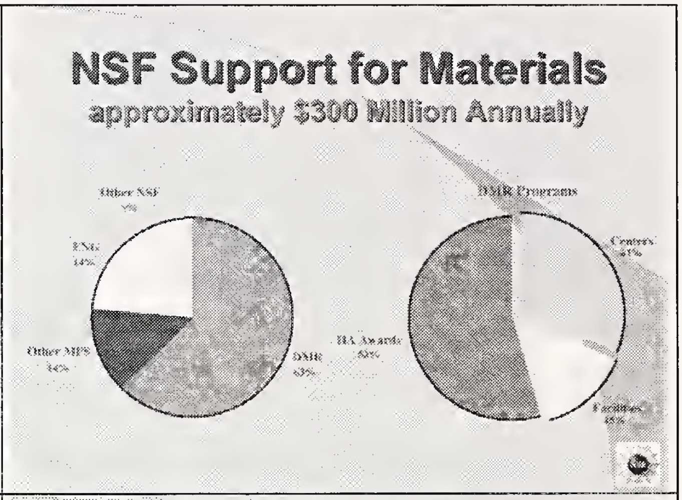
Materials Programs at NSF

K.L. Murty, NSF (National Science Foundation), Arlington, VA

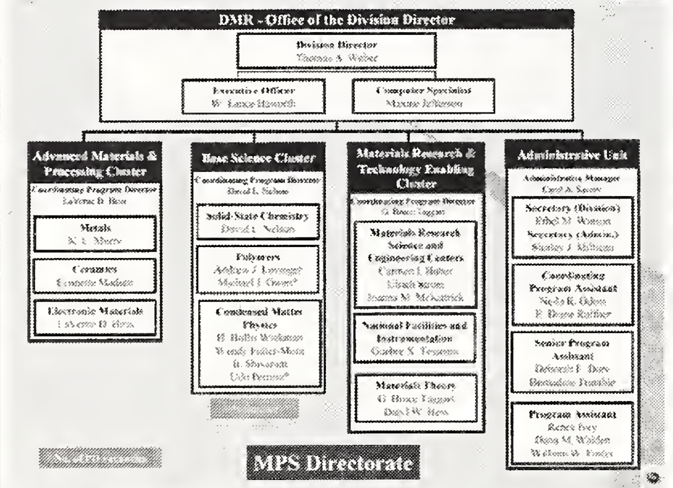


DMR/Metals Research at NSF

K. Linga (KL) Murty
Program Director (IPA), Metals Research, DMR
National Science Foundation
&
Department of Nuclear Engineering and
Department of Materials Science & Engineering
North Carolina State University
Raleigh NC USA



NSF Support for Materials
approximately $300 Million Annually



DMR - Office of the Division Director

Division Director
Thomas A. Weber

Executive Officer
W. Lance Haworth

Computer Specialist

Advanced Materials & Processing Cluster

Coordinating Program Director

Metals
K. L. Murty

Ceramics

Electronic Materials

Base Science Cluster

Coordinating Program Director

Solid-State Chemistry

Polymers

Condensed Matter Physics

Materials Research & Technology Enabling Cluster

Coordinating Program Director

Materials Research Science and Engineering Centers

National Facilities and Instrumentation

Materials Theory

Administrative Unit

Administrative Manager

Secretary (Division)

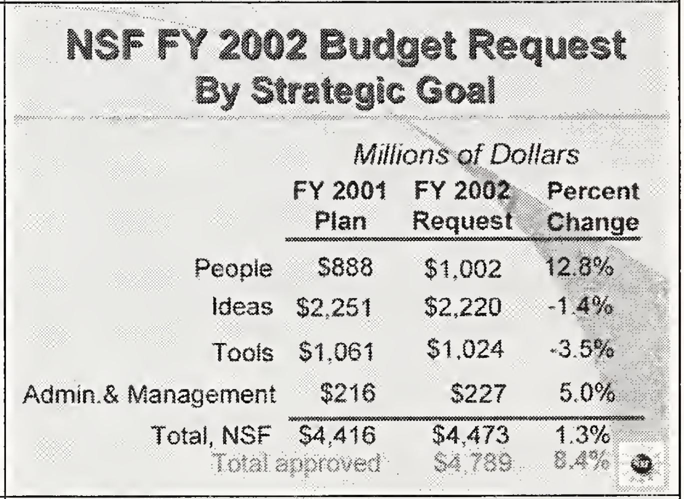
Secretary (Admin.)

Coordinating Program Assistant

Senior Program Assistant

Program Assistant

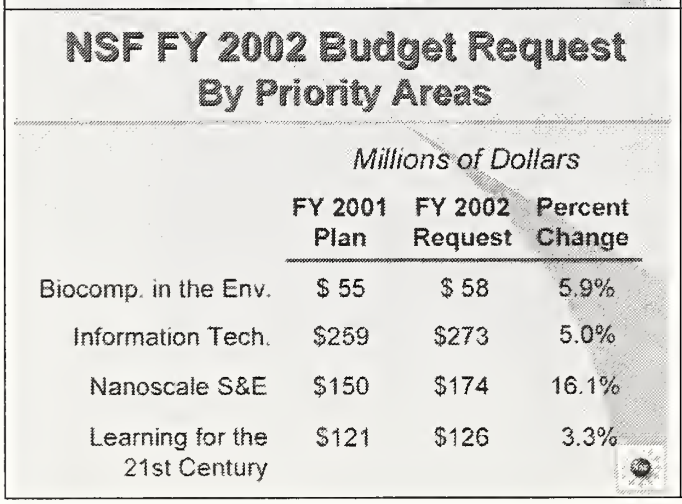
MPS Directorate



NSF FY 2002 Budget Request
By Strategic Goal

Millions of Dollars

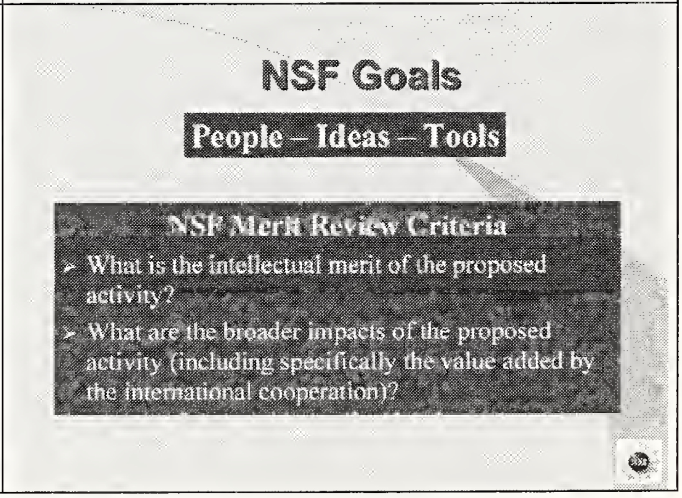
	FY 2001 Plan	FY 2002 Request	Percent Change
People	$888	$1,002	12.8%
Ideas	$2,251	$2,220	-1.4%
Tools	$1,061	$1,024	-3.5%
Admin.& Management	$216	$227	5.0%
Total, NSF	$4,416	$4,473	1.3%
Total approved		$4,789	8.4%



NSF FY 2002 Budget Request
By Priority Areas

Millions of Dollars

	FY 2001 Plan	FY 2002 Request	Percent Change
Biocomp. in the Env.	$ 55	$ 58	5.9%
Information Tech.	$259	$273	5.0%
Nanoscale S&E	$150	$174	16.1%
Learning for the 21st Century	$121	$126	3.3%



NSF Goals

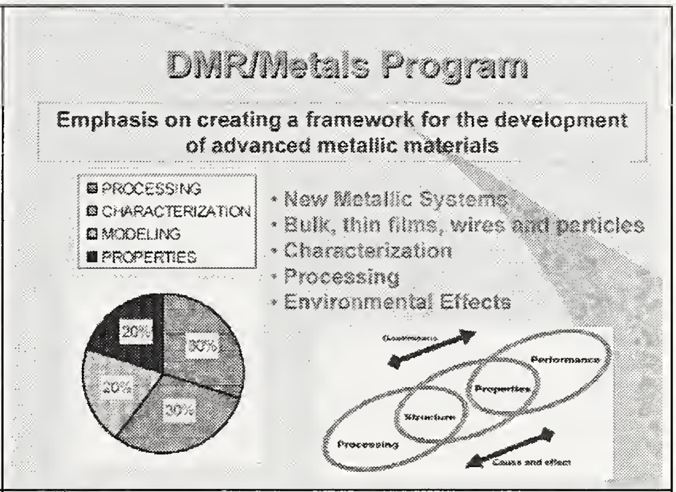
People – Ideas – Tools

NSF Merit Review Criteria

- What is the intellectual merit of the proposed activity?
- What are the broader impacts of the proposed activity (including specifically the value added by the international cooperation)?

Types of Individual Investigator Grants

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

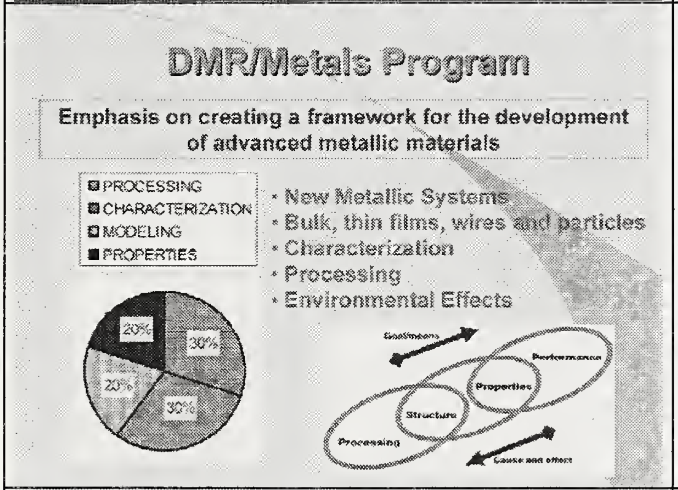


DMR/Metals Program

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

▨ PROCESSING
▨ CHARACTERIZATION
☐ MODELING
■ PROPERTIES

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



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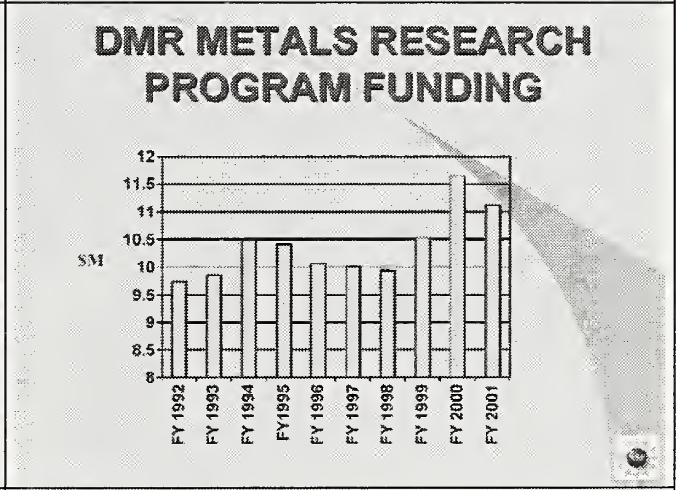
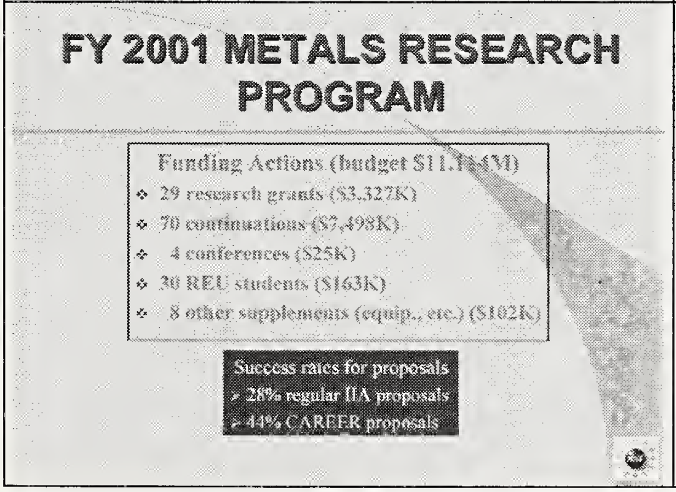


DMR METALS RESEARCH PROGRAM FUNDING



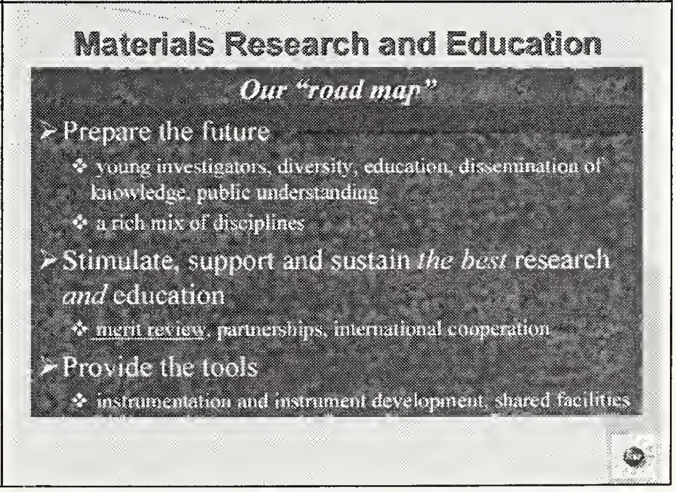
FY 2001 METALS RESEARCH PROGRAM

Funding Actions (budget $11.114M)

- 29 research grants ($3,327K)
- 70 continuations ($7,498K)
- 4 conferences ($25K)
- 30 REU students ($163K)
- 8 other supplements (equip., etc.) ($102K)

Success rates for proposals

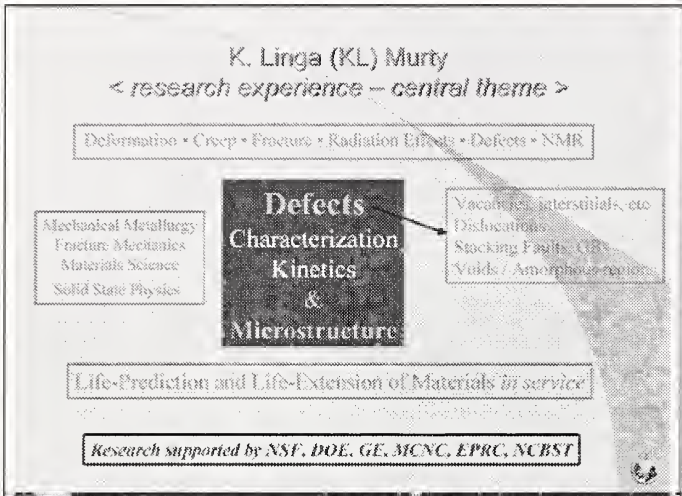
- 28% regular IIA proposals
- 44% CAREER proposals



Materials Research and Education

Our "road map"

- Prepare the future
  - young investigators, diversity, education, dissemination of knowledge, public understanding
  - a 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 >

Deformation • Creep • Fracture • Radiation Effects • Defects • NMR

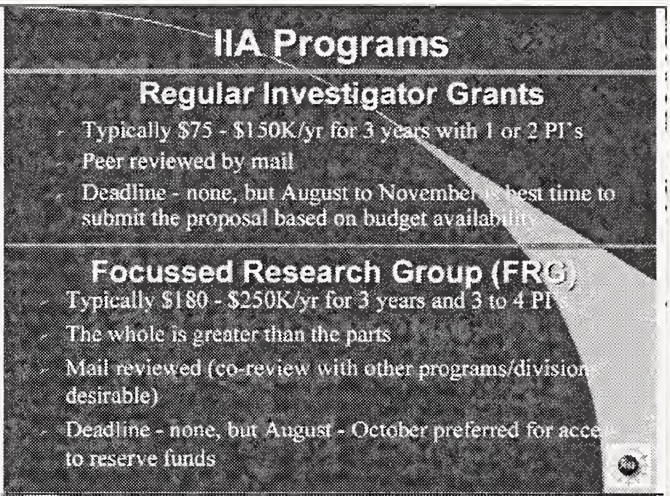
Mechanical Metallurgy
Fracture Mechanics
Materials Science
Solid State Physics

Defects
Characterization
Kinetics
&
Microstructure

Vacancies, interstitials, etc
Dislocations
Stacking Faults, GB
Voids / Amorphous regions

Life-Prediction and Life-Extension of Materials *in service*

Research supported by NSF, DOE, GE, MCNC, EPRC, NCBST



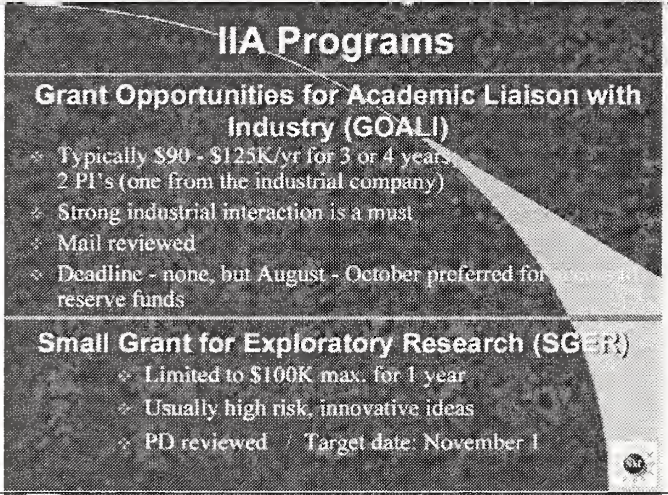
IIA Programs

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 acce to reserve funds



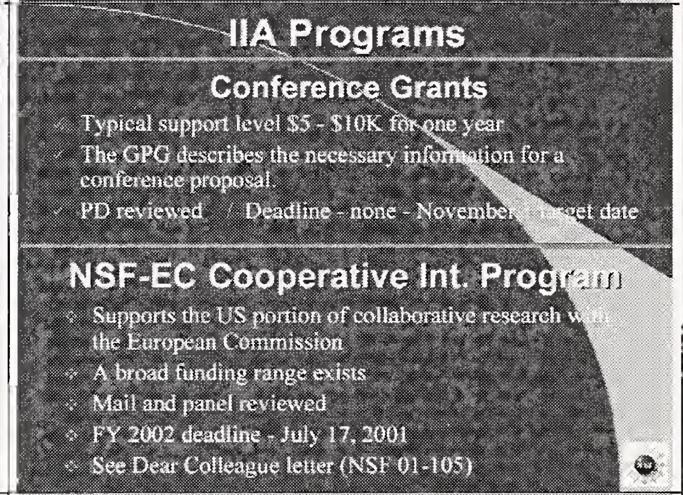
IIA Programs

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 reserve funds

Small Grant for Exploratory Research (SGER)

- Limited to $100K max. for 1 year
- Usually high risk, innovative ideas
- PD reviewed / Target date: November 1



IIA Programs

Conference Grants

- Typical support level $5 - $10K for one year
- The GPG describes the necessary information for a conference proposal.
- PD reviewed / Deadline - none - November 1 target date

NSF-EC Cooperative Int. Program

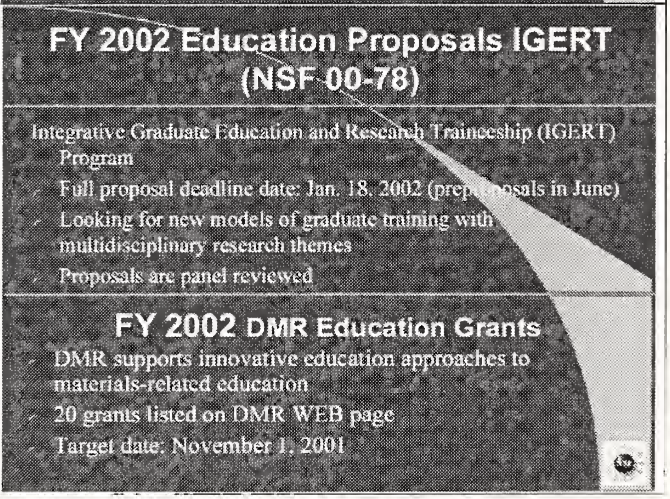
- Supports the US portion of collaborative research with the European Commission
- A broad funding range exists
- Mail and panel reviewed
- FY 2002 deadline - July 17, 2001
- See Dear Colleague letter (NSF 01-105)

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 see (NSF 01-84)

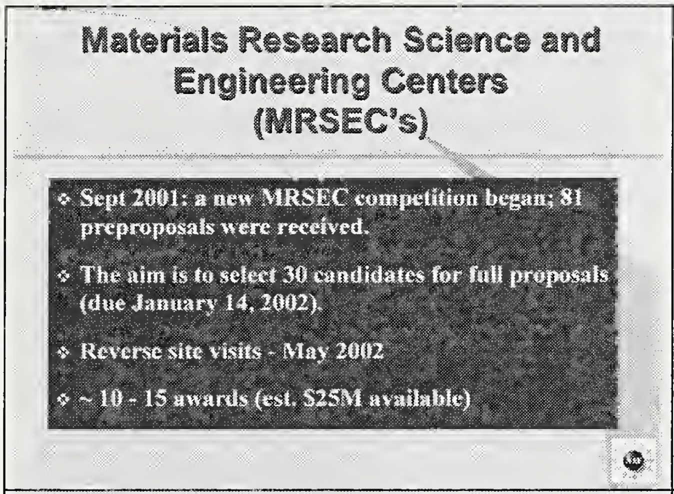


FY 2002 Education Proposals IGERT (NSF 00-78)

Integrative Graduate Education and Research Traineeship (IGERT) Program
- Full proposal deadline date: Jan. 18, 2002 (preproposals 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



Materials Research Science and Engineering Centers (MRSEC's)

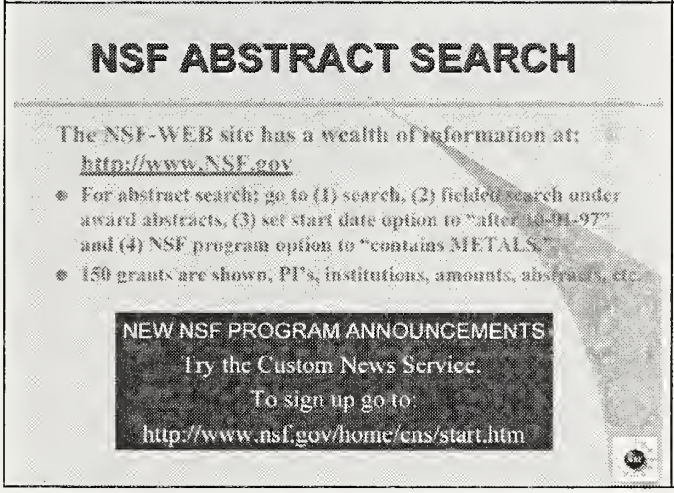
- Sept 2001: a new MRSEC competition began; 81 preproposals were received.
- The aim is to select 30 candidates for full proposals (due January 14, 2002).
- Reverse site visits - May 2002
- ~ 10 - 15 awards (est. $25M available)

FY 2002 Equipment Proposals (IMR & MRI)

Instrumentation for Materials Research (IMR)
  Smaller groups: avg. award size $170K
  Deadline: early January 2002
Major Research Instrumentation (MRI)
  Larger multidisciplinary groups: avg. award [illegible]K
  Deadline: late January 2002

New Programs for International Cooperation

US International Materials Institute
  To enhance US materials research and education interactions with foreign investigators
New interactive research activities
  US/Europe US/Canada US/Mexico



NSF ABSTRACT SEARCH

The NSF-WEB site has a wealth of information at: http://www.NSF.gov

- For abstract search: go to (1) search, (2) fielded search under award abstracts, (3) set start date option to "after 10-01-97" and (4) NSF program option to "contains METALS."
- 150 grants are shown, PI's, institutions, amounts, abstracts, etc.

NEW NSF PROGRAM ANNOUNCEMENTS
Try the Custom News Service.
To sign up go to:
http://www.nsf.gov/home/cns/start.htm

<u>Additional points made by speaker:</u>

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

Aluminum alloys & products

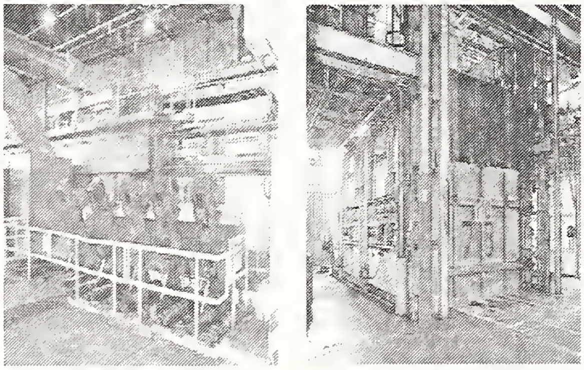
Non-heat treatable - Work-hardened	Heat treatable - Precipitation hardened	Other
1xxx Al-Fe-Si •Commercial purity Al •Litho sheet •Bright sheet	6xxx Al-Mg-Si •6061 - Medium strength structural alloys •6063 - soft alloy extrusions, architectural applications •6262 - free machining	Casting alloys Powder met alloys
3xxx Al-Mn •3003 foil •3004 can sheet	2xxx Al-Cu-X •2x24 - aerospace alloy: high strength, damage tolerant •2x19 weldable higher temperature alloy	
5xxx Al-Mn-Mg •5182 – end stock •Lighting sheet •Architectural sheet	7xxx Al-Mg-Zn-X •7x75 high strength, corrosions resistant •7x50 high strength, better corrosion resistance, less quench sensitivity	

Production of Body Stock Alloys

courtesy of Tom Rouns, Alcoa Technical Center

Scalping removes the as-cast surface of the ingot

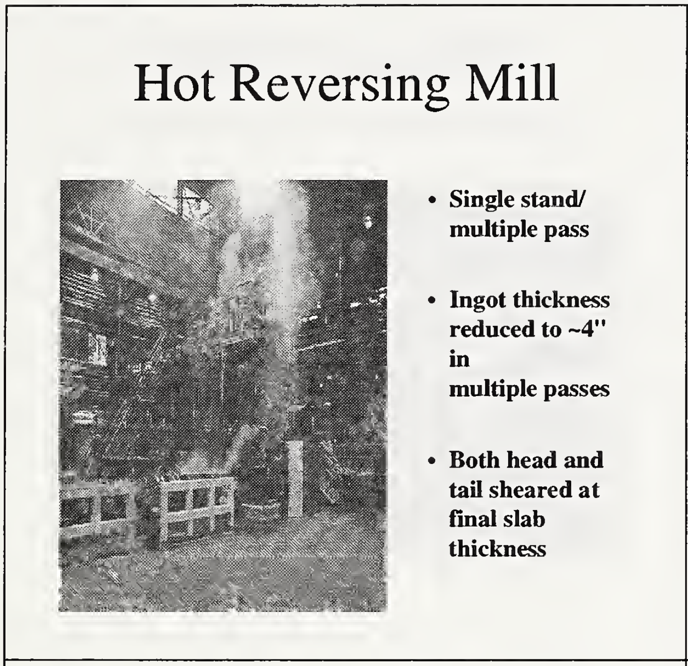
Preheating heats the metal for hot rolling and produces the correct microstructure for hot rolling and subsequent operations



Microstructural Changes During Preheating

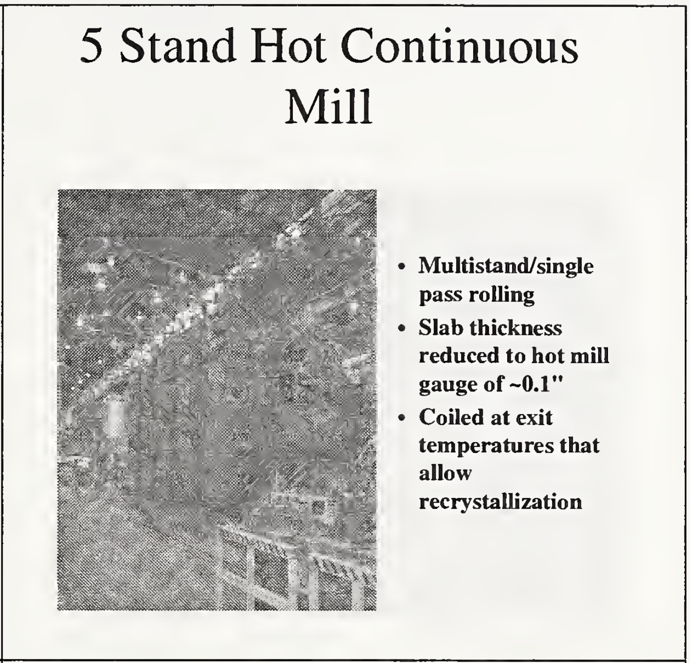
Many complex simultaneous reactions:

- **Dissolution of Mg_2Si**
- **Precipitation of $Al_{12}Mn_3Si$ dispersoids**
- **Transformation of $Al_6[Fe,Mn]$ to $Al_{12}[Fe,Mn]_3Si$ insoluble constituents**
- **Partial dissolution of $Al_{12}Mn_3Si$ dispersoids**
- **Growth of insoluble constituents by Mn diffusion**
- **Growth of $Al_{12}Mn_3Si$ dispersoids**



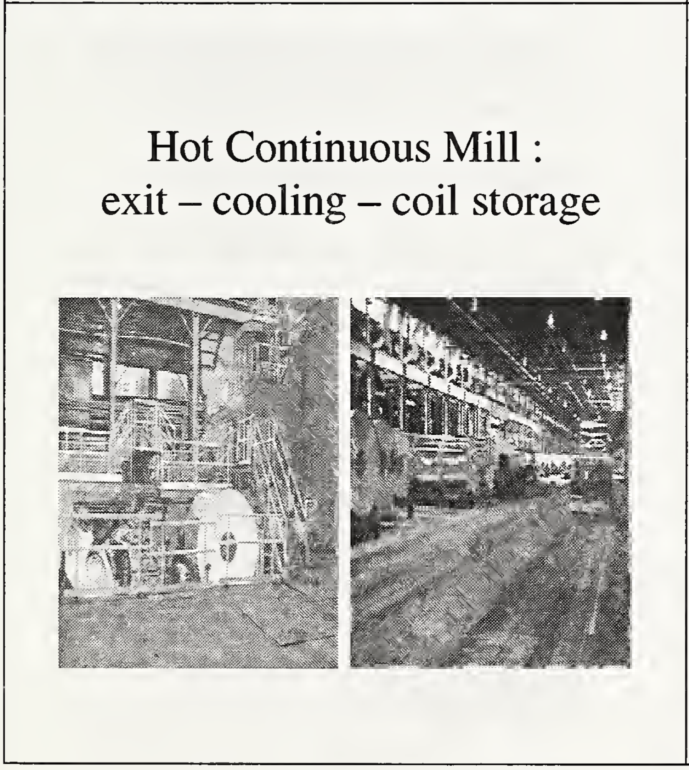
Hot Reversing Mill

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

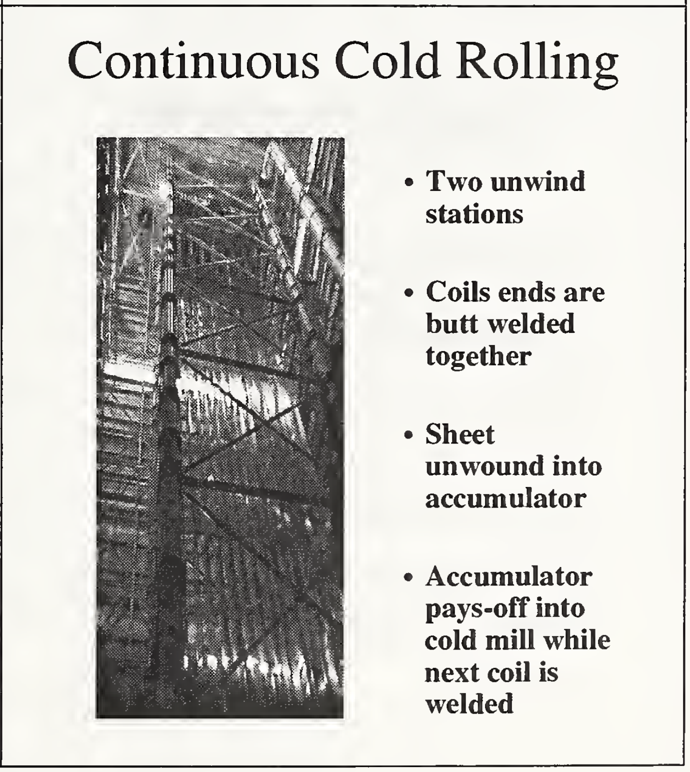


5 Stand Hot Continuous Mill

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



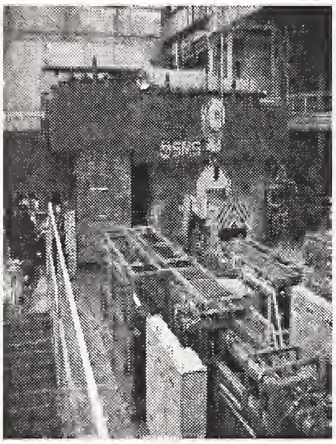
Hot Continuous Mill : exit – cooling – coil storage



Continuous Cold Rolling

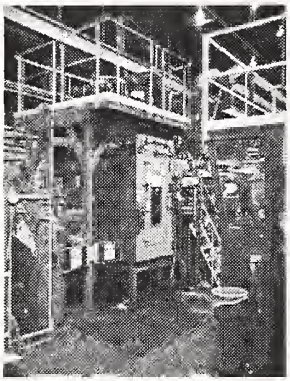
- Two unwind stations
- Coils ends are butt welded together
- Sheet unwound into accumulator
- Accumulator pays-off into cold mill while next coil is welded

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

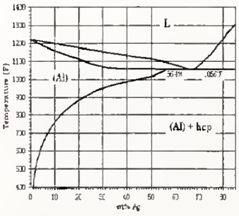
Example research goals

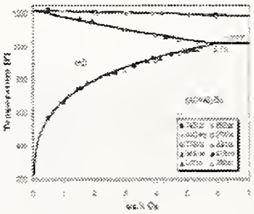
- Preheat and solution treatment practice improvement and simplification
- Reduce end-to-end variability
- Continuous casting
- Grain structure control
- Development of aging practices
- Reduce through thickness variability

Alloying additions and/or impurities

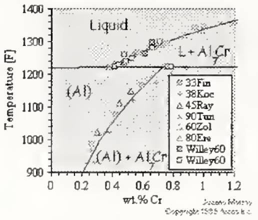
No element is completely soluble in aluminum, most solubilities are quite limited

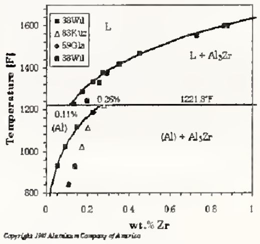
- Major: Ag, Cu, Li, Mg, Mn, Si, Zn





•Minor: Cr, Zr, V,Mn, Fe, Si

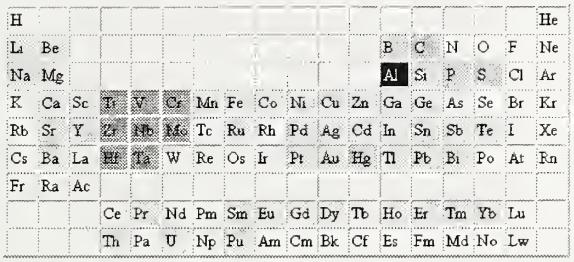




Almost all systems have eutectic reactions

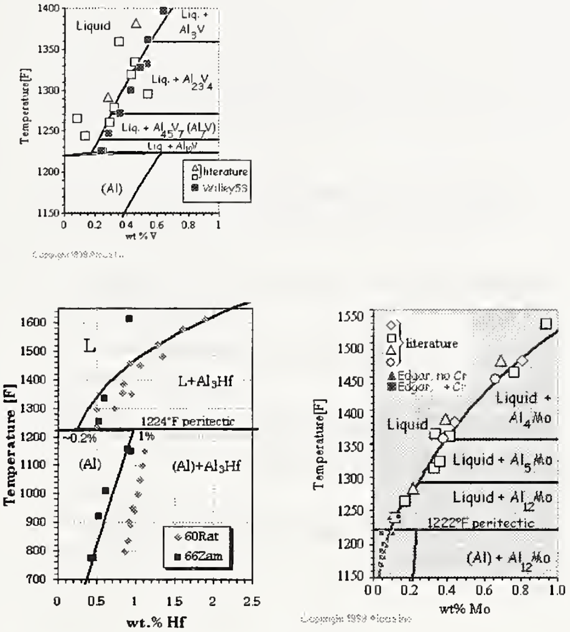
Melting reaction data:

eutectic	
peritectic	▨
~nil solubility	▨



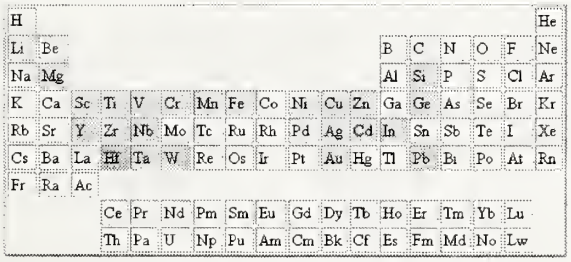
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Dy	Tb	Ho	Er	Tm	Yb	Lu	
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw	

Peritectic systems that need work



Solvus data

known	
discrepancy	▨



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Dy	Tb	Ho	Er	Tm	Yb	Lu	
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw	

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

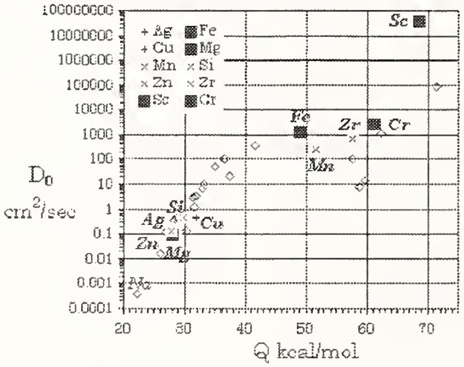
Modeling requires (in addition to the usual suspects) the phase diagram under pressure

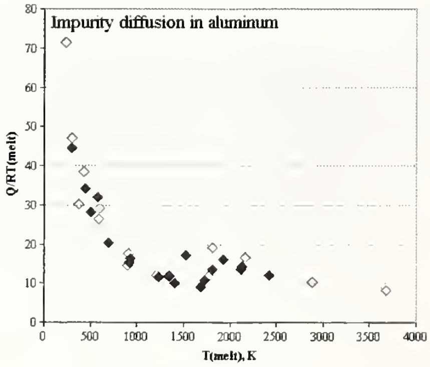
Thermodynamic properties to support modeling of aging processes (esp. nucleation)

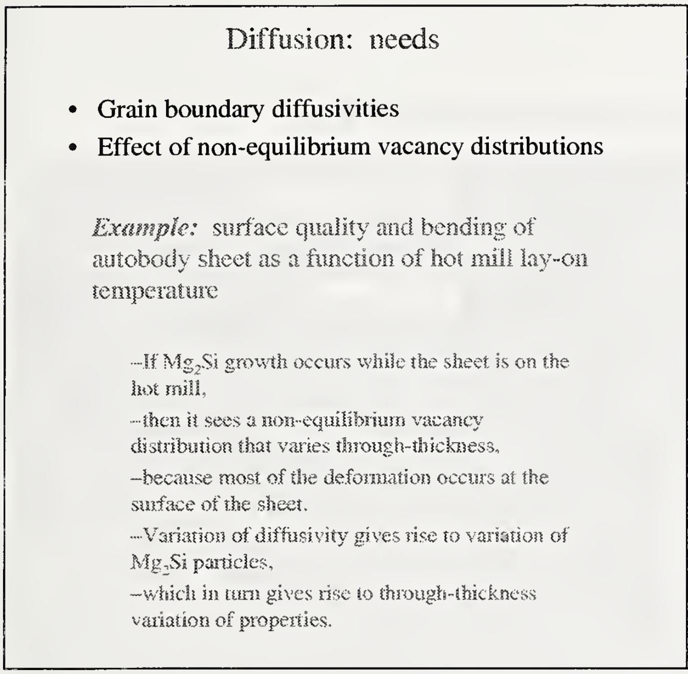
- Free energies of the non-equilibrium crystal structures
- Interfacial strain and energies for 2nd phase particles
- Bulk modulus(T)
- (Also - heats of formation of phases for which we have no measurements)

Via VASP or other first principles techniques

Impurity diffusion data





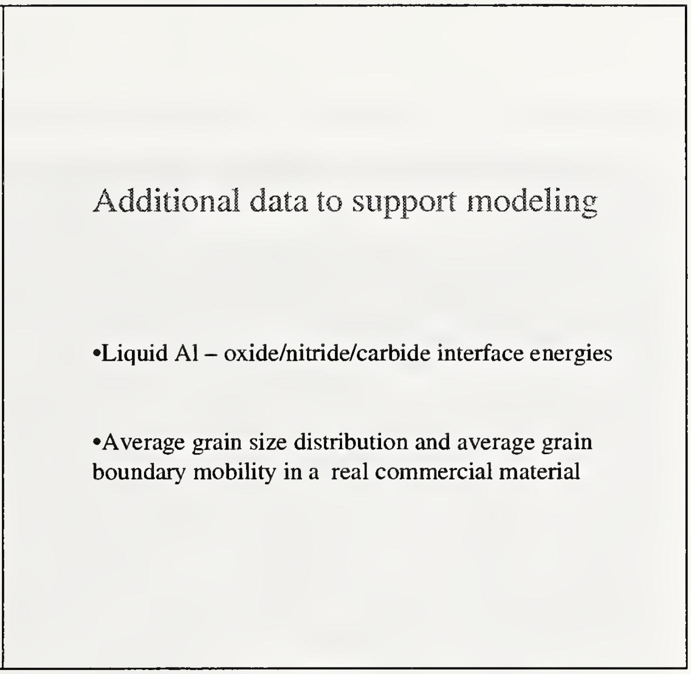


Diffusion: needs

- 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_2Si 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_2Si 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

<u>Additional points made by speaker:</u>

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.

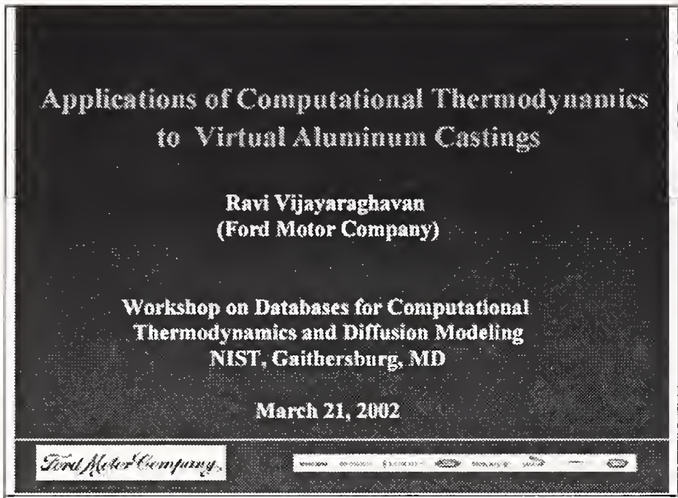
Modeling opportunities abound in the area of heat treatable alloys. To optimize homogenization heat treats, one needs standard phase diagrams and relatively simple diffusion models, but the solvus and melting temperatures are needed with very good precision (*i.e.,* < 2.5 °C (5 °F)). More sophisticated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

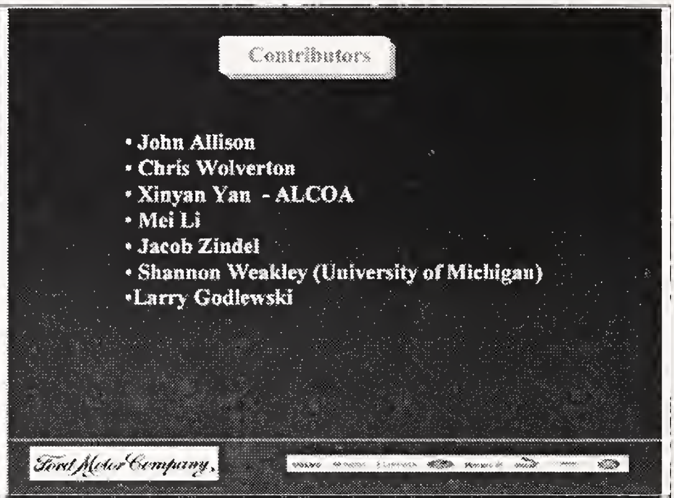


Applications of Computational Thermodynamics to Virtual Aluminum Castings

Ravi Vijayaraghavan
(Ford Motor Company)

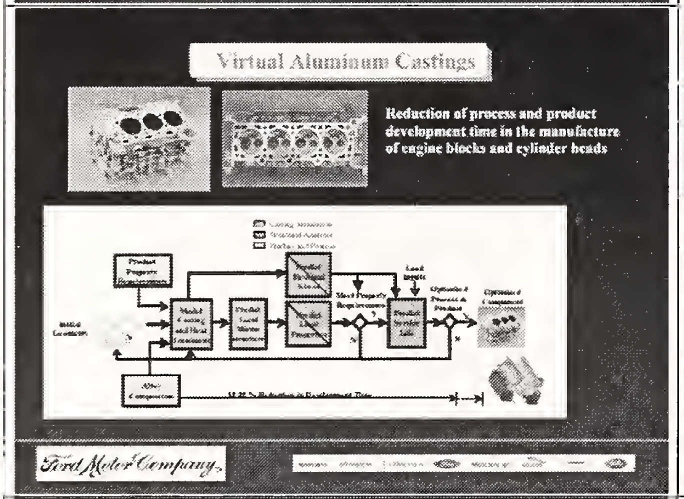
Workshop on Databases for Computational Thermodynamics and Diffusion Modeling
NIST, Gaithersburg, MD

March 21, 2002



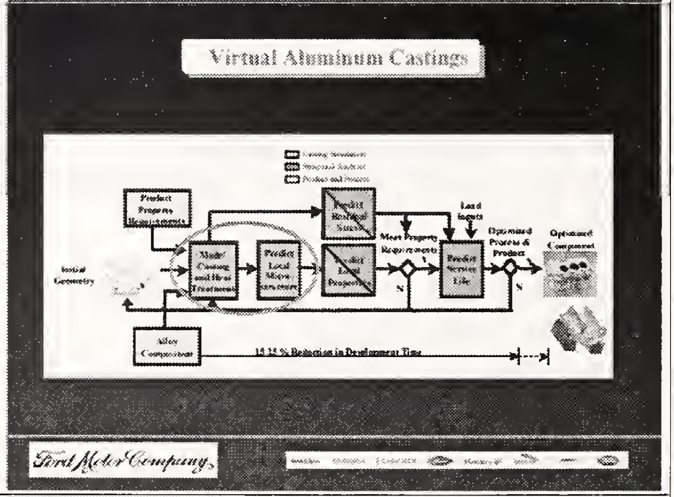
Contributors

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

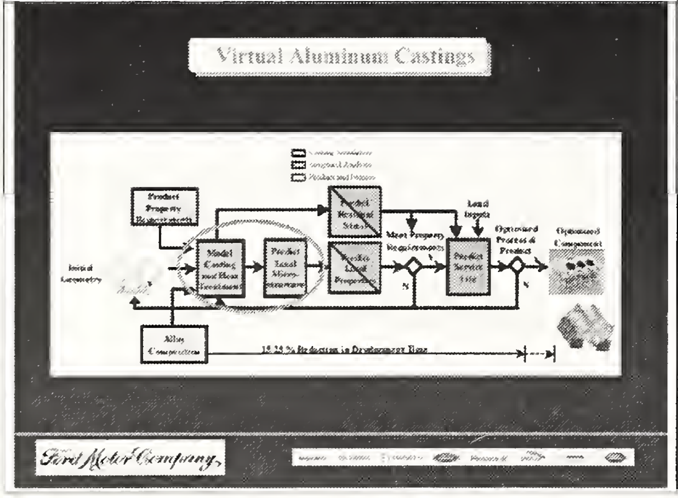


Virtual Aluminum Castings

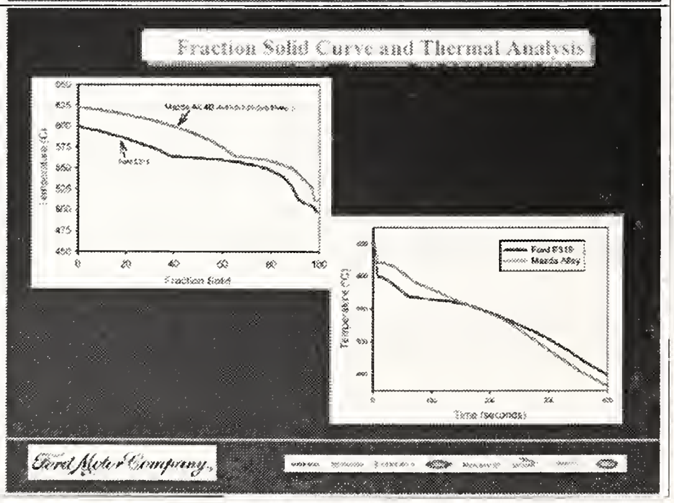
Reduction of process and product development time in the manufacture of engine blocks and cylinder heads



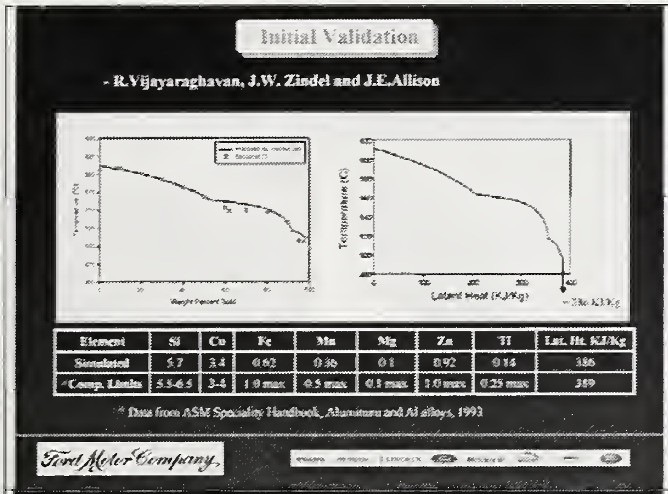
Virtual Aluminum Castings



Virtual Aluminum Castings



Fraction Solid Curve and Thermal Analysis

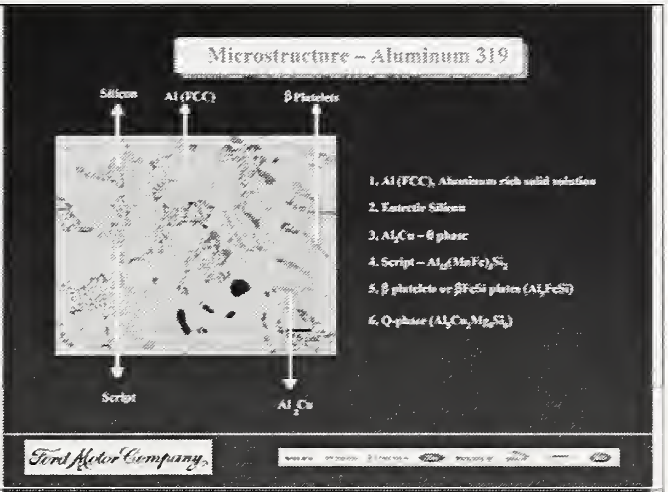


Initial Validation

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

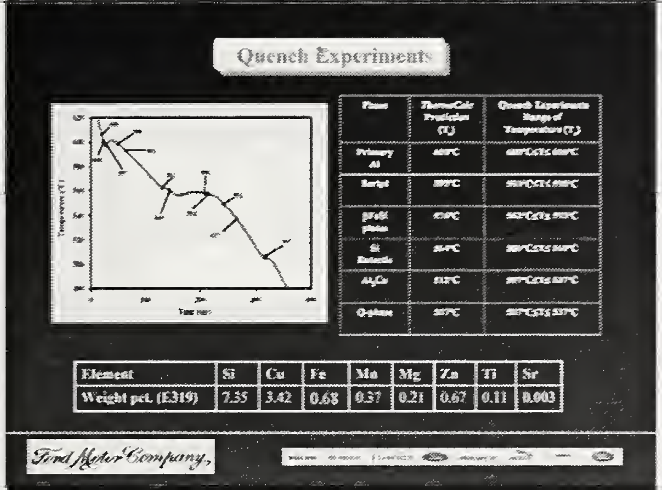
Element	Si	Cu	Fe	Mn	Mg	Zn	Ti	Lat. Ht. KJ/Kg
Simulated	5.7	3.4	0.62	0.36	0.1	0.92	0.14	386
*Comp. Limits	5.5-6.5	3-4	1.0 max	0.5 max	0.1 max	1.0 max	0.25 max	389

* Data from ASM Specialty Handbook, Aluminum and Al alloys, 1993



Microstructure – Aluminum 319

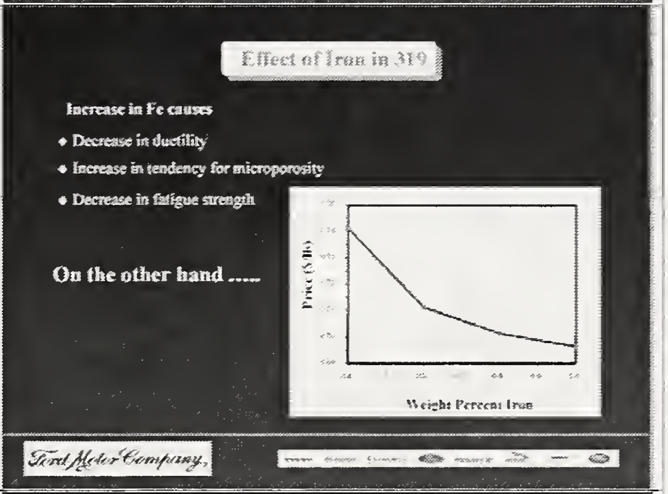
1. Al (FCC), Aluminum rich solid solution
2. Eutectic Silicon
3. Al_2Cu – θ phase
4. Script – $Al_{15}(MnFe)_3Si_2$
5. β platelets or βFeSi plates (Al_5FeSi)
6. Q-phase ($Al_5Cu_2Mg_8Si_6$)



Quench Experiments

Phase	ThermoCalc Prediction (°C)	Quench Experiments Range of Temperature (°C)
Primary Al	[illegible]	[illegible]
Script	[illegible]	[illegible]
βFeSi plates	[illegible]	[illegible]
Si Eutectic	[illegible]	[illegible]
Al_2Cu	[illegible]	[illegible]
Q-phase	[illegible]	[illegible]

Element	Si	Cu	Fe	Mn	Mg	Zn	Ti	Sr
Weight pct. (E319)	7.35	3.42	0.68	0.37	0.21	0.67	0.11	0.003

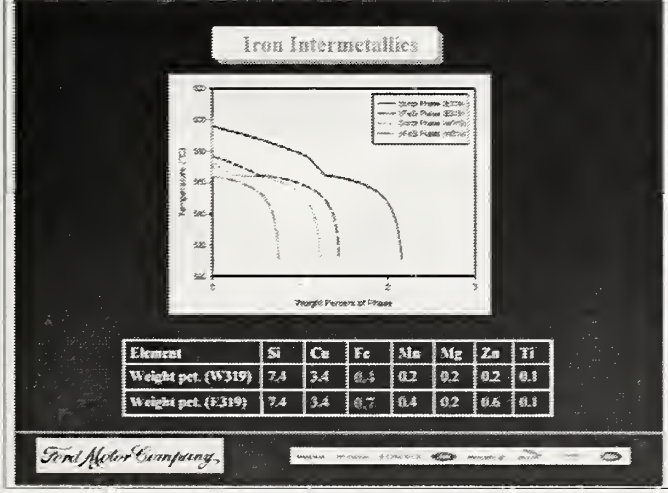


Effect of Iron in 319

Increase in Fe causes

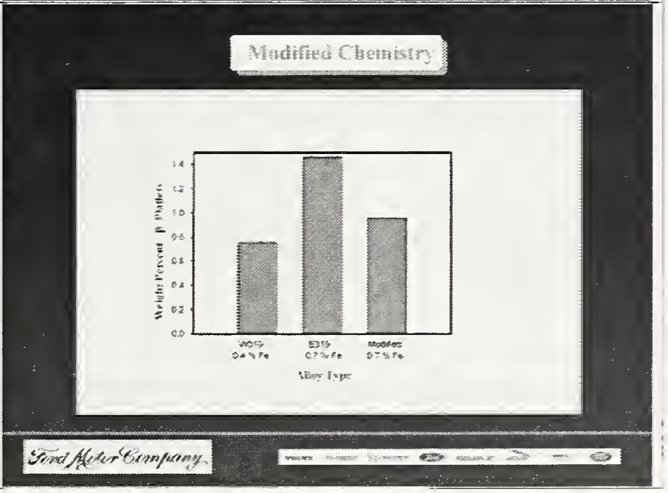
- Decrease in ductility
- Increase in tendency for microporosity
- Decrease in fatigue strength

On the other hand .....

