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The primary goal of the proposed research was to study and develop alloying concepts for understanding intermetallic alloys as derived from a first principles quantum mechanical approach. Thus, a major part of our effort was to study and determine ductilizing effects of alloying elements in several intermetallic compounds and to work closely with experimental efforts to evaluate the applicability of the theoretical approach to alloy design. Specifically, highly precise all-electron quantum mechanical electronic structure methods were applied to the study of a number of materials problems in order to obtain from first principles information of relevance to alloy stability on the design of structural materials. Using our recently developed state-of-the-art all-electron self-consistent total energy methods which gives precise solutions of the local density equations, fundamental information was sought about the structural and electronic properties of these alloys in order to predict stable and metastable phases and how alloying effects bonding, crystal ordering and crystal symmetry. The first principles approach used here addresses questions of a metallurgical nature, such as phase stability, crystal structure, equilibrium lattice constants and mechanical properties including the effect of atomic relaxation.

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# Quantum Mechanical Approach to Understanding Microstructural and Mechanical Properties of Intermetallics

by Arthur J. Freeman
PRINCIPAL INVESTIGATOR

PERIOD OF PERFORMANCE: January 1, 1992 through January 31, 1995

# Quantum Mechanical Approach to Understanding Microstructural and Mechanical Properties of Intermetallics

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## I. INTRODUCTION AND BACKGROUND PERSPECTIVE

The high temperature intermetallics have become a major focus of efforts - both experimental and theoretical - driven in large part by their potential for important aerospace applications. In the theoretical area of this research, our work has been at the forefront and has already stimulated similar efforts at other laboratories. Indeed, the work initiated and carried out under AFOSR support reflects the present state of the field and the reaching of a threshold: advanced theoretical - computational techniques combined with the power of supercomputers provide an understanding of matter at the atomic-scale with an unprecedented level of detail and accuracy. It is this capability that has given birth to a new branch of scientific endeavor: Computational Materials Science. Not only can we simulate experiment, but using the computational approach, we are now beginning to design new materials and to predict their properties without actually synthesizing them. In contrast to an analytic-theoretical approach, which isolates and idealizes real systems to unravel fundamental relations and laws, the computational approach is synthetic: its goal is to simulate more and more details of the systems studied including as much of the environment as possible.

Designing new materials with specific mechanical, thermal, chemical, electronic, magnetic and optical properties hinges on one basic assumption: the properties of the macroscopic ensemble are related to and can be derived from the properties of individual molecules and atomic building blocks (such as crystallographic unit cells in solids). But which atomic-scale physical quantities and observables need to be looked at? This is the important question today and the key to successful materials by design in the future.

Today much of the theoretical efforts are focused on the atomic scale since the theoretical concepts and methodologies being developed are bringing us closer to the goal of a unified approach. The theoretical approach, density functional theory, that underlies all the calculations discussed here 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 materials applications.

Our goal was to study and develop alloying concepts for understanding intermetallic alloys as derived from a first principles quantum mechanical approach. Thus, a major part of our effort was to study and determine effects of alloying elements in several intermetallic compounds and to work closely with experimental efforts to evaluate the applicability of the theoretical approach to alloy design. Specifically, as seen from the publications listed, our highly precise all-electron quantum mechanical electronic structure methods were applied to the study of a number of materials problems in order to obtain from first principles, information of relevance to alloy stability and the design of structural materials. Using our recently developed state-of-the-art all-electron self-consistent total energy methods which give precise solutions of the local density equations, fundamental information was obtained about the structural and electronic properties of these alloys in order to predict stable and metastable phases and how alloying affects bonding, crystal ordering and crystal symmetry. The first principles local density approach used addresses questions of a metallurgical nature, such as phase stability, crystal structure, equilibrium lattice constants, and some mechanical properties including the effect of atomic relaxation.

We have attempted in the above to describe how our first principles approaches have been employed to study some key problems in understanding high temperature intermetallics. It needs to be understood that the problems posed are as complex and challenging as any in materials science today. Thus, while significant, the progress made by us and others constitute (of necessity) only the first steps taken to "bridge the gap" - see the accompanying table (developed by Rosenstein & Freeman) - of relating the macroscopic properties to the atomic scale properties. This table encompasses not only a philosophy but also a working principle, that bridging the gap requires a strong collaboration between the materials science and metallurgy community (Dimiduk, Frazer and others) and computational materials scientists.

