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MATERIALS BY DESIGN

A HIERARCHICAL APPROACH TO THE DESIGN OF NEW MATERIALS

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MATERIALS BY DESIGN A HIERARCHICAL APPROACH TO THE DESIGN OF NEW MATERIALS

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ABSTRACT

Major developments in materials characterization instrumentation over the past decade have helped significantly to elucidate complex processes and phenomena connected with the microstructure of materials and interfacial interactions. Equally remarkable advances in theoretical models and supercomputers also have been taking place during this period. These latter now permit, for example, in selected cases the computation of material structures, bonding and the prediction of some material properties. Two assessments of the state-of-the-art of instrumental techniques and theoretical methods for the study of material structures and properties have recently been conducted. This paper will discuss aspects of computational theoretical methods applied to materials from these assessments. In addition, an approach will be presented which uses advanced instrumentation and complementary theoretical computational techniques in tandem in an effort to construct and verify hierarchies of models to translate engineering materials performance requirements into microscopic and atomic level materials specifications (composition, structure and bonding). Areas of practical interest include: catalysis, tribology (contacting surfaces in relative motion), protective coatings and metallurgical grain boundaries. A first attempt involving modeling of grain boundary adhesion in Ni_3Al will be discussed.

INTRODUCTION

The concept of using a hierarchy of structural models to design materials is based upon the presumption that the properties exhibited by a material ultimately can be causally related to and based upon the composition, structure (including defects) and bonding in the assembly of atoms of which a material is composed. It is of interest, therefore, to determine how such relationships may be established to permit a priori design of materials. This paper outlines an approach and gives a synopsis of two recent studies which address various aspects of the state of our knowledge in constructing models to establish these linkages among composition, structure, bonding and materials properties at the most fundamental levels (electronic, atomic/ molecular) of the hierarchy. An outline of some research needed to achieve the objective of materials-by-design through such hierarchies also is presented.

MATERIALS-BY-DESIGN - DEFINITION AND HIERARCHY OF MODELS

Materials-by-design (MBD) can be defined as the use of scientific principles to predict materials properties and performance characteristics. In this age of computers, scientific principles, more often than not, are expressed in terms of computational models having predictive capabilities. Accordingly, for the purpose of designing a priori new materials for specific

functions, it is useful to conceive of a hierarchy of models which can relate the performance characteristics of a material to its structural features. Figure 1 shows such a conceptual hierarchy; this also could be called an "expert system" because the models embody the knowledge and judgement of many kinds of experts across the many fields of knowledge needed to form the hierarchy. Some materials related disciplines whose knowledge is required for MSD are indicated along the ordinate in Figure 1. It should be noted also that the size of features modeled declines as one proceeds down the hierarchy from right to left. Microscopic level models include microstructural, atomic/molecular and electronic.

Examples of systems performance models are CAD/CAM models for performance desired, say, from an automobile engine. This desired engine performance implies materials requirements and properties such as high temperature capability. The desired material performance capabilities imply certain types of materials (e.g. ceramic, metal alloy) and other properties (ductility, corrosion resistance) determined by microstructure. Ultimately, the description of the material properties can be reduced to the two lowest levels of the hierarchy viz. atomic/molecular level simulations and electronic structure. It is the state of the art of the models at these latter two levels of the hierarchy which have been the subject of the two recent assessments ^{1,2}, which are being summarized here.

The concept of designing materials is not new. Zener³ refers to the design of a "new high-temperature alloy for steam turbines" as early as 1956 and von Hippel⁴ wrote eloquently of the quest to design new materials in 1962. However, four major developments over the past fifteen years are resulting in the historic convergence of theory and experiment at these two lowest levels in the hierarchy. These developments are: 1) advances in electronic and atomic/molecular level theoretical computational methods (and associated software), 2) computer architectures suitable for mapping onto the mathematical formulation of physical phenomena (e.g. approximating solutions to second order non-linear partial differential equations via the matrix-eigenvalue mathematical formulation), 3) developments in solid-state electronic devices and 4) proliferation of new, more powerful materials characterization instrumentation. It is this historical convergence which is new and these developments taken together give us confidence that at long last we are on the verge of being able to design new materials to meet the future needs of our civilization.