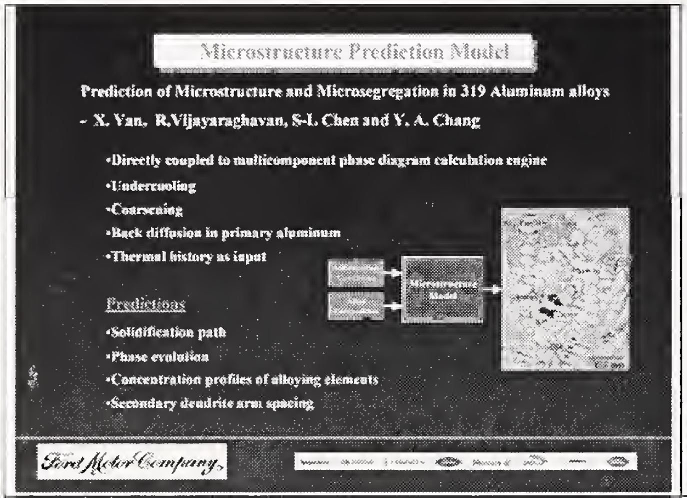


Iron Intermetallics

Element	Si	Cu	Fe	Mn	Mg	Zn	Ti
Weight pct. (W319)	7.4	3.4	0.4	0.2	0.2	0.2	0.1
Weight pct. (E319)	7.4	3.4	0.7	0.4	0.2	0.6	0.1



Modified Chemistry



Microstructure Prediction Model

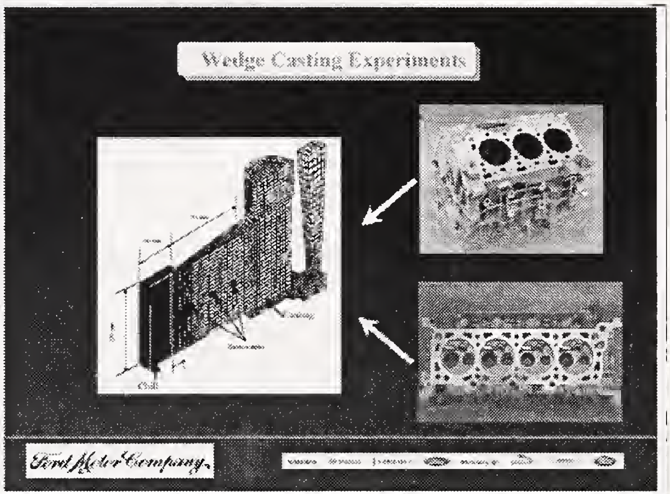
Prediction of Microstructure and Microsegregation in 319 Aluminum alloys

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

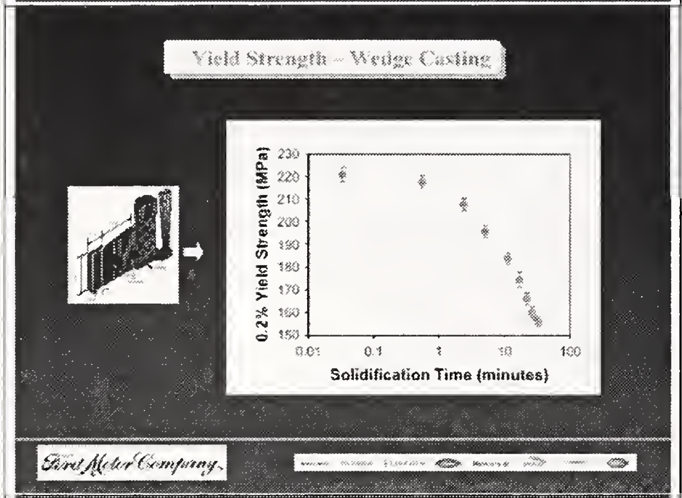
- Directly coupled to multicomponent phase diagram calculation engine
- Undercooling
- Coarsening
- Back diffusion in primary aluminum
- Thermal history as input

Predictions

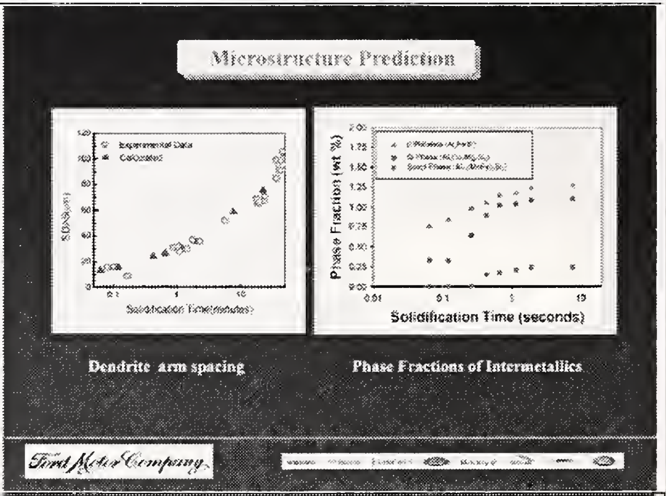
- Solidification path
- Phase evolution
- Concentration profiles of alloying elements
- Secondary dendrite arm spacing



Wedge Casting Experiments



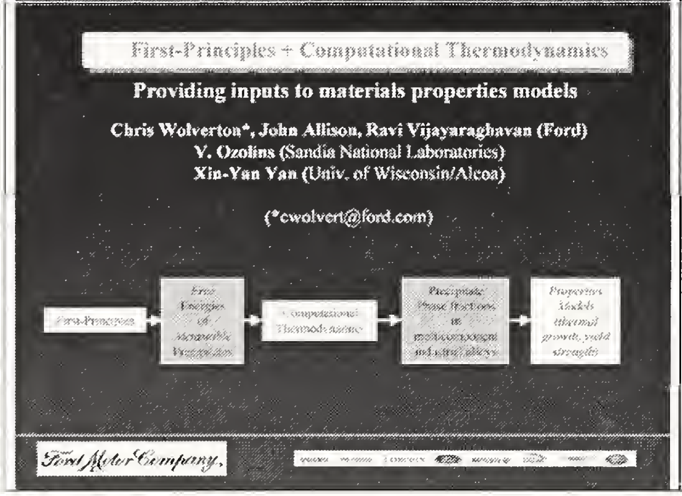
Yield Strength – Wedge Casting



Microstructure Prediction

Dendrite arm spacing

Phase Fractions of Intermetallics



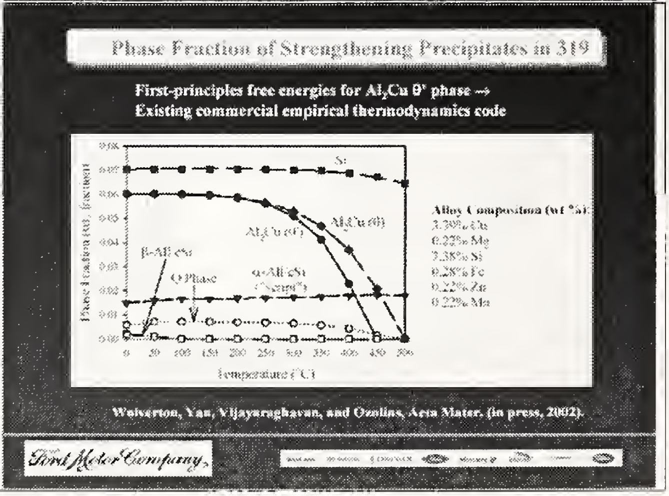
First-Principles + Computational Thermodynamics

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)

(*cwolvert@ford.com)

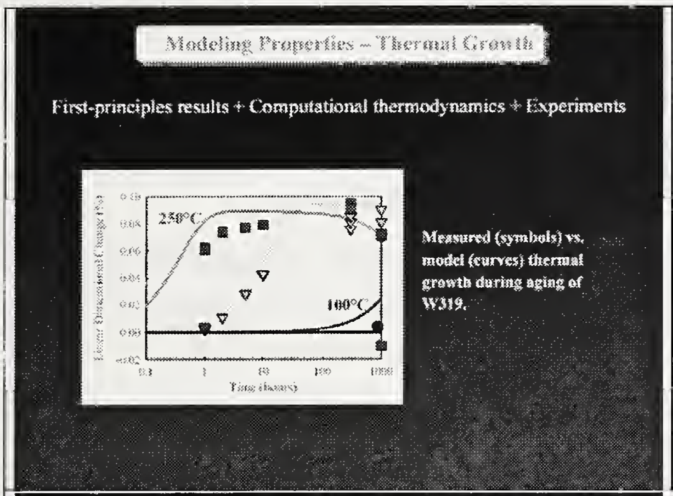
First-Principles → Free Energies of Metastable Precipitates → Computational Thermodynamics → Precipitate Phase fractions in multicomponent industrial alloys → Properties Models thermal growth, yield strength



Phase Fraction of Strengthening Precipitates in 319

First-principles free energies for Al_2Cu θ' phase →
Existing commercial empirical thermodynamics code

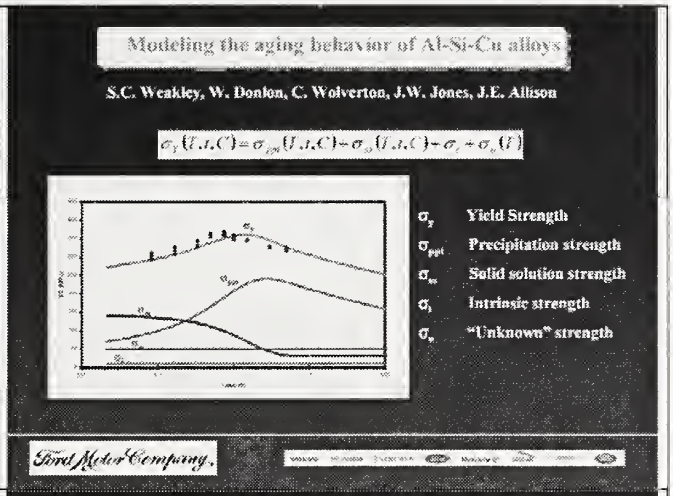
Wolverton, Yan, Vijayaraghavan, and Ozolins, Acta Mater. (in press, 2002).



Modeling Properties – Thermal Growth

First-principles results + Computational thermodynamics + Experiments

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

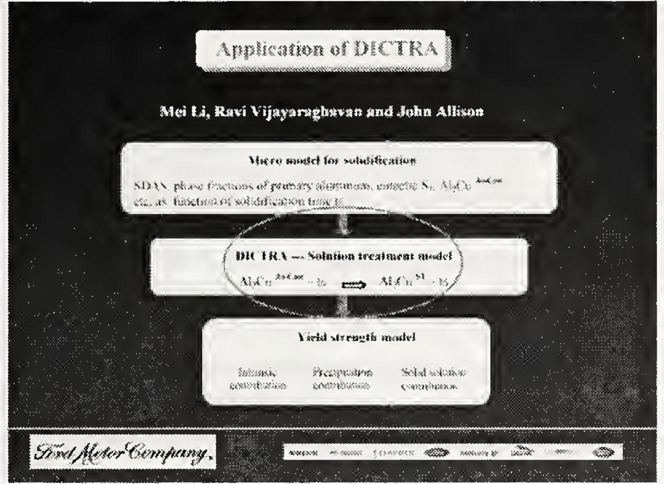


Modeling the aging behavior of Al-Si-Cu alloys

S.C. Weakley, W. Donlon, C. Wolverton, J.W. Jones, J.E. Allison

$$\sigma_Y(T,t,C)=\sigma_{ppt}(T,t,C)+\sigma_{ss}(T,t,C)+\sigma_i+\sigma_u(T)$$

σ_y Yield Strength
σ_{ppt} Precipitation strength
σ_{ss} Solid solution strength
σ_i Intrinsic strength
σ_u "Unknown" strength



Application of DICTRA

Mei Li, Ravi Vijayaraghavan and John Allison

Micro model for solidification

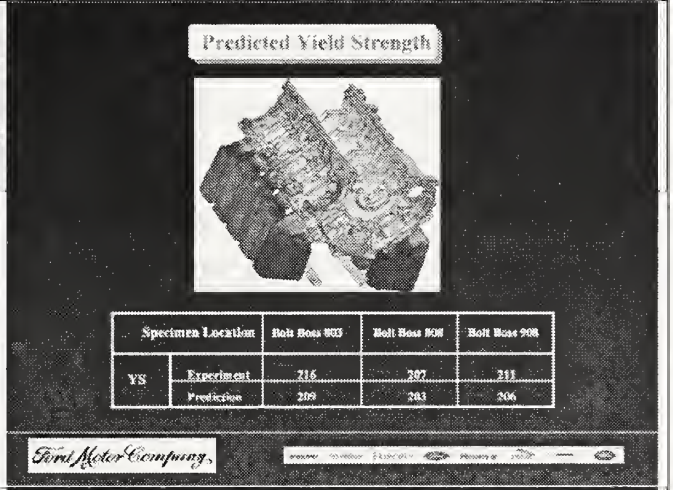
SDAS, phase fractions of primary aluminum, eutectic Si, $Al_2Cu^{2nd\,Cast}$ etc. as function of solidification time (s)

DICTRA — Solution treatment model

$Al_2Cu^{2nd\,Cast}$ - t_s ⟹ Al_2Cu^{ST} - t_s

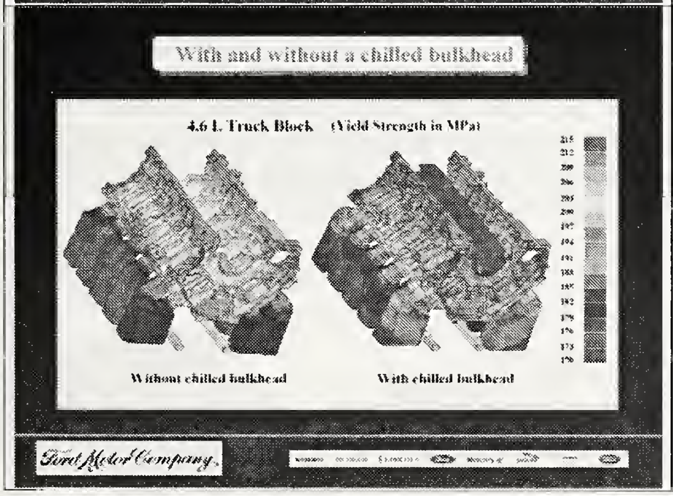
Yield strength model

Intrinsic contribution | Precipitation contribution | Solid solution contribution



Predicted Yield Strength

Specimen Location		Bolt Boss 803	Bolt Boss 808	Bolt Boss 908
YS	Experiment	216	207	211
	Prediction	209	203	206

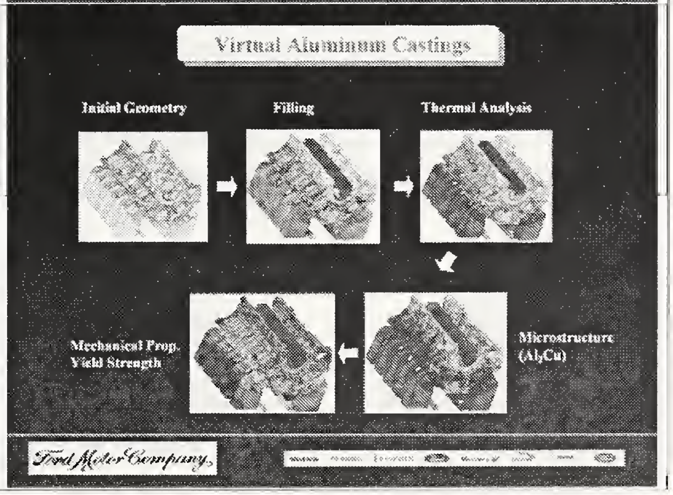


With and without a chilled bulkhead

4.6 L Truck Block (Yield Strength in MPa)

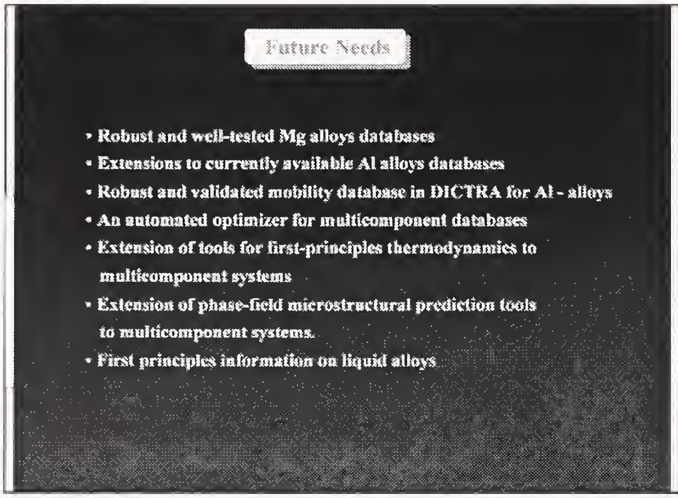
Without chilled bulkhead

With chilled bulkhead



Virtual Aluminum Castings

Initial Geometry → Filling → Thermal Analysis → Microstructure (Al_2Cu) → Mechanical Prop. Yield Strength



Future Needs

- Robust and well-tested Mg alloys databases
- Extensions to currently available Al alloys databases
- Robust and validated mobility database in DICTRA for Al - alloys
- An automated optimizer for multicomponent databases
- Extension of tools for first-principles thermodynamics to multicomponent systems
- Extension of phase-field microstructural prediction tools to multicomponent systems.
- First principles information on liquid alloys

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.

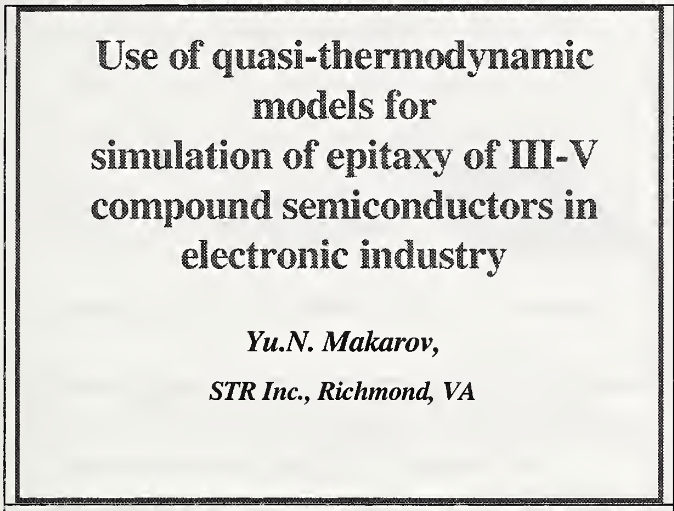
Solution and aging heat treatment is an area of great opportunity in the cast aluminum systems. Work is beginning with kinetic modeling of phase transformation using the DICTRA software program. Although empirical modeling of properties such as hardness exists for these processes, it is hoped that more 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

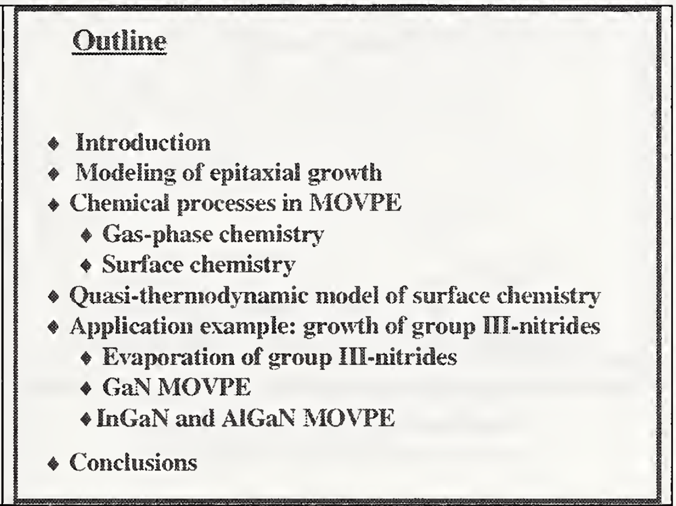
Yuri N.Makarov, Semiconductor Technology Research Inc., Richmond, VA



Use of quasi-thermodynamic models for simulation of epitaxy of III-V compound semiconductors in electronic industry

Yu.N. Makarov,

STR Inc., Richmond, VA



Outline

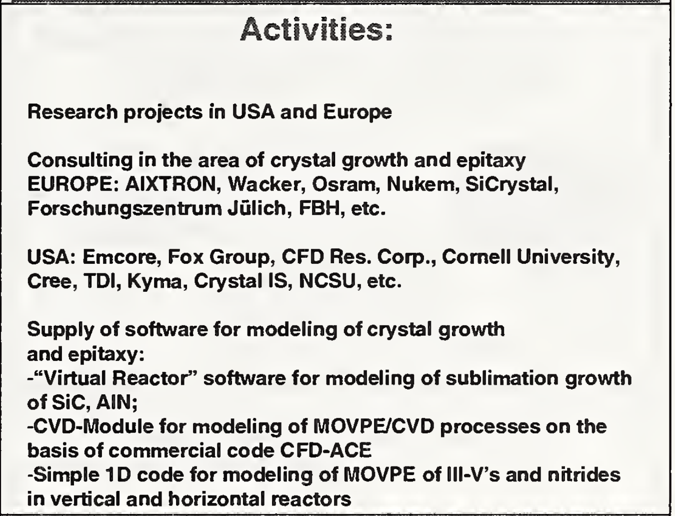
- Introduction
- Modeling of epitaxial growth
- Chemical processes in MOVPE
  - Gas-phase chemistry
  - Surface chemistry
- Quasi-thermodynamic model of surface chemistry
- Application example: growth of group III-nitrides
  - Evaporation of group III-nitrides
  - GaN MOVPE
  - InGaN and AlGaN MOVPE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

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;



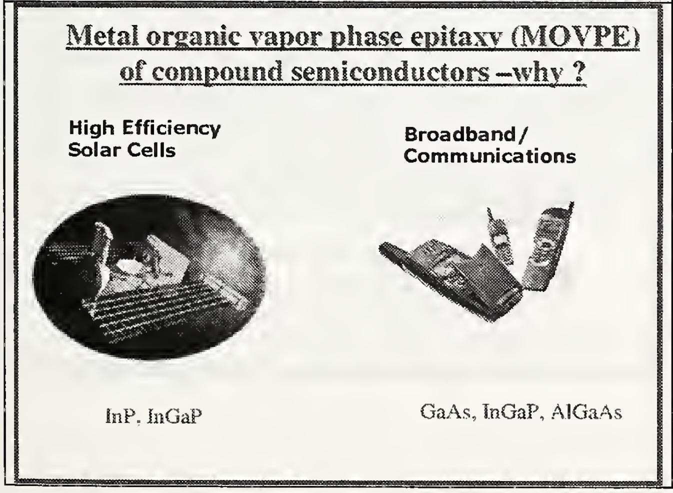
Activities:

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



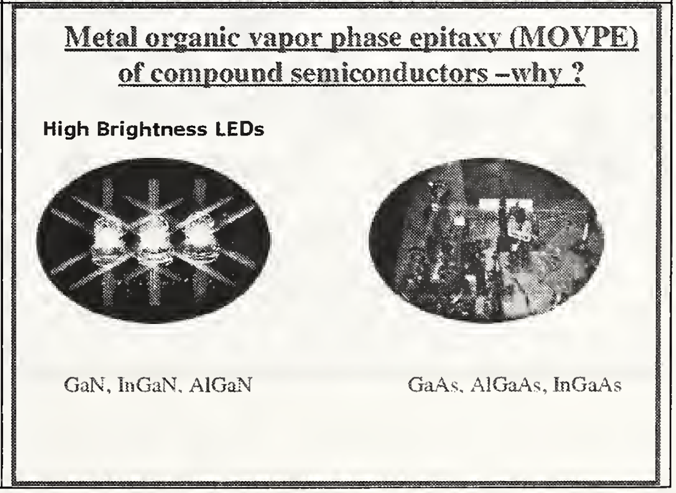
Metal organic vapor phase epitaxy (MOVPE) of compound semiconductors –why ?

High Efficiency Solar Cells

Broadband / Communications

InP, InGaP

GaAs, InGaP, AlGaAs

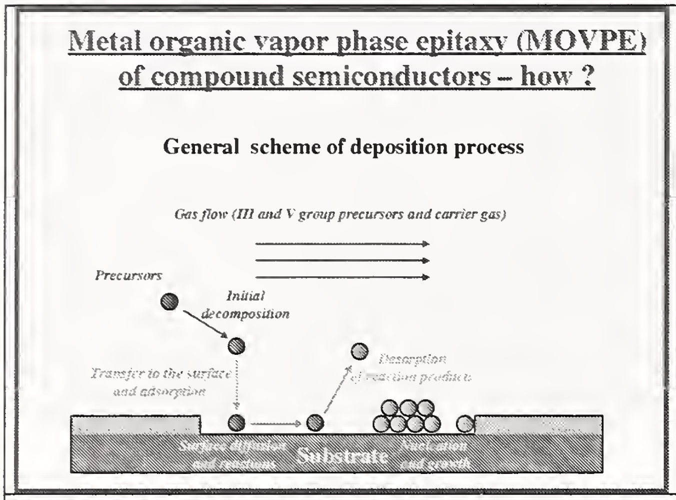


Metal organic vapor phase epitaxy (MOVPE) of compound semiconductors –why ?

High Brightness LEDs

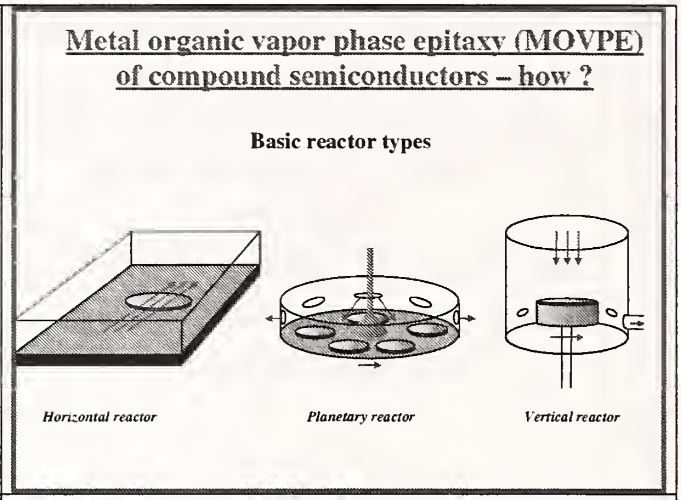
GaN, InGaN, AlGaN

GaAs, AlGaAs, InGaAs



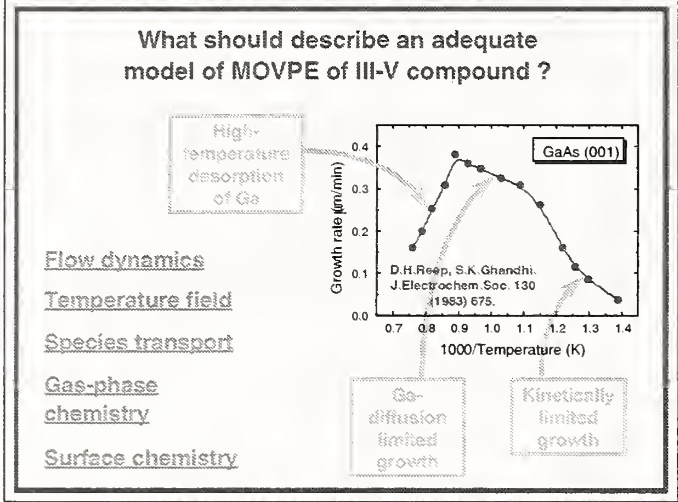
Metal organic vapor phase epitaxy (MOVPE) of compound semiconductors – how ?

General scheme of deposition process



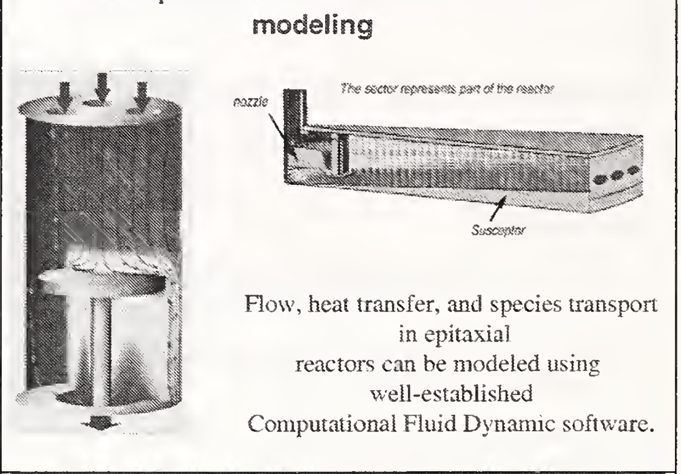
Metal organic vapor phase epitaxy (MOVPE) of compound semiconductors – how ?

Basic reactor types



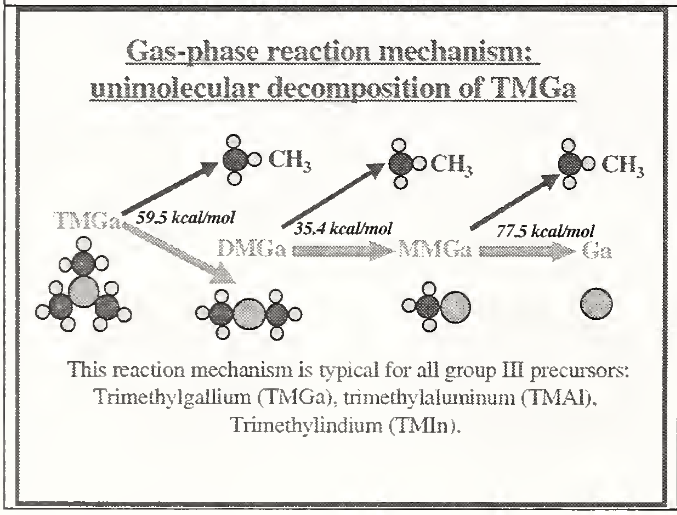
What should describe an adequate model of MOVPE of III-V compound ?

- Flow dynamics
- Temperature field
- Species transport
- Gas-phase chemistry
- Surface chemistry



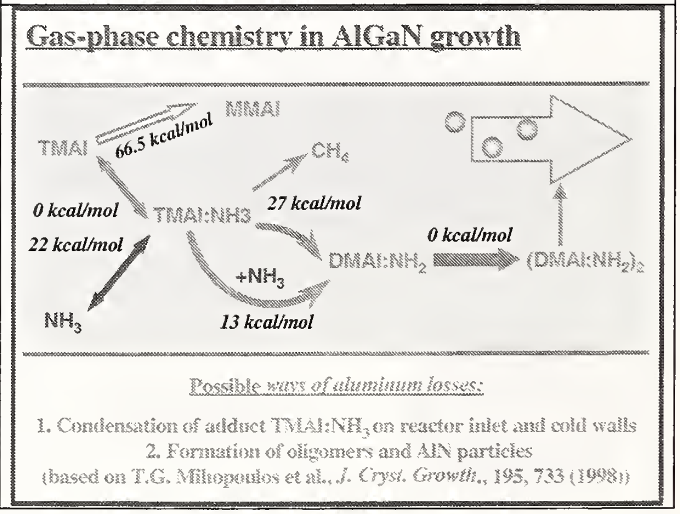
Examples of flow and heat transfer modeling

Flow, heat transfer, and species transport in epitaxial reactors can be modeled using well-established Computational Fluid Dynamic software.



Gas-phase reaction mechanism: unimolecular decomposition of TMGa

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



Gas-phase chemistry in AlGaN growth

Possible ways of aluminum losses:

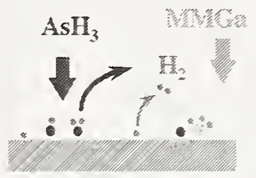
1. Condensation of adduct $TMAl:NH_3$ on reactor inlet and cold walls
2. Formation of oligomers and AlN particles

(based on T.G. Mihopoulos et al., *J. Cryst. Growth.*, 195, 733 (1998))

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 "bottlneck" in MOVPE modeling is the description of surface chemical processes.

Full kinetic model for surface processes



Drawback:

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

... A total of 60 species and 232 reactions are considered in the gas together with 19 species and 115 processes at the surface –

S1 $AsH + V \Leftrightarrow AsH(a)$
S2 $AsH_2 + V \Leftrightarrow AsH_2(a)$
S3 $AsH_3 + V \Leftrightarrow AsH_3(a)$
S4 $H + V \Leftrightarrow H(a)$
S5 $CH_3 + V \Leftrightarrow CH_3(a)$
S6 $AsH(a) + H(a) \Leftrightarrow AsH_2 + 2V$
S7 $AsH_2(a) + H(a) \Leftrightarrow AsH_3 + V$
S8 $AsH_2(a) + H(a) \Leftrightarrow AsH_3(a) + V$
....

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

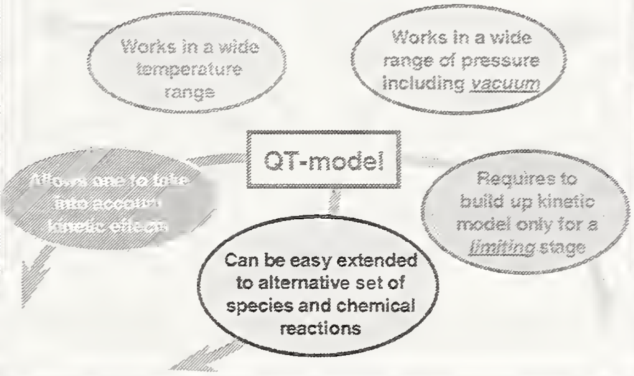
Basic assumptions:

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/evaporation 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 thermochemical properties of gaseous and solid substances;
- **the accounts of the** elastic strain effect via a contribution to the Gibbs energy of solid phase

Advantages of quasi-thermodynamic model for surface processes



Works in a wide temperature range

Works in a wide range of pressure including *vacuum*

QT-model

Allows one to take into account kinetic effects

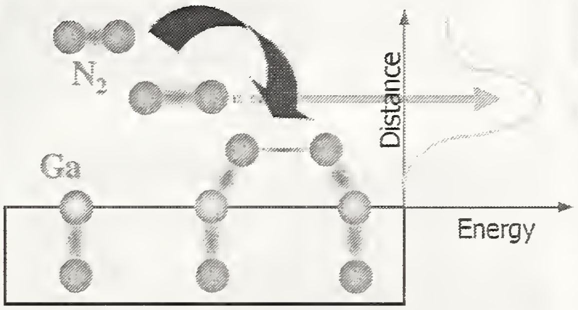
Requires to build up kinetic model only for a *limiting* stage

Can be easy extended to alternative set of species and chemical reactions

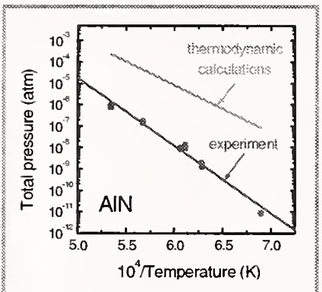
Group III–nitrides – metastable materials with unusual properties

- 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

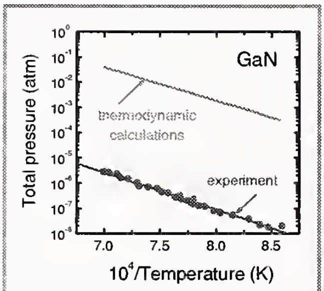
Formation of kinetic barrier in adsorption and desorption of nitrogen



Kinetics of nitrogen evaporation and condensation – reason for the metastability

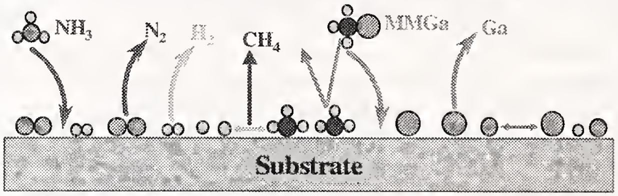


Experiment: L.H. Dreger, et all, J.Phys.Chem. 66 (1962) 1556



Experiment: Z.A. Munir, A.W. Searcy, J.Chem.Phys. 42 (1965) 4223

Surface chemical processes during GaN growth



Rate-limiting processes

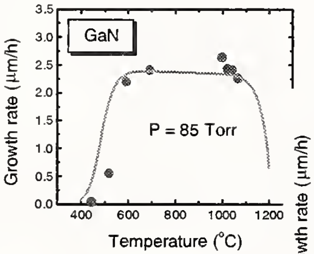
- *Low temperatures:* sites for Ga adsorption are blocked by methyl radicals
- *Intermediate temperatures:* transport of Ga containing species to the growing surface
- *High temperatures:* Ga desorption

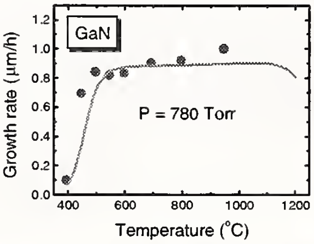
There is the strong experimental trend to move towards the high GaN growth temperatures because of the better quality of the material. Accurate description of gallium desorption from the growing surface is necessary for predictive modeling.

MOVPE growth of GaN (comparison with experiment)

Precursors: TMGa, NH_3

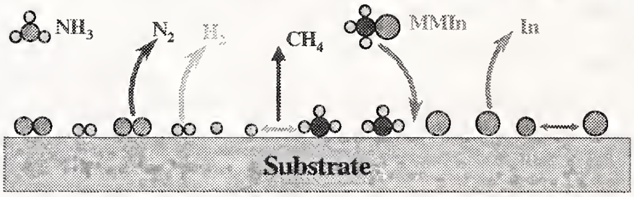
Carrier gas: H_2





Experiment: C.H. Chen et al, J.Electron.Mat. 25 (1996) 1004

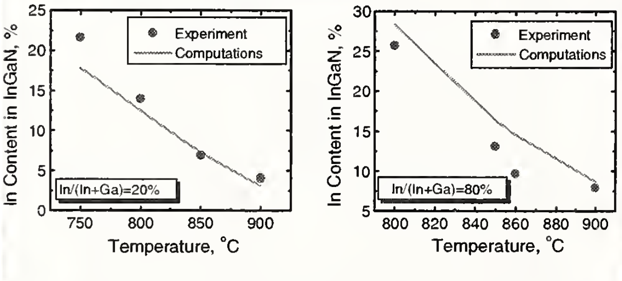
Surface chemical processes during InGaN growth



Primary reaction pathways

- Adsorption of gaseous species
- Ammonia cracking on the surface giving rise to N_2 and H_2
- Indium, gallium, and nitrogen incorporation into the crystal
- Desorption of indium: the limiting process for indium incorporation at elevated temperatures.

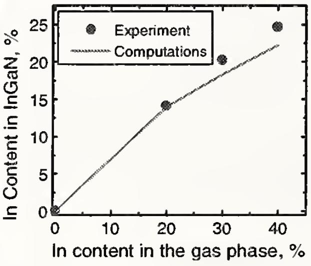
2D modeling of InGaN MOVPE in AIX 200 RF reactor: comparison to experimental data



Experimental data from: M. Schwambera et al. J. Crystal Growth, 203, 340 (1999)

Operating conditions: total flow rate 4.5 SLM, pressure 50 mbar, V/III ratio ~ 3000; carrier gas nitrogen

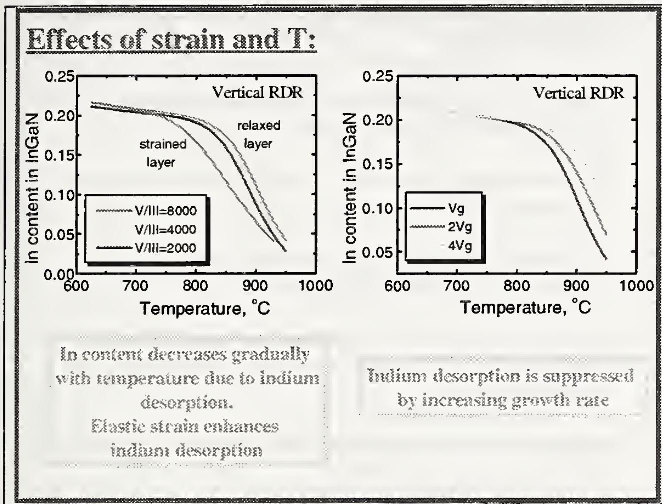
2D modeling of InGaN MOVPE in AIX 200 RF reactor: comparison to experimental data



Experimental data from: MRS Internet J. Nitride Semicond. Res., 4, 5 (1999)

Operating conditions:
temperature 750 °C,
total flow rate 4.5 SLM,
pressure 50 mbar,
V/III ratio 20000÷30000,
carrier gas nitrogen

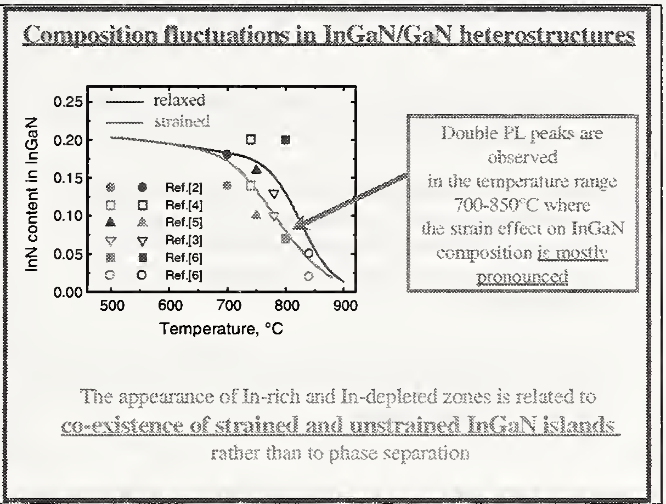
The model provides a good quantitative reproduction of the experimental data without any parameter fitting. Account of the strain effect is very important.



Effects of strain and T:

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

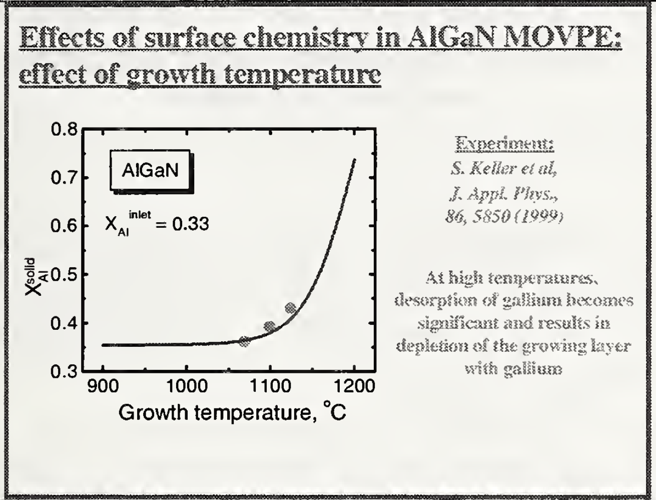
Indium desorption is suppressed by increasing growth rate



Composition fluctuations in InGaN/GaN heterostructures

Double PL peaks are observed in the temperature range 700-850°C where the strain effect on InGaN composition is mostly pronounced

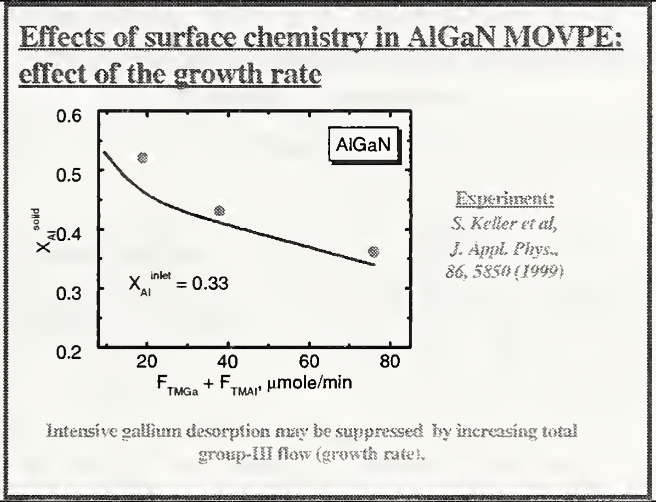
The appearance of In-rich and In-depleted zones is related to co-existence of strained and unstrained InGaN islands rather than to phase separation



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

Experiment:
S. Keller et al, J. Appl. Phys., 86, 5850 (1999)

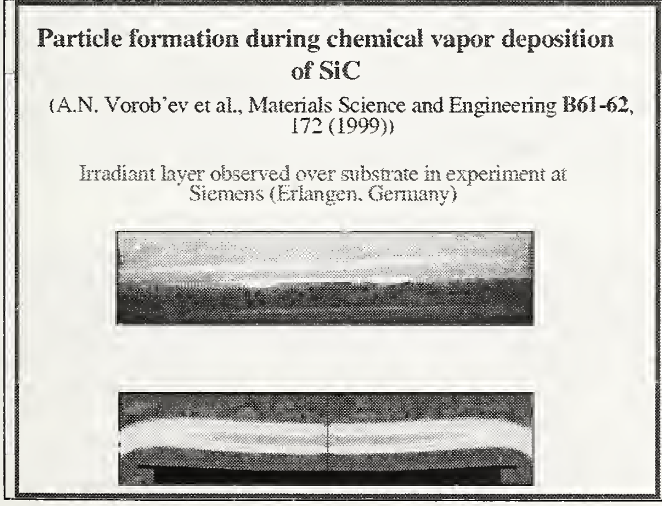
At high temperatures, desorption of gallium becomes significant and results in depletion of the growing layer with gallium



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

Experiment:
S. Keller et al, J. Appl. Phys., 86, 5850 (1999)

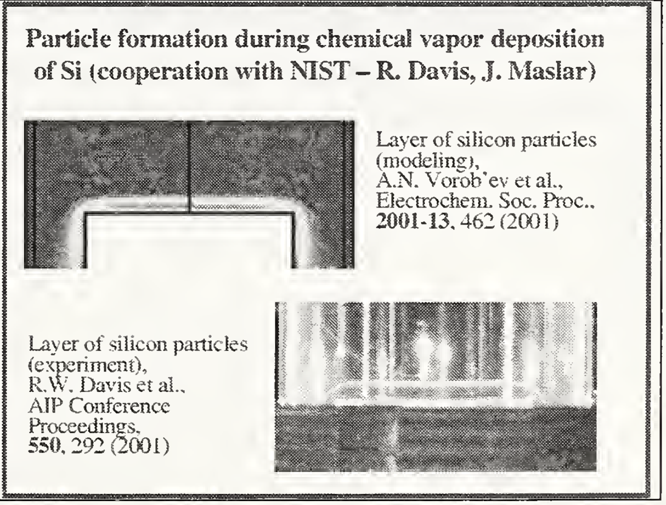
Intensive gallium desorption may be suppressed by increasing total group-III flow (growth rate).



Particle formation during chemical vapor deposition of SiC

(A.N. Vorob'ev et al., Materials Science and Engineering **B61-62**, 172 (1999))

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



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

Layer of silicon particles (modeling),
A.N. Vorob'ev et al.,
Electrochem. Soc. Proc.,
2001-13, 462 (2001)

Layer of silicon particles (experiment),
R.W. Davis et al.,
AIP Conference Proceedings,
550, 292 (2001)

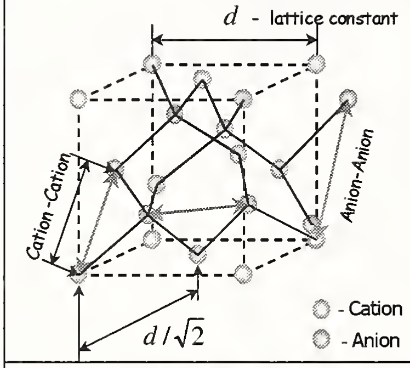
Summary

- 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?

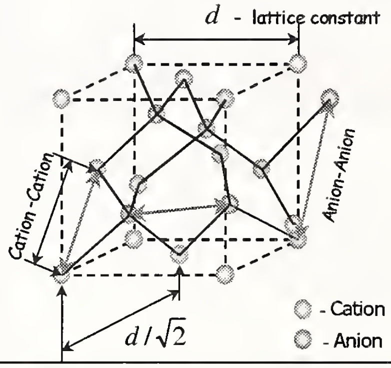
- Reliable thermodynamic properties of GaN, AlN. InN, AlGaN, InGaN, AlGaInN, AlInN
- Thermodynamic properties of vapor species and products of decomposition
- Thermodynamic properties of different adducts between metalorganic species and ammonia
- Kinetic parameters of rate-limiting processes (diffusion 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



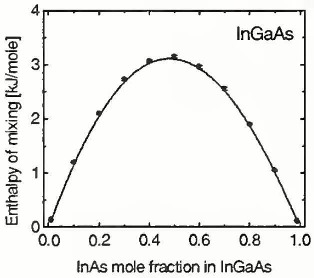
Elastic energy of lattice distortion is described in terms of stretching and bending of tetrahedral covalent bonds

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



Elastic energy of lattice distortion is described in terms of stretching and bending of tetrahedral covalent bonds

Enthalpy of mixing for ternary compounds



⇑

Agrees well with available data

Comparison with experimental data

Interaction parameter W is defined by the expression

$$H_{mix} = W \cdot x(1-x)$$

Compound	VFF-modeling (kJ /mole)	Experiment (kJ /mole)
InGaAs	12.985	11.76–12.56
InGaP	16.112	13.36–18.45
InGaN	30.464	□
GaAsP	4.283	4.19

Contributors:

R. Talalaev, E. Yakovlev, I.N. Przhevalskii, S.Yu. Karpov, A.N. Vorob'ev, A.V. Lobanova, N. Podol'skaya and I.Zmakin

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

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

Supported by NSF DMR-0073836

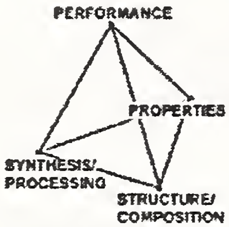
Zi-Kui Liu* (liu@matse.psu.edu)
Long-Qing Chen, Karl Spear and Carlee Allison

Department of Materials Science and Engineering
The Pennsylvania State University

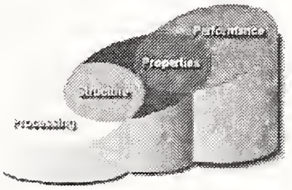
Objective

- 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.

Materials Science and Engineering



From http://www.erc4mse.org



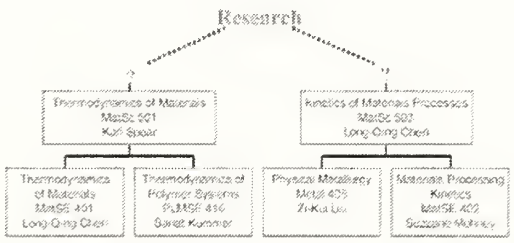
From http://www.nwu.edu

The core is not reflected.

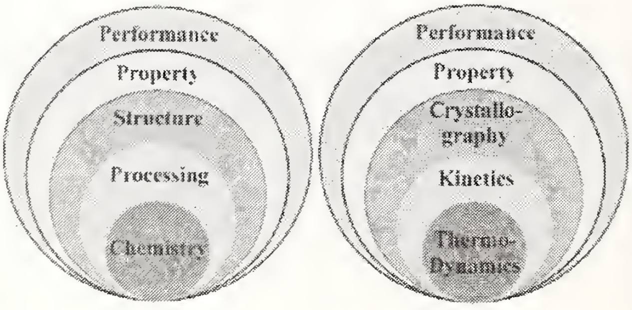
Conventional Situation

- 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.

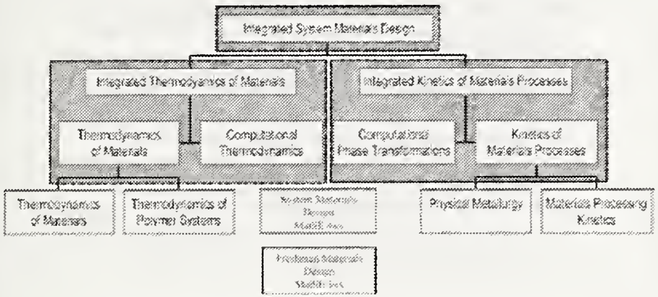
Current Graduate Curriculum



Materials Science and Engineering



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



Development in Recent Years

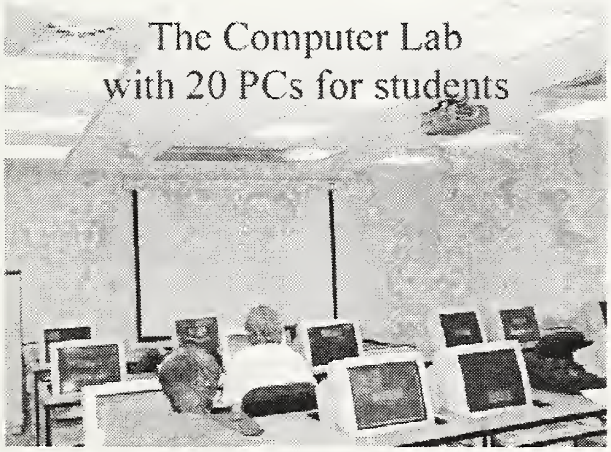
- Computational Thermodynamics
  - Coupling of phase equilibrium and thermochemistry (CALPHAD)
  - First-principles calculations
- Phase transformation simulation
  - Sharp interface
  - Diffuse interface (phase-field)
- System materials design based on the above
  - Northwestern University and Questek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

Faculty Expertise at Penn State

- MSE: 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-Kui Liu
  - Thermodynamic modeling of alloys
  - Teach undergraduate phase transformation
  - Knowledge of system materials design

The Project

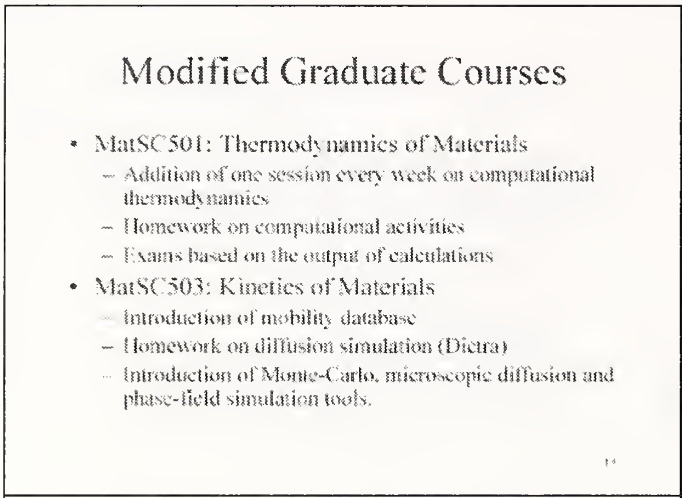
- Time Period: 09/01/00-08/31/03.
- Financial support: NSF, University matching and in-kind.
- Build a new PC lab in the department
- Web site: http://nsfedu.metsce.psu.edu



The Computer Lab with 20 PCs for students

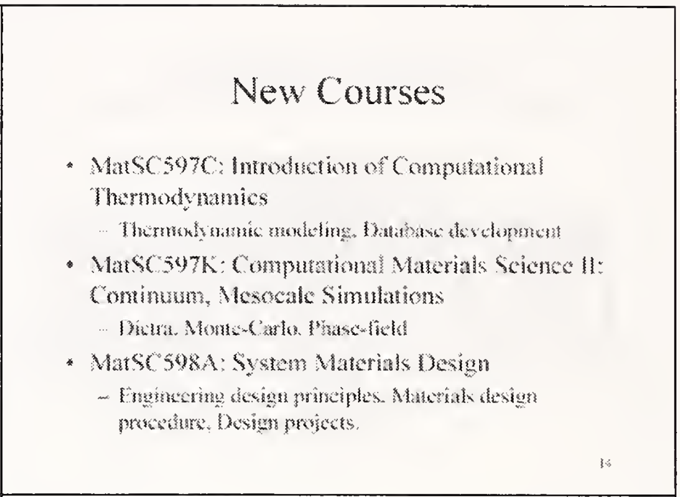
Modified Undergraduate Courses

- MatSE401: Thermodynamics of Materials
  - Introduction of computational thermodynamics: P-T diagrams of pure element.
- Metal 405: Phase Transformations in Alloys
  - Calculation of phase diagrams and equilibrium phase fractions
- Metal 435: Metallurgy Lab II
  - Experimental and calculated phase diagrams
- Metal 436: Metallurgy Lab III
  - A computational lab on avoiding clogging in a continuous casting process



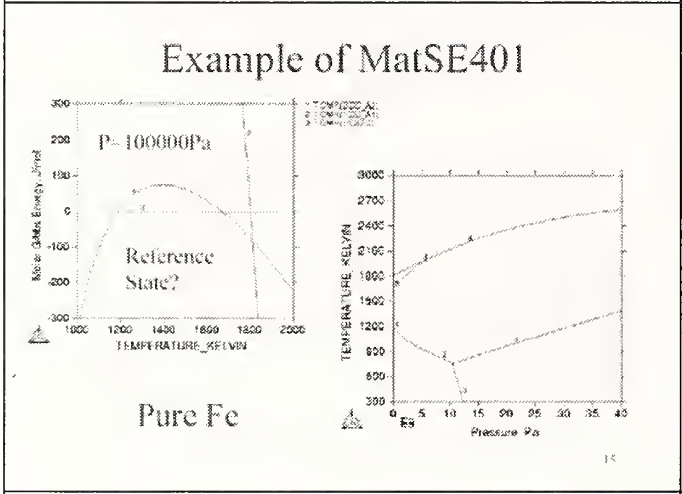
Modified Graduate Courses

- 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.



