First principles study of Ti_5Si_3 intermetallic compounds with Cu additions: Elastic properties and electronic structure

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Abstract. The structural stabilities, elastic and electronic properties of Ti_5Si_3 intermetallic compounds with Cu additions have been studied by density functional theory. The calculated lattice constants (a, c) and the equilibrium volume are found to decrease with the increasing of Cu atomic number.Then the independent elastic constants are calculated, the results shows that all the elastic constants of compounds satisfy the mechanical stability criteria, which indicates all these hexagonal structures are mechanically stable, furthermore, the elastic constants (C11, C44 and C66) decrease with the increasing of Cu atomic number. The calculated bulk modulus B, shear modulus G and Young's modulus E decrease, while Poisson's ratio σ and Cauchy pressure increase with the increasing of Cu atomic number, and the ductility is slightly improved. The calculated DOS showed that the density of states (DOSs) of the Feimi level increases and the stability of compounds decreases with the increasing of Cu atomic number.

1. Introduction

Titanium silicide (Ti_5Si_3) has attracted considerable attention due to its low density (4.32 g/cm^3), high melting temperature (2130℃), good strength at elevated temperatures, high oxidation resistance, and excellent creep resistance [1-2]. Nevertheless, the defect of Ti_5Si_3, such as low fracture toughness (2.5 Mpa/m^2) below the ductile-brittle transition temperature [3], severely restricted its practical applications.

In fact, by adding Cu to the structure, Ti_5Si_3 becomes a considerably more hopeful material for engineering applications by improving mechanical property and electronic structure [4]. This study is to combine experimentally determined structural data with first-principle calculations to fully understand bonding changes that occur with the addition of Cu to Ti_5Si_3. The main purpose of the this study is to investigate the lattice constants, formation enthalpy, density of states (DOS) and elastic constants of Ti_5Si_3 intermetallic compounds with Cu additions.

2. Calculation methods

The structural, electronic and elastic properties of Ti_5Si_3 intermetallic compounds with Cu additions was calculated by First-principles of Cambridge Serial Total Energy Package (CASTEP). The density functional theory (DFT) was used by this software package that employed the plane wave pseudo-potential method as a basically theory [5]. The generalized gradient approximation of Perdew Burke Ernzerhof (GGA-PBE) parameterized by PERDEW described to the exchange and correlation terms [6]. The electron-ion interaction was described by Ultrasoft pseudo-potential with the cutoff energy 400 eV. The calculations of total energy and electronic are followed by cell optimization with self-consistant field below 5.0×10^{-6} eV/atom, the maximum force on the atom was below 0.01eV/ Å, the

maximum displacement between cycles was below 5.0×10^{-4} and the maximum stress was below 0.02 GPa.

3. Results and discussion

3.1. Structure and stability

Ti-Si-Cu system intermetallics possess the $D8_8$ crystal structure of Ti_5Si_3 prototype with the space group $P6_3/mcm$ (No. 193). As shown in Fig. 1, the unit cell of Ti_5Si_3 contains 10 Ti atoms and 6 Si atoms in which Ti atoms occupy at 4d (0.33, 0.67, 0), 6g (0.23, 0, 0.25) sites and Si atoms are at 6g (0.60, 0, 0.25). Cu is incorporated in the intermetallic phase of Ti_5Si_3 by occupation at sites 4d (0.33, 0.67, 0) or 6 g (0.23, 0, 0.25). This is gave rise to $Ti_{10}Si_5Cu_1$, $Ti_9Si_6Cu_{1\text{-}4d}$ and $Ti_9Si_6Cu_{1\text{-}6g}$ intermetallic phases. Fig. 2 given is the crystal structures of these compounds. Considering the phase stability, formation enthalpy of intermetallic phases are calculated as follows:

$$\Delta H = \frac{1}{a+b+c}\left(E_{tot} - aE_{solid}^{Ti} - bE_{solid}^{Si} - cE_{solid}^{Cu}\right) \qquad (1)$$