Since most of our recent effort focussed on $\gamma$-TiAl, we describe some of this work here. This will also serve to illustrate the approach taken in tackling some complex problems, the computational/theoretical capabilities brought to bear in their solution and the meaningful results obtained.

## II. PROGRESS MADE

### A. Electronic Structure, Ti-Ti Bonding and Properties of $\gamma$-TiAl

Recently, several authors[12,13,14] have tried to understand the cause of the poor ductility of $\gamma$-TiAl in terms of the type and character of available deformation mechanisms. Some[15,16,6,17] have tried to examine possible effects of bonding on mechanical properties

# COMPUTATIONAL MATERIALS DESIGN: HIGH TEMPERATURE INTERMETALLICS

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**PREMISE**: MACROSCOPIC PROPERTIES ARE RELATED TO ATOMIC-SCALE PROPERTIES.

| RESEARCH VEHICLE | ATOMIC SCALE PROPERTIES MODELED | "BRIDGING THE GAP" <---------------------> | MECHANISMS INFLUENCED: (MICROMECHANICAL/ MICROSTRUCTURAL) | EXPERIMENTAL VERIFICATION OF MECHANICAL PROPERTIES |
|---|---|---|---|---|
| FUNDAMENTAL PHYSICS<br>All-electron total energy quantum mechanical approach<br>• Periodic Lattice<br>• Large Clusters Broken Symmetry | Bonding | THE PULL ACROSS THE "GAP" MUST BE SUPPLIED BY REQUIREMENTS FROM THE MORE MACROSCOPIC COMMUNITY. | Bonding Directionality, Strength, Type | Deformation Processes |
| | Cohesion | | Interfacial Phenomena<br>Grain Boundary Sliding<br>Void Formation | Fracture, Creep |
| | Phase Stability Cubic Structure ($L1_2$) | | Slip Systems Available<br>[111] Planes Promote Easier Slip/Deformation | Ductility, Toughness |
| COMPUTATIONAL TOOL<br>Use supercomputers to perform otherwise formidable amount of calculations | Alloying Microalloying | | Solid Solution Strengthening<br>Solute/Dislocation Interactions | Strength, Ductility Fatigue |
| | Phase Transformations | | Control of Microstructure<br>Role of Ternary Additions<br>Transformation Toughening | All Properties |
| | Fault Energies (APB, Twins, Stacking, etc.) | | Dislocation Mobility<br>Interfacial Energies<br>Activation of Specific Slip Systems | Deformation, Fracture |

Electronic Materials Experience

Materials Science .... Metallurgy
Microstructure/Property Relationships
Lots of Experience!!

and to understand the dislocation behavior in terms of the underlying bulk electronic structure. Studying the effects of substitutional ternary additions using a cluster linear muffin-tin orbital (LMTO) method, Morinaga et al.[15] observed that ternary additions (such as Mn) which weaken the Ti-Al d-p interactions and enhance the Ti-Ti d-d interactions may improve its ductility. Using the full-potential linearized augmented plane wave (FLAPW) method[1], Fu and Yoo studied the elastic constants and various fault energies of TiAl and found a fairly large elastic shear anisotropy ($A_2$) along the [011] direction, and a high APB energy due to the strong cohesion between Ti and Al layers. From charge densities and planar fault energies calculated using a layered Korringa-Kohn-Rostoker method, Woodward et al.[17] observed that the hierarchy of fault energies was consistent with the number of disrupted p-d and d-d bonds. Greenberg et al.[6] suggested that Ti d-d bonding in the (001) plane forms a rigid framework and that this charge anisotropy results in a Peierls stress anisotropy in $\gamma$-TiAl. In their view, the presence of deep Peierls valleys may be one factor responsible for both brittleness and the anomalous flow-stress versus temperature behavior.