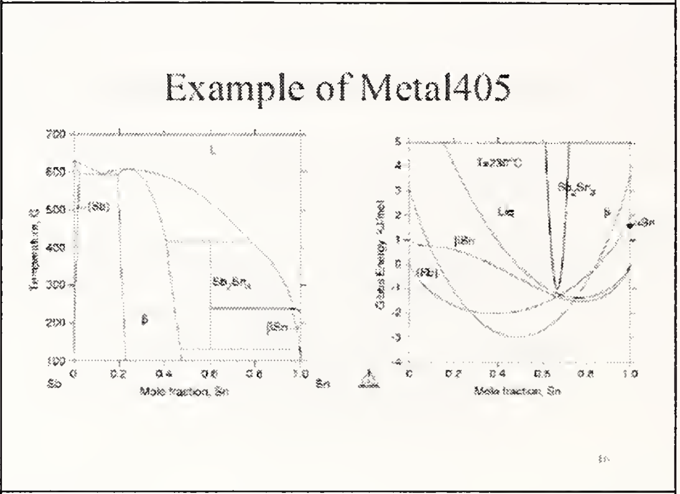
New Courses

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

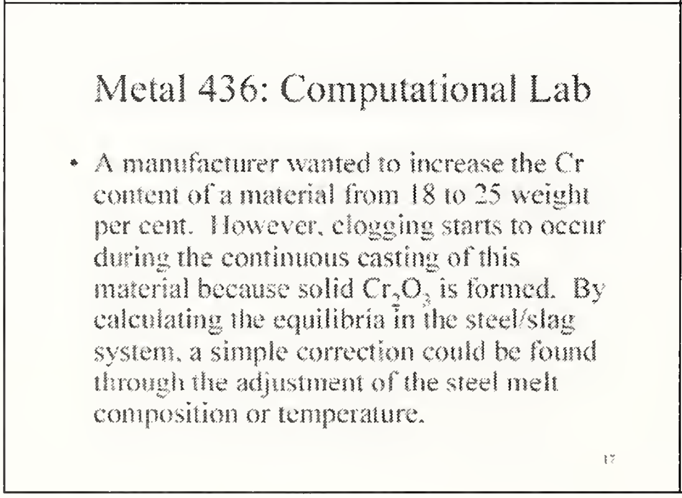


Example of MatSE401

Pure Fe

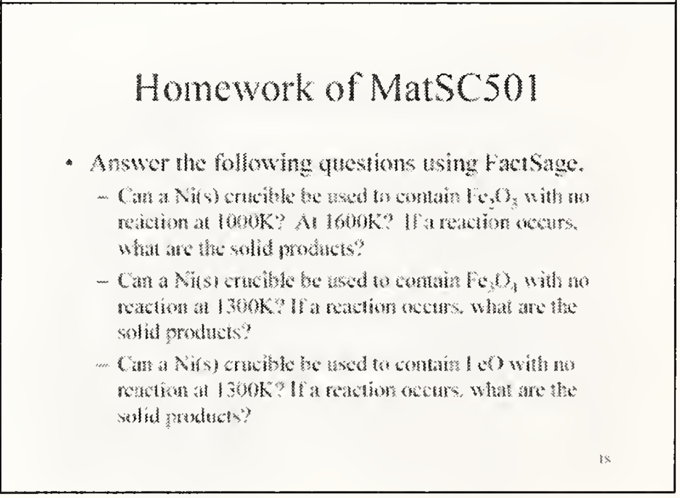


Example of Metal405



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 Cr_2O_3 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 Fe_2O_3 with no reaction at 1000K? At 1600K? If a reaction occurs, what are the solid products?
  - Can a Ni(s) crucible be used to contain Fe_3O_4 with no reaction at 1300K? If a reaction occurs, what are the solid products?
  - Can a Ni(s) crucible be used to contain FeO with no reaction at 1300K? If a reaction occurs, what are the solid products?

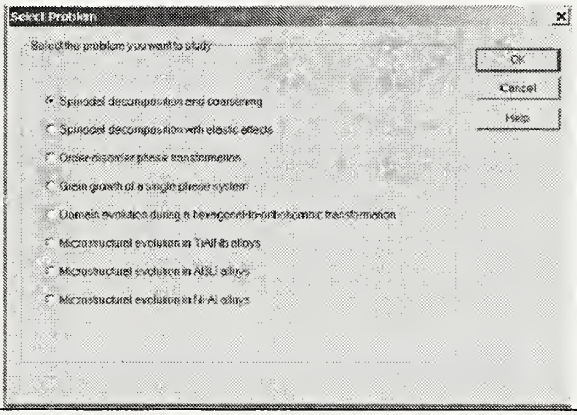
Homework of MatSC501

- A flowing H_2O/H_2 gas mixture is equilibrated with a large quantity of a Ti(s)/TiO(s) mixture at 1900K before it passes over small separated samples of Sc, V, Mn, Cr, Zn, Cu, Co, and Ni heated at 1000K. The gas is passed over these samples until they finally equilibrate with the H_2O/H_2 ratio produced by equilibration with the 1900K Ti(s)/TiO(s) 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

Homework of MatSC503

- Label the phase regions in the attached two Fe-Si-C isopleth diagrams with 0.45%C and 0.49%C, respectively. The numbers indicate the phase boundaries with the shown phases in equilibrium with each other.
- Simulate the up hill diffusion of the Fe-Si-C diffusion couple.
- Explain, thermodynamically and kinetically, why carbon diffuses from the low carbon concentration region (A) to the high carbon concentration region (B).
- Simulate the time needed to homogenize the carbon concentration at 1323K.
- Make another simulation at a higher temperature where the two alloys are still in the single fcc phase region and find out the time needed to homogenize the carbon concentration.

Software in MatSC503



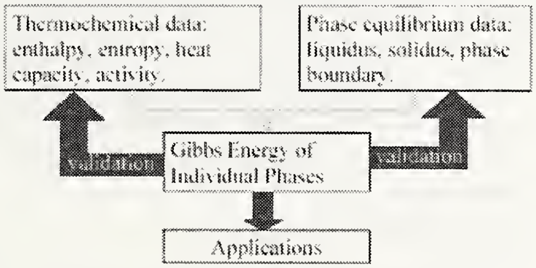
Select the problem you want to study

● Spinodal decomposition and coarsening
○ Spinodal decomposition with elastic effects
○ Order-disorder phase transformations
○ Grain growth of a single phase system
○ Domain evolution during a hexagonal-to-orthorhombic transformation
○ Microstructural evolution in TiAl-Nb alloys
○ Microstructural evolution in Al-Li alloys
○ Microstructural evolution in Ni-Al alloys

MatSC597C: 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 sublattice 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
- Miniproject of the course

Thermodynamic Modeling



Thermochemical data: enthalpy, entropy, heat capacity, activity.

Phase equilibrium data: liquidus, solidus, phase boundary.

Gibbs Energy of Individual Phases

Applications

Special Issue of CALPHAD on Computational Tools: ExTHERM, FACT, MTDATA, PANDAT, THERMOCALC, THERMOSUITE

MatSC597K: Continuum, Mesocale Simulations

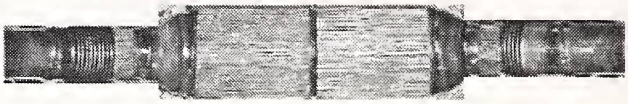
- Dr. Liu
  - Review thermodynamic and kinetic principles
  - Modeling of atomic mobility
  - Simulation of diffusional phase transformations
- Dr. DebRoy
  - Monte-Carlo simulation of grain growth
  - Time-Temperature-Transformation simulation for inclusions
- Dr. Chen
  - Kinetic Monte Carlo simulation: ordering and phase separation
  - Microscopic diffusion equation: modeling of diffusional processes
  - Time-dependent Ginzburg-Landau equations: order parameters and Landau expansions, and antiphase domain coarsening
  - Cahn-Hilliard equations: phase separation, precipitate coarsening
  - Coherency strain energy and applied stress: coherent precipitate morphologies, ferroelectric and ferroelastic domains
  - Phase-field simulation: solidification, grain growth
  - Project of the course

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

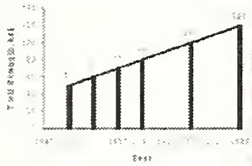
MatSC598A: Project One:

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 everyday. 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 56kgf/mm^2 or 550MPa). 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.

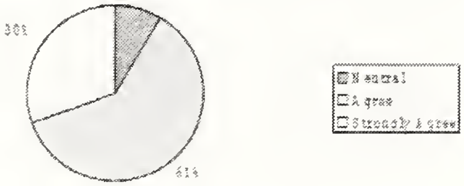


Evaluation Procedures

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

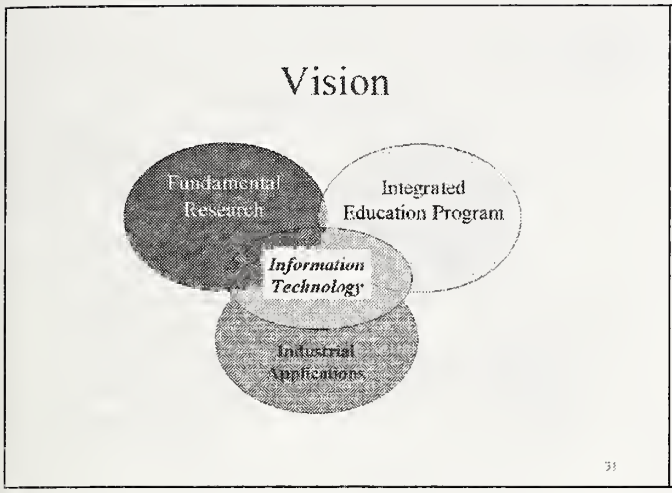
Survey Results

- 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.metsce.psu.edu



Vision

Fundamental Research

Integrated Education Program

Information Technology

Industrial Applications

<u>Additional points made by speaker:</u>

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

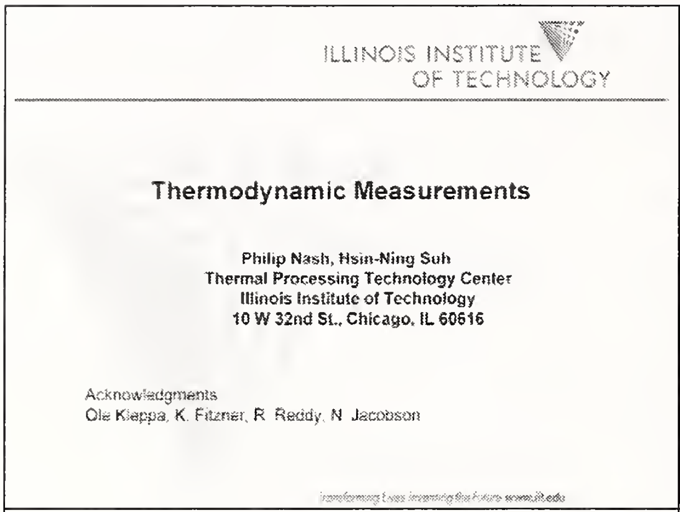
<u>Questions/comments from workshop attendees:</u>

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

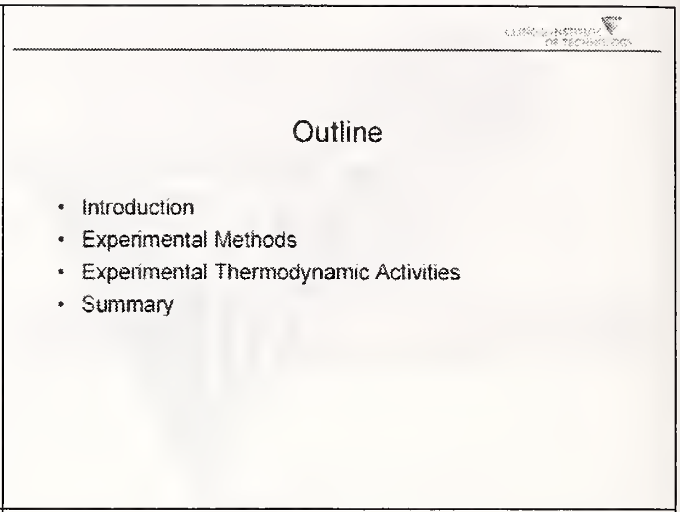


ILLINOIS INSTITUTE
OF TECHNOLOGY

Thermodynamic Measurements

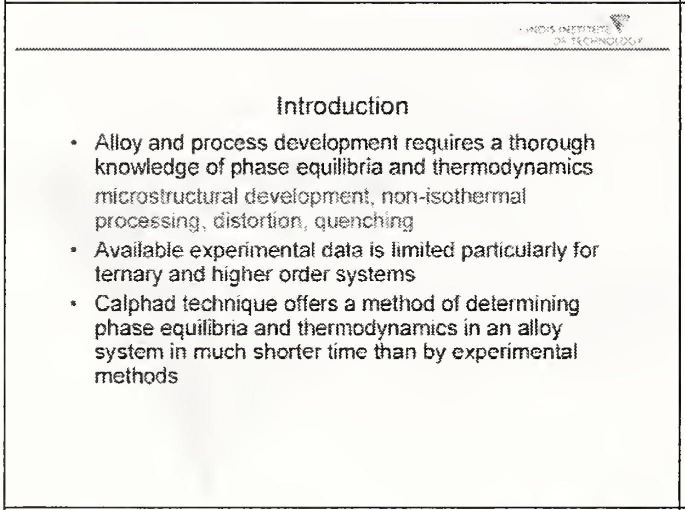
Philip Nash, Hsin-Ning Suh
Thermal Processing Technology Center
Illinois Institute of Technology
10 W 32nd St., Chicago, IL 60616

Acknowledgments
Ole Kleppa, K. Fitzner, R. Reddy, N. Jacobson



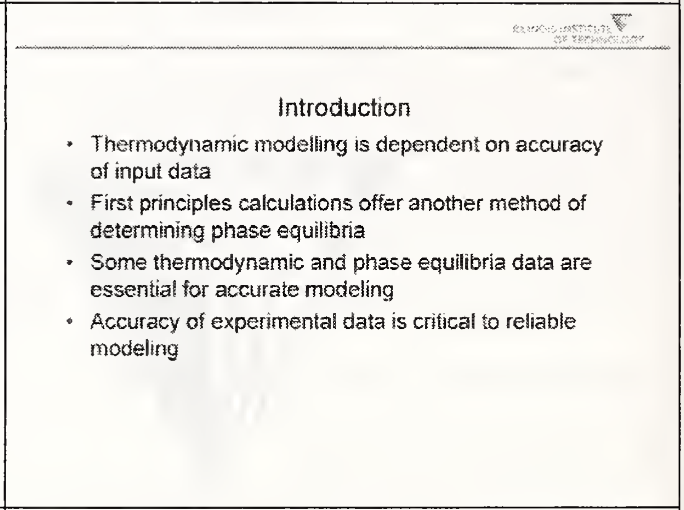
Outline

- Introduction
- Experimental Methods
- Experimental Thermodynamic Activities
- Summary



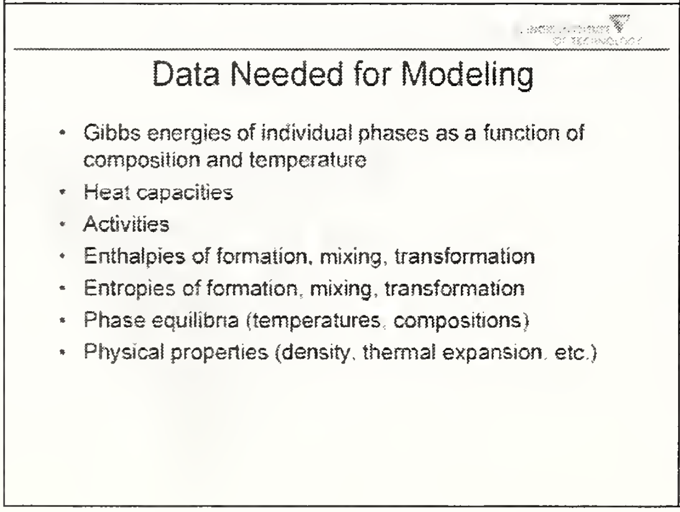
Introduction

- 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



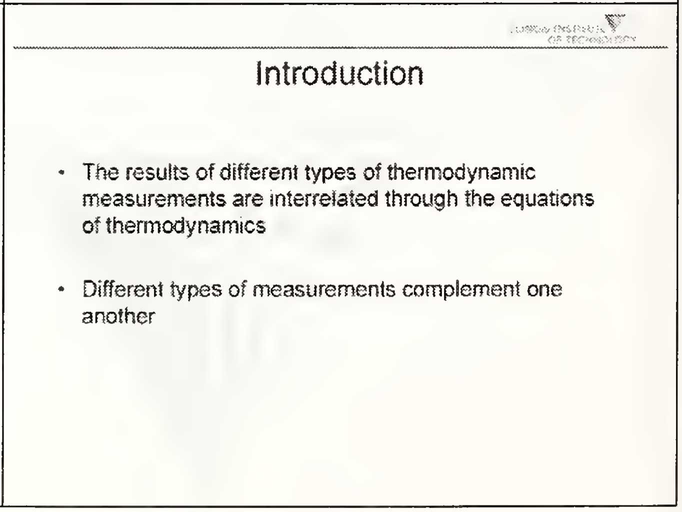
Introduction

- Thermodynamic modelling is dependent on accuracy of input data
- First principles calculations offer another method of determining phase equilibria
- Some thermodynamic and phase equilibria data are essential for accurate modeling
- Accuracy of experimental data is critical to reliable modeling



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.)



Introduction

- The results of different types of thermodynamic measurements are interrelated through the equations of thermodynamics
- Different types of measurements complement one another

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 ±1kJ/mole

The measurements are generally made with the calorimeter set at 1473±2K, 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

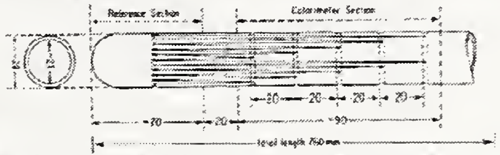


Fig. 18 Schematic view of calorimeter section ("working section") and "reference section" of the new calorimeter.

Kleppa Calorimeter

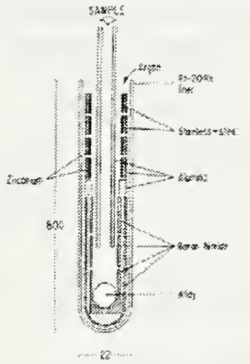
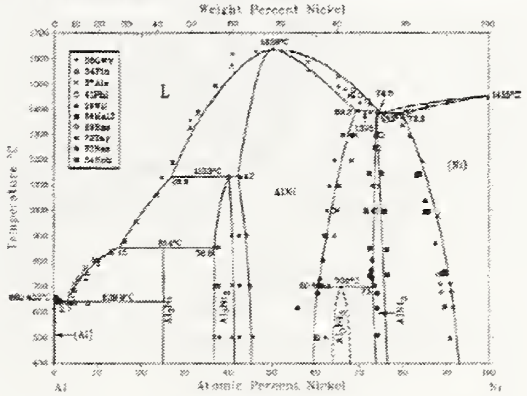


Fig. 19 Schematic diagram of the calorimetric cell assembly showing part of the PtRh liner, the boron nitride crucible, the boron nitride protective cylinder and stirrer, the alumina protective crucible and protective cylinders, as well as parts of the final gettering system for the argon gas.

Fig. 1 Assessed Al-Ni Phase Diagram



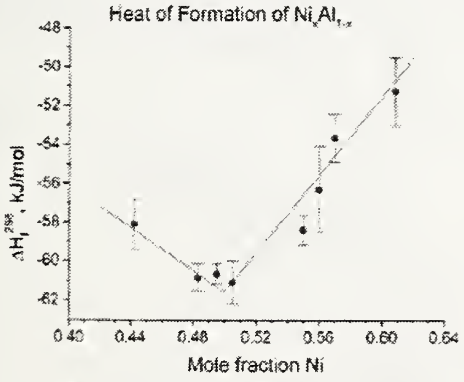
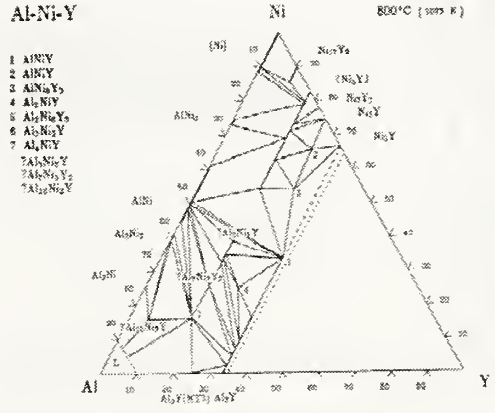


Fig. 2 Enthalpies of formation for Ni_xAl_{1-x} alloys determined in this work.

Al-Ni-Y Isothermal section [3]



Results

By using direct synthesis, the standard enthalpy of formation, ΔH_f^{298K}, is calculated from:

$$aAl(s, 298K) + bNi(s, 298K) + cY(s, 298K) = Al_aNi_bY_c(1473\ K) \quad \Delta H_{Reaction} \quad (1)$$

$$Al_aNi_bY_c(s, 298\ K) = Al_aNi_bY_c(1473\ K) \quad \Delta H_{Heat\ Content} \quad (2)$$

From reaction (1) and (2) we get

$$aAl(s, 298K) + bNi(s, 298K) + cY(s, 298K) = Al_aNi_bY_c\ (s, 298\ K)$$

The standard enthalpy of formation is thus obtained.

$$\Delta H_f^{298K} = \Delta H_{Reaction} - \Delta H_{Heat\ Content}$$

$\Delta H_{Reaction}$ and $\Delta H_{Heat\ Content}$ are molar enthalpy changes for reaction (1) and (2).

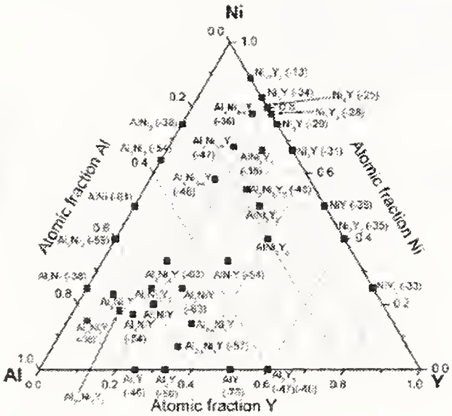
Table 2. Summary of high temperature reaction calorimetry results and Miedema's semi-empirical model results. Calorimeter temperature set at 1473K except as noted

Compound	$\Delta H_{Reaction}$, kJ/mole	$\Delta H_{Heat\ Content}$, kJ/mole	Experimental $\Delta H_{formation}$, kJ/mole	$\Delta H_{formation}$ Miedema's model	Melting point
Al[illegible]Ni[illegible]Y[illegible]	-29.0 ± 0.5	52.0 ± 0.5	-55.0 ± 0.8	-44.8	1244K
Al[illegible]Ni[illegible]Y[illegible]	-31.6 ± 1.5	31.2 ± 0.2	-62.8 ± 1.5	-51.6	1418K
Al[illegible]Ni[illegible]Y[illegible]	0.0 ± 1.0	48.5 ± 0.8	-48.5 ± 1.5	-45.3	1250K
Al[illegible]Ni[illegible]Y[illegible]*	-10.3 ± 0.5	40.5 ± 1.1	-55.7 ± 1.4	-25.8	1467K
Al[illegible]Ni[illegible]Y[illegible]	-22.9 ± 1.0	32.8 ± 1.1	-66.7 ± 1.6	-40.8	-
Al[illegible]Ni[illegible]Y[illegible]†	-12.5 ± 1.4	39.0 ± 1.2	-	-58.6	1423K
Al[illegible]Ni[illegible]Y[illegible]	-6.96 ± 0.6	47.3 ± 0.3	-56.3 ± 0.9	-54.3	1453K
Al[illegible]Ni[illegible]Y[illegible]	-29.55 ± 1.2	32.87 ± 1.0	-62.8 ± 2.3	-49.2	1423K
Al[illegible]Ni[illegible]Y[illegible]	-3.10 ± 0.8	44.89 ± 1.0	-48.3 ± 2.9	-42.3	1426K
Al[illegible]Ni[illegible]Y[illegible]	-11.13 ± 0.72	26.26 ± 0.55	-37.44 ± 1.1	-37.6	1479K
Al[illegible]Ni[illegible]Y[illegible]	-4.02 ± 1.08	35.02 ± 1.08	-39.14 ± 1.8	-39.1	1569K
Al[illegible]Ni[illegible]Y[illegible]	-8.2 ± 1.8	33.3 ± 1.1	-37.9 ± 2.5	-39.2	-
Al[illegible]Ni[illegible]Y[illegible]				-48.2	1408K

* Calorimeter set at 1373K

† Reacted sample was not predominantly single phase

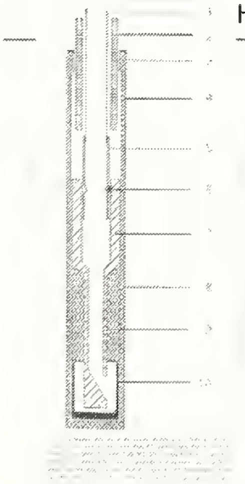
Enthalpies of Formation of Al-Ni-Y intermetallics



Advantages and Limitations of Direct Synthesis Calorimetry

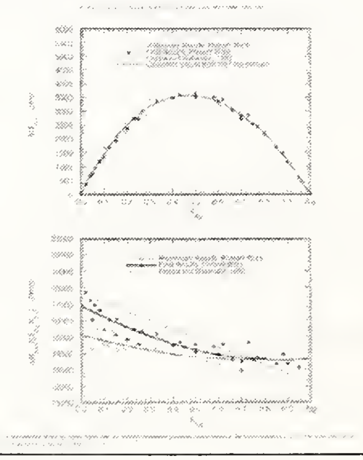
- Advantages
  - Only two heat effects need be measured
  - Absolute temperature measurement not needed
  - High accuracy (typically ± 1kJ/mole)
  - Experiment directly yields enthalpy of formation at 298K
- Limitations
  - Some systems give incomplete reactions, particularly very high melting point compounds
  - Temperature drift
  - Reduction in sensitivity over time

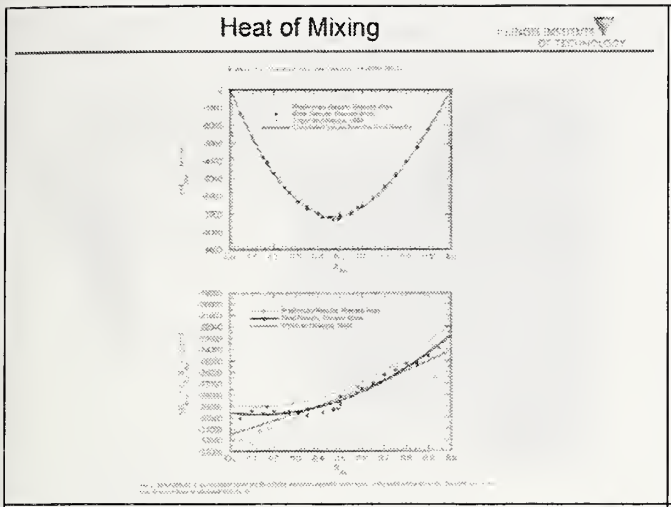
Heat of Mixing



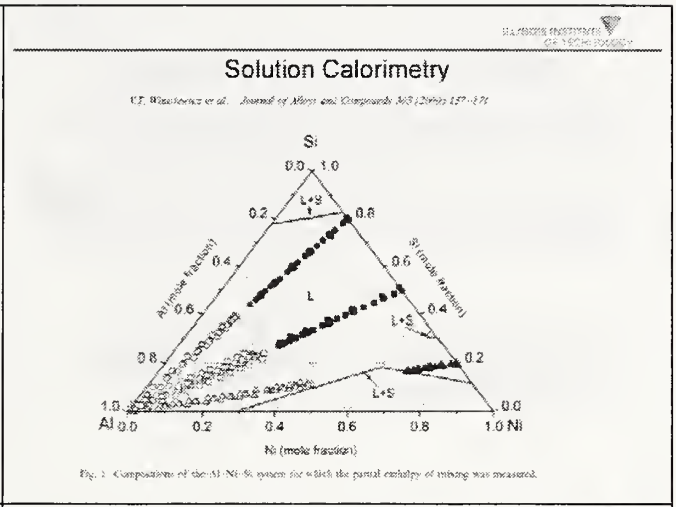
Schematic of calorimeter set-up for mixing measurements. Solute reaches thermal equilibrium with solvent before being dropped

Heat of Mixing





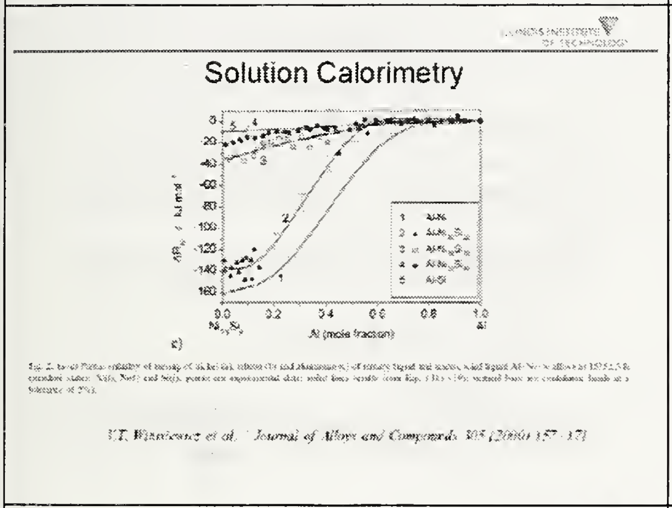
Heat of Mixing



Solution Calorimetry

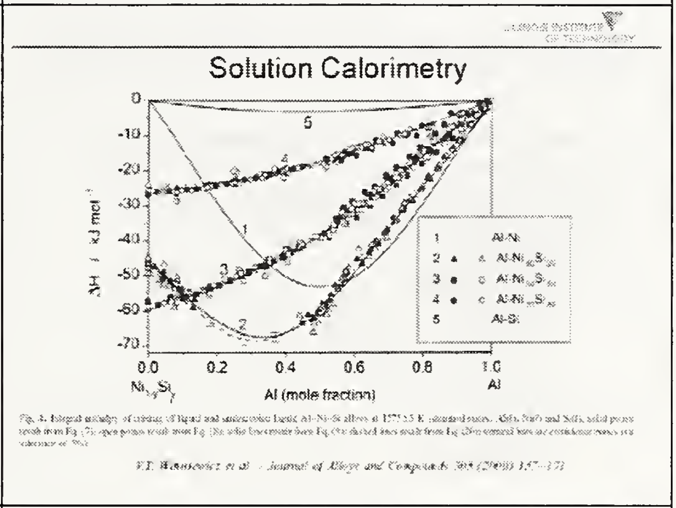
V.T. Witusiewicz et al. / Journal of Alloys and Compounds 305 (2000) 157–171

Fig. 1. Compositions of the Al–Ni–Si system for which the partial enthalpy of mixing was measured.



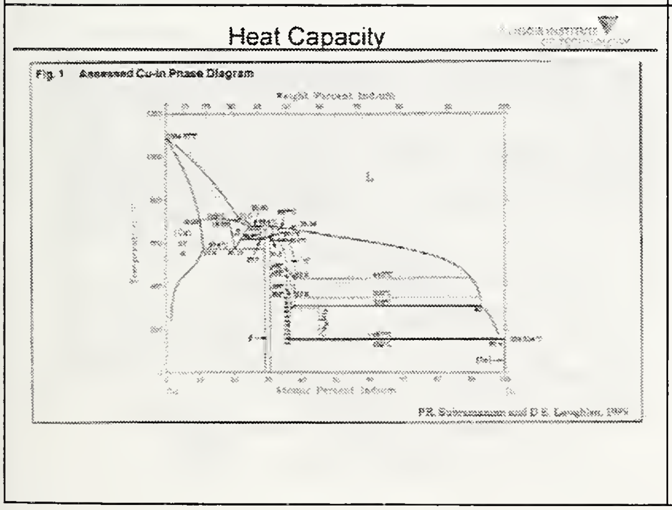
Solution Calorimetry

V.T. Witusiewicz et al. / Journal of Alloys and Compounds 305 (2000) 157–171



Solution Calorimetry

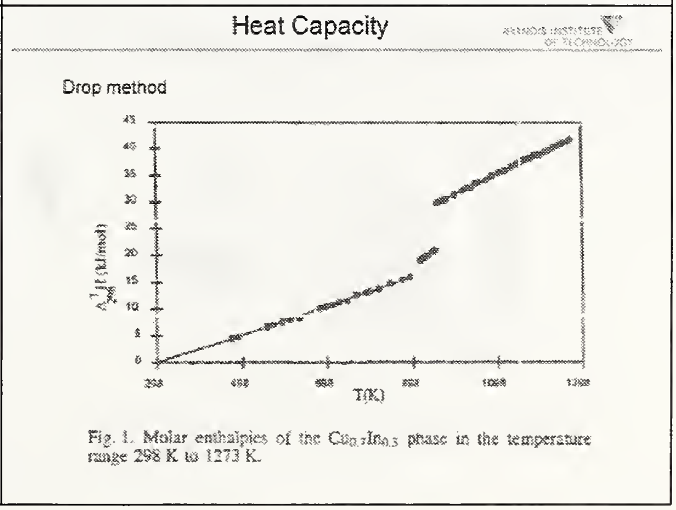
V.T. Witusiewicz et al. / Journal of Alloys and Compounds 305 (2000) 157–171



Heat Capacity

Fig. 1 Assessed Cu-In Phase Diagram

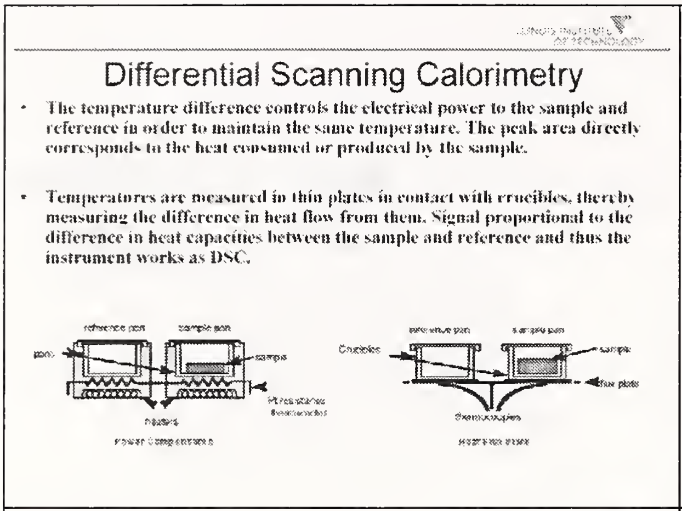
P.R. Subramanian and D.E. Laughlin, 1989



Heat Capacity

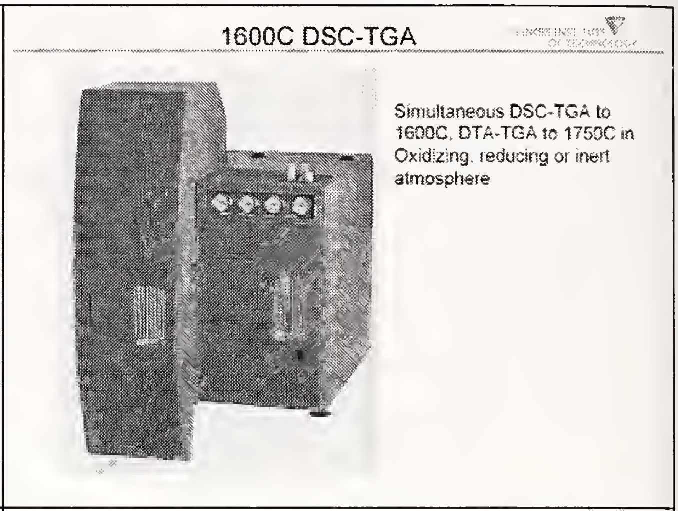
Drop method

Fig. 1. Molar enthalpies of the $Cu_{0.7}In_{0.3}$ phase in the temperature range 298 K to 1273 K.



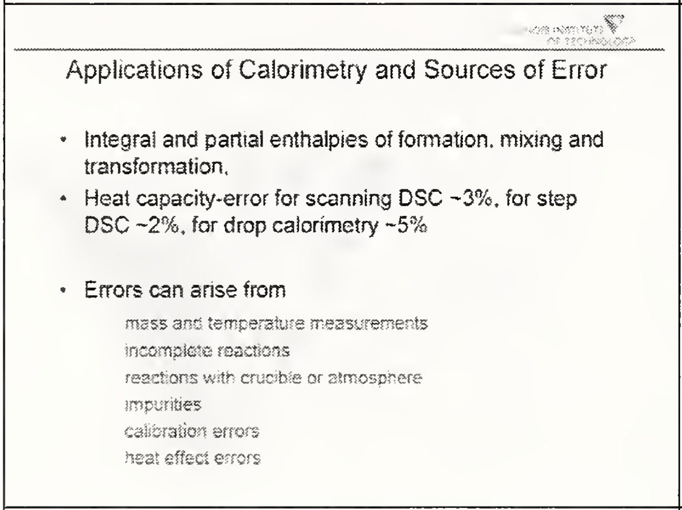
Differential Scanning Calorimetry

- **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.**



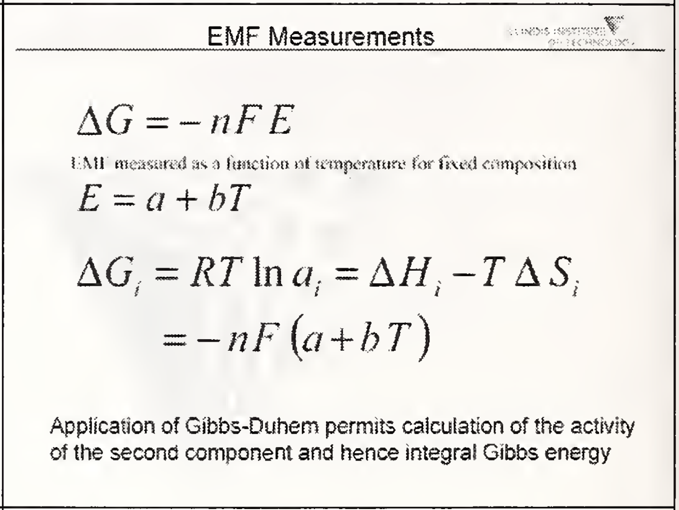
1600C DSC-TGA

Simultaneous DSC-TGA to 1600C, DTA-TGA to 1750C in Oxidizing, reducing or inert atmosphere



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

$$\Delta G = -nFE$$

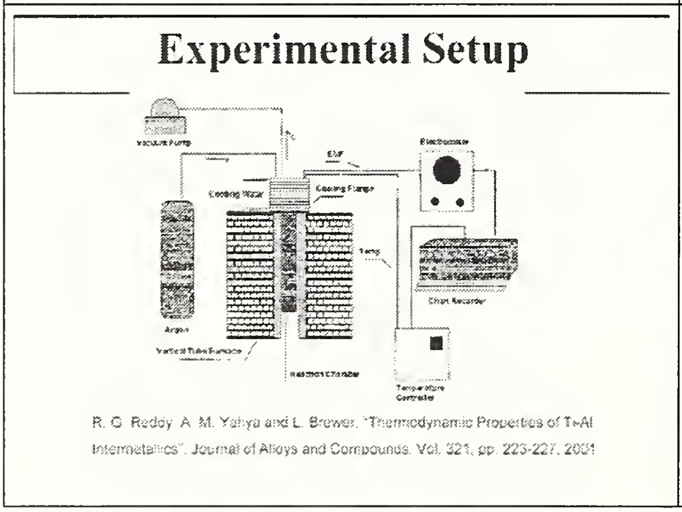
EMF measured as a function of temperature for fixed composition

$$E = a + bT$$

$$\Delta G_i = RT \ln a_i = \Delta H_i - T\,\Delta S_i$$

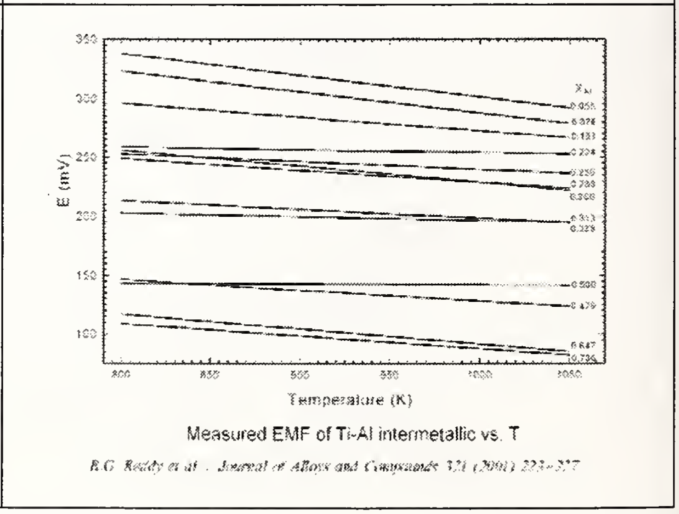
$$= -nF\,(a + bT)$$

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



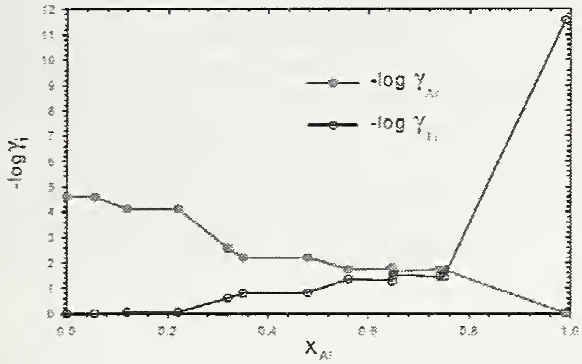
Experimental Setup

R. G. Reddy, A. M. Yahya and L. Brewer, "Thermodynamic Properties of Ti-Al Intermetallics", Journal of Alloys and Compounds, Vol. 321, pp. 223-227, 2001



Measured EMF of Ti-Al intermetallic vs. T

R.G. Reddy et al. , Journal of Alloys and Compounds 321 (2001) 223–227



Activity coefficient vs. X_{Al} at 850 K

R.G. Reddy et al. / Journal of Alloys and Compounds 321 (2001) 223–227

Applications and Sources of Error

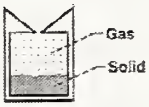
- Activities, partial and integral Gibbs energies, enthalpies and entropies
- Major limitation is in maximum temperature
- Errors can arise from
  - mass and temperature measurements
  - reactions with atmosphere
  - impurities
  - multiple valence states
  - thermal gradients in cell

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

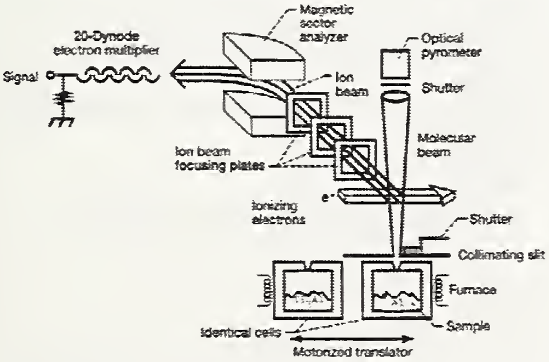
Knudsen Cell Technique

- Equilibrate alloy/vapor in small cell
- Sample vapor with mass spectrometer.
  - Pressure ∝ IT
- Best accuracy—requires internal standard
  - Double or Triple cell system
- Modified commercial magnetic sector instrument
  - Windows based Data acquisition system



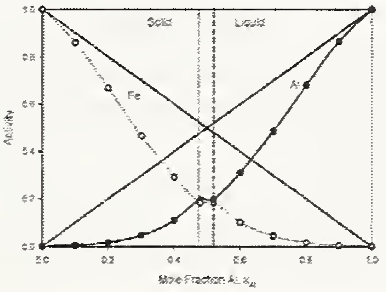
Measurement of Thermodynamic Activities

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

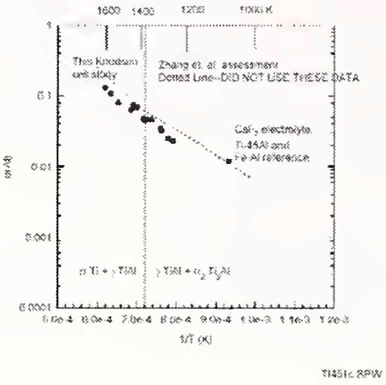


Fe-Al System at 1573 K

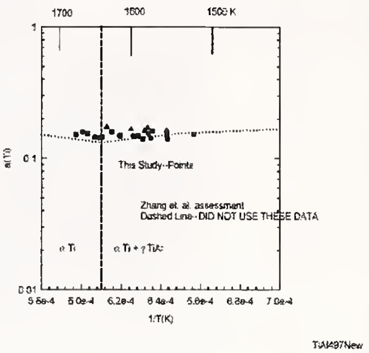
(Ion Current Ratio Technique)



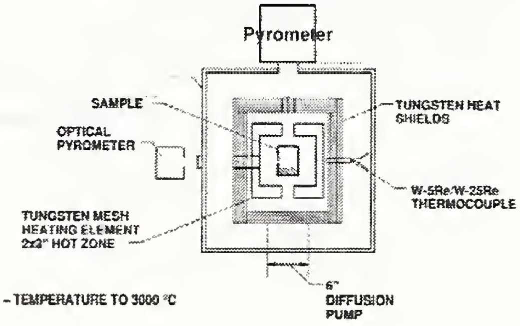
Al Activities in α_2 Ti_3Al + γ TiAl
(Double Cell Technique)



Ti Activities in α_2 Ti_3Al + γ TiAl
(Double Cell Technique)



High Temperature Vacuum Furnace— Liquidus Data for Refractory Containing Systems



– TEMPERATURE TO 3000 °C

Other Methods

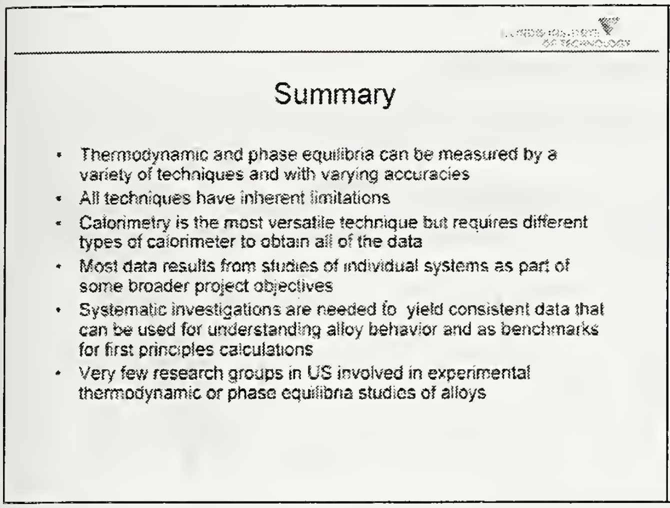
- Equilibrium phase composition by WDS or EDS analysis
- Metallography-phase amounts by lever rule
- XRD-phase boundaries, site occupancy
- DTA-phase boundaries
- Dilatometry-phase boundaries, CTE's
- Diffusion couples-phase boundaries

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
  - Fitzner& Moser-IMMS-Krakow
- Japan
  - Yamaguchi-Iwate U., Jacob-Tohoku U., Shoji-Nagoya U., Yamana-Kyoto U., Sheng-ONRI
- Austria
  - A. Mikula & H. Ipser-U. Vienna
- Italy
  - Borzone-U. Rome, Ferro-U. Genoa



Summary

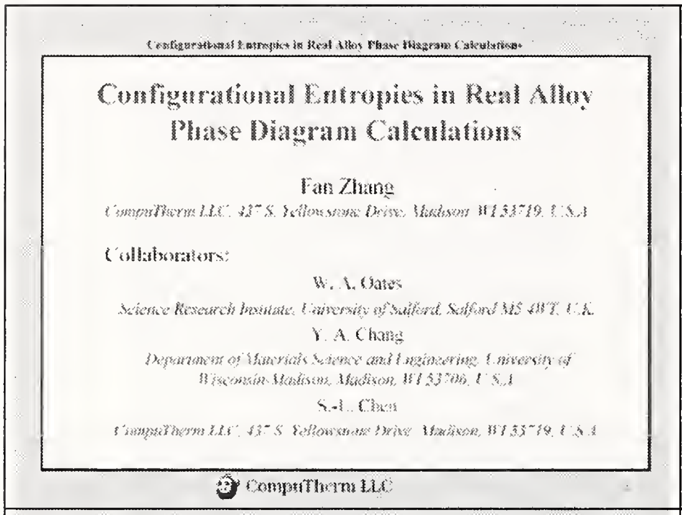
- Thermodynamic and phase equilibria can be measured by a variety of techniques and with varying accuracies
- All techniques have inherent limitations
- Calorimetry is the most versatile technique but requires different types of calorimeter to obtain all of the data
- Most data results from studies of 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



Configurational Entropies in Real Alloy Phase Diagram Calculations

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Collaborators:
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Science Research Institute, University of Salford, Salford M5 4WT, U.K.
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Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, WI 53706, U.S.A
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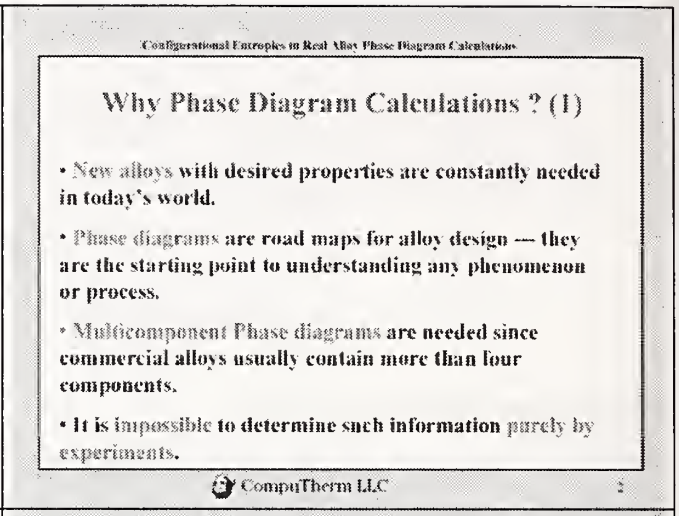
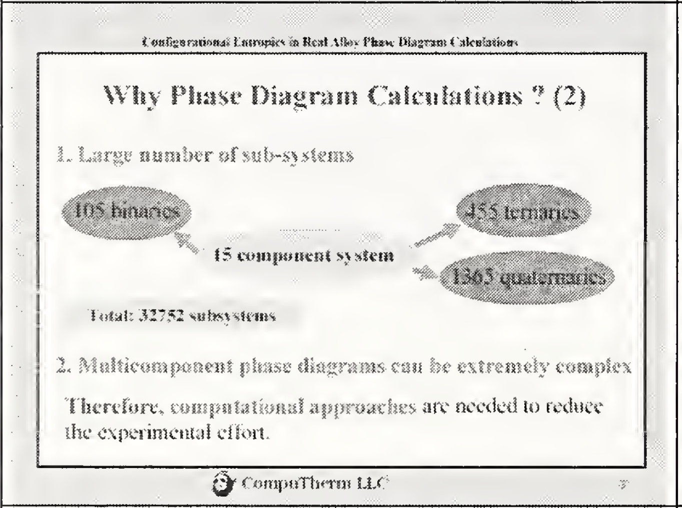
CompuTherm LLC, 437 S. Yellowstone Drive, Madison, WI 53719, U.S.A



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.**



Why Phase Diagram Calculations ? (2)

1. Large number of sub-systems

105 binaries

15 component system

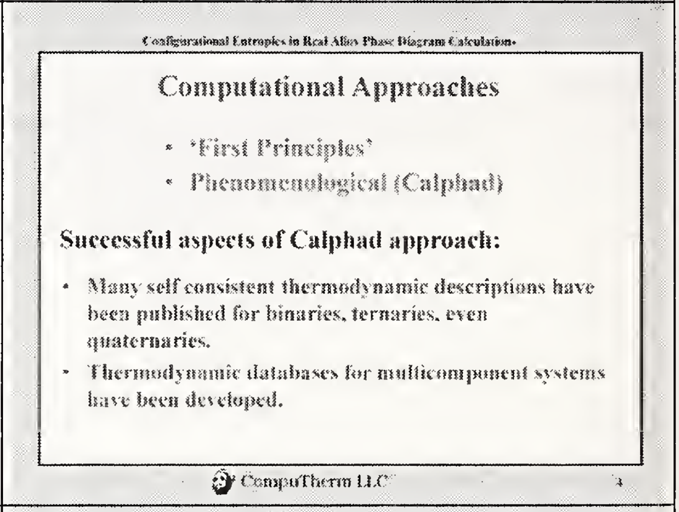
455 ternaries

1365 quaternaries

Total: 32752 subsystems

2. Multicomponent phase diagrams can be extremely complex

Therefore, computational approaches are needed to reduce the experimental effort.

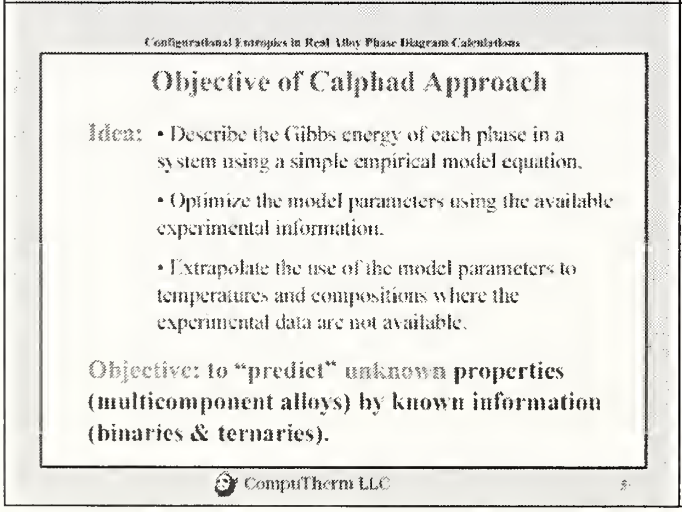


Computational Approaches

- 'First Principles'
- Phenomenological (Calphad)

Successful aspects of Calphad approach:

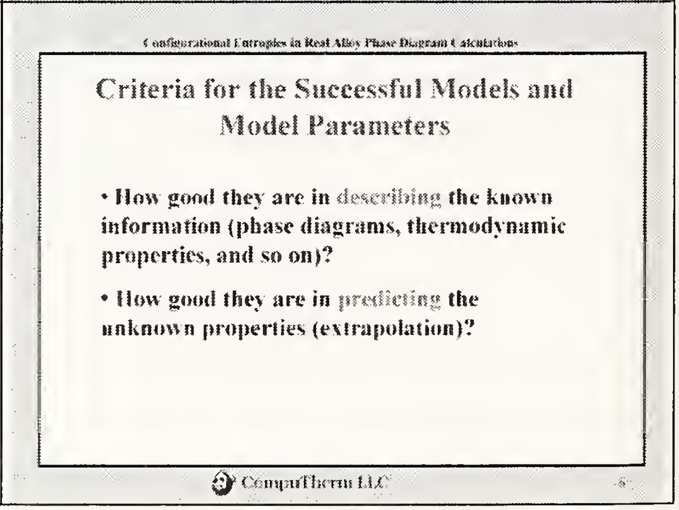
- Many self consistent thermodynamic descriptions have been published for binaries, ternaries, even quaternaries.
- Thermodynamic databases for multicomponent systems have been developed.



