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Alloy Design and Phase Stability of the Ternary Alloy Titanium-Aluminum-Niobium

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Abstract

This is the final report of a three-year, Laboratory Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). We have used high-precision electronic-structure and cluster-variational method (CVM) techniques to study aspects of alloy design involving the phase stability and ordering tendencies of the ternary system Ti-Al-Nb, and the correlation with these to changes in the electronic structure of these materials. This system is of great interest for aerospace applications due to its desirable mechanical properties and low densities. Total energies were computed for 18 binary and ternary bcc superstructures in order to derive parameters for CVM calculations, which showed important strong ordering tendencies in the alloy phase diagram as a function of temperature and alloy concentration. Structural optimization calculations were used to analyze structural instabilities for bcc, fcc, hcp, O-phase, and ω -phase structures. We discovered the mechanism for the role of Nb in the structural stability of the O-phase of the ternary intermetallic Ti_2AlNb . Calculations were also done to investigate the electronic properties associated with the structural stability of a related class of Laves Phase high-temperature structural materials NbCr_2 and HfV_2 .

Background and Research Objectives

Because of their excellent high-temperature properties and low density, Ti-Al alloys are considered to be important candidates for aircraft engine applications. The key technical impediment currently preventing these applications is their poor room-temperature ductility and low fracture toughness. Much research has been directed at trying to improve the ductility of these alloys by examining the effects of ternary additions, stoichiometry, and processing conditions.

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The work performed under this proposal was focused on gaining an understanding of the effect of ternary additions to Ti-Al alloys, especially Nb, since the ternary Ti-Al-Nb is a promising new alloy, particularly near the composition Ti_2AlNb . This alloy is much more ductile than conventional Ti-Al alloys, yet retains the light-weight and desirable high-temperature properties. There is much current work on optimizing microstructure and processing of Ti_2AlNb -based materials in order to achieve the best balance of mechanical properties.

To understand how the addition of Nb to Ti-Al alloys improves the room-temperature ductility and fracture toughness requires important theoretical input. If we knew the role that Nb plays, we might be able to suggest new alternative alloys (perhaps by adding yet other alloying elements or finding a better compositional mix of the three elements). There is likely to be an important interplay between electronic-structure properties, crystal structure, and alloying effects (including temperature and disorder) which modifies the microstructure that controls the mechanical strengths and ductility of these materials.

In addition, an understanding of the phase stability and metastable phases of the ternary alloys is needed for input into the industrial processing of these materials. Because such processing often involves materials reactions that take place under non-equilibrium conditions, metastable phases can often affect the way in which materials with the correct mechanical properties are made. It is important to elucidate candidate reaction pathways to metastable and intermediate phases so that the processing does not get trapped in some undesired transient phase.

Our goal in this project has been to theoretically calculate the phase stability and thermodynamic properties of the Ti-Al-Nb alloy system near the interesting composition of Ti_2AlNb . We have provided information on both the perfectly stoichiometric compounds at zero temperature as well as the effects of temperature, composition, and substitutional disorder in the alloyed material. More generally, we have tried to understand how materials science issues of ternary compounds connects to new techniques and concepts beyond those that were previously developed for binary alloys. We have studied the interplay between electronic-structure properties, crystal structure, and alloying effects (including temperature and disorder) which modifies the microstructure that controls the mechanical strength and ductility of these materials. We have also studied the Laves phase compounds NbCr_2 and HfV_2 in order to get insight into related ternary materials.

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

Core Los Alamos competencies and capabilities include both "theory, modeling, and high-performance computing," and "nuclear and advanced materials." This project, which concerns modeling of advanced materials, clearly enhances and relates to both of these in a fairly direct fashion. More specifically, it involves developing the theory of ternary alloys 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" *ab-initio* electronic structure approaches. The calculations being performed under this proposal apply these methods to structural alloys and involves the development of new calculational techniques for dealing with complex materials systems. In addition, we are bringing a new technology, the cluster variation method, for modeling complex systems to Los Alamos.

More generally, in the past, most theoretical investigations of alloy properties have focused on simpler binary (two-element) alloys. However, the number of ternary (three-element) alloys is exceedingly vast and these alloys are much more likely to have the desired properties needed for industrial applications and needs. This project explores the materials science issues and physics of ternary alloys and focuses on a specific systems of great importance to the aircraft industry and of interest to the laboratory.

Scientific Approach and Accomplishments:

In order to understand the properties and alloying strategies for Ti-Al-Nb alloys, it is important to develop a detailed knowledge of the equilibrium phase boundaries and their metastable extensions. Experimental work has established that ternary extensions of the binary phase fields span relatively wide ranges of composition. Additionally, ordering of Ti and Nb atoms on the Ti-sublattice of the hexagonal Ti_3Al structure gives rise to a compound (the O-phase) with an orthorhombic structure, which is stable at low temperatures for compositions near Ti_2AlNb . Ordering also occurs in the bcc-based (β) solid solution, giving rise to the β_0 -phase with a B2 (CsCl) structure for compositions rich in Ti and Nb. Metastable bcc phase with B2-type order have also been observed in quenched Nb-rich Nb-Al alloys both with and without ternary Ti additions.

