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First-principles study of site occupancy of 3*d*, 4*d* and 5*d* transition-metal elements in $L1_0$ TiAl

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ABSTRACT

Using a statistical-mechanical Wagner-Schottky model parametrized by first-principles density-functional (DFT-GGA) calculations on 32-atom supercells, we predict the lattice site occupancy of 3*d* (Ti-Cu), 4*d* (Zr-Ag) and 5*d* (Hf-Au) transition-metal elements in $L1_0$ TiAl intermetallic compound as a function of both alloy composition and temperature. The effects of local atomic relaxations, anisotropic lattice distortions, as well as magnetism on point defect energetics are fully taken into account. Our calculations show that, at all alloy compositions and temperatures, Zr and Hf consistently show a preference for the Ti sublattice, while Co, Ru, Rh, Pd, Ag, Re, Os, Ir, Pt and Au consistently show a preference for the Al sublattice. In contrast, the site preference of V, Cr, Mn, Fe, Ni, Cu, Nb, Mo, Tc, Ta and W strongly depend on both alloy stoichiometry and temperature. Our calculated results compare favorably with existing theoretical and experimental studies in the literature.

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1. Introduction

TiAl intermetallic compound with an ordered $L1_0$ (space group P4/mmm, prototype CuAu) crystal structure has been widely considered a promising high-temperature structural material for aerospace applications due to its low density, high strength, and good oxidation resistance [1-3]. However, practical applications of TiAl are still hindered by its lack of room temperature ductility [4-6]. One way to improve the ductility of TiAl is through microalloying with ternary elements. For example, Morinaga *et al.* [7] suggested that the intrinsic ductility of TiAl is due to the directional Al *p*-Ti *d* covalent bonds. Therefore, ternary additions that can weaken the *p-d* interactions may effectively enhance the ductility of TiAl. Chubb *et al.* [8] also proposed that alloying elements that can reduce the axial *c/a* ratio of TiAl to be close to unity may lead to an increase in the number of deformation modes and thus improved ductility.

To gain a fundamental understanding of the role of ternary alloying elements in modifying the structural, electronic, and mechanical properties of TiAl, precise knowledge of their lattice site occupancy behavior is indispensable. The present work aims at presenting a unified picture of the T=0K site preference of 3*d* (Ti-Cu), 4*d* (Zr-Ag) and 5*d* (Hf-Au) transition-metal elements in TiAl using first-principles calculations based on density functional theory. By combining our first-principles calculated defect formation enthalpies with a statistical-mechanical Wagner-Schottky model based on the canonical ensemble, the finite temperature site occupancy behaviors of ternary additions in TiAl are further predicted. As will be shown, the present calculated results compare favorably with existing experimental and theoretical studies in the literature.

2. Mean-field formalism

In perfectly ordered stoichiometric TiAl, Ti and Al atoms alternatively occupy the (002) planes of a tetragonally distorted $L1_0$ unit cell (see Fig. 1). Deviations from the ideal stoichiometry are necessarily accommodated by the formation of constitutional (structural) point defects, *e.g.*, antisite defects formed by atoms located on the wrong sublattice (Ti_{Al}, Al_{Ti}) or vacancies formed by removing an atom from its regular lattice position (Va_{Al}, Va_{Ti}). Here i_α denotes species i on the α sublattice and Va denotes vacancy. When alloyed with TiAl, a ternary element X can occupy either the Al sublattice (X_{Al}) or the Ti sublattice (X_{Ti}), or both. In addition to the substitutional lattice positions, a ternary element may also reside in the interstitial voids of the TiAl lattice [9]. However, formation of such interstitial defects will be energetically very unfavorable since the atomic sizes of transition-metal elements are significantly larger than the size of interstitial sites in TiAl.

In studying the site preference of ternary alloying elements in TiAl, it is assumed that the defect concentrations are sufficiently dilute to allow use of the Wagner-Schottky model, *i.e.*, a gas of non-interacting point defects on well-defined sublattices [10]. We consider in this treatment a canonical ensemble [11-13], which is convenient for a single-phase alloy at fixed composition. Here the total number of atoms is fixed while the total number of lattice sites is allowed to vary when vacancies are present. According to the Wagner-

Schottky model, the formation enthalpy (per atom) of a ternary TiAl-X alloy can be written as a linear function of the point defect concentrations:

$$\Delta H = \Delta H_{TiAl} + \sum_{d} H_d x_d \qquad (1)$$

where ΔH_{TiAl} is the formation enthalpy of perfect, defect-free TiAl. x_d is the atomic concentration [11] defined as the total number of point defects of type d divided by the total number of atoms in the system, with d={Va_{Al}, Va_{Ti}, Ti_{Al}, Al_{Ti}, X_{Al} and X_{Ti}}. H_d is the formation enthalpy of isolated point defects of type d to be determined from first-principles.

