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Substitution behavior of Si in Al_3Ti (D0_{22}): a first-principles study

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Abstract

A first-principles total-energy plane-wave pseudopotential method based on density functional theory has been used to investigate the site preference of Si in Al_3Ti . The site preference parameter S has been calculated and the value of S decreases on increasing Si concentration, but is always greater than 1 while the Si concentration is lower than 25 at.%, indicating Si has a strong site preference for the Al sublattice. The physical origin of the site preference of Si in Al_3Ti was studied by calculating the densities of states (DOSs) of the Al_3Ti -Si systems. The heat of formation and the DOS of the position of the Fermi energy level were also studied to analyze the site preference of Si in Al_3Ti .

1. Introduction

Si is a very important alloying element in casting aluminum alloys. However, it always reacts with Al and other impurity elements, such as Fe, to form Si-rich phases, which are detrimental to the mechanical properties of pure aluminum and high strength aluminum alloys [1, 2]. So far, many attempts have been made to remove impurity Si from the Al melt, for instance, calcium was introduced to react with Si and Al and to form compounds Ca_2Si and CaSi_2Al_2 in the Al melt with 5 wt% Si, and the Si-rich compounds were separated from the Al melt by filtration [3]. However, the similarities of density, atomic radius and chemical properties between Al and Si, and the much smaller activity of Si compared to Al, led to difficulties in the removal of Si with low concentration (<1 wt%). Moreover, the separation of Si and Cu from the Al-1%Si-1%Cu melt was executed by using the electromagnetic centrifugal solidification method. The result indicated that the electromagnetic and centrifugal forces have little influence on the distribution of Si, and the Si also presents disorder under the forces [4].

It is well known that Ti can react with Al to form Al_3Ti (D0_{22} , body-centered tetragonal structure) particles, which are blocky and have a higher density and a higher melting point than Al. The size of the Al_3Ti particle is strongly influenced by the processing conditions, such as formation temperature. The particles range in size from several to 40 μm in general. It was reported that the solubility of Si in Al_3Ti can reach as

high as 15 at.% [5]. Enlightened by these facts, we recently made an attempt to purify low concentration impurity Si from the Al melt via a new method. Ti was introduced into the Al melt by the addition of K_2TiF_6 powder. In this process [6], then, Al_3Ti particles were precipitated and the growth of Al_3Ti particles and the solid solution of Si were finished in the heat preservation time. Si can be removed by the separation of $(\text{Al}, \text{Si})_3\text{Ti}$ particles from the Al melt. The results indicated that this method is effective, but the purification efficiency, to a large extent, is related to the initial Si concentration in the Al melt, and the solubility of Si in Al_3Ti is finite when the initial Si concentration is lower than 0.2 wt%. In order to improve purification efficiency, it is important to introduce some useful means to enhance the solubility of Si in Al_3Ti when the initial Si concentration is lower. So, study of the limit solubility of Si in Al_3Ti becomes important for understanding the purification ability of this method. We should make it clear that the site preference of Si in Al_3Ti has an important impact on the calculation of the limit solubility.

So far, the substitution behaviors of Si in Al_3Ti are seldom investigated. At present, all conclusions concerning Al sites in Al_3Ti partly substituted by Si were found by composition analysis, x-ray diffraction and other experimental methods [5, 7–10]. Almost no one has studied the substitution behavior of Si in Al_3Ti in theory, including the effect of Si substitution on the crystal structure, the site preference and the underlying physical properties.

First-principles calculations were used to understand and predict the properties of materials and structural stability. Over

