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**FIRST-PRINCIPLES STUDY OF INTERMETALLIC PHASE
STABILITY IN THE TERNARY Ti-Al-Nb ALLOY SYSTEM**

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ABSTRACT

The stability of bcc-based phases in the Ti-Al-Nb alloy system has been studied from first-principles using a combination of *ab-initio* total energy and cluster variation method (CVM) calculations. Total energies have been computed for 18 binary and ternary bcc superstructures in order to determine low temperature ordering tendencies. From the results of these calculations a set of effective cluster interaction parameters have been derived. These interaction parameters are required input for CVM computations of alloy thermodynamic properties. The CVM has been used to study the effect of composition on finite-temperature ordering tendencies and site preferences for bcc-based phases. Strong ordering tendencies are observed for binary Nb-Al and Ti-Al bcc phases as well as for ternary alloys with compositions near Ti_2AlNb . For selected superstructures we have also analyzed structural stabilities 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 ternary bcc compounds.

INTRODUCTION

Ti-Al-Nb based materials are currently of great interest for aerospace applications due to their desirable mechanical properties and low densities¹. Since the development of these materials can be greatly aided by a detailed knowledge of equilibrium phase boundaries and their metastable extensions, the phase diagram of Ti-Al-Nb has been the subject of extensive research recently (for a review see Kattner and Boettinger²). 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 (α_2) structure gives rise to a compound (referred to as the O-phase) with an orthorhombic structure which is stable at low temperatures for compositions near Ti_2AlNb ³. 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^{2,4-6}. Metastable bcc phases with B2-type order have also been observed in quenched Nb-rich Nb-Al alloys both with and without ternary Ti additions⁷. In this paper we present preliminary results of a first-principles study of phase stability in Ti-Al-Nb. In particular, we will discuss results related to the effects which temperature and alloy composition have on ordering, site-selection tendencies, and structural stabilities for bcc-based phases in this system.

COMPUTATIONAL METHOD

The details of the computational approach will be given in a future publication and are summarized only briefly here. Finite-temperature ordering tendencies and site-selection preferences for bcc-based Ti-Al-Nb alloys have been studied within the framework of the cluster variation method (CVM)^{8,9}. The CVM is a generalized mean-field, statistical-mechanical method which allows one to compute a variational estimate of the free energy for an ordered or disordered alloy phase by minimizing a functional expressed in terms of a set of cluster-correlation variables⁹. The values of these correlation variables which minimize the free energy provide valuable information about the degree of atomic short- and long-range order present in the alloy phase. From this information the site-preferences for particular atomic species can be determined.

In the CVM the enthalpy is parametrized in terms of the so-called effective cluster interaction (ECI) coefficients which can be readily computed by fitting to energies of a large number of alloy

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RESEARCH

superstructures⁹. For the purpose of computing values for the ECI's in the present study, we have performed *ab-initio* total energy calculations for bcc Nb, Ti and Al, as well as the 18 binary and ternary alloy superstructures which can be stabilized by nearest- and second-nearest-neighbor effective pair interactions on a bcc lattice¹⁰. These 18 alloy structures include $D0_3$ (Fe_3Al), $B2$ (CsCl), $B32$ (NaTi), and Heusler $L2_1$ (Cu_2AlMn), as well as an additional ternary compound with A_2BC composition and $F\bar{4}3m$ space-group symmetry¹⁰. Total energy calculations have also been performed in order to determine the structural stability of various bcc-based compounds, as will be discussed further below.

Total energies have been computed within the framework of density functional theory using a full-potential implementation¹¹ of the linear muffin-tin orbital (LMTO) method¹². Special-point¹³ k-point sampling was used in all calculations and total energies were converged to an accuracy estimated to be within 0.5 mRy/atom.

RESULTS AND DISCUSSION

Ordering Tendencies for BCC-Based Phases

In Fig. 1 a ground-state ($T=0$ K) phase diagram for bcc-based Ti-Al-Nb phases is shown. Solid and dashed lines in this figure form the boundaries of three-phase triangles. The phase diagram was constructed from the total energies calculated for the bcc-based structures discussed above. The ground-state compounds and the three-phase triangles were determined by computing, as a function of composition, the combinations of bcc superstructures which minimize the energy.