Objective of Calphad Approach

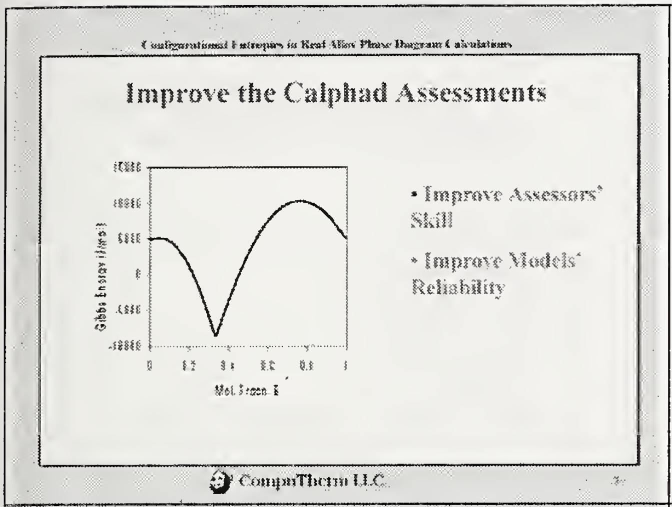
Idea:
- Describe the Gibbs energy of each phase in a system using a simple empirical model equation.
- Optimize the model parameters using the available experimental information.
- Extrapolate the use of the model parameters to temperatures and compositions where the experimental data are not available.

Objective: to "predict" unknown properties (multicomponent alloys) by known information (binaries & ternaries).



Criteria for the Successful Models and Model Parameters

- **How good they are in describing the known information (phase diagrams, thermodynamic properties, and so on)?**
- **How good they are in predicting the unknown properties (extrapolation)?**



Configurational Entropies in Real Alloy Phase Diagram Calculations

Improve the Calphad Assessments

- Improve Assessors' Skill
- Improve Models' Reliability

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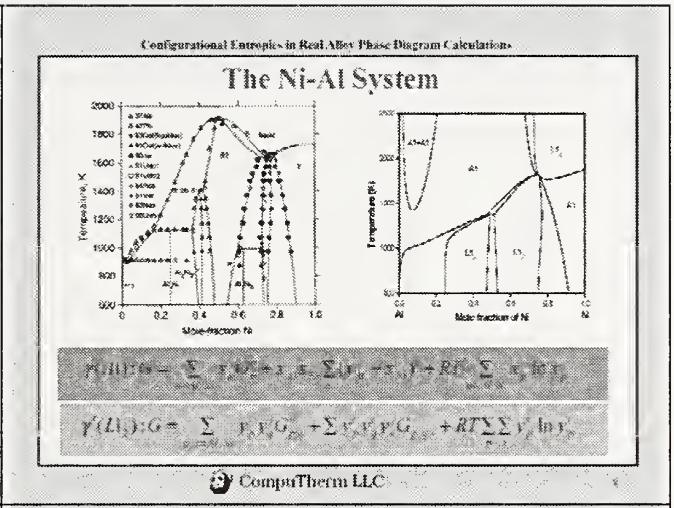

Configurational Entropies in Real Alloy Phase Diagram Calculations

The Ni-Al System

$\gamma(A1): G = $ [illegible]

$\gamma'(L1_2): G = \sum y_i y_j G_{ij} + \sum y_i y_j y_k G_{ijk} + RT\sum\sum y_i \ln y_i$

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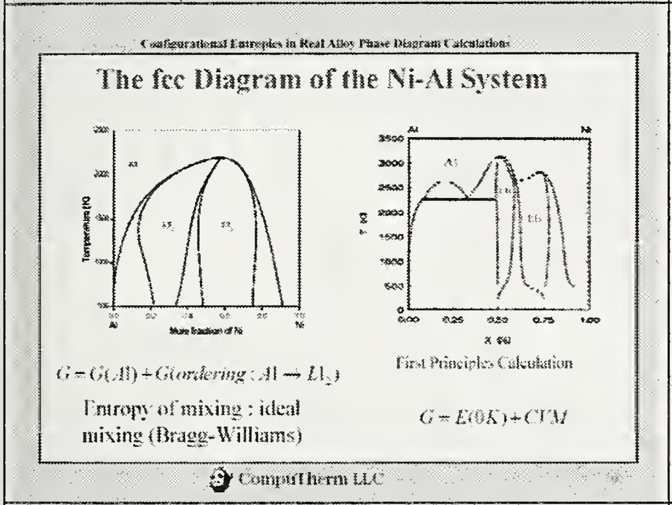

Configurational Entropies in Real Alloy Phase Diagram Calculations

The fcc Diagram of the Ni-Al System

$G = G(A1) + G(ordering: A1 \rightarrow L1_2)$

Entropy of mixing : ideal mixing (Bragg-Williams)

First Principles Calculation

$G = E(0K) + CVM$

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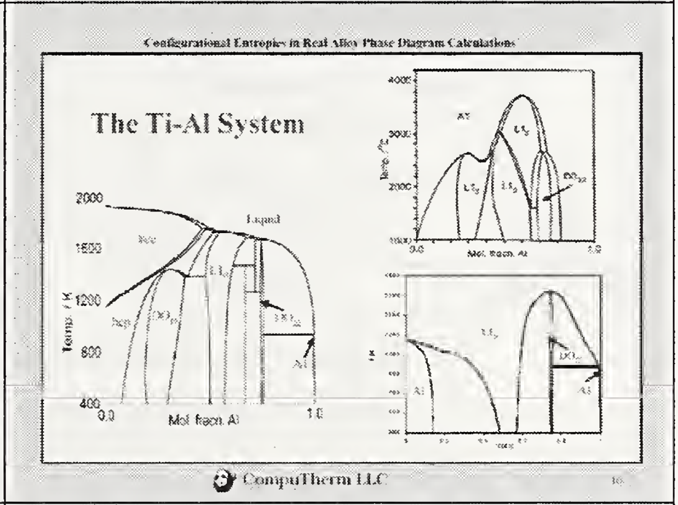

Configurational Entropies in Real Alloy Phase Diagram Calculations

The Ti-Al System

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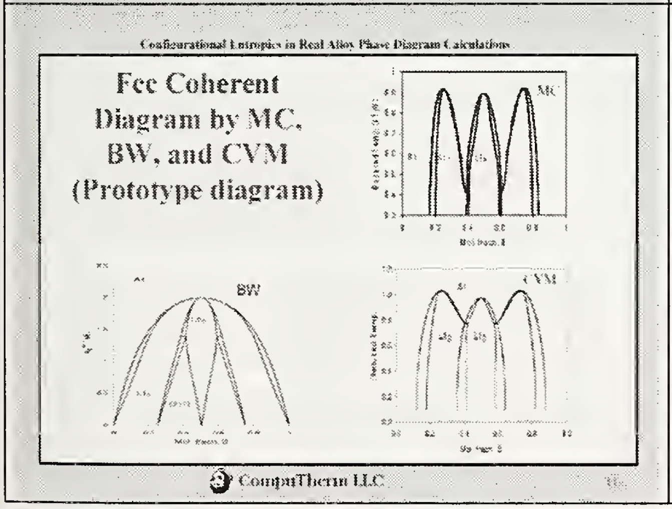

Configurational Entropies in Real Alloy Phase Diagram Calculations

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

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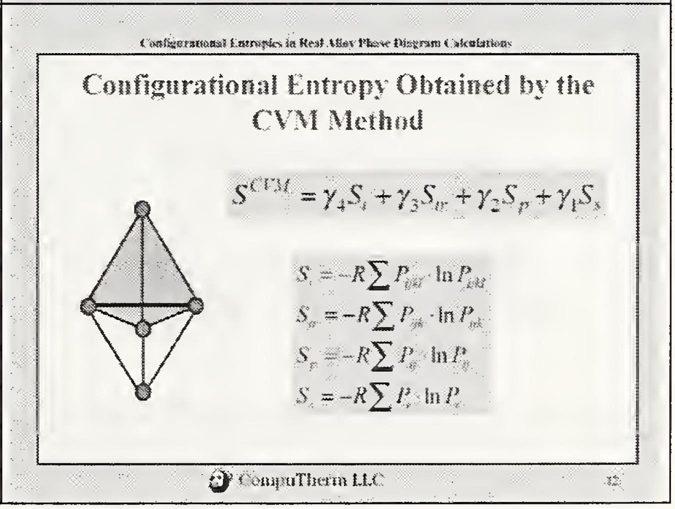

Configurational Entropies in Real Alloy Phase Diagram Calculations

Configurational Entropy Obtained by the CVM Method

$$S^{CVM} = \gamma_4 S_t + \gamma_3 S_{tr} + \gamma_2 S_p + \gamma_1 S_x$$

$$S_t = -R\sum P_{ijkl} \cdot \ln P_{ijkl}$$

$$S_{tr} = -R\sum P_{ijk} \cdot \ln P_{ijk}$$

$$S_p = -R\sum P_{ij} \cdot \ln P_{ij}$$

$$S_x = -R\sum P_i \cdot \ln P_i$$

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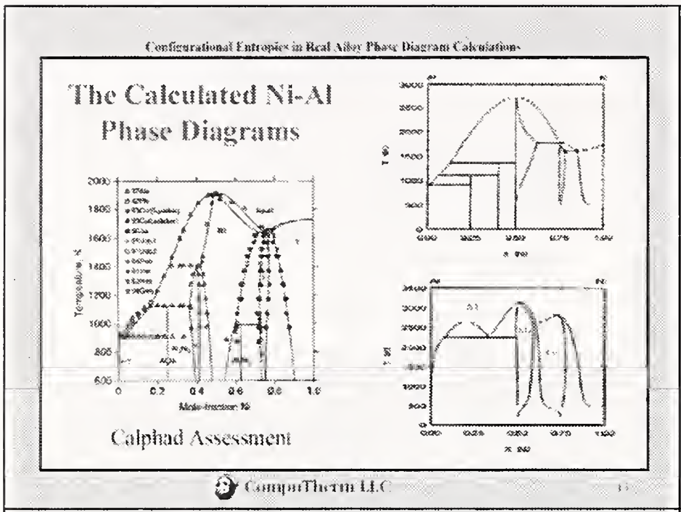

Configurational Entropies in Real Alloy Phase Diagram Calculations

The Calculated Ni-Al Phase Diagrams

Calphad Assessment

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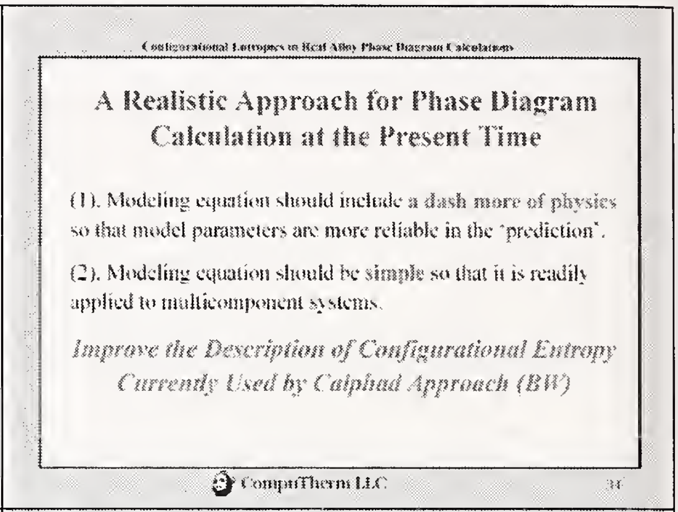

Configurational Entropies in Real Alloy Phase Diagram Calculations

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)

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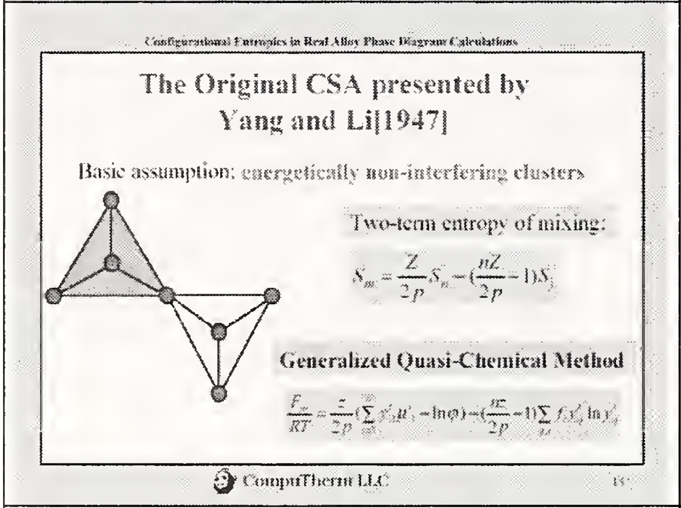

Configurational Entropies in Real Alloy Phase Diagram Calculations

The Original CSA presented by Yang and Li[1947]

Basic assumption: energetically non-interfering clusters

Two-term entropy of mixing:

$$S_m = \frac{Z}{2p} S_n - (\frac{nZ}{2p} - 1) S_1$$

Generalized Quasi-Chemical Method

$$\frac{F_m}{RT} = \frac{z}{2p}(\sum_{ijkl} x_{ijkl} u_{ijkl} - \ln\varphi) - (\frac{nz}{2p} - 1)\sum_{ij} f_i x_{ij}^1 \ln x_{ij}^1$$

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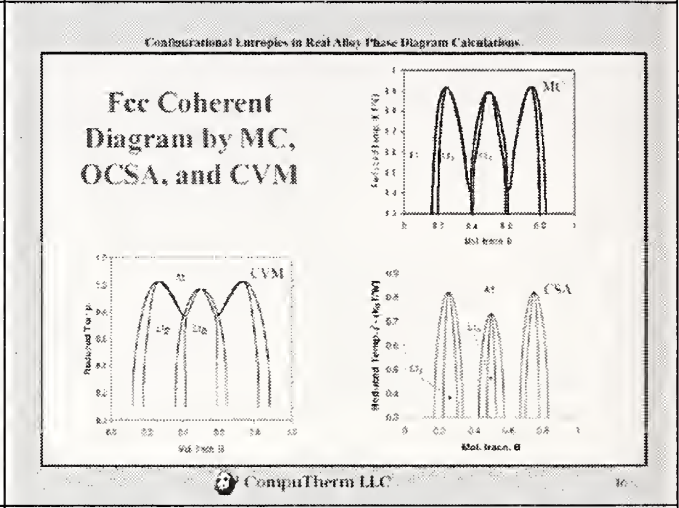

Configurational Entropies in Real Alloy Phase Diagram Calculations

Fcc Coherent Diagram by MC, OCSA, and CVM

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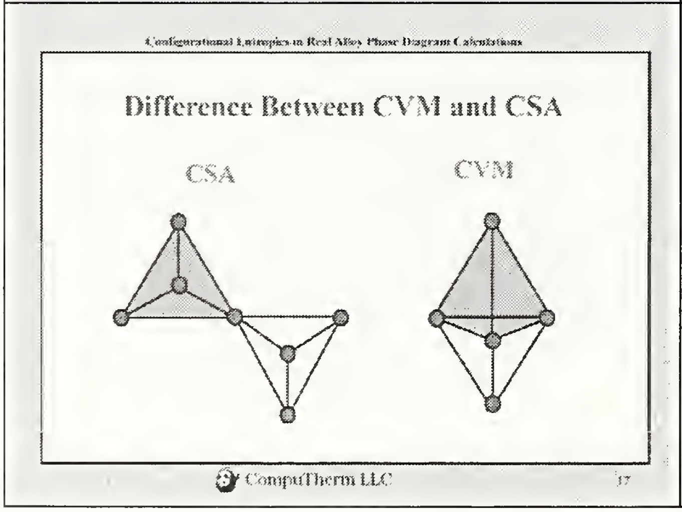

Configurational Entropies in Real Alloy Phase Diagram Calculations

Difference Between CVM and CSA

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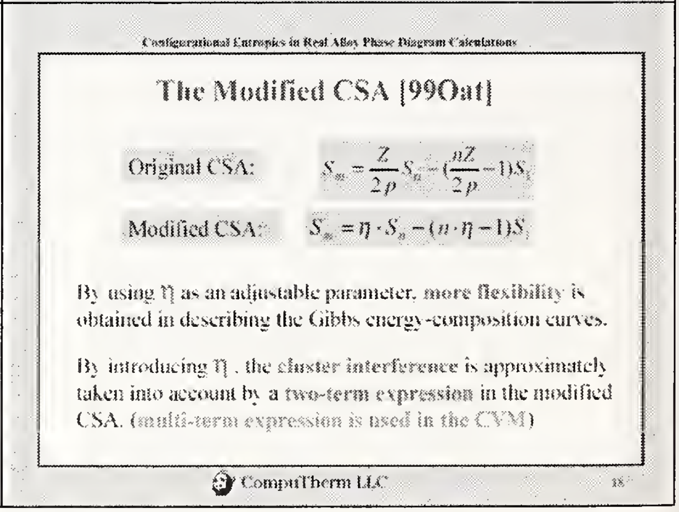

Configurational Entropies in Real Alloy Phase Diagram Calculations

The Modified CSA [99Oat]

Original CSA: $S_m = \frac{Z}{2p} S_n - (\frac{nZ}{2p} - 1) S_1$

Modified CSA: $S_m = \eta \cdot S_n - (n \cdot \eta - 1) S_1$

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

By introducing η, 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)

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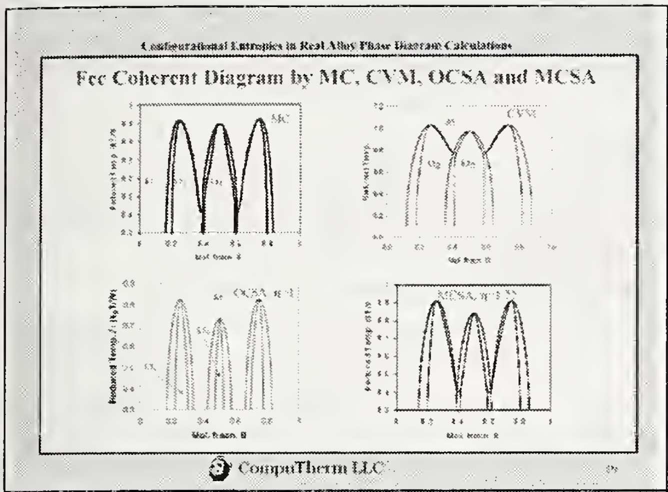
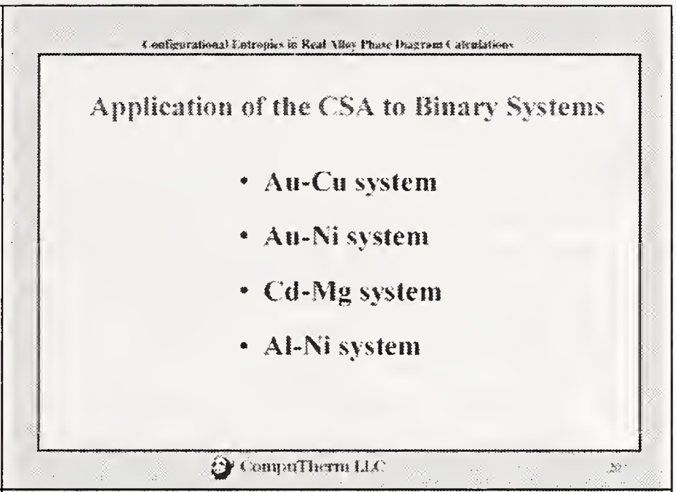
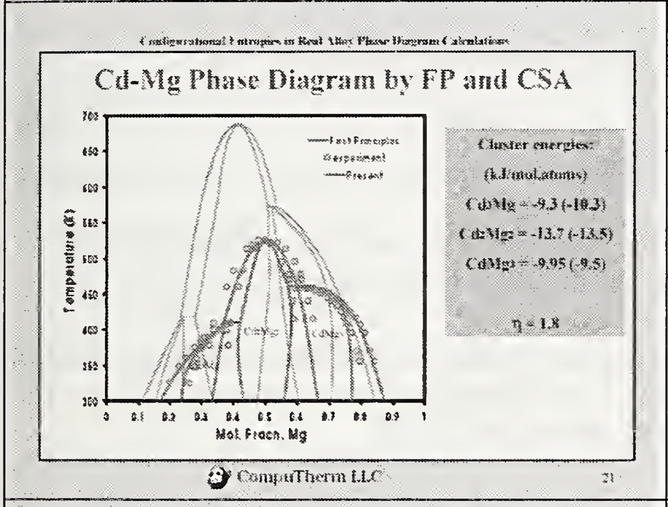


Fcc Coherent Diagram by MC, CVM, OCSA and MCSA



Application of the CSA to Binary Systems

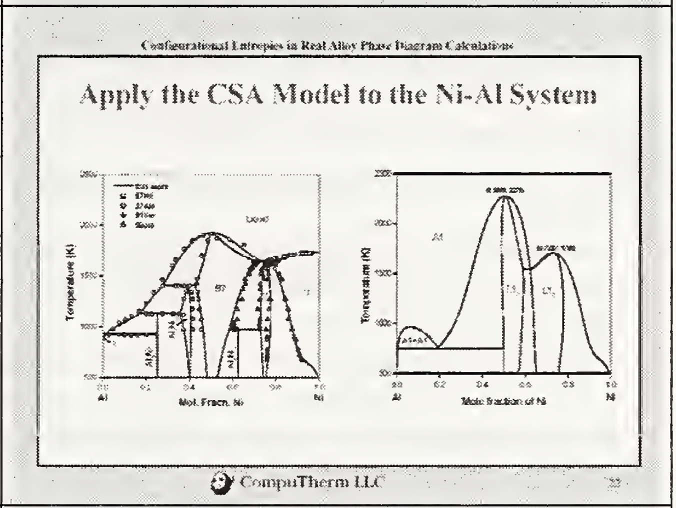
- Au-Cu system
- Au-Ni system
- Cd-Mg system
- Al-Ni system



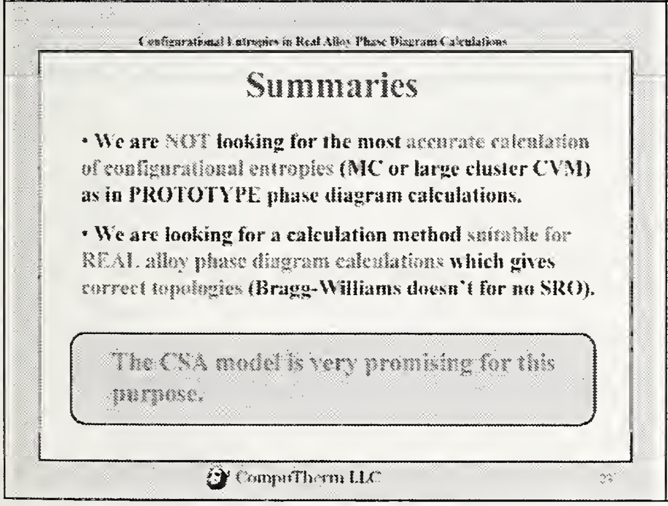
Cd-Mg Phase Diagram by FP and CSA

Cluster energies:
(kJ/mol.atoms)
Cd_3Mg = -9.3 (-10.3)
Cd_2Mg_2 = -13.7 (-13.5)
$CdMg_3$ = -9.95 (-9.5)

η = 1.8



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

The End !

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 γ/γ' 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 γ and γ' 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:

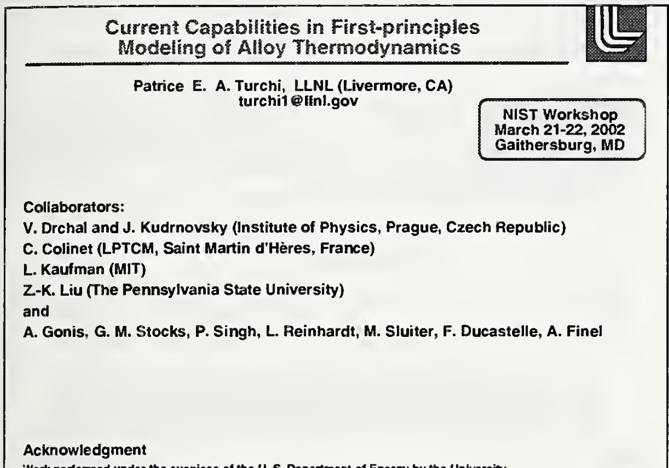
- Bragg-Williams as a point approximation method cannot describe all order/disorder transformations correctly.
- The expression for the entropy in CVM is a too complex for practical purposes. Although these phase diagrams are topologically correct, the accuracy of results is insufficient for practical 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



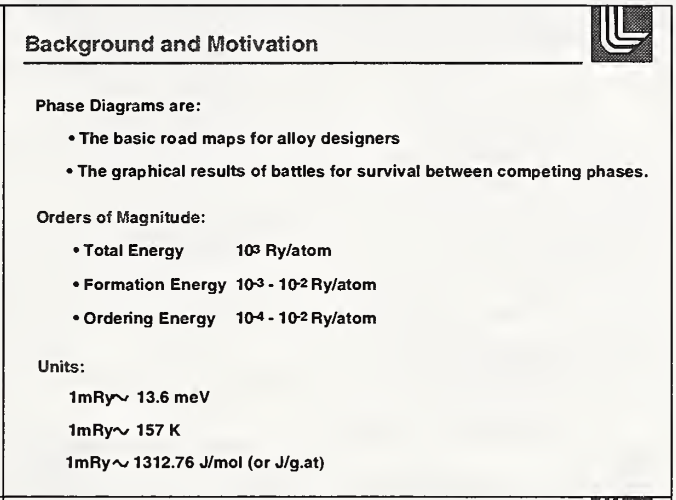
Current Capabilities in First-principles Modeling of Alloy Thermodynamics

Patrice E. A. Turchi, LLNL (Livermore, CA)
turchi1@llnl.gov

NIST Workshop
March 21-22, 2002
Gaithersburg, MD

Collaborators:
V. Drchal and J. Kudrnovsky (Institute of Physics, Prague, Czech Republic)
C. Colinet (LPTCM, Saint Martin d'Hères, France)
L. Kaufman (MIT)
Z.-K. Liu (The Pennsylvania State University)
and
A. Gonis, G. M. Stocks, P. Singh, L. Reinhardt, M. Sluiter, F. Ducastelle, A. Finel

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.



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:

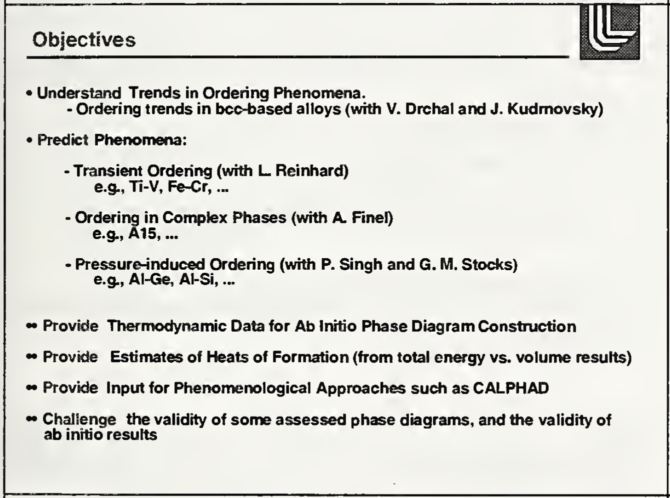
• Total Energy	10^3 Ry/atom
• Formation Energy	10^{-3} - 10^{-2} Ry/atom
• Ordering Energy	10^{-4} - 10^{-2} Ry/atom

Units:

1mRy$\sim$ 13.6 meV

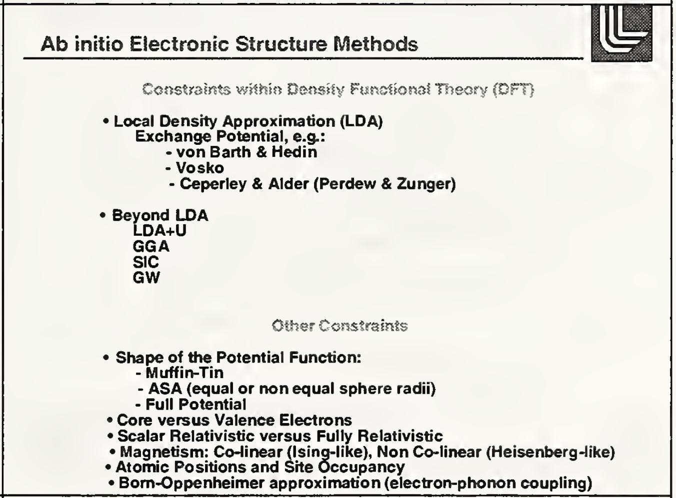
1mRy$\sim$ 157 K

1mRy$\sim$ 1312.76 J/mol (or J/g.at)



Objectives

- Understand Trends in Ordering Phenomena.
  - Ordering trends in bcc-based alloys (with V. Drchal and J. Kudrnovsky)
- Predict Phenomena:
  - Transient Ordering (with L. Reinhard) e.g., Ti-V, Fe-Cr, ...
  - Ordering in Complex Phases (with A. Finel) e.g., A15, ...
  - Pressure-induced Ordering (with P. Singh and G. M. Stocks) e.g., Al-Ge, Al-Si, ...
- 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



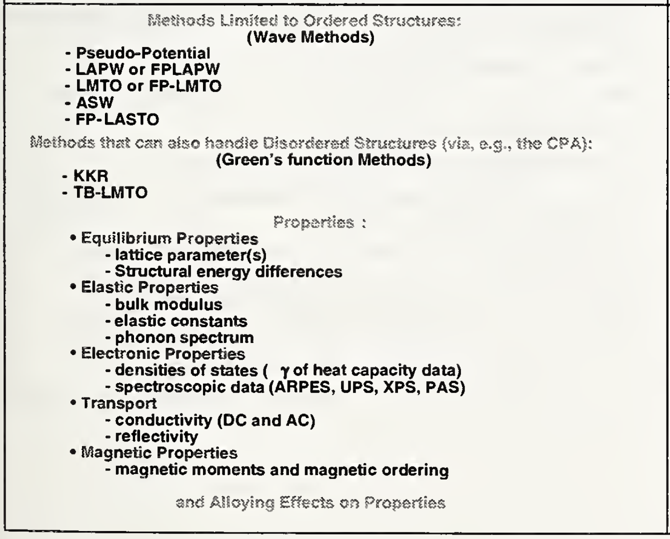
Ab initio Electronic Structure Methods

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
  SIC
  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)



Methods Limited to Ordered Structures:
(Wave Methods)

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

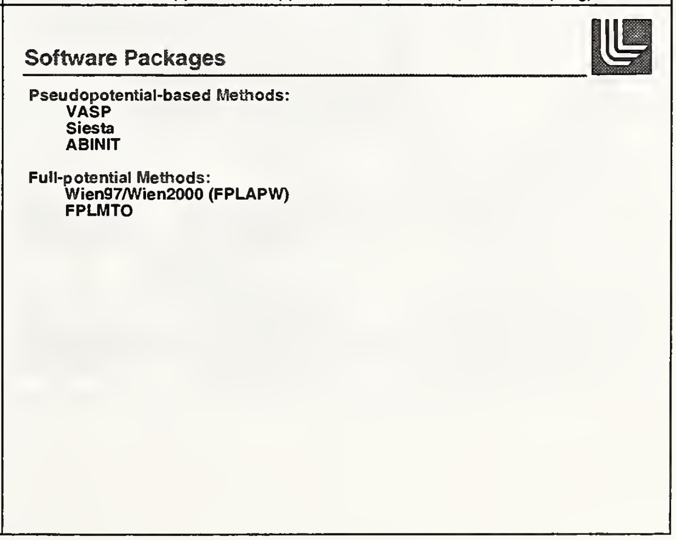
Methods that can also handle Disordered Structures (via, e.g., the CPA):
(Green's function Methods)

- 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, XPS, PAS)
- Transport
  - conductivity (DC and AC)
  - reflectivity
- Magnetic Properties
  - magnetic moments and magnetic ordering

and Alloying Effects on Properties



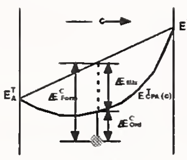
Software Packages

Pseudopotential-based Methods:
VASP
Siesta
ABINIT

Full-potential Methods:
Wien97/Wien2000 (FPLAPW)
FPLMTO

Order versus Disorder for a Binary Alloy $A_{1-c}B_c$

From the Disordered State



$\Delta E^C_{Form} = E^C - (1-c^C)E^T_A - c^C E^T_B = \Delta E_{Mix}(c^C) + \Delta E^C_{Ord}$

Mixing Energy

$\Delta E_{Mix}(c) = E^T_{CPA}(c) - (1-c)E^T_A - cE^T_B$

Ordering Energy of Configuration C

$\Delta E^C_{Ord} = \frac{1}{2N}\sum_{n,m}(p^C_n - c^C)(p^C_m - c^C)V_{nm}(c^C) \quad p^C_n = 0 \text{ or } 1$

$\Delta E^C_{Ord} = \sum_s q^C_s V_s$ where $q^C_s = c^C(n^{BB}_s - c^C n_s)/2$

$V_s = V^{AA}_s + V^{BB}_s - 2V^{AB}_s$

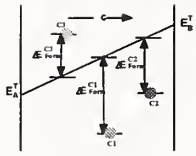
$V_s > 0$ → $(A\text{-}B)_s$ pairs favored → ORDERING

$V_s < 0$ → $(A\text{-}A)_s$ or $(B\text{-}B)_s$ paira favored → CLUSTERING

"Ordering" Energy associated with Segregation if $n^{BB}_s = n_s$

$V^{ij}_{nm} = -\frac{\mathrm{Im}}{\pi}\int^{E_F} t^i_n G^{ij}_{nm} t^j_m G^{ji}_{mn}\,dz$ i,j=species n,m=sites

From the Ordered State



$\Delta E^C_{Form} = E^C - (1-c^C)E^T_A - c^C E^T_B$

Formation Energy of Configuration C

$\Delta E^C_{Form} = V_0 + \sum_\alpha \sigma^C_1 \sigma^C_2 \ldots \sigma^C_\alpha V_\alpha \quad \sigma^C_n = 2p^C_n - 1 = -1 \text{ or } +1$

$[V]_{Volume} = [\sigma]^{-1}.[\Delta E_{Form}]_{Volume}$

From the Disordered State	From the Ordered State
$\Delta E_{Mix}(c)$ and $\Delta E^C_{Ord} = \frac{1}{2N}\sum_{n,m}(p_n - c)(p_m - c)V_{nm}(c)$	$\Delta E^C_{Form} = V_0 + \sum_\alpha \sigma^C_1 \sigma^C_2 \ldots \sigma^C_\alpha V_\alpha \quad \sigma^C_n = 2p^C_n - 1 = -1 \text{ or } +1$
Requirement Green's function-based method	Requirement Wave (or Green's function) method
Advantages • Decoupling between the energy of the disordered state and the ordering energy • Fast convergence of the expansion in terms of effective interactions • Concentration-dependent interactions • Actual prediction of the ground-state properties	Advantages • Easy to implement • Not limited to simple structures • In some instances, no constraint on the shape of the potential (FP-LAPW, FP-LMTO)
Limitations • Implementation so far within ASA and Muffin-tin • Questions related to charge transfer effects • In an *ab initio* context, only simple structures (fcc, bcc, hcp) are dealt with	Limitations • Selection of the number and type of clusters • Selection of the ordered configurations • The interactions are concentration-independent, except via volume effect • Slow convergence of the expansion i terms of effective interactions • Very questionable predictability

Unified Approach to Alloy Stability?
Can the physics of the chemically disordered state and of any ordered configuration of an alloy be described within a unique framework?

CALPHAD Thermodynamics

Multi-component Phases

$$G^\phi(\{c_i\},T) = {}^{ref}G^\phi(\{c_i\},T) + {}^{id}G^\phi(\{c_i\},T) + {}^{xs}G^\phi(\{c_i\},T)$$

$${}^{ref}G^\phi(\{c_i\},T) = \sum_i c_i\, G^\phi_i(\{c_i\},T)$$

$$(1) \qquad {}^{id}G^\phi(\{c_i\},T) = RT\sum_i c_i \ln c_i$$

$${}^{xs}G^\phi(\{c_i\},T) = \sum_{i,j>i} c_i c_j \sum_{p=0}^{n} {}^pL^\phi_{ij}(T)(c_i - c_j)^p \qquad {}^pL^\phi_{ij}(T) = u + vT + \ldots$$

Two-sublattice Model of a Binary Alloy

$${}^{ref}G^\phi(\{y^s_i\},T) = \sum_{i,j} y^I_i y^{II}_j G^\phi_{i:j}$$

$$(2) \qquad {}^{id}G^\phi(\{y^s_i\},T) = RT\sum_{s=I,II} N_s \sum_i y^s_i \ln y^s_i$$

$${}^{xs}G^\phi(\{y^s_i\},T) = y^I_A y^I_B\Big[\sum_i y^{II}_i \sum_{p=0}^{n} {}^pL^\phi_{A,B:i}(T)(y^I_A - y^I_B)^p\Big]$$

$$+\, y^{II}_A y^{II}_B\Big[\sum_i y^I_i \sum_{p=0}^{n} {}^pL^\phi_{i:A,B}(T)(y^{II}_A - y^{II}_B)^p\Big] \qquad {}^pL^\phi_{i,j:k} = {}^pL^\phi_{i,j:k'}$$

Ordering

$$G^C(\{c_i\},T) = G^{Dis}(\{c_i\},T) + \Delta G^{Ord}(\{y^s_i\},T)$$

Eqs. (1)

$$\Delta G^{Ord}(T) = {}^{xs}G^{Ord}(\{y^s_i\},T) - {}^{xs}G^{Ord}(\{c_i\},T)$$ Eqs. (2)

Ab Initio to CALPHAD

Ab Initio (AI)

$$\Delta G^{AI}(c,T) = \Delta E_{Mix}(c) + \Delta E_{Ord}(c,T) - T\Delta S^{CVM}_{Conf}(c,T) \text{ where } \Delta E_{Mix}(c) = c(1-c)[{}^0L + (2c-1)\,{}^1L]$$

CALPHAD (CP)

$$\Delta G^{CP}(c,T) = G(c,T) - \sum_i c_i G^0_i$$

$$= +RT\sum_i c_i \ln c_i + \sum_{i,j>i} c_i c_j \sum {}^pL_{ij}(c_i - c_j)^p \quad \text{where } {}^pL_{ij} = u + vT + \ldots$$

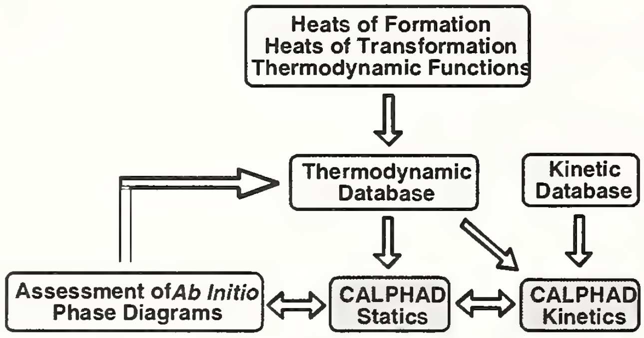
Determination of the {u,v} parameters by minimizing the difference

$$\Delta G^{AI} - \Delta G^{CP}(c,T)$$

The assessment can be performed with the following input from *ab initio*:

- Gibbs energies and enthalpies of formation as functions of temperature and alloy composition.
- Phase diagram information

The Role of *Ab Initio* in CALPHAD



Heats of Formation
Heats of Transformation
Thermodynamic Functions

Thermodynamic Database

Kinetic Database

Assessment of *Ab Initio* Phase Diagrams

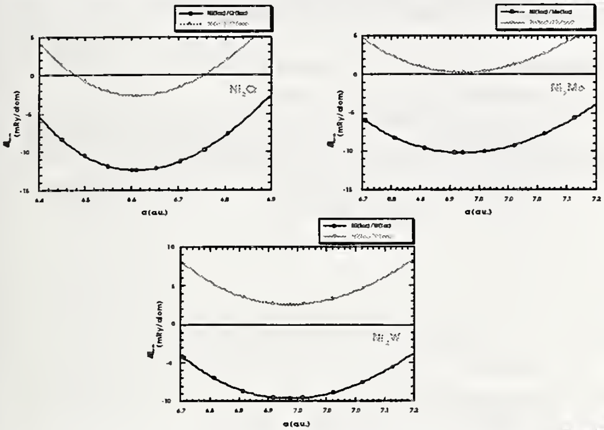
CALPHAD Statics

CALPHAD Kinetics

Ab Initio Methodology

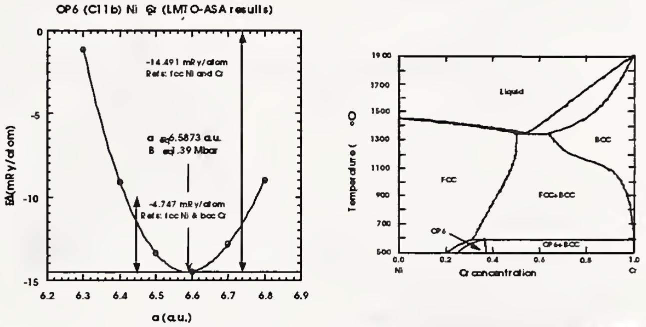
- Tight-Binding Linear Muffin-Tin Orbital (TB-LMTO) method for the description of the electronic structure
- Atomic Sphere Approximation (ASA)
- Unequal sphere radii, zero-charge transfer (i.e., local charge neutrality)
- von Barth Hedin exchange potential
- fully relativistic treatment of the (core 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

Input from *Ab Initio:* Heats of Formation



Interface between *Ab Initio* and CALPHAD: The Ni-Cr case

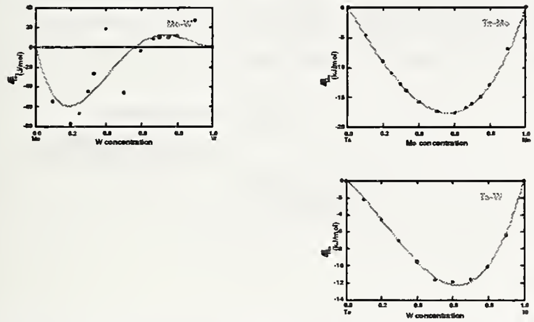
Ni $_2$Cr Heat of Formation obtained from *ab initio* was used to include the ordered phase C11b (or OP6) in the phase diagram of Ni-Cr.



Ab Initio Results: Formation Energy of the Chemically Random Solid Solution

$\Delta E^{c}_{Form} = \Delta E_{Mix}(c^{c}) + \Delta E^{c}_{Ord}$

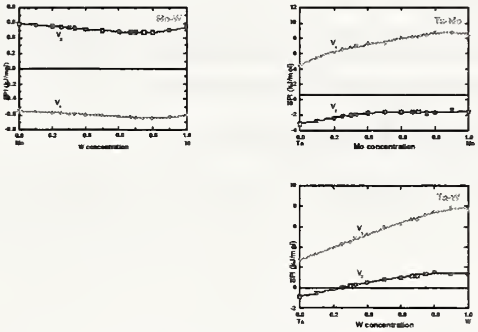
$\Delta E_{Mix}(c^{c}) = c(1-c)[L + (2c-1) L]$



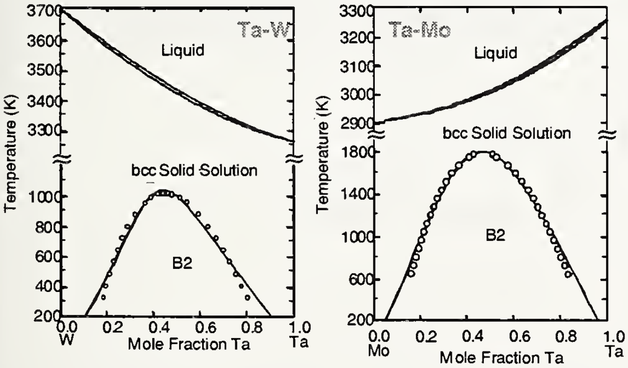
Ab Initio Results: Ground-state Analysis

$\Delta E^{c}_{Form} = \Delta E_{Mix}(c^{c}) + \Delta E^{c}_{Ord}$

$\Delta E^{c}_{Ord} = \sum \alpha^{c}_{s} V_s$

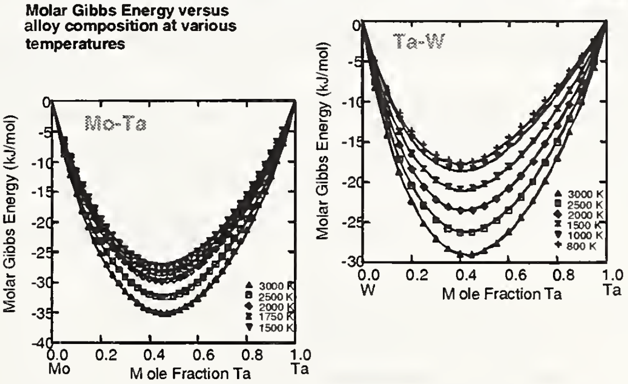


Comparison between *Ab Initio*+ CVM and *Ab Initio* + CALPHAD Results for Ta-W and Ta-Mo Alloys

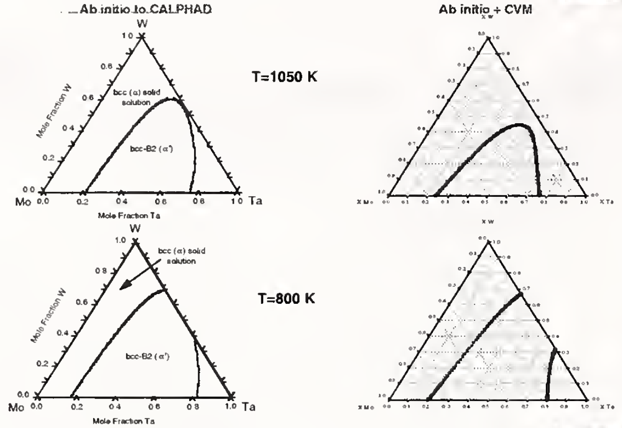


Comparison between *Ab Initio* + CVM and *Ab Initio* + CALPHAD Results for Ta-W and Ta-Mo

Molar Gibbs Energy versus alloy composition at various temperatures



Ab initio + CALPHAD Predictions of Phase Diagrams for Mo-Ta-W Alloys



Conclusions

Ab initio approaches provide information on:
- ground-state properties and ordering trends
- the origin of stability and local order in alloys
- thermodynamic functions and phase diagrams
- short-range order, validated by experiments

The *ab initio*-CALPHAD approach can be used to:
- supplement thermodynamic databases
- reproduce the main features of predicted ab initio phase diagrams
- predict the impact of *ab initio* predictions for binary alloys on multi-component phase diagrams
- validate the *ab initio* data by using the CALPHAD predictions on multi-component phase diagrams

Future Directions for *Ab Initio*

- Electronic Structure Methods
  - Electron-electron correlations
  - "Charge transfer" effects
  - Relativistic effects
- Unified Approach to Alloy Stability: SRO vs. LRO
  - Can the <u>physics</u> of the chemically disordered state and of any ordered configuration of an alloy be described within a unique framework?
- More accurate prediction of the free energy
  - Relaxations
  - Vibrations
  - Magnetic contribution
- Treatment of Multi-component Alloys: Connection to CALPHAD approach, and user-friendly interface to software applications such as Thermo-Calc
- Description of the Liquid and Amorphous states
- Kinetics of Transformation
  - Under isothermal conditions (TTT diagrams)
  - Under non-isothermal conditions
- Dynamics of Transformation
  - Fundamental understanding of complex phase formation and transformation

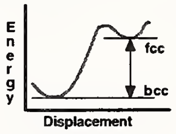
Examples of "still" challenging systems:

- Liquid state
- Hydrides (e.g., Pd-H)
- Transition metal carbides, nitrides, and oxides
- Magnetic alloys (e.g., Ni-Cr)
- Shape memory alloys (e.g., Ni-Ti)
- Correlated systems (e.g., rare earth and actinide-based alloys)

Issue pertaining to lattice stability

Even in the simplest description of the vibrational properties within the Debye Model, the Free energy is given as:

$F(r,T) = E_{el}(r) - k_BT.[D(\Theta_D/T) + 3\ln(1-e^{-\Theta_D/T})] + 9/8k_B\Theta_D$ ← zero-point energy



Instable Phase:

θ_D is not defined, hence the total energy is not defined

<u>Additional points made by speaker:</u>

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 *ab initio*:

- Liquid phase
- X - H systems
- Transitionelementcarbides, -nitrides, etc.
- Magnetic properties

See also “Some Notes on First-Principles Electronic Structure Methods and Calculations,” page 17.

Database Development and Industrial Applications

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Thermodynamic Database Development and Industrial Applications

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NIST – Gaithersburg – March 21, 2002

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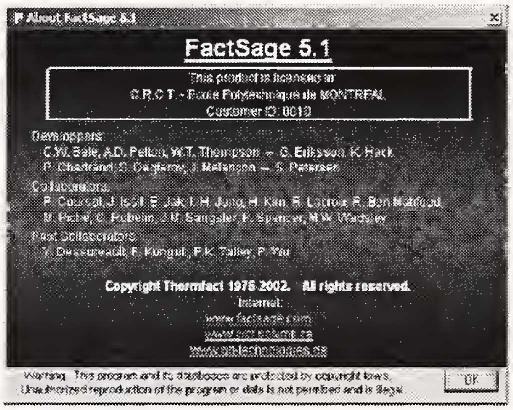
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Developers:
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Collaborators:

Past Collaborators:

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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.

Choice of models

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

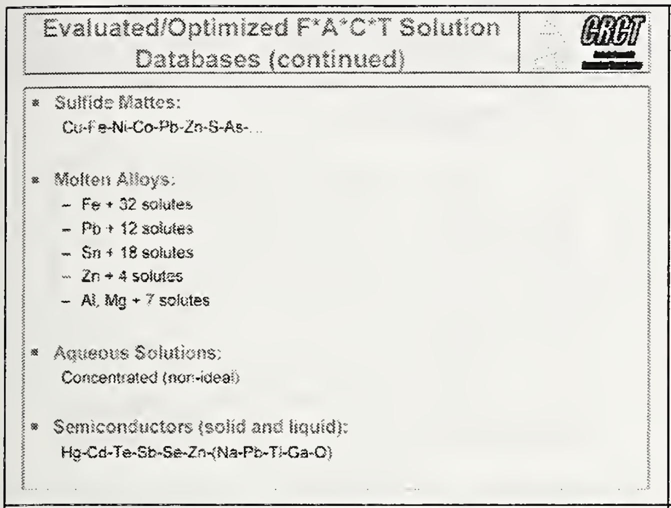
The predictions are only as good as the models. The proper choice of a model which correctly reflects the structure, ordering and speciation of a given solution is essential.