Theoretical models can provide: 1) complementary information or insights unobtainable by experiment (as, for example, information on short lived species); 2) scientific as opposed to heuristic foundation for design efforts; 3) framework to guide design and 4) methods for prescreening and testing of design prior to experimental verification. Here it is well to reemphasize the complementarity of theoretical techniques to experimental methods as opposed to the displacement of experiment by theory.

SOME TECHNOLOGIES OF INTEREST

Three technological areas were addressed by one study ² as being of particular interest for treatment by microscopic computational structural models: heterogeneous catalysis, tribological phenomena (lubrication and wear), and material interfaces e.g. bonding of solid coatings to solid substrates, and interactions involved in grain boundary adhesion. The fundamental mechanisms describing phenomena of interest in all three of these areas are: defect stability/ movement, physisorption, chemisorption, surface reactivity, interfacial bonding (adhesion), intermolecular bonding and electron transfer at surfaces.

These fundamental mechanisms, in turn, can be described by the electronic states and geometrical configurations of the atoms and molecules during the various stages of the process of interest and, as such, these mechanisms are amenable to being simulated by models at the electronic and atomic/molecular levels of the hierarchy.

ELECTRONIC AND ATOMIC/MOLECULAR LEVEL SIMULATION MODELS

TABLE I shows an outline of the two lowest levels of microscopic computer simulation techniques (electronic level calculations and atomic/molecular level simulations), the scientific disciplines generally involved in their development and the relationship of the electronic level to the atomic/molecular level models.

Electronic level calculations are computations in which the "electron locations" (more correctly, electron probability distributions) are computed in the potential field of a fixed nuclear framework (the so-called Born-Oppenheimer Approximation). These in turn are divided into techniques developed with either of chemical (Quantum Chemistry) or solid state (Solid State Physics) features in mind. There is some overlap between the two schools, of course, but in general the solid state techniques were pursued as alternatives to constructing approximate solutions to the many-body problem which is the approach of the quantum chemists. This was necessary because the computational difficulty of ab initio quantum chemistry techniques scales by at least a factor of N^4 , where N is the number of particles (electrons) in the physical system of interest. Since many more atoms of high atomic number (particularly metal alloys) are of interest in solid state systems, the development of alternate methods to those being pursued by chemists was desirable. TABLE II lists some of the more common quantum chemistry techniques, related acronyms and a short description of each. TABLE III does the same thing for the solid state physics methods.

Atomic/molecular level simulations are computations in which atomic locations are predicted. These computations require a description of the interactions (forces) among the atoms in the system of interest. These many-body interaction potentials can, in principle, be derived from the electronic level computations but because of the enormous amount of computing required (e.g. the electronic wave function would have to be recomputed for a wide range of interatomic distances) generally are not available. For this reason, atomic/molecular level simulations usually are carried out using assumed analytical potentials of a simple form such as the Lennard-Jones or Morse Potential. It is this lack of accurate, transferable many-body potentials which is hampering the realistic simulation of many of the fundamental mechanisms involving defect structures in materials. TABLE IV summarizes the two predominant atomic/molecular level simulation methods and gives a brief description of the approach and limitations of each.

Phenomenological models. To describe the macroscopic properties of materials involving defects, grain boundaries, dislocations and other microstructures, phenomenological theories need to be employed to address issues such as fracture, ductility, and brittleness in metals. In this paper we shall not attempt to address theories at this level of the hierarchy except to state that the goal of a Materials-by-Design approach is to provide more quantitative information on the parameters used in these macroscopic approaches on the basis of the micro-scope simulations discussed above.

CURRENT AND FUTURE CAPABILITY OF ELECTRONIC/ATOMIC/MOLECULAR LEVEL SIMULATION MODELS FOR PREDICTION OF MATERIALS STRUCTURES AND PROPERTIES

Electronic level. The electronic properties of a particular system can be determined in principle by solving the Schroedinger equation for the electronic wavefunction, from which one can derive such information as charge distribution and densities of electronic states for the material. These calculations are carried out with fixed nuclear coordinates, since the Born-Oppenheimer Approximation allows separation of the problem into electronic and nuclear motion. By carrying out calculations as a function of nuclear geometries and by computing the total energy of the system at each point, one can compute the equilibrium structure, the bulk modulus and other measures of the interaction potentials among the constituent atoms.

