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It is now clear that the high temperature intermetallics have become a major focus of research effort -both experimental and theoretical- driven in large part by their potential for important aerospace applications at elevated temperatures. State-of-the-art first-principles total-energy electronic structure calculations based on the *full-potential* linear-muffin-tin-orbital method were employed to study systematically issues of metallurgical nature, such as bonding, cohesion and phase stability and the role of ternary additions on their electronic and mechanical properties. More specifically, we have investigated: 1) The effect of impurities (boron and hydrogen) in Ni_3Al; 2) The contrasting effect of boron and sulfur impurities on the ideal cleavage cleavage fracture; 3) The variation of the elastic constants with chemical environment across the Ni_3X (X = Al, Si, Ga, Mn) intermetallics and their correlation to plastic deformation; and 4) The anisotropy of the antiphase boundary (APB) energy between the (001) and (111) slip planes, responsible for the anomalous temperature dependence of the yield strength.

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FINAL PROGRESS REPORT

I. Statement of the problem studied

During the 1993-1997 grant period we have carried out first principles electronic structure calculations of the $L1_2$-type ordered nickel-based, Ni_3X (X = Mn, Al, Si), and TiAl intermetallics, exhibiting unique mechanical properties that make them attractive for aerospace and U.S. Army structural applications at elevated temperatures. This research work is supported by the US Army Grant (DAAH04-93-G-0427). The immediate motivation of this research work is the unusual mechanical properties of this class of intermetallics (high melting temperature, low density, good oxidation resistance, and *increase* of yield stress with *increasing* temperature in contrast to conventional compounds) and their importance in designing new ductile ordered super alloys and the need for a theoretical understanding at the atomistic level of the electronic and mechanical properties.

In Sec. II, we present the summary of the most important results. The impact of the 1994 Northridge earthquake on the research work is presented in Sec. III. The list of publications resulted from this research work during the 1993-97 period is presented in Sec. IV. The scientific personnel involved in the research work is listed in Sec. V. The bibliography is presented in Sec. VI.

The past two decades have witnessed dramatic growth in both the experimental and theoretical activity in intermetallic compounds and ordered alloys, because of their potential use in a wide variety of technological aerospace applications.[1] Among the intermetallic compounds, the $L1_2$-type ordered nickel intermetallics, Ni_3X (X=Al, Si, Ga, Ge, Mn), exhibit unique mechanical properties that make them attractive for structural applications at elevated temperatures. Of central interest are the high melting temperatures, the low densities, the resistance to oxidation,[2] and the *increase* of yield stress with *increasing* temperature,[3] *in contrast* to conventional compounds or disordered alloys. However, as with many other intermetallics, an inherent drawback to using Ni_3Al as a structural material, however, is the tendency of polycrystalline ordered stoichiometric alloys to undergo brittle intergranular fracture,[4] even though single crystals of Ni_3Al are highly ductile.

Micro alloying studies have shown[2] that doping with certain impurities (boron), which strongly segregate to grain boundaries, can significantly improve the ductility of polycrystalline Ni_3Al.[3] On the other hand, sulfur reduces ductility and causes embrittlement. At room temperature, the addition of only 0.05 wt % (0.25 at %) of boron increases the elongation of polycrystalline Ni_3Al from a few percent to values of 45-50 %.[5] This effect, however, is only observed in specimens that contain excess Ni. Because boron is known to segregate preferentially to grain boundaries, one explanation for its dramatic effect on ductility is that it promotes better cohesion across the grain boundary plane.[6-11] More recent experiments have shown that boron improves the ductility of single Ni_3Al crystals,[12] suggesting that a "bulk effect" should be considered in addition to the grain boundary strengthening effect of boron when explaining the improvement in ductility of polycrystalline Ni_3Al due to B additions.

While the *intrinsic* factors are important -in many cases dominant- in limiting ductility, recent work by Liu *et al* has shown[13] that *extrinsic* factors, in particular the humidity, can be a major cause of low ductility in some systems. Their results demonstrate that the poor ductility commonly observed in air tests is an extrinsic effect due to the conditions of the tests. This "environmental embrittlement" effect involves a mechanism of dissociation of H_2O to generate atomic hydrogen, which diffuses into the region of the crack tip and promotes brittle crack propagation. Their results suggest that the principal role of boron in ductilizing Ni_3Al is to suppress the environmental embrittlement.