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

- Alloys-Carbonitrides:
  SGTE Solution Databases (ferrous and non-ferrous)
- Molten Oxide Slag/Glass:
  - Oxides of: Al, As, B, Ca, Cr^{2+}, Cr^{3+}, Cu, Fe^{2+}, Fe^{3+}, K, Mg, Mn, Na, Ni, Pb, Si, Ti^{3+}, Ti^{4+}, Ti, Zn, Zr.
  - Dilute: S, SO_4, PO_4, CO_3, F, Cl, I, H_2O/OH
- Solid Oxides (ceramic):
  - Ilmenite $(Fe, Mg, Mn, Ti)TiO_3$
  - Pseudobrookite $(Fe, Mg, Mn, Ti)Ti_2O_5$
  - Monoxide $(Ca, Cu, Fe^{2+}, Fe^{3+}, Mg, Mn, Ni, Ti, Zn, Zr, Al)O$
  - Garnet $(Ca, Fe)_3(Cr, Al, Fe)_2Si_3O_{12}$
  - Spinels $(Fe, Zn, Al, Mg, Co, Ni, Cr, Mn)_3O_4$
  - Forsterite $(Mg, Zn)_2SiO_4$
  - Olivine $(Ca, Mg, Fe)_2SiO_4$
  - Corundum $(Al, Cr, Fe)_2O_3$

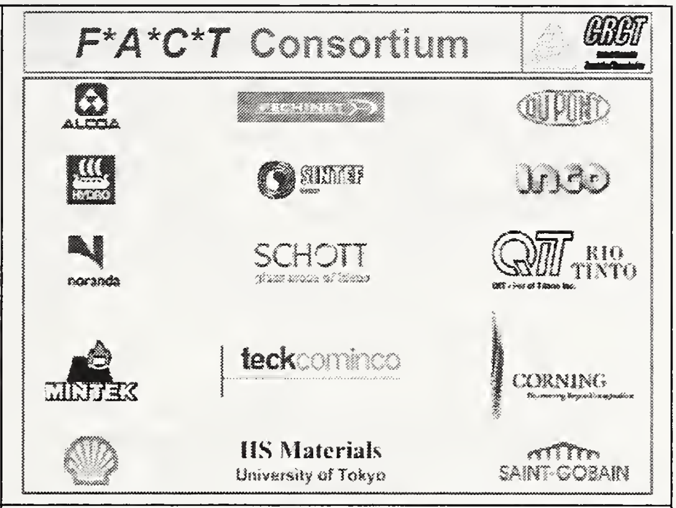
Evaluated/Optimized F*A*C*T Solution Databases (continued)

- Solid Oxides (ceramic, continued):
  - Melilite $(Ca, Pb)_2(Zn, Fe^{2+}, Fe^{3+}, Al)(Fe^{3+}, Al, Si)_2O_7$
  - Pyroxenes $(Ca, Mg, Fe)(Mg, Fe)Si_2O_6$ (ortho, clino, proto)
  - Spinels $(Fe, Mg, Mn)Ti_2O_4$
  - Perovskites
  - ZrO_2-based solutions
  - Feldspars
  - Wollastonite
  - Pseudowollastonite
  - Etc…
- Salts (liquid and solid)
  - Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Al, Fe [2^+, 3^+], La, Ce, Nd / F, Cl, Br, I, OH, NO_3, CO_3, SO_4
  - Cryolite-CaF_2-Al_2O_3-Al-Na
  - $FeCl_2$-$FeCl_3$-$CoCl_2$-$NiCl_2$-$MnCl_2$-$MgCl_2$-$AlCl_3$-…



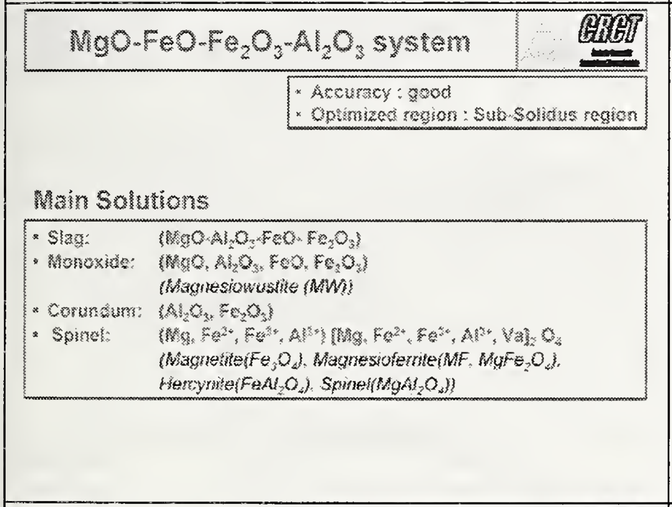
Evaluated/Optimized F*A*C*T Solution Databases (continued)

- 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-Ga-O)



F*A*C*T Consortium

ALCOA
PECHINEY
DUPONT
HYDRO
SINTEF
INCO
noranda
SCHOTT
QIT RIO TINTO
MINTEK
teckcominco
CORNING
IIS Materials
University of Tokyo
SAINT-GOBAIN

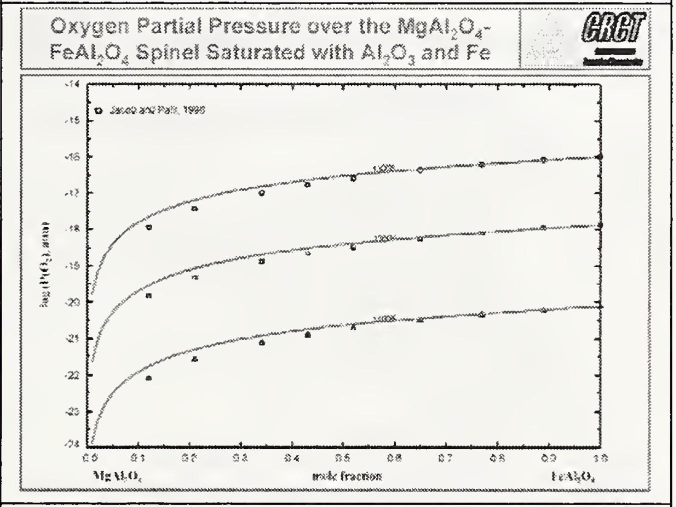


MgO-FeO-Fe_2O_3-Al_2O_3 system

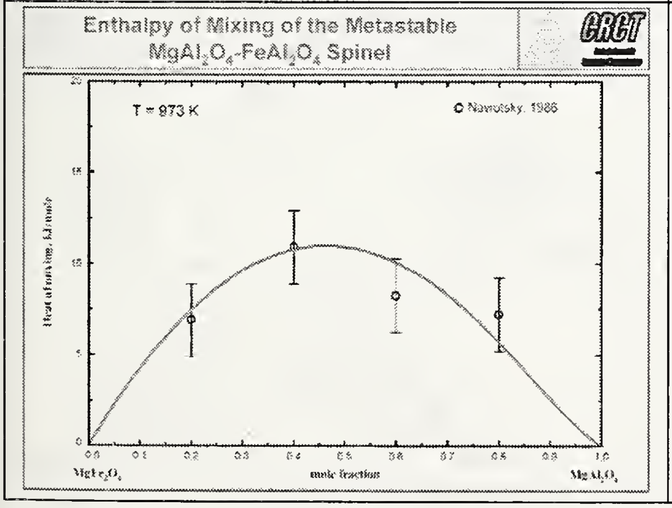
- Accuracy : good
- Optimized region : Sub-Solidus region

Main Solutions

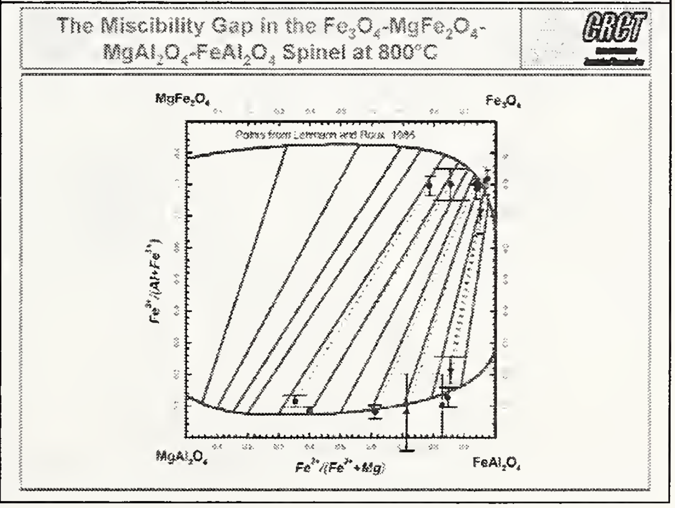
- Slag: (MgO-Al_2O_3-FeO-Fe_2O_3)
- Monoxide: (MgO, Al_2O_3, FeO, Fe_2O_3)
  (Magnesiowustite (MW))
- Corundum: (Al_2O_3, Fe_2O_3)
- Spinel: (Mg, Fe^{2+}, Fe^{3+}, Al^{3+}) [Mg, Fe^{2+}, Fe^{3+}, Al^{3+}, Va]$_2$ O_4
  (Magnetite(Fe_3O_4), Magnesioferrite(MF, $MgFe_2O_4$), Hercynite($FeAl_2O_4$), Spinel($MgAl_2O_4$))



Oxygen Partial Pressure over the $MgAl_2O_4$-$FeAl_2O_4$ Spinel Saturated with Al_2O_3 and Fe

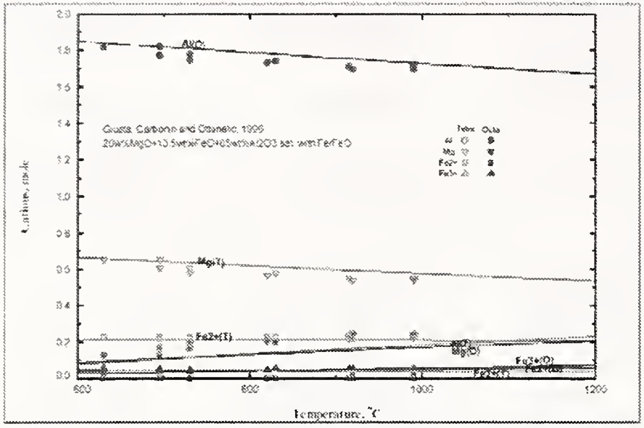


Enthalpy of Mixing of the Metastable $MgAl_2O_4$-$FeAl_2O_4$ Spinel

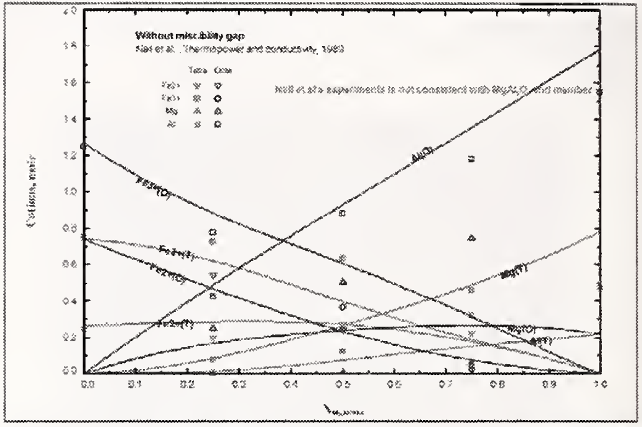


The Miscibility Gap in the Fe_3O_4-$MgFe_2O_4$-$MgAl_2O_4$-$FeAl_2O_4$ Spinel at 800°C

Cation Distribution in Spinel (Fe-Mg-Al-O)



Cation Distribution in Fe_3O_4-$MgFe_2O_4$ Spinel Solution



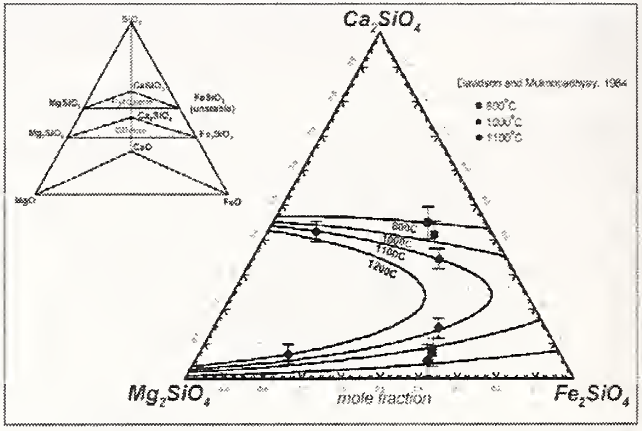
CaO-MgO-FeO-Fe_2O_3-SiO_2 System

- Accuracy: good
- Optimized region: Whole system except Ca_2SiO_4 region

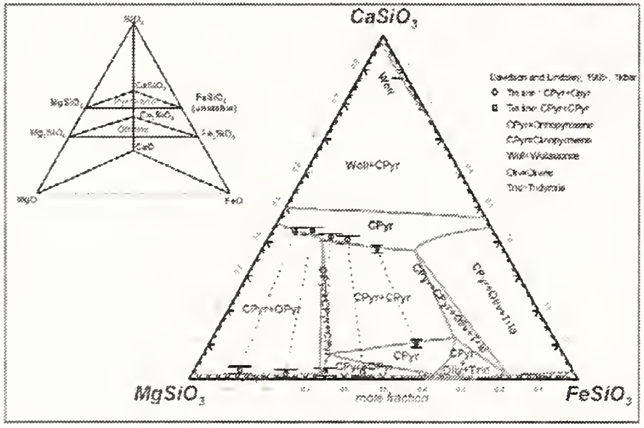
Main Solutions

- Slag : $\{CaO\text{-}MgO\text{-}FeO\text{-}Fe_2O_3\text{-}SiO_2\}$
- Monoxide : $\{CaO,MgO,FeO,Fe_2O_3\}$ *(Lime, Wustite)*
- Spinel : $\{Fe^{2+}, Fe^{3+}, Mg\} [Fe^{2+}, Fe^{3+}, Mg, Va]_2 O_4$
  (Magnetite(Fe_3O_4), Magnesioferrite(MF, $MgFe_2O_4$))
- Olivine : $\{Ca, Mg, Fe^{2+}\} [Ca, Mg, Fe^{2+}] SiO_4$
  (Forsterite(Mg_2SiO_4), Fayalite(Fe_2SiO_4), Monticellite($CaMgSiO_4$), γ-Ca_2SiO_4)
- Pyroxene : $\{Ca, Mg, Fe^{2+}\}^{M2} \{Mg,Fe^{2+}\}^{M1} \{Si\}^{B} Si^{A} O_6$
  - proto pyroxene, ortho pyroxene, clino pyroxene, low clino pyroxene
- Wollastonite : $\{Ca,Mg\}SiO_3$
- α'-Ca_2SiO_4 : $\{Ca,Mg\}_2SiO_4$
- α-Ca_2SiO_4 : $\{Ca,Mg,Fe^{2+}\}_2SiO_4$
- Melilite : $Ca_2 [Mg, Fe^{2+}]Si_2O_7$ *(Akermanite, Fe-Akermanite)*
- Fe-Liquid : F*A*C*T

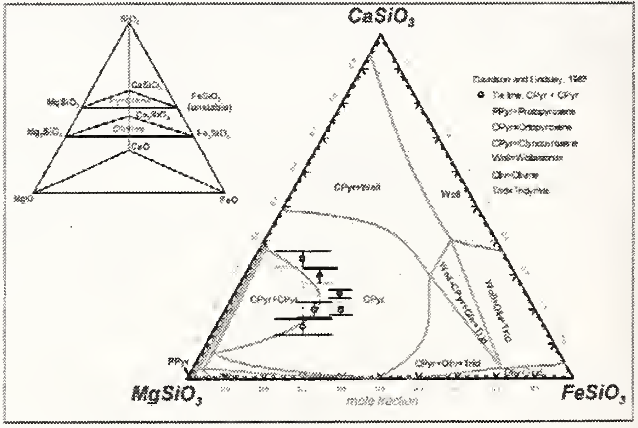
The Miscibility Gap in the Ca_2SiO_4-Fe_2SiO_4-Mg_2SiO_4 Olivine

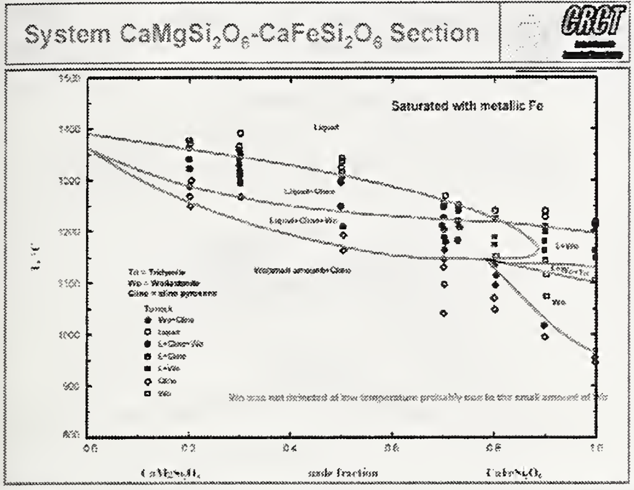


The $CaSiO_3$-$FeSiO_3$-$MgSiO_3$ Phase Diagram at 900°C

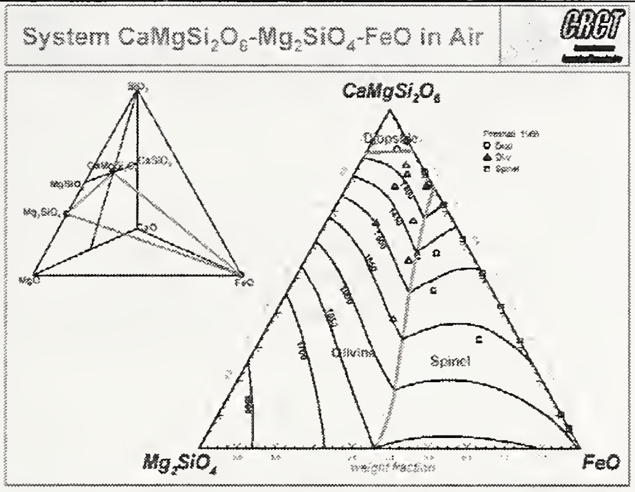


The $CaSiO_3$-$FeSiO_3$-$MgSiO_3$ Phase Diagram at 1200°C

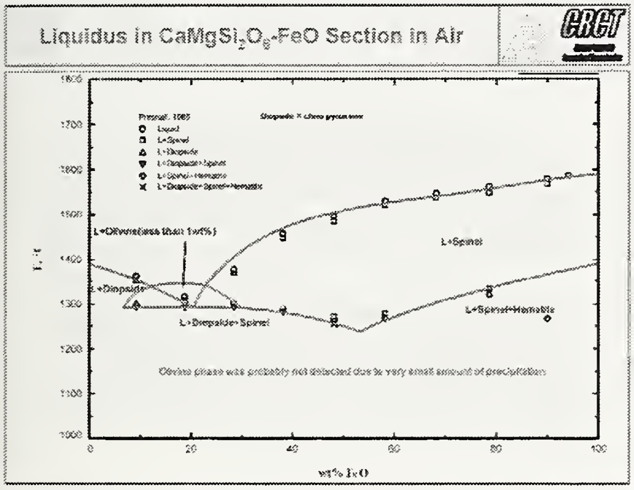




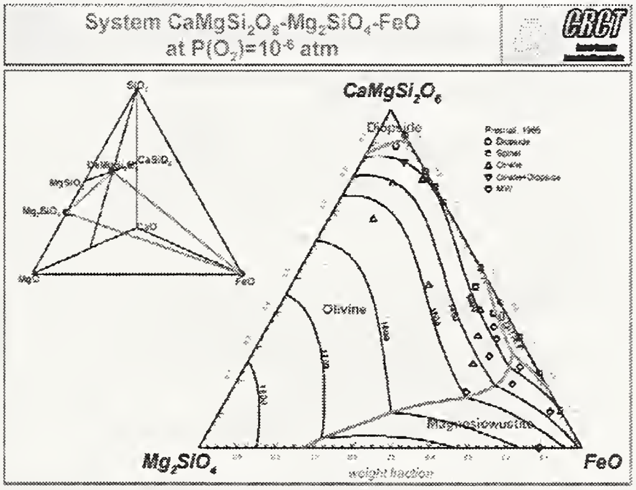
System $CaMgSi_2O_6$-$CaFeSi_2O_6$ Section



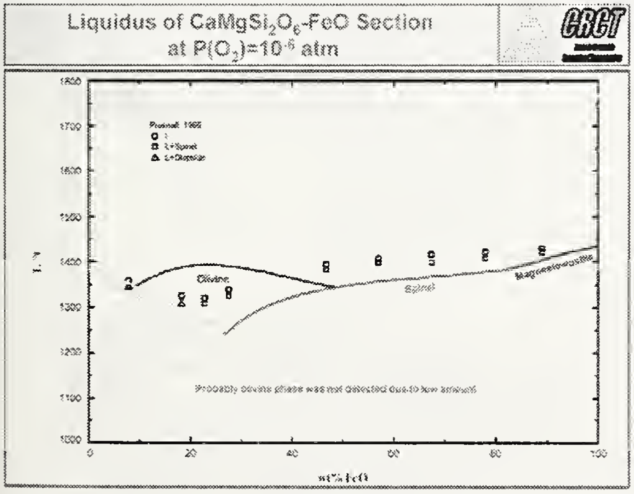
System $CaMgSi_2O_6$-Mg_2SiO_4-FeO in Air



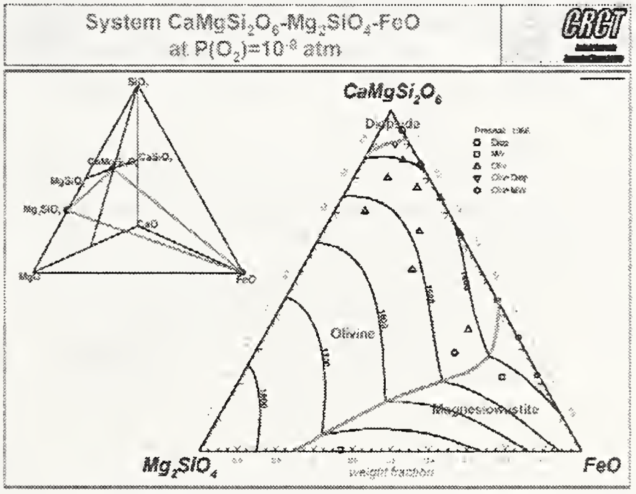
Liquidus in $CaMgSi_2O_6$-FeO Section in Air



System $CaMgSi_2O_6$-Mg_2SiO_4-FeO at $P(O_2)=10^{-6}$ atm

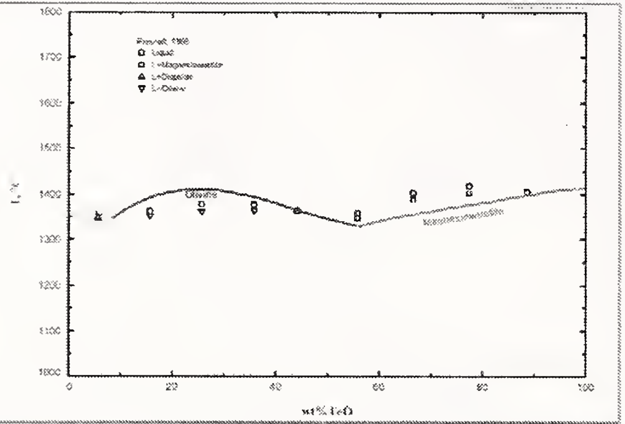


Liquidus of $CaMgSi_2O_6$-FeO Section at $P(O_2)=10^{-6}$ atm



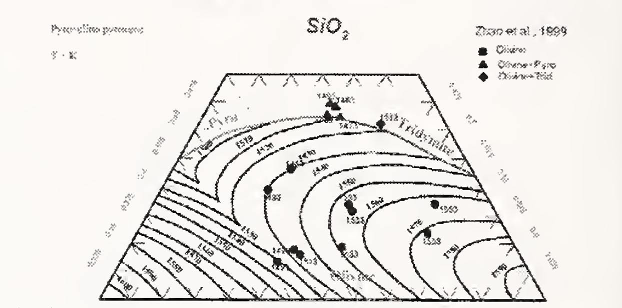
System $CaMgSi_2O_6$-Mg_2SiO_4-FeO at $P(O_2)=10^{-8}$ atm

Liquidus of $CaMgSi_2O_6$-FeO Section at $P(O_2)=10^{-8}$ atm



Liquidus on Olivine(Fayalite) primary region at 5 wt% MgO

Saturated with Metallic Fe



Some Applications of Oxide Databases

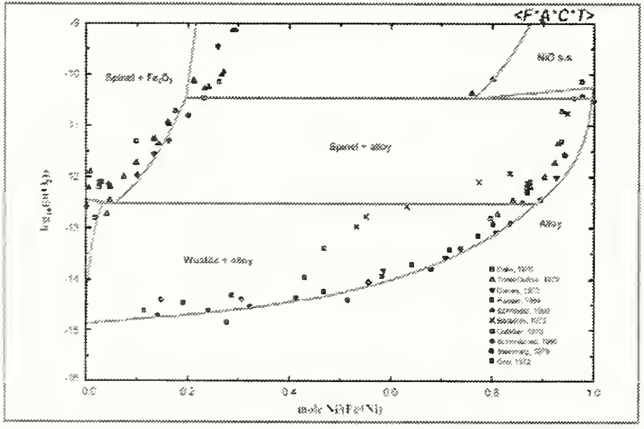
- Metallurgical Processing (slags)
- Inclusion Engineering
- Refractories
- Ceramics
- Glass Technology
- Geology
- Combustion, Gasification
- Hot Corrosion

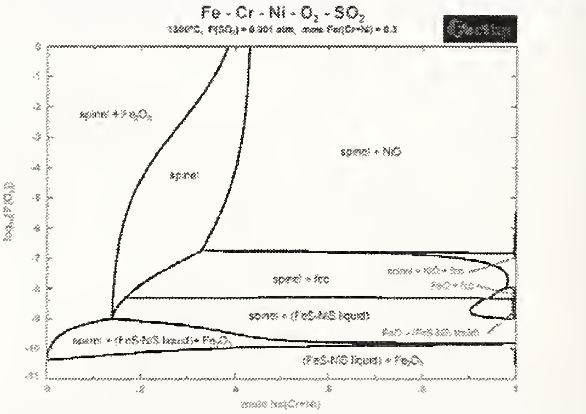
ASSET Project

(Shell Development, Dr Randy John)

- A database for hot corrosion kinetics of Fe-Cr-Co-Ni-C-N alloys in oxygen-, sulfur-, nitrogen- and carbon-containing atmospheres.
- 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

FactSage™

Feb., 2002

In-Ho Jung, Youn-Bae Kang and Arthur D. Pelton

CRCT, École Polytechnique de Montréal, Canada

- Inclusion modification:
  Al_2O_3 modification by Ca treatment
- Minimizing the losses of Ti in low carbon steel
- Inclusions in stainless steel:
  [N], [Ti] and [C]

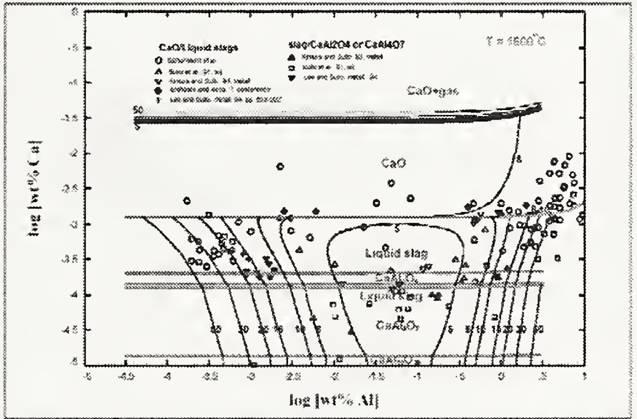
---

1. Inclusion modification:

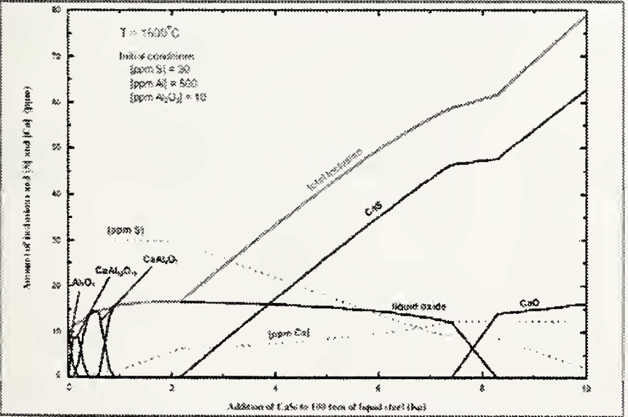
Al_2O_3 modification by Ca treatment

- Al_2O_3 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 Al_2O_3 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

Inclusion Diagram of Fe-Al-Ca-O System



Simulation of Ca treatment (CaSi wire injection)



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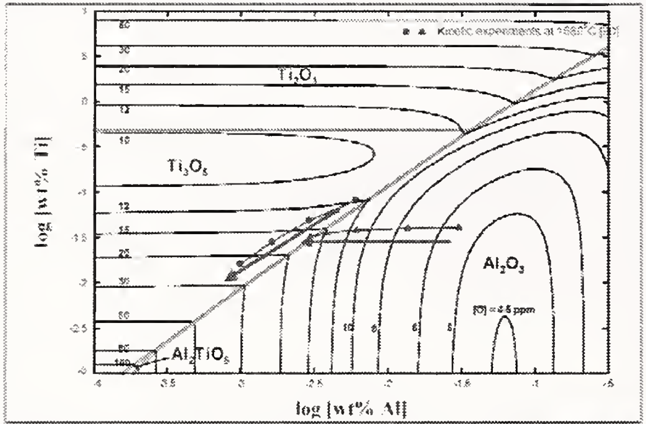
2. Minimizing the losses of Ti in low carbon steel

- 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 TiO_x inclusion
- To minimize the losses of expensive Ti, the inclusion diagram of Ti and Al is necessary

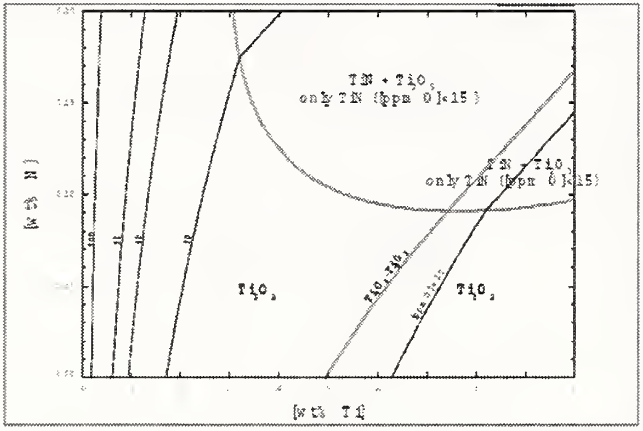
Inclusion Diagram of Fe-Al-Ti-O System at 1600°C



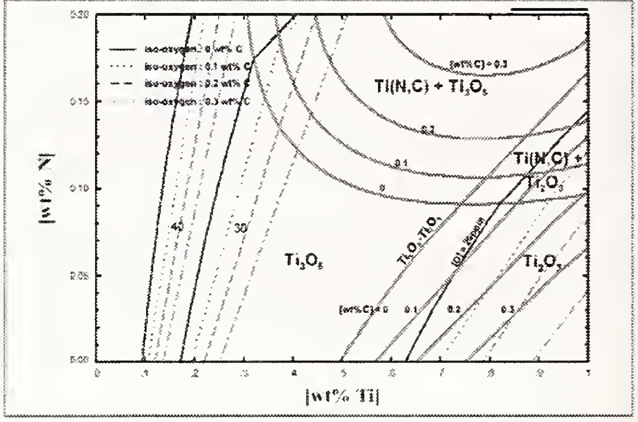
3. Inclusions in stainless steel: [N], [Ti] and [C]

- 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 in Fe-18 wt%Cr-8 wt% Ni-Ti-N-O at 1600°C



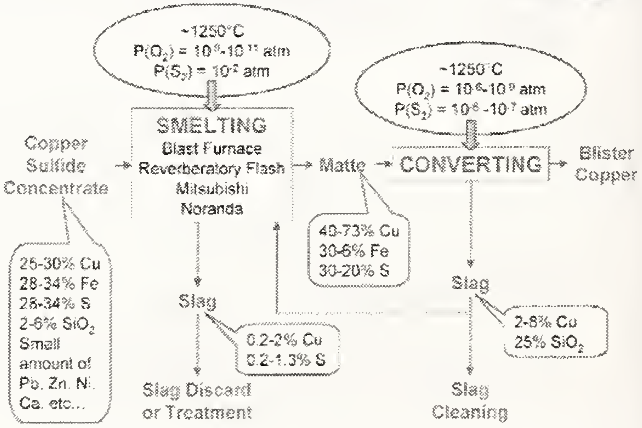
Inclusion Diagram in Fe-18 wt%Cr-8wt% Ni-Ti-N-O-C at 1600°C



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
$P(O_2) = 10^{-8}$-10^{-11} atm
$P(S_2) = 10^{-2}$ atm

~1250°C
$P(O_2) = 10^{-6}$-10^{-9} atm
$P(S_2) = 10^{-6}$-10^{-7} atm

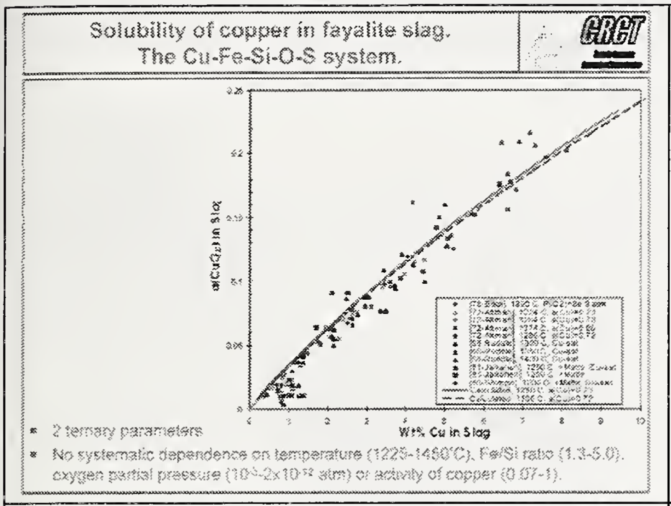
Copper Sulfide Concentrate → **SMELTING** (Blast Furnace, Reverberatory Flash, Mitsubishi, Noranda) → Matte → CONVERTING → Blister Copper

25-30% Cu
28-34% Fe
28-34% S
2-6% SiO_2
Small amount of Pb, Zn, Ni, Ca, etc...

40-73% Cu
30-6% Fe
30-20% S

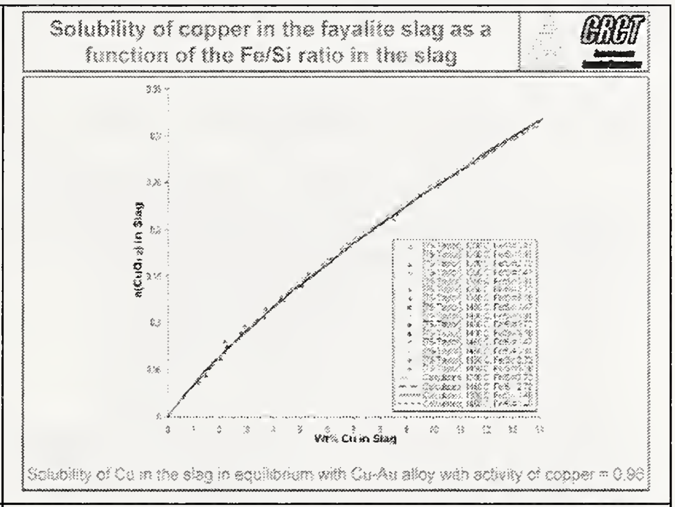
Slag
0.2-2% Cu
0.2-1.3% S
Slag Discard or Treatment

Slag
2-8% Cu
25% SiO_2
Slag Cleaning



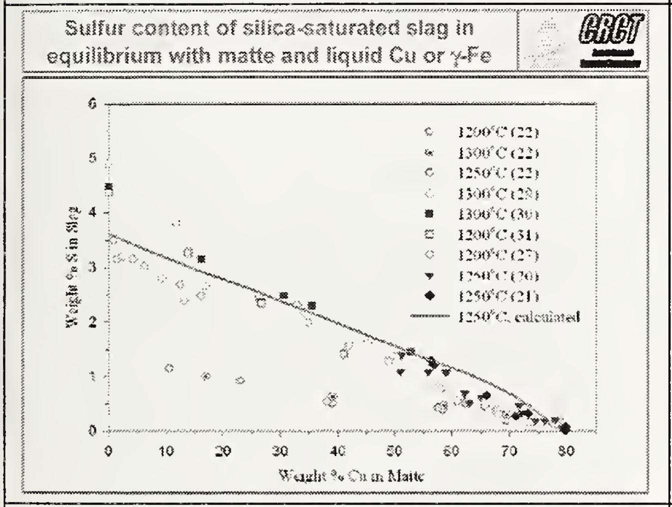
Solubility of copper in fayalite slag. The Cu-Fe-Si-O-S system.

- 2 ternary parameters
- No systematic dependence on temperature (1225-1460°C), Fe/Si ratio (1.3-5.0), oxygen partial pressure (10^{-5}-$2x10^{-12}$ atm) or activity of copper (0.07-1).

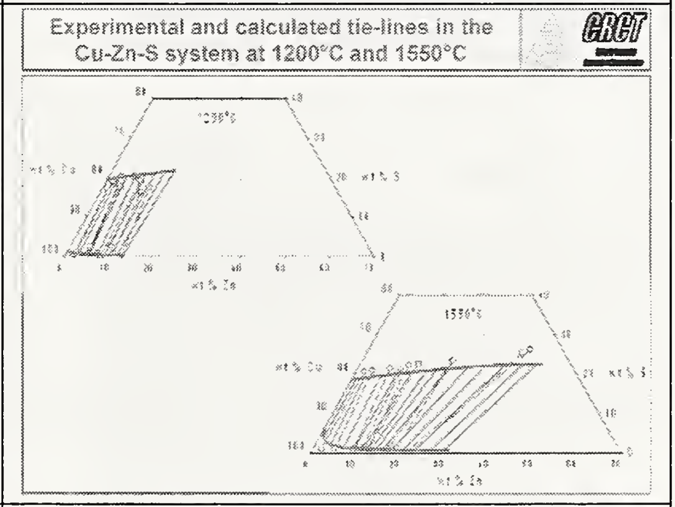


Solubility of copper in the fayalite slag as a function of the Fe/Si ratio in the slag

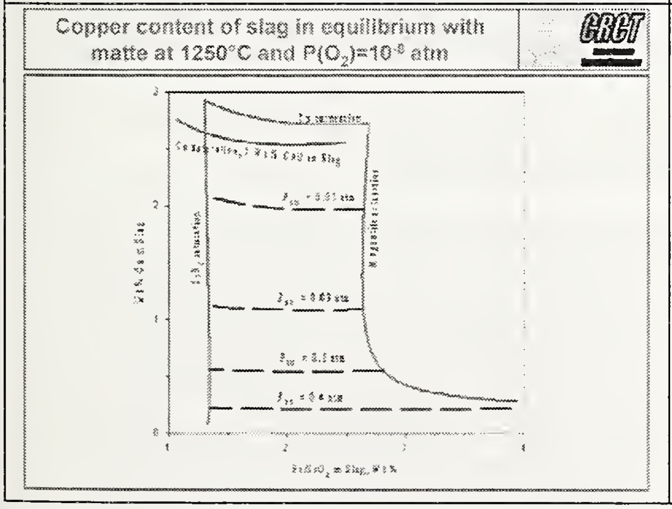
Solubility of Cu in the slag in equilibrium with Cu-Au alloy with activity of copper = 0.98



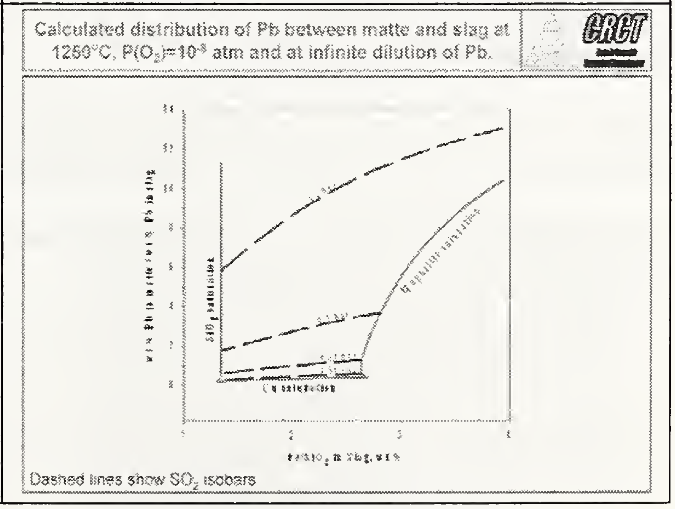
Sulfur content of silica-saturated slag in equilibrium with matte and liquid Cu or γ-Fe



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

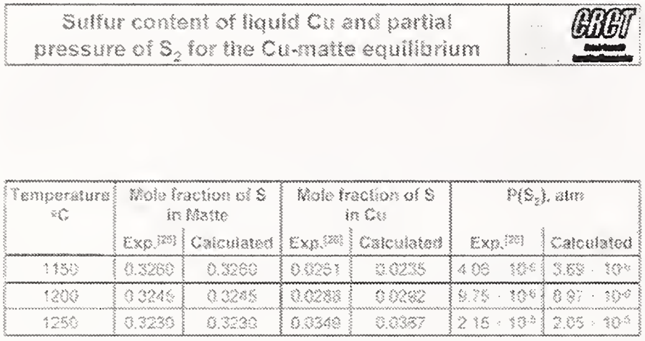


Copper content of slag in equilibrium with matte at 1250°C and P(O$_2$)=10^{-8} atm



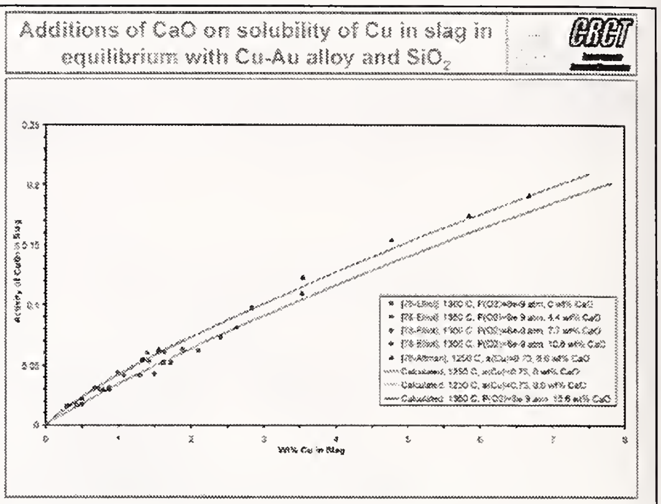
Calculated distribution of Pb between matte and slag at 1250°C, P(O$_2$)=10^{-8} atm and at infinite dilution of Pb.

Dashed lines show SO$_2$ isobars

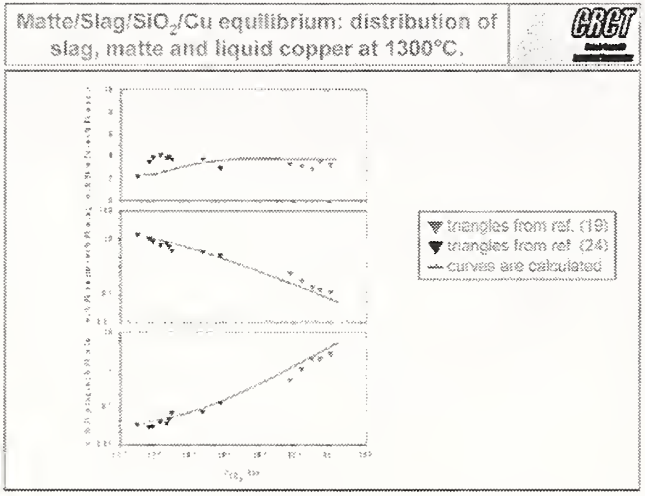


Sulfur content of liquid Cu and partial pressure of S_2 for the Cu-matte equilibrium

Temperature °C	Mole fraction of S in Matte		Mole fraction of S in Cu		$P(S_2)$, atm	
	Exp.[20]	Calculated	Exp.[20]	Calculated	Exp.[20]	Calculated
1150	0.3260	0.3260	0.0251	0.0235	$4.06 \cdot 10^{-6}$	$3.69 \cdot 10^{-6}$
1200	0.3245	0.3245	0.0288	0.0282	$9.75 \cdot 10^{-6}$	$8.97 \cdot 10^{-6}$
1250	0.3239	0.3230	0.0349	0.0367	$2.15 \cdot 10^{-5}$	$2.05 \cdot 10^{-5}$



Additions of CaO on solubility of Cu in slag in equilibrium with Cu-Au alloy and SiO_2



Matte/Slag/SiO_2/Cu equilibrium: distribution of slag, matte and liquid copper at 1300°C.

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.

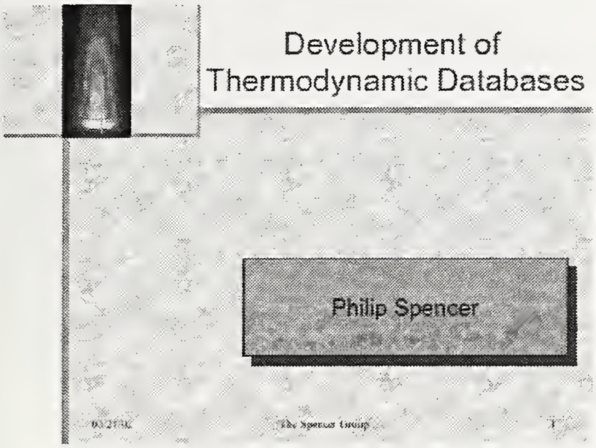
Cluster pair approximation and quasichemical models are used in the slag/glass and sulfide mattes databases.

F*A*C*T 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



Development of Thermodynamic Databases

Philip Spencer

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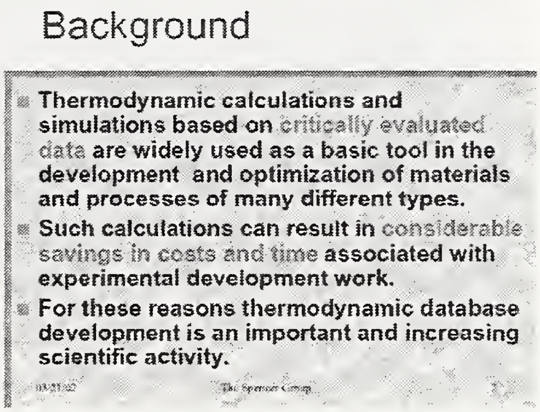

Background

- 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 costs and time associated with experimental development work.
- For these reasons thermodynamic database development is an important and increasing scientific activity.

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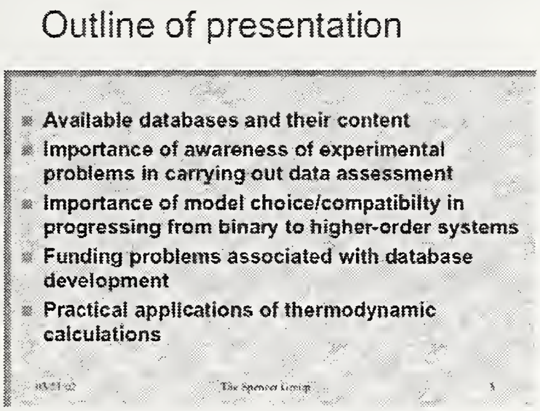

Outline of presentation

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

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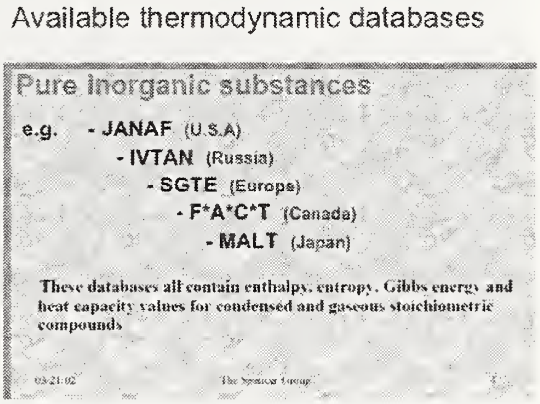

Available thermodynamic databases

Pure inorganic substances

e.g. - JANAF (U.S.A)
- IVTAN (Russia)
- SGTE (Europe)
- F*A*C*T (Canada)
- MALT (Japan)

These databases all contain enthalpy, entropy, Gibbs energy and heat capacity values for condensed and gaseous stoichiometric compounds

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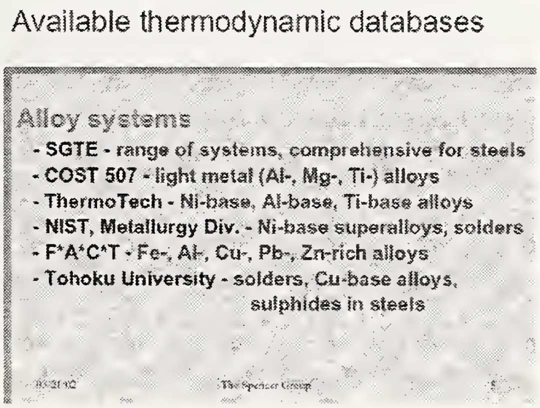

Available thermodynamic databases

Alloy systems

- SGTE - range of systems, comprehensive for steels
- COST 507 - light metal (Al-, Mg-, Ti-) alloys
- ThermoTech - Ni-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

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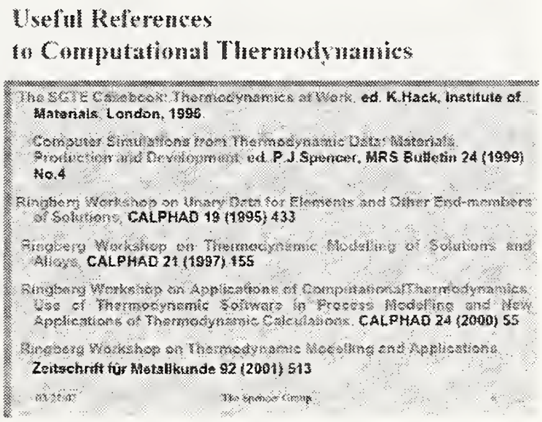

Useful References to Computational Thermodynamics

The SGTE Casebook: Thermodynamics at Work. ed. K.Hack, Institute of Materials, London, 1996.

Computer Simulations from Thermodynamic Data: Materials Production and Development. ed. P.J.Spencer, MRS Bulletin 24 (1999) No.4

Ringberg Workshop on Unary Data for Elements and Other End-members of Solutions, CALPHAD 19 (1995) 433

Ringberg Workshop on Thermodynamic Modelling of Solutions and Alloys, CALPHAD 21 (1997) 155

Ringberg Workshop on Applications of ComputationalThermodynamics. Use of Thermodynamic Software in Process Modelling and New Applications of Thermodynamic Calculations. CALPHAD 24 (2000) 55

Ringberg Workshop on Thermodynamic Modelling and Applications Zeitschrift für Metallkunde 92 (2001) 513

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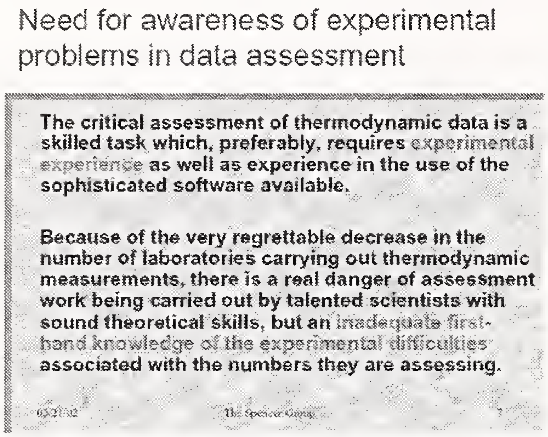
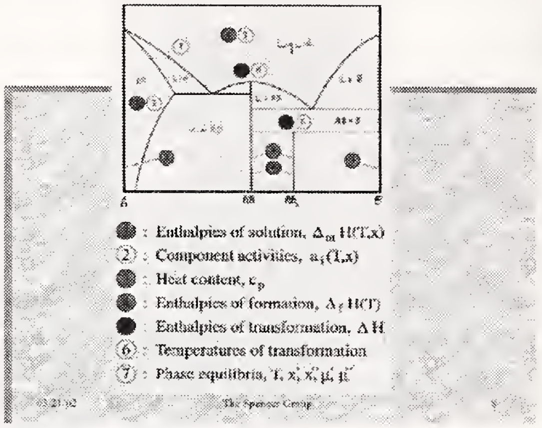


Need for awareness of experimental problems in data assessment

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.