For periodic systems traditional solid-state approaches employ local density techniques wherein the problem is reduced to the solution within a given unit cell. In these approaches, which have become practical for a variety of metallic, ionic and covalent solids, the electron-electron interactions are described by local potentials for the classical coulomb and nonclassical exchange potentials. In addition, electron correlation effects have been incorporated into the "exchange-correlation" potentials. Within this local density formalism (including methods with acronyms such as KKR, CPA, APW, LMTD and ASW) systems ranging from elemental solids with one atom per unit cell to alloys with 20 or more atoms per unit cell typically can be treated.

Ab initio quantum chemical approaches differ from the solid state approaches in the two important respects that (1) the "infinite" cluster of atoms in a solid state material is represented by a finite cluster of atoms to treat the solid or surface and (2) the exchange interactions are described by a nonlocal potential in the Hartree-Fock approximation. These approaches have proven useful in describing properties that are not dependent on the long-range interactions of the solid, such as the description of chemisorption and dangling bonds at surfaces, defects in semiconductors and mechanisms of catalytic reactions. Techniques are now available to treat aggregates of 40 to 50 atoms reliably within the ab initio (Hartree-Fock) framework.

Finally semiempirical techniques can be used to understand a broad range of materials without explicitly having to perform first principles calculations on each to understand the overall trends. Such approaches as the tight binding method (TBM) and the empirical pseudopotential method (EPM), which parametrize the matrix elements needed in the theory from experimental or theoretical information, have proved very valuable for global searches of materials and in correlating structural properties with electronic properties.

Atomic/Molecular level simulations. Once the interactions among the atoms are known, either from electronic structure calculations or from experimental information, simulations can be performed to determine thermodynamic and kinetic properties of the material. These properties can include the equilibrium structures and energies of grain boundaries in metals and ceramics and the diffusion rates of species on metal surfaces. The two major approaches can be divided into molecular dynamics and Monte Carlo techniques. In the

former, the classical equations of motion are solved for all the atoms or molecules in the system (or a unit cell of the system), and the results can be used to obtain information on processes occurring in real time intervals of picoseconds to nanoseconds. In the latter, one finds the thermodynamically stable configurations of the system at a given temperature and pressure by varying the positions of the atoms according to Boltzmann weighted probabilities. Typically 100 to 1000 atoms can be treated in such simulation studies.

TABLE V. is a synopsis of the types of materials, structural features and properties which are commonly within reach of current atomic/molecular and electronic level simulation techniques. These generally fall in the categories of materials having strongly ionic bonding, materials (especially molecules with covalent bonds) composed primarily of first and second row atoms and alkali metals. The computation of the electronic structure of clusters of transition metal atoms presently constitutes a very active research area. Simulation of materials interfaces and point defect dependent phenomena, such as impurities in non-crystalline solids, interaction of point defects with surfaces, some types of diffusion, and high-temperature behavior of point defects may be feasible over the next five to ten years. Simulation of extended defects (dislocations, microstructures, rapid transients, vibronic and diffuse electronic states) also fall into this category of simulations which are generally five years or more away. Problems which require revolutionary methods or advances in computing power include the simulation of the electronic structure of a dissociated edge or a dissociated screw dislocation (The electronic structure near an extended defect is needed to address the issue of whether or not an atom will segregate at that location.), point defect/extended defect interactions and materials processing (sintering, forging, machining).¹

DESIGN PROBLEM OF "REAL WORLD"INTEREST

The potential for MBD using simulations based on electronic and atomic structures may perhaps best be seen in the case of ordered metallic alloys. It has been known that many long-range ordered (LRO) alloys and ordered intermetallic compounds have strength and temperature capabilities exceeding those of normal disordered solid solution alloys and even approaching those of ceramics; however, in its search for new high temperature structural materials, the general technical community more or less by-passed this general class of materials in favor of ceramics because of a perceived lack of any, or very little, ductility without the very high temperature capability of the ceramics. However, recent work² at the Oak Ridge National Laboratory and elsewhere has shown the feasibility of producing very ductile (30-50% elongation at room temperature) LRO alloys based on the $(\text{FeNi})_{3}\text{V}$ system and the intermetallic alloys based on the Ni_3Al system. Such alloys should eventually find use in many high temperature applications such as heat engines and high temperature industrial reactors and heat exchangers.

