



be developed. The current research will combine the Nano- and Micro-scale Inclusion Nucleation and Growth Phenomena with the Macro-scale Flow Pattern and Inclusion Transport.

## Computational Thermodynamics and Phase Transformations: First Principles and Atomistic Calculations of Phase and Alloy Thermodynamics II

*Sponsored by:* The Minerals, Metals and Materials Society, ASM International, TMS Electronic, Magnetic, and Photonic Materials Division, TMS Materials Processing and Manufacturing Division, ASM Materials Science Critical Technology Sector, TMS: Chemistry and Physics of Materials Committee, TMS/ASM: Computational Materials Science and Engineering Committee

*Program Organizers:* Corbett Battaile, Sandia National Laboratories; James Morris, Oak Ridge National Laboratory

Monday PM                      Room: Europe 11  
February 26, 2007              Location: Dolphin Hotel

*Session Chair:* Hamish Fraser, Ohio State University; Anton Van der Ven, University of Michigan

### 2:00 PM Invited

**Kinetics of Phase Transformations from First Principles:** *Anton Van der Ven*<sup>1</sup>; <sup>1</sup>University of Michigan

While much progress has been made in the first-principles prediction of the thermodynamics of multi-component solids, predicting the kinetics of solid-state phase transformations remains a major challenge. A large class of phase transformations in multi-component solids involves a redistribution of its constituents, which requires atomic diffusion. First-order phase transformations also require the passage of interfaces separating new phases from old phases. One approach to simulate first-order diffusional phase transformations from first-principles is through parameter passing, whereby kinetic coefficients describing atomic diffusion and interface mobilities are implemented in a continuum description. In this talk, I will describe first-principles approaches to predict diffusion coefficients in multi-component solids and focus on a class of first-order phase transformations in intercalation compounds and metal hydrides in which the moving interface is coherent and migrates through dislocation glide.

### 2:30 PM Invited

**Precipitation in Al-Mg-Si from First-Principles:** *Christopher Wolverton*<sup>1</sup>; Yi Wang<sup>2</sup>; Chinnappan Ravi<sup>3</sup>; Hui Zhang<sup>2</sup>; Tao Wang<sup>2</sup>; Long Qing Chen<sup>2</sup>; Zi-Kui Liu<sup>2</sup>; <sup>1</sup>Ford Motor Company; <sup>2</sup>Pennsylvania State University; <sup>3</sup>Indira Gandhi Centre for Atomic Research

Precipitation in Al-Mg-Si alloys has been extensively studied, since this ternary forms the basis of a wide variety of commercial alloys (e.g., 6xxx series alloys). The observed precipitation sequence is complex and involves a wide variety of metastable phases (e.g., GP zones,  $\beta''$ ,  $\beta'$ ). We have undertaken an extensive first-principles study of many key precipitate properties: T=0 energetics and crystal structures, vibrational entropies, interfacial structure and energies, and lattice-mismatch and coherency strain energies. By incorporating these first-principles results into CALPHAD databases, we can predict the metastable phase equilibria and phase fractions of precipitate phases in a wide variety of 6xxx alloys. Interfacial and strain energies can be used to elucidate the key factors in controlling the morphologies of precipitates in this system, and we incorporate these energetics in phase-field models and predict the resulting precipitate shapes.

### 3:00 PM

**Stress Anisotropy Controls Pathway of Martensitic Transformation in Titanium:** *Richard Hennig*<sup>1</sup>; Dallas Trinkle<sup>2</sup>; <sup>1</sup>Cornell University; <sup>2</sup>University of Illinois Urbana-Champaign

The pressure-driven martensitic phase transformation in titanium from the ductile hcp to the brittle omega phase can limit titanium's mechanical properties. Under hydrostatic stress conditions this phase transition proceeds via a six-atom pathway with an energy barrier of 9 meV/atom. Ab-initio calculations characterize how non-hydrostatic stresses affect the transformation barriers

of the two lowest-energy pathways and show under which conditions the anisotropic stresses result in a change of transformation pathway. The results indicate that the two orientation relationships observed in diamond anvil and shock experiments are caused by different stress conditions.