● : Enthalpies of solution, $\Delta_{sol} H(T,x)$

② : Component activities, $a_i(T,x)$

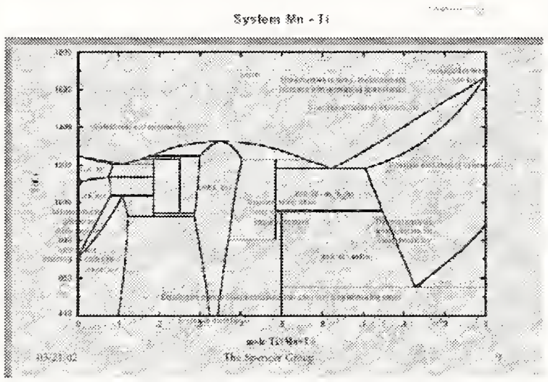
● : Heat content, c_p

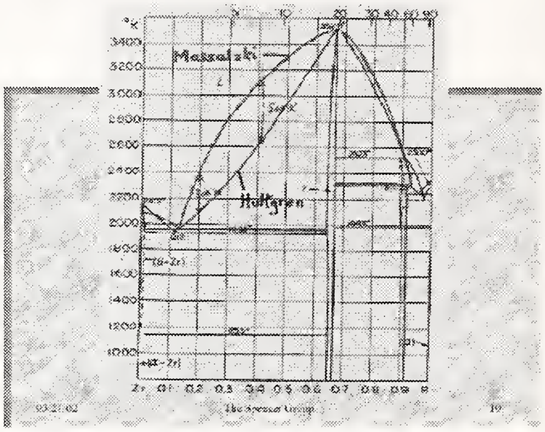
● : Enthalpies of formation, $\Delta_f H(T)$

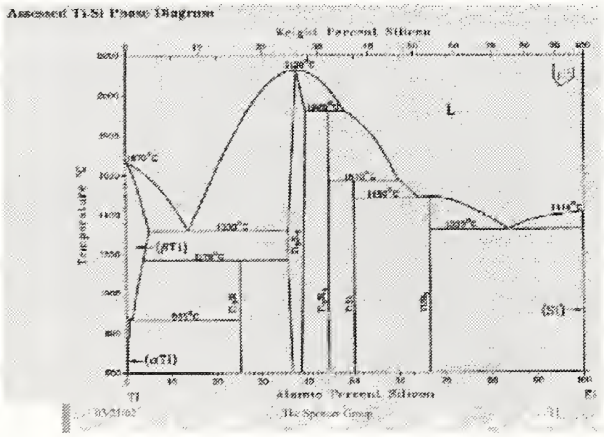
● : Enthalpies of transformation, ΔH

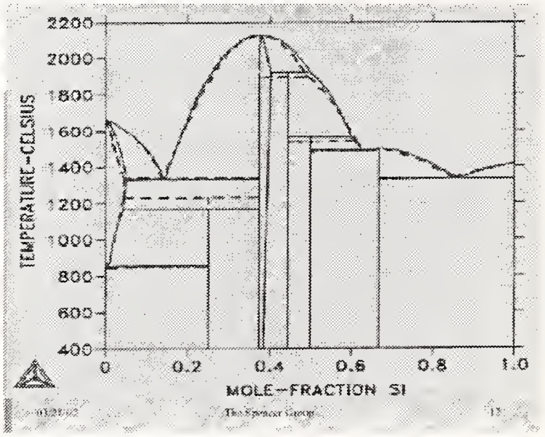
⑥ : Temperatures of transformation

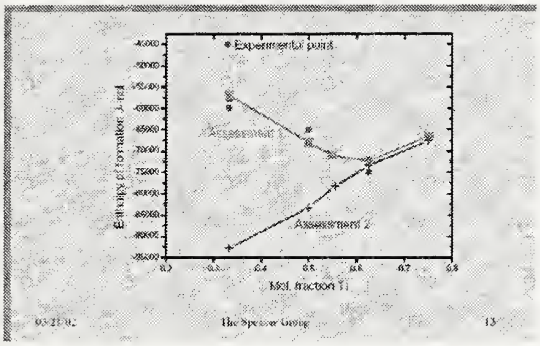
⑦ : Phase equilibria, T, x', x'', μ', μ''

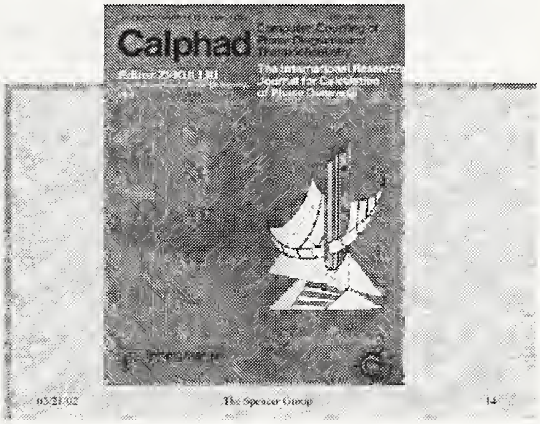




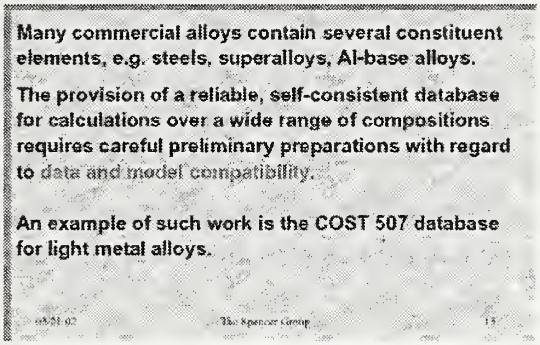








Important considerations in thermodynamic database development for alloys



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: Measurement and evaluation of thermochemical and thermophysical properties to provide a database for the development of new light alloys

Signatory Countries:

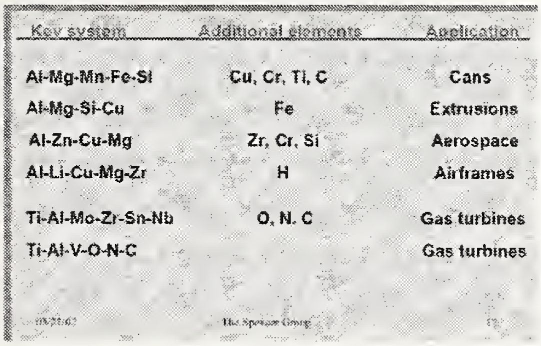
Austria, Belgium, France, Finland, Germany, Greece, Italy, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland, United Kingdom

Participant: Baikov Institute of Metallurgy, Russia

Co-ordination Groups:

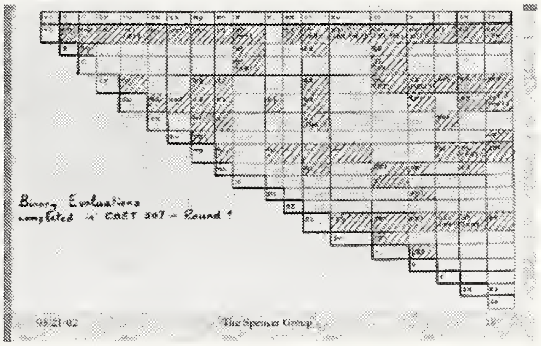
A. Experimental thermodynamic investigations
B. Phase diagram evaluations and compilations
C. Thermodynamic assessments and calculations
D. Measurement and compilation of thermophysical data

COST Action 507: Light alloy systems of potential interest

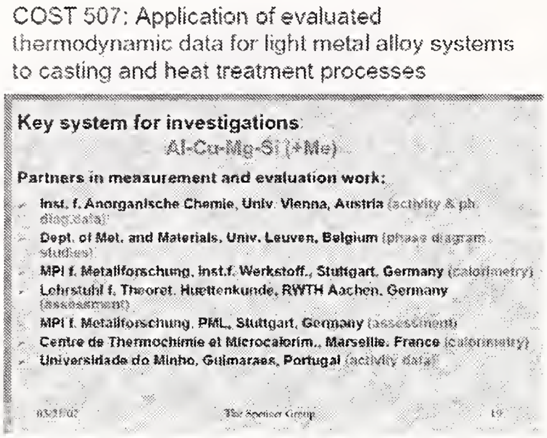


Key system	Additional elements	Application
Al-Mg-Mn-Fe-Si	**Cu, Cr, Ti, C**	**Cans**
Al-Mg-Si-Cu	**Fe**	**Extrusions**
Al-Zn-Cu-Mg	**Zr, Cr, Si**	**Aerospace**
Al-Li-Cu-Mg-Zr	**H**	**Airframes**
Ti-Al-Mo-Zr-Sn-Nb	**O, N, C**	**Gas turbines**
Ti-Al-V-O-N-C		**Gas turbines**

COST 507: Matrix of binary systems representing building blocks for alloys of potential commercial interest



Binary Evaluations
completed in COST 507 – Round 1



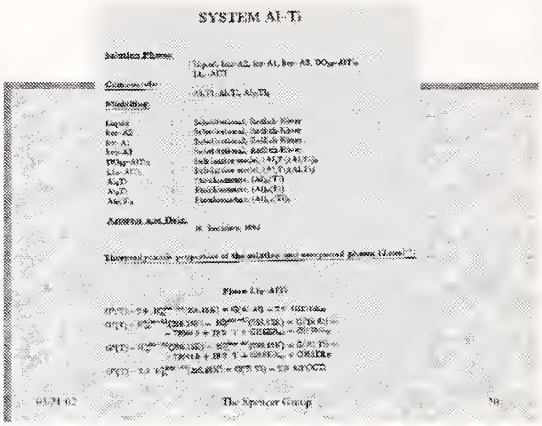
COST 507: Application of evaluated thermodynamic data for light metal alloy systems to casting and heat treatment processes

Key system for investigations:

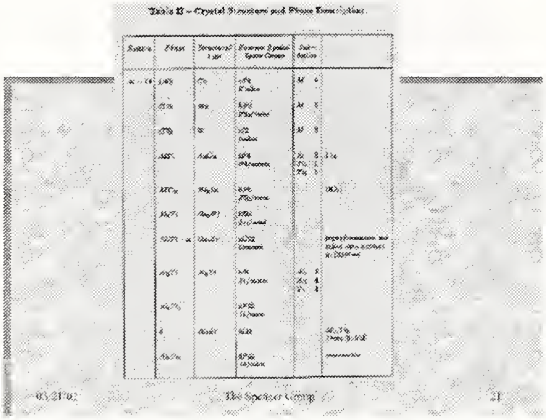
Al-Cu-Mg-Si (+Me)

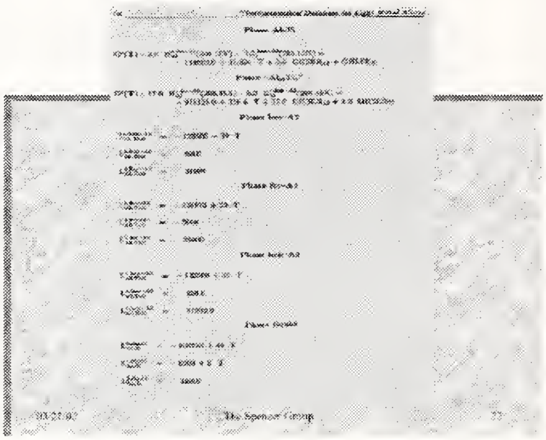
Partners in measurement and evaluation work:

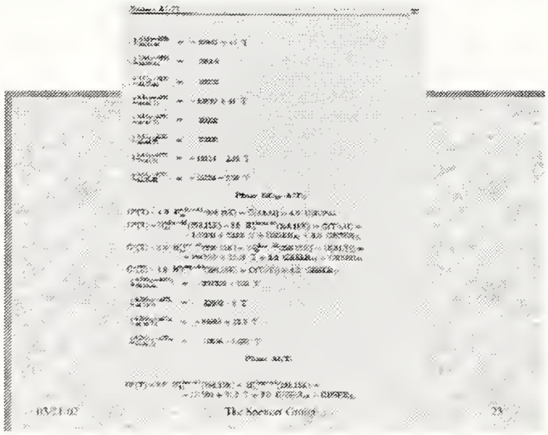
- **Inst. f. Anorganische Chemie, Univ. Vienna, Austria** (activity & ph. diag.data)
- **Dept. of Met. and Materials, Univ. Leuven, Belgium** (phase diagram studies)
- **MPI f. Metallforschung, Inst.f. Werkstoff., Stuttgart, Germany** (calorimetry)
- **Lehrstuhl f. Theoret. Huettenkunde, RWTH Aachen, Germany** (assessment)
- **MPI f. Metallforschung, PML, Stuttgart, Germany** (assessment)
- **Centre de Thermochimie et Microcalorim., Marseille, France** (calorimetry)
- **Universidade do Minho, Guimaraes, Portugal** (activity data)

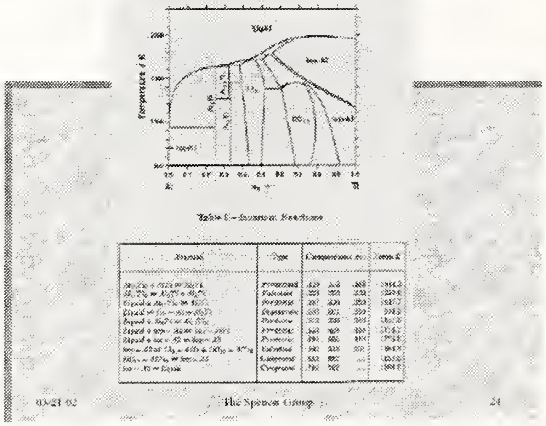


SYSTEM Al-Ti







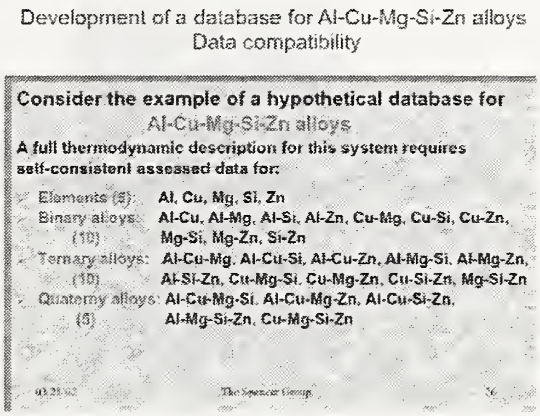


COST 507

Definition of thermochemical and thermophysical properties to provide a database for the development of new light alloys

Thermochemical database for light metal alloys

Volume 2

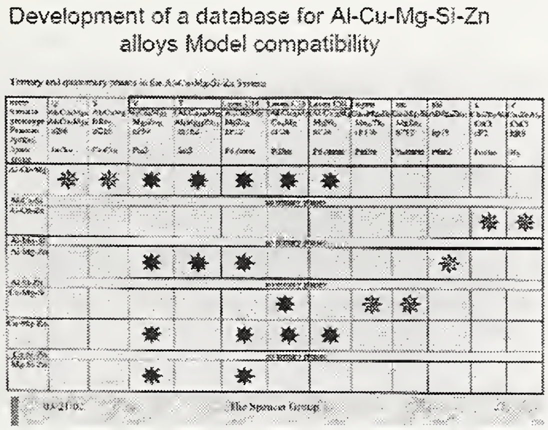


Development of a database for Al-Cu-Mg-Si-Zn alloys Data compatibility

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

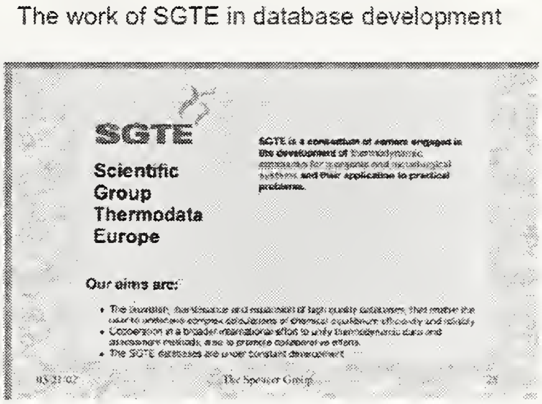
A full thermodynamic description for this system requires self-consistent assessed data for:

- Elements (5): **Al, Cu, Mg, Si, Zn**
- Binary alloys (10): **Al-Cu, Al-Mg, Al-Si, Al-Zn, Cu-Mg, Cu-Si, Cu-Zn, Mg-Si, Mg-Zn, Si-Zn**
- Ternary alloys (10): **Al-Cu-Mg, Al-Cu-Si, Al-Cu-Zn, Al-Mg-Si, Al-Mg-Zn, Al-Si-Zn, Cu-Mg-Si, Cu-Mg-Zn, Cu-Si-Zn, Mg-Si-Zn**
- Quaternary alloys (5): **Al-Cu-Mg-Si, Al-Cu-Mg-Zn, Al-Cu-Si-Zn, Al-Mg-Si-Zn, Cu-Mg-Si-Zn**



Development of a database for Al-Cu-Mg-Si-Zn alloys Model compatibility

Ternary and quaternary phases in the Al-Cu-Mg-Si-Zn System



The work of SGTE in database development

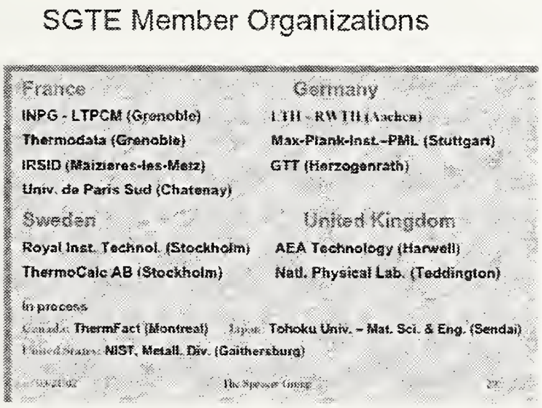
SGTE

Scientific
Group
Thermodata
Europe

SGTE is a consortium of centers engaged in the development of thermodynamic databases for inorganic and metallurgical systems and their application to practical problems.

Our aims are:

- The creation, maintenance and expansion of high quality databases that enable the user to undertake complex calculations of chemical equilibrium efficiently and reliably
- Cooperation in a broader international effort to unify thermodynamic data and assessment methods, also to promote collaborative efforts.
- The SGTE databases are under constant development



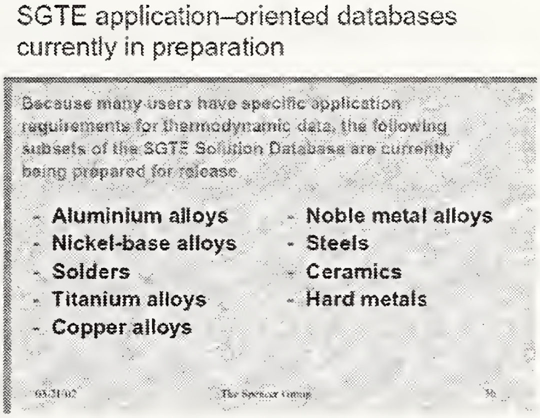
SGTE Member Organizations

France	Germany
INPG - LTPCM (Grenoble)	LTH - RWTH (Aachen)
Thermodata (Grenoble)	**Max-Plank-Inst.-PML (Stuttgart)**
IRSID (Maizieres-les-Metz)	**GTT (Herzogenrath)**
Univ. de Paris Sud (Chatenay)	
Sweden	**United Kingdom**
Royal Inst. Technol. (Stockholm)	**AEA Technology (Harwell)**
ThermoCalc AB (Stockholm)	**Natl. Physical Lab. (Teddington)**

in process

Canada: **ThermFact (Montreal)** Japan: **Tohoku Univ. – Mat. Sci. & Eng. (Sendai)**

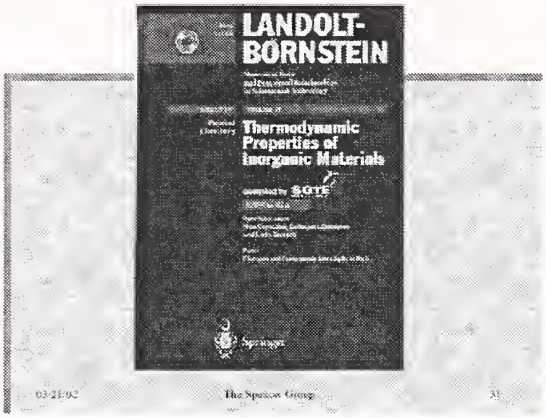
United States: **NIST, Metall. Div. (Gaithersburg)**

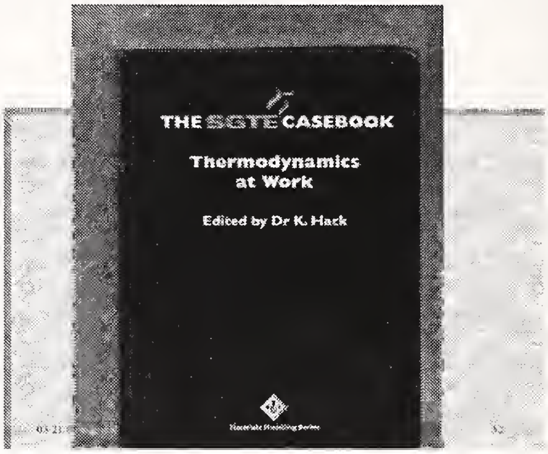


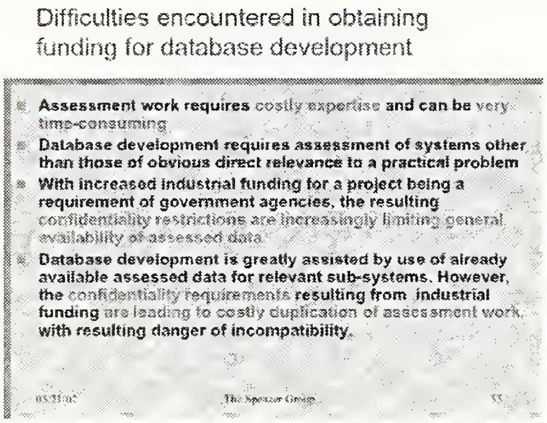
SGTE application–oriented databases currently in preparation

Because many users have specific application requirements for thermodynamic data, the following subsets of the SGTE Solution Database are currently being prepared for release

- **Aluminium alloys**
- **Nickel-base alloys**
- **Solders**
- **Titanium alloys**
- **Copper alloys**
- **Noble metal alloys**
- **Steels**
- **Ceramics**
- **Hard metals**

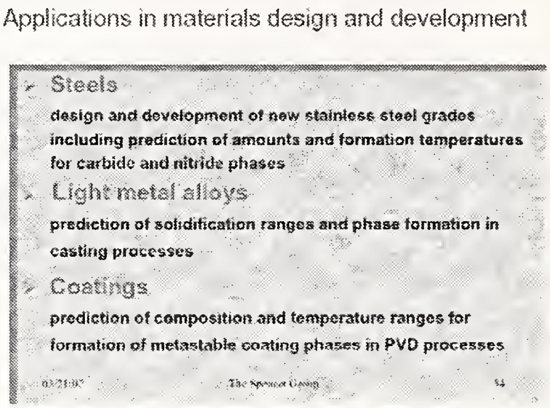






Difficulties encountered in obtaining funding for database development

- 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.



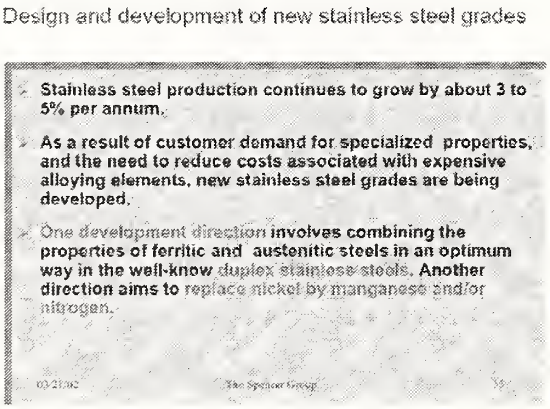
Applications in materials design and development

- Steels

  design and development of new stainless steel grades including prediction of amounts and formation temperatures for carbide and nitride phases
- Light metal alloys

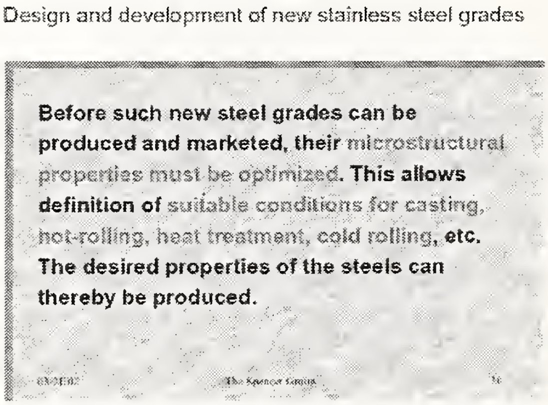
  prediction of solidification ranges and phase formation in casting processes
- Coatings

  prediction of composition and temperature ranges for formation of metastable coating phases in PVD processes



Design and development of new stainless steel grades

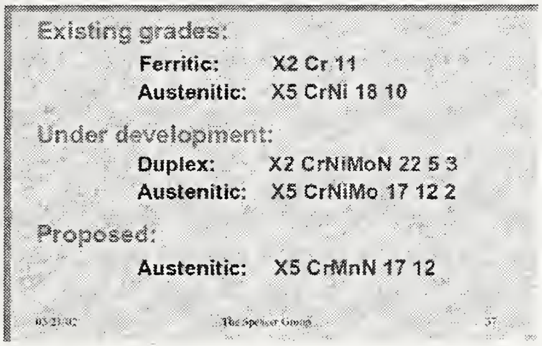
- Stainless steel production continues to grow by about 3 to 5% per annum.
- As a result of customer demand for specialized properties, and the need to reduce costs associated with expensive alloying elements, new stainless steel grades are being developed.
- One development direction involves combining the properties of ferritic and austenitic steels in an optimum way in the well-know duplex stainless steels. Another direction aims to replace nickel by manganese and/or nitrogen.



Design and development of new stainless steel grades

Before 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:

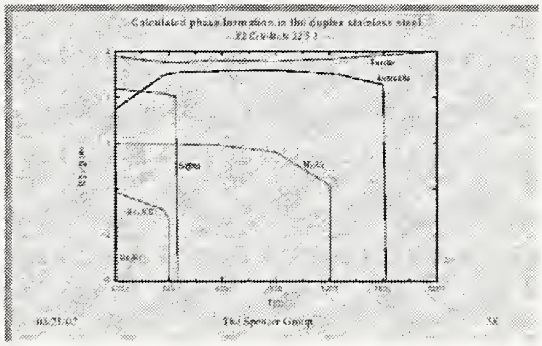
Ferritic: X2 Cr 11
Austenitic: X5 CrNi 18 10

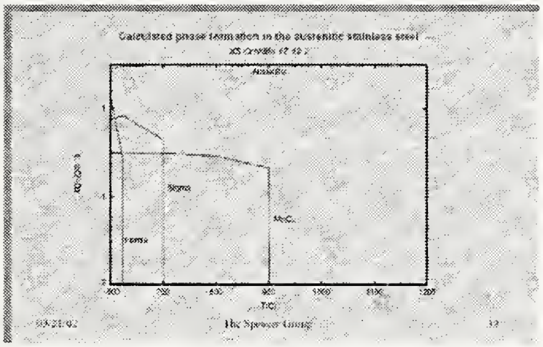
Under development:

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

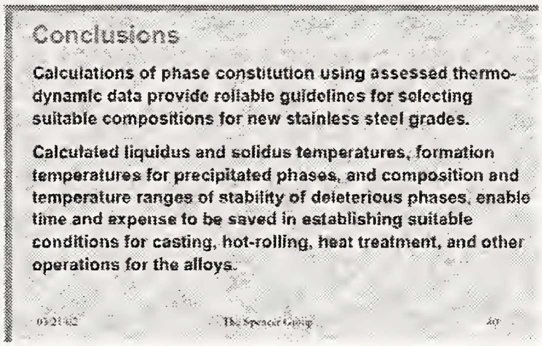
Proposed:

Austenitic: X5 CrMnN 17 12


Calculated phase formation in the duplex stainless steel X2 CrNiMoN 22 5 3


Calculated phase formation in the austenitic stainless steel X5 CrNiMo 17 12 2

Design and development of new stainless steel grades

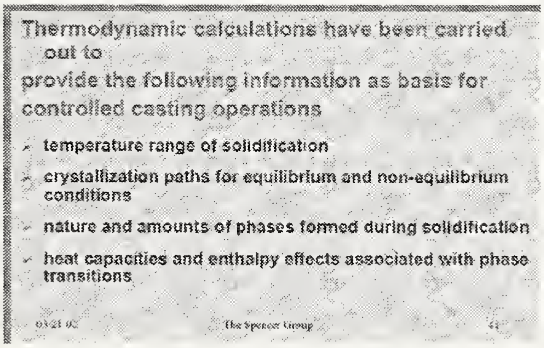


Conclusions

Calculations of phase constitution using assessed thermodynamic 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.

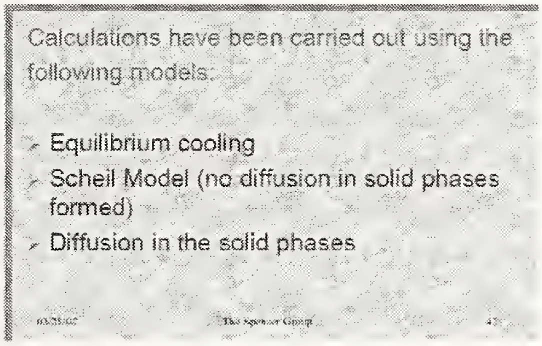
Casting of light metal alloys



Thermodynamic calculations have been carried out to
provide the following information as basis for controlled casting operations

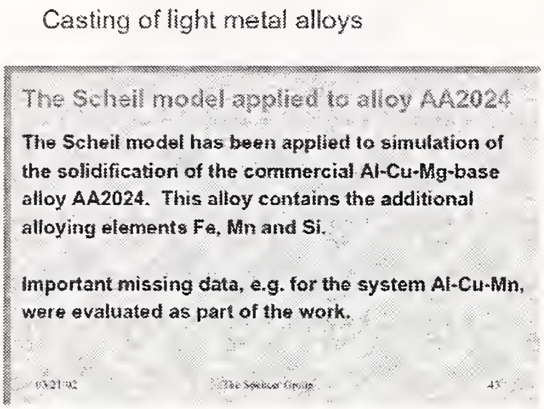
- temperature range of solidification
- crystallization paths for equilibrium and non-equilibrium conditions
- nature and amounts of phases formed during solidification
- heat capacities and enthalpy effects associated with phase transitions

Casting of light metal alloys



Calculations have been carried out using the following models:

- Equilibrium cooling
- Scheil Model (no diffusion in solid phases formed)
- Diffusion in the solid phases

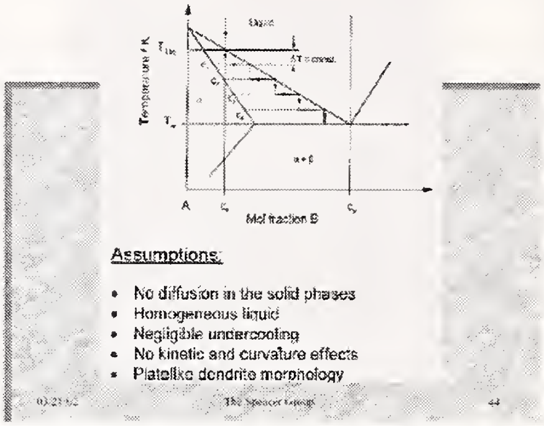


Casting of light metal alloys

The Scheil model applied to alloy AA2024

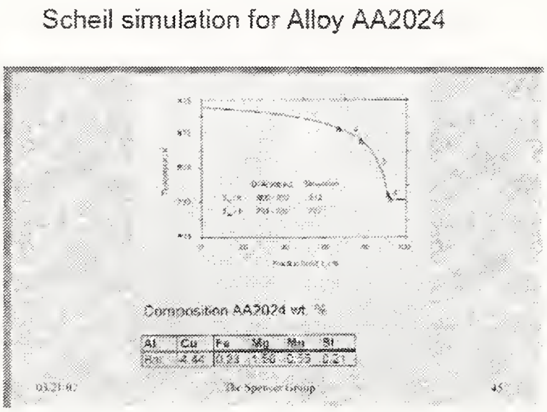
The Scheil model has been applied to simulation of the solidification of the commercial Al-Cu-Mg-base alloy AA2024. This alloy contains the additional alloying elements Fe, Mn and Si.

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



Assumptions:

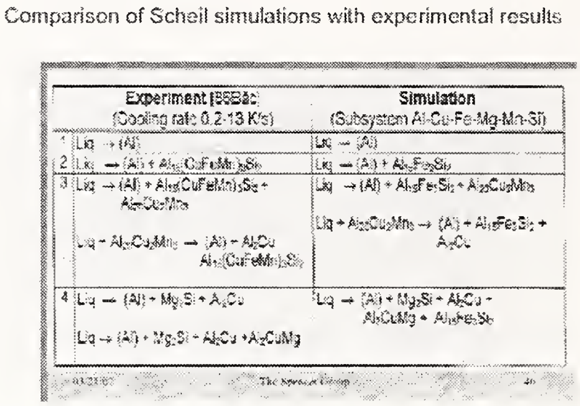
- No diffusion in the solid phases
- Homogeneous liquid
- Negligible undercooling
- No kinetic and curvature effects
- Platelike dendrite morphology



Scheil simulation for Alloy AA2024

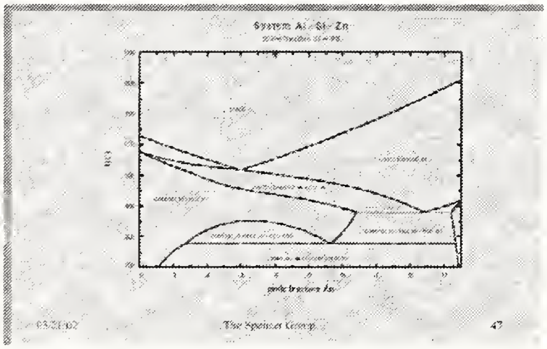
Composition AA2024 wt. %

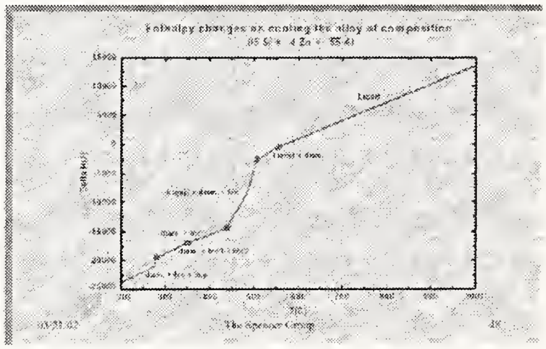
Al	Cu	Fe	Mg	Mn	Si
Bal.	4.44	0.23	1.50	0.55	0.21

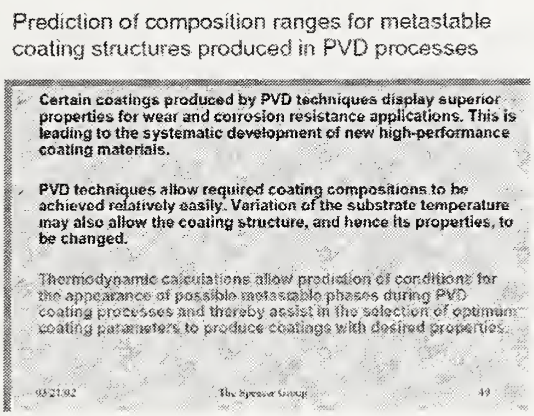


Comparison of Scheil simulations with experimental results

	Experiment [88Bäc] (Cooling rate 0.2-13 K/s)	Simulation (Subsystem Al-Cu-Fe-Mg-Mn-Si)
1	Liq → (Al)	Liq → (Al)
2	Liq → (Al) + $Al_{15}(CuFeMn)_3Si_2$	Liq → (Al) + Al_8Fe_2Si
3	Liq → (Al) + $Al_{15}(CuFeMn)_3Si_2$ + $Al_{20}Cu_2Mn_3$ Liq + $Al_{20}Cu_2Mn_3$ → (Al) + Al_2Cu $Al_{15}(CuFeMn)_3Si_2$	Liq → (Al) + Al_8Fe_2Si + $Al_{20}Cu_2Mn_3$ Liq + $Al_{20}Cu_2Mn_3$ → (Al) + Al_8Fe_2Si + Al_2Cu
4	Liq → (Al) + Mg_2Si + Al_2Cu Liq → (Al) + Mg_2Si + Al_2Cu + Al_2CuMg	Liq → (Al) + Mg_2Si + Al_2Cu + Al_2CuMg + Al_8Fe_2Si

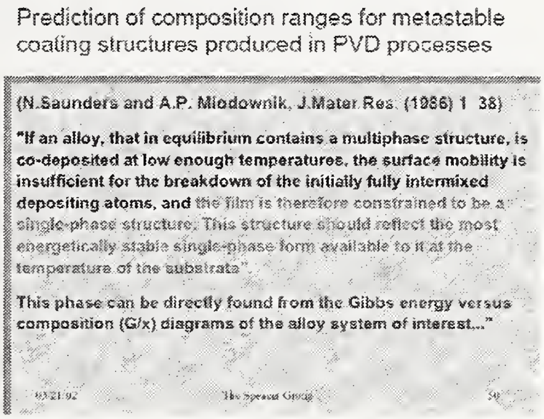






Prediction of composition ranges for metastable coating structures produced in PVD processes

- 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.

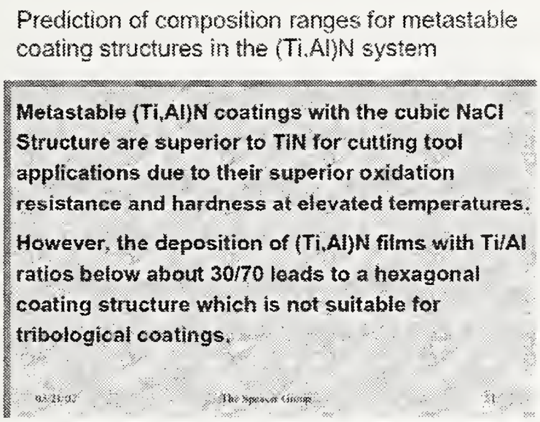


Prediction of composition ranges for metastable coating structures produced in PVD processes

(N.Saunders and A.P. Miodownik, J.Mater.Res. (1986) 1 38)

"If an alloy, that in equilibrium contains a multiphase structure, is co-deposited at low enough temperatures, the surface mobility is insufficient for the breakdown of the initially fully intermixed depositing atoms, and the film is therefore constrained to be a single-phase structure. This structure should reflect the most energetically stable single-phase form available to it at the temperature of the substrate".

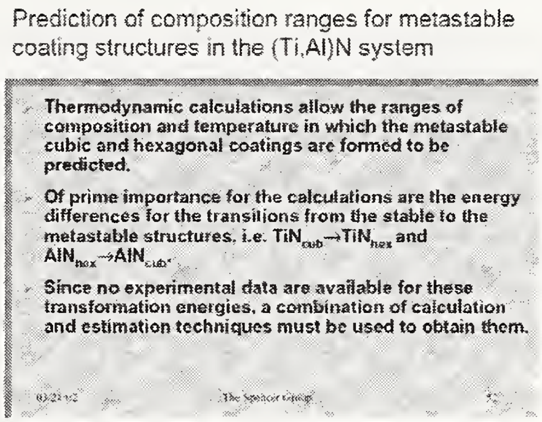
This phase can be directly found from the Gibbs energy versus composition (G/x) diagrams of the alloy system of interest..."



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

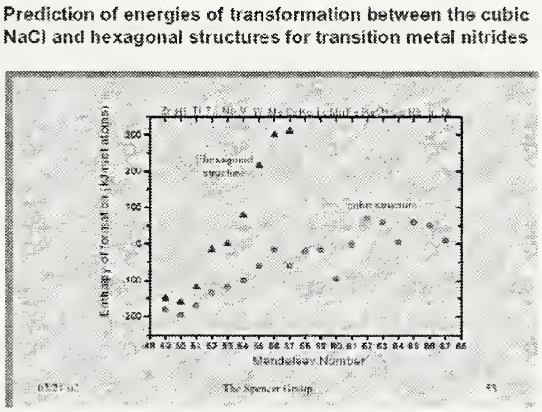
Metastable (Ti,Al)N coatings with the cubic NaCl Structure are superior to TiN for cutting tool applications due to their superior oxidation resistance and hardness at elevated temperatures.

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.

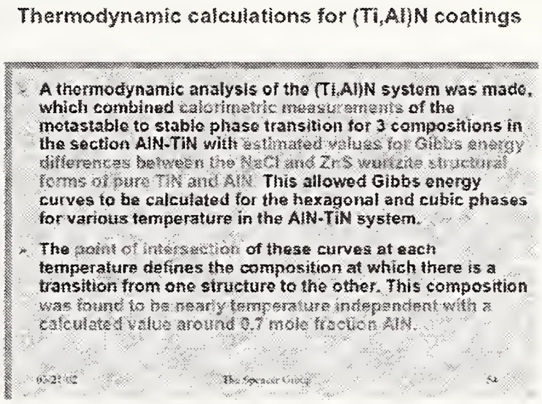


Prediction of composition ranges for metastable coating structures in the (Ti,Al)N system

- Thermodynamic calculations allow the ranges of composition and temperature in which the metastable cubic and hexagonal coatings are formed to be predicted.
- Of prime importance for the calculations are the energy differences for the transitions from the stable to the metastable structures, i.e. $TiN_{cub} \rightarrow TiN_{hex}$ and $AlN_{hex} \rightarrow AlN_{cub}$.
- Since no experimental data are available for these transformation energies, a combination of calculation and estimation techniques must be used to obtain them.

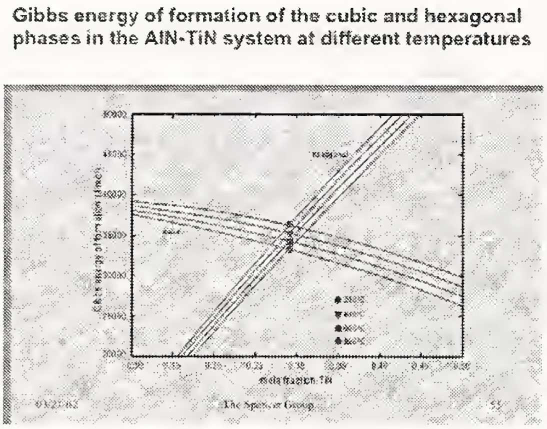


Prediction of energies of transformation between the cubic NaCl and hexagonal structures for transition metal nitrides



Thermodynamic calculations for (Ti,Al)N coatings

- 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 temperature 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

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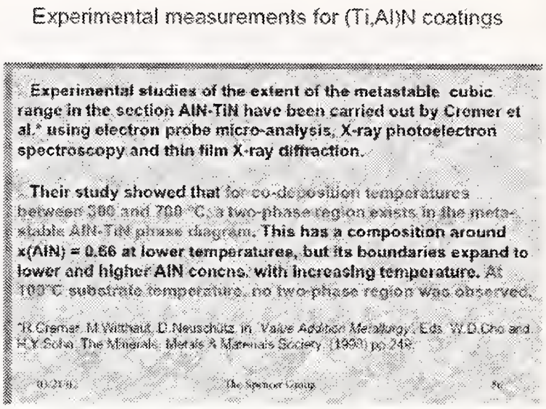


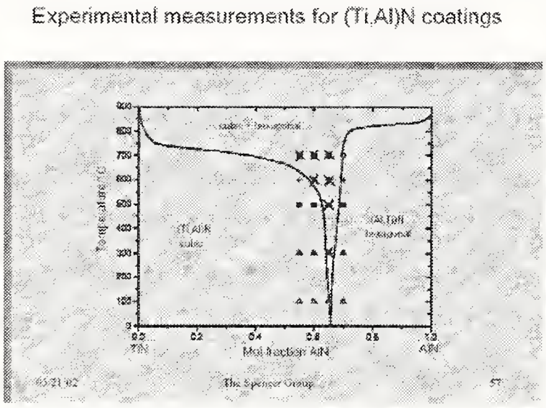
Experimental measurements for (Ti,Al)N coatings

Experimental studies of the extent of the metastable cubic range in the section AlN-TiN have been carried out by Cremer et al.* using electron probe micro-analysis, X-ray photoelectron spectroscopy and thin film X-ray diffraction.

Their study showed that for co-deposition temperatures between 300 and 700 °C, a two-phase region exists in the meta-stable AlN-TiN phase diagram. This has a composition around x(AlN) = 0.66 at lower temperatures, but its boundaries expand to lower and higher AlN concns. with increasing temperature. At 100°C substrate temperature, no two-phase region was observed.

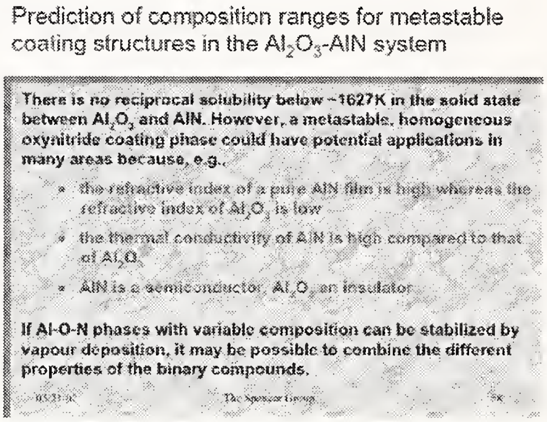
*R.Cremer, M.Witthaut, D.Neuschütz, in: Value Addition Metallurgy, Eds. W.D.Cho and H.Y.Sohn, The Minerals, Metals & Materials Society, (1998) pp.249.

03/21/02 The Spencer Group 56



Experimental measurements for (Ti,Al)N coatings

03/21/02 The Spencer Group 57



Prediction of composition ranges for metastable coating structures in the Al_2O_3-AlN system

There is no reciprocal solubility below ~1627K in the solid state between Al_2O_3 and AlN. However, a metastable, homogeneous oxynitride coating phase could have potential applications in many areas because, e.g.,

- the refractive index of a pure AlN film is high whereas the refractive index of Al_2O_3 is low
- the thermal conductivity of AlN is high compared to that of Al_2O_3
- AlN is a semiconductor, Al_2O_3 an insulator

If Al-O-N phases with variable composition can be stabilized by vapour deposition, it may be possible to combine the different properties of the binary compounds.

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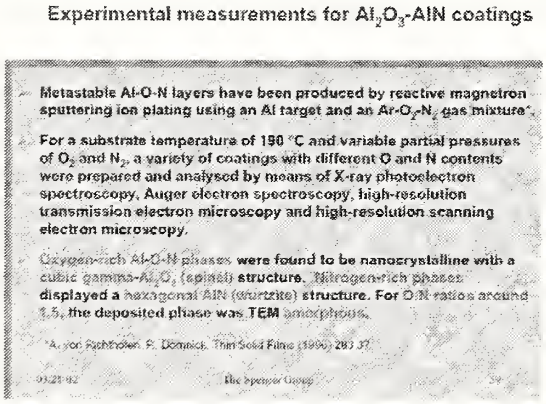
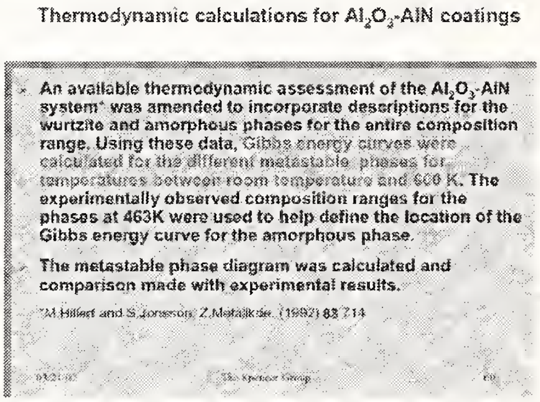


Experimental measurements for Al_2O_3-AlN coatings

- Metastable Al-O-N layers have been produced by reactive magnetron sputtering ion plating using an Al target and an Ar-O_2-N_2 gas mixture*.
- For a substrate temperature of 190 °C and variable partial pressures of O_2 and N_2, 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-Al_2O_3 (spinel) structure. Nitrogen-rich phases displayed a hexagonal AlN (wurtzite) structure. For O:N ratios around 1.5, the deposited phase was TEM amorphous.

*A. von Richthofen, R. Domnick, Thin Solid Films (1996) 283 37

03/21/02 The Spencer Group 59



Thermodynamic calculations for Al_2O_3-AlN coatings

- An available thermodynamic assessment of the Al_2O_3-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 463K 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.

*M.Hillert and S.Jonsson, Z.Metallkde. (1992) 83 714

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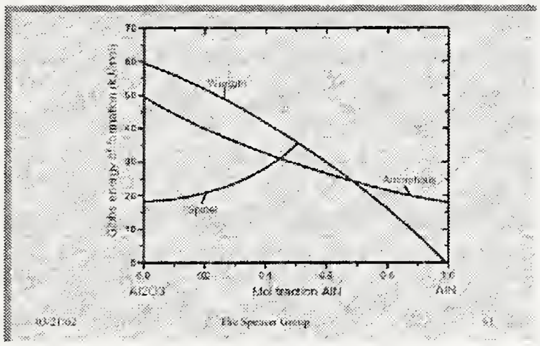
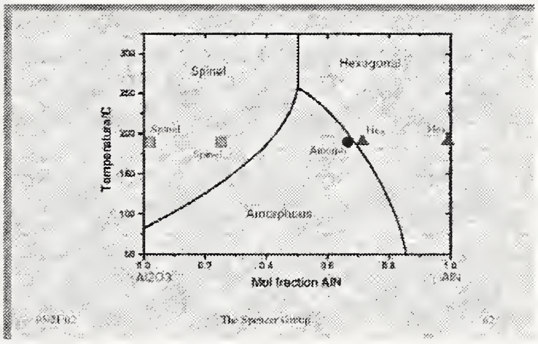
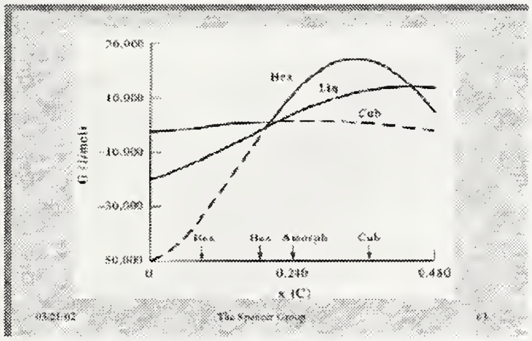
Gibbs energy of formation of the spinel, amorphous and wurtzite phases in the Al_2O_3-AlN system at 463K



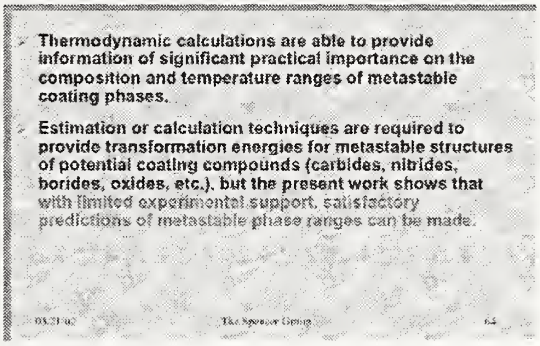
Calculated metastable phase ranges in the Al_2O_3-AlN system



Calculated metastable phase ranges in the TiB_2-TiC system

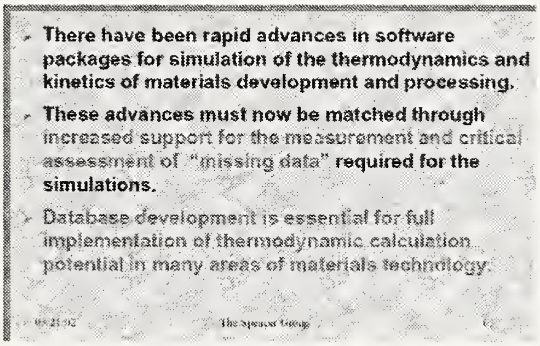


Conclusions



- 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 focussing on important subsystems: Example Al-Cu-Mg-Si-Zn
- Modeling of the intermediate phases and the subsystems must be compatible

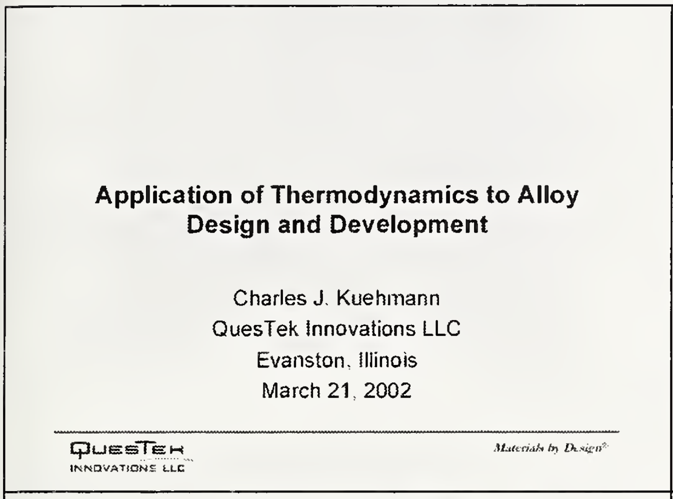
SGTE and its aims:

- 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



Application of Thermodynamics to Alloy Design and Development

Charles J. Kuehmann
QuesTek Innovations LLC
Evanston, Illinois
March 21, 2002

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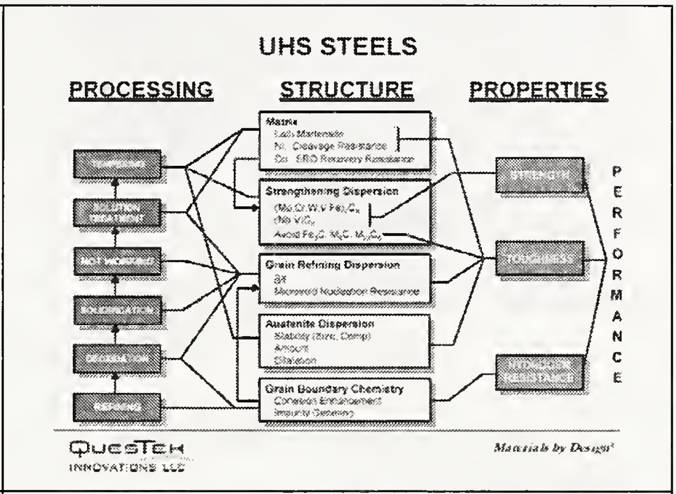

UHS STEELS

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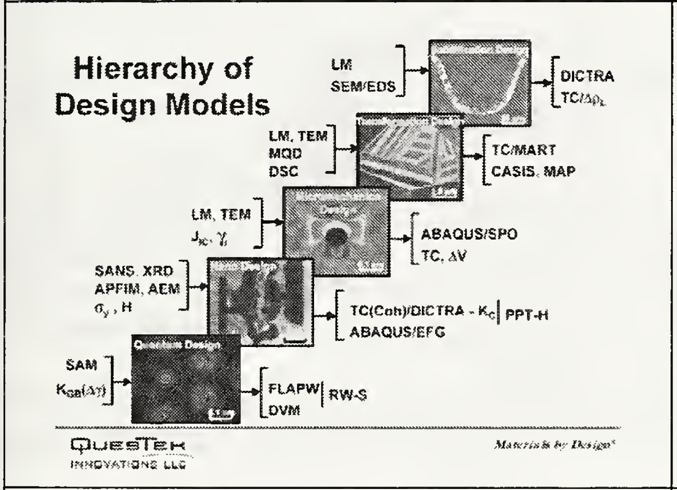

Hierarchy of Design Models

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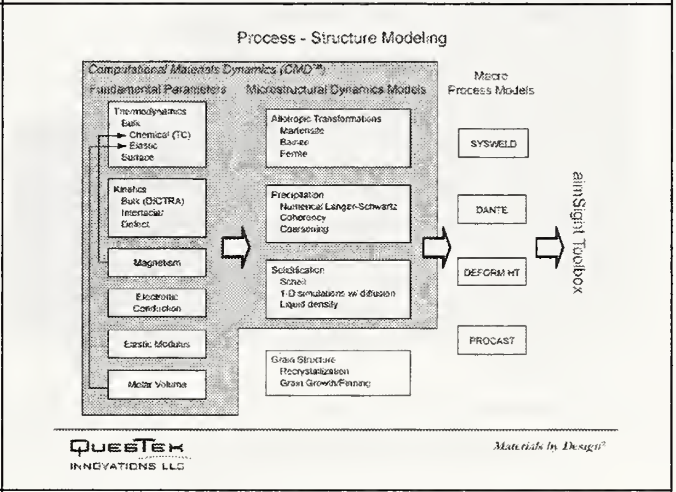

Process - Structure Modeling

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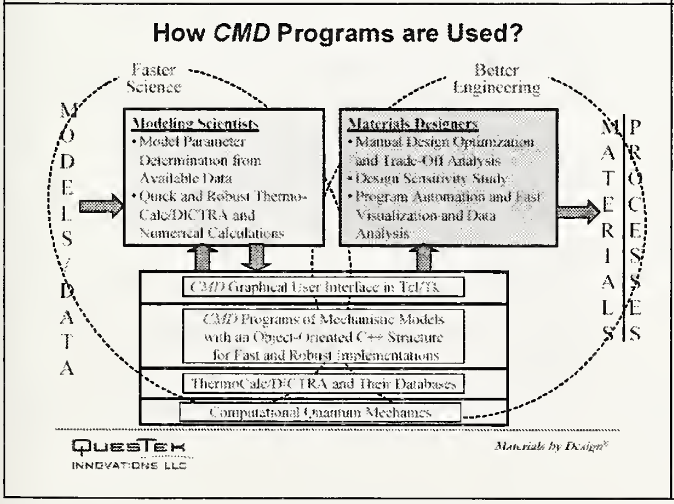

How *CMD* Programs are Used?

Modeling Scientists
- Model Parameter Determination from Available Data
- Quick and Robust Thermo-Calc/DICTRA and Numerical Calculations

Materials Designers
- Manual Design Optimization and Trade-Off Analysis
- Design Sensitivity Study
- Program Automation and Fast Visualization and Data Analysis

CMD Graphical User Interface in Tcl/Tk

CMD Programs of Mechanistic Models with an Object-Oriented C++ Structure for Fast and Robust Implementations

ThermoCalc/DICTRA and Their Databases

Computational Quantum Mechanics

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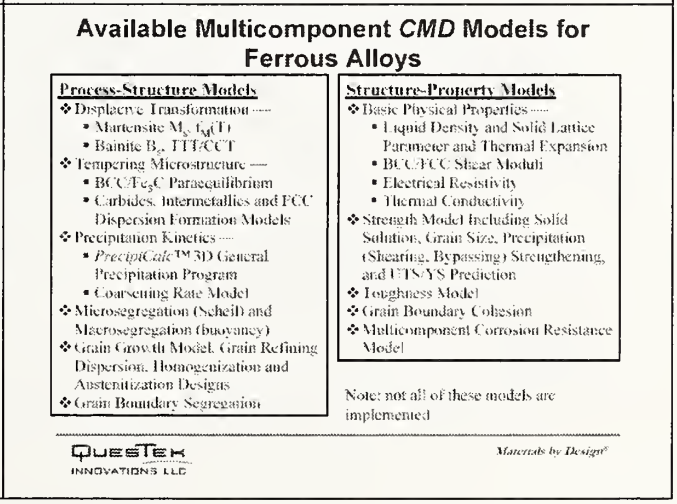

Available Multicomponent *CMD* Models for Ferrous Alloys

Process-Structure Models
- ❖ Displacive Transformation —
  - Martensite M_s, $f_M(T)$
  - Bainite B_s, TTT/CCT
- ❖ Tempering Microstructure —
  - BCC/Fe$_3$C Paraequilibrium
  - Carbides, Intermetallics and FCC Dispersion Formation Models
- ❖ Precipitation Kinetics —
  - *PrecipiCalc*™ 3D General Precipitation Program
  - Coarsening Rate Model
- ❖ Microsegregation (Scheil) and Macrosegregation (buoyancy)
- ❖ Grain Growth Model, Grain Refining Dispersion, Homogenization and Austenitization Designs
- ❖ Grain Boundary Segregation

Structure-Property Models
- ❖ Basic Physical Properties —
  - Liquid Density and Solid Lattice Parameter and Thermal Expansion
  - BCC/FCC Shear Moduli
  - Electrical Resistivity
  - Thermal Conductivity
- ❖ Strength Model Including Solid Solution, Grain Size, Precipitation (Shearing, Bypassing) Strengthening, and UTS/YS Prediction
- ❖ Toughness Model
- ❖ Grain Boundary Cohesion
- ❖ Multicomponent Corrosion Resistance Model

Note: not all of these models are implemented

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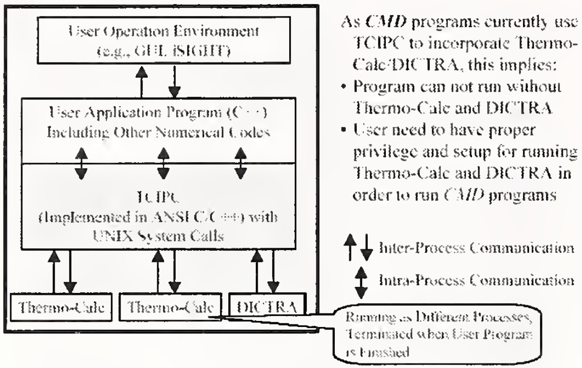
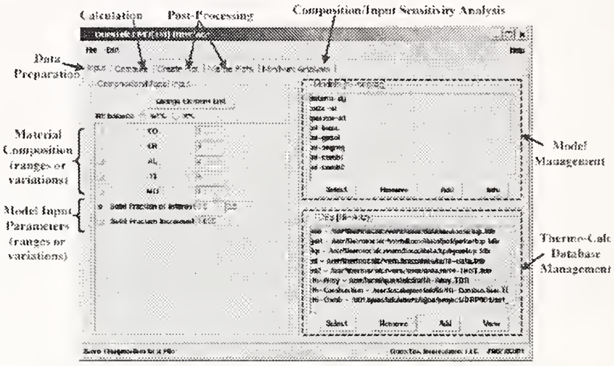
More About TCIPC



As *CMD* programs currently use TCIPC to incorporate Thermo-Calc/DICTRA, this implies:

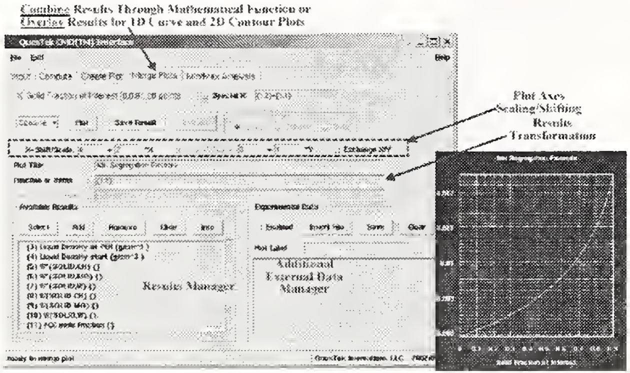
- Program can not run without Thermo-Calc and DICTRA
- User need to have proper privilege and setup for running Thermo-Calc and DICTRA in order to run *CMD* programs

CMD User Interface — Pre-Processor

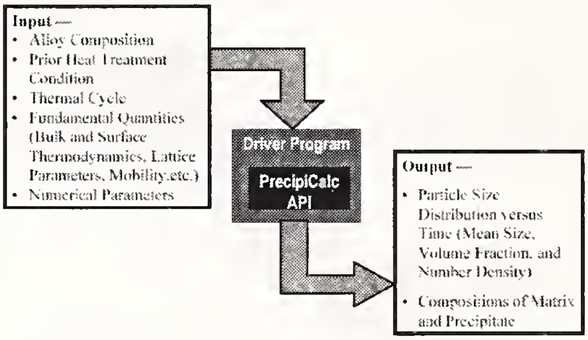


CMD User Interface — Post-Processor

Combine Results Through Mathematical Function or Overlay Results for 1D Curve and 2D Contour Plots



PrecipiCalc™ Input/Output



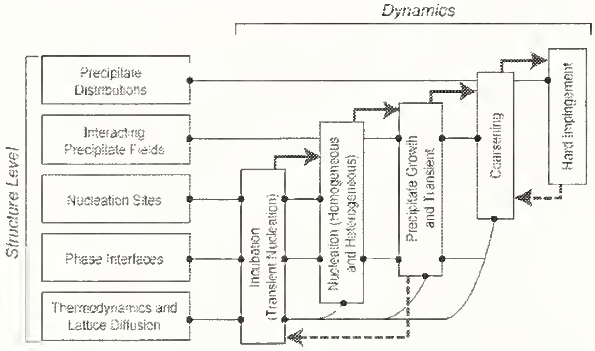
Input —

- Alloy Composition
- Prior Heat Treatment Condition
- Thermal Cycle
- Fundamental Quantities (Bulk and Surface Thermodynamics, Lattice Parameters, Mobility, etc.)
- Numerical Parameters

Output —

- Particle Size Distribution versus Time (Mean Size, Volume Fraction, and Number Density)
- Compositions of Matrix and Precipitate

Modeling Structure of PrecipiCalc™ Software



Basic Multicomponent PrecipiCalc™ Equations

Continuity $\frac{\partial f}{\partial t} + \frac{\partial\left(f\frac{dR}{dt}\right)}{\partial R} = e^{-t/\tau} J_{SS}$ with transient nucleation (incubation time τ)

$$\frac{dR}{dt} = \frac{\left(1 - R\sqrt{4\pi N_v \langle R\rangle}\right)}{R\Gamma}\left[\Delta G_m - \frac{2\sigma \bar{V}_m^\beta}{R}\right]$$

where $\Delta G_m \approx \overline{[\Delta C_i]}^T \left[\frac{\partial^2 \bar{G}^\alpha}{\partial C_i \partial C_j}\right][\Delta C_j^\alpha] + [\bar{X}_\alpha^\beta]\cdot\left([\bar{\mu}_\alpha^\alpha] - [\bar{\mu}_\alpha^\beta]\right)$

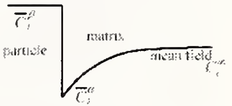
$\Gamma = \overline{[\Delta C_i]}^T \left[\frac{\partial^2 \bar{G}^\alpha}{\partial C_i \partial C_j}\right][\bar{D}_{jk}]^{-1}[\Delta C_k^*]$ and $\overline{[\Delta C_i]}^T = \left[(\bar{C}_2^\beta - \bar{C}_2^\alpha), \ldots, (\bar{C}_n^\beta - \bar{C}_n^\alpha)\right]$

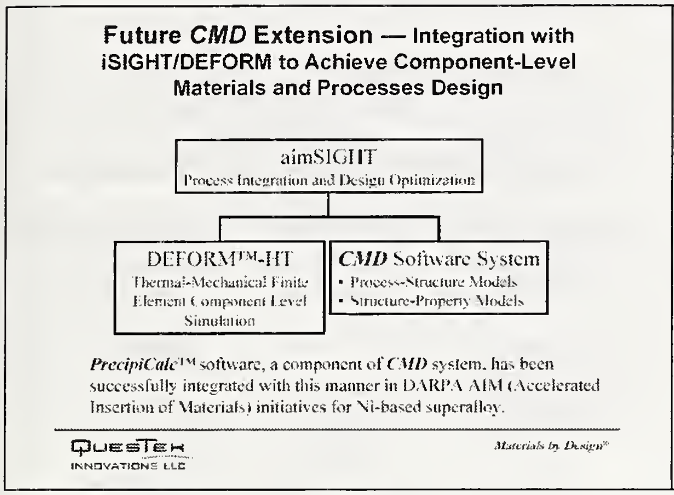
$[\Delta C_j^\alpha]^T = \left[(\bar{C}_2^\alpha - C_2^\infty), \ldots, (\bar{C}_n^\alpha - C_n^\infty)\right]$ and $[\Delta C_k^*]^T = \left[(C_2^{\beta\alpha} - C_2^{\alpha\beta}), \ldots, (C_n^{\beta\alpha} - C_n^{\alpha\beta})\right]$

with α = Γ, ..., n and i, j, k = 2, ..., n component, component 1 is balanced

Mass Balance $C_i^0 = \frac{4\pi}{3}\int_0^\infty fR^3\bar{C}_i^\beta(R)\,dR + C_i^\infty(1-\phi)$ where $\phi = \frac{4\pi}{3}\int_0^\infty fR^3\,dR$

R — particle radius
t — time
$f(R,t)$ — particle frequency distribution (1/m⁴)
N_v — total number density of particle (1/m³)
μ — chemical potential
G — Gibbs free energy
C_i — solute concentration
D_{ij} — diffusivity matrix
σ — surface energy
V_m — molar volume





Future *CMD* Extension — Integration with iSIGHT/DEFORM to Achieve Component-Level Materials and Processes Design

aimSIGHT
Process Integration and Design Optimization

DEFORM™-HT
Thermal-Mechanical Finite Element Component Level Simulation

CMD Software System
- Process-Structure Models
- Structure-Property Models

PrecipiCalc™ software, a component of *CMD* system, has been successfully integrated with this manner in DARPA AIM (Accelerated Insertion of Materials) initiatives for Ni-based superalloy.