the years, many researchers had investigated the substitution behavior of alloying additions theoretically based on first-principles calculations. The site preference of W in B2 and L1₀ TiAl were studied by Lu *et al* [11], while the electronic structure and total energies were calculated using the full-potential linearized augmented plane-wave method [12]. The result indicated that W was predicted to occupy Al sites in the B2 TiAl, but Ti sites in the L1₀ TiAl. The site preference of Zr in Ti₃Al was also investigated by Ravi *et al* [13]. The values of equilibrium lattice parameters and heat of formation were calculated to determine the site preference of Zr, which were calculated by using the tight-binding linear muffin-tin orbital method [14]. It is shown that Zr atoms prefer to occupy the Ti sites. Sluiter [15] has studied the site preference of ternary additions in Ni₃Al. A simple site preference parameter *S* was introduced and results for a large number of ternary additions were discussed, Si and Ge were found to substitute preferentially for Al, whereas Fe, Co and Pd were found to have a strong preference for the Ni sites. The local-density linear muffin-tin orbital method [16] with the atomic-sphere approximation was used to calculate the energies of Ni₃Al configurations in which some sites were occupied by ternary additions. Most of the above calculation results are consistent with experimental and other calculational results, which indicates that the first-principles method is reasonable and feasible. Moreover, the first-principle method does not rely on any experimental data and the effect of experiment diversity on the result is avoided.

In this paper, by using the first-principles total-energy plane-wave ultrasoft pseudopotential (USP) method based on density functional theory, we have studied the site preference of Si in Al₃Ti. The site preference is determined by comparing the total energies of atomic configurations where the Al or Ti sites are occupied by Si. The calculation of the electronic structure of atomic configurations was also executed to compare the system stability of the configurations where Si occupied Al or Ti sites.

2. Method

In analogy with [15], the site preference parameter *S* was used to investigate the substitution behavior of Si in Al₃Ti and is defined as

$$S = \frac{\Delta E_{3-4} + \Delta E_{1-2}}{\Delta E_{3-4} - \Delta E_{1-2}}. \quad (1)$$

In this equation, ΔE_{1-2} can be obtained by subtracting the E_2 from E_1 , and ΔE_{3-4} can be obtained by subtracting the E_4 from E_3 . E_1 is the total energy of configuration (1) (Al_{0.75})(Ti_{0.25-x}Si_x), where Si atoms occupy Ti sites, E_2 represents the total energy of configuration (2) (Al_{0.75-x}Si_x)(Ti_{0.25-x}Al_x), where Si occupy Al sites and force Al atoms onto the Ti sites, and E_3 denotes the total energy of configuration (3) (Al_{0.75-x}Ti_x)(Ti_{0.25-x}Si_x), where Si occupy Ti sites and, as a consequence, force Ti atoms to move to the Al sites. Finally E_4 indicates the total energy of configuration (4) (Al_{0.75-x}Si_x)(Ti_{0.25}), where Si atoms occupy Al sites.

The calculations of the electronic structure and total energy of configurations were done using the first-principles

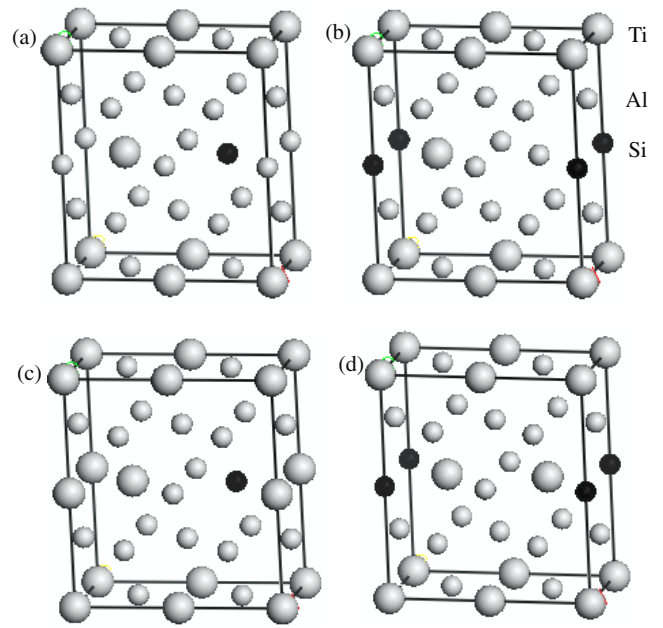


Figure 1. Models of the supercells of Al₃Ti (D0₂₂) with 6.25 at.% Si. (a) Al₁₂(Ti₃Si), (b) (Al₁₁Si)(Ti₃Al), (c) (Al₁₁Ti)(Ti₃Si) and (d) (Al₁₁Si)Ti₄.