It is well-known that the flow and fracture of high temperature intermetallic alloys is strongly influenced by the propagation and cross slip of ordinary and super dislocations. In TiAl, there is an apparently large Peierls stress, or lattice friction stress for the glide of ordinary (1/2<110>) dislocations. This Peierls relief is intimately related to the underlying crystal and electronic structure of TiAl, and specific bonding states have been identified by some investigators as contributing to the pinning of dislocations along certain line directions. In our study, we quantify the relative strength of these bonds using several complementary electronic structure methods.

Many factors have been found to affect the ductility of this material, such as ternary additions, microstructure, and especially stoichiometry. For example, the ductility of $\gamma$-TiAl increases with (i) decreasing aluminum concentration (i.e., depends on the stoichiometry), (ii) decreasing amounts of impurity concentration (such as, oxygen or carbon etc.), (iii) doping few percent ternary additions ( such as, Mn, Cr, and V etc.). Many speculations were proposed to discover a mechanism for improving its mechanical properties. One such conjecture is that the increase in metallic bonding with decreasing aluminum content may be responsible for improving the ductility.

In what follows, aspects of the electronic structure, equilibrium lattice constants and bond energies of $\gamma$-TiAl are compared with hypothetical fcc Ti as obtained by the full-potential linearized augmented plane wave (FLAPW) method[1], the DMol molecular cluster method[3] and the linear muffin-tin orbital-Green's function (LMTO-GF) method[4]. Pair energies, bond occupations of Ti-Ti and Ti-Al bonds in $L1_0$ TiAl and fcc Ti are calculated using the LMTO-GF method. Comparing the $d_{xy}$ bonding states for these two crystal structures, we find that the in-plane directional d-d bonding between Ti atoms on the (001) plane are strengthened in TiAl relative to fcc Ti. These observations suggest that the alternating (001) planes of Al and Ti atoms enhance these bonding states. Conversely, transition metal ternary additions substituted on the Al sites in TiAl are expected to weaken these bonding states. Using the FLAPW method, we examined the changes in charge density in the (001) Ti planes when Mn atoms are substituted on Al sites in TiAl and LMTO-GF methods were used to study the effect of Mn substitutional point defects on the (001) Ti $d_{xy}$ bonding states. The elastic constants of TiAl and Al rich TiAl were determined using the FLMTO method and compared with those of fcc Ti. Most recently, the effects of ternary additions on the twin energy and site preference in $\gamma$-TiAl were investigated as was the role of impurities such as C and O (see below).

### B. Effect of Stoichiometry

It is known[12] that $\gamma$-TiAl has the ordered face-centered tetragonal $L1_0$ structure with c/a= 1.02, and that single phase $\gamma$-TiAl exists only on the Al-rich side with a composition range about 50 - 65 at.%Al. At off-stoichiometric compositions, excess titanium and aluminum atoms occupy anti-sites without creating vacancies. On the other hand, the phase diagram shows that Ti-rich TiAl decomposes into a mixture of two phases, TiAl and $Ti_3Al$ ($\alpha 2/\gamma$).

For studying the effect of stoichiometry theoretically, we constructed a 16-atom $L1_0$ structured supercell as a model to simulate the Al-rich (or Ti-rich) TiAl according to the center site occupied by Al (or Ti). In order to judge the phase stability, we calculated the formation energy[18] for each phase, and compared with that of its decomposed components or existing equilibrium compounds (e.g., we compared the formation energy of $Ti_7Al_9$ with that of $7TiAl+2Al$ or $6TiAl+TiAl_3$). The calculated formation energy results show that Al-rich TiAl (i.e., $Ti_7Al_9$) is energetically stable as compared to its decomposed counterparts (either $7TiAl+2Al$ or $6TiAl+TiAl_3$). On the other hand, $Ti_9Al_7$ is unstable with respect to a mixture phases of TiAl and $Ti_3Al$ (cf., Table.1 of our as yet unpublished results) in agreement with observations.[12]

Table I. Equilibrium lattice constant (in Å) and formation energy (in eV/atom) of Al-rich TiAl and Ti-rich TiAl. As comparison, the formation energy of the decomposed components or existing stable compounds were also listed (unpublished).

| | Lattice Constant | Formation Energy |
|---|---|---|
| $Ti_7Al_9$ | 3.97 | 0.649 |
| $7TiAl+2Al$ | | 0.472 |
| $6TiAl+TiAl_3$ | | 0.509 |
| $Ti_9Al_7$ | 3.98 | 0.340 |
| $6TiAl+Ti_3Al$ | | 0.477 |

