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EOS, Thermodynamic, and Structural-Mechanical Properties of Intermetallic Compounds

John M. Wills*, Galen Straub, and
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Abstract

This is the final report of a of a three-year, Laboratory-Directed Research and Development (LDRD) project at Los Alamos National Laboratory (LANL). Several classes of binary intermetallic compounds have important potential application as high temperature structural materials because of their high melting temperature, low density, and high strength, but their use is limited by their poor low temperature ductility and fracture toughness. The goal of this project was to further the development of techniques for performing *ab-initio* calculations of the electronic, structural, and elastic properties of these materials in an investigation of the relation between structure, composition, and mechanical properties of intermetallics. Materials properties to be addressed in these calculations included the equation of state (EOS), defect structure energetics, and elastic constants and phonons. Major accomplishments included calculations of stacking fault and twin energies in layered TiAl, structural stability in binary and ternary Ti-Al-Nb compounds, and point defect energies and elastic moduli of Laves phase intermetallics.

Background and Research Objectives

Intermetallic compounds possess many properties that make them attractive in technological applications. Many of the ordered intermetallics exhibit high melting points and large elastic moduli, implying high strength at elevated temperatures; these materials are thus strong candidates for use as high-temperature structural materials. Ti-Al alloys, for example, because of their low densities, are potentially useful for aerospace applications. Despite these attractive properties, a major barrier to the widespread use of ordered intermetallics is that most of them lack room temperature ductility and/or toughness. There has been much research directed at improving the ductility of these alloys. A possible means for achieving this lies in stabilizing these alloys in different structures. Polysynthetically twinned TiAl, for example, exhibits improved low temperature ductility under uniaxial stress. Different structures may also be stabilized by ternary additions. The mechanism for this improved ductility, is not well understood.

Although the mechanical properties of intermetallics are determined by phenomena occurring over several length scales, an accurate understanding of the electronic structure of these materials is essential for any predictive, first principles theory of mechanical behavior. Methods for calculating the electronic structure of materials from first principles

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have been developed extensively over the last few years, to the point where accurate calculation of complex material properties is becoming feasible. The goal of this project was to further this development in application to the calculation of material properties such as extended and point defects, structural stability, elastic moduli, and phonon spectra both on and off stoichiometry in binary and ternary intermetallic compounds and alloys. The calculations performed in the course of this research were based on highly accurate *ab-initio* electronic structure calculations. We sought to improve the *ab-initio* understanding of the elastic properties of these materials and, more generally, the relationship between structure, composition, and mechanical properties in intermetallics.

Importance to LANL's Science and Technology Base and National R&D Needs

Of primary importance in attempting to engineer the properties of intermetallic compounds is a theoretical understanding of the nature of structure, composition, and elastic response in these alloys. Studying the energetics of point and extended defects in intermetallics has the potential to significantly increase our understanding of mechanical behavior in intermetallics while providing detailed theoretical data on a system of potential technological importance. The study of elasticity in binary intermetallics as a function of composition addresses relationships between composition and elasticity experimentally observed but not well understood. The work performed under this project furthered the development of the capability to calculate the equation of state (EOS) of materials from first principles. This capability is highly desirable, theoretically as well as in application to weapons and industrial technology. Our work develops and enhances Laboratory capabilities in the core areas of advanced computing, modeling, and simulation and integrated defense science and technology competencies. This work developed the theory of intermetallic compounds at a fundamental level while providing practical information on materials of technological importance. The electronic structure methods that we use are "state-of-the-art" in *ab-initio* electronic structure; the calculations performed under this proposal push these methods to the limit and involve the development of new calculational techniques for dealing with complex systems.