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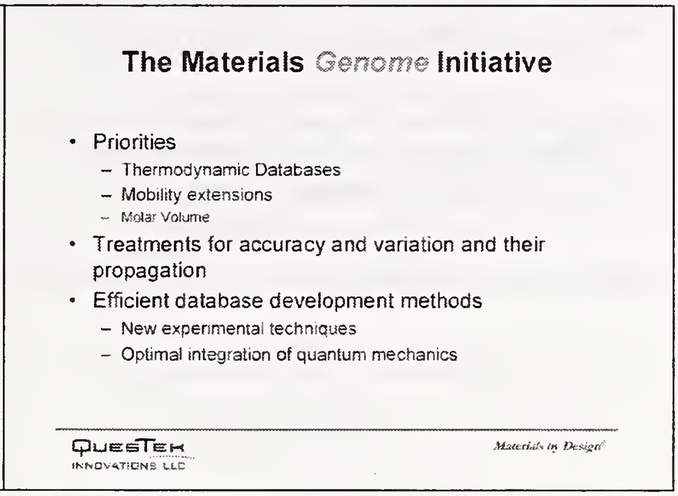


The Materials *Genome* Initiative

- Priorities
  - Thermodynamic Databases
  - Mobility extensions
  - Molar Volume
- Treatments for accuracy and variation and their propagation
- Efficient database development methods
  - New experimental techniques
  - Optimal integration of quantum mechanics

QuesTek Innovations LLC

Materials by Design®

<u>Additional points made by speaker:</u>

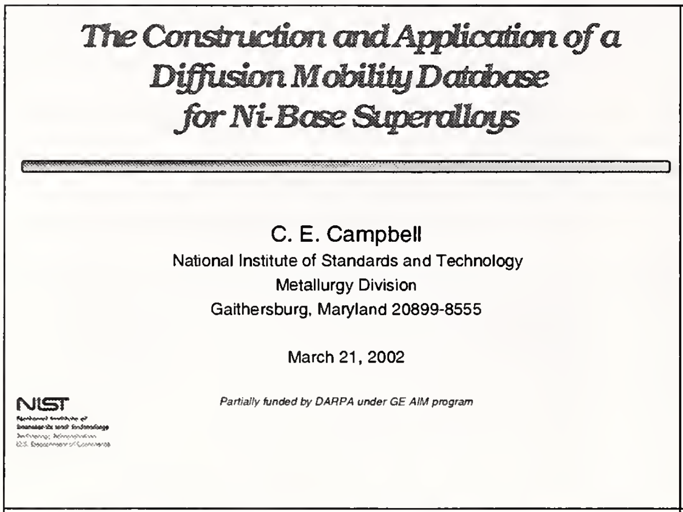
Performance ↔ properties ↔ structure ↔ processing
Modeling employs thermodynamic quantities.

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



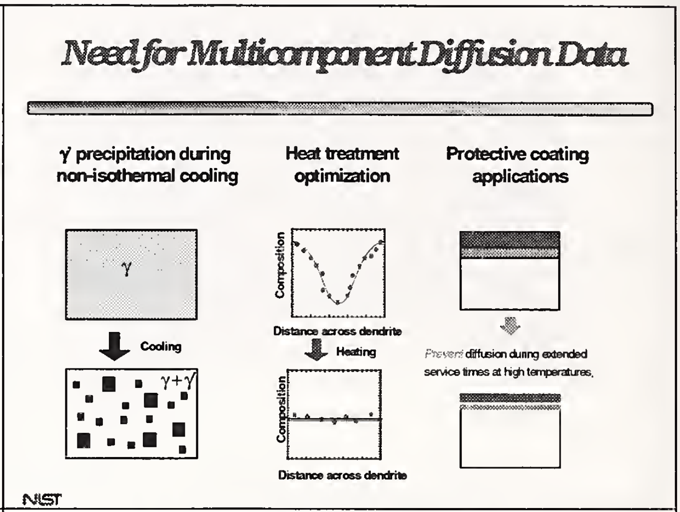
The Construction and Application of a Diffusion Mobility Database for Ni-Base Superalloys

C. E. Campbell
National Institute of Standards and Technology
Metallurgy Division
Gaithersburg, Maryland 20899-8555

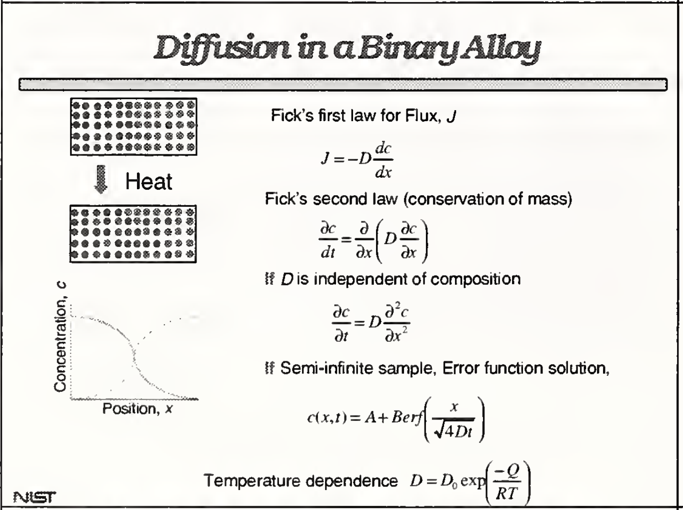
March 21, 2002

Partially funded by DARPA under GE AIM program

NIST



Need for Multicomponent Diffusion Data



Diffusion in a Binary Alloy

Fick's first law for Flux, *J*

$$J = -D\frac{dc}{dx}$$

Fick's second law (conservation of mass)

$$\frac{\partial c}{dt} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right)$$

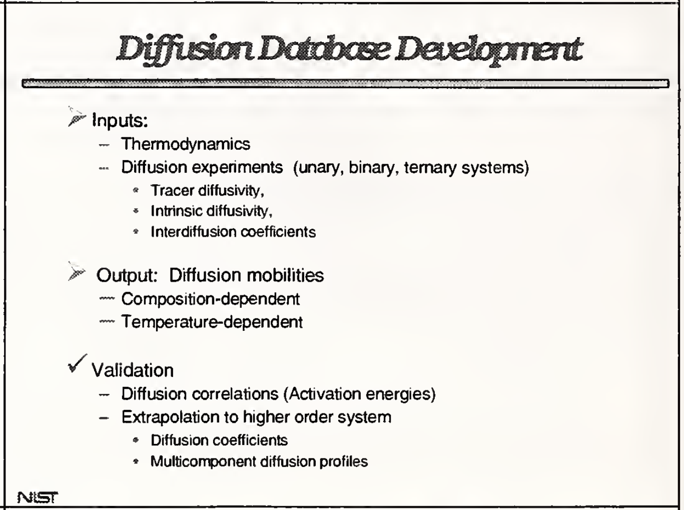
If *D* is independent of composition

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

If Semi-infinite sample, Error function solution,

$$c(x,t) = A + B\,\mathrm{erf}\left(\frac{x}{\sqrt{4Dt}}\right)$$

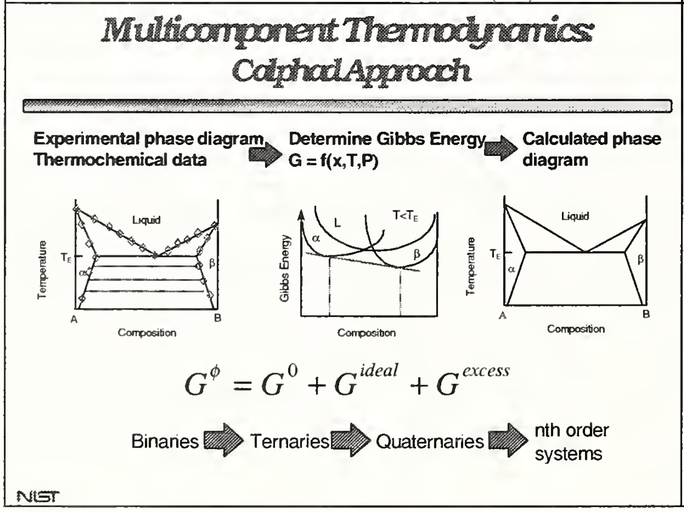
Temperature dependence $D = D_0\exp\left(\frac{-Q}{RT}\right)$



Diffusion Database Development

- Inputs:
  - Thermodynamics
  - Diffusion experiments (unary, binary, ternary systems)
    - Tracer diffusivity,
    - Intrinsic diffusivity,
    - Interdiffusion coefficients
- Output: Diffusion mobilities
  - Composition-dependent
  - Temperature-dependent
- ✓ Validation
  - Diffusion correlations (Activation energies)
  - Extrapolation to higher order system
    - Diffusion coefficients
    - Multicomponent diffusion profiles

NIST



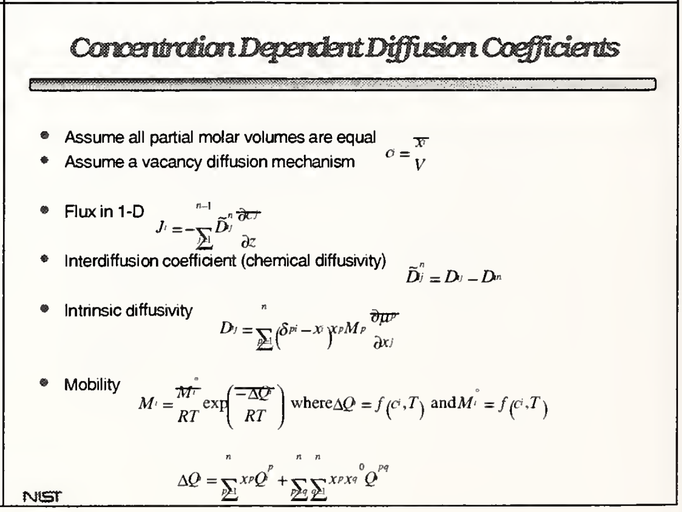
Multicomponent Thermodynamics: Calphad Approach

Experimental phase diagram, Thermochemical data → **Determine Gibbs Energy G = f(x,T,P)** → **Calculated phase diagram**

$$G^{\phi} = G^{0} + G^{ideal} + G^{excess}$$

Binaries → Ternaries → Quaternaries → nth order systems

NIST

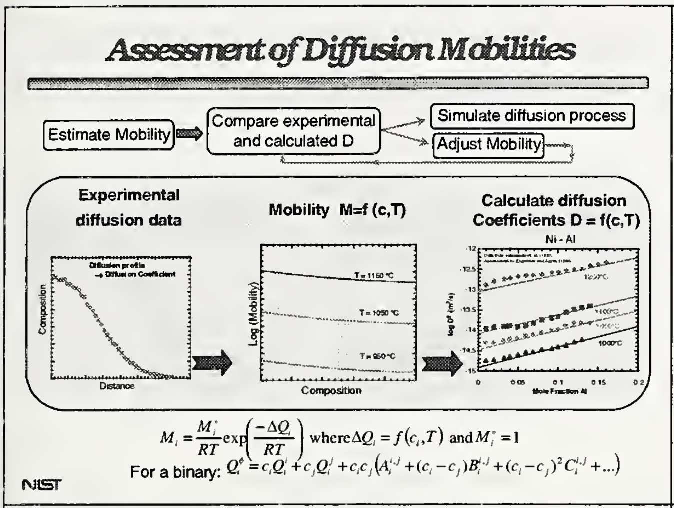


Concentration Dependent Diffusion Coefficients

- Assume all partial molar volumes are equal
- Assume a vacancy diffusion mechanism $c_i = \frac{x_i}{V}$
- Flux in 1-D $J_i = -\sum_{j=1}^{n-1}\tilde{D}_{ij}^{n}\frac{\partial c_j}{\partial z}$
- Interdiffusion coefficient (chemical diffusivity) $\tilde{D}_{ij}^{n} = D_{ij} - D_{in}$
- Intrinsic diffusivity $D_{ij} = \sum_{p=1}^{n}\left(\delta_{pi} - x_i\right)x_p M_p\frac{\partial \mu_p}{\partial x_j}$
- Mobility $M_i = \frac{M_i^{\circ}}{RT}\exp\left(\frac{-\Delta Q_i}{RT}\right)$ where $\Delta Q_i = f(c_i, T)$ and $M_i^{\circ} = f(c_i, T)$

$$\Delta Q = \sum_{p=1}^{n} x_p Q^{p} + \sum_{p=1}^{n}\sum_{q>p}^{n} x_p x_q\, {}^{0}Q^{pq}$$

NIST



Assessment of Diffusion Mobilities

Estimate Mobility → Compare experimental and calculated D → Simulate diffusion process

Adjust Mobility

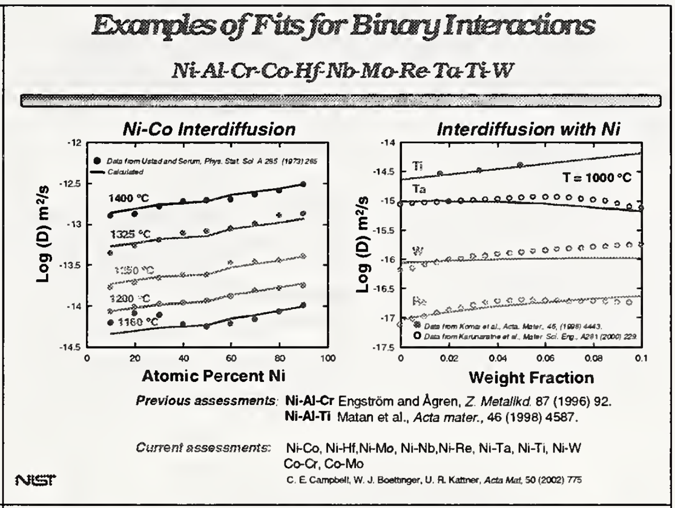
Experimental diffusion data

Mobility M=f (c,T)

Calculate diffusion Coefficients D = f(c,T)

$$M_i = \frac{M_i^*}{RT}\exp\left(\frac{-\Delta Q_i}{RT}\right) \text{ where } \Delta Q_i = f(c_i,T) \text{ and } M_i^* = 1$$

For a binary: $Q_i^{\phi} = c_i Q_i^i + c_j Q_i^j + c_i c_j \left(A_i^{i,j} + (c_i - c_j) B_i^{i,j} + (c_i - c_j)^2 C_i^{i,j} + \ldots\right)$



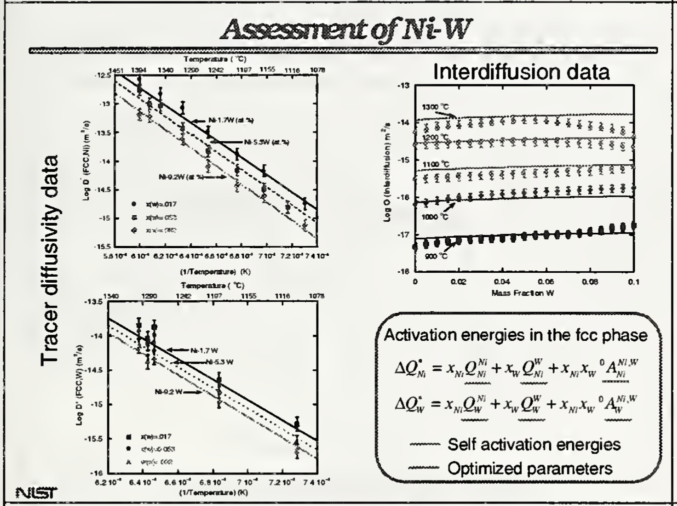
Examples of Fits for Binary Interactions

Ni-Al-Cr-Co-Hf-Nb-Mo-Re-Ta-Ti-W

Previous assessments: **Ni-Al-Cr** Engström and Ågren, *Z. Metallkd.* 87 (1996) 92.
Ni-Al-Ti Matan et al., *Acta mater.*, 46 (1998) 4587.

Current assessments: Ni-Co, Ni-Hf, Ni-Mo, Ni-Nb, Ni-Re, Ni-Ta, Ni-Ti, Ni-W
Co-Cr, Co-Mo

C. E. Campbell, W. J. Boettinger, U. R. Kattner, *Acta Mat*, 50 (2002) 775



Assessment of Ni-W

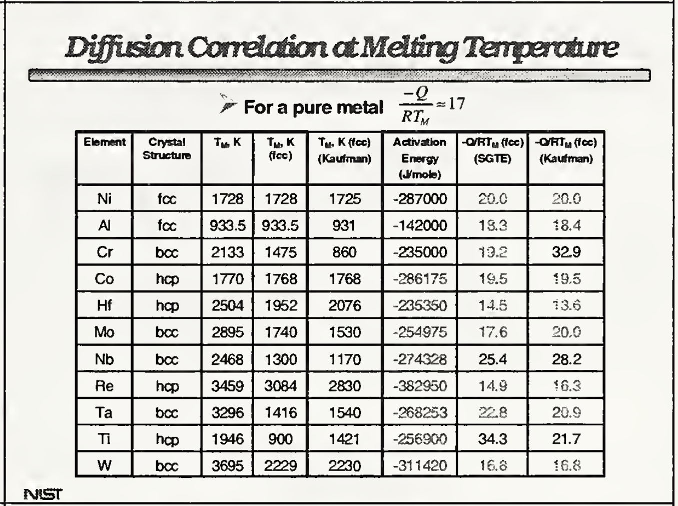
Activation energies in the fcc phase

$$\Delta Q_{Ni}^* = x_{Ni} \underline{Q_{Ni}^{Ni}} + x_W \underline{Q_{Ni}^{W}} + x_{Ni} x_W \, {}^{0}\underline{A_{Ni}^{Ni,W}}$$

$$\Delta Q_{W}^* = x_{Ni} \underline{Q_{W}^{Ni}} + x_W \underline{Q_{W}^{W}} + x_{Ni} x_W \, {}^{0}\underline{A_{W}^{Ni,W}}$$

Self activation energies

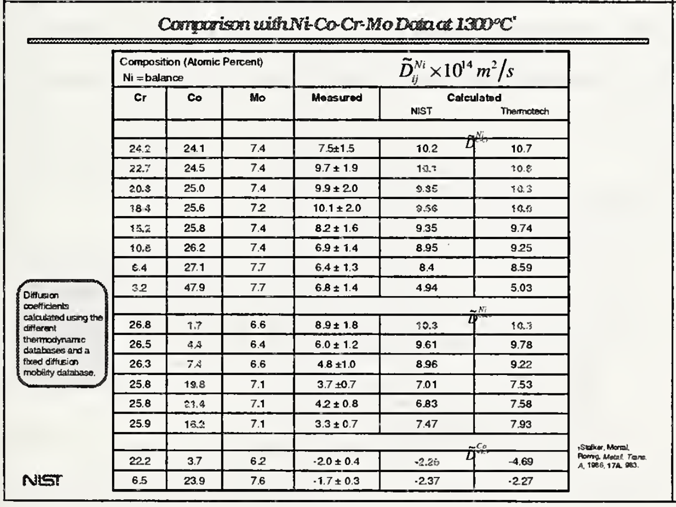
Optimized parameters



Diffusion Correlation at Melting Temperature

- For a pure metal $\frac{-Q}{RT_M} \approx 17$

Element	Crystal Structure	T_M, K	T_M, K (fcc)	T_M, K (fcc) (Kaufman)	Activation Energy (J/mole)	$-Q/RT_M$ (fcc) (SGTE)	$-Q/RT_M$ (fcc) (Kaufman)
Ni	fcc	1728	1728	1725	-287000	20.0	20.0
Al	fcc	933.5	933.5	931	-142000	18.3	18.4
Cr	bcc	2133	1475	860	-235000	19.2	32.9
Co	hcp	1770	1768	1768	-286175	19.5	19.5
Hf	hcp	2504	1952	2076	-235350	14.5	13.6
Mo	bcc	2895	1740	1530	-254975	17.6	20.0
Nb	bcc	2468	1300	1170	-274328	25.4	28.2
Re	hcp	3459	3084	2830	-382950	14.9	16.3
Ta	bcc	3296	1416	1540	-268253	22.8	20.9
Ti	hcp	1946	900	1421	-256900	34.3	21.7
W	bcc	3695	2229	2230	-311420	16.8	16.8

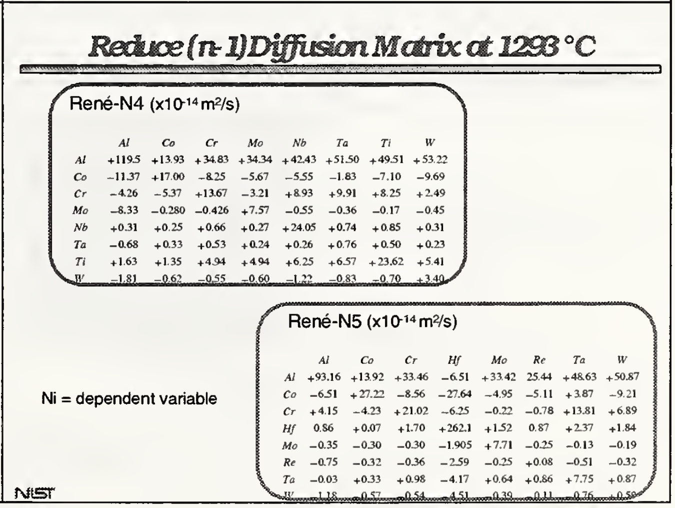


Comparison with Ni-Co-Cr-Mo Data at 1300°C*

Composition (Atomic Percent) Ni = balance			$\tilde{D}_{ij}^{Ni} \times 10^{14}\, m^2/s$		
Cr	Co	Mo	Measured	Calculated NIST	Thermotech
				D^{Ni}	
24.2	24.1	7.4	7.5±1.5	10.2	10.7
22.7	24.5	7.4	9.7 ± 1.9	10.3	10.8
20.8	25.0	7.4	9.9 ± 2.0	9.35	10.3
18.4	25.6	7.2	10.1 ± 2.0	9.56	10.6
15.2	25.8	7.4	8.2 ± 1.6	9.35	9.74
10.8	26.2	7.4	6.9 ± 1.4	8.95	9.25
6.4	27.1	7.7	6.4 ± 1.3	8.4	8.59
3.2	47.9	7.7	6.8 ± 1.4	4.94	5.03
				$\tilde{D}^{Ni}$	
26.8	1.7	6.6	8.9 ± 1.8	10.3	10.3
26.5	4.4	6.4	6.0 ± 1.2	9.61	9.78
26.3	7.4	6.6	4.8 ±1.0	8.96	9.22
25.8	19.8	7.1	3.7 ±0.7	7.01	7.53
25.8	21.4	7.1	4.2 ± 0.8	6.83	7.58
25.9	16.2	7.1	3.3 ± 0.7	7.47	7.93
				$\tilde{D}^{Co}$	
22.2	3.7	6.2	-2.0 ± 0.4	-2.25	-4.69
6.5	23.9	7.6	-1.7 ± 0.3	-2.37	-2.27

Diffusion coefficients calculated using the different thermodynamic databases and a fixed diffusion mobility database.

*Stalker, Morral, Romig, *Metall. Trans. A*, 1986, 17A, 983.



Reduce (n-1) Diffusion Matrix at 1293 °C

René-N4 (x10⁻¹⁴ m²/s)

	Al	*Co*	*Cr*	*Mo*	*Nb*	*Ta*	*Ti*	*W*
Al	+119.5	+13.93	+34.83	+34.34	+42.43	+51.50	+49.51	+53.22
Co	−11.37	+17.00	−8.25	−5.67	−5.55	−1.83	−7.10	−9.69
Cr	−4.26	−5.37	+13.67	−3.21	+8.93	+9.91	+8.25	+2.49
Mo	−8.33	−0.280	−0.426	+7.57	−0.55	−0.36	−0.17	−0.45
Nb	+0.31	+0.25	+0.66	+0.27	+24.05	+0.74	+0.85	+0.31
Ta	−0.68	+0.33	+0.53	+0.24	+0.26	+0.76	+0.50	+0.23
Ti	+1.63	+1.35	+4.94	+4.94	+6.25	+6.57	+23.62	+5.41
W	−1.81	−0.62	−0.55	−0.60	−1.22	−0.83	−0.70	+3.40

Ni = dependent variable

René-N5 (x10⁻¹⁴ m²/s)

	Al	*Co*	*Cr*	*Hf*	*Mo*	*Re*	*Ta*	*W*
Al	+93.16	+13.92	+33.46	−6.51	+33.42	25.44	+48.63	+50.87
Co	−6.51	+27.22	−8.56	−27.64	−4.95	−5.11	+3.87	−9.21
Cr	+4.15	−4.23	+21.02	−6.25	−0.22	−0.78	+13.81	+6.89
Hf	0.86	+0.07	+1.70	+262.1	+1.52	0.87	+2.37	+1.84
Mo	−0.35	−0.30	−0.30	−1.905	+7.71	−0.25	−0.13	−0.19
Re	−0.75	−0.32	−0.36	−2.59	−0.25	+0.08	−0.51	−0.32
Ta	−0.03	+0.33	+0.98	−4.17	+0.64	+0.86	+7.75	+0.87
W	−1.18	−0.57	−0.54	−4.51	−0.39	−0.11	−0.76	+0.59

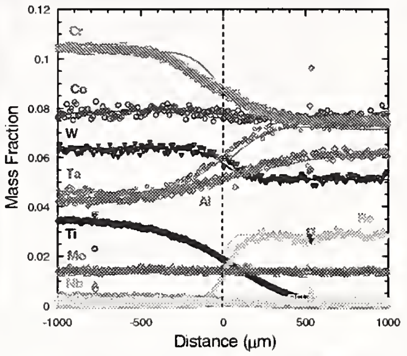
René-N4/René-N5 at 1293 °C for 100 h

- Databases used
  - Thermodynamics: Thermotech
  - Diffusion mobilities: NIST Ni-mob

René-N4	René-N5
γ	γ

6.35 mm 6.35 mm

Double geometric grid: 200 points

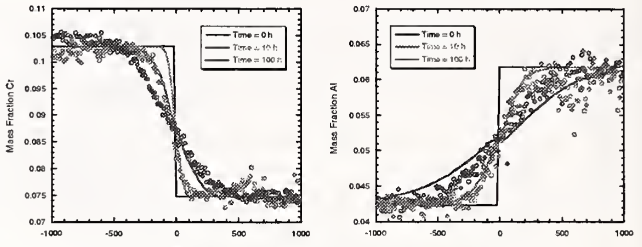


Experimental work performed by T. Hansen, P. Merewether, B. Mueller, Howmet Corporation, Whitehall, MI.

NIST Howmet Castings

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

Cr profile Al profile



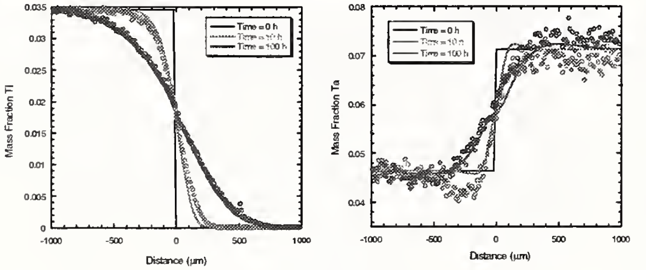
René-N4	René-N5

6.35 mm 6.35 mm

NIST Howmet Castings

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

Ti profile Ta profile



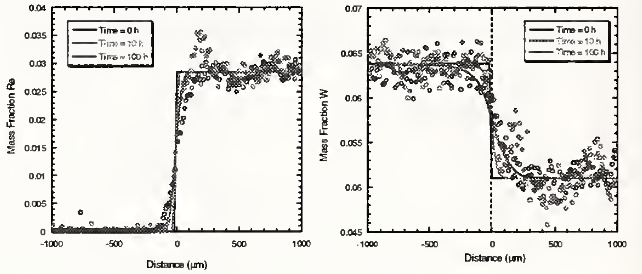
René-N4	René-N5

6.35 mm 6.35 mm

NIST Howmet Castings

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

Re profile W profile

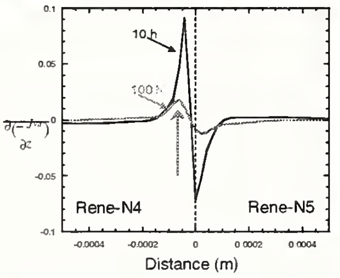


René-N4	René-N5

6.35 mm 6.35 mm

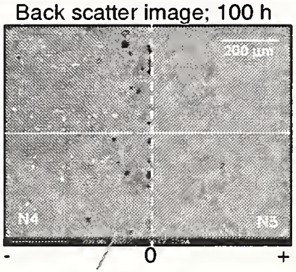
NIST Howmet Castings

Porosity Prediction



Maximum gives location of pore formation.

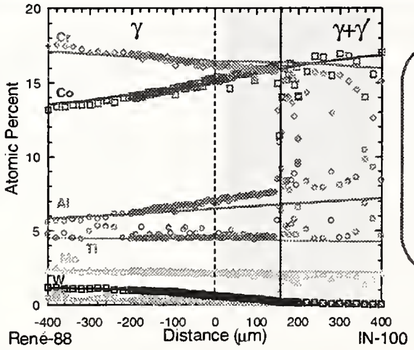
Back scatter image; 100 h



Predicted position for maximum pore formation

Howmet Castings

René-88/IN-100; 1000 h at 1150 °C



At 1150 °C equilibrium phase fractions

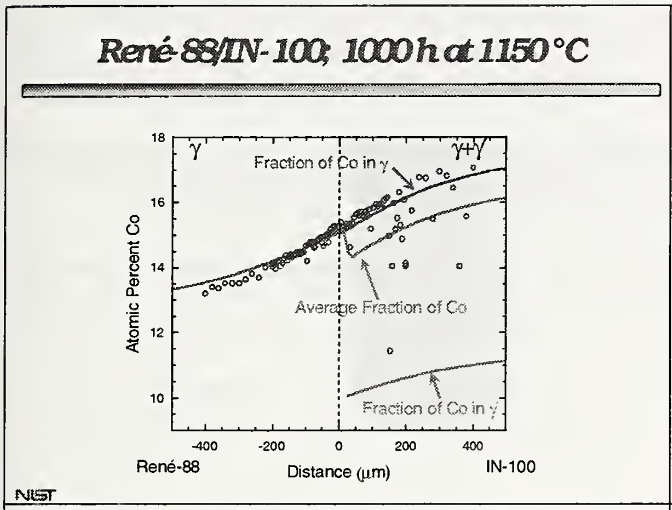
- René-88: $f_{\gamma} = 1$
- IN-100: $f_{\gamma} = 0.638$ $f_{\gamma'} = 0.362$

René-88	IN-100

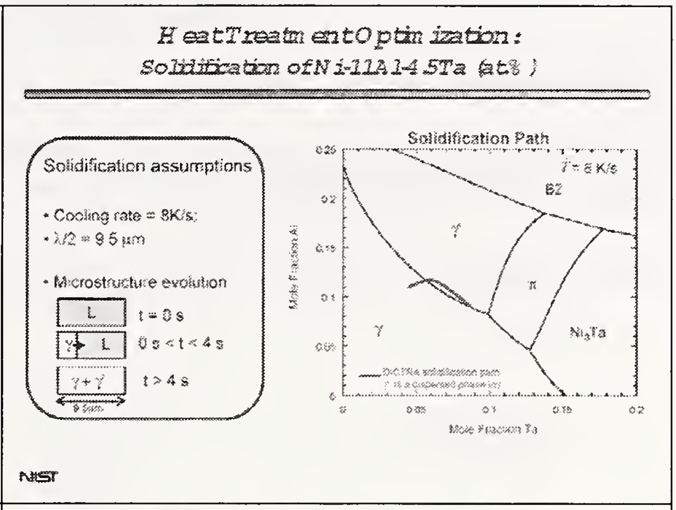
4 mm 4 mm

NIST

Experimental data from J. C. Zhao, GE-CRD, Schenectady, NY



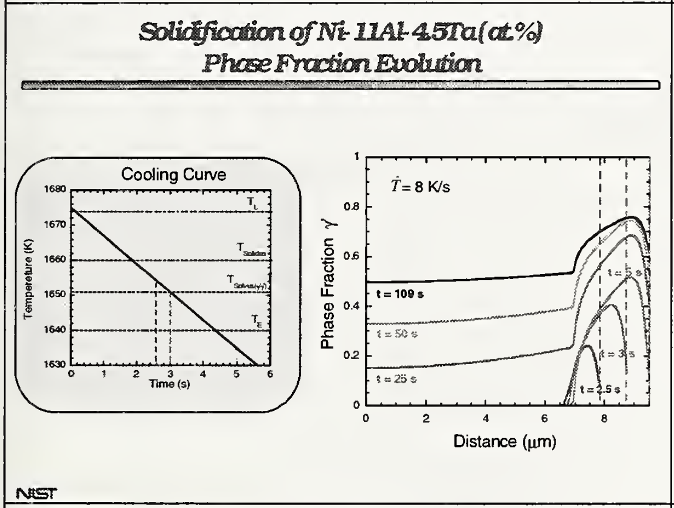
René-88/IN-100; 1000 h at 1150 °C



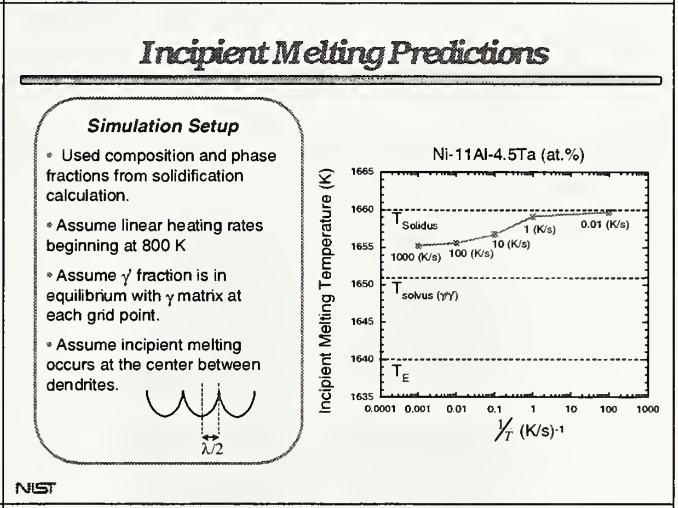
Heat Treatment Optimization: Solidification of Ni-11Al-4.5Ta (at%)

Solidification assumptions

- Cooling rate = 8K/s;
- λ/2 = 9.5 μm
- Microstructure evolution



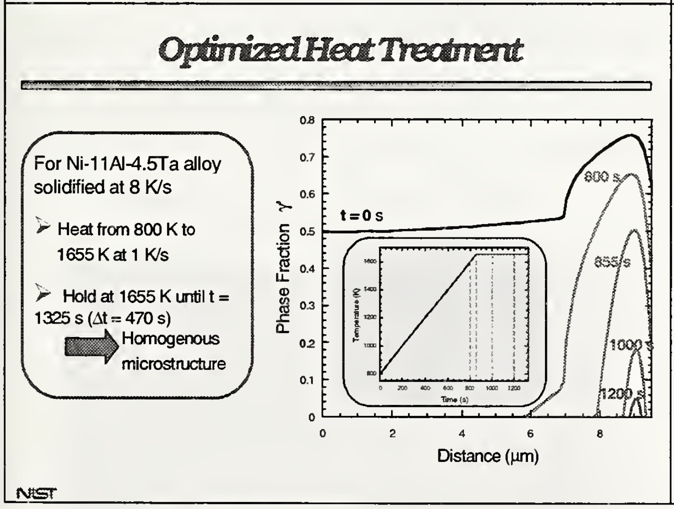
Solidification of Ni-11Al-4.5Ta (at.%) Phase Fraction Evolution



Incipient Melting Predictions

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 (Δt = 470 s) ⇒ Homogenous microstructure

Summary

- Database Development
  - Ni-base superalloys:
    - Ni-Al-Co-Cr-Hf-Mo-Nb-Re-Ta-Ti-W (Fe)
    - FCC (γ) phase, γ', B2
  - Comparisons with
    - Diffusion correlations at melting temperature
    - Experimental quaternary diffusion coefficients
    - Multicomponent diffusion couples: (René-N4/René-N5; René-88/IN-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: $-Q/RT_M \approx 17$.

Porosity prediction: Position of maximum in vacancy flux gives position for maximum pore formation.

Incorporation of CALPHAD Calculations into Phase Field Modeling

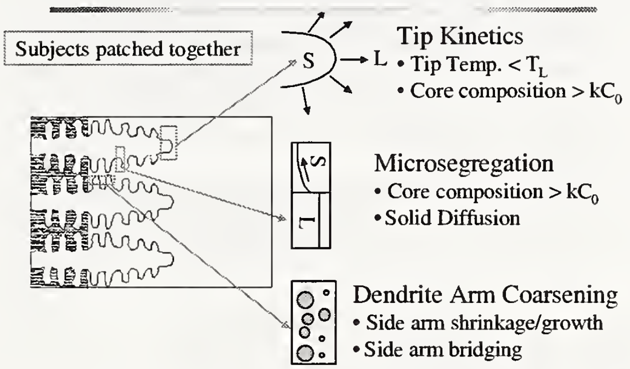
William J. Boettinger, NIST, Gaithersburg, MD

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



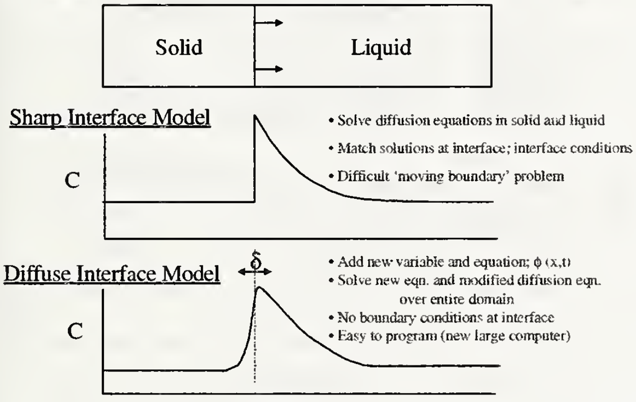
Subjects patched together

Tip Kinetics
- Tip Temp. < T_L
- Core composition > kC_0

Microsegregation
- Core composition > kC_0
- Solid Diffusion

Dendrite Arm Coarsening
- Side arm shrinkage/growth
- Side arm bridging

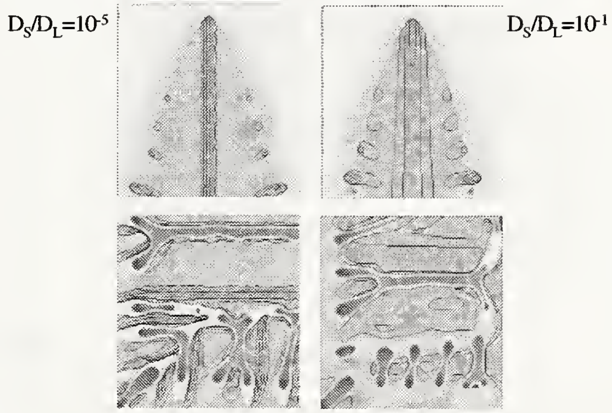
Sharp vs. Diffuse Interface



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

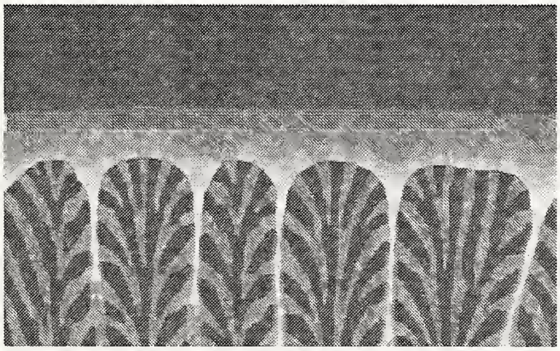
Diffuse Interface Model
- Add new variable and equation: $\phi(x,t)$
- Solve new eqn. and modified diffusion eqn. over entire domain
- No boundary conditions at interface
- Easy to program (new large computer)

Microsegregation (Warren and Boettinger, 1996)



Binary Eutectic with Dilute Ternary Impurity

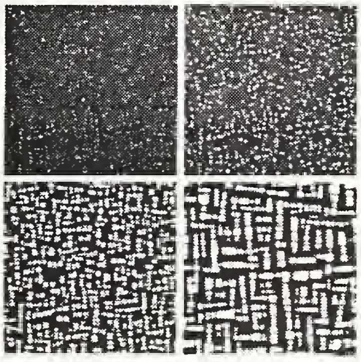
M. Plapp and A. Karma 1999



Simulation of γ' Precipitation w/Coherency Strains

Y. Wang, D. Banerjee, C.C. Su, (OSU) & A. Khachaturyan, (Rutgers)

Acta Mat. 46 (1998) 2983



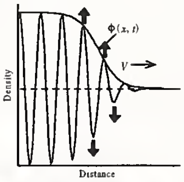
Active researchers: Phase Field Modeling attempting "Calphad"Thermodynamic Databases

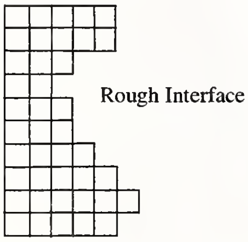
- Y. Wang, D. Banjeree, C.C. Su and A.G. Khachaturyan, Acta Mat. 46(1998) 2983. *Ni-Ni$_3$Al polynomial 4 sublattice stress*
- U. Grafe, B. Bottger, J. Tiaden, S.G. Fries, Mod. & Sim. Mat. Sci. & Eng. 8(2000) 871. *TQ interface Ni-Al-Cr-Co Ti solidification*
- I. Loginova, G, Amberg , J. Agren, Seattle 2001 TMS
- Miyazaki, Calphad 25 (2001) 231. Discrete lattice Fe-Co-Al and InGaAsP, w/stress
- L.Q. Chen, C. Wolverton V. Vaithyanathan, Z.K. Liu, MRS Bulletin 26(2001) 197. *Al-Cu* θ'& θ ' *ppt. First principles free and interface energy used to get phase field parameters.*

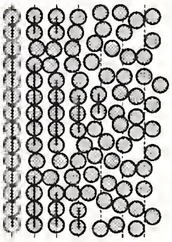
Phase Field vs. Order Parameter(s)

- 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.

What is the Phase Field variable for solidification?







Gradient Thermodynamics

$$F=\int_V\left[f(c,\phi,T)+\frac{\varepsilon_\phi^{\,2}}{2}|\nabla\phi|^2+\frac{\varepsilon_C^2}{2}|\nabla c|^2\right]dV$$

$\boxed{\text{Equilibrium}}$

$$\begin{cases}\dfrac{\delta F}{\delta\phi}=\dfrac{\partial f}{\partial\phi}-\varepsilon_\phi^2\nabla^2\phi=0\\[2ex]\dfrac{\delta F}{\delta c}=\dfrac{\partial f}{\partial c}-\varepsilon_C^2\nabla^2 c=\text{constant}\end{cases}$$

$$\begin{cases}\dfrac{\partial\phi}{\partial t}=-M_\phi\left[\dfrac{\partial f}{\partial\phi}-\varepsilon_\phi^2\nabla^2\phi\right]\\[2ex]\dfrac{\partial c}{\partial t}=\nabla\cdot\left[\underbrace{M_C\nabla\left(\dfrac{\partial f}{\partial c}-\varepsilon_C^2\nabla^2 c\right)}_{-\mathbf{J}}\right]\end{cases}$$

M_ϕ = *Interface Kinetics*

M_C = *Diffusion Mobility*

$\boxed{\text{Dynamics}}$

Coupled Cahn-Hilliard & Cahn-Allen Equations

Combined Alloy Free Energy Function for independent α & β phases

$\boxed{\text{Wheeler, Boettinger, McFadden:}}$

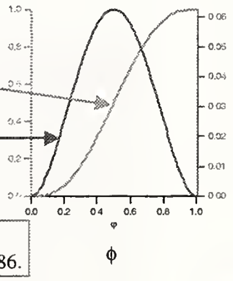
$$f(\phi,c,T)=(1-p(\phi))f^\alpha(c,T)+p(\phi)f^\beta(c,T)+W(c,T)g(\phi)$$

Interpolating function

Double-Well function

$$p(\varphi)=\varphi^3\left(6\varphi^2-15\varphi+10\right)$$

$$g(\varphi)=\varphi^2(1-\varphi)^2$$

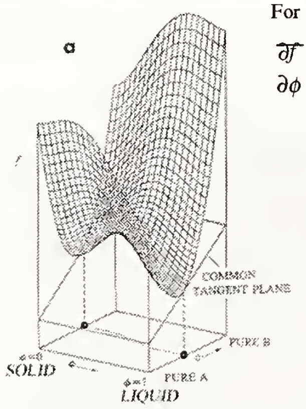


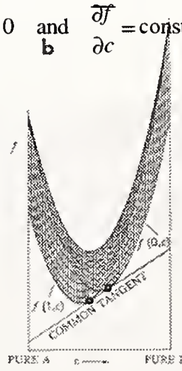
Alternate method:
Kim, Kim & Suzuki, Phys. Rev E 60(1999) 7186.

Alloy Free Energy Function

For equilibrium far from the interface

$$\frac{\partial f}{\partial\phi}=0\quad\text{and}\quad\frac{\partial f}{\partial c}=\text{constant}$$





Interface Energies via Thermodynamic Functions; *natural order parameters*

Dregia & Wynblatt, Acta Met. 39(1991)774

Ternary Regular Solution Ag-Au-Cu with Ω_{ij} heats of mixing

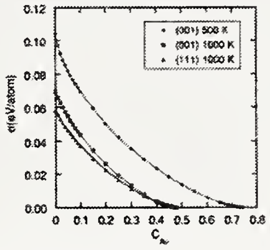
$$F=\int\left\{f(c_1,c_2,T)+k_{11}(\nabla c_1)^2+k_{12}(\nabla c_1\cdot\nabla c_2)+k_{22}(\nabla c_2)^2\right\}dV$$

$$k_{11}=2Z_v d^2\Omega_{13}$$

$$k_{22}=2Z_v d^2\Omega_{23}$$

$$k_{12}=2Z_v d^2(\Omega_{13}+\Omega_{23}-\Omega_{12})$$

d = interatomic distance
Z_v= interface coordination number
= 3 for {111}
= 4 for{100}



Similarly, gradient energy coefficients can be obtained for order/disorder cases! Braun, et al. Phil. Trans. R. Soc Lon. A (1997) Wang et al., Acta Mat.(1998)

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, $L_{ij}''(\phi)$, for the dynamic constitutive law.

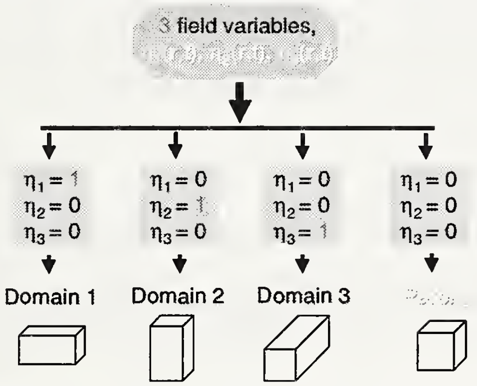
$$\boxed{J_i=-\sum_{j=1}^{n-1}L_{ij}''\frac{\delta F}{\delta X_i}=\sum_{j=1}^{n-1}L_{ij}''\nabla\left(\frac{\partial f(X_1,\ldots,X_{n-1})}{\partial X_j}\right)=\sum_{j=1}^{n-1}L_{ij}''\nabla(\mu_j-\mu_n)}$$

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

$L''=PMP^T$ (matrix multiplication)
where
$P_{ij}=\delta_{ij}-X_i$

- Then $\boxed{L''(\phi)=p(\phi)L_1''+(1-p(\phi))L_2''}$ where L_1'' and L_2'' are for each phase.

Elastic effects: Cubic → Tetragonal Transformation



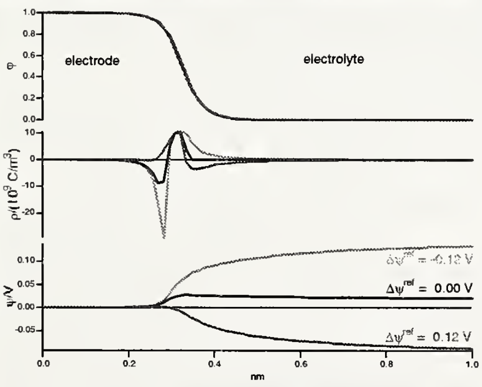
Stress free strain, function of η; add elastic energy to free energy functional

Electrochemistry

$$F(\varphi,C_j,\psi)=\int_V\left(f_V(\varphi,C_j)+\frac{1}{2}\rho\psi+\frac{\kappa_\varphi}{2}|\nabla\varphi|^2\right)dV$$

F	Helmholtz free energy
f_V	Helmholtz free energy per unit volume
φ	phase field
C_j	concentration of species j
ψ	electrostatic potential
$\rho=\sum_N z_j C_j F$	charge density
κ_φ	phase field gradient energy coefficient

Application to Electrochemistry, Jon Guyer at NIST



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 these 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.

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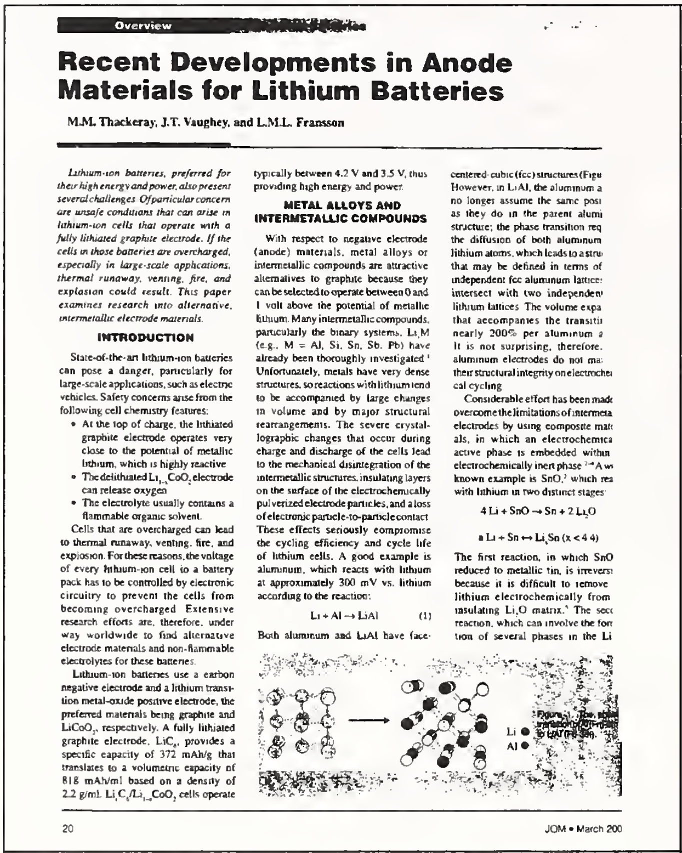


Overview

Recent Developments in Anode Materials for Lithium Batteries

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

Lithium-ion batteries, preferred for their high energy and power, also present several challenges. Of particular concern are unsafe conditions that can arise in lithium-ion cells that operate with a fully lithiated graphite electrode. If the cells in those batteries are overcharged, especially in large-scale applications, thermal runaway, venting, fire, and explosion could result. This paper examines research into alternative, intermetallic electrode materials.