The binary superstructures which were found to be ground-states in the present study are shown in Fig. 1 to be the following: $B32$ TiNb and NbAl, $D0_3$ Ti_3Al and Nb_3Al , and $B2$ TiAl. Two ternary compounds, with compositions Ti_2AlNb and Nb_2AlTi are also present in Fig. 1. The structure of Nb_2AlTi has $F\bar{4}3m$ space-group symmetry and is obtained when Al and Ti atoms order on the Al sublattice of the NbAl $B32$ compound. For Ti_2AlNb the $L2_1$ (Heusler) structure is found to be the stable bcc ground-state. In the $L2_1$ Ti_2AlNb structure Al and Nb atoms are ordered

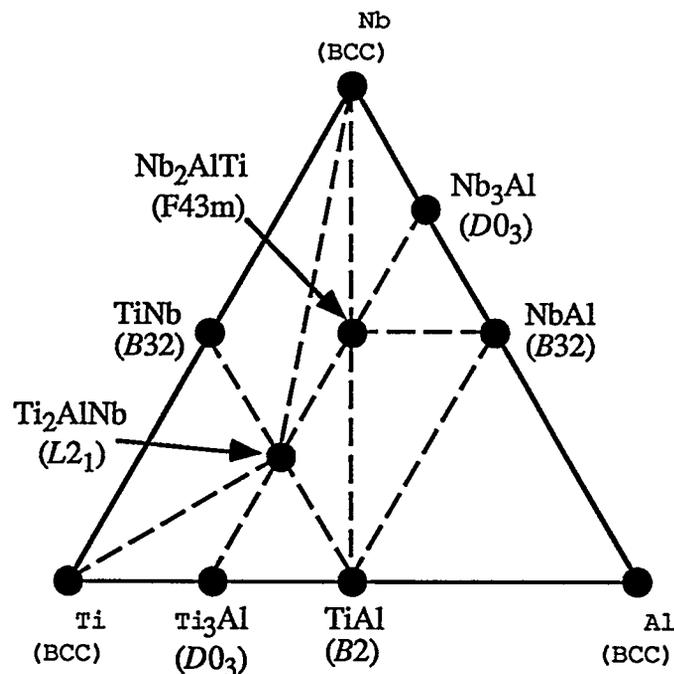


Figure 1: Calculated ground-state ($T=0$ K) phase diagram for bcc-based Ti-Al-Nb superstructures. Dashed and solid lines form the boundaries of three-phase triangles.

on the Al simple-cubic sublattice of the $B2$ TiAl compound.

The CVM has been used to calculate finite-temperature bcc-based phase diagrams for each of the Ti-Al, Ti-Nb and Al-Nb binary alloy systems. It is found that Ti-Nb shows the weakest ordering tendencies: we calculate that the ground-state $B32$ TiNb phase is stable only for temperatures below 200 K. The calculated bcc-based Nb-Al phase diagram includes a miscibility gap for the Al-rich bcc solid-solution at high-temperatures, as well as extensive phase fields for ordered $B32$ NbAl and DO_3 Nb₃Al at Nb-rich compositions. The strongest ordering tendencies for bcc-based phases are found in Ti-Al. Our calculations predict that $B2$ TiAl remains ordered to temperatures well above the experimentally measured liquidus in this system.

The effect of ternary composition on the order-disorder transition temperatures for the $B2$ phase has also been studied with the CVM. The results of these ternary CVM calculations are shown in Figs. 2 (a) and (b) for pseudo-binary TiAl-TiNb and Ti₃Al-Nb₃Al sections, respectively. The transitions between all phases shown in Fig. 2 were calculated to be second-order. In Fig. 2 (a) it can be seen that the substitution of Nb for Al is found to give rise to a strong decrease in the calculated BCC- $B2$ transition temperature (T_c). In the Ti₃Al-Nb₃Al section, Fig. 2 (b) shows that the addition of Nb initially gives rise to an increase in the value of T_c until a composition near 20 % Nb; further increases in the Nb concentration cause T_c to drop rapidly. The results of our calculations concerning the qualitative effect of Nb composition on the BCC- $B2$ critical temperature are in excellent agreement with those of recent experimental studies^{5,6}. Quantitative agreement with experiment is not as good however; the best experimental estimates⁵ of T_c for $B2$ alloys near Ti₂AlNb compositions are roughly 600 K lower than our calculated values.