### C. Electronic Structure of TiAl

In order to gain insight at the microscopic level into the bonding character of TiAl, we considered tetragonal $L1_0$ TiAl along with hypothetical fcc Ti because, except for c/a=1.02, tetragonal face-centered $L1_0$ is indeed a fcc-like structure. One can view $L1_0$ TiAl as stacking alternatively one fcc Ti layer on one fcc Al layer. To understand the bonding character of γ-TiAl, we studied the electronic structures of both $L1_0$ TiAl and fcc Ti using the FLAPW method, and obtained the equilibrium lattice constants for both fcc Ti and $L1_0$ TiAl. The calculated lattice constant for γ-TiAl agrees well with the observed value. It is interesting to note that the calculated interatomic distance (i.e., bond length) of the Ti-Ti bond in the fcc structure is quite close to the observed bond length of Ti in the bcc structure, and about 3% smaller than that of Ti in the hcp structure. However, it is 1% larger than the Ti-Ti bond length in TiAl. This means that when one Ti (001) layer and one Al(001) layer are successively stacked together along the <001> direction to form TiAl, it keeps the fcc-like structure; the only modification seen is the appearance of a shrinkage of its lattice constant (or the bond length) in the (001) plane.

To visualize the bonding character, we plotted the charge density of Ti-plane in the pure fcc Ti, compared it with its counterpart in $L1_0$ TiAl and found that the charge becomes more directional ($d_{xy}$) in TiAl as compared with that in fcc Ti. This implies that the existence of Al in the alternating plane in TiAl may be responsible for this more directional bonding.

### D. Bond Energy and Occupation of the Ti-Ti bonding in TiAl

In order to have a quantitative description of the bonding character, we calculated pair energies and occupation numbers of the bond with the LMTO-Green Function method. The in-plane Ti-Ti pair energy increases from fcc Ti, to $L1_0$ Ti, to $L1_0$ TiAl. This means that the bond strength between the nearest neighbor Ti atoms increases in going from fcc Ti to TiAl. On the other hand, the inter-plane nearest neighbor bond strength remains approximately the same value for all three cases. This is consistent with the shrinkage of the in-plane lattice constant for TiAl compared with fcc Ti.

Furthermore, by studying the bond energy and occupation for different orbitals, we found that in the Ti-Ti in-plane bond, the bonding state with the largest number of electrons is the $d_{xy}$-$d_{xy}$ bond. The occupation number of the $d_{xy}$-$d_{xy}$ bond increases from fcc Ti, to $L1_0$ Ti to in TiAl, and the bond energy increases from fcc Ti, to $L1_0$ Ti, to $L1_0$ TiAl. It is obvious that there are more electrons and a higher bond energy in the Ti$d_{xy}$-Ti$d_{xy}$ bond in TiAl compared with fcc Ti. These first bond strengths reported for TiAl provide strong evidence to support the argument that there is a strengthened Ti$d_{xy}$-Ti$d_{xy}$ bond in TiAl.

### E. Effect of Mn Addition on Ti-Ti Bonding in TiAl

We also considered the effect of ternary additions on the in-plane d-d bonding by replacing one of the atoms in the Al layer by a Mn atom. The charge density shows that fewer electrons are accumulated in the Ti-Ti bond and that the in-plane d-d bonding is less directional. With the LMTO-GF calculations, the Ti-Ti pair energy in $Ti_8Al_7Mn$ is found to be smaller than that in TiAl; the Ti-Al pair energy in $Ti_8Al_7Mn$ (Ti-43.75 at % Al - 6.25% Mn) remains close to the Ti-Al pair energy in TiAl; the Ti $d_{xy}$-Ti $d_{xy}$ bonding state in $Ti_8Al_7Mn$ has fewer electrons and a lower energy than in TiAl. These results show that the in-plane d-d bonding is weaker and less directional when Mn substitutes Al in TiAl.

Noting the experimental results that Mn additions occupy Al sites[19] and improves the ductility[20] of Ti rich $\gamma$-TiAl, our results are consistent with previous models that suggest that the strengthened in-plane directional bonding in TiAl is among the factors responsible for the poor ductility of $\gamma$-TiAl.