In considering the effects of finite temperatures, the vibrational entropy is neglected since such calculations are extremely demanding. Assuming random distribution of point defects, the configurational entropy (per atom) is calculated using the mean-field approximation as:

$$S_{conf} = k_B(1 + x_{Va_{Al}} + x_{Va_{Ti}})\ln\left(\frac{1 + x_{Va_{Al}} + x_{Va_{Ti}}}{2}\right) - k_B \sum_{\alpha} \sum_{i} x_{i_\alpha} \ln(x_{i_\alpha}) \qquad (2)$$

where the summation goes over all species i={Al, Ti, X, Va} and sublattices α={Al, Ti}. k_B is Boltzmann's constant. The concentrations of all point defects in thermodynamic equilibrium can now be rigorously obtained through a minimization of the Gibbs free energy of the system ($\Delta G = \Delta H - T S_{conf}$) under the mass-balance constraints, leading to the following set of non-linear equations:

$$\frac{2x_{Va_{Al}} x_{Al_{Ti}}}{x_{Va_{Ti}}(1-2x_{Ti_{Al}}-2x_{X_{Al}}-x_{Va_{Al}}+x_{Va_{Ti}})} = \exp[-\frac{H_{Al_{Ti}}-H_{Va_{Ti}}+H_{Va_{Al}}}{k_B T}] \tag{3a}$$

$$\frac{2x_{Va_{Ti}} x_{Ti_{Al}}}{x_{Va_{Al}}(1-2x_{Al_{Ti}}-2x_{X_{Ti}}+x_{Va_{Al}}-x_{Va_{Ti}})} = \exp[-\frac{H_{Ti_{Al}}+H_{Va_{Ti}}-H_{Va_{Al}}}{k_B T}] \tag{3b}$$

$$\frac{x_{X_{Al}} x_{Va_{Ti}}}{x_{X_{Ti}} x_{Va_{Al}}} = \exp[-\frac{H_{X_{Al}}-H_{X_{Ti}}-H_{Va_{Al}}+H_{Va_{Ti}}}{k_B T}] \tag{3c}$$

$$\frac{4x_{Va_{Al}} x_{Va_{Ti}}}{(1+x_{Va_{Al}}+x_{Va_{Ti}})^2} = \exp[-\frac{H_{Va_{Al}}+H_{Va_{Ti}}}{k_B T}] \tag{3d}$$

$$\frac{1}{2}(1-2x_{Al_{Ti}}+2x_{Ti_{Al}}-2x_{X_{Ti}}+x_{Va_{Al}}-x_{Va_{Ti}}) = x_{Ti} \tag{3e}$$

$$x_{X_{Al}} + x_{X_{Ti}} = x_X \tag{3f}$$

where x_{Ti} and x_X are the mole fractions of Ti and X in the alloy, respectively. A numerical solution of Eqs. (3a)-(3f) gives the equilibrium point defect concentrations at a given alloy composition and temperature.

3. First-principles methods

A first-principles supercell approach [11-17] is employed to obtain the formation enthalpies of isolated point defects in L1$_0$ TiAl. We use 32-atom 2×2×2 supercells (see

Fig. 1), each containing a single point defect (vacancy, antisite or ternary element) at its center. First-principles calculations are performed using projector augmented wave (PAW) [18] pseudopotentials within the generalized gradient approximation (PW91-GGA) [19], as implemented in Vienna *ab initio* simulation package (VASP) [20]. The semi-core 3*p* electrons of Ti, V, Cr and Mn, the semi-core 4*p* electrons of Nb, Mo and Tc, the semi-core 5*p* electrons of Hf, Ta and W, and both the semi-core 4*s* and 4*p* electrons of Zr are explicitly treated as valence. The plane wave cutoff energy is set at 350 eV. The *k*-point meshes for Brillouin zone sampling are constructed using the Monkhorst–Pack scheme [21] and a 9×9×9 *k*-point mesh for the 32-atom supercells (corresponding to 75 irreducible *k*-points in the Brillouin zone) is found to be sufficient to give fully converged point defect energetics. Spin-polarized calculations are performed for Cr, Mn, Fe, Co, and Ni. According to our calculations, Mn, Fe and Co develop large localized magnetic moments ($>1.5\mu_B$) when they occupy the Ti sites in TiAl, but become essentially non-magnetic when placed at the Al sites. In their experimental investigation of a series of $Ti_{0.5-x}Al_{0.5}Mn_x$ alloys, Coletti *et al.* [22] observed that Mn substitutes for the Ti sites and carries a large local moment of $2.3\mu_B$ that is nearly independent of the doping level x. In contrast, Babu *et al.* [23] also found that Cr is essentially non-magnetic when doped in TiAl. Those experimental observations are in complete agreement with the present calculations.

By computing the quantum-mechanical forces and stress tensor, each supercell is fully relaxed with respect to unit cell volume, shape (*c*/*a* ratio), as well as all internal atomic positions using a conjugate-gradient scheme. Our predicted equilibrium lattice constants of the ideal $L1_0$ TiAl structure (a=3.987 Å, c=4.072 Å, c/a=1.021) are in excellent agreement with the experimental values of a=3.99 Å, c=4.07 Å , and c/a=1.02 [24].

