Site preference of Zr in Ti$_3$Al and phase stability of Ti$_2$ZrAl

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Abstract. The site preference of Zr atoms in Ti$_3$Al and the phase stability of Ti$_2$ZrAl are examined using first-principles electronic structure total energy calculations. Of the sixteen possible ways in which Ti, Zr and Al atoms can be arranged, in the lattice sites corresponding to D0$_{19}$ structure of Ti$_3$Al, to obtain Ti$_2$ZrAl, it is shown that Zr atoms prefer to get substituted at the Ti sites. It is further shown that among the seven crystal structures considered, D0$_{19}$-like and L1$_2$-like are the competing ground-state structures of Ti$_2$ZrAl. The above results are in agreement with the experimental results reported in the literature. Calculated values of equilibrium lattice parameters, heat of formation and bulk modulus of Ti$_2$ZrAl are presented. The basis for the structural stability and bonding are analysed in terms of the density of states. Between the two possible B2-like structures, Ti$_2$ZrAl shows enhanced stability for the one where Zr is substituted in the Ti sublattice, which again is in agreement with the experimental observation.

Keywords. Site preference; phase stability; first-principles calculations; Ti$_3$Al.

1. Introduction

Ti$_3$Al has been studied extensively during the past two decades because of its low density, good high-temperature strength and oxidation resistance at elevated temperatures (Lipsit 1993). However, Ti$_3$Al suffers from poor room-temperature ductility and fracture toughness. There have been a number of studies to understand the effects of alloying additions on the properties of Ti$_3$Al based alloys. Substitutional alloying affects the physical properties at the microscopic level and hence knowledge of substitutional behaviour of alloying additions is not only of great practical interest but also of fundamental theoretical interest. Several first-principles studies (Xu and Freeman 1994; Song et al 1998) show that the site preference of alloying elements is a key factor in describing properties such as twin-boundary energy and dislocation mobility of the alloys. Several techniques such as X-ray diffraction, transmission electron microscopy, atom probe field ion microscopy (Munroe and Baker 1991; Larson and Miller 1998), etc are available for experimental investigation of site occupancy. Over the years, various models have also been developed to study the substitutional behaviour of alloying additions theoretically. The first among them is the Ising model with nearest neighbour effective pair interactions and it was studied in detail using the cluster variation method (Wu et al 1989). Ruban and Skriven (1997) have developed a model based on the empirical parametrization of the ordering energy (obtained from first-principles calculation of the total energy of partially ordered alloys), which is the analogue of the rectangular $d$-band model of the cohesive energy developed by Friedel (1969). A thermodynamic model incorporating results of first-principles total energy calculations introduced by Woodward and Kajihara (1998) describes substitutional behaviour of alloying additions in terms of the change in the chemical potentials of the system obtained by minimization of free energy. Jiang (1999) modeled sublattice occupancy in ternary intermetallic compounds by an analytical approach wherein an atom pair transition occurs between two sublattices whenever the energy change caused by this process is negative. Another approach, which is used in the present work, is to compare the heat of formation of pure and defect unit cells from the first-principles calculation of the total energy of the system (Kim et al 2000).

In this paper, we present the results of a systematic study of site preference of Zr atoms in Ti$_2$ZrAl by considering all 16 ways of arranging (henceforth referred to as decoration) Ti, Zr and Al atoms at the atomic sites in the D0$_{19}$ unit cell of Ti$_3$Al consistent with the required stoichiometry. The stability of the crystal structure of Ti$_2$ZrAl is then examined by considering six other competing structures. Section 2 describes the possible inequivalent decorations of D0$_{19}$ unit cell to study the site preference of Zr atoms in Ti$_3$Al. The various crystal structures employed to understand the phase stability of Ti$_2$ZrAl are also described. Section 3 gives the computational details and in §4, we discuss the results of the calculations. Section 5 analyses the density of states of Ti$_2$ZrAl to obtain information regarding the structural stability and bonding. The last section is devoted to a brief summary of the results.
2. Crystal structure details

Several engineering alloys, Ti$_{3-x}$M$_x$Al (M is a transition metal), based on CsCl-D0$_{19}$-Ti$_3$Al, have been developed in the recent times. It is believed that in this structure, the M atoms occupy the Ti sites. Banerjee (1995) and Yang et al (2000) have confirmed that Zr indeed gets substituted at the Ti sites in Ti$_3$Al. The X-ray powder diffraction study (Sornadurai et al 2000a) reports that Ti$_2$ZrAl remains in the D0$_{19}$ structure of the parent compound, Ti$_3$Al.