Scientific Approach and Accomplishments

Underlying the techniques used in this proposal was an *ab-initio*, all-electron, total-energy, electronic-structure method developed at LANL. Computer codes based on this method are currently providing state-of-the-art calculations for elements, alloys, and compounds throughout the periodic table. Three techniques were developed based on this

method during the course of this work. These techniques were all taken to the point of practical application, although further development is desirable and underway. A basic extension of the electronic structure method was the development of the method to be able to efficiently handle very large unit cells. This involved devising and/or implementing new algorithms for calculating and storing basis functions, potentials, and charge densities, and new algorithms for matrix diagonalization and construction. The principal calculation that was used as the focus for this development was the calculation of stacking fault and twin energies in layered TiAl. The geometry for this calculation consisted of stacked (111) planes of gamma-TiAl contained in a periodic supercell that contained as many as 72 transition and simple metallic atoms. Calculations for geometries containing both stacking faults and twins were taken to convergence. The change in energy and electronic structure (bands and EOS) were calculated and are being used to analyze extended defects in this material. The improvements made in the electronic structure code have since allowed the all-electron calculation of materials with unit cells containing 256 atoms, a record for all-electron, full potential, electronic structure calculations.

Extremely useful for the study of structural properties and defect structures in intermetallics was the development of *ab-initio* force calculations. The forces obtained from a density functional electronic structure calculation are Hellman-Feynman forces with corrections; the difficult part of such a force calculation is in recognizing and implementing the corrections. For any basis set not containing its gradients, Pulay (or Incomplete Basis Set—IBS) corrections are essential. This correction is particularly tedious to implement on a site-centered basis such as that used in the electronic structure method being developed here, but the force method developed implements this correction fairly efficiently. Other necessary corrections, such as core and kinetic energy corrections, (Yu, 1991) were implemented without problem. Force calculations were then used in several calculations. Zone boundary phonons were calculated for TiAl and NiAl as a function of volume. These are being used, together with calculated elastic constants, to fit interatomic potentials to be used in the calculation of the EOS of these materials (Straub, 1994). Calculations of vacancy structures and formation energies in the Laves phase intermetallic NbCr₂ were performed using 24-atom supercells. These calculations were done with full relaxation and will be used together with calculated elastic moduli to investigate ductility in this material.

Several methods exist for the calculation of the electronic and structural properties of random alloys, ranging from the Virtual Crystal Approximation (VCA) to the Coherent Potential Approximation (CPA). Although the CPA is the theoretically most appealing of these methods, it is difficult to implement in full-potential calculations. The VCA has useful application in alloys containing constituents with similar electronic energy levels and, as a step toward a general capability for calculating the electronic structure and

structural energy of random alloys, we have implemented this method in our full-potential electronic structure code. In essence, this amounts to constructing an average Hamiltonian obtained by connecting alloy constituents with a common interstitial medium. This capability was used to investigate the energetics of (Ti, Zr, Hf)-(V,Ta) alloy structural stability and is currently being used to study volumes and Young's modulus in the metastable bcc phase of Nb-Cr alloys observed experimentally.

Other properties were studied under this project, making use of and testing the computational capability developed. The structural stability of stoichiometric Ti-Al-Nb alloys (Ti(3)Al, Ti(2)AlNb, and Nb(3)Al) was studied. The orthorhombic phase of Ti(2)AlNb is particularly interesting as it exhibits enhanced room-temperature ductility. A result of this study was the discovery that the stability of the orthorhombic phase is almost entirely due to lattice relaxation, and the source, in the electronic structure, of the lattice relaxation was identified (Asta 1994). This study was continued by investigating the stability of bcc-based binary and ternary alloys, motivated by the observation that Ti-Al and Nb-Al intermetallics do not form in simple bcc based structures, while the ternary Ti(2)AlNb has a stable high-temperature bcc-based phase (the Heusler phase). The energy along the Bain path was calculated for bcc based TiAl and NbAl and the Heusler structure in Ti(2)AlNb. The stability has been found to result from the additional electrons donated by Nb, essentially filling a set of valence bands (Asta, 1995). In the last year of the project, material properties of Laves phase intermetallics were studied, in part because of the potential availability of new experimental data (Ormeci, 1996). Calculations of the structural phase stability, formation energy, and elastic moduli of NbCr(2) and HfV(2) were completed as well as the vacancy formation energy discussed above.

Publications

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