In order to study the phase stability of the bcc-based phases in the Ti-Al-Nb alloy system, we used a combination of *ab initio* total energy and cluster variation method (CVM) calculations. The electronic-structure calculations employed a state-of-the-art full-potential technique developed at Los Alamos by John Wills. These zero-temperature

calculations were used to understand the electronic structure of these alloys and how they affect mechanical properties such as bulk moduli and elastic constants.

Total energies were computed for 18 binary and ternary bcc superstructures (including Ti_3Al , Ti_2AlNb , and Nb_3Al) in order to determine a set of effective cluster interaction parameters, which are the input needed by the CVM method. With CVM it is possible to calculate thermodynamic properties such as free energies for all of the phases of interest, even metastable ones, as functions of composition and temperature. The CVM technique was developed by Professor Didier de Fontaine's Group at UC Berkeley. One of the collaborators of this project (M. Asta) was a former student of de Fontaine's.

The CVM was used to study the effects of composition on finite-temperature ordering tendencies and site preferences for bcc-based phases. Strong ordering tendencies were found for binary Nb-Al and Ti-Al bcc phases as well as for ternary alloys with compositions near Ti_2AlNb . For selected superstructures we also analyzed the structural stability with respect to tetragonal distortions, which transform the bcc into an fcc lattice. Instabilities with respect to such distortions are found to exist for binary, but not for ternary bcc compounds.

Besides the needed input for the CVM method, the electronic structure code was used to investigate a number of fundamental properties of various Ti-Al-Nb alloys. In particular, we have calculated the cohesive energies, equilibrium volumes, and bulk moduli of Ti_3Al in the D019 structure, Ti_2AlNb in the O-phase (orthorhombic), and Nb_3Al in the A15 structure (the experimentally observed structure) and in the D019 structure. The structural parameter (c/a) in the D019 structures were optimized. In O-phase Ti_2AlNb , calculations were performed both for the ideal structural parameters and for the experimentally observed structural parameters. The results are in excellent agreement with experimental data. The formation energy of Ti_2AlNb was extracted from these calculations. Cluster variation method (CVM) calculations of the stability of Ti_2AlNb considering only the effect of configurational ordering on an ideal hcp lattice were performed.

A significant result of this work was the discovery that the stability of Ti_2AlNb has little to do with "chemical" forces driving the atoms to rearrange in an ordered structure; rather, the elastic energy associated with the structural relaxation is almost entirely responsible for the stability of the ordered O-phase. This result implies that study of ternary alloys, at least those considered here, will require a significantly greater degree of sophistication than the study of binary alloys due to the increased number of degrees of freedom. In particular, meaningful *ab-initio* results for the composition-temperature (c - T) dependent phase stability will need to be based on cohesive energies for relevant ordered structures minimized with respect to all the degrees of freedom. Practical calculations of

these energies will require simultaneous calculation of total energies and the full thermodynamic stress tensor.

Quenching the bcc-phase alloys of Ti leads to a metastable precipitate known as the ω -phase. This phase is related to a wide class of displacive or martensitic phase transitions, which makes this system of particular interest. From a materials point of view the ω -phase is considered a strengthening element. The ω -phase structure can be derived from the bcc phase through a continuous distortion of the unit cell. We have studied the reaction pathway of this displacive transition by calculating the total energy of the crystal as a function of the path. For TiAl we find an energy barrier between the two phases. Similar calculations for $\text{Ti}_3\text{Al}_2\text{Nb}$ show that the addition of Nb removes this barrier. We are continuing investigations to look for an electronic-structure feature of the Nb alloy that could cause this change.

Given the importance of elastic energy in the stability of these alloys, we thought that it was useful to investigate elasticity in different alloys of Ti and Nb to gain a general understanding of elastic response in related transition-metal alloys. Recent experiments at Los Alamos performed by D. J. Thoma and Ricardo Schwarz on metastable structures of Nb-Cr and Nb-Ti-Cr alloys have found deviations in lattice constants and Young's moduli from the "rule of mixtures." We have performed alloy calculations of the equilibrium lattice parameters and, more generally, the relationship between the electronic and structural properties of NbCr_2 and a related compound, HfV_2 . We investigated lattice constants, bulk moduli, density of states, charge contours, cohesive energy, and heats of formations for both compounds in the C15 and C14 Laves phase structures. From these calculations we found a stacking fault energy of 90 mJ m^{-2} for C15 NbCr_2 , which is in good agreement with experiment. The small cohesive energy found between the C15 and C14 phases implies low stacking fault energies in these structures, suggesting that deformability through a synchro-shear mechanism is physically reasonable. The Poisson's ratio provides a measure of the directionality of bonding. The high values of these ratios for these two materials suggest that directional effects are weak. Charge-density contour plots from our calculations confirm this observation.

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