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Lawrence Berkeley Laboratory
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Materials Sciences Division

Presented at the MRS 1992 Spring Meeting (Symposium W),
San Francisco, CA, April 27–May 1, 1992,
and to be published in the Proceedings

Received by OSTI
NOV 0 6 1992

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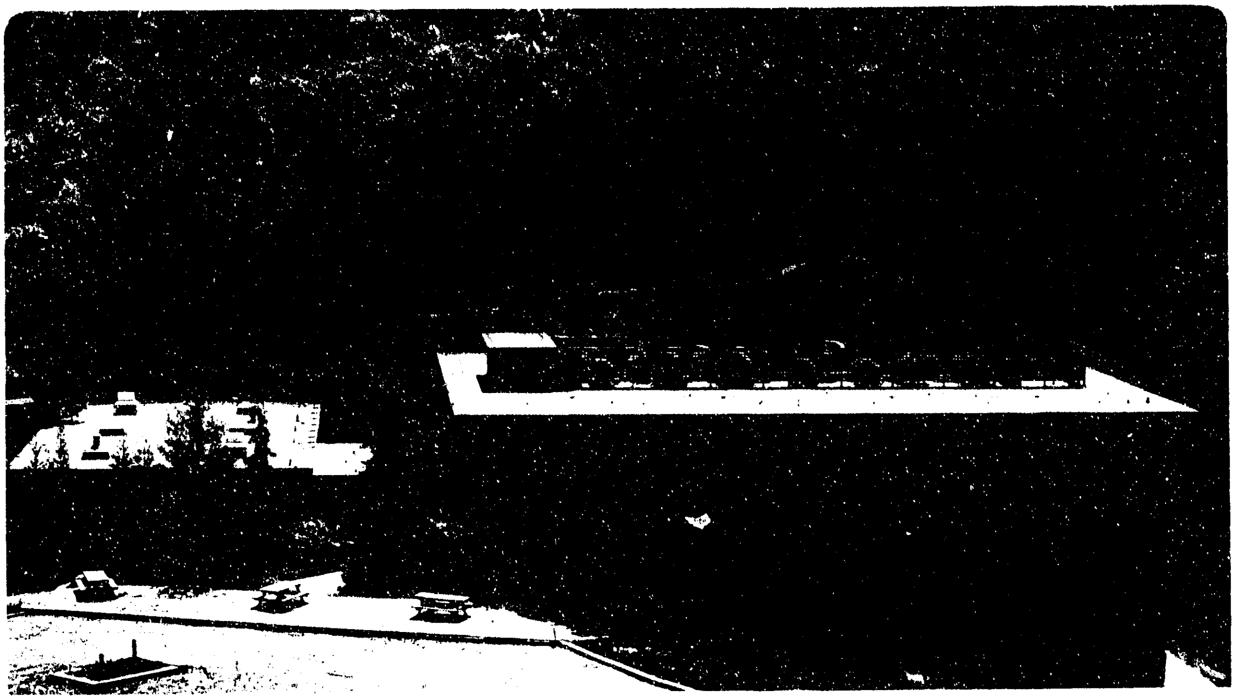
April 1992



Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098

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This work was supported by the Institute for Scientific Computing Research at the Lawrence Livermore National Laboratory, Livermore, CA, and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

A FIRST-PRINCIPLES STUDY OF THE PHASE STABILITY OF FCC-BASED Ti-Al ALLOYS

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ABSTRACT

In this paper we present results of a first-principles phase stability study of fcc-based Ti-Al alloys. In particular, the full-potential linear muffin tin orbital method has been used to determine heats of formation and other zero-temperature properties of 9 fcc ordered superstructures as well as fcc and hcp Ti, and fcc Al. From these results a set of effective cluster interactions are determined which are used in a cluster variation method calculation of the thermodynamic properties and the composition-temperature phase diagram of fcc-based alloys.