The $(\text{FeNi})_3\text{V}$ alloys were "designed" using a standard metallurgical rule of thumb guide, namely, the electron-to-atom ratio, in order to achieve a ternary alloy with a cubic crystal structure. Obtaining a cubic crystal structure now seems to be the first and foremost criterion for achieving

ductility in an ordered alloy because such high symmetry structure provides a greater number of slip systems than other crystal structures. The logic behind the "design" of the $(\text{FeNi})_3\text{V}$ alloys has been described in detail elsewhere (1); suffice it to say that the design worked in that case because of a base of experimental data and certain empirical correlations which happened to hold for these specific atoms. If more sophisticated models were available to predict that certain combinations of atoms might have cubic ordered crystal structures and therefore be amenable to suitable macro- or microalloying to form a useful structural material, what other alloys might be identified? The development and use of models to predict the existence of heretofore unknown compounds with ordered crystal structures has already been reported^{6,7}.

In the case of the Ni_3Al alloys the "design" was based on knowledge⁸ that single crystals of Ni_3Al , which naturally has a cubic crystal structure, are quite ductile even at room temperature even though the normal, polycrystalline form of Ni_3Al is very brittle, usually failing by intergranular fracture, as shown in Figure 1. Following the logic that there must be something "wrong" with polycrystalline Ni_3Al grain boundaries, several dopants known to act as grain boundary "strengtheners" for other alloy systems were added systematically and one, boron, was indeed found to dramatically alter the ductility properties. The "design" of the ductile Ni_3Al alloys has also been described elsewhere⁹. Had models been employed to predict the properties of grain boundaries in ordered alloys, perhaps the empirical search used in the Ni_3Al work could have shortened. The use of these kinds of models has now begun to be applied to an extension of the solution of the Ni_3Al grain boundary embrittlement problem to other possible A_3B alloy systems. This ongoing work is described below.

There is still another opportunity for modeling in the case of Ni_3Al and perhaps other ordered alloys. Ni_3Al alloys lose much of their strengths and ductilities at temperatures above about 900°C (Figure 3) despite the fact that they remain ordered all the way up to the melting point of Ni_3Al at around 1400°C . The reasons for these reductions in strengths and ductilities are not known. Perhaps models of the dislocation structures in ordered alloys could help to explain the reasons and indicate approaches for extending the use temperatures of such alloys even higher.

CURRENT THEORETICAL APPROACHES TO THE Ni_3Al PROBLEM

Electronic level. Currently several theoretical approaches are being employed to understand the relationship between the electronic properties of Ni_3Al in the bulk and at grain boundaries and the influence of solute atoms in the bulk and at grain boundaries. TABLE 6 outlines the types of models being employed and the kinds of information expected from them. Local density methods, such as the Linear Muffin-Tin Orbital (LMTO) method, are being applied to pure Ni_3Al and to supercells of 20 to 40 atoms representing the interface region of a high-angle grain boundary. From these results one should obtain information on the bulk cohesive energy, the cohesive energy of the grain boundaries with and without solute atoms such as boron, and correlations of such energies with densities of states (DOS) and charge distributions in the solid. The coherent potential approximation (CPA) method for random alloys is

also being explored to study similar properties and to investigate the role of vacancies in the lattice (as in $\text{Ni}_3\text{Al}_{1-5}$) and of B atoms in the lattice.

The tight binding method (TBM) is being used to make global searches of binary alloys and ternary alloys which are expected to have cubic ordered crystal structures and, hence, to have high ductility.