Also shown in Fig. 2 are the CVM-calculated boundaries for transitions between the $B2$ and $L2_1$ Ti₂AlNb phases. We find that the critical temperature of the $L2_1$ phase has a maximum value at composition Ti₂AlNb which is roughly 70 percent of the BCC- $B2$ T_c at the same composition. Experimentally, the $L2_1$ phase has not been observed. At low temperatures and for compositions near Ti₂AlNb, the O-phase, with an orthorhombic hcp-based crystal structure³, is known to be stable. We have analyzed the stability of the O-phase with respect to $L2_1$ Ti₂AlNb by performing a series of electronic structure calculations for each structure. As will be discussed in further detail in a future publication, we find that the stability of the O-phase with respect to the ordered bcc superstructure at $T=0$ K can be attributed to the large energy associated with experimentally-observed¹⁴, symmetry-allowed displacements of atoms away from ideal close-packed positions for the structure of the former.

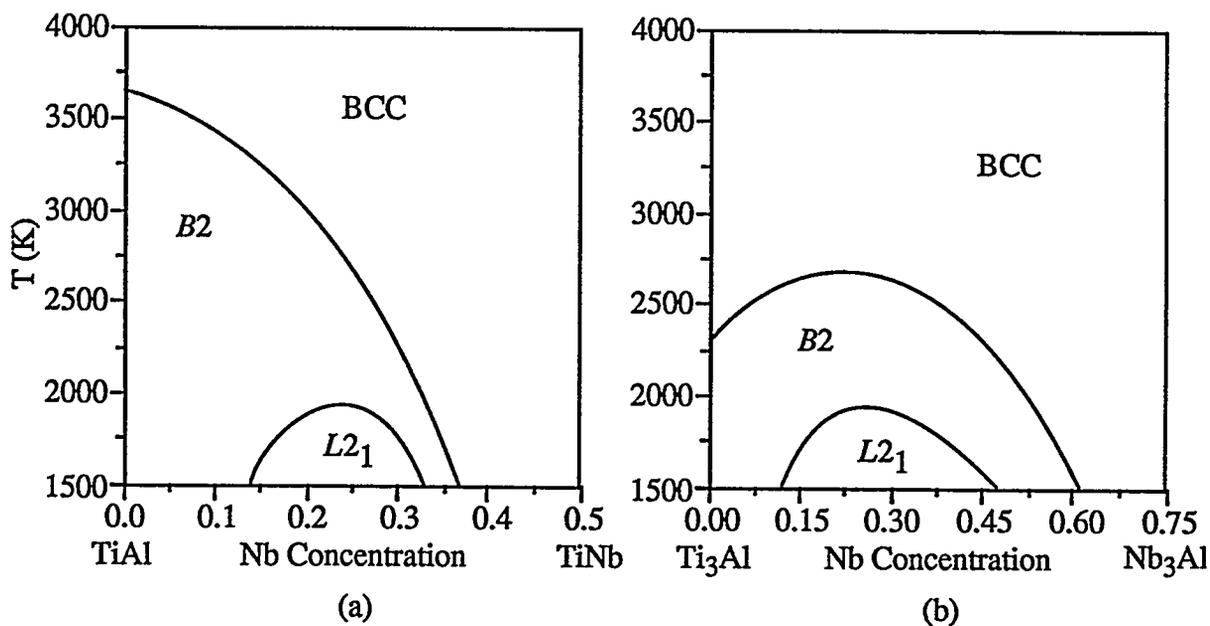


Figure 2: Calculated second-order transition temperatures for bcc-based phases along the TiAl-TiNb (a) and Ti₃Al-Nb₃Al (b) sections of the ternary phase diagram.

Site-Selection Preferences for the B2 Phase

CVM calculations have been performed in order to determine the effect of composition on the site-occupation preferences for Ti, Al and Nb atoms in the *B2* phase. The results of these calculations at temperatures corresponding to 75 % of the computed BCC-*B2* T_c are presented in Figs. 3 (a) and (b) for TiAl-NbAl and TiAl-TiNb pseudo-binary sections, respectively. In Fig. 3, $f_1(\text{Ti})$ and $f_2(\text{Al})$ correspond, respectively, to the average fraction of Ti and Al which occupy sublattices "1" and "2" of the *B2* structure. Similar definitions hold for $f_1(\text{Nb})$ and $f_2(\text{Nb})$. The values of $f_1(\text{Ti})$ and $f_2(\text{Al})$ are shown in Fig. 3 to be greater than 0.5 for all compositions considered. In other words, we find that Ti and Al atoms always preferentially occupy different sublattices in the *B2* structure, in agreement with the results of two recent experimental measurements for *B2* phases with $\text{Ti}_{65}\text{Al}_{25}\text{Nb}_{10}$ ¹⁵ and $\text{Ti}_{43}\text{Al}_{41}\text{Nb}_{16}$ ¹⁶ compositions.