INTRODUCTION

In the last ten years or so, techniques for accurately calculating the bandstructures of crystalline solids within the local density approximation (LDA) [1] have been combined with statistical mechanical methods such as the cluster variation method (CVM) [2] to allow the calculation of thermodynamic and structural properties of alloys from a knowledge of only the atomic numbers of the constituents. We present here preliminary results of such a first-principles study of the composition-temperature phase diagram of the Ti-Al system; only the phase stability of alloy compounds with fcc-based structures are considered in this paper.

Ti-Al alloys are of technological interest due to the excellent high-temperature mechanical properties of the intermetallic compounds found in this system [3]. Ti-Al is also of theoretical interest because the equilibrium phase diagram contains phases with structures based on three different lattice types, and because atomic ordering and composition have non-trivial effects on the structural and thermodynamic properties of these alloys [4].

The phase diagram of Ti-Al is shown in figure 1 which is redrawn from an article by Murray [5]. For compositions less than 50 atomic percent aluminum (at. % Al), alloy phases have hcp-based structures which transform to a bcc solid solution at higher temperatures. For larger concentrations of Al, a series of long-range-ordered alloy compounds with fcc-based structures are found. In particular, the γ (TiAl) compound forms in the $L1_0$ structure and is stable over an extended composition range near 50 at. % Al. By contrast, at 75 at. % Al, the $TiAl_3$ phase with the $D0_{22}$ structure has a very narrow range of stability (in figure 1 this phase is shown as a line compound). Both of the TiAl and $TiAl_3$ compounds remain ordered up to their melting points. Between 55 and 75 at. % Al, long period superstructures (LPS) and two $TiAl_2$ compounds (a high temperature and low temperature phase) are stable; these phases have structures which contain periodically, conservatively or nonconservatively antiphased unit cells described in detail by Loiseau et al. [6]. On the Al-rich side of the phase diagram, the maximum solubility of Ti is reached just below the melting point of Al (660°C) and amounts to only a few atomic percent. At low temperatures near 75 at. % Al, experimental evidence suggests the presence of another ordered compound as indicated by the dashed horizontal line in figure 1. The dashed box in figure 1 surrounds a portion of the phase diagram which has been shown to be incorrect [7].

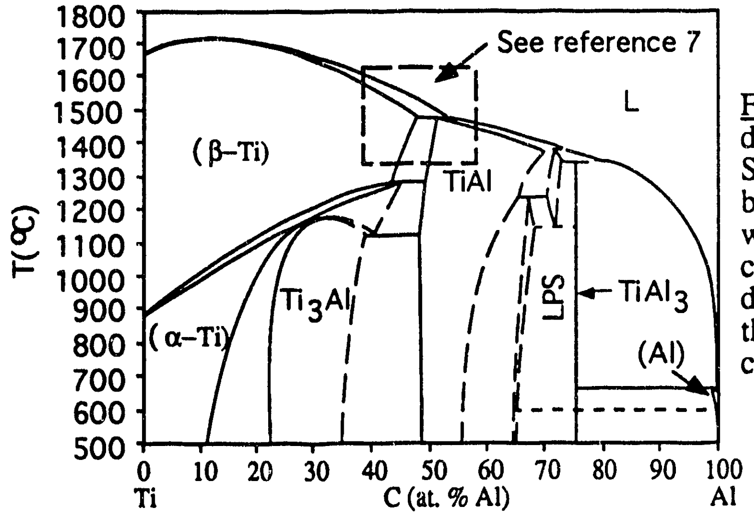

Figure 1: Experimental Ti-Al phase diagram as assessed by Murray [5]. Solid and dashed lines indicate phase boundaries which are, respectively, well determined or based on incomplete experimental data. The dashed box surrounds a portion of the phase diagram which is incorrect; see reference 7.

Several first-principles calculations have been undertaken to study the stability and structural and mechanical properties of Ti-Al compounds (see references listed in [4]). The results of these calculations are in excellent agreement with experimental observations and measurements; however, previous theoretical studies have focussed primarily on perfectly ordered, stoichiometric alloy compounds. An important feature of this work is that alloy properties are calculated as a function of composition and for any given state of atomic order. Previous calculations [8] have shown that the effect of tetragonal distortion on the energy of the $TiAl_3$ ($D0_{22}$) compound is large and that only when this structural relaxation is taken into account can the stability relative to the cubic $L1_2$ structure be correctly predicted. Clearly the effect of structural relaxation must be included in a phase stability study such as this one.

