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PHASE STABILITY OF FCC- AND HCP-BASED INTERMETALLICS: THE Ti-Al AND Cd-Mg SYSTEMS

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ABSTRACT

In this paper we summarize results of first-principles phase stability studies of fcc- and hcp-based Ti-Al alloys and of the hcp-based Cd-Mg system. In particular, heats of formation for ordered alloy compounds are calculated with the linear muffin tin orbital method; effective cluster interactions are determined from the results of these calculations and are used to derive thermodynamic properties and composition-temperature phase diagrams.

INTRODUCTION

In the last ten years or so, techniques for accurately calculating the bandstructures of crystalline solids have been combined with statistical mechanical methods such as the cluster variation method[1] (CVM) to allow ab-initio calculations of thermodynamic and structural properties of alloys. Therefore, the calculation of alloy phase diagrams has become possible from a knowledge of only the atomic numbers of the constituents. In this paper we present results of first-principles studies of phase stability in the Ti-Al and Cd-Mg systems.

In addition to being of great technological interest as potential high-temperature structural materials, Ti-Al alloys are also theoretically interesting for several reasons. For example, the equilibrium phases in this system have fcc-, bcc- and hcp-based structures[2]. Therefore, the relative stability of alloy phases on each lattice and the structural energy difference between the different types of lattices must be described well in order to calculate the phase diagram of this system. A first-principles study of phase stability for fcc-based Ti-Al alloys has been recently reported[3] and preliminary results for hcp-based structures will be presented here.

Although much research has been devoted to the study of phase stability in fcc- and bcc-based alloy systems, far less work on hcp alloys has been undertaken. Recently, the CVM was used to calculate prototype ordering phase diagrams for the hcp Ising model with isotropic and anisotropic nearest-neighbor effective pair interactions (EPI's)[4]. Additionally, the composition-temperature phase diagram for the Cd-Mg system has been calculated from first-principles. Cd-Mg is of interest because the phase diagram of this system[5] contains continuous hcp solid solution which transforms to three ordered phases at compositions 25, 50 and 75 atomic percent Mg (at. %) as the temperature is lowered; all of the ordered compounds can be stabilized by nearest-neighbor EPI's. Therefore, the Cd-Mg system provides a straightforward test of a first-principles approach to the calculation of hcp-based

alloy phase diagrams. In the next section of the paper the computational approach taken in this work will be discussed and results for Ti-Al and Cd-Mg will then be presented.

COMPUTATIONAL APPROACH

We will make use of a theorem due to Sanchez, Ducastelle and Gratias[6] 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:

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

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. In equation (1) the sum is over all clusters (α) of atomic positions, the cluster functions (Φ_α) specify the atomic configuration on the lattice, and the expansion coefficients (E_α) are referred to as effective cluster interactions (ECI's). The ECI's can be uniquely defined[6] and are either dependent or independent of concentration depending on the form of the cluster functions used in equation (1)[7]. In this work concentration-independent ECI's are used.

We have calculated the ECI's using a method first proposed by Connolly and Williams[8]. The basis for this method is that ECI's have been shown to decay in magnitude rapidly for many alloy systems so that only a small number of terms (~ 10) are needed to parametrize the dependence of the alloy energy on atomic configuration[7,10]. Therefore, the total energy can be calculated from first-principles for a set of ordered structures, the lattice average of the cluster functions can be determined by inspection for these compounds, and the ECI's are then determined by solving the resulting set of linear equations from (1).

Once a set of ECI's has been calculated, equation (1) can be used to determine the groundstates of the alloy system. In particular, the groundstate structures are defined as those which minimize the energy (1) subject to a set of linear constraints which arise because the cluster functions should describe a physically realizable configuration of atoms on the lattice. If concentration-independent ECI's are used, the energy and the constraints are linear in the cluster function variables, and the determination of the groundstates reduces to a problem in linear programming for which global energy minima can be obtained. In this work the constraints are constructed by using the CVM formalism and requiring that the probabilities for all states on a cluster be between zero and one[9].

The phase diagram for the system under consideration can be constructed from the free energies of the groundstate structures and the disordered alloy through standard common-tangent constructions. The CVM has been used in this work to calculate these free energies as a function of composition and temperature. In particular, for the Cd-Mg system the tetrahedron-octahedron approximation of the CVM for hcp structures[11] has been used.