total-energy plane-wave ultrasoft pseudopotential (USP) method based on density functional theory (DFT). The calculations were performed using special point integration over the Brillouin zone [17, 18] and a plane-wave basis set for the expansion of the wavefunctions [19, 20]. The electronic exchange–correlation energy was treated by the generalized gradient approximation (GGA) of Perdew *et al* [21]. The Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm [22] was used to minimize the interatomic forces acting on atoms in the supercell. The selected plane-wave cutoff energy was 340 eV, which can ensure a total energy convergence of 10⁻⁶ eV/atom. The number of *k*-points was reduced as the atom number of the supercell increases, and Brillouin zone sampling was performed using 3 × 6 × 3 and 3 × 3 × 3 Monkhorst–Pack *k*-point meshes for 16-atom supercells and 32-atom supercells, respectively. The substitution behavior is mainly influenced by the interactions with atoms in the nearest-neighbor shell [15], so supercells with a limited number of atoms were employed.

Al₃Ti (D0₂₂) crystallizes in the *I*₄/*mmm* space group and the lattice constants were fixed at the values of $a = 0.3851$ nm and $c = 0.8611$ nm ($c/a = 2.236$) found in previous experimental studies [23], which are in satisfactory agreement with other experimental and calculation results of $a = 0.3851$ nm and $c = 0.8610$ nm ($c/a = 2.236$) [24], $a = 0.384$ nm and $c = 0.8614$ nm ($c/a = 2.237$) [25], and $a = 0.3846$ nm and $c = 0.8594$ nm ($c/a = 2.234$) [26]. In order to study the Si concentration relationship to the site preference in Al₃Ti, first-principles calculations have been performed for pure Al₃Ti and Al₃Ti alloys containing 3.125, 6.25, 12.5, 18.75 and 25 at.% Si, respectively. The supercells containing 6.25 at.% Si are investigated, corresponding to the following chemical formulae: Al₁₂(Ti₃Si), (Al₁₁Si)(Ti₃Al), (Al₁₁Ti)(Ti₃Si) and (Al₁₁Si)Ti₄, which are shown in figure 1,

Table 1. Calculated and experimental values of the heat of formation of Al_3Ti (D_{022} structure). id, d and fr refer to ideal, distorted and fully relaxed structure, respectively.

Structures	ΔH (eV/atom)	Comments	Reference
D_{022} (fr)	0.43	DFT	Present work
D_{022} (id)	0.44	DFT	Present work
D_{022}	0.42	LMTO-ASA	[27]
D_{022} (d)	0.43	FLAPW	[28]
D_{022} (d)	0.43	FPLMTO	[29]
D_{022} (d)	0.38	Calorimetry	[30]
D_{022} (d)	0.38	Calorimetry	[31]

and the energies of those configurations were expressed as E_1 , E_2 , E_3 and E_4 , respectively. Other supercells of $\text{Al}_{12}\text{Ti}_4$ with different Si concentrations are similar; just the number of substituted atoms is increased with the Si concentration. The supercells of $\text{Al}_{24}\text{Ti}_8$ were applied to describe the substitution situation when the Si concentration is 3.125 at.%. For Ti atoms, there is just one location in the Al_3Ti unit cell, but there are two distinct locations of Al atoms existing in the Al_3Ti unit cell configuration. So, there were many configurational possibilities for substitutions in the supercells, including the substitution of different atoms and the different ways of arrangement. As shown in figure 1, in this work, the Al sites which are surrounded by four Ti atoms in the nearest-neighbor shell were occupied by Si with a loose arrangement.

In the present calculations, the total energy of the $\text{Al}_{12}(\text{Ti}_3\text{Si})$ cell deviates only 0.02 eV/atom from the sum of the total energy of Al_6Ti_2 and $\text{Al}_6(\text{TiSi})$. The total energy of the $(\text{Al}_{11}\text{Si})\text{Ti}_4$ cell deviates only 0.024 eV/atom from the sum of the total energy of Al_6Ti_2 and $(\text{Al}_5\text{Si})\text{Ti}_2$. As this energy deviation is small compared with energies involved with the site preference, it is confirmed that the 16-atom supercell selected in this study is sufficient.