To interpret the anomalous yield behavior of the $L1_2$ alloys, Yoo[14] proposed that the effect of elastic anisotropy on the temperature dependence of yield stress is as important as the anisotropy of antiphase boundary energy[15] in describing the dynamical breakaway of super partial screw dislocations from cross-slipped segments.[16] Recent measurements[17] of single-crystal elastic constants for this series indicate a large elastic anisotropy shear factor, A, ranging from 3.1 to 3.7, except for Ni_3Ge (A = 1.72). It was suggested that the relatively high shear anisotropy factor across the $L1_2$ Ni_3X series tends to *elastically* enhance the cross slip.[17] The available experimental data indicate a strong effect of chemistry on the tendency of grain boundaries for brittle intergranular fracture, with the resistance to fracture increasing in the order $X= Ge < Si < Ga< Al <Mn$.[18] The trend of grain-boundary energy in Ni_3X has been found to correlate well with the difference in valence[19] and the difference in atomic (Pauling) electronegativity[18] of the atomic constituents of the compound.

In the theoretical area of this research, the focus of our effort has centered on developing and applying highly precise all-electron quantum mechanical electronic structure calculations, based on the full-potential linear-muffin-tin orbital (FLMTO) method,[20] to study a number of properties of this class of nickel-based intermetallics. The theoretical approach, density functional theory, that underlies all these calculations is appealing because it promises to provide such a unified approach, which is particularly suited for bridging the gap between our understanding of atomic scale properties and the macroscopic properties essential for producing useful material applications. The "full potential" capability is *essential* when dealing with intermetallic compounds, which combine those characteristics common to covalently bound materials with metallic properties - a fairly uncommon combination. In contrast to atomistic simulations based on empirical potentials or the embedded-atom method involving the process of fitting parameters, first principles electronic structure calculations provide insight into the chemical bonding characteristics which ensue the cohesiveness of interatomic forces that control mechanical properties, and allow the possibility of not only studying "clean" intermetallics, but also intermetallics containing chemically different impurities.

Using our recently developed state-of-the-art self-consistent total energy calculations we addressed questions of metallurgical nature, such as bonding, cohesion and phase stability of the intermetallics and the role of ternary additions on their electronic and mechanical properties. A major part of our effort was focused on applying first principles electronic structure calculations to study systematically:

1) The effects of boron and hydrogen on the electronic structure of Ni_3Al;
2) The effects of impurities on the ideal cleavage properties of Ni_3Al;
3) The electronic structure and elastic properties of the Ni_3X (X = Al, Ga, Si, Ge, Mn) intermetallics; and
4) The electronic structure of antiphase boundaries in Ni_3Al and Ni_3Si (currently continuing).

II. Summary of the most important results

1. Effects of boron and hydrogen on the electronic structure of Ni_3Al

In the pure Ni_3Al system, the depletion of electron density at the aluminum sites is accompanied by significant anisotropic buildup of the directional d-bonding charge at the nickel sites. The bonding charge accumulation at the Ni site is along the nearest-neighbor Ni-Al and next-nearest-neighbor Ni-Ni directions. The bonding directionality is caused mainly by the polarization of p electrons at the Al sites as a result of the *p-d* hybridization effect. It is important to state that it is the *non spherical* corrections to the spherical potential, that yield the directionality of the d-bonding charge at the Ni sites. Thus, the bonding mechanism in Ni_3Al involves the combination of charge transfer and strong Al-*p*/ Ni-*d* hybridization effects. This is one of the most remarkable features of intermetallics.

We find that changes in the electronic structure induced by boron in Ni_3Al result from the hybridization of the *d* states of the nearest-neighbor Ni atoms with adjacent B-*p* states. Boron prefers to occupy Ni-rich octahedral interstices. Boron is found to enhance the interplanar metallic bonding between the NiAl layers in the [001] direction, and to reduce the bonding-charge directionality near the more distant Ni atoms. Thus, we conclude that in such an environment boron acts to increase the cohesion of the crystal. In contrast, hydrogen is found to enhance the bonding-charge directionality near the more distant atoms, and provides virtually no interstitial charge enhancement. This suggests that hydrogen does not promote local cohesion. When with boron and hydrogen are present in the system, the dominant changes in the electronic structure (density of states, induced charge densities) are induced by boron, and hydrogen seems to have very little effect. Overall, we find that our calculations are in qualitative accord with the known behavior of boron and hydrogen in Ni_3Al, and they suggest that the origin of the remarkable effects of these solutes may lie primarily in the fundamental changes they induce in the electronic structure of this material.

2. Effects of impurities on the ideal cleavage properties of Ni_3Al

Poor cleavage strength is considered to be one of the major causes of brittleness in intermetallics. The brittleness is associated with weak atomic bonding across certain crystallographic planes. The fracture mode of brittle intermetallics is either cleavage, i.e., fracture along specific crystallographic planes in either a single-crystal or polycrystalline sample, or intergranular, i.e. fracture along the grain boundaries in a polycrystalline sample. Understanding the properties and nature of the brittle fracture process are of practical interest. However, not much theoretical work has been done on correlating cleavage strength with electronic structure in these intermetallics.