In the D0$_{19}$ unit cell there are two formula units of atoms arranged in two planes. Let \( \{A, B, C, D\} \) and \( \{E, F, G, H\} \) refer to the atomic positions in the planes I and II. The coordinates of these atoms are the following:

\[
\begin{align*}
&\text{I: (1) } A (\text{Ti})(1/6, 5/6, 3/4); (2) B (\text{Ti})(1/6, 1/3, 3/4); (3) C (\text{Al})(2/3, 1/3, 3/4); (4) D (\text{Ti})(2/3, 5/6, 3/4); \\
&\text{II: (5) } E (\text{Al})(1/3, 2/3, 1/4); (6) F (\text{Ti})(1/3, 1/6, 1/4); (7) G (\text{Ti})(5/6, 1/6, 1/4); (8) H (\text{Ti})(5/6, 2/3, 1/4).
\end{align*}
\]

By using the freedom in the choice of directions of the basis vectors \( \vec{a} \) and \( \vec{b} \) and the origin, it can be shown that all the 24 ways of arranging atoms in each of the planes (considered in isolation) of the D0$_{19}$ unit cell are equivalent. However, when both the planes are considered together, there are many inequivalent ways of arranging the atoms. After accounting for the symmetries present in the system, it can be shown that there are 16 inequivalent decorations of the atomic sites \( A \ B \ C \ D \ E \ F \ G \ H \) (with 4 Ti, 2 Al and 2 Zr) as given in table 1. Since each of these decorations of D0$_{19}$ unit cell imply different interplanar and intraplanar atomic interactions, it is necessary to calculate the total energy of each of these to determine the structure with lowest energy. Since the equilibrium lattice parameters of each of these decorations can be different, in principle, it is important to optimize the total energy by relaxing the lattice parameters \( (a \text{ and } c) \) simultaneously. Hence, we have carried out total energy calculations, for each of the 16 decorations, at \( 11 \times 11 \) different values of each of \( (a, c) \) in the range \( 0.92 \leq a/c_{\text{expt}} \leq 1.10 \), where \( a_{\text{expt}} \) and \( c_{\text{expt}} \) are the values of the lattice parameters obtained in the experiments. It may be noted that the symmetry of the unit cell is retained to be the same as that of the parent compound, but the symmetry of the basis lowered, in these calculations. To find the site preference of Zr atoms in Ti$_3$Al, the heats of formation were calculated for each of the above 16 decorations using their respective equilibrium total energies.

To examine the phase stability of Ti$_2$ZrAl in relation to the D0$_{19}$-like structure, six other competing structures (described below) are also studied. Banerjee (1995) has reported that Zr atoms get substituted at the Ti sublattice in the B2(cP2) ternary phase with Ti$_2$AlZr composition. The B2(CsCl) structure can be described in terms of the two interpenetrating sc lattices with one lattice displaced with respect to the other by the vector \( \frac{1}{2} (111) \). An equivalent way of describing the B2 structure is to consider a sc lattice with a diatomic basis. For the B2-Ti$_2$ZrAl we have constructed two B2-like unit cells with a 4 atom basis obtained by stacking two B2(CsCl) unit cells one over the other to ensure the desired composition. In one of the B2-like cells (designated as B2-I) the stacking is TiAltZr, while in the other (B2-II) it is TiTiAlZr. These are the only two inequivalent stacking for Ti$_2$ZrAl (with 4 atoms) in the B2-like unit cell. Sketches of the unit cells of the crystal structures considered for Ti$_2$ZrAl are given in figure 1.

**Table 1.** Lattice constants (in a.u.) and heat of formation, \( \Delta H \) (in eV/atom) for the 16 inequivalent decorations of the D0$_{19}$ unit cell obtained by substituting one of the Ti atoms with Zr in Ti$_3$Al. \( A \ B \ C \ D \ E \ F \ G \ H \) are labels corresponding to the 8 atomic positions in the D0$_{19}$ unit cell.