3. Results and discussion

The heat of formation of pure Al_3Ti bulk (containing four atoms) was obtained from the calculated total energies of $\text{Al}_{12}\text{Ti}_4$, fcc Al and hcp Ti. The result is 0.43 eV/atom, which is in good agreement with the experimental and other calculation results (see table 1). Though the results were obtained with different methods, the discrepancies are within the uncertainties of the respective methods, so the method of calculation of the heat of formation is proven to be reliable.

Table 2 lists the change in volume of different 8-atom configurations. From this table we observe that the volume is generally decreased when the Ti or Al sublattice was occupied by Si atoms. The atomic Goldschmidt radius of Al (1.43 Å) is smaller than Ti (1.47 Å) (table 3), but the volumes of the supercells where Si atoms occupy Al sites are always smaller than those of supercells where Si atoms occupy Ti sites. We can find a very good argument to explain the shrinking of the supercell volumes if we focus on the electronegativity and the standard values of Allred and Rochow of table 3. The discrepancy of electronegativity between Ti and Si is 0.42 eV, which is more obvious than that between Al and Si, i.e. 0.27 eV. Ranking the interactions of these elements

we argue that the Ti–Si and Ti–Al bonds are stronger than the Al–Al and Si–Al bonds because the latter do not involve d electrons. The Ti–Si bonds appear while the Ti–Al bonds disappear in the nearest-neighbor shell of Si atoms which occupy the Al sites, and Ti–Al bonds disappear while the Si–Al bonds appear when Si atoms occupy the Ti sites. If we further consider that the Ti–Si bonds are stronger than Ti–Al and Si–Al bonds and to be shorter than Ti–Al and Si–Al bonds, it is reasonable that the volumes of supercells with Si-occupied Al sites are smaller than those of supercells with Si-occupied Ti sites, which indicates that Si has a site preference for Al sites. The values of lattice constants a and b are increased with Si concentration in Al_3Ti supercells with Si-occupied Ti sites, because of the disappearance of partial stronger Ti–Al bonds. But the lattice constant c is sharply decreased with Si concentration, which may be caused by the difference in atomic radius between Ti and Si, and the volume of Al_3Ti supercells with Si-occupied Ti sites decreases with increased Si concentration.

Si may have a strong preference for the Ti(Al) sublattice, or have only a weak site preference, or may have no particular site preference at all. The relationship between the total energies of these four configurations and the site preference can be extracted:

- (1) When ΔE_{1-2} and ΔE_{3-4} are both negative, Si has a strong preference for the Ti sites both in Ti-rich and Ti-poor alloys, and S is less than -1 .
- (2) When ΔE_{1-2} and ΔE_{3-4} are both positive, Si has a strong preference for the Al sites both in Al-rich and Al-poor alloys, where S is not less than 1.
- (3) If ΔE_{1-2} is negative and ΔE_{3-4} is positive, Si does not have a strong preference for either site and will occupy Al sites in Al-poor alloys ($1 > S > 0$) and Ti sites in Ti-poor alloys ($0 > S > -1$).

The result that ΔE_{1-2} is positive and ΔE_{3-4} is negative is not possible.

The calculation results of different supercells are listed in table 4. E_1 , E_2 , E_3 and E_4 were the energies of four atoms obtained from the total energies of 16 atoms or 32 atoms. $\text{Al}_3(\text{Ti}, \text{Si})$ represents Si substituting Ti, the configuration of $(\text{Al}, \text{Si})_3(\text{Ti}, \text{Al})$ indicates the preference of Si for the Al sublattice is so strong that Al atoms are forced onto the Ti sublattice, while the configuration of $(\text{Al}, \text{Ti})_3(\text{Ti}, \text{Si})$ denotes the preference of Si for the Ti sublattice is so strong that Ti atoms are forced onto the Al sublattice. The situation that Si substitutes Al is represented by the configuration of $(\text{Al}, \text{Si})_3\text{Ti}$.

In Ti-poor supercells, the total energy increases with the Si concentration, which is caused by the discrepancy between Si atoms and Ti atoms, where the energy of Si is larger than that of Ti. Similarly, the energy of Si is smaller than that of Al, so the total energy decreases with the Si concentration in Al-poor supercells.