The formation enthalpy of a ternary $Ti_{1-x-y}Al_xX_y$ alloy is calculated from the following equation:

$$\Delta H = E(Ti_{1-x-y}Al_xX_y) - (1-x-y)E(Ti) - xE(Al) - yE(X) \tag{4}$$

where $E(Ti)$, $E(Al)$, $E(X)$ and $E(Ti_{1-x-y}Al_xX_y)$ are, respectively, the first-principles calculated total energies (per atom) of the constituent pure elements Ti, Al, X and the corresponding alloy, each relaxed to their equilibrium geometries. Finally, we obtain the defect formation enthalpies using finite differencing [25] as:

$$H_d = \frac{\partial \Delta H}{\partial x_d} \approx \frac{\Delta H_d - \Delta H_{TiAl}}{x_d} \tag{5}$$

where ΔH_d is the formation enthalpy (per atom) of a 32(31)-atom TiAl supercell containing one single point defect of type d. We have x_d=1/32 for antisites and ternary substitutional elements and x_d=1/31 for vacancies.

4. Results and discussion

4.1. Intrinsic point defects in binary TiAl alloys

Before addressing the site preference of ternary additions in TiAl, it is necessary to first have a good understanding of the types of intrinsic point defects in binary TiAl alloys. At T=0K, the point defect structure of an ordered compound is solely determined by enthalpy and the point defects stable at this temperature are called constitutional defects. Table 1 reports our first-principles calculated formation enthalpies of the intrinsic point defects in $L1_0$ TiAl. It can be seen that antisite defects have much lower formation enthalpies than vacancies, indicating that the constitutional defects in TiAl are antisites on both sides of stoichiometry. We note that, such a conclusion is in accordance with previous experimental [26, 27] and theoretical [28-30] studies. We also find that the formation enthalpy of Al antisites is much lower than that of Ti antisites, which may explain why the homogeneity range of TiAl is significantly shifted toward Al-rich compositions in the equilibrium Ti-Al phase diagram [31].

4.2. Site preference of ternary alloying elements at T=0K

The T=0K site preference of ternary elements in TiAl is governed only by enthalpy. For a Al-rich $Ti_{0.5-x}Al_{0.5}X_x$ alloy, there are two possible lattice configurations depending on the location of ternary element X: (i) X occupies the Ti sites and the configuration is simply (Ti,X)(Al). (ii) X occupies the Al sites at the cost of forming Al antisites to yield the configuration (Ti,Al)(Al,X). The creation of vacancies is not considered since they are energetically very unfavorable compared to antisite defects (see Table 1). It is the formation enthalpy *difference* between configuration (i) and (ii) that determines the site preference of X: X preferentially occupies the Ti sites when $\Delta H_i - \Delta H_{ii} < 0$ and vice versa. Such an enthalpy difference is given below normalized per atom of X:

$$\Delta H_i - \Delta H_{ii} = H_{X_{Ti}} - H_{X_{Al}} - H_{Al_{Ti}} \tag{6}$$

Similarly, there are also two possible lattice configurations for a Ti-rich $Ti_{0.5}Al_{0.5-x}X_x$ alloy: (i) X occupies the Ti sites at the cost of forming Ti antisites to yield the configuration (Ti,X)(Al,Ti). (ii) X occupies the Al sites and the configuration is simply (Ti)(Al,X). The formation enthalpy difference between the two configurations normalized per atom of X now becomes:

$$\Delta H_i - \Delta H_{ii} = H_{X_{Ti}} - H_{X_{Al}} + H_{Ti_{Al}} \tag{7}$$

Finally, for a stoichiometric $Ti_{0.5-x/2}Al_{0.5-x/2}X_x$ alloy, there are three possible lattice configurations: (i) X occupies the Ti sublattice accompanied by the formation of Ti antisites and the configuration is (Ti,X)(Al,Ti). (ii) X occupies the Al sublattice accompanied by the creation of Al antisites and the configuration is (Ti,Al)(Al,X). (iii) X randomly occupies both Al and Ti sublattices to yield the (Ti,X)(Al,X) configuration, in which 1/2 of the X atoms occupy the Ti sites and the remaining 1/2 occupy the Al sites. The formation enthalpy differences between configurations (i) and (iii) and between configurations (iii) and (ii) are:

$$\Delta H_{i} - \Delta H_{iii} = \frac{H_{X_{Ti}} - H_{X_{Al}} + H_{Ti_{Al}}}{2} \tag{8a}$$

$$\Delta H_{iii} - \Delta H_{ii} = \frac{H_{X_{Ti}} - H_{X_{Al}} - H_{Al_{Ti}}}{2} \tag{8b}$$

Based on Eqs. (6)-(8), the T=0K site occupancy behavior of substitutional ternary elements in TiAl can be generally classified into the following three types:

(i) $H_{X_{Ti}} - H_{X_{Al}} + H_{Ti_{Al}} < 0$: X always prefers the Ti sites in TiAl independent of composition, *i.e.*, X exhibits strong Ti site preference.

(ii) $H_{X_{Ti}} - H_{X_{Al}} - H_{Al_{Ti}} > 0$ (or equivalently $H_{X_{Ti}} - H_{X_{Al}} + H_{Ti_{Al}} > H_{Ti_{Al}} + H_{Al_{Ti}}$): X always prefers the Al sites in TiAl independent of composition, *i.e.*, X exhibits strong Al site preference.