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A ternary ordering for the bcc Ti₃NbAl, where all the three atoms occupy distinct sublattices is more likely to lead to a structure based on $L2_1(Fm3m)$ symmetry (Banerjee et al 1988) which is also being inferred by Mark Asta et al (1995). Hence we consider $L2_1$ structure for Ti₃ZrAl in this calculation. In view of the fact that both $D0_{19}$ and $L1_2$ structures are degenerate (Banerjee and Cahn 1983; Hong et al 1991; Watson and Weinert 1998) for Ti₃Al and Zr₃Al, an $L1_2$-like structure also is considered as a possible structure for Ti₃ZrAl. Since ordered ternary orthorhombic phase of Ti₃NbAl and Ti₃VAl with $Cmcm$ space-group symmetry are observed (Banerjee et al 1988; Banerjee 1995; Ravi et al 1999), we have included the orthorhombic structure as yet another possible structure for Ti₃ZrAl. There are only three distinctive ways of arranging the Ti, Al and Zr atoms in the orthorhombic structure consistent with the fact that the glide plane parallel to the $(1\bar{1}00)$ plane of $D0_{19}$ structure is retained in the orthorhombic structure. The three possible ways of arranging the atoms are: (i) Zr atoms occupy a distinct sublattice of their own or they occupy a sublattice which was previously associated with Ti atoms, (ii) Zr atoms occupy a distinct sublattice of their own but interchanged with the Al sublattice on the $c/2$ plane and (iii) Zr atoms randomly substitute Ti, or Al or both sites. In such a situation the sublattices remain identical to that of Ti₃Al structure. As the case (iii) represents a disordered alloy, it is not included in the present calculation. The coordinates of atoms in cases (i) and (ii) are the following: (i) Ti(1/4, 1/12, 3/4); Zr(0, 1/3, 3/4); Al(0, 1/6, 1/4); (2) Ti(1/4, 1/3, 3/4); Zr(0, 1/12, 3/4); Al(0, 5/12, 1/4), respectively.

### 3. Computational details

The total energy calculations were carried out using the tight binding-linear muffin-tin orbital (TB-LMTO) method (Andersen and Jepsen 1984). The conventional LMTO method and its tight-binding versions are well described in the literature (Andersen 1975; Skriver 1984; Horsfield and Bratkovsky 2000). The sphere radii were chosen so as to achieve a good compromise between the sphere overlaps (about 8%) and the proper charge transfer between spheres. The von Barth–Hedin (1972) exchange-correlation potential was used in this calculation. About 340 irreducible $k$-points have been used for the $B2$-like, $L1_2$-like and $L2_1$ structures and about 460 irreducible $k$-points have been used for $D0_{19}$-like and the orthorhombic structures. These calculations employ a minimal basis set consisting of $s$, $p$ and $d$ orbitals for Al and Ti, and $s$, $p$, $d$ and $f$ orbitals for Zr atoms. Combined correction terms that correct errors due to overlapping spheres in the atomic sphere approximation have been incorporated in the calculation. The valence states were calculated in a semi-relativistic approximation and the core states were treated fully relativistically. The new version of tetrahedron method has been used for Brillouin zone integration (Blochl et al 1994), which avoids improper weighting and also corrects for errors due to the linear approximation of bands inside each tetrahedron. The self-consistency iterations were continued until the total energy difference between two consecutive iterations was less than a microrydberg.
4. Site preference and ground-state properties

Calculation of the formation energy is carried out to facilitate a comparison of the site preference, phase stability and bonding (Robbins and Falicov 1984; Watson and Weinert 1998). In order to determine the formation energy, we first obtained the total energy of Ti, Zr and Al elements for their respective equilibrium lattice parameters. The difference between total energy of the compound and the concentration-weighted sum of the total energy of the constituent elements gives the heat of formation. The systematic errors in the total energy arising due to atomic sphere approximation get cancelled significantly, leading to a reasonably accurate formation of energy. The total energy of Ti$_2$ZrAl for each of the 16 inequivalent decorations of $D0_{19}$-Ti$_3$Al unit cell (obtained by replacing one of the three Ti atoms with a Zr atom) have been optimized with respect to both the lattice parameters, $a$ and $c$, simultaneously. Figure 2 gives the total energy as a function of lattice parameters corresponding to decoration 15 given in table 1.