In table 4, we can see that both the site preference energies of ΔE_{1-2} and ΔE_{3-4} are positive. In Ti-poor supercells, the total energies of supercells with Si-occupied Ti sites are larger than those of supercells with Si-occupied Al sites and Al

Table 2. Change in volumes of eight atoms (in Å³) with Si concentration varied from 3.125 to 25 at.% in Al₃Ti.

Concentration (at.%)	0	3.125	6.25	12.5	18.75	25
Ti ₂ (Al, Si) ₆	127.7029	121.4477	120.5838	118.9421	116.5552	114.2799
(Ti, Si) ₂ Al ₆	127.7029	122.6109	122.3831	120.6185	120.3566	118.9584
ΔV	0	-1.1632	-1.7993	-1.6764	-3.8014	-4.6785

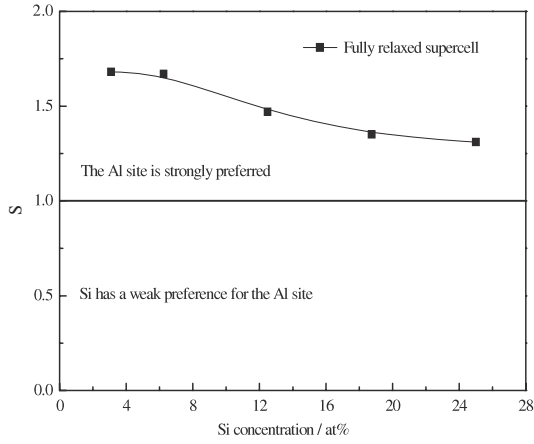


Figure 2. The calculated site preference parameter S versus Si concentration.

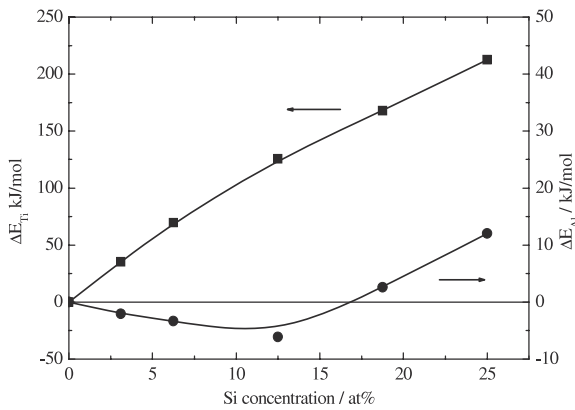


Figure 3. ΔE_{Ti} and ΔE_{Al} versus Si concentration.

atoms are forced onto Ti sites. Likewise, the total energies of supercells with Si-occupied Ti sites and Ti atoms are forced onto Al sites are larger than those of supercells with Si-occupied Al sites directly in Al-poor supercells. So, Si has a preference for Al sites both in Al-poor and Ti-poor supercells. Moreover, E_4 is smaller than E_2 , which indicates that Si prefers to occupy the Al sites directly.

Figure 2 presents the site preference parameter S with different Si concentrations. As can be found in this figure, the S value is larger than 1 in the checked Si concentration range and decreases with increased Si concentration. Si still has a strong preference to occupy Al sites when the Si concentration levels are up to 25 at.%, where the value of S is 1.31.

The calculation of S is based on the assumption that all substitution behaviors are feasible. In fact, the substitution of Si onto the Al (or Ti) sublattice may become infeasible with the increased Si concentration as can be deduced from the variation

Table 3. Atomic Goldschmidt radii R in Å according to Hansen [32], and the electronegativity, EN, whose standard values are from Allred and Rochow [33].

Elements	R (Å)	EN
Ti	1.47	1.32
Al	1.43	1.47
Si	1.34	1.74

of the total energy of the system, which was calculated as [34]

$$\Delta E_{\text{Ti}} = E_{\text{Al}_3(\text{Ti}_{1-4x}\text{Si}_{4x})} + 4xE_{\text{Ti}} - E_{\text{Al}_3\text{Ti}} - 4xE_{\text{Si}} \quad (2)$$

$$\Delta E_{\text{Al}} = E_{(\text{Al}_{3-4x}\text{Si}_{4x})\text{Ti}} + 4xE_{\text{Al}} - E_{\text{Al}_3\text{Ti}} - 4xE_{\text{Si}} \quad (3)$$