In contrast to Ti and Al, the nature of the site-selection preference for Nb depends on the composition of the alloy. In Fig. 3 (a) it is shown that when the concentration of Al is maintained at 50 %, a majority of Nb atoms occupy the same sublattice as Ti. The opposite trend is found in Fig. 3 (b): Nb atoms prefer the Al sublattice sites when the concentration of Ti is fixed at $c=0.5$. CVM calculations of Nb site occupancies have also been performed for *B2* phases having equal concentrations of Ti and Al. In this case, a very weak preference is found for Nb atoms to occupy Ti sites. Our results for Nb site-occupancies are also consistent with the experimental measurements referenced in the previous paragraph: for the alloy containing a Ti-rich composition, a strong preference for Nb atoms to occupy Al-sublattice sites was found experimentally¹⁵. By contrast, for the *B2* phase with nearly equal concentrations of Ti and Al, approximately the same fraction of Nb was measured on each of the two sublattices¹⁶.

The nature of the atomic site preferences for the *B2* can be understood qualitatively in terms of a simple bond-counting argument. Since the strongest driving force for *B2* ordering exists for Ti-Al, nearest-neighbor (nn) "bonds" between these atoms are significantly more favorable than for Ti-Nb and Al-Nb. Preferential occupation of different sublattices by Ti and Al therefore arises in order to increase the number of favorable nn bonds between these atoms. Nb is left to occupy whichever sites remain: Al-sublattice sites when the concentration of Ti is high and vice-versa.

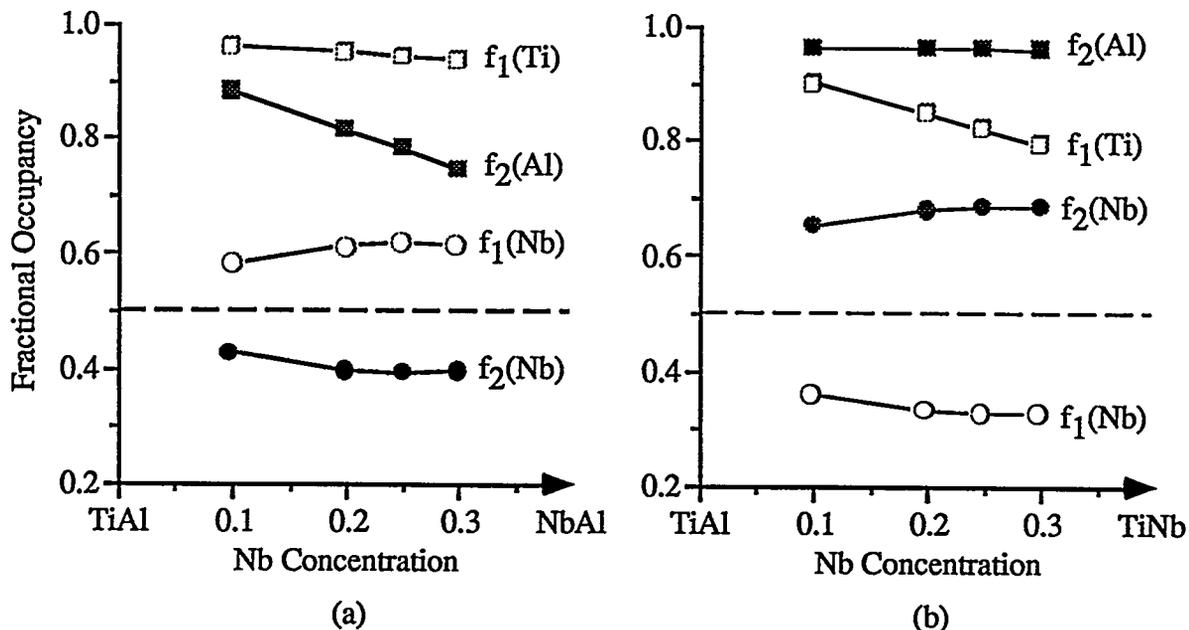


Figure 3: CVM-calculated fractional occupancies for Ti, Al and Nb atoms on the two different sublattices in the *B2* phase. (a) and (b) show results for TiAl-NbAl and TiAl-TiNb pseudo-binary sections, respectively. The variables $f_1(\text{Ti})$, $f_2(\text{Al})$, $f_1(\text{Nb})$ and $f_2(\text{Nb})$ are defined in the text.