The formation energies along with the relaxed lattice parameters are given in table 1. The relatively large value of heat of formation of decoration 16 establishes the fact that Zr atoms prefer to get substituted at the Ti sites in the $D0_{19}$ structure of Ti$_3$Al which is in agreement with the experimental report. Any of the decorations where Zr is getting substituted fully or partially in the Al sublattice is found to have significantly less negative heat of formation.

The results of total energy calculations as a function of unit cell volume are presented in figure 3 which can be used for examining the crystal structure stability of Ti$_2$ZrAl. In table 2 we give the calculated value of lattice parameters, heat of formation ($\Delta H$) and bulk modulus ($B_0$) of Ti$_2$ZrAl for the seven structures considered in this calculation. From the total energy curves (open circle and open box in figure 3) and from the values of heat of formation, this calculation (within the error bars of TB–LMTO method) shows that both $D0_{19}$-like and $L1_2$-like phases are almost degenerate and hence they are competing ground-state structures of Ti$_2$ZrAl.

The calculated lattice parameters of $D0_{19}$-like ($a = 10.994$ a.u. and $c = 8.961$ a.u.) and $L1_2$-like ($a = 7.748$ a.u.) phases are found to be in good agreement with the experimental values ($D0_{19}$: $a = 11.265$ a.u. and $c = 9.057$ a.u.; $L1_2$: $a = 7.753$ a.u.). The bulk modulus and equilibrium volume were obtained by fitting the total energy as a function of volume to the universal equation of state (Vinet et al 1986) for solids under compression. Due to non-availability of experimental values, we could not make a comparison of the calculated heat of formation and bulk modulus ($-0.273$ eV/atom and 1.410 Mbar for the $D0_{19}$-like phase). However, these values are found to be comparable to those (Yoo et al 1995) of Ti$_3$Al ($-0.26 \pm 0.02$ eV/atom and 1.30 Mbar).

As stated earlier, Ti$_2$ZrAl is found (Sornadurai et al 2000a) to have the same $D0_{19}$ type crystal structure of parent compound, Ti$_3$Al, with random replacement of Ti atoms by Zr. The same authors have observed (Sornadurai et al 2000b) that Ti$_2$ZrAl transforms to a cubic ($L1_2$ structure with a lattice parameter of 7.7535 a.u.) phase under 85 keV Ar$^+$ irradiation at a dose of $1 \times 10^{17}$ ions/cm$^2$. These experimental findings have to be compared with the results of the present calculation which shows that the total energy of the $L1_2$-like structure is lower than that of the $D0_{19}$-like structure by 0.054 eV. It must also be pointed out that the results of the present calculation are consistent with an earlier first-principles calculation (Zou et al 1995) which has shown that Zr is a candidate element for stabilizing the cubic $L1_2$ structure for Ti$_3$Al. It should be noted that Ti$_2$ZrAl

**Figure 2.** Total energy as a function of lattice parameters corresponding to the decoration 15 (in table 1) for Ti$_2$ZrAl in the $D0_{19}$ structure of Ti$_3$Al.

**Figure 3.** Total energy as a function of unit cell volume of Ti$_2$ZrAl for the different competing structures considered in this calculation.
was prepared (Sornadurai et al 2000a) by arc-melting technique where the synthesis takes place at high temperature and the sample is quenched to a relatively low temperature. If \( D_{019} \) structure has a larger entropy than \( L1_2 \) structure, it is possible that free energy of the \( D_{019} \) structure is lower than that of the \( L1_2 \) structure at high temperatures, even though the \( L1_2 \) structure has a lower internal energy than that of the \( D_{019} \) structure. If that were indeed the case, then \( Ti_2ZrAl \) would form in the \( D_{019} \) structure at high temperature and the very same structure would be preserved upon quenching to low temperature. It is plausible that irradiation would provide the necessary energy for the rearrangement of atoms so as to bring about the transition from the \( D_{019} \) phase to the more stable \( L1_2 \) phase at low temperature.

The third and seventh (open diamond and star in figure 3) curves correspond to two different site occupations of the Ti, Zr and Al atoms in the ordered ternary orthorhombic structure. The significant energy difference (0.132 Ry) between these two curves indicate that, though both \( O(1) \) and \( O(2) \) are base-centred orthorhombic structures, site occupancy difference plays an important role in deciding the relative stability of the phases. We also observe that between the two possible site occupancy of atoms in the \( B2-2 \) -like structures (triangle-down and triangle-up in figure 3), \( B2-II \) (where Zr is substituted in the Ti sublattice) shows enhanced stability, which is in agreement with Banerjee’s (1995) report. The energy of the \( L2_1 \) structure lies in between that of the two \( B2-2 \) -like structures.