where ΔE_{Ti} and ΔE_{Al} represent the energy variations of the systems when Ti and Al are substituted, respectively. x is the Si concentration in the Al₃Ti supercell, $E_{\text{Al}_3(\text{Ti}_{1-4x}\text{Si}_{4x})}$ and $E_{(\text{Al}_{3-4x}\text{Si}_{4x})\text{Ti}}$ are the total energies of the systems when Si occupies $4x$ Ti and $4x/3$ Al sites, respectively. $E_{\text{Al}_3\text{Ti}}$ is the total energy of the Al₃Ti supercell, and E_{Ti} and E_{Al} are the atomic energies of Ti and Si, respectively. A negative ΔE indicates that the total energy of the system is decreased after substitution and the substitution behavior is feasible, while a positive one suggests that the total energy of the system is increased and the substitution behavior is infeasible.

Figure 3 plots ΔE_{Ti} and ΔE_{Al} versus Si concentration. As can be found in the figure, ΔE_{Ti} is positive and increases monotonically with the Si concentration. In contrast, ΔE_{Al} is decreased firstly with Si concentration, and after reaching a minimum at a concentration of about 12.5 at.%, it is increased. As the figure shows, ΔE_{Al} stays negative before the Si concentration exceeds a value of about 16–17 at.%. That is to say, the substitution of Si onto the Al sublattice is feasible when the Si concentration is lower than this limiting value. According to the experimental work [3], the Si limit solubility in Al₃Ti is 15 at.% at 973 K. Obviously, this value is in satisfactory agreement with our calculated limit value though the temperature effect has been neglected in the calculation. Considering the accuracy of the first-principles calculation, the temperature effect on the Si limit solubility in Al₃Ti may be rather finite. Therefore, in the experiment, raising the temperature may be not be very effective in enhancing the solid solubility of Si in Al₃Ti.

The comparison of the site preference, phase stability and bonding of different substitution behaviors is also executed by the calculation of the heat of formation [35, 36]. At first, the total energies of Al, Ti and Si elements for the irrespective equilibrium lattice parameters are calculated to decide the heat of formation. The heat of formation is obtained by the calculation of the difference between the total energy of the compound and the sum of the concentration-weighted total

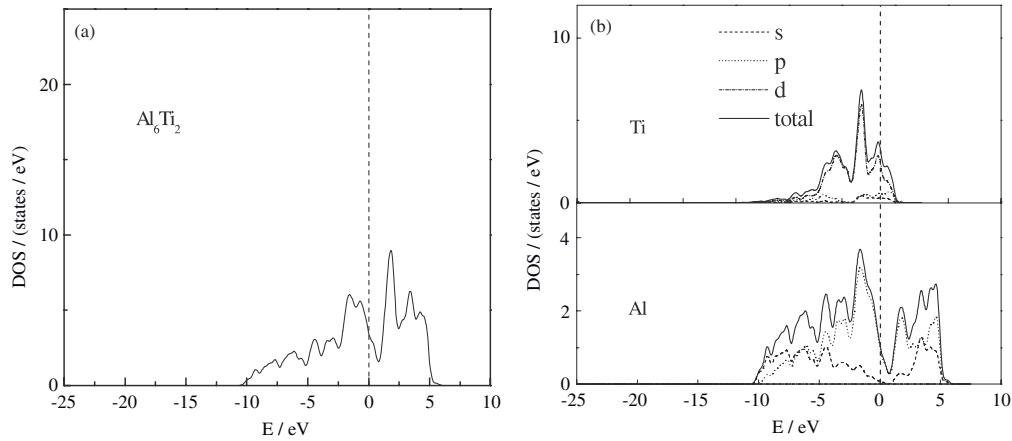


Figure 4. The calculated DOS curves of pure Al_6Ti_2 supercell: (a) the total DOS curve of Al_6Ti_2 and (b) the PDOS curves of Al_6Ti_2 .

Table 4. The total energies and site preference energies ΔE_{1-2} and ΔE_{3-4} (in eV) of fully relaxed supercells with different substitution behaviors.