### 3:20 PM

**On Some Aspects of Phase Transitions in Mechanically Driven Alloys:** *Jong Lee*<sup>1</sup>; <sup>1</sup>Michigan Technological University

An interesting feature observed in mechanical alloying is temporal oscillations in phase fractions. For example, the microstructure of a binary Ni-Zr alloy is shown to vary cyclically between a crystalline and an amorphous state. In our earlier work, such cyclical phase transitions were described in terms of a thermodynamic model which shows a time-dependent free energy function. In this work, we present non-equilibrium molecular dynamics (NEMD) results. For a model Ni-Zr alloy, both compressive and shearing deformation modes are applied to mimic a ball milling process. Atomic interactions are expressed through a many-body, tight-binding as well as a Lennard-Jones potential. Both compressive and shearing deformation modes display amorphization from the homogeneous, elastically deformed crystalline state at high strain rates. Shearing deformation, however, is shown to be much more effective for phase transitions, forming a 2-dimensional layered structure at high shear strain rates.

### 3:40 PM Break

### 4:00 PM Invited

**Reliable First-Principles Prediction of Alloy Thermodynamic Characterization Data via Cluster Expansion Methods:** *Duane Johnson*<sup>1</sup>; Teck Tan<sup>1</sup>; N. Zarkevich<sup>1</sup>; <sup>1</sup>University of Illinois

Using cluster expansion (CE) techniques and a database of structural formation energies from first-principles electronic-structure calculations, we predict phase stability and structural phase transformations in multicomponent alloys. We present results from our automated thermodynamic toolkit (TTK) that controls all facets of the CE fitting and density-functional calculation and includes two methods for constructing CE basis sets: our published optimal truncation method and a genetic algorithm method that uses a niching algorithm to prevent solution stagnation, where reliability from these approaches can be estimated. We then show that there are two mean-field limits that permit rapid and accurate estimates of concentration-dependent order-disorder transformations without Monte Carlo, with the appropriate limiting choice determined a priori by the CE interactions. We exemplify these various results in a number of alloy systems, including combining defect calculations with elasticity theory to establish design maps for improving materials properties.

### 4:30 PM Invited

**The Tensorial Cluster Expansion:** *Axel van de Walle*<sup>1</sup>; <sup>1</sup>California Institute of Technology

While the cluster expansion formalism is traditionally used to parametrize the configurational-dependence of scalar properties (such as the total energy), this talk introduces a generalization of this formalism to tensorial quantities (such as elastic constants, phase-transformation-induced strains, permanent dielectric dipoles, etc). This new method generates a suitable orthogonal basis for the space of all mappings from lattice configurations to tensors. It also provides symmetry rules to determine which terms in the Tensorial Cluster Expansion are equivalent by symmetry and must therefore share a common coefficient. The proposed framework encompasses, as special cases, a number of existing tools, including the local cluster expansion (used for modeling the properties of point defects), the "symmetrized" cluster expansions (used for predicting tensorial properties of disordered phases), and transferable force constants (used for efficient lattice dynamics calculations). This formalism also provides a simple language to describe the coupling between symmetry-breaking phase transformations and materials properties.

### 5:00 PM

**Using Multi-Body Energy Expansions from Ab Initio Calculations for Computation of Alloy Phase Structures:** *Nicholas Zabaras*<sup>1</sup>; *Veera Sundararaghavan*<sup>1</sup>; <sup>1</sup>Cornell University

Cluster expansion methods (CEM) are quite successful for modeling energies of substitutional and interstitial alloys. However, in alloys involving constituents with large size differences, structural relaxations play an important role and convergence properties of the CEM diminish. In such cases, long-ranged and many-body interactions are necessary to model the

energy accurately. We construct such many-body expansion through statistical learning over a very large database of ab-initio energies. Modern regression and cross validation techniques allow efficient handling of the continuous degrees of freedom in the expression for N-body potentials and ensure optimal selection of parameters for convergence of the expansion. This approach provides a more realistic energy functional for use in MC simulations of thermodynamic properties of alloy systems. As an improvement over the cluster expansion method, the methodology enables identification of stable phase structures that do not fall within the superstructures of FCC, HCP or BCC parent lattices.