The fracture properties of Ni_3Al under tensile stress were studied by employing a repeated slab geometry. The FLMTO ab initio electronic structure calculations can provide accurate information on the tensorial/directional properties of the bonding forces across and parallel to the cleavage plane in terms of the anisotropy of the detailed induced bonding charge characteristics. We find that sulfur reduces the ideal cleavage energy of Ni_3Al by 35%, while boron reduces it only by 5%. Furthermore, we find that while boron increases the maximum cleavage stress (ideal yield stress) by about 2% compared to that of the pure Ni_3Al system, sulfur causes a significant reduction of the ideal yield stress by 29%. The impurity-induced charge density results indicate that there is a large charge accumulation between the boron and the nickel atoms across the cleavage plane, while there is a large depletion of charge between the sulfur and the nickel atoms. The strong accumulation of bonding charge which "hangs on" across the interface much longer, explains the fact that the ideal cleavage strength for $Ni_3AlB_{1/2}$ is larger than that of $Ni_3AlS_{1/2}$. The electronic bonding mechanism underlying the contrasting effects of the boron and sulfur impurities seems to be strong d-p hybridization for the boron impurity and a more embedded-like (electrostatic) interaction for the sulfur impurity.

3. The electronic structure and elastic properties of the Ni_3X (X = Al, Ga, Si, Ge, Mn) intermetallics

We have carried out first-principles total-energy electronic structure calculations of the elastic constants of the $L1_2$ -type ordered nickel-based intermetallics Ni_3X (X = Mn, Al, Ga, Si, Ge). The elastic constants determine the response of the crystal to external forces and play an important part in determining the strength of the material. They provide valuable information on the bonding characteristics between adjacent atomic planes and the anisotropic character of the bonding. There is also a tendency toward correlation between the elastic constants and the melting temperature of a solid.[21] Pugh[22] introduced the quotient of bulk to shear modulus of polycrystalline phases, B/G, as an indication of the extent of fracture in metals. A high (low) B/G value is associated with ductility (brittleness). The purpose of this work is to study the origins in the electronic structure of the variation of the elastic constants with chemical environment across the series, to correlate the trends of B/G with changes of orbital electronegativity of the constituent atoms, and to understand the nature of chemical bonds responsible for the unusual mechanical behavior of this class of systems. We have also examined how the charge redistribution that accompanies strain can be related to the material's elastic properties. From an electronic structural point of view, the obvious difference on going from Ni_3Al to Ni_3Si and from Ni_3Ga to Ni_3Ge is the addition of an extra *p* electron in the X atom.

We have calculated the electronic structure, equilibrium volume, and elastic properties across the series. The results are in overall agreement with experiment. The shear moduli increase on going from Ni_3Mn to Ni_3Si. The relatively high shear anisotropy factor, which tends to enhance the cross slip, is due to the anisotropic bonding charge density. The bonding charge density can be described by the combination of charge transfer from X to Ni and strong X*p* - Ni*d* (Mn/*d* - Ni/*d* in Ni_3Mn) hybridization effect. The more pronounced directional bonding between the Ni and Si atoms compared to that between the Ni and Al atoms is responsible for the larger shear moduli of NiSi. Thus, the addition of an extra *p*-electron on going from Ni_3Al to Ni_3Si and from Ni_3Ga to Ni_3Ge results in more directional bonding charge density and hence larger resistance to shear. The rearrangement of the bonding charge when the systems undergo deformation indicates that the redistribution is small for Ni_3Al and large for Ni_3Si. These results are consistent with the larger shear moduli of Ni_3Si. The bonding charge directionality changes in Ni_3Mn due to the Ni/*d* - Mn/*d* hybridization.

The calculated isotropic shear moduli for polycrystalline phases are in overall agreement with experiment. Even though adopting any single characteristic as indicative of ductile behavior is highly simplistic, our electronic structure results indicate that the B/G ratio, proposed by Pugh[22] to provide a simple rule for measuring the ease of plastic deformation, decreases from Ni_3Mn to Ni_3Si; and that the trend of B/G across the series correlates well with the absolute difference in the *s* -orbital electronegativity between the atomic constituents, the difference in energy, $E_d(Ni)-E_p(X)$, ($E_d(Ni)-E_d(Mn)$ for Ni_3Mn), and the total density of states at the Fermi energy E_F.This trend for B/G is similar to that found for the tendency for brittle intergranular fracture, with the grain-boundary cohesive strength changing in the order X = Mn > Al > Ga > Ge > Si.