Si concentration at. %	E_1 $\text{Al}_3(\text{Ti}, \text{Si})$	E_2 $(\text{Al}, \text{Si})_3(\text{Ti}, \text{Al})$	E_3 $(\text{Al}, \text{Ti})_3(\text{Ti}, \text{Si})$	E_4 $(\text{Al}, \text{Si})_3\text{Ti}$	ΔE_{1-2}	ΔE_{3-4}
3.125	-1591.565 14	-1591.655 03	-1785.127 74	-1785.481 37	0.089 89	0.353 63
6.25	-1404.092 91	-1404.223 48	-1791.391 13	-1791.909 26	0.130 57	0.518 13
12.50	-1029.281 42	-1029.337 86	-1804.376 35	-1804.693 78	0.056 44	0.317 43
18.75	-654.615 40	-654.688 67	-1816.884 87	-1817.505 57	0.073 27	0.620 70
25.00	-279.920 42	-279.996 73	-1829.758 00	-1830.236 77	0.076 31	0.478 77

Table 5. The heats of formation (in eV) of four-atom units of different supercells.

Si concentration (at. %)	Ti were substituted	Al were substituted
0	-1.75	-1.75
3.125	-1.38	-1.77
6.25	-1.03	-1.78
12.50	-0.45	-1.81
18.75	-0.01	-1.72
25.00	0.45	-1.62

energies of the constituent elements. The calculated results reduced to four-atom units are shown in table 5. As can be anticipated, the heats of formation of the systems with Si-occupied Al sites are always smaller than those of the systems with Si-occupied Ti sites, indicating the formation of systems with Si-occupied Al sites are more preferred.

Concerning the supercells where Si atoms occupy Al sites, the heat of formation of supercells with Si-occupied Al sites is lower than pure Al_3Ti until the Si concentration exceeds 12.5 at.%. Therefore the substitution behaviors are feasible and the compounds are stable under this Si-doped concentration. The heat of formation is large when the Si concentration is 3.125 at.% and 6.25 at.%, where the heat of formation is -1.77 eV and -1.78 eV, respectively. But the driving force is dependent on the discrepancy of the heat of formation between the supercells with Si-occupied Al sites and the perfect Al_3Ti supercell, and the discrepancy is -0.02 eV and -0.03 eV, respectively. So, the driving force is small and the substitution process is slow, which agrees well with the experimental phenomenon that 60 min is needed to finish this substitution process [6].

In order to gain further insight into the physical origin of the site preference of Si in Al_3Ti and the feasibility of the substitution behavior, the density of states (DOS) of the Al_3Ti -Si systems was investigated in this work. The calculated DOS of the pure Al_6Ti_2 supercell is shown in figure 4. One can see that the densities of states display a similar shape characterized by a strong hybridization between d states of titanium and p states of aluminum. The presence of a pseudo-gap in the densities of states with the Fermi energy residing close to the minimum could also be observed. The results are in good overall agreement with the literature [28, 37].

The hybridization character between different atoms reflects the site preference of Si. Figure 5 shows the DOS of the supercells with Si-occupied Ti or Al sites, with the same Si concentration 6.25 at.%. For the $\text{Al}_{12}(\text{Ti}_3\text{Si})$ supercell, the DOS is similar to that of the pure Al_3Ti supercell. The main peaks from the hybridization of Ti d states and Al p states occur at -1.5 and 1.46 eV, but the Ti-Si hybridization is absent in bonding states, which indicated that there is not a strong interaction between Ti atoms and Si atoms. So the substitution of Si on the Ti sublattice seems to be unsuitable. Comparing to the $\text{Al}_{12}(\text{Ti}_3\text{Si})$ supercell, the densities of states of $(\text{Al}_{11}\text{Si})\text{Ti}_4$ present hybridizations between Al p, Ti d and Si p states. A new strong hybridization between Ti d states and Si p states occurs at -1.4 eV below the Fermi level, suggesting that the substitution of Si on the Al sublattice seems to be favorable. Moreover, the total DOS of the $(\text{Al}_{11}\text{Si})\text{Ti}_4$ supercell at the Fermi level, $N(E_F)$, is lower than that of $\text{Al}_{12}(\text{Ti}_3\text{Si})$, so the $(\text{Al}_{23}\text{Si})\text{Ti}_8$ supercell should be more stable according to the correlation of phase stability with low $N(E_F)$ [38].