#### 5:20 PM

**Vibrational Thermodynamics of Vanadium Alloys:** *Oliver Delaire*<sup>1</sup>; Max Kresch<sup>1</sup>; Matthew Lucas<sup>1</sup>; Tabitha Swan-Wood<sup>1</sup>; Brent Fultz<sup>1</sup>; <sup>1</sup>California Institute of Technology

We investigated the effects of alloying on the lattice dynamics and electronic structure of bcc vanadium. Using inelastic neutron scattering, we have measured the phonon density of states and vibrational entropy of random solid solutions of vanadium with transition metal impurities. The effect of alloying on the phonon DOS is thermodynamically significant, comparable in magnitude to the configurational entropy of mixing. A clear trend was observed for solutes across the 3d-series, and down the Ti, V and Ni columns. Using density functional theory, we calculated the geometry and electronic structure for the alloys, and computed the stiffness of certain vibrational modes. The electronic entropy of alloying was calculated and found to follow the same trend as the vibrational entropy, although it is smaller in magnitude. Experimental investigations of the phonon DOS were also conducted on concentrated V-Cr alloys and Al<sub>5</sub>V-based compounds.

## Diffusion in Advanced Materials and Processing: Interfaces, Surfaces and Nanostructures

*Sponsored by:* The Minerals, Metals and Materials Society, TMS Structural Materials Division, ASM Materials Science Critical Technology Sector, TMS: Alloy Phases Committee, TMS: High Temperature Alloys Committee, ASM-MSCTS: Atomic Transport Committee, TMS/ASM: Nuclear Materials Committee, TMS: Solidification Committee

*Program Organizers:* Yong-Ho Sohn, University of Central Florida; Carelyn Campbell, National Institute of Standards and Technology; Daniel Lewis, Rensselaer Polytechnic Institute; Afina Lupulescu, Union College

Monday PM Room: Europe 2  
February 26, 2007 Location: Dolphin Hotel

*Session Chairs:* Graeme Murch, University of Newcastle; Yuri Mishin, George Mason University

#### 2:00 PM Invited

**Growth Kinetics on Nanoscale: Finite Diffusion Permeability of Interfaces:** *Dezso Beke*<sup>1</sup>; Zoltán Erdélyi<sup>1</sup>; <sup>1</sup>University of Debrecen

Growth kinetic is either diffusion or interface reaction controlled process, characterized by parabolic or linear relationships, respectively. The well known diffusion paradox, predicting infinitely fast diffusion kinetics at short times (distances) for diffusion control will be discussed and resolved, by showing that the diffusion permeability across the interface should be finite at the very beginning of the process. Thus one can arrive at an *atomistic interpretation of the interface transfer coefficient, K*, and at *linear growth kinetics* even if there is no extra potential barrier present at the interface, usually assumed in the interpretation of interface reaction control. It is also shown that this phenomenon is a typical nanoeffect: after a certain diffusion distance (lying between 0.01 and 300 nm, depending on the composition dependence of the diffusion coefficient) the finite permeability of the interface will not restrict the growth and normal diffusion control will be observed.

#### 2:30 PM

**Diffusion Mechanisms in Nanocrystalline and Nanolaminated Au-Cu:** *Alan Jankowski*<sup>1</sup>; <sup>1</sup>Lawrence Livermore National Laboratory

The development of pulsed electro-deposition leads to the synthesis of Au-Cu alloys (0-20 wt.% Cu) with grain sizes less than 5 nm. However,

the nanocrystalline grain structure is thermally unstable. Anneal treatments are used to identify the temperature range of the two dominant diffusion mechanisms – bulk and grain boundary. To assess the transition between mechanisms, the low temperature range for bulk diffusion is established utilizing the decay of static concentration waves in composition-modulated nanolaminates. A transition in the dominant mechanism for grain growth from grain boundary to bulk diffusion occurs with an increase in temperature. The activation energy for bulk diffusion is found to be 1.8 eV/atom whereas that for grain growth at low temperatures is only 0.2 eV/atom. The temperature for transitioning from the dominant mechanism of grain boundary to bulk diffusion is found to be dependent on composition, generally trending at 57% the alloy melt temperature.