Total energy calculations of ordered alloy compounds have been performed using the Linear Muffin Tin Orbitals (LMTO)[12] method. For Cd-Mg the atomic sphere approximation (ASA)[12] was invoked to calculate the total energies of the nine groundstates of the hcp Ising model with nearest-neighbor EPI's[13]; ideal crystal structures were assumed and all energies were optimized with respect to atomic volume. For Ti-Al, a full-potential version of the LMTO method (FLMTO) was used[14] to calculate total energies of eleven of the second-nearest-neighbor fcc groundstates[15], and presently some of the hcp groundstate energies have also been calculated. Next-nearest-neighbor fcc groundstates were considered because in Ti-Al some of the equilibrium structures can only be stabilized by EPI's beyond the range of the nearest-neighbor[2]. The total energies for Ti-Al compounds were minimized with respect to all structural degrees of freedom, owing to the importance of structural relaxation in this system[16]; a full-potential bandstructure approach was necessary to reliably determine energies of relaxed Ti-Al compounds.

RESULTS

In figure 1(a) the results of the FLMTO total energy calculations for fcc and hcp Ti and Al, and twelve ordered fcc and hcp superstructures are plotted as heats of formation versus
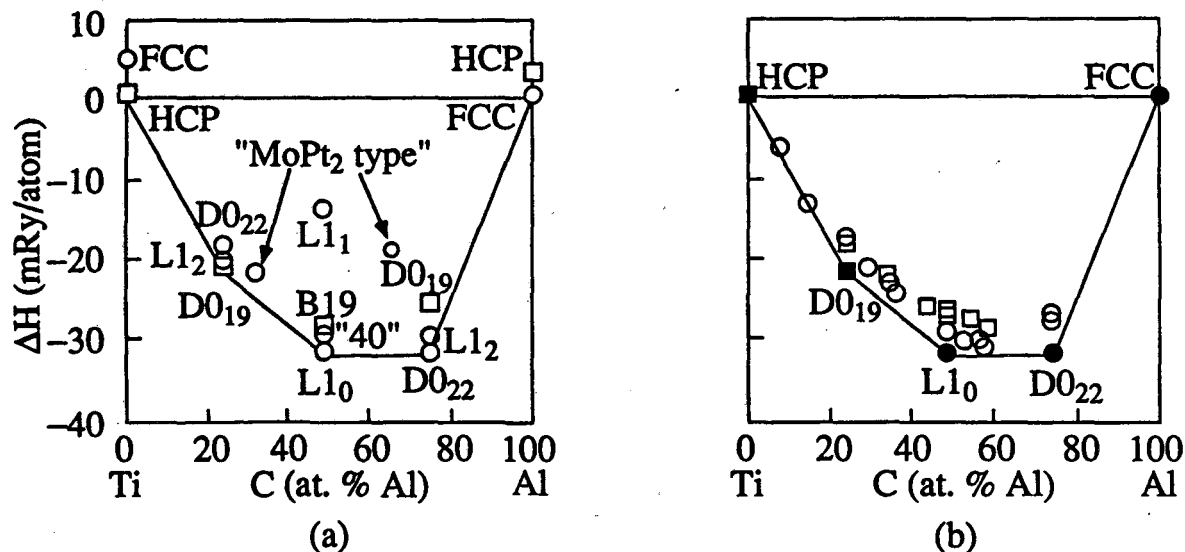
Figure 1. Heats of formation for ordered Ti-Al alloys. (a) FLMTO calculated heats of formation for fcc- and hcp-based alloy compounds are shown as open circles and squares, respectively. Solid lines connect energetically stable structures. (b) Calculated heats of formation for the most *energetically stable structures* are shown as solid circles and squares for fcc- and hcp-based structures, respectively. Open squares (circles) are from the 1960 (1955) calorimetry measurements of Kubaschewski et al.[17]. The vertical scale is the same as in figure 1 (a).

the concentration of Al. For the pure elements, the correct close-packed crystal structures are predicted with energy differences between hcp and fcc of -4.4 mRy/atom and 2.6 mRy/atom for Ti and Al, respectively. Furthermore, figure 1 (a) shows that of the compounds considered in these calculations, only the DO_{19} Ti$_3$Al, Ll_0 TiAl and DO_{22} TiAl$_3$ phases are energetically stable with respect to other compounds at the same composition and phase separation to alloy structures at other concentrations, in agreement with the experimental phase diagram[2]. In figure 1 (b) the heats of formation of the energetically stable compounds are again plotted against the concentration of Al; the results of calorimetry experiments[17] are included as open symbols for comparison. The agreement between the experimental measurements and calculated results is excellent.