(iii) $0 < H_{X_{Ti}} - H_{X_{Al}} + H_{Ti_{Al}} < H_{Ti_{Al}} + H_{Al_{Ti}}$: The site preference of X is strongly composition-dependent. X prefers the Ti sites in Al-rich TiAl and the Al sites in Ti-rich TiAl, and shows no site preference in stoichiometric TiAl by randomly occupying both Al and Ti sites.

It is worth noting that a similar methodology has been employed by Ruban and Skriver [32] in classifying the site substitution behavior of ternary additions to Ni_3Al. Clearly, the T=0K site preference of any substitutional ternary element in TiAl can be characterized by a single parameter $E_X^{Al\rightarrow Ti} = H_{X_{Ti}} - H_{X_{Al}} + H_{Ti_{Al}}$, which has the physical meaning as the energy required in transferring a X atom from a Al site to a Ti site via the reaction:

$X_{Al} + Ti_{Ti} \rightarrow X_{Ti} + Ti_{Al}$. Its value can be directly obtained from first-principles calculated total energies of four 32-atom supercells as follows:

$$E_X^{Al \rightarrow Ti} = E(Ti_{15}Al_{16}X) - E(Ti_{16}Al_{15}X) + E(Ti_{17}Al_{15}) - E(Ti_{16}Al_{16}) \qquad (9)$$

The calculated values of $E_X^{Al \rightarrow Ti}$ for each of the 3*d* (Ti-Cu), 4*d* (Zr-Ag) and 5*d* (Hf-Au) transition-metal elements are shown in Fig. 2. The formation enthalpy of the exchange antisite defect in TiAl, $H_{Ti_{Al}} + H_{Al_{Ti}}$, is calculated to be 1.01 eV, in good agreement with the theoretical value of 1.20 eV from Woodward *et al.* [29]. In the cases of Cr, Mn, Fe, Co and Ni, both spin-polarized and non-spin-polarized calculations are performed. For Mn, Fe and Co, the magnetic effect shifts their site preference towards the Ti sublattice by stabilizing the X_{Ti} defects. For Mn and Fe, the magnetic effect is even strong enough to change their site preference behavior from type (ii) to type (iii). In comparison, the magnetic effect does not much influence the site preference of Cr and Ni. We note that, a similar strong effect of magnetism on site preference has also been observed by Sluiter *et al.* [17] and in our previous study [13]. According to Fig. 2, Zr and Hf fall into type (i), Co, Ru, Rh, Pd, Ag, Re, Os, Ir, Pt and Au fall into type (ii), and V, Cr, Mn, Fe, Ni, Cu, Nb, Mo, Tc, Ta and W fall into type (iii). The general trend is that the tendency of transition metals to occupy the Al sublattice in TiAl increases with increasing *d*-electron number along a series. Such a trend is obeyed by all 3*d*, 4*d* and 5*d* transition-metal elements except for those at the very end of a series.

4.3. Site preference at finite temperatures

It should be noted that, the classification as proposed in Section 4.2 is strictly valid only at T=0K. At finite temperatures, entropy will also play an important role in determining the site preference of ternary elements. In Fig. 3, the fraction of X atoms occupying the Al sites in TiAl alloys containing 1% of X at 1173K is plotted as a function of Ti concentration. Fig. 4 further shows the equilibrium partitioning of X atoms between Al and Ti sites in Al-rich, Ti-rich and stoichiometric TiAl alloys as a function of temperature. The horizontal dashed lines indicate random occupation of Al and Ti sites by X atoms, *i.e.*, no site preference. At all alloy compositions and temperatures, type (i) and type (ii) elements consistently show a predominant preference for the Ti and Al sublattices, respectively. By contrast, the site preference of type (iii) elements exhibits a strong dependence on both composition and temperature. At constant temperature, the general trend is that the preference for the Al sublattice increases with decreasing Al concentration. In Al-rich TiAl (Fig. 4(a)), all type (iii) elements show a preference for the Ti sublattice at low temperatures. However, with increasing temperature, the fractions of Cr, Mn, Fe, Ni, Cu, Tc and W in the Ti sublattice decrease to such extent that their site preference is reversed. We note that, such a entropically-driven site preference reversal has also been observed by Ruban and Skiver [32] and in our previous study [13]. In Ti-rich TiAl (Fig. 4(b)), all type (iii) elements instead show a preference for the Al sublattice at low temperatures. When the temperature is increased, the fractions of V, Nb and Ta in the Al sublattice decrease to the extent that site preference reversal occurs. Finally, in stoichiometric TiAl (Fig. 4(c)), all type (iii) elements partition randomly between Al and Ti sites at low temperatures. As temperature is increased, Cr, Mn, Fe, Ni, Cu, Tc and W start to show a preference for the Al sublattice, while V, Nb and Ta start to show a preference for the Ti sublattice. At all temperatures, Mo remains randomly partitioned between Al and Ti sites.