Atomic/molecular level simulations. Monte Carlo atomistic simulations are being carried out using empirically derived potentials and theoretically based variants of the Embedded Atom Method (EAM) to study the equilibrium geometries and energies of grain boundaries in Ni_3Al . Improved potentials for use in molecular dynamics calculations also are being investigated.

EXPERIMENTAL TECHNIQUES APPLIED TO THE Ni_3Al SYSTEM

Currently, several experimental approaches are being applied to explain the observed Boron effect on Ni_3Al by either obtaining direct experimental evidence or by experimentally verifying predictions coming out of the simulation calculations. The experimental studies, the investigators and the goals are summarized in TABLE VII. In all likelihood, no one experimental technique will be able to provide a definitive understanding of the boron effect any more than any one type of simulation calculation will. Through the use of theory and experiment in tandem the probability of gaining the desired understanding is increased. It then may be possible to extend this understanding through the simulation models to the effects of dopants and impurities on metallic grain boundaries in general.

RESEARCH NEEDS

While the present state of the art of microscopic simulation techniques provides hope that computational techniques can significantly aid our quest toward the objective of Materials-by-Design, a number of areas for additional research are evident from this analysis. Better methods of displaying simulation results are needed to permit extraction of qualitatively meaningful features from the computations. Reliable techniques are needed to obtain rigorously transferable and predictive many-body potentials for atomic/molecular level simulations and simple analytical expressions (a la Lennard-Jones) are needed for these many-body potentials. Models relating parameters in models at one level in the hierarchy to models at another level in the hierarchy (e.g. quantum statistical mechanics) are needed. Algorithms for rapid, accurate estimates of the total energy of any given geometrical configuration of atoms are needed. New, more sophisticated numerical procedures are required to significantly reduce computation time. "Smart" systems should be developed to assist researchers to select appropriate computational techniques

for a given problem of interest. Efficient algorithms which take maximum advantage of computer architectural features such as parallelism and vectorization must be developed. Finally, combinations of several simulation and modeling techniques must be pursued to treat extended defect phenomena such as brittle fracture in ceramics, yield phenomena and creep/fatigue in alloys. This list is by no means exhaustive.

SUMMARY

To summarize, a hierarchy of models has been outlined to structure our thinking on the kinds of models necessary in order to be able to design a priori materials with desired performance specifications. The state of the art is such that microscopic computational methods at the electronic and atomic/molecular level can contribute significantly to gaining insights into the mechanisms functioning in and in predicting properties of several types of materials. However, presently there is no one computational technique which can best simulate all kinds of material's features. The most urgent need appears to be for the development of many-body potentials to permit the simulation of dynamic phenomena such as the movement of atoms or vacancies in material structures.

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FIG. 1 - MATERIALS-BY-DESIGN HIERARCHY OF MODELS - "EXPERT SYSTEM"

**INTERMETALLIC ALLOYS BASED ON NICKEL ALUMINIDES
CAN BE MADE MORE DUCTILE THAN STAINLESS STEELS**

**UNMODIFIED
 Ni_3Al**

**Ni_3Al DOPED
WITH B AND Mo**

**STAINLESS
STEEL**

**• THE ALUMINIDES ARE MUCH STRONGER THAN STAINLESS
STEELS AND SUPERALLOYS AT ELEVATED TEMPERATURES**

FIG. 2

FIG. 3 - Yield strength as a function of temperature of Ni_3Al compared to selected conventional alloys

TABLE 1
FUNDAMENTAL MECHANISMS CAN BE DESCRIBED AT
THE LOWEST LEVELS OF THE HIERARCHY

- I. Electronic-Level Simulations
 - Quantum Chemistry
 - 1. ab initio
 - 2. semiempirical
 - Solid State Physics
 - 1. first principles approaches
 - 2. semiempirical