The heats of formation of fcc-based structures have been used to calculate a set of ECI's
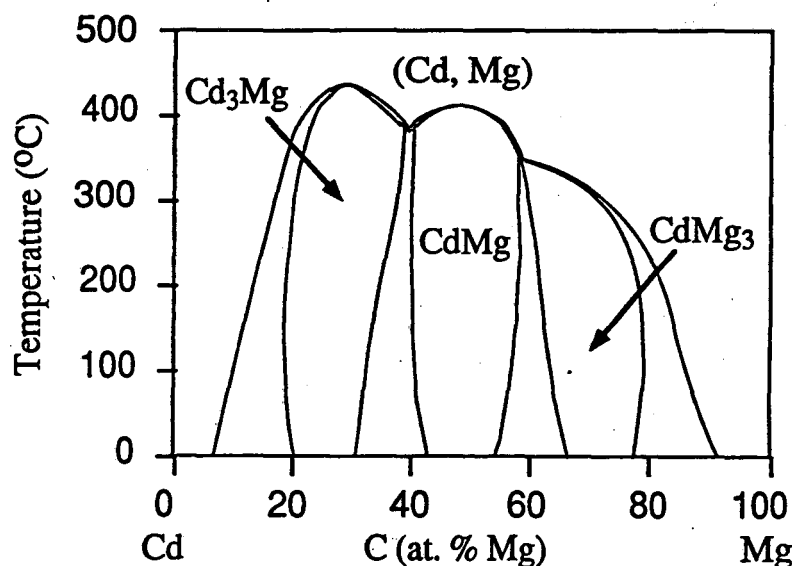

Figure 2. Calculated composition-temperature phase diagram for the Cd-Mg system. Equilibrium phase boundaries were calculated from the CVM using ECI's obtained from LMTO-ASA calculations of heats of formation for ordered Cd-Mg compounds. (Cd, Mg) indicates hcp solid solution.