where E_{tot} is the total energy of the unit cell, E_{solid}^{Ti}, E_{solid}^{Cu} and E_{solid}^{Si} are the total electronic energies per atom of Ti and Cu, and Si, and a, b and c are to the numbers of Ti, Si and Cu atoms in unit cell. Table 1 gives the calculation results of formation enthalpy(△H). It can be seen that all the formation enthalpies of the compounds are negative, which indicates these intermetallic compounds are stable. Except $Ti_{10}Si_6$ phase, $Ti_9Si_6Cu_{1\text{-}4d}$ phase possess the lowest formation enthalpy when Cu occupied 4d (0.33, 0.67, 0) or 6 g (0.23, 0, 0.25) sites, which indicates that the $Ti_9Si_6Cu_{1\text{-}4d}$ phase possess the highest structure stability, and then followed by$Ti_9Si_6Cu_{1\text{-}6g}$ and $Ti_{10}Si_5Cu_1$. Therefore, Cu preferentially occupies 4d-Ti site of Ti_5Si_3.

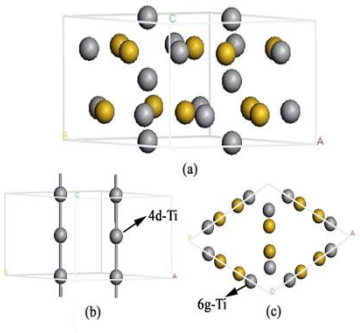

Fig.1 (a) $D8_8$ crystal structure of Ti_5Si_3; (b) Schematic diagram of 4d-Ti arrangement; (c) Schematic diagram of 6g-Ti arrangement.

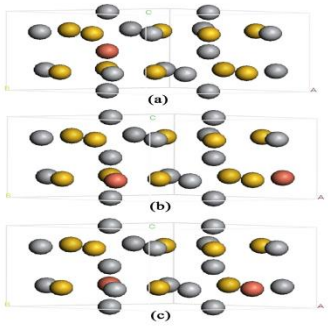

Fig.2 (a) Cu doped 4d-Ti sites of Ti_5Si_3; (b) Cu doped 6g-Ti sites of Ti_5Si_3; (c) Cu doped Si sites of Ti_5Si_3.

Table 1 Calculated formation enthalpy (△ H) of Cu atom to dope Ti sites of Ti_5Si_3

Compound	$Ti_{10}Si_6$	$Ti_{10}Si_5Cu_1$	$Ti_9Si_6Cu_{1\text{-}4d}$	$Ti_9Si_6Cu_{1\text{-}6g}$
△ H (eV/atom)	-6.377	-5.203	-5.462	-5.341

Table 2 gives the calculation value of lattice parameters and equilibrium volume by different Cu atomic number occupying of Ti_5Si_3 stable sites, and the lattice parameters (a c) decrease. Because of the atomic radius of Ti is bigger than that of Cu, which induces lattice distortion of compound. At the same time, the equilibrium volume also decreases.

Table 2 Calculated lattice parameter of different Cu atom to dope 4d-Ti sites of Ti_5Si_3.

Compound	a/(Å)	b/(Å)	c/(Å)	V/(Å)^3
$Ti_{10}Si_6$	7.4716	7.4716	5.132	248.119
$Ti_9Si_6Cu_{1\text{-}4d}$	7.4004	7.4004	5.124	243.79
$Ti_8Si_6Cu_{2\text{-}4d}$	7.2783	7.2783	5.114	239.681
$Ti_7Si_6Cu_{3\text{-}4d}$	7.2623	7.2623	5.014	232.681
$Ti_6Si_6Cu_{4\text{-}4d}$	7.2592	7.2592	5.012	228.704

3.2. Elastic properties

Table 3 gives the calculated elastic constants Cij in Cu-Ti-Si intermetallic compounds. In Table 3, the values of C11, C44, C66 decrease with the increasing of Cu atomic number. The traditional mechanical stability criteria for hexagonal crystal systems are given as [7]:

$$C_{11} > 0,\ C_{11} - C_{12} > 0,$$
$$C_{44} > 0,\ (C_{11} + C_{12})C_{33} - 2C_{13}^2 > 0 \quad (2)$$

Table 3 Calculated elastic constants of different Cu atom to dope 4d-Ti sites of Ti_5Si_3.