5. Density of states

In order to gain more information on the structural stability and bonding of \( Ti_2ZrAl \), we looked at its density of states in figure 4 we present the density of states of \( L1_2 \)-like phase of \( Ti_2ZrAl \), and the total density of states of other structures considered in this calculation are shown in figure 5. In these figures, the Fermi level is taken as the zero of energy. The plots of the density of states reveal a low-lying band at about –0.4 Ry dominated by Al 3s states and separated from other bands by a narrow forbidden region that is quite prominent for \( L1_2 \)-like, \( D_{019} \)-like, \( O(1) \) and \( L2_1 \) structures. But, this (pseudo) gap is less prominent in \( B2-2 \) -like and \( O(2) \) structures. The bands from about –0.34 Ry up to the Fermi level are due to hybridized Ti 3d, Zr 4d and Al 3p states with dominant contribution from Ti 3d states. The peaks near the Fermi level are due to the Ti 3d and Zr 4d states. For the \( L1_2 \)-like phase, the Fermi level falls at a non-bonding Ti 3d state. Moreover, the density of states of \( Ti_2ZrAl \) in \( L1_2 \)-like and \( D_{019} \)-like structures share a number of common features present in that of (Hong et al 1991; Ravindran and Asokamani 1994) \( TiAl \) and \( Zr_2Al \). It can be seen that the density of states of \( Ti_2ZrAl \) in \( D_{019} \)-like and in \( O(1) \) structures have almost similar features. In both \( D_{019} \)-like and \( O(1) \) structures we find that the Fermi level lies at a point very close to the pseudogap. The density of states at Fermi level \( (N(E_F)) \) for \( D_{019} \)-like, \( O(1) \) and \( L1_2 \)-like structures are 37, 29 and 52 (states/Ry/f.u.), respectively. The correlation (Gelatt et al 1983; Hong and Freeman 1991; Paxton 1992) of phase stability to low

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* Sornadurai et al (2000a); † Sornadurai et al (2000b)
$N(E_F)$ and Fermi level falling at the pseudogap is not so obvious from these pictures. This further indicates that the phase stability of Ti$_2$ZrAl (in $D0_{19}$-like and $L1_2$-like structures) is due to a competition between temperature effects and symmetry of the underlying lattices. However, the dependence of phase stability to the shape of the density of states may explain the unstable nature of $B2$-like, $L2_1$ and $O(2)$ structures, where the pseudogap is absent and Fermi level lies at a peak in the density of states leading to large $N(E_F)$. It may also be noted that even though $O(1)$ and $O(2)$ are base-centred orthorhombic structures, their density of states differ significantly indicating presence or absence of pseudogap at Fermi level is not only controlled by the symmetry of the underlying lattice (Weinert and Watson 1998) but also on the symmetry of the basis atoms.

**Figure 5.** Density of states of Ti$_2$ZrAl for the $D0_{19}$-like, $O(1)$, $O(2)$, $L2_1$, $B2$-like (I), and $B2$-like (II) structures. Energies are taken relative to the Fermi level, $E_F$.

6. **Summary of the results**

This calculation clearly shows that Zr additions to $D0_{19}$-Ti$_3$Al prefer to get substituted in the Ti sites. Among the seven probable structures considered, we find that both $D0_{19}$-like and $L1_2$-like structures are competing ground-states of Ti$_2$ZrAl. The calculated lattice parameters of Ti$_2$ZrAl in $D0_{19}$-like and $L1_2$-like structures are found to be in good agreement with experimental values. The heat of formation and bulk modulus of $D0_{19}$-like Ti$_2$ZrAl are found to be comparable with those of Ti$_3$Al. Between the two $B2$-like structures, Ti$_2$ZrAl shows preference to the one ($B2$-II) where Zr is substituted in the Ti sublattice. Optimization of total energy by relaxing the lattice parameters for $L1_2$-like and $B2$-like structures shows enhanced stability for slight deviation from cubicity. Analysis
of the density of states shows that phase stability need not necessarily follow from the presence of a pseudogap.

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