4.4. Comparisons with previous studies in the literature

The site occupancy of Nb, Mo, Ta and W in TiAl at T=1473K has been predicted by Woodward *et al.* [29] using first-principles methods. Their study showed that the site preference of Mo and W changes with alloy stoichiometry, which is in agreement with our classification of Mo and W as type (iii) elements. Interestingly, although Nb and Ta are both type (iii) elements and thus exhibit strongly composition-dependent site preference at T=0K, they actually show a consistent preference for the Ti sublattice over the whole composition range at high temperatures, although such a preference is weaker than that of type (i) elements (see Fig. 3). Such a conclusion also agrees with the study by Woodward *et al.* [29].

Using X-ray diffraction and atom probe techniques, Kim *et al.* [33] observed that Ru strongly prefers the Al sites in TiAl. Their results are in support of our classification of Ru as a type (ii) element. Using atom location by channeling enhanced microanalysis (ALCHEMI), Chen *et al.* [34, 35] and Rossouw *et al.* [36] found that Zr and Hf exclusively occupy the Ti sites, while Cr, Mn and Mo occupy both Al and Ti sites in TiAl. Those experimental evidences are consistent with our classification of Zr and Hf as type

(i) elements and of Cr, Mn and Mo as type (iii) elements. Using the same technique, Hao *et al.* [37, 38] observed that the site preference of V, Cr and Mn changes considerably with alloy composition, which can be understood since V, Cr and Mn are all type (iii) elements. They also found that Nb consistently prefers the Ti sites while Fe consistently prefers the Al sites regardless of alloy composition. Although Fe and Nb are both type (iii) elements, the experimental observations can be explained by the fact that Fe and Nb actually behave like a type (ii) and type (i) element at high temperatures, respectively (see Fig. 3). Finally, Fig. 5 shows our predicted site occupancy of Ta, Zr, Nb, Mo, V, Cr, Mn, Fe and Ni in $Ti_{0.47}Al_{0.51}X_{0.02}$ alloys in direct comparison with the experimental data from Hao *et al.* [37]. All calculations are performed at the experimental annealing temperature of 1173K. With the exception of Cr and Fe, the agreement is quite satisfactory. Presumably, the origin of such discrepancies may be due to the large experimental uncertainties as well as the neglect of vibrational entropy and defect-defect interactions in our calculations.

4.5. Lattice distortion due to ternary alloying

Since the lattice tetragonality of TiAl has been associated with its poor ductility [8], it is important to investigate the effects of ternary additions on the *c/a* ratio of TiAl. Table 2 summarizes our first-principles optimized equilibrium *c/a* ratio of various $Ti_{15}Al_{16}X$ (X substitutes for Ti) and $Ti_{16}Al_{15}X$ (X substitutes for Al) supercells, which correspond to a doping level of ~3%. In agreement with previous studies by Erschbaumer *et al.* [39] and Song *et al.* [40], Table 2 clearly shows that the effects of ternary elements on the lattice tetragonality of TiAl strongly depend on their lattice site occupation. We find that Cr, Mn, Mo, Tc, W and Re strongly reduce the *c*/*a* ratio of TiAl when occupying the Al sites, while Pd and Pt significantly decrease the *c*/*a* ratio of TiAl when occupying the Ti sites. We however wish to point out that, since Pd and Pt are both type (ii) elements, they will exclusively occupy the Al sites and instead lead to an increase in the *c*/*a* ratio of TiAl. Furthermore, since the site occupation of type (iii) elements in TiAl change significantly with temperature (see Fig. 4), it is expected that the *c*/*a* ratio of ternary TiAl alloys doped with type (iii) elements will also exhibit a strong dependence on temperature, which is yet to be verified experimentally.

5. Summary

In summary, using a combination of first-principles calculations and a statistical-mechanical Wagner-Schottky model, we systematically predict the site preference of all 3*d*, 4*d* and 5*d* transition-metal elements in the technologically important $L1_0$ TiAl compound. For Mn and Fe, the effect of magnetism is to strongly promote their preference for the Ti sublattice. Regardless of alloy composition and temperature, type (i) elements Zr and Hf have a predominant preference for the Ti sites, while type (ii) elements Co, Ru, Rh, Pd, Ag, Re, Os, Ir, Pt and Au have a predominant preference for the Al sites. For type (iii) elements V, Cr, Mn, Fe, Ni, Cu, Nb, Mo, Tc, Ta and W, their site preference will depend quite sensitively on alloy stoichiometry as well as heat treatment, e.g., annealing temperature and cooling rate.

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Table 1. First-principles calculated formation enthalpies (eV/defect) of the intrinsic point defects in $L1_0$ TiAl. Reference states: fcc Al and hcp Ti.

Defect type	Ti_{Al}	Al_{Ti}	Va_{Al}	Va_{Ti}
H_d	0.84	0.17	2.20	1.46

Table 2. First-principles optimized *c*/*a* ratio of various $Ti_{15}Al_{16}X$ (X substitutes for Ti) and $Ti_{16}Al_{15}X$ (X substitutes for Al) supercells.