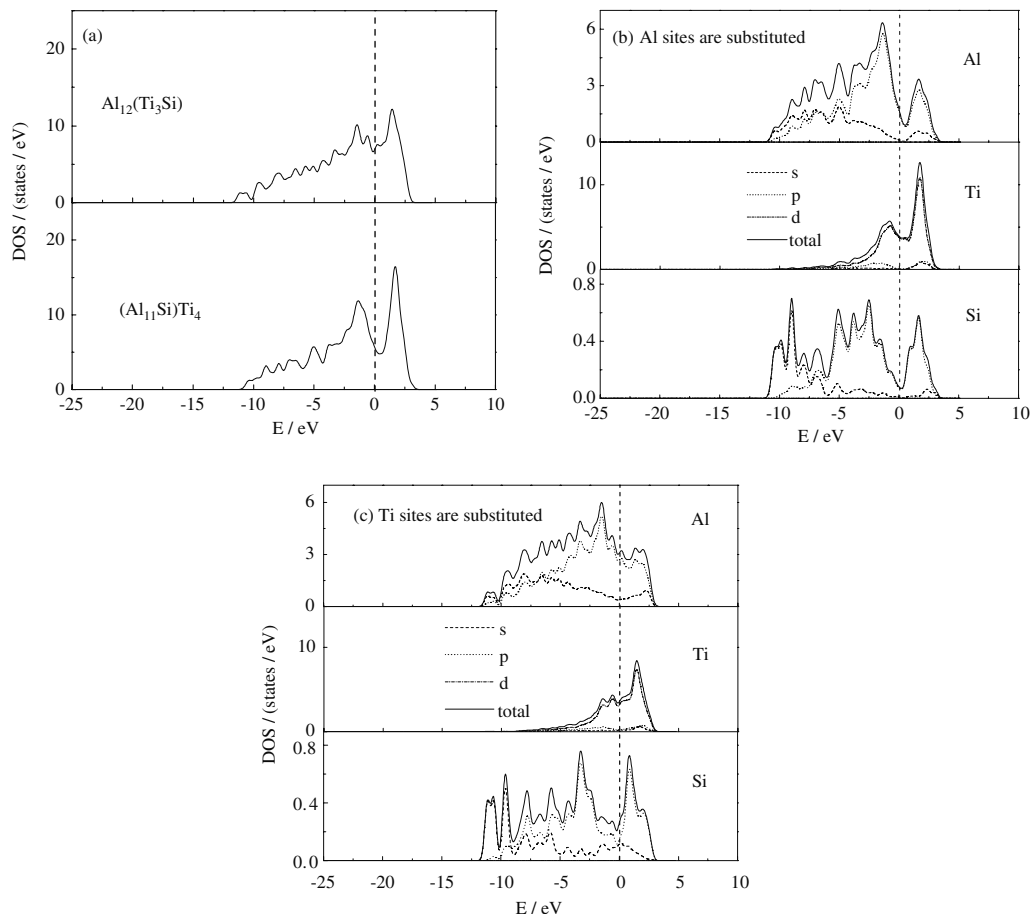


Figure 5. The calculated DOS curves of $\text{Al}_3\text{Ti-Si}$ supercell containing 6.25 at.% Si: (a) the total DOS curves of $\text{Al}_{12}(\text{Ti}_3\text{Si})$ and $(\text{Al}_{11}\text{Si})\text{Ti}_4$, (b) the PDOS curves of $(\text{Al}_{11}\text{Si})\text{Ti}_4$ and (c) the PDOS curves of $\text{Al}_{12}(\text{Ti}_3\text{Si})$.

4. Conclusions

The site preference of Si in Al_3Ti with different Si concentrations has been computed from the first-principles total-energy plane-wave pseudopotential method based on density functional theory. According to our study, both the site preference energies of ΔE_{1-2} and ΔE_{3-4} are positive, which means the energies of supercells with Si-occupied Al sites are smaller than those of supercells with Si-occupied Ti sites with the same Si concentration. The site preference parameter S is calculated and all the values of S of supercells with Si-occupied Al sites are larger than 1, which shows that Si atoms have a clear preference to substitute Al which is due to the energy stabilization effect.

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