COMPUTATIONAL APPROACH

In this work, we will make use of a theorem due to Sanchez, Ducastelle and Gratias [9], which states that any function of the atomic configuration on a given lattice in an alloy system can be expanded in a complete orthonormal set of so-called cluster functions. In particular, the expansion for the energy takes the form:

$$E(\sigma) = E_0 + \sum_{\alpha} E_\alpha \, \Phi_\alpha(\sigma) \qquad (1)$$

where $E(\sigma)$ denotes the total energy of a crystalline alloy with a lattice decorated by A and B atoms in a manner specified by the compositional variable σ. To each site p of the lattice we assign a pseudo-spin variable σ_p which takes on values +1 or -1 depending on which type of atom occupies the site. σ is a vector with components σ_p, and the cluster functions $\Phi_\alpha(\sigma)$ are defined as a product of the pseudo-spin variables for a set of lattice sites which make up the cluster α. Equation (1) expresses the energy as a sum over all clusters of the cluster function multiplied by the expansion coefficient (E_α). The E_α are referred to as effective cluster interactions (ECI's) and can be rigorously defined since the cluster functions are orthonormal with respect to an inner product involving a trace over all configurations. If the ECI's can be determined, equation (1) provides a rigorous method for evaluating the energy of a crystalline alloy for any possible arrangement of atoms.

Several ways exist to calculate the ECI's from first-principles, and in this study we will use a method first proposed by Connolly and Williams [10]. We assume that equation (1) converges rapidly so that only a small set (~ 10) of terms are needed to parametrize well the energy of the alloy. Then, the total energy is calculated from first-principles for a set of ordered structures which, by definition, possess translational symmetry. For these structures, the cluster functions can be evaluated by inspection, so that two of the three terms in equation (1) are determined. The ECI's are calculated by solving the resulting set of equations. In practice, the energy of a large set of alloy compounds should be calculated in order to check that the resulting truncated expansion of the energy predicts accurately the energy of structures not used in the determination of the ECI's.

From equation (1) the internal energy can be defined in terms of the correlation functions which are the ensemble averages of the cluster functions. The CVM can be used to express the configurational entropy of the alloy also in terms of correlation functions [11]. A free energy functional of these variables is therefore formulated and can be minimized at any composition and temperature to yield the equilibrium free energy and other thermodynamic properties. The phase diagram can be determined from the free energy through standard common-tangent constructions.

In this study, the full-potential linear muffin tin orbital (FLMTO) method [12, 13] has been used to calculate the total energies of 11 of the ground states of the fcc Ising model with nearest and next-nearest pair interactions [14 and references therein]. Because of the large effect of structural relaxation, the energy of each compound was minimized with respect to all structural degrees of freedom allowed by symmetry; a full-potential bandstructure technique is needed to determine the effect of structural relaxation on the energies of the compounds in this system [15]. A set of 9 ECI's were obtained by performing a weighted least-squares fit of a truncated version of (1) to these 11 total energies as discussed in detail in reference 4. Therefore, the effect of structural relaxation on the phase diagram is taken into account in this study by using fully relaxed compounds to determine the ECI's. Furthermore, ECI's were calculated as a function of the molar volume of the alloy by using total energies of compounds at several volumes. Including volume-dependence in equation (1) explicitly in the ECI's leads to a more rapidly convergent expansion (1); also, with volume-dependent ECI's, the equilibrium molar volume and bulk modulus can be calculated for partially ordered or disordered alloys with any composition [4].

In calculating the phase diagram, the tetrahedron-octahedron approximation [11] of the CVM was used to obtain the free energy of the energetically stable structures and the disordered fcc alloy phase as a function of composition and temperature. In this study, one of the ECI's was too long-ranged to be included in the tetrahedron and octahedron approximation of the CVM, and the term corresponding to this cluster interaction in the internal energy was treated in an approximate manner as discussed in reference 4.