Alloying element	*c*/*a*		Alloying element	*c*/*a*	
	$Ti_{15}Al_{16}X$	$Ti_{16}Al_{15}X$		$Ti_{15}Al_{16}X$	$Ti_{16}Al_{15}X$
V	1.025	1.014	Rh	1.011	1.024
Cr	1.025	1.008	Pd	1.007	1.037
Mn	1.019	1.009	Ag	1.013	1.037
Fe	1.020	1.015	Hf	1.020	1.018
Co	1.021	1.020	Ta	1.024	1.011
Ni	1.014	1.031	W	1.025	1.003
Cu	1.018	1.033	Re	1.026	1.005
Zr	1.020	1.016	Os	1.024	1.013
Nb	1.024	1.010	Ir	1.017	1.022
Mo	1.025	1.002	Pt	1.009	1.035
Tc	1.025	1.005	Au	1.013	1.039
Ru	1.022	1.014			

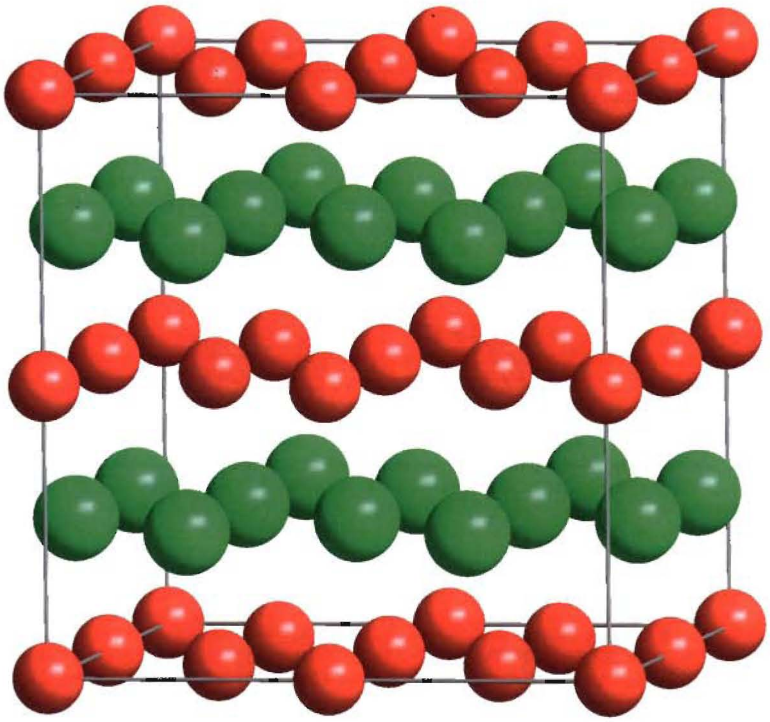


Fig. 1. The 32-atom TiAl supercell used in our calculations. Red and green spheres represent Ti and Al atoms, respectively.

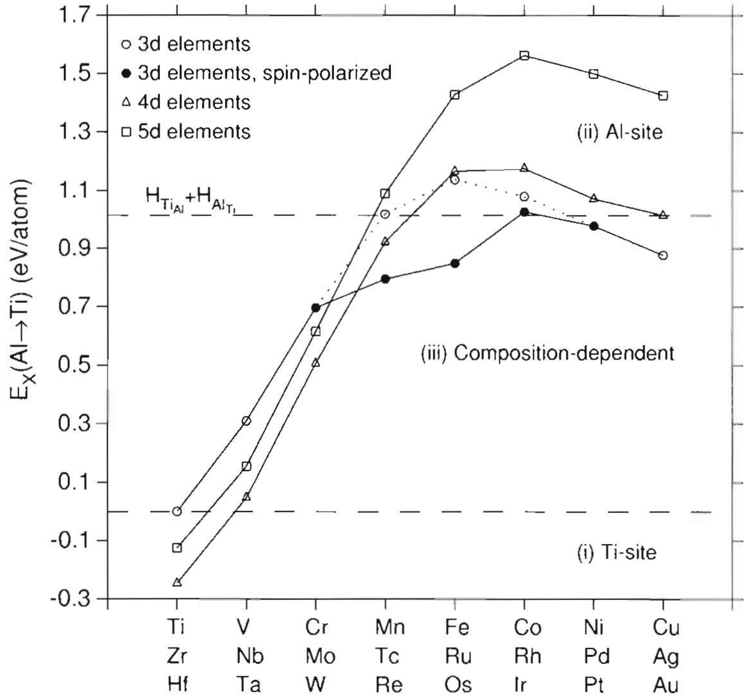


Fig. 2. Classification of the T=0K site preference behavior of 3*d*, 4*d* and 5*d* transition-metal elements in L1_0 TiAl based on $E_X^{Al\rightarrow Ti}$ obtained from first-principles calculations on 32-atom supercells. For Cr, Mn, Fe, Co and Ni elements, the filled and unfilled circles represent results from spin-polarized and non-spin-polarized calculations, respectively.