This finding leads us to expect that any ternary additions substituted on the Al sites and contributing d-electrons may reduce the in-plane Ti-Ti directional bonding and reduce the Peierls anisotropy in TiAl. Indeed, this view may explain the beneficial effect of some other d-additions (such as Cr and V) in $\gamma$-TiAl.

## F. Phase Stability, Bonding Character and Elastic Constants of TiAl and Al rich TiAl

For a structural material, it is important to study its elastic constants, because the elastic constants give a direct measure of the stiffness of the materials. As was done for the determination of the equilibrium lattice constants, the elastic constants can be obtained by means of total energy calculations under several uniform distortions. Using the FLMTO method[2], we determined and compared the elastic constants for fcc Ti, TiAl and $Ti_7Al_9$. These unpublished results are listed in Table 2, which is taken from Appendix A, the preprint of a paper scheduled to appear in Phys. Rev. B.

As shown in Table 2, except for $C_{44}$, $C_{66}$ and $C_{66}$, all the other elastic constants for TiAl and the Al-rich compound, $Ti_7Al_9$, remain more or less the same as that of pure fcc Ti. On the other hand, $C_{44}$, which corresponds to a [010] shear strain on the (001) plane, has been dramatically enhanced - from 0.73 x $10^{11}$ $N/M^2$ in fcc Ti, to 1.21 x $10^{11}$ $N/M^2$ in TiAl, to 1.12 x $10^{11}$ $N/M^2$ in $Ti_7Al_9$ . Note that $C'_{66}$ is the only one that increases monotonically upon going from fcc Ti, to TiAl to $Ti_7Al_9$. Since $C'_{66}=(C_{11}-C_{12})/2$ corresponds to the [110] shear strain on the (110) plane, this indicates that intrinsic hardness increases from fcc Ti, to TiAl to $Ti_7Al_9$, which may possibly be correlated with the lack of <110] dislocations in Al-rich $Ti_{48}Al_{52}$.[21]

Table 2. Elastic constants (in unit of $10^{11}$ $N/M^2$) of fcc Ti, TiAl and $Ti_7Al_9$ calculated with the FLMTO method. The percent number in the parentheses are the difference from the TiAl results listed in the second column. the last column lists the FLAPW results by Fu *et al.* for comparison.

| Elastic Constants | fcc Ti | TiAl | $Ti_7Al_9$ | TiAl (FLAPW, Ref. 15) |
|---|---|---|---|---|
| $C_{11}$ | 1.67(-5%) | 1.76 | 1.97(+12%) | 1.90(+8%) |
| $C_{12}$ | 1.01(+2%) | 0.99 | 0.93(-6%) | 1.05(+6%) |
| $C_{13}$ | 1.01(+3%) | 0.98 | 0.89(-9%) | 0.90(-8%) |
| $C_{33}$ | 1.67(-7%) | 1.79 | 1.75(-2%) | 1.85(+3%) |
| $C_{44}$ | 0.73(-40%) | 1.21 | 1.12(-7%) | 1.20(-1%) |
| $C_{66}$ | 0.73(+22%) | 0.60 | 0.87(+45%) | 0.50(-17%) |
| $C'_{66}$ | 0.33(+15%) | 0.39 | 0.52(+33%) | 0.42(+8%) |

### G. Effects of ternary additions on the twin energy in γ-TiAl

It has been known that in the Ti-48% Al alloys the additions of Mn, V and Cr results in increased twinning activity, and improves the ductility[20]. We have attempted to understand this behavior from a microscopic point of view, and studied the (111) twin boundary energy of stoichiometric TiAl, of TiAl with ternary additions (Mn and V), and the effect of stoichiometry on the twin energy[22]. The calculations were performed using a supercell scheme and the total energy linear muffin-tin orbital method. Both Al-rich and Ti-rich γ-TiAl were simulated with the use of $Ti_5Al_7$ and $Ti_7Al_5$ supercells, respectively. While the calculated results presented may be viewed as only qualitative, the trends observed are probably correct.