RESULTS

In figure 2 (a) the results of the FLMTO total energy calculations for fcc Al, fcc and hcp Ti, and 9 ordered fcc superstructures are plotted as heats of formation versus the concentration of Al. The heat of formation is defined as the difference between the energy of a compound and the concentration-weighted average of the energies of hcp Ti and fcc Al. The hcp structure for Ti is correctly predicted to be lower in energy than fcc, and the calculated energy difference is 4.4 mRy/atom. From figure 2 (a) it can be seen that of the fcc compounds considered in these calculations, only $L1_2$ Ti_3Al, $L1_0$ TiAl and $D0_{22}$ $TiAl_3$ are energetically stable. This result is in agreement with the experimental phase diagram where the TiAl and $TiAl_3$ phases are found to have the $L1_0$ and $D0_{22}$ structures, respectively. Previous calculations by Hong et al. [16] have shown that the $L1_2$ structure is higher in energy than the experimentally found $D0_{19}$ structure at composition Ti_3Al by approximately 1 mRy/atom. It should be emphasized that although most of the fcc structures considered in the FLMTO calculations will not be observed in the phase diagram, the energies of these compounds are needed in order to obtain the ECI's which are used to determine thermodynamic properties; furthermore, all structures must be fully relaxed with respect to all structural degrees of freedom in the total energy calculations in order to describe well phase stability in this system.

In figure 2 (b) the heats of formation of the energetically stable fcc compounds are again plotted against the concentration of Al, and the results of calorimetry experiments [17] are also included for comparison (experimental data are plotted as open symbols). The agreement