Stability of BCC-Based Structures

The phase diagram of Fig. 1 shows that $B32$ is predicted to be the most stable bcc superstructure for NbAl. Recent experimental studies, however, have determined that metastable phases in quenched Nb-Al alloys show signs of $B2$ rather than $B32$ order (see Menon et al.⁷ and references therein). In particular, selected-area-diffraction patterns taken from Nb-rich quenched alloys for $[100]$ orientations show superlattice spots in positions which are characteristic of the $B2$ structure. However, an analysis of the diffraction pattern for an $[011]$ orientation shown in Fig. 2 (b) of the paper by Menon et al.⁷ leads us to conclude that the ordered phase seen in quenched Nb-Al alloys has tetragonal rather than cubic symmetry. We propose that diffraction patterns obtained for quenched Nb-Al samples are consistent with a tetragonal $L1_0$ (CuAu) structure which is related to the $B2$ through the well-known Bain transformation which takes a bcc into an fcc lattice. We will now show that results of total energy calculations support this interpretation.

The effect of tetragonal distortions on the total energies of the $B2$ and $B32$ NbAl compounds have been calculated from first principles using the full-potential LMTO method mentioned above. The results of these calculations are shown in Fig. 4 where the formation energy (ΔE) is plotted as a function of the tetragonal distortion for a constant volume per unit cell. ΔE is defined as the difference between the total energy of a given NbAl structure and the average of the calculated energies for ideal bcc Nb and Al. In Fig. 4 the degree of tetragonal distortion is parametrized by the ratio of the c to a lattice parameters; c/a ratios of 1 and $(2)^{1/2} = 1.4142\dots$ correspond to ideal bcc and fcc lattice geometries, respectively.

In Fig. 4 (a) it can be seen that the $B2$ structure for NbAl is unstable with respect to tetragonal distortions since the curvature of the energy is negative for $c/a=1$. The dependence of ΔE on c/a shows a "double-well" structure with two minima located on either side of $c/a=1$. The lowest calculated energy for the NbAl compound with $B2$ order is obtained for a value of c/a roughly equal to 1.45. This c/a ratio is very close to the value for an fcc lattice where the distorted $B2$ is equivalent to an ideal $L1_0$ structure. In Fig. 4 (b) the calculated values of ΔE for $B32$ NbAl are also seen to depend strongly on the degree of tetragonal distortion. At $c/a=1$ the curvature of the $B32$ energy is found to be very close to zero; the lowest value of the energy for $B32$ NbAl