- II. Atomic/Molecular Level Simulations
 - Molecular Dynamics
 - Monte Carlo

TABLE II

ELECTRONIC-LEVEL SIMULATIONS

Quantum Chemistry Techniques

<u>Name</u>	<u>Description</u>
<u>Ab Initio Methods</u>	
Hartree-Fock (HF)	Single particle description in terms of orbitals in average field of electrons
	Electron correlation effects not included
	Predicts molecular structures well but chemical energies only qualitatively well
	Treat electron correlation effects and proper dissociation of molecule (lattice)
	Accurate description of potential energy surfaces and chemical energies
	Non-local exchange interaction replaced by local potential
	Good description of one-electron properties
	Total energies reliable only in non-muffin tin calculations
	Matrix elements determined from experiment or rigorous calculations
	Permits global correlation with experiment and of structure-reactivity relations
<u>Correlated wave functions</u>	
- Configuration Interaction (CI)	
- Generalized valence bond (GVB)	
- Multi-configuration SCF (MC-SCF)	
- Green's function	
- Moeller-Plesset Perturb Theory (MPPT)	
<u>Local density methods</u>	
- Rigorous approaches (X α -DVM)	
- Muffin-tin approaches (X α -SM)	
<u>Semiempirical methods</u>	
- Extended Hückel	
- (INDO, INDO, Fenske-Hall)	

TABLE III
ELECTRONIC-LEVEL SIMULATIONS
Solid State Physics Methods

<u>Name</u>	<u>Description</u>
<u>First Principles Approaches</u>	
Local Density Functional (LDF) Approaches	
- Korringa-Kohn-Rostoker (KKR)	Local potential describes exchange and correlation effects
- Augmented plane wave (APW)	Predicts lattice spacings, densities of states, modulus, elastic constants
- Coherent potential approximation (CPA)	
- Linear muffin tin orbitals (LMTO)	Linearization of energy minimization search and muffin tin approximation for starting potential result in order of magnitude savings in computations
- Augmented spherical wave (ASW)	
<u>Semiempirical Approaches</u>	
- Tight binding (TB)	Matrix elements determined from experiment or from rigorous calculations
- Empirical pseudopotential method (EPM)	Global studies of structure-properties relationships

TABLE IV
ATOMIC/MOLECULAR-LEVEL SIMULATION TECHNIQUES

<u>Name</u>	<u>Description</u>
Molecular dynamics	Integrates classical equations of motion of particles Determines dynamical (e.g. transport coefficients, rate constants) and equilibrium properties of systems
Monte Carlo approaches	Determines stable equilibrium structures by Boltzmann-weighted probabilities Determines equilibrium (not dynamical) properties of system
Both approaches	Requires description of interaction potential between particles Higher than pairwise interactions necessary for accurate properties

Calculations for systems of 100 to 1000 particles and time evolutions on order of nanoseconds are presently possible. Simulations of microsecond (infrequent) phenomena must wait for increased computational power.

TABLE V

Materials/Properties Within Reach of Current Theoretical Techniques

Ionic Materials (halides, binary oxides)	
o Accurate potentials based on shell model	o Sangster and Dixon (1976); Stoneham (1981)
o Applications to point defects, surfaces, dislocations and grain boundaries	o Catlow and Mackrodt (1982)
o Self-trapped holes in KCl	o Tasker and Stoneham (1971)
o Quantum mechanical models for localized regions of lattice	o Vail (1984); Baroff et al (1983)
Related ionic and semi-ionic materials	
o Bulk properties and defects in sulfides	o Pandey and Harding (1984)
o Charge transfer and interstitials in selenides	o Newman (1980)
Complex oxides	
o Electrical & magnetic properties and properties at high T and P using similar techniques for ionic materials (above)	o Lewis and Catlow (1983)
Minerals and silicates	
o Structural properties	o Toselli (1977), Parker et al. (1984)
o Binding sites in zeolites	o Sanders et al (1984)
Semiconductors	
o Structural properties and defects using valence-force potentials	o Stoneham (1985)
Metals	
o Vacancy formation enthalpies	o Taylor (1982)
o Interstitials in Al and Cu	o Chakraborty et al (1981)
o Positron - annihilation characteristics	o Chakraborty and Siegal (1983)
o Electric field gradients for hyperfine probes and nuclear quadrupole resonance	o Michert (1982); Minier et al (1978)

TABLE V (CONTINUED)