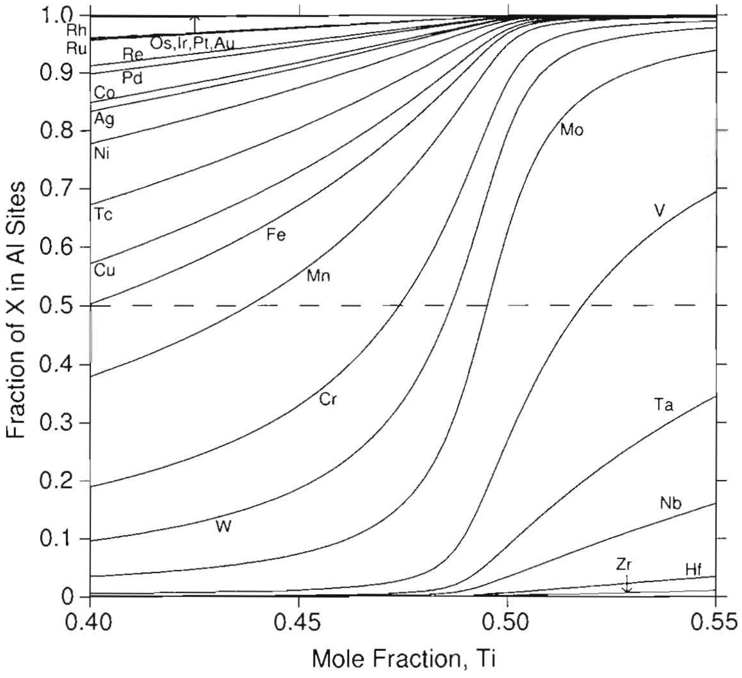
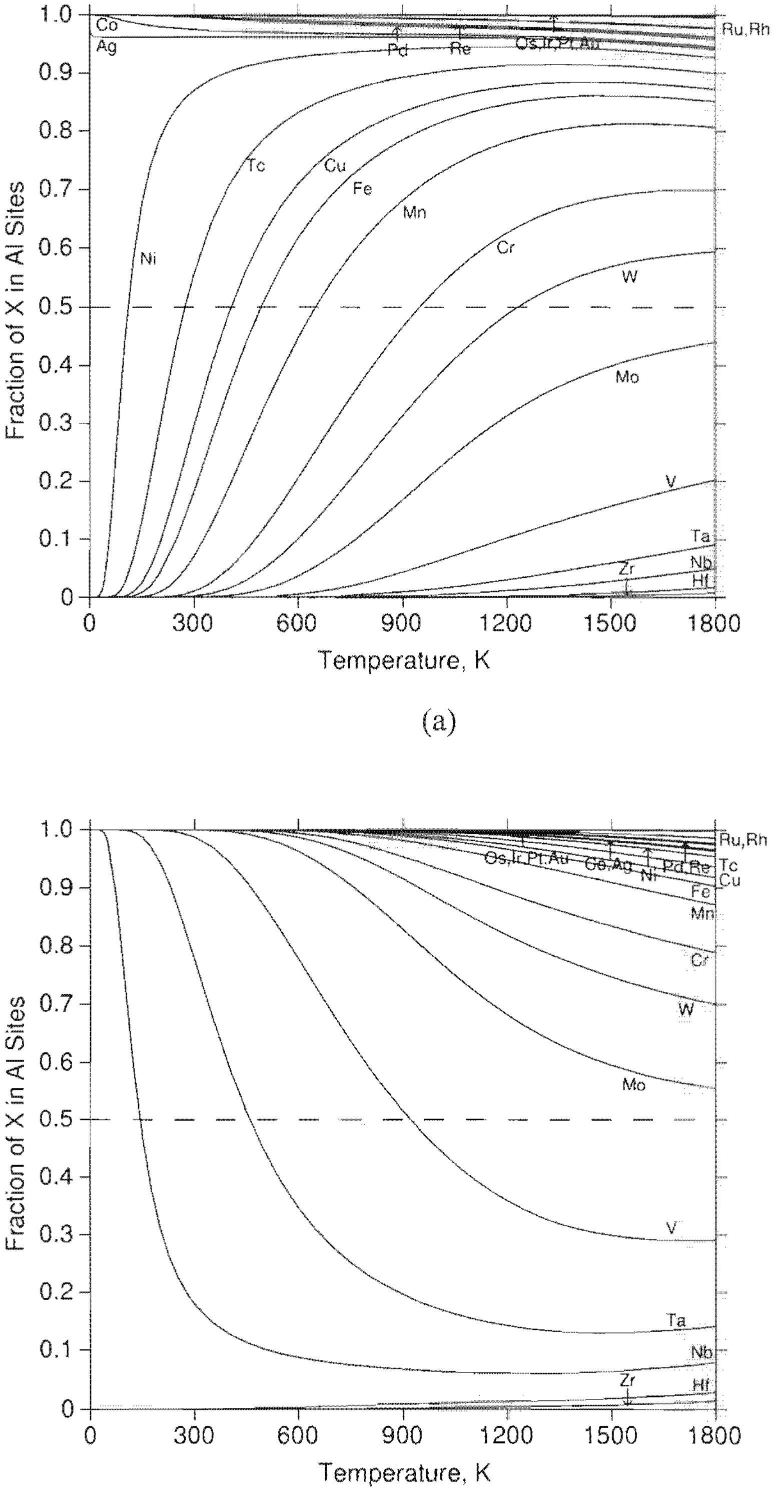
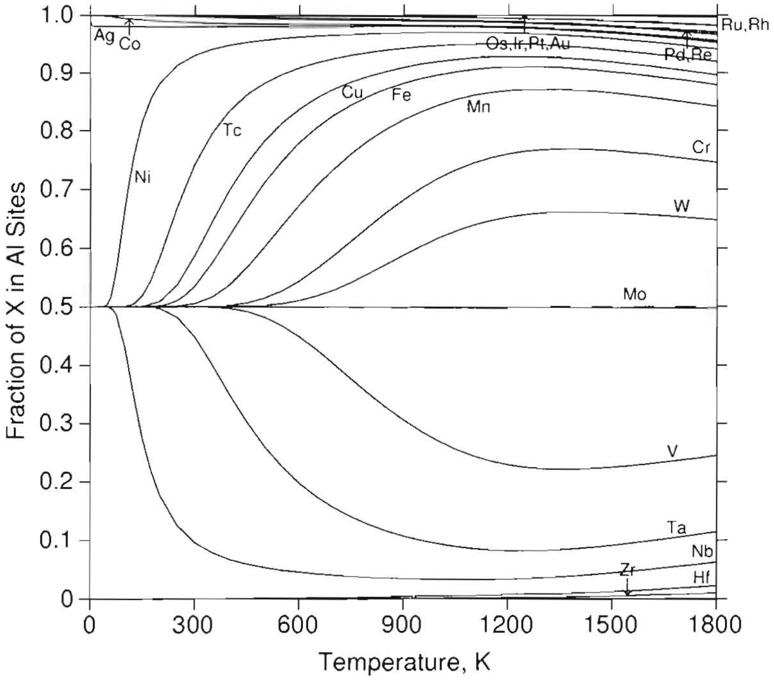