from which an fcc-based Ti-Al phase diagram has been calculated with the CVM[3]. It was found that the TiAl and TiAl3 compounds remain ordered well above their experimental melting points and that the former phase is stable over a much wider composition range than the latter, in agreement with the experimental phase diagram[2].
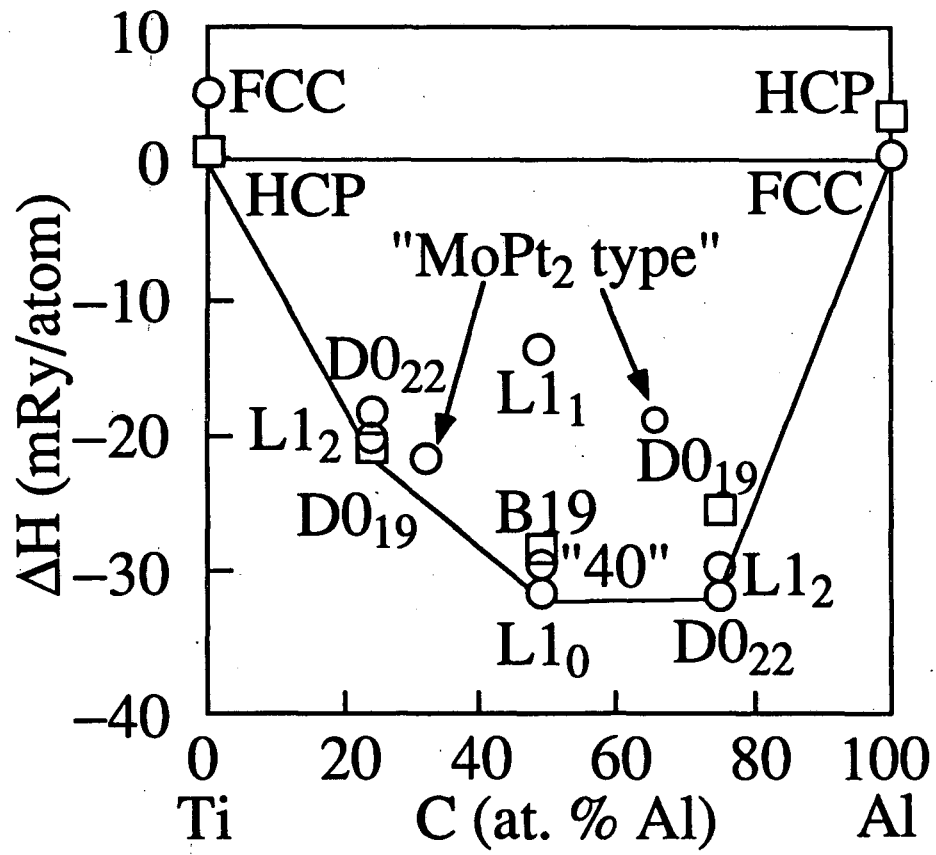
In figure 2 the calculated Cd-Mg phase diagram is shown. Nearest- and next-nearest-neighbor pair as well as nearest-neighbor triplet and tetrahedron ECI's were determined from the results of the LMTO-ASA total energy calculations. A groundstate search using these ECI's was performed and only the B19 CdMg, DO_{19} Cd3Mg and DO_{19} CdMg3 structures were found to be stable at zero Kelvin, in agreement with experimental observations[5]. In the experimental Cd-Mg phase diagram, the equiatomic phase undergoes a congruent order-disorder reaction