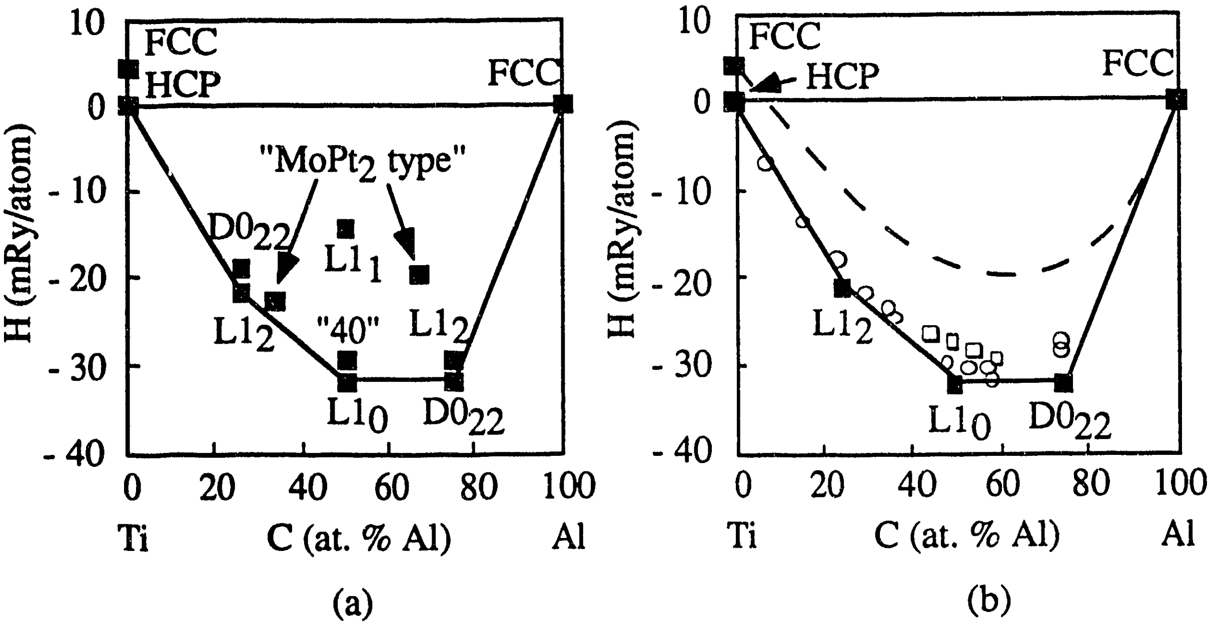

Figure 2: Heats of formation for fcc-based Ti-Al alloys. (a) FLMTO calculated heats of formation for fcc-based alloy compounds. Solid lines connect energetically stable structures. The fcc superstructures are described in reference 4. (b) Calculated heats of formation for the most energetically stable structures are shown as solid squares. Open symbols are results of experimental calorimetry experiments performed by Kubaschewski et al. [17]. The dashed line corresponds to the heats of formation of a random arrangement of Ti and Al atoms on the fcc lattice as calculated from the cluster expansion of the energy (1).

between the calculated and experimental results is excellent. The dashed line in figure 2(b) gives the heats of formation of a random mixture of Ti and Al atoms on the fcc lattice, as calculated from equation (1) with ECI's determined from the total energies of the ordered compounds. At 50 and 75 at. % Al, the random alloys are, respectively, 13.1 and 13.5 mRy/atom higher in energy than the ordered alloy compounds at these compositions. This large energy difference is consistent with the fact that fcc disordered alloys are never observed in the experimental phase diagram because the TiAl and Ti_3Al phases remain ordered up to their melting points. In reference 4 it is shown that the calculated dependence of molar volume on alloy composition shows significant deviation from Vegard's law, with a minimum value corresponding to alloys with 75 at. % Al, in agreement with experimental findings [18].

In figure 3, the phase diagram for fcc-based Ti-Al alloys, as calculated with the CVM and ECI's obtained in the manner described above, is shown. In the calculation of the phase diagram, only the $L1_2$ Ti_3Al, $L1_0$ TiAl and $D0_{22}$ $TiAl_3$ and fcc disordered alloy phases were considered. The dashed horizontal line in figure 3 indicates the temperature above which Ti-Al alloys are observed to be liquid at all compositions in the experimental phase diagram. The stability regions for each of the phases are indicated by their structure types and two-phase regions are designated by a series of parallel, horizontal, solid lines.

The experimentally determined phase diagram shown in figure 1 contains phase boundaries between hcp, bcc and liquid as well as fcc phases while only the latter have been considered in our calculations. Therefore, a comparison between our computed phase diagram and experiment can only be made for solid-state phase equilibria at concentrations greater than 50 at. % Al. We predict that both the $L1_0$ TiAl and $D0_{22}$ $TiAl_3$ compounds are ordered up to their experimentally observed melting points, in agreement with the experimental phase diagram. In fact, our calculations [4] predict that the $L1_0$ TiAl phase would undergo an order-disorder transition at 4100 K and the $D0_{22}$ $TiAl_3$ compound would transform in a peritectoid reaction to TiAl + fcc at 3000 K if these alloys did not melt first. Additionally, we find a much narrower