Compound	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	$C_{66}=\frac{1}{2}(C_{11}-C_{12})$
$Ti_{10}Si_6$	282.62	107.91	54.00	271.63	94.17	87.36
$Ti_9Si_6Cu_{1\text{-}4d}$	272.89	110.65	45.03	281.85	73.34	80.93
$Ti_8Si_6Cu_{2\text{-}4d}$	264.72	111.97	49.83	284.05	59.63	76.38
$Ti_7Si_6Cu_{3\text{-}4d}$	258.20	112.45	53.33	269.69	49.32	72.88
$Ti_6Si_6Cu_{4\text{-}4d}$	243.60	113.33	46.08	251.63	14.6	65.13

In Table 3, all the elastic constants of phase satisfy the mechanical stability criteria of Eq. (2), and all these hexagonal structures are excellent mechanical stability. Shear modulus (BV, BR, GV, GR) in terms of the elastic constants Cij’ s are given by[7]. And the final values can be taken as:

$$B = (B_V + B_R)/2 \quad (3)$$
$$G = (G_V + G_R)/2 \quad (4)$$
$$E = \frac{9BG}{3B+G} \quad (5)$$
$$\sigma = \frac{1}{2}\left(1 - \frac{E}{3B}\right) \quad (6)$$

According to expression (3-6), Shear modulus (BV, BR, GV, GR) can be calculated in Table 4. The calculated bulk modulus and the shear modulus decrease with the increasing of Cu atomic number in Table 4, which indicates the resistance of volume change by applied pressure and the resistance of reversible deformations upon shear stress is decreased, respectively.

The ratio of the bulk to B/G represents the ductility of materials. When The B/G is higher than 1.75, suggesting that the material shows a ductile behavior. In Table 4, the value of $Ti_{10}X_6$ and $Ti_9Si_6Cu_{1\text{-}4d}$ are 1.46 and 1.60, respectively, which indicates $Ti_{10}X_6$ and $Ti_9Si_6Cu_{1\text{-}4d}$ are brittle material. While the values of the other phases are higher than 1.75, which indicates that the others are ductile materials.

Table 4 Calculated bulk modulus B, shear modulus G, Young's modulus E and Poisson's ratio σ of different Cu atom to dope 4d-Ti of Ti_5Si_3.

Compound	B	G	E	σ	B/G
$Ti_{10}Si_6$	140.32	95.82	237.16	0.36	1.46
$Ti_9Si_6Cu_{1\text{-}4d}$	136.21	85.37	225.25	0.39	1.60
$Ti_8Si_6Cu_{2\text{-}4d}$	132.68	67.29	209.18	0.41	1.97
$Ti_7Si_6Cu_{3\text{-}4d}$	131.47	59.35	198.74	0.42	2.21
$Ti_6Si_6Cu_{4\text{-}4d}$	127.19	41.37	188.37	0.45	3.07

From Table 4, it can be also seen that Young's modulus (B) of $Ti_{10}Si_6$ is largest, this indicates $Ti_{10}Si_6$ is the stiffest, and then followed by $Ti_9Si_6Cu_{1\text{-}4d}$, $Ti_8Si_6Cu_{2\text{-}4d}$, $Ti_7Si_6Cu_{3\text{-}4d}$ and $Ti_6Si_6Cu_{4\text{-}4d}$. For another, Poisson's ratio σ increased with the increasing of Cu atomic number, which indicates the ductility of materials increases with the increasing of Cu atomic number.

Besides B/G, Young's modulus E and Poisson's ratio σ, Cauchy pressure (C12-C44) is another important parameter for the mechanical properties of materials [8]. The higher values of Cauchy pressure (C12-C44) correspond to better toughness of materials. Fig. 3 shows the effect of the number of Cu atom on Cauchy pressure (C12-C44). It can be seen that the toughness of materials increases with the increasing of Cu atomic number, which the same with above calculation results.