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B-Effect in Ni_3Al and Extension to New Materials

Current Theoretical Activities

Method - Investigators

Electronic Properties

- Supercell LUMO -- F. Hehlker, S. Buehlerp (LAME)
- CPA alloy studies - A.M. Boring (LAME)
- Semiempirical TMB studies - D. Pettifor (UK)

Goals

- Properties of high-angle Ni_3Al grain boundaries with and without B atoms; extraction of many body potentials
 - Properties of lattices with defects and with B atoms
 - Global search for cubic ordered intermetallics
-
- Relaxed geometries and energies of grain boundaries. Thermodynamic properties of segregation & disorder.
 - Interface properties of alloys
 - Diffusion and segregation of grain boundaries

Atomistic simulations

- Monte Carlo studies - D. Srolovitz, S. Chen, A. Voter (LAME)
- Embedded atom studies - B. Besker, M. Dow (SILL)
- Geometric models of grain boundaries - Farkas (VP) & Su)

TABLE VII

**B-Effect in Ni₃Al and Extension to New Materials
Current Experimental Activities**

<u>Transmission Electron Microscopy</u>	<u>Goals</u>
o Structure of Grain Boundaries in B-Doped Polycrystalline Ni ₃ Al...J. Norton et al. (ORNL)	o Elucidate grain boundary structural features in "real" Ni ₃ Al in order to provide conceptual guidance as to where B may prefer to reside.
o Effects of B on dislocation structures of boundaries between epitaxially grown Ni ₃ Al thin films... Sass et al (Cornell)	o Understand effect of B on dislocation structures at interface between two epitaxially thin films of Ni ₃ Al.
o Effects of Deformation on Ni ₃ Al. M. Birnbaum et al. (Illinois)	o Understand phenomena associated with in-situ deformation and fractures in vicinity of Ni ₃ Al grain boundary
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o Effects of Deformation on Ni ₃ Al. M. Birnbaum et al. (Illinois)	o Understand phenomena associated with in-situ deformation and fractures in vicinity of Ni ₃ Al grain boundaries.

Field Emission Ion Microscope (Atom Probe)

- o Structure and compositions of Ni₃Al grain boundaries...M. Miller (ORNL) and S. Bremer (Pittsburgh)

Diffusion and Segregation

- o Electron microprobe studies of diffusion in polycrystalline and bicrystal Ni₃Al... Chou et al (Lehigh)
- o Auger Electron Spectroscopy Studies of segregation of B to grain boundaries and free surfaces of Ni₃Al
- o Radioactive tracer studies of diffusion in Ni₃Al...A. Peterson, S. Rothman (Argonne)
- o Measure the rates of diffusion of Ni, Al, B and other species both within the grains and in the grain boundaries and determine possible effects of various structural defects on those rates.

TABLE VII

B-Effect-In Ni₃Al and Extensions to New Materials
Current Experimental Activities (Continued)

<u>Positron Annihilation</u>	<u>Goals</u>
o Positron annihilation studies of vacancies in B-doped Ni ₃ Al...A. Des Gupta et al. (ORNL) and K. Lynn (Brookhaven)	o Elucidate numbers and types of vacancies on Ni and Al sublattices of Ni ₃ Al stoichiometries in order to explain possibilities of influences on B effect
<u>Photoelectron Spectroscopy</u>	
o XPS and UPS investigations of bonding of B in rapidly solidified and annealed B-doped Ni ₃ Al...K. Lynn (Brookhaven)	o Determine possible shifts in bonding state of B as it segregates to Ni ₃ Al grain boundaries.
<u>Microscopic Deformation Processes</u>	
o Studies of the effects of grain size on deformation of Ni ₃ Al... E.M. Schwalson et al. (Dartmouth)	o Establish trend of yield strength as function of grain size in order to provide possible support to grain boundary dislocation hypothesis of effect of B in Ni ₃ Al.
<u>Ion Channeling</u>	
o Ion Channeling studies of B-doped Ni ₃ Al... C.T. Liu et al. (ORNL)	o Establish locations of B in Ni ₃ Al grain boundaries.