Fig. 3. Predicted fraction of X occupying the Al sublattice in $Ti_xAl_{0.99-x}X_{0.01}$ alloys at T=1173K as a function of Ti concentration.


Fraction of X in Al Sites
Temperature, K
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
300
600
900
1200
1500
1800
Co
Ag
Pd
Re
Os,Ir,Pt,Au
Ru,Rh
Ni
Tc
Cu
Fe
Mn
Cr
W
Mo
V
Ta
Nb
Zr
Hf
(a)
Fraction of X in Al Sites
Temperature, K
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
300
600
900
1200
1500
1800
Ru,Rh
Os,Ir,Pt,Au
Co,Ag
Ni
Pd
Re
Tc
Cu
Fe
Mn
Cr
W
Mo
V
Ta
Nb
Zr
Hf
(b)



(c)

Fig. 4. Predicted fraction of X occupying the Al sublattice in (a) Al-rich $Ti_{0.48}Al_{0.5}X_{0.02}$, (b) Ti-rich $Ti_{0.5}Al_{0.48}X_{0.02}$, and (c) stoichiometric $Ti_{0.49}Al_{0.49}X_{0.02}$ alloys as a function of temperature.

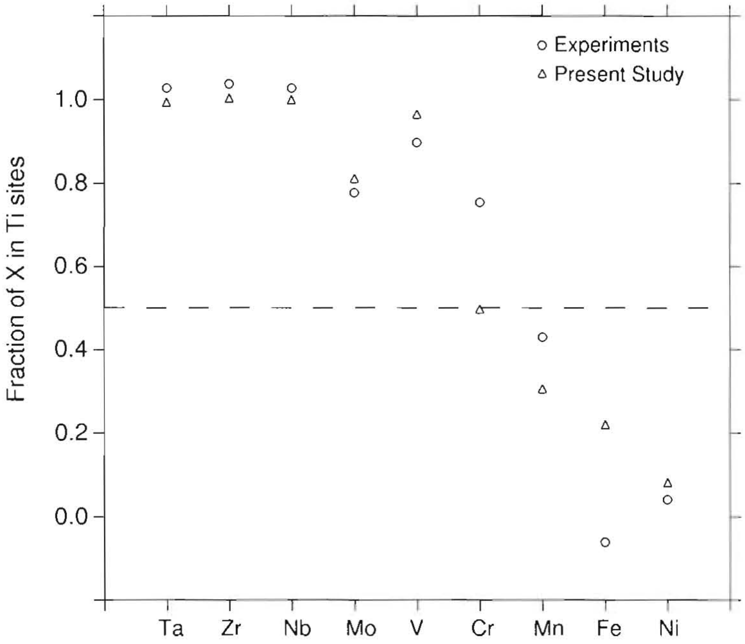


Fig. 5. Comparison between calculated and experimentally measured [37] site occupancy of X={Ta, Zr, Nb, Mo, V, Cr, Mn, Fe, Ni} in L1$_0$ Ti$_{0.47}$Al$_{0.51}$X$_{0.02}$ alloys at T=1173K.