4. Electronic structure of antiphase boundaries in intermetallics

One of the outstanding features of plastic deformation of the Ni_3X (X=Al, Si) intermetallics is the anomalous increase in flow stress with increasing temperature. It has been recently proposed experimentally that the anisotropy of antiphase boundary (APB) energy between the (001) and (111) slip planes is responsible for the anomalous temperature dependence of tensile strength in polycrystalline intermetallics.

To date, we have investigated the electronic structure of the (001) and (111) APB using supercell calculations. The total number of unit cells in the supercell were increased to minimize the effects of interactions between two consecutive APBs. The APB energy for the (111) plane for Ni_3Si is found to be larger than that for Ni_3Al. Detailed comparison of the density of states and the charge densities for the two APB's indicate that the larger APB energy for Ni_3Si is due to the more pronounced directional bonding between the Ni and Si atoms compared to that between Ni and Al atoms. This research work is continuing.

III. Northridge Earthquake Impact on Research

The delay in submitting the technical progress report is due to the January 17, 1994 Northridge earthquake. Situated approximately one mile from the epicenter, the California State University Northridge (CSUN) campus suffered extensive damage, including structural damage to facilities and biological and chemical contamination resulting from fire in the science complex. Faculty and staff were barred from entering university buildings until the buildings could be inspected for safety. Each aftershock brought another inspection. After nine weeks, access was finally granted, but was limited to a few hours and only for the purpose of removing the most necessary papers and materials. The rest of our books, folders, papers, etc. was put in large boxes and placed in storage. Because of these conditions and the need to continue my research program, I requested and received a temporary office in the Physics Department at UCLA. We moved workstations, folders and books and basically started from scratch. We had to repeat certain lengthy calculations because some results had been lost.

After several months of commuting to UCLA, we were given temporary office space in trailers on the CSUN campus. This entailed another move, into the trailers, where we remained until Fall 1997. Nonetheless, it was in a trailer that the Theoretical/Computational Materials Research Center was born and where our work continues to go forward despite the unanticipated delays and inconveniences resulting from the Northridge earthquake.

IV. Publications

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2. Impurity Effects on Atomic Bonding in Ni_3Al, S. Sun, N. Kioussis, S. Lim, A. Gonis, W. Gourdin, Phys. Rev. B **52,** 14421 (1995).

3. First principles determination of the Effects of Boron and Sulfur on the Cleavage Fracture in Ni_3Al, S. Sun, N. Kioussis, A. Gonis, and M. Ciftan, Mat. Res. Soc. Symp. Proc. **409**, 183 (1996).

4. Effects of Boron and Sulfur on the Ideal Yield Stress of Ni_3Al - A First Principles Study S. Sun, N. Kioussis, M. Ciftan, A. Gonis, NATO, ASI Series **355**, 413-418 (1996).

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7. First Principles Total-Energy Calculations of the Elastic Constants of the Nickel-Based $L1_2$ Intermetallics, D. Iotova, N. Kioussis, S. P. Lim, S. Sun, and R. Wu, Mat. Res. Soc. Symp. Proc. **408**, 557 (1996).

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9. Electronic Structure and Elastic Properties of the Ni_3X (X = Mn, Al, Ge, Ga, Si) Intermetallics, D. Iotova, N. Kioussis, and S. P. Lim, Phys. Rev. **B 54**, 14413 (1996).

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V. Participants and scientific personnel

The following scientific personnel was involved in the research program during the 1993-97 grant period and was supported by the US Army grant award:

Prof. Nicholas Kioussis (PI); Dr. Sheng Sun (Post doctoral fellow); two graduate students, Ms. D. Iotova (MS, Spring 1996) and Mr. Gang Lu (Ph. D., Spring 1998); two undergraduate students, Mr. Steve Agoston and Mr. Jason Pruet, (currently at Yale). Dr. Sheng Sun was supported 70% from the US army grant and 30% with *matching funds* from the Department of Physics at California State University Northridge.

The program has provided undergraduate and graduate students the opportunity to get hands-on experience with active researchers and to build a solid foundation for further scientific study and research careers. Students attend seminars that have grown out of the research program and participate in research via projects in upper level Solid State courses. A new graduate course, *Advanced Topics in Solid State*, has been added to the curriculum to introduce students to topics such as density functional theory, correlated electron systems, computational materials science, etc. Collaboration with the Los Alamos National Laboratory, and the Lawrence Livermore National Laboratory, has brought the students into contact with Ph.D.-granting institutions and national laboratories, and has enhanced the research environment at California State University.

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