The calculated results showed that the twin energy for γ-TiAl is about 9 - 10 mRy/cell, (equivalently, 70 - 80 erg/$cm^2$), which is comparable with the FLAPW result[16] (60 erg/$cm^2$). Note that from the twin energy, γ-TiAl is close to the category of materials such as, aluminium, that have high twin energy (75 erg/$cm^2$)[23]. The fact that only few twins are observed in Al-rich γ-TiAl may be understood from its relatively high twin energy. Indeed, for the Al-rich case the nearly same value (75 - 80 erg/$cm^2$) of the twin energy is obtained as that for stoichiometric γ-TiAl. On the other hand, a significantly reduced twin energy (60 erg/$cm^2$) was found for the Ti-rich case as compared to stoichiometric γ-TiAl. This appears to agree qualitatively with the observation of increasing twin activity when the Al content is decreased to 48% in TiAl[12], but note that we have not considered the mobility of twinning dislocations which should be influenced by solutes.

For studying the effects of ternary additions on the twin energy in γ-TiAl, we constructed $(Ti_5X)Al_6$ $(Ti_{50-x}X_xAl_{50})$ and $Ti_6Al_5X$ $(Ti_{50}Al_{50-x})$ (where X = Mn or V) supercells, representing V substitutions on Ti and Al sites.[22] For the case of substitutions on the Al sites, the calculated twin energies turn out to be 55 - 60 erg/$cm^2$, which is about the same value as the twin energy of Ti-rich TiAl but markedly lower than that of stoichiometric γ-TiAl. The observation of the increase of twin activity in Ti-48% Al manganese alloys[19] may be understood in terms of lowering the twin energy due to the presence of these ternary additions in γ-TiAl. On the other hand, when V is substituted on the Ti sites the calculated twin energy is slightly lower than that of pure γ-TiAl. When Mn occupies Ti sites, an exceptionally small twin energy is obtained.

In order to understand this from the microscopic point of view, we inspected the density of states (DOS) for $Ti_6Al_5Mn$ (or V). Near the interface, the characteristic p-d peak located at about 2.0 eV below $E_F$ in stoichiometric γ-TiAl[16] was found to be spread out which indicates that the degree of p-d (directional) bonding has been reduced. As a result, the general feature of the total DOS for $Ti_6Al_5Mn$ (or V) resembles pure fcc titanium (in the region between $E_F$ and -3 eV) plus a parabolic-like tail (from -3 eV to -9 eV (mainly) due to Al contributions). From the calculated partial DOS, it is clear that the main contributions from the ternary addition are the d-states located near (or above) $E_F$, which are hybridized strongly with the Ti-d states. This hybridization determines the major feature of the DOS near $E_F$, and restores the d-d interactions between the Ti layer and the neighboring d-substituted Al layer. As a result, the in-plane Ti d-Ti d directional bonding is weakened, as found also above. Thus, both reduced p-d bonding and restored d-d bonding between neighboring layers may play a positive role towards improving the intrinsic ductility. (We should note that a similar analysis for the γ/α2 and γ/γ interfaces proposed later, will yield important information there as well.)

### H. Molecular Cluster Studies of the Effect of Impurities in TiAl

A number of recent experiments show that the mechanical properties of γ-TiAl and $TiAl/Ti_3Al$ lamellar vary under different environments such as in $O_2$, $H_2$, air or vacuum. The cause of these environmental effects is still, however, unclear. The molecular cluster model represents a convenient method for studying those electronic properties that are primarily a function of the local environment of the system, such as vacancies, interstitial and substitutional defects, and local moments. Thus, we have carried out DMol molecular cluster calculations[3], to investigate the role of these low level impurities on the properties of TiAl. With this approach, the site preference, lattice relaxation, and bonding character can be obtained for these interstitial impurities.

From these calculations, results such as total binding energy of the cluster, the charge density, the deformation density, molecular orbitals and density of states were obtained. When determined for several geometries or for different electronic states, this information can be used to predict such properties as relative energetics and stabilities, and ground state electron configurations. With atomic force calculations, we also determined the impurity-induced lattice relaxation, which is an important part of the study.