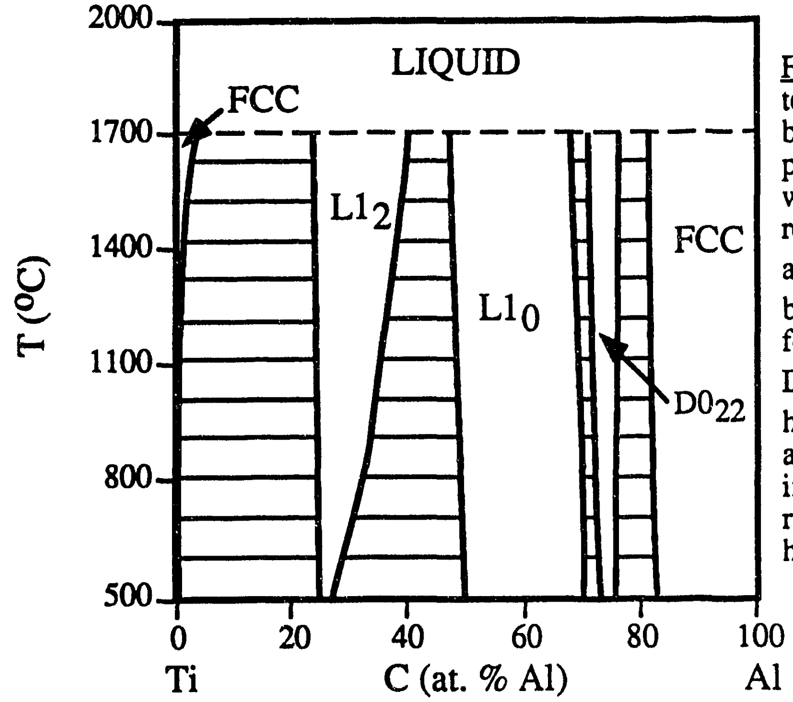

Figure 3: Calculated composition-temperature phase diagram for fcc-based Ti-Al alloys. Equilibrium phase boundaries were calculated with the CVM. The stability regions for the ordered Ti_3Al, TiAl and $TiAl_3$ compounds are indicated by the Strukturbericht designation for their structures: $L1_2$, $L1_0$ and $D0_{22}$, respectively. The dashed horizontal line indicates the pcint above which all Ti-Al alloys exist in the liquid phase. Two-phase regions are indicated by sets of horizontal lines.

concentration range for the stability of the $D0_{22}$ than for the $L1_0$ phase, also in agreement with experimental observations. Furthermore, the small energy difference (2 mRy/atom) between the $D0_{22}$ and $L1_2$ $TiAl_3$ structures calculated by the FLMTO is indicative of a small (100) antiphase boundary energy which is consistent with the many experimentally observed LPS in this system.

A shortcoming of the calculated phase diagram is our prediction that solid solution of Ti in Al is stable over an extended composition range at low temperatures while experimentally it is found that Ti is soluble only up to a maximum of 2 at. % below the melting point of Al. We have found that this discrepancy can be explained by the fact that several ordered compounds are lower in energy than phase separation between fcc Al and the $D0_{22}$ $TiAl_3$ compound, as determined from the cluster expansion of the energy (1), in possible agreement with experimental findings [5]. In order to determine the absolute lowest energy structure in this part of the phase diagram, a ground-state search must be performed by finding the minimum value of the energy out of all realizable arrangements of atoms on the fcc lattice. Such a ground-state search can be performed using expansion (1) as described in references 14, 19 and 20 (and references listed therein), and is currently being undertaken for this system.

The Ti-rich portion of the phase diagram contains hcp- and bcc-based phases in reality so that the fcc solid solution and $L1_2$ Ti_3Al compound are actually unstable in this system. A comparison with the experimental phase diagram for concentrations less than 50 at. % Al will be possible when the hcp and bcc phases are included in our calculations.

SUMMARY

We have presented the results of a first-principles study of the phase stability of fcc-based Ti-Al alloys. The FLMTO method has been used to calculate the formation energy and other properties of ordered alloy compounds with fcc-based structures. The energy associated with structural relaxation in many of the non-cubic Ti-Al fcc superstructures is large and plays an important role in, for example, the stability of the $D0_{22}$ relative to the $L1_2$ structure at 75 at. % Al [8]. Therefore, all energy calculations must take into account this effect, and a full potential bandstructure is needed [15]. From the results of the FLMTO calculations, a set of ECI's have been determined which enable us to calculate alloy properties for any composition and state of atomic order. The phase diagram shown in figure 3 for fcc-based Ti-Al alloys has been obtained using the CVM with the calculated ECI's. Results of the FLMTO and CVM calculations are in excellent agreement with experimental measurements and observations, particularly considering that no adjustable parameters were used in this study. We are therefore encouraged to continue this study by including hcp and bcc phases in our calculations.

ACKNOWLEDGEMENTS

The research at the University of California was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76F00098 and by the Institute for Scientific Computing Research at the Lawrence Livermore National Laboratory, Livermore, CA.

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