INTRODUCTION

State-of-the-art lithium-ion batteries can pose a danger, particularly for large-scale applications, such as electric vehicles. Safety concerns arise from the following cell chemistry features:

- At the top of charge, the lithiated graphite electrode operates very close to the potential of metallic lithium, which is highly reactive.
- The delithiated $Li_{1-x}CoO_2$ electrode can release oxygen.
- The electrolyte usually contains a flammable organic solvent.

Cells that are overcharged can lead to thermal runaway, venting, fire, and explosion. For these reasons, the voltage of every lithium-ion cell in a battery pack has to be controlled by electronic circuitry to prevent the cells from becoming overcharged. Extensive research efforts are, therefore, under way worldwide to find alternative electrode materials and non-flammable electrolytes for these batteries.

Lithium-ion batteries use a carbon negative electrode and a lithium transition metal-oxide positive electrode, the preferred materials being graphite and $LiCoO_2$, respectively. A fully lithiated graphite electrode, LiC_6, provides a specific capacity of 372 mAh/g that translates to a volumetric capacity of 818 mAh/ml based on a density of 2.2 g/ml. $Li_xC_6/Li_{1-x}CoO_2$ cells operate typically between 4.2 V and 3.5 V, thus providing high energy and power.

METAL ALLOYS AND INTERMETALLIC COMPOUNDS

With respect to negative electrode (anode) materials, metal alloys or intermetallic compounds are attractive alternatives to graphite because they can be selected to operate between 0 and 1 volt above the potential of metallic lithium. Many intermetallic compounds, particularly the binary systems, Li_xM (e.g., M = Al, Si, Sn, Sb, Pb) have already been thoroughly investigated.[1] Unfortunately, metals have very dense structures, so reactions with lithium tend to be accompanied by large changes in volume and by major structural rearrangements. The severe crystallographic changes that occur during charge and discharge of the cells lead to the mechanical disintegration of the intermetallic structures, insulating layers on the surface of the electrochemically pulverized electrode particles, and a loss of electronic particle-to-particle contact. These effects seriously compromise the cycling efficiency and cycle life of lithium cells. A good example is aluminum, which reacts with lithium at approximately 300 mV vs. lithium according to the reaction:

$$Li + Al \rightarrow LiAl \qquad (1)$$

Both aluminum and LiAl have face-centered-cubic (fcc) structures (Figu However, in LiAl, the aluminum a no longer assume the same posi as they do in the parent alumi structure; the phase transition req the diffusion of both aluminum lithium atoms, which leads to a stru that may be defined in terms of independent fcc aluminum lattice: intersect with two independen lithium lattices. The volume expa that accompanies the transiti nearly 200% per aluminum a It is not surprising, therefore, aluminum electrodes do not ma their structural integrity on electroche cal cycling.

Considerable effort has been mad overcome the limitations of intermeta electrodes by using composite mat als, in which an electrochemica active phase is embedded within electrochemically inert phase.[2-4] A w known example is SnO,[5] which rea with lithium in two distinct stages:

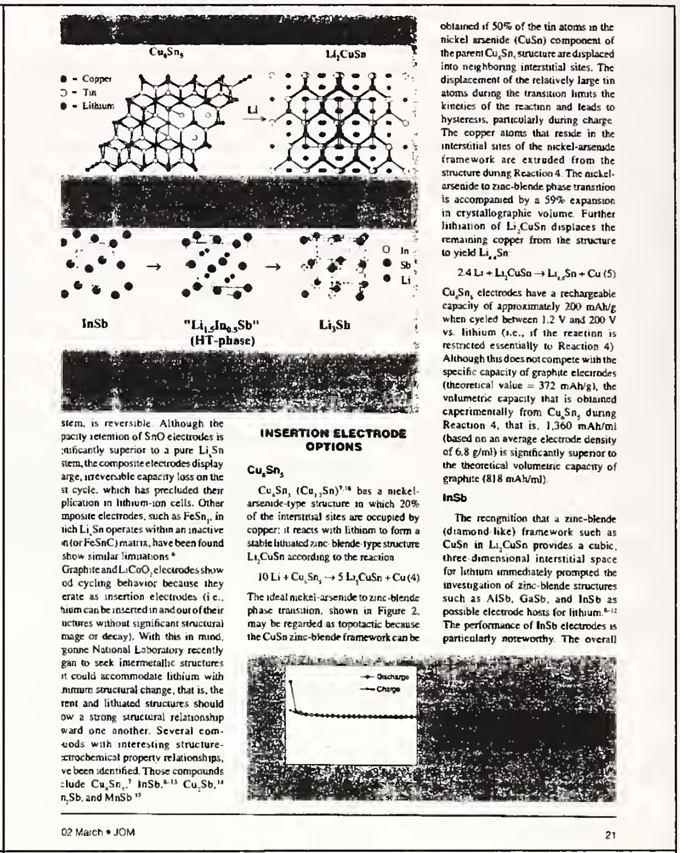
$$4\,Li + SnO \rightarrow Sn + 2\,Li_2O$$

$$x\,Li + Sn \leftrightarrow Li_xSn\ (x < 4.4)$$

The first reaction, in which SnO reduced to metallic tin, is irreversi because it is difficult to remove lithium electrochemically from insulating Li_2O matrix.[5] The seco reaction, which can involve the for tion of several phases in the Li

Li ●
Al ●

Figure 1. [illegible]



Cu$_6$Sn$_5$ Li$_2$CuSn

● - Copper
○ - Tin
● - Lithium

Li

○ In
● Sb
● Li

InSb "Li$_{1.5}$In$_{0.5}$Sb" (HT-phase) Li$_3$Sb

stem, is reversible. Although the pacity retention of SnO electrodes is gnificantly superior to a pure Li_xSn stem, the composite electrodes display arge, irreversible capacity loss on the st cycle, which has precluded their plication in lithium-ion cells. Other mposite electrodes, such as $FeSn_2$, in iich Li_xSn operates within an inactive n (or FeSnC) matrix, have been found show similar limitations.[6]

Graphite and $LiCoO_2$ electrodes show od cycling behavior because they erate as insertion electrodes (i.e., hium can be inserted in and out of their uctures without significant structural mage or decay). With this in mind, gonne National Laboratory recently gan to seek intermetallic structures it could accommodate lithium with nimum structural change, that is, the rent and lithiated structures should ow a strong structural relationship ward one another. Several comuods with interesting structure-ctrochemical property relationships, ve been identified. Those compounds clude Cu_6Sn_5,[7] InSb,[8-13] Cu_2Sb,[14] n_2Sb, and MnSb.[15]

INSERTION ELECTRODE OPTIONS

Cu$_6$Sn$_5$

Cu_6Sn_5 $(Cu_{1.2}Sn)$[7,16] has a nickel-arsenide-type structure in which 20% of the interstitial sites are occupied by copper; it reacts with lithium to form a stable lithiated zinc-blende-type structure Li_2CuSn according to the reaction

$$10\,Li + Cu_6Sn_5 \rightarrow 5\,Li_2CuSn + Cu \quad (4)$$

The ideal nickel-arsenide to zinc-blende phase transition, shown in Figure 2, may be regarded as topotactic because the CuSn zinc-blende framework can be obtained if 50% of the tin atoms in the nickel arsenide (CuSn) component of the parent Cu_6Sn_5 structure are displaced into neighboring interstitial sites. The displacement of the relatively large tin atoms during the transition limits the kinetics of the reaction and leads to hysteresis, particularly during charge. The copper atoms that reside in the interstitial sites of the nickel-arsenide framework are extruded from the structure during Reaction 4. The nickel-arsenide to zinc-blende phase transition is accompanied by a 59% expansion in crystallographic volume. Further lithiation of Li_2CuSn displaces the remaining copper from the structure to yield $Li_{4.4}Sn$:

$$2.4\,Li + Li_2CuSn \rightarrow Li_{4.4}Sn + Cu \quad (5)$$

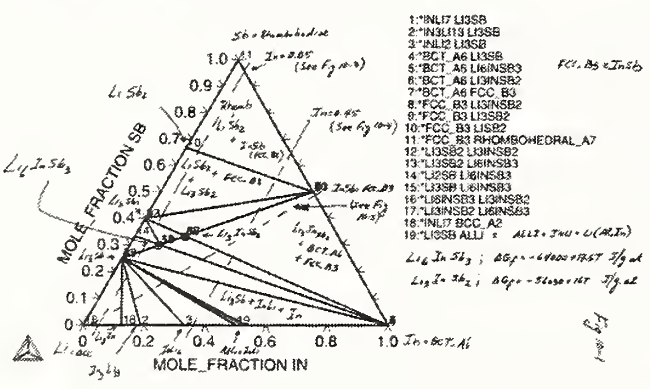
Cu_6Sn_5 electrodes have a rechargeable capacity of approximately 200 mAh/g when cycled between 1.2 V and 200 V vs. lithium (i.e., if the reaction is restricted essentially to Reaction 4). Although this does not compete with the specific capacity of graphite electrodes (theoretical value = 372 mAh/g), the volumetric capacity that is obtained experimentally from Cu_6Sn_5 during Reaction 4, that is, 1,360 mAh/ml (based on an average electrode density of 6.8 g/ml) is significantly superior to the theoretical volumetric capacity of graphite (818 mAh/ml).

InSb

The recognition that a zinc-blende (diamond-like) framework such as CuSn in Li_2CuSn provides a cubic, three-dimensional interstitial space for lithium immediately prompted the investigation of zinc-blende structures such as AlSb, GaSb, and InSb as possible electrode hosts for lithium.[8-12] The performance of InSb electrodes is particularly noteworthy. The overall

—●— Discharge
—— Charge

THERMO-CALC (2001.05.23:23.28) :INLISB3 27 °C



1:*INLI7 LI3SB
2:*IN3LI13 LI3SB
3:*INLI2 LI3SB
4:*BCT_A6 LI3SB
5:*BCT_A6 LI6INSB3
6:*BCT_A6 LI3INSB2
7:*BCT_A6 FCC_B3
8:*FCC_B3 LI3INSB2
9:*FCC_B3 LI3SB2
10:*FCC_B3 LISB2
11:*FCC_B3 RHOMBOHEDRAL_A7
12:*LI3SB2 LI3INSB2
13:*LI3SB2 LI6INSB3
14:*LI2SB LI6INSB3
15:*LI3SB LI6INSB3
16:*LI6INSB3 LI3INSB2
17:*LI3INSB2 LI6INSB3
18:*INLI7 BCC_A2
19:*LI3SB ALLI = ALLI + InLi + Li(Al,In)

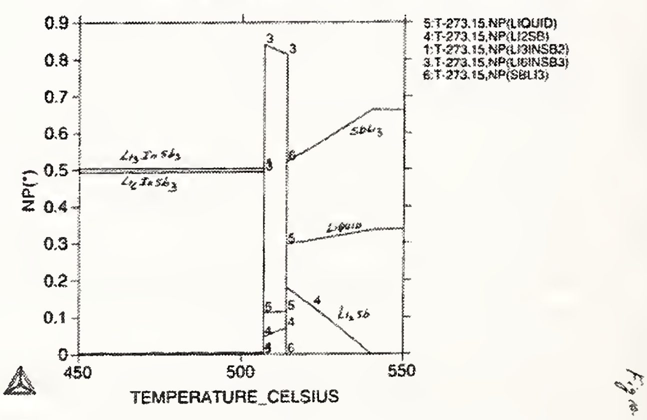
FCC. B3 = InSb

Li_6InSb_3 ; $\Delta G_f = -64000 + 17.5T$ J/g at

Li_3InSb_2 ; $\Delta G_f = -56050 + 14T$ J/g at

Fig 10

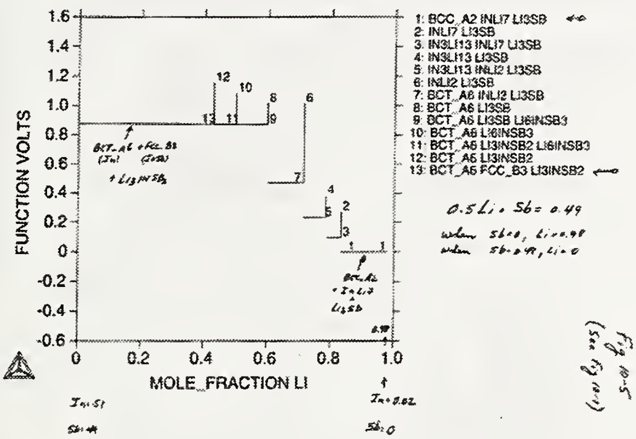
THERMO-CALC (2001.05.21:16.49) :INLISBNP1



5:T-273.15,NP(LIQUID)
4:T-273.15,NP(LI2SB)
1:T-273.15,NP(LI3INSB2)
3:T-273.15,NP(LI6INSB3)
6:T-273.15,NP(SBLI3)

Fig 10-c

THERMO-CALC (2001.05.23:23.08) :IN(LI2SB.98)31



0.5 Li + Sb = 0.49

when Sb = 0, Li = 0.98

when Sb = 0.49, Li = 0

(see fig 10-5)

Stable and metastable evaluation of the Cu-Co-Fe Phase diagrams

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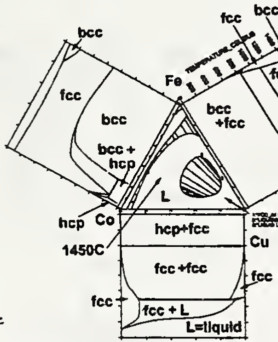
The Thermo-Calc SSOL database for the Cu-Co-Fe ternary system was modified according to experimental data obtained by electromagnetic levitation. Using the modified database, the solidus and the liquidus temperatures were calculated. Very good agreement was obtained between the calculated and the experimental 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)(1,2), namely a large drop in the electrical resistance under the influence of a magnetic field. For example, a supersaturated $Cu_{90}Co_{10}$ 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 decomposion, 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 Co or Fe rich (called L1)(3-6). 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-Fe-Co diagram.

Recently, some experimental data for the melting temperatures were published concerning the Cu-Co-Fe system(11). Based on the Fe-Cu(7,8) and Co-Cu(8,9) binary phase diagrams, approximate isothermal sections have been constructed(10).

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.



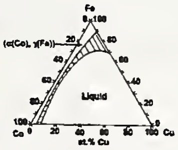


Figure 3) Computed isothermal section at 1400°C in the Cu-Co-Fe system using the modified data-base

L, Fcc

Co = 5000 J/mol

Cu = -80000

Fe = 10000

$x_{Co}x_{Cu}x_{Fe}$

Figure 2a) Computed isothermal section at 1450C surrounded by the edge binary Systems.

Alloy No	Composition in wt.%			Melting Temperature(°C)	
	Cu	Co	Fe	Measured	Calculated
1	95	3	2	1100	1080
2	90	5	5	1120	1205
3	84	8	8	1230	1245
4	80	10	10	1240	1250
5	80	5	15	1300	1310
6	75	10	15	1280	1270
7	72	5	23	1315	1350
8	65	25	10	1280	1280
9	64	18	18	1300	1280
10	60	30	10	1280	1285
11	60	20	20	1320	1290
12	55	30	15	1330	1300
13	55	10	35	1340	1360
14	48	18	34	1340	1380
15	45	37	18	1325	1335
16	38	35	27	1300	1390

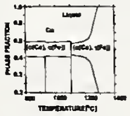
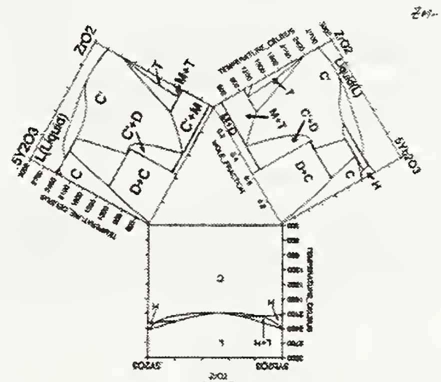
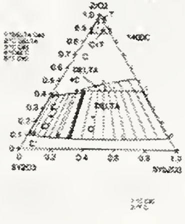


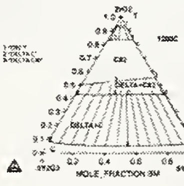
Figure 5) Computed phase formation in a Cu 20 wt. % Co-30 wt. % Fe alloy using the modified database.

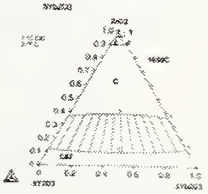
16 NS

2m-4m-8m

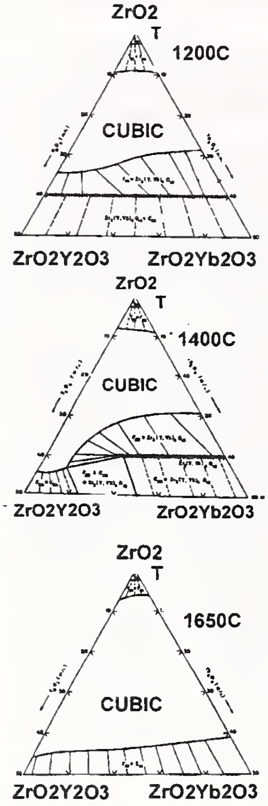




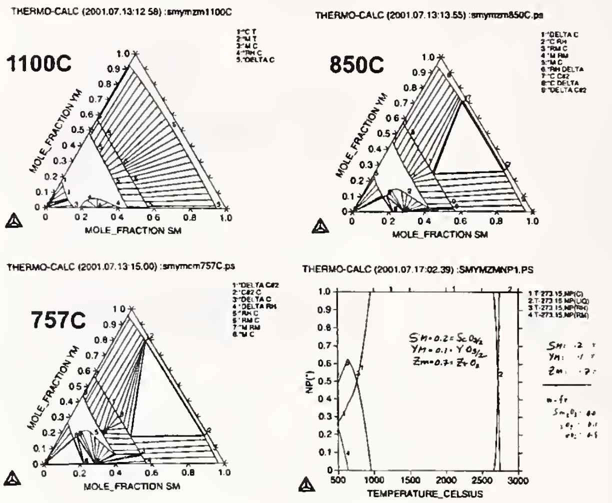




17 NJ
Zn_YM-BM



ZrO2-0.5Y2O3-0.5Sc2O3



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 *at* from 300°*C* to liquidus temperatures. Thermochemical measurements and phase diagram data were used to model the Gibbs free energies of seven phases. Additionally, the ordered interstitial HCP-based solutions were included and considered as simple line compounds. By using the PARROT module in Thermo-Calc, it was possible to optimize the parameters of the models used to describe the Gibbs free energies of the *HCP*, *BCC*, *liquid*, $\gamma\ ZrO_{2-x}$, $\beta\ ZrO_{2-x}$ and $\alpha\ ZrO_{2-x}$ phases. The *Gas* phase was considered to behave ideally. Although phase diagrams including the stoichiometric zirconia phases have been assessed, this is the first time, to the best of our knowledge that a complete assessment of this system is published

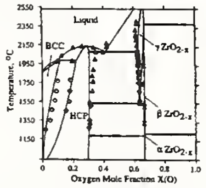


Figure 2: Experimental data vs. calculated phase diagram. Experimental data obtained from [7], [14], [13] and [10]

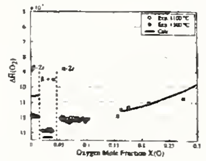


Figure 3. Experimental [17], [16] vs. calculated partial molar enthalpies of oxygen, $\Delta\bar{H}_{O_2}$, within the *BCC*, *BCC/HCP* and *HCP* phase fields

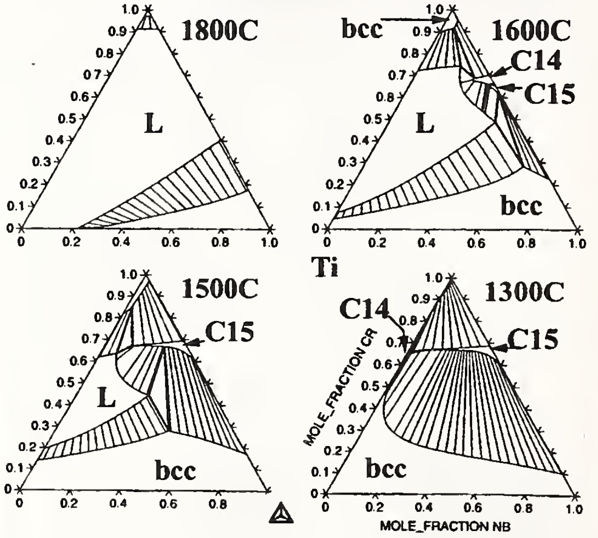


Figure 2. Calculated Isothermal Sections in Nb-Ti-Cr at 1800C, 1600C,1500C and 1300C.Two-Phase Regions are identified by Tie-Lines,Three-Phase Regions by Triangles and Single Phase Regions are labled.

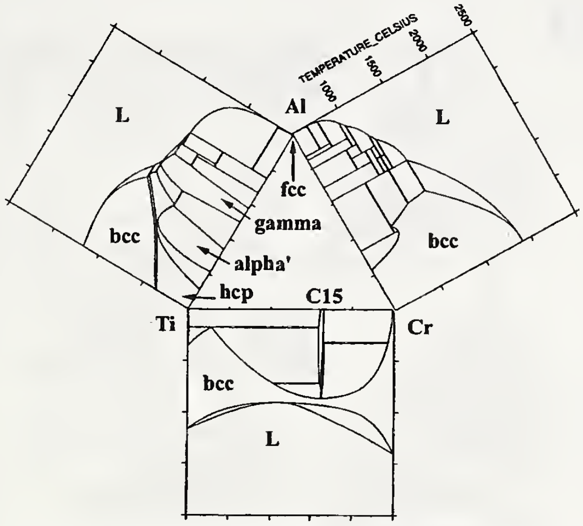


Figure 3.Calculated Binary Phase Diagram Components of the Ti-Al-Cr System.The Liquid Phase is designated by L

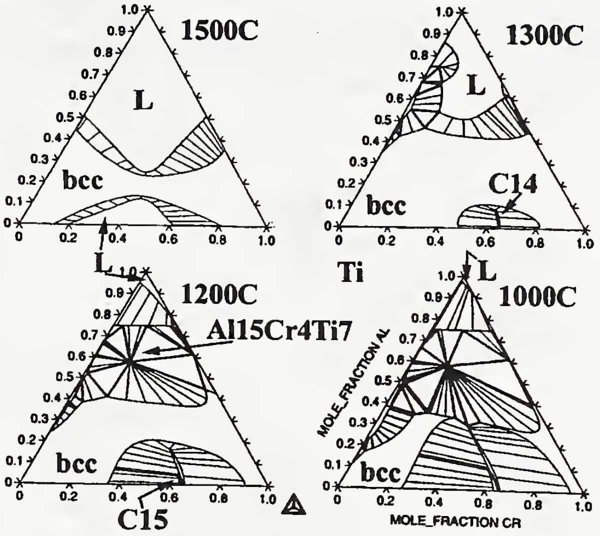


Figure 4. Calculated Isothermal Sections in Ti-Al-Cr at 1500C, 1300C,1200C and 1000C.Two-Phase Regions are identified by Tie-Lines,Three-Phase Regions by Triangles and Single Phase Regions are labled.

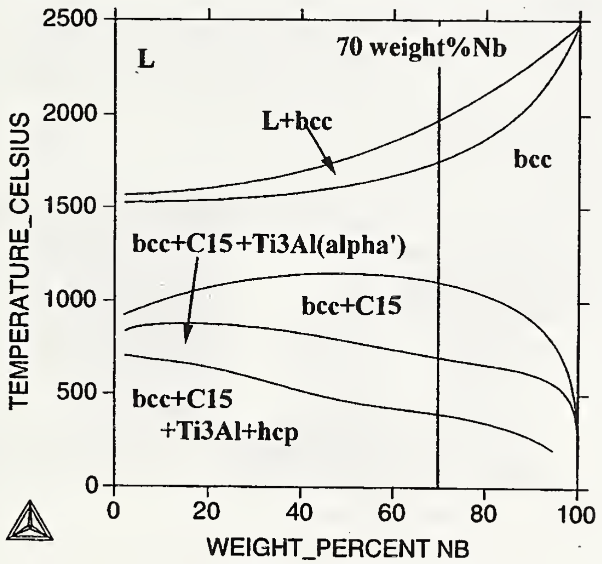


Figure 13.Calculated Isopleth constrained by the Conditions that weight%Cr=4wt.%Al and wt%Ti=3wt%Cr.

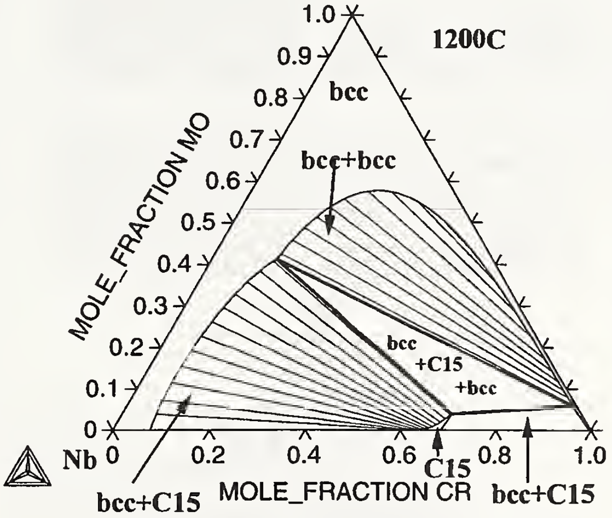
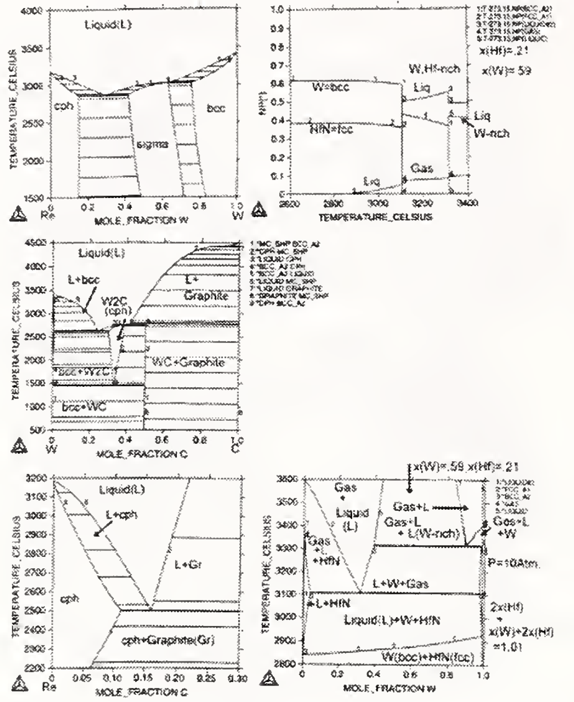
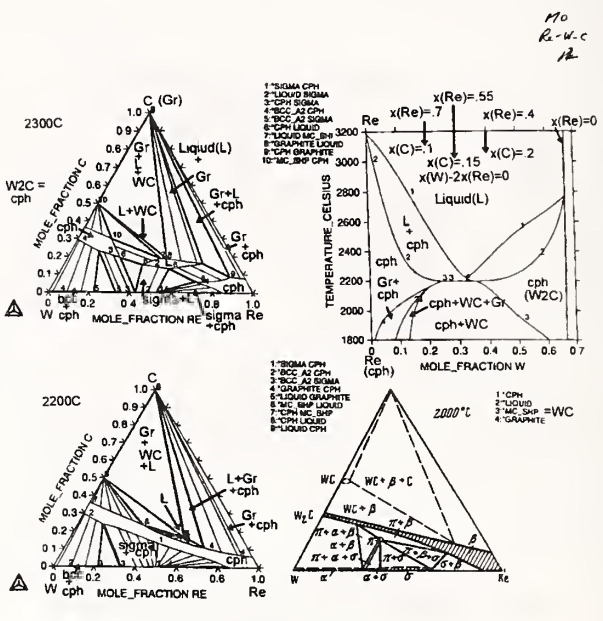


Figure 17.Calculated Isothermal Section in the Nb-Cr-Mo System at 1200C.

Mo II and 15/11
Re-C, Re-W, WC and Hf-W-N



Mo
Re-W-C
12



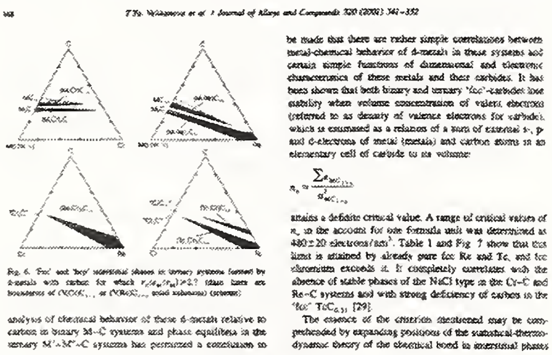

T.Ya. Velikanova et al. / Journal of Alloys and Compounds 320 (2001) 341–352

Fig. 6. 'Fcc' and 'hcp' interstitial phases in ternary systems formed by d-metals with carbon for which [illegible]

analysis of chemical behavior of these d-metals relative to carbon in binary M–C systems and phase equilibria in the ternary M′–M″–C systems has permitted a conclusion to be made that there are rather simple correlations between metal-chemical behavior of d-metals in these systems and certain simple functions of dimensional and electronic characteristics of these metals and their carbides. It has been shown that both binary and ternary 'fcc'-carbides lose stability when volume concentration of valent electrons (referred to as density of valence electrons for carbides), which is estimated as a relation of a sum of external s-, p- and d-electrons of metal (metals) and carbon atoms in an elementary cell of carbide to its volume:

$$n_e = \frac{\sum e_{MC_{1\pm x}}}{a^3_{MC_{1\pm x}}}$$

attains a definite critical value. A range of critical values of n_e in the account for one formula unit was determined as 480±20 electrons/nm³. Table 1 and Fig. 7 show that this limit is attained by already pure fcc Re and Tc, and for chromium exceeds it. It completely correlates with the absence of stable phases of the NaCl type in the Cr–C and Re–C systems and with strong deficiency of carbon in the 'fcc' TcC$_{0.33}$ [29].

The essence of the criterion mentioned may be comprehended by expanding positions of the statistical-thermodynamic theory of the chemical bond in interstitial phases

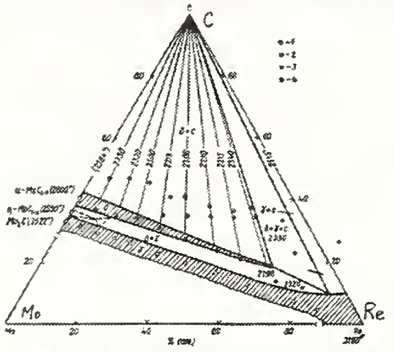
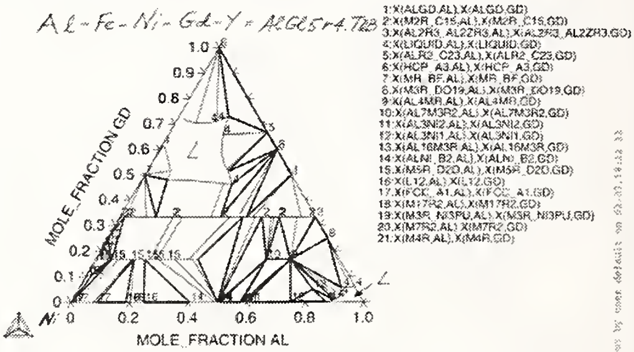


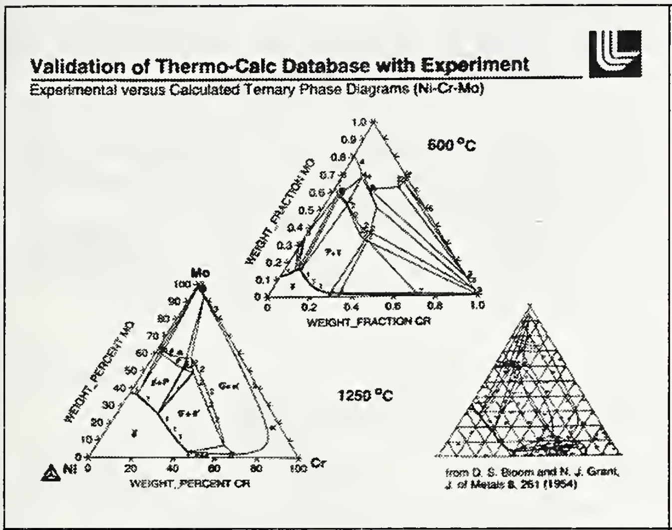
Рис. 4.28. Проекция поверхности солидуса внутренней системы Mo — Re — C в области Mo$_2$C — Re — C [181]:

N Erymenko, T. Ya. Velikanova and A. M. Khartova, Kiev, IPM An USSR 181) pp 3-28

THERMO-CALC (02.03.18:12.33) :algdni107r1.ps = 800°C

Al-Fe-Ni-Gd-Y = AlGd5r4.T2B

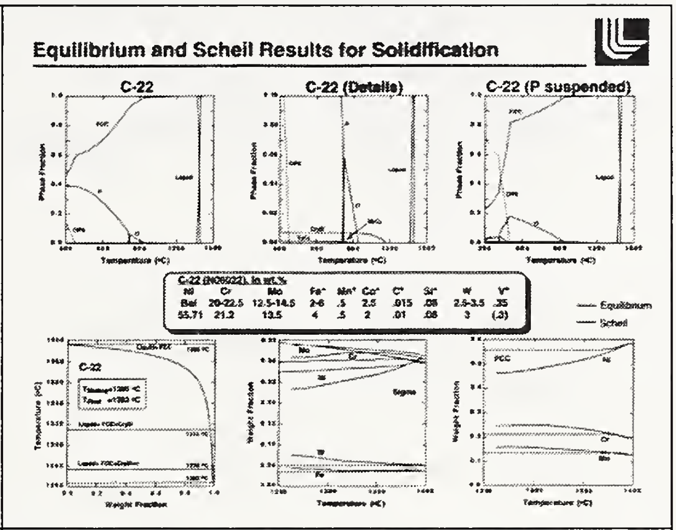




Validation of Thermo-Calc Database with Experiment

Experimental versus Calculated Ternary Phase Diagrams (Ni-Cr-Mo)

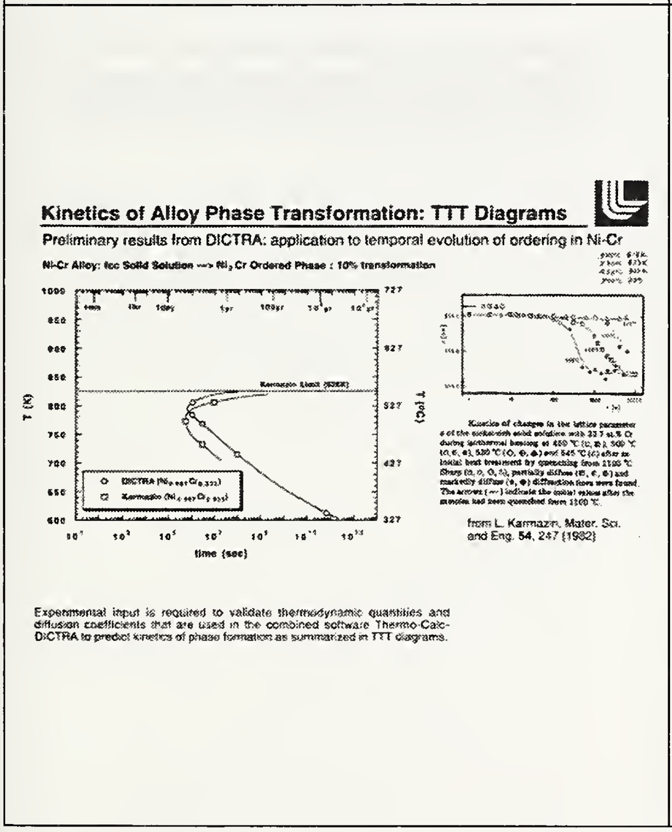
from D. S. Bloom and N. J. Grant, J. of Metals 6, 261 (1954)



Equilibrium and Scheil Results for Solidification

C-22 (N06022), in wt.%

Ni	Cr	Mo	Fe*	Mn*	Co*	C*	Si*	W	V*
Bal	20-22.5	12.5-14.5	2-6	.5	2.5	.015	.08	2.5-3.5	.35
55.71	21.2	13.5	4	.5	2	.01	.08	3	(.3)



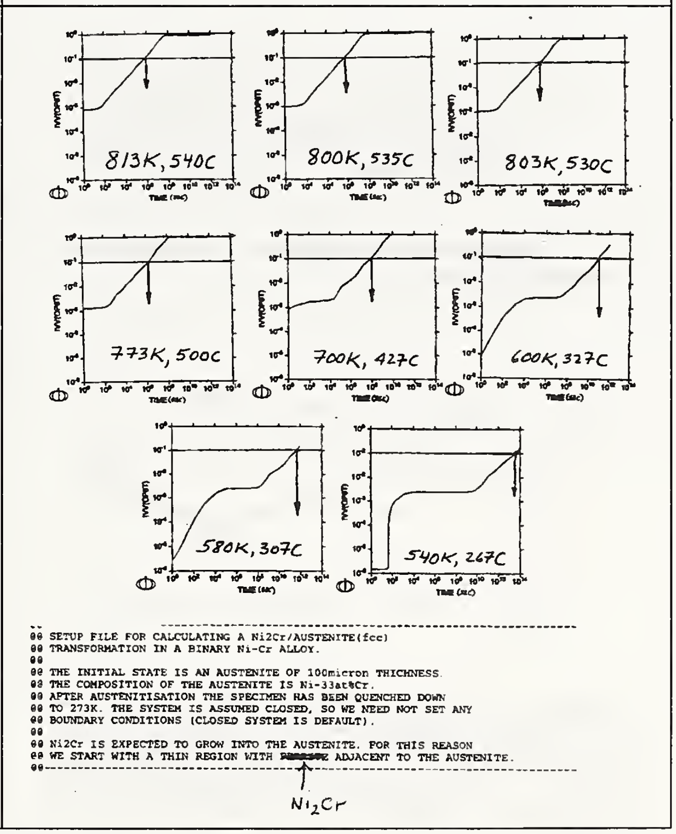
Kinetics of Alloy Phase Transformation: TTT Diagrams

Preliminary results from DICTRA: application to temporal evolution of ordering in Ni-Cr

Ni-Cr Alloy: fcc Solid Solution ---> Ni_2Cr Ordered Phase : 10% transformation

from L. Karmazin, Mater. Sci. and Eng. 54, 247 (1982)

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.



```
@@ SETUP FILE FOR CALCULATING A Ni2Cr/AUSTENITE(fcc)
@@ TRANSFORMATION IN A BINARY Ni-Cr ALLOY.
@@
@@ THE INITIAL STATE IS AN AUSTENITE OF 100micron THICHNESS.
@@ THE COMPOSITION OF THE AUSTENITE IS Ni-33at%Cr.
@@ AFTER AUSTENITISATION THE SPECIMEN HAS BEEN QUENCHED DOWN
@@ TO 273K. THE SYSTEM IS ASSUMED CLOSED, SO WE NEED NOT SET ANY
@@ BOUNDARY CONDITIONS (CLOSED SYSTEM IS DEFAULT).
@@
@@ Ni2Cr IS EXPECTED TO GROW INTO THE AUSTENITE. FOR THIS REASON
@@ WE START WITH A THIN REGION WITH [illegible] ADJACENT TO THE AUSTENITE.
@@------------------------------------------------------------------------
```

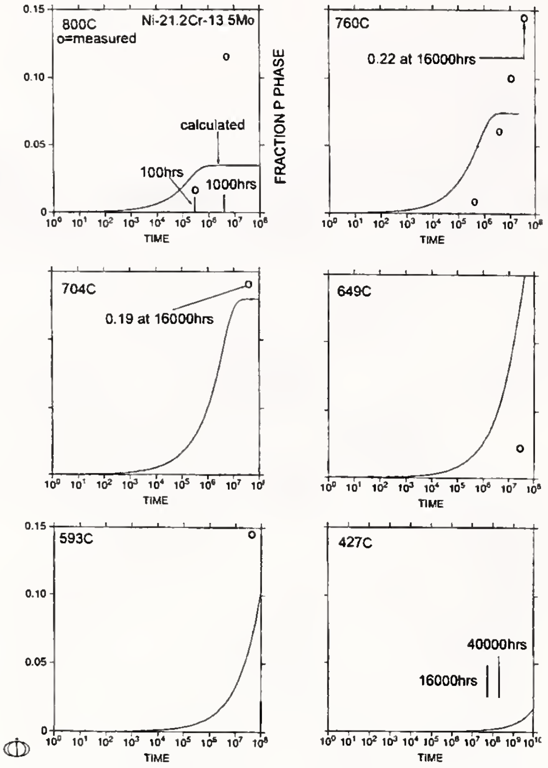


Fig.14 Experimental measurment of TCP phase formation in C-22 by Tammy Summers and Sharon G. Torres compared with calculation of P_Phase formation in a Ni-21.1-13.5Cr Alloy.

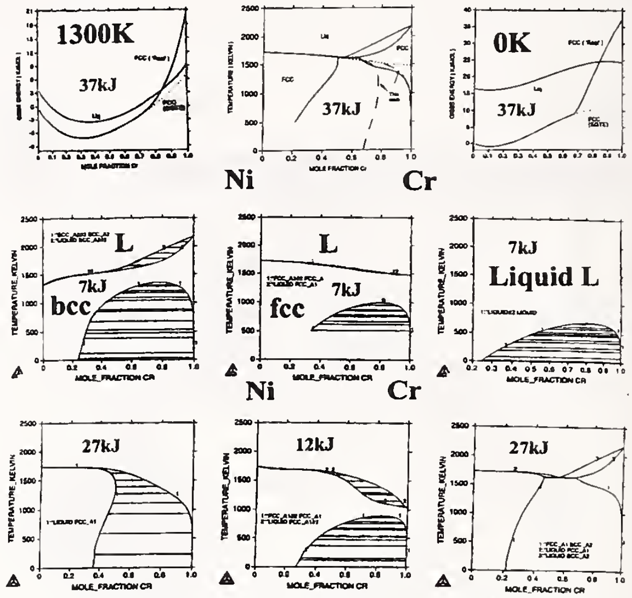
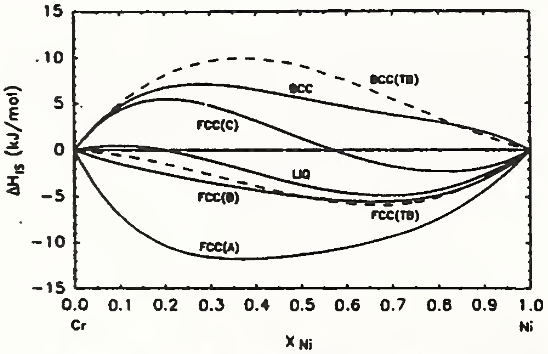


Figure.16 Examination of the stability and phase diagram of the fcc and bcc phases in the Cr-Ni System.Top row(95Cha),Middle row SSOL,Bottom row(01Kau).

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 that the LS values that are employed.Initially(**89Kos,9SCha and 98Gri**) it was suggested that these differences

Isostructural Enthalpies of Formation for the Ni-Cr System



Calculated using the phenomenological (solid lines) and the first-principles TB-CPA (dashed lines) models. Curves (A), (B), and (C) correspond, respectively, to Skriver's (35.56 kJ/mol), an intermediate (23.01 kJ/mol), and Kaufman's (10.46 kJ/mol) values of $H_{\mathrm{Cr}}^{\mathrm{fcc/bcc}}$.

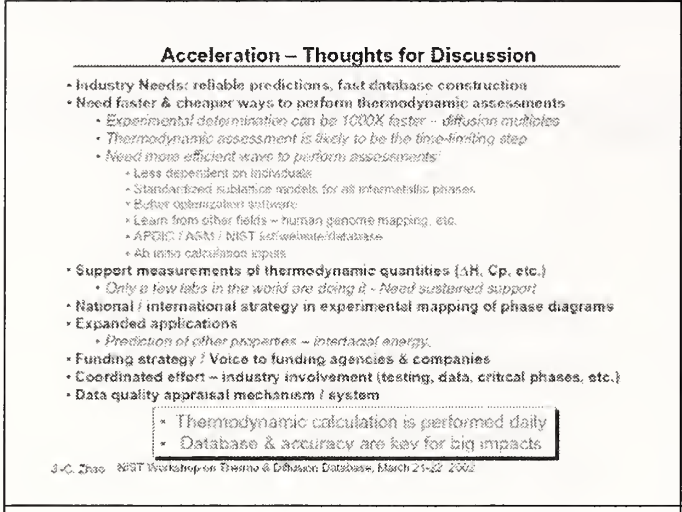
Additional points made by speaker:

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



Acceleration – Thoughts for Discussion

- Industry Needs: reliable predictions, fast database construction
- Need faster & cheaper ways to perform thermodynamic assessments
  - *Experimental determination can be 1000X faster – diffusion multiples*
  - *Thermodynamic assessment is likely to be the time-limiting step*
  - *Need more efficient ways to perform assessments:*
    - Less dependent on individuals
    - Standardized sublattice models for all intermetallic phases
    - Better optimization software
    - Learn from other fields – human genome mapping, etc.
    - APDIC / ASM / NIST1st/website/database
    - Ab initio calculation inputs
- Support measurements of thermodynamic quantities (ΔH, Cp, etc.)
  - *Only a few labs in the world are doing it - Need sustained support*
- National / international strategy in experimental mapping of phase diagrams
- Expanded applications
  - *Prediction of other properties – interfacial energy.*
- Funding strategy / Voice to funding agencies & companies
- Coordinated effort – industry involvement (testing, data, critical phases, etc.)
- Data quality appraisal mechanism / system

- Thermodynamic calculation is performed daily
- Database & accuracy are key for big impacts

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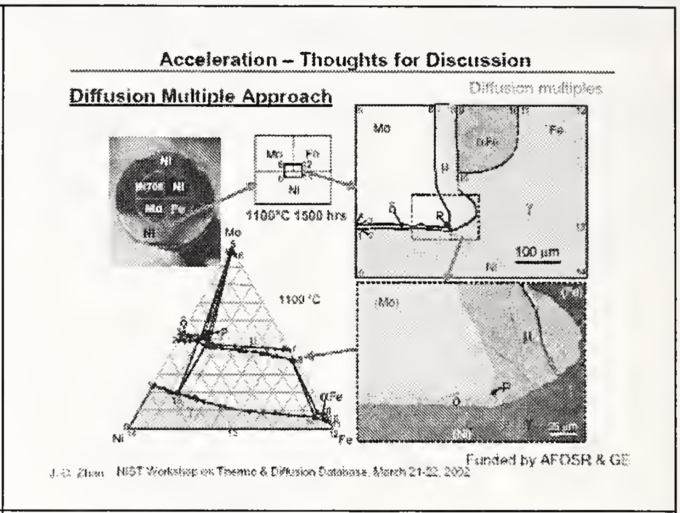

Acceleration – Thoughts for Discussion

Diffusion Multiple Approach

Diffusion multiples

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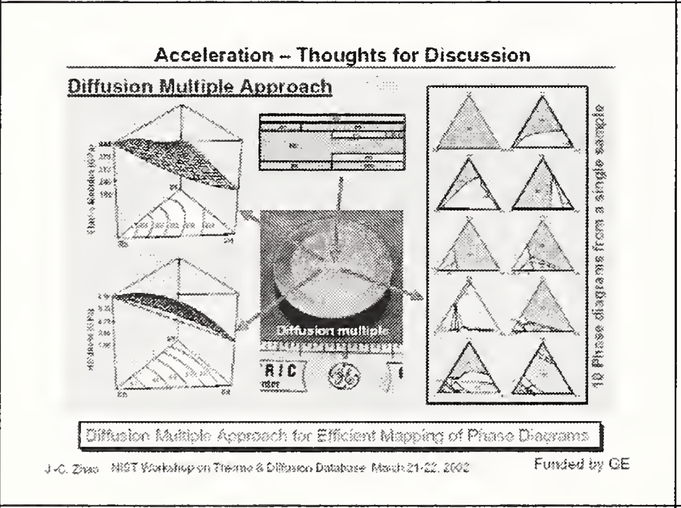

Acceleration – Thoughts for Discussion

Diffusion Multiple Approach

Diffusion Multiple Approach for Efficient Mapping of Phase Diagrams

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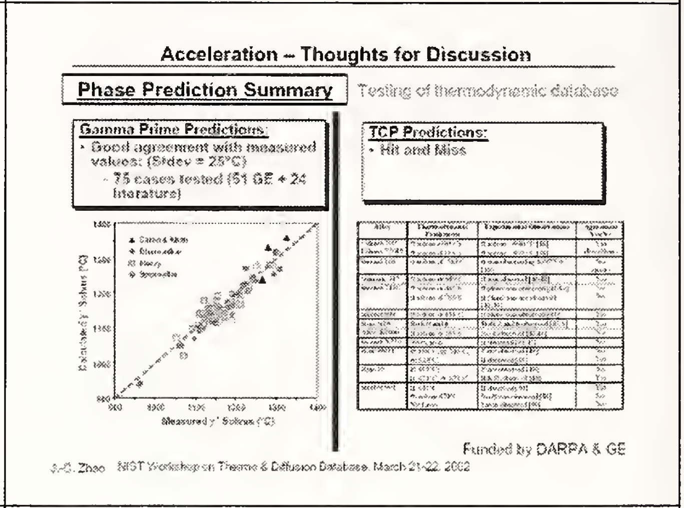

Acceleration – Thoughts for Discussion

Phase Prediction Summary

Testing of thermodynamic database

Gamma Prime Predictions:
- Good agreement with measured values: (Stdev = 25°C)
  - 75 cases tested (51 GE + 24 literature)

TCP Predictions:
- Hit and Miss

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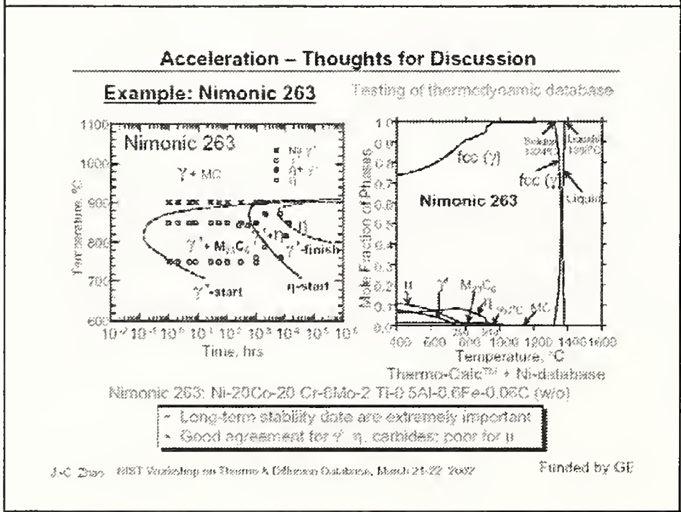

Acceleration – Thoughts for Discussion

Example: Nimonic 263

Testing of thermodyamic database

Thermo-Calc™ + Ni-database

Nimonic 263: Ni-20Co-20 Cr-6Mo-2 Ti-0.5Al-0.6Fe-0.06C (w/o)

- Long-term stability data are extremely important
- Good agreement for γ', η, carbides; poor for μ

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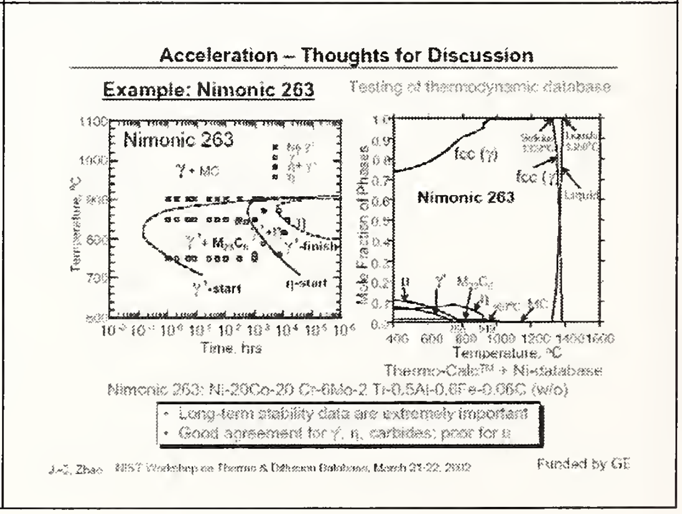

Acceleration – Thoughts for Discussion

Example: Nimonic 263

Testing of thermodynamic database

Thermo-Calc™ + Ni-database

Nimonic 263: Ni-20Co-20 Cr-6Mo-2 Ti-0.5Al-0.6Fe-0.06C (w/o)

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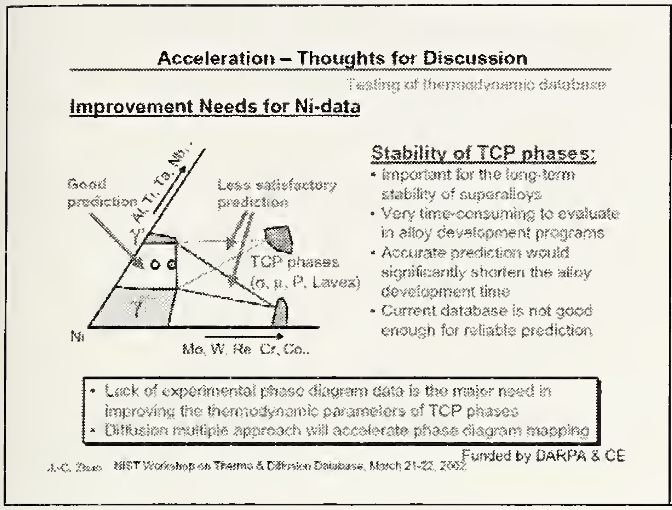

Acceleration – Thoughts for Discussion

Testing of thermodynamic database

Improvement Needs for Ni-data

Stability of TCP phases:
- Important for the long-term stability of superalloys
- Very time-consuming to evaluate in alloy development programs
- Accurate prediction would significantly shorten the alloy development time
- Current database is not good enough for reliable prediction

- Lack of experimental phase diagram data is the major need in improving the thermodynamic parameters of TCP phases
- Diffusion multiple approach will accelerate phase diagram mapping

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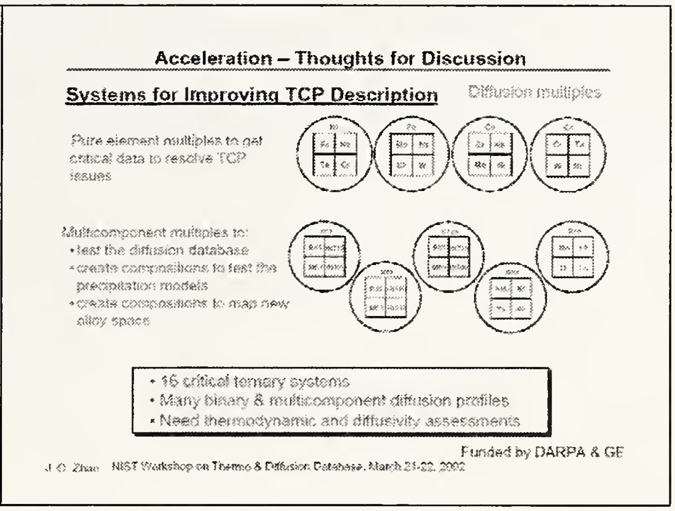

Acceleration – Thoughts for Discussion

Systems for Improving TCP Description

Diffusion multiples

Pure element multiples to get critical data to resolve TCP issues

Multicomponent multiples to:
- test the diffusion database
- create compositions to test the precipitation models
- create compositions to map new alloy space

- 16 critical ternary systems
- Many binary & multicomponent diffusion profiles
- Need thermodynamic and diffusivity assessments

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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.