We began by studying the electronic structure of TiAl using the total energy and atomic force capabilities of the DMol method with several cluster models ranging from 6 to 47 atoms. We found that clusters as small as 6 atoms can give the basic properties such as the bonding between atoms - even though there exists a significant surface effect. More precise calculations should include atoms at least to the second nearest neighbors. The results show that in the (001) pure Ti plane, the Ti-Ti directional bonding dominates, which is mainly the contribution of the Ti-$d_{xy}$ component. In the pure (001) Al plane, the charge density around Al sites is quite flat, indicating metallic bonding between the Al atoms; in the (010) mixed Ti-Al plane, the Ti-d and Al-$p_z$ forms a mixture of s and p bonding states. This p-d bonding state gives a high peak in the DOS curve at 2 eV below $E_F$. These results are in good agreement with other theoretical calculations[16,17] and those reported above.

To obtain insight into how the Ti-Ti bonding is changed from the pure Ti metal to the TiAl compound, we constructed a $Ti_{40}$ cluster with fcc structure and calculated the deformation charge between Ti atoms in the (001) plane. It turns out that there is no obvious directional bonding between Ti atoms in fcc Ti, in contrast with that in TiAl. This again implies that Al may play a role in enhancing the directionality of Ti-Ti bonding in TiAl. Accordingly, one can expect that adding more Al to TiAl may further enhance the directional in-plane Ti-Ti bonding. Our calculations on an Al-rich cluster, do show that Ti-Ti in-plane bonding is stronger than that in a Ti-rich cluster. The increase in Ti-Ti in-plane bonding results in a shrinkage of the lattice constant in the basal plane - which explains the observation that the lattice constant of the basal plane in TiAl is smaller than that of pure fcc Ti metal. This was separately confirmed by our FLAPW total energy calculations (reported above) which showed that the horizontal lattice constant of TiAl shrinks by 1% compared to fcc Ti. These results support the idea of Greenberg et al.[6] that Ti-Ti bonding is also an important factor in determining the structure of TiAl.

Knowing the basic electronic structure of pure TiAl, we next began to study the effect of impurities on the atomic and electronic structure of TiAl and to determine the possible connection between these effects and the mechanical properties of TiAl. We studied two impurities, namely, carbon and oxygen using two clusters models, $Ti_4Al_2X_1$ and $Ti_{20}Al_{20}X_1$, with X representing the impurity atom at the octahedral center of TiAl. There are two possible choices for the impurity atom position. One is in the Ti plane, another in the Al plane. Our calculation on the 40 atom cluster shows that both C and O prefer to stay in the Ti plane, since the binding energy of this site is more than 1.9 eV higher than when C and O stay in the Al plane. Table 3 lists the calculated (as yet unpublished) results. It can be seen from this Table that C has a higher binding energy than O indicating a stronger interaction between C and its neighboring atoms. Without considering the lattice relaxation, C and O have very little hybridization with either Ti and Al implying that they do not form visible covalent bonding with metal atoms. This can be seen from both density of states and deformation charge contour plots, separately obtained.

Table 3: Binding energies (in eV) of 40 atom cluster with and without impurity atom. $X_1Ti_{20}Al_{20}$ denotes an impurity in the Ti plane; and $X_1Al_{20}Ti_{20}$ denotes an impurity in the Al plane.

| | $X_1Ti_{20}Al_{20}$ | $Ti_{20}Al_{20}$ | $\Delta E$ |
|---|---|---|---|
| X=C | 186.91 | 177.24 | 9.67 |
| X=O | 185.50 | 177.24 | 8.26 |
| | $X_1Al_{20}Ti_{20}$ | $Al_{20}Ti_{20}$ | $\Delta E$ |
| X=C | 184.91 | 177.40 | 7.51 |
| X=O | 183.75 | 177.40 | 6.35 |

Table 4: Relaxation of the nearest neighbor atoms when impurities are placed at octahedral sites in the Ti plane. E (in eV) is the binding energy and $\Delta E$ (in eV) is the energy gain after relaxation. $P_{X\text{-}Ti}$ and $P_{X\text{-}Al}$ stand for the percentage change of X-Ti and X-Al bond length.

| $X_1Ti_{20}Al_{20}$ | E(relaxed) | E(unrelaxed) | $\Delta E$ | $P_{X\text{-}Ti}$ | $P_{X\text{-}Al}$ |
|---|---|---|---|---|---|
| X=C | 187.22 | 186.91 | 0.31 | 3.5% | 0.6% |
| X=O | 185.96 | 185.50 | 0.46 | 3.5% | 4.2% |

An important result from the calculation is that we found a significant relaxation for both X-Ti and X-Al bond lengths when O is placed on the Ti plane, while C only induces relaxation for the X-Ti bond length. These results are listed in Table 4.