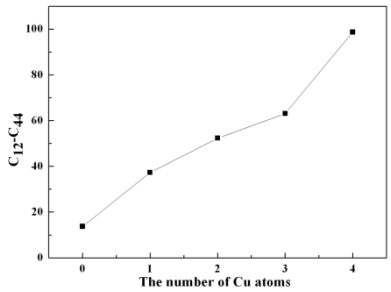

Fig. 3 Cauchy pressure (C12 – C44).

3.3. Electronic structure

Fig. 4 gives the total and partial electronic density of states (DOSs) for Ti_5Si_3. It can be seen that the values of total DOS at Fermi level (Ef) are all higher than 0, which implying that Ti_5Si_3 exhibits metallic behavior. From Fig. 4, it can be also seen that the main bonding peaks between -10 eV and -5 eV mainly originate from the contribution of valence electron numbers of Si(3s) orbits, the main bonding peaks between -5 eV and -2 eV are the result of the bonding Ti(3d), Ti(4s) and Si(3s) hybridized. The main bonding peaks from -2 to 2 eV are the contribution of Ti(3d) with little Si(3p) and Ti(4s). Furthermore, from the total density of states (DOS) for Ti_5Si_3, it can be also seen that the pseudogap is wider and deeper, and the Feimi level is close proximity to the valley bottom. The pseudogap at the Fermi level was always associates with stronger stability, which indicates Ti_5Si_3 is stable.

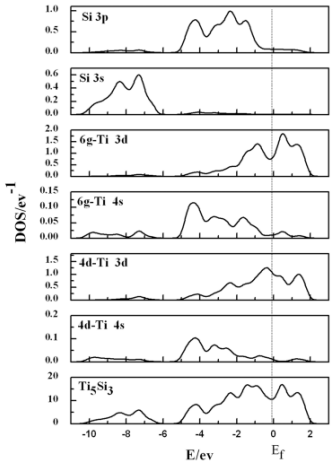

Fig. 4 The total and partial density of states (DOS) of Ti_5Si_3.

Fig. 5 shows the total density of states (DOSs) of different Cu atom to dope 4d-Ti of Ti_5Si_3. It is noted that the Feimi level of Ti_5Si_3 is the lowest, the Feimi level of $Ti_6Si_6Cu_{4\text{-}4d}$ is the highest, which indicates that the density of states (DOSs) of the Feimi level increases and the stability of compounds decreases with the increasing of Cu atomic number. Furthermore, the Feimi level moves toward the high pseudogap side, which indicates the valence electron occupies the anti-bonding states of d(Ti-4d)- d(Ti-4d).

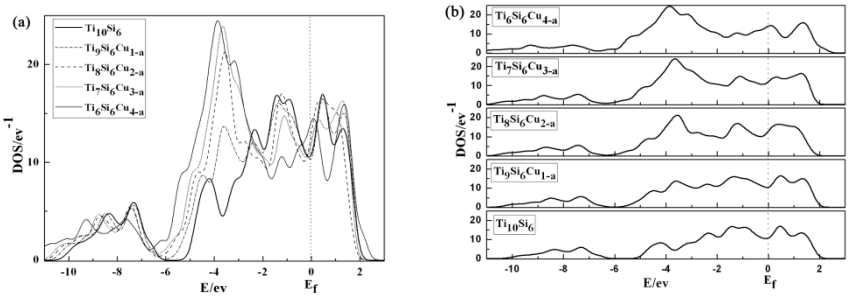

Fig. 5 The total density of states (DOS) of different Cu atom to dope 4d-Ti of Ti_5Si_3.

4. Conclusions

Structural stability, elastic and electronic properties of Cu-Ti-Si system intermetallic compounds with $D8_8$ hexagonal structure were investigated.

The calculated lattice constants (a, c) and elastic constants (C11, C44 and C66) decrease with the increasing of Cu atom.

The polycrystalline elastic modulus were obtained by the VRH method, and the obtained B, G and E decreased and Poisson’ s ratio σ_{xy} and Cauchy pressure (C12-C44) increased with the increasing of Cu atomic number, whereas the ductility was improved.

The calculated DOS showed that the density of states (DOSs) of the Feimi level increases and the stability of compounds decreases with the increasing of Cu atomic number.

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