#### 2:50 PM

**Modeling of Oxygen Diffusion and Segregation at Interfaces in Ag-MgO Composites:** Thomas Fiedler<sup>1</sup>; Nilindu Muthubandara<sup>2</sup>; Andreas Ochsner<sup>1</sup>; *Irina Belova*<sup>2</sup>; Graeme Murch<sup>2</sup>; <sup>1</sup>University of Aveiro; <sup>2</sup>University of Newcastle

The presence of atomic oxygen at internal metal-ceramic oxide interfaces significantly affects the physical properties of the interfaces which in turn affects the bulk properties of the composite (metal+ceramic oxide) material. We address this problem for the conditions of a constant source of oxygen at the surface(s) and various periodic and random arrangements of ceramic oxide inclusions (MgO) embedded in the metal matrix Ag. With experimentally determined atomic transport quantities we simulate the concentration depth profiles and segregation of oxygen to the interfaces using independent Monte Carlo and Finite Element methods.

#### 3:10 PM

**Stability and Shrinkage by Diffusion of Hollow Nanospheres:** Alexander Evteev<sup>1</sup>; Elena Levchenko<sup>1</sup>; *Irina Belova*<sup>1</sup>; *Graeme Murch*<sup>1</sup>; <sup>1</sup>University of Newcastle

Recently, hollow nanospheres of cobalt selenide and cobalt sulphide have been formed from cobalt nanocrystals in Se or S environments (Y. Yin et al. Science Vol.304 ,p711 (2004)). The process of formation is believed to be driven by interdiffusion with an extreme Kirkendall effect as Co is replaced by incoming vacancies. There has been considerable interest in the stability of hollow nanospheres compared with the corresponding solid nanospheres. Using Molecular Dynamics we have analyzed single metallic systems exemplified by Pd. We found that small hollow nanospheres (up to about 10 000 atoms) collapsed quickly, but not by classical vacancy-assisted mechanisms, but by mechanisms involving Shockley partial dislocations. For larger systems, too much energy appears to be required for such mechanisms, and the collapse is mediated by the usual vacancy mechanism.

#### 3:30 PM Break

#### 3:50 PM Invited

**Diffusion along Dislocation Cores in Metals:** G. Pun<sup>1</sup>; *Y. Mishin*<sup>1</sup>; <sup>1</sup>George Mason University

Diffusion along dislocations can control the kinetics of many processes in materials, including coarsening of disperse particles, dislocation bypass, dynamic strain ageing, creep and sintering. The amount of experimental data on dislocation diffusion is very limited and theoretical understanding of the relevant atomic mechanisms is rudimentary, if existent. We give a brief overview of current knowledge of dislocation diffusion and discuss possible approaches to the modeling of this process on the atomic level. Results of atomistic simulations of dislocation diffusion in Al, Ni, and Ni-Al alloys are presented. The simulations reveal the dominant atomic mechanisms and point to the nearly equal role of vacancies and interstitials. The effect of solute interaction with the dislocation core on the rates of solute and solvent diffusion is examined for edge, screw and mixed dislocations in Al. The impact of this work on understanding of diffusion kinetics in plastically deformed materials is discussed.

#### 4:20 PM

**Anomalous Diffusion along Interfaces in Crystalline Solids:** *Raghavan Narayanan*<sup>1</sup>; Alexander King<sup>1</sup>; <sup>1</sup>Purdue University

It is often neglected that Fick's law depends on a particular set of assumptions concerning the nature of Einstein's random walk theory. We elucidate the conditions under which Fick's diffusion law can be applied to a