These results show that O produces large relaxations in both the Ti and Al bond length whereas C interacts much more strongly with Ti than with Al atoms. From the difference charge density in the X-Ti plane, it can be seen that there is an obvious bonding between C and the nearest Ti atoms. For O in TiAl, this bonding is weak.

## III. MOST RECENT ACTIVITIES ON FIRST PRINCIPLES REAL-SPACE CALCULATIONS OF FAULT ENERGETICS (INCLUDING IMPURITIES) IN TiAl

In this part of the work, we are starting to develop real-space methods for calculating fault energies. As spelled out below, this is being attempted by combining the first-principles tight-binding Hamiltonian[24,25] with an effective real-space method for calculating the local DOS[26]. This will hopefully provide the ability to study systems with strongly reduced symmetry, even amorphous metals and alloys[27,28] and also impurity states[29].

Accurate ab-initio calculations of stacking fault energetics are difficult from a computational point of view. In supercell calculations[30,31], the numerical work increases with the third power of the numbers of layers; in layer KKR[32,17] the planar defects are treated in a less costly way; however, such calculations are restricted only to planar defects. Moreover, the numerical accuracy of these methods is challenged by attempting to calculate small fault energies by taking the difference of two large total energies.

For systematic calculations we need methods which simplify the computational difficulties but that are still ab-initio and precise. Thus, we need to find a compromise between our wishes to simulate complicated defects (such as dislocations) and to carry out precise ab-initio band structure calculations. From our investigations to date, the combination of the ab-initio tight-binding like method (TB-LMTO)[24,25] with the recursion method[26] (we use the notation R-TBLMTO method) and the "frozen potential" approximation[33,34] or the Harris-Foulks functional[35] appears to provide a reliable approach for the systematic study of systems with reduced symmetry, such as stacking faults in doped aluminides. The advantages of the TB-LMTO formalism in this case includes: (i) dividing the problem into two parts - the (structural) screened structure constant part and the potential function part[24,25] - provides a natural way to use "frozen" potentials[33] and Harris-Foulks functional[35] approximations in order to avoid the problem of subtracting the huge total energy values to find small defect energies. We note that frozen potentials have been used successfully for calculating the energetics of intrinsic faults in Ag using an Ising model[36]). (ii) The influence of environmental changes (chemical or structural) on the structural part can also be taken into account by real space calculations[28,37].

Unlike previous supercell band structure[30,31] and layer KKR approaches[17,38], the R-TBLMTO method may provide us with the ability to simulate (i) impurities in stacking faults by going beyond the single site approximation (as done in [38]) and, (ii} the influence of a finite concentration of impurities, or a cluster of impurities (for treating the effects of local fluctuations of the concentration).

We believe that developing real space methods for studying aluminide materials is one possible way to consider faults more complex than planar faults, such as dislocations which are characterized by a pronounced reduction of crystal symmetry which is incompatible with traditional supercell methods. The precision and real capabilities of the proposed R-TBLMTO method were verified for the case of simple planar faults determined previously by other methods.

If all goes well, we hope to use this technique to study the influence of impurities (i.e., the chemical effects of alloying) on the changes of of fault energies in TiAl - including relaxations at the faults. This method appears to allow us to calculate self-consistently several hundred atoms in a cluster containing several thousand atoms[28] and so may well provide a basis for the theoretical description of the faults and the influence of impurities on those energy parameters.

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1. "Phase Stability and Role of Ternary Additions on Electronic and Mechanical Properties of Aluminum Intermetallics", A.J. Freeman, T. Hong, W. Lin and J.-h. Xu, in *High-Temperature Ordered Intermetallic Alloys IV*, L.A. Johnson, D.P. Pope and J.O. Stiegler, eds., Mater. Res. Soc. Symp. Proc. **213**, (1991) p. 3.
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## CONFERENCES, SEMINARS, WORKSHOPS

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