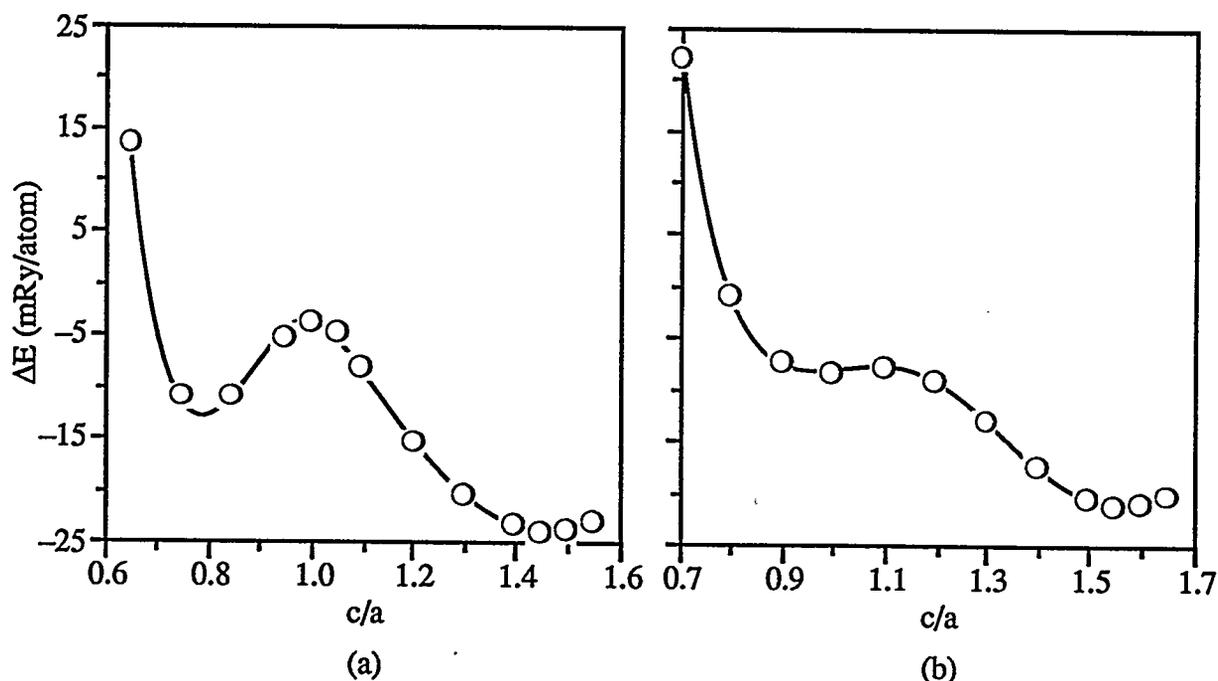


Figure 4: Effect of tetragonal distortions on the formation energies of $B2$ (a) and $B32$ (b) structures for NbAl. The definition of the formation energy is given in the text. For both (a) and (b) the same energy scale applies.

corresponds to a c/a ratio roughly equal to 1.58. The minimum value of the energy for the distorted $B2$, i.e. the $L1_0$, structure is shown in Fig. 4 to be lower than that for the $B32$ by 2.5 mRy/atom. Therefore, the results in Fig. 4 indicate that $B2$ -type order is preferred for bcc-based Nb-Al alloys at low temperatures. Furthermore, this type of ordering must be accompanied by a tetragonal distortion of the lattice, giving rise to an $L1_0$ structure with a geometry close to ideal fcc.

The effect of tetragonal distortions on the energies of $B2$ TiAl and $L2_1$ Ti₂AlNb has also been studied. An instability similar to that found for $B2$ NbAl also exists for $B2$ TiAl. By contrast, tetragonal distortions only increase the energy of $L2_1$ Ti₂AlNb. It therefore appears that the ternary additions to binary bcc alloys in Ti-Al-Nb have the effect of stabilizing ordered bcc superstructures. The features of the electronic structure which give rise to a structural instability for binary $B2$ TiAl and NbAl and which cause the $L2_1$ Ti₂AlNb structure to be stable with respect to tetragonal distortions will be the subject of future work.

Summary:

Results of a first-principles study of the stability, ordering-tendencies and site-selection preferences for bcc-based Ti-Al-Nb alloy phases have been presented. A ground-state ($T=0$ K) phase diagram has been computed which shows ordered bcc superstructures for Nb₃Al, NbAl, TiAl, Ti₃Al, TiNb, Ti₂AlNb and Nb₂AlTi compositions. The strongest ordering tendencies are found for Ti-Al bcc-based alloys. Addition of Nb to TiAl has been shown to lead to a decrease in the calculated BCC- $B2$ order-disorder transition temperature (T_c). Along the Ti₃Al-Nb₃Al pseudo-binary section we find that the BCC- $B2$ T_c has a maximal value near 20 % Nb. Calculations for site occupancies in ternary $B2$ phases show that, independent of the composition of the alloy, Ti and Al preferentially occupy different sublattice sites. By contrast, the sublattice occupancy preference for Nb atoms in this phase is found to change with composition: Nb atoms prefer Al sublattice sites for Ti-rich compositions and vice-versa. The effect of tetragonal distortions on the energies of cubic TiAl, NbAl and Ti₂AlNb bcc superstructures has been examined and structural instabilities are found for binary, but not ternary, compounds. We show large tetragonal distortions are associated with $B2$ -type ordering in Nb-Al. This result is consistent with diffraction patterns shown in the paper of Menon et al.⁷ for quenched Nb-rich Nb-Al alloys.

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