near 50 at. % Mg at 253 °C while the Cd3Mg and CdMg3 phases undergo peritectoid reactions to two-phase mixtures of the solid solution and CdMg phases at 125 and 186 °C, respectively[5]. Therefore, for concentrations greater than 50 at. % Mg, the agreement between the calculated and experimentally determined phase diagrams is very good, with calculated transition temperatures which are about 150 °C too high. For the CdMg3 phase, the agreement between calculated and experimentally determined phase boundaries is not as good, which is likely due to our neglect of the effect of structural relaxation on the energy of these alloys. This effect should be more important for Cd-rich alloys because of the distorted geometry of the elemental Cd structure[5].
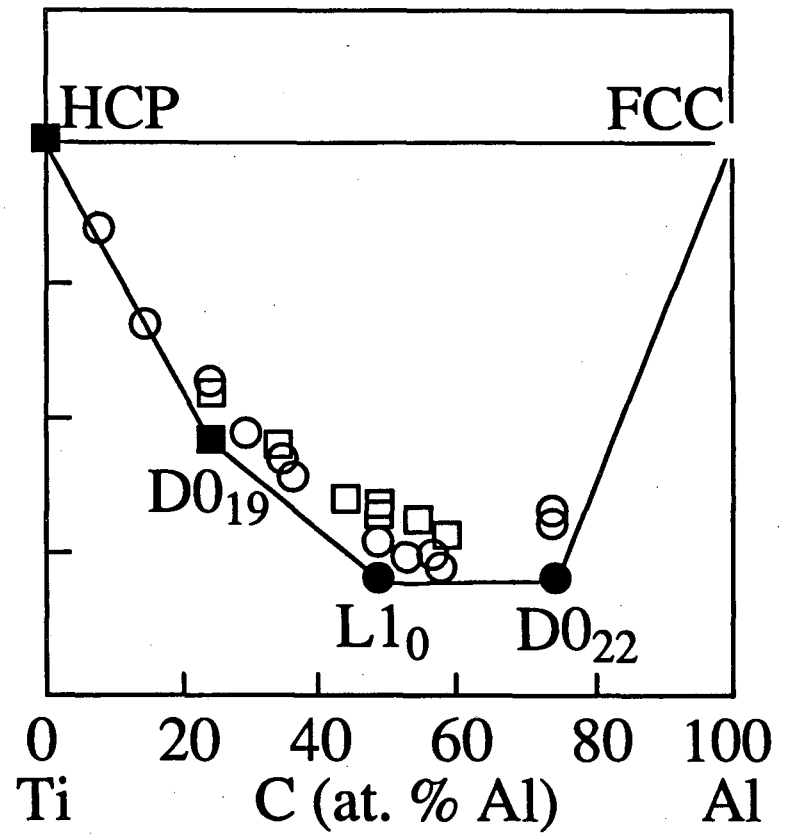
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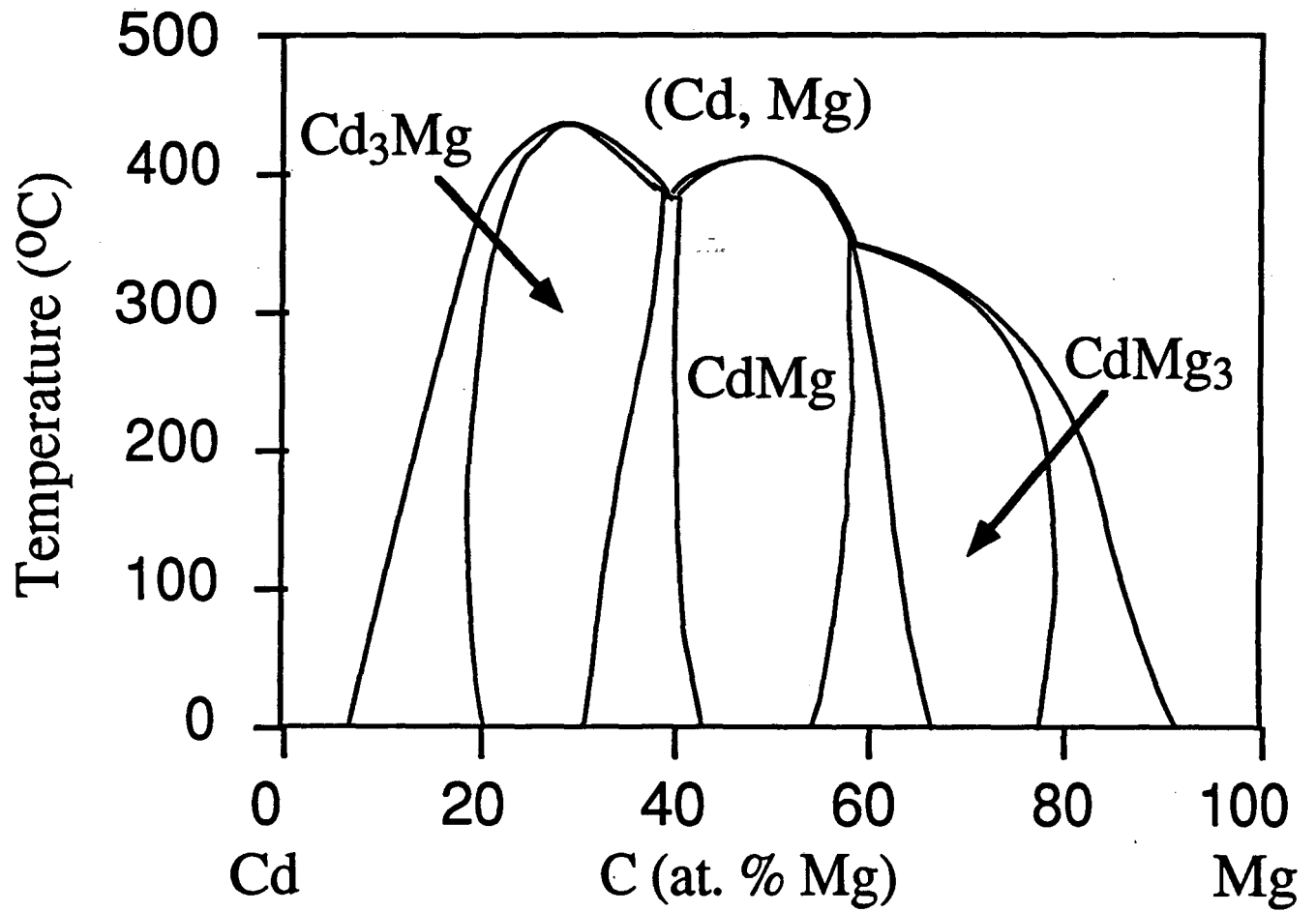
Figure 1

Figure 2