Effects of Alloying Elements Ti, Cr, Al, and Hf on β-Nb₅Si₃ from First-principles Calculations

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Abstract

The energy, lattice parameters, electronic structures, and elastic constants of the intermetallic compound β-Nb₅Si₃ alloyed by Ti, Cr, Al, and Hf elements are investigated using first-principles methods based on plane-wave pseudopotential theory. From the impurity formation energy calculated, it is found that Ti, Cr, and Hf prefer to occupy the Nb₁, Nb₂, and Nb₃ site, respectively, and that Al decreases the stability of β-Nb₅Si₃. Ti and Cr atoms reduce the c/a ratio of crystalline lattices and Hf atom transforms the tetragonal system to the orthorhombic system. The total state density of pure β-Nb₅Si₃ system and Ti, Cr, and Hf doped systems shows that Ti, Cr, and Hf improve the ductility of β-Nb₅Si₃ system. The bulk modulus, shear modulus, and elastic modulus are obtained using Voight approximation equation. Ti and Cr increase the hardness and reduce the ductility of β-Nb₅Si₃. In contrast, Hf decreases the hardness and improves the ductility.

Keywords: intermetallics; silicide; site occupancy; hardness; ductility

1. Introduction

The efficiency and performance of the jet engines strongly depend on the highest temperature in the engines—the inlet temperature of the high-pressure turbine. To achieve higher thrust, higher operating temperature must be realized. However, advanced Ni-based superalloy that widely applies as turbine materials at present cannot satisfy the urgent requirements of the increase in operating temperature since the melting temperature of most superalloy is about 1 350 °C. In this case, it is obvious that a completely new family of materials must be developed, with higher melting point, lower density and greater intrinsic strength. Recent researches have shown that Nb-Si based superalloy can lead to the room-temperature brittleness, and the high-speed internal diffusion of oxygen leads to the inactivation of Nb-Si based in-situ composites. In order to balance the properties in a single composition, including low temperature toughness, high-temperature strength, creep resistance, and oxidation resistance, alloying elements such as Ti, Cr, Al, and Hf are considered to add to binary Nb-Si system. Therefore, it is important to study the effects of alloying elements Ti, Cr, Al, and Hf on the properties of Nb-Si based in-situ composites. In the Nb-Si-X ternary or multiple systems, there are Nb₅Si₃, α-Nb₅Si₃, and β-Nb₅Si₃ silicide phases. Since the translation from β-Nb₅Si₃ to α-Nb₅Si₃ needs high temperature and the translation process is very slow, the high-temperature stable phase—β-Nb₅Si₃ can exist at room temperature as a main composition phase. However, there are few investigations about the influence of elements on α-Nb₅Si₃ by first-principles and no reports on β-Nb₅Si₃. Therefore, the aim of this article is to investigate how Ti, Cr, Al, and Hf elements affect the stability, electronic structure, and stress characters of β-Nb₅Si₃.

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2. Models and Method of Calculation

Fig.1 shows the crystal structure model of β-Nb5Si3 used for calculation. There are 32 atoms in the structure cell shown in Fig.1. The structure type of β-Nb5Si3 is D8m with the space group of I4/mcm (No. 140). The lattice parameters of the unit cell are \(a = b = 10.020\, \text{Å}, c = 5.069\, \text{Å}\) from joint committee on powder diffraction standards (JCPDS) card (No.30-0875). And the atomic equivalent positions are Nb (0, 0.50, 0.25), Nb (0.074, 0.223, 0), Si (0.17, 0.67, 0)\(^9\), which are defined to be NbI, NbII, SiI, and SiII from their geometry position, respectively. Therefore, the number of possible substituted groups of equivalent sites for alloying elements is 4. The total atom number of each equivalent group is 4 for NbI, 16 for NbII, 4 for SiI, and 8 for SiII in a 32-atom \(\beta\)-Nb5Si3 cell. In every calculation, only one atom is replaced in the 32-atom \(\beta\)-Nb5Si3 cell.

All the first-principles calculations are carried out with cambridge serial total energy package (CASTEP)\(^{10}\), which uses the density functional theory (DFT)\(^{11-12}\) plane-wave pseudopotential method. The function of generalized gradient approximation (GGA) of J. P. Perdew\(^{13}\) with ultrasoft pseudopotentials is selected for the exchange-correlation energy of all elements in the models. The cutoff energy is set at 320 eV. A regular Mokhorst-Pack grid of special \(k\)-point is used to define the accuracy of the Brillouin zone sampling, which is \(2 \times 2 \times 4\) for all models. The finite basis set correction\(^{14}\) and the Pulay scheme of density mixing are specified to evaluate energy and stress. In the calculations for doped systems, Broyden-Fletcher-Goldfarb-Shanno (BFGS) geometry optimization task is performed to obtain a stable structure with minimum total energy, and in the optimization processes, all atomic positions in our models are relaxed until the forces are less than 0.05 eV/Å and the stresses less than 0.1 GPa.

3. Results and Discussion

3.1. Impurity formation energy

The lowest energy theory indicates that the system with the lowest formation energy is most stable, so the stability of doped system depends on the change of formation energy before and after doping. The less the formation energy, the more stable the system. Therefore, we define the impurity formation energy for the change of formation energy. The following function is used to calculate the impurity formation energy.

\[
E_{f-im}^X = E_{f}^{X-Nb-Si} - E_{f}^{Nb-Si} = (E_{f}^{X-Nb-Si} - mE_{Nb} - nE_{Si} - uE_{Nb} - vE_{Si}) = E_{f}^{X-Nb-Si} - E_{f}^{Nb-Si} - (m - u)E_{Nb} - (n - v)E_{Si} - E_X
\]

where \(X\) is the doping element, \(X-Nb-Si\) and Nb-Si denote the doped and pure \(\beta\)-Nb5Si3 system, \(E_{f-im}^X\), \(E_f\), and \(E_r\) refer to the impurity formation energy, the formation energy, and the total energy of the unit cell. In addition, \(E_{Nb}\), \(E_{Si}\), and \(E_X\) represent the monoatomic energy of Nb, Si, and alloying element in their bulk pure states, and \(m\), \(n\), \(u\), and \(v\) denote the number of Nb and Si atoms in the unit cell.

Table 1 shows the calculated impurity formation energies of doped systems. The results show that in the Ti-doped system, the impurity formation energy increases from \(-1.01\) eV to \(1.71\) eV, when the groups of sites NbI, NbII, SiI, and SiII are substituted, respectively. According to the negative impurity formation energy, the groups of sites NbI and NbII are the possible sites to be replaced in the Ti-doped system. And in the Cr-doped systems, the only negative \(E_{f-im}^X\) appears when the NbI site is doped, which means that the NbI site doped by Cr atom is feasible. Aside from that the formation energy is reduced when Hf is introduced to the NbII site. However, the impurity formation energy is lower when NbI site is substituted than when NbII site is substituted, which proves that Ti atoms replace atoms on the NbI sublattice in \(\beta\)-Nb5Si3 first. And in the Cr-doped systems, the only negative \(E_{f-im}^X\) appears when the NbI site is doped, which means that the NbI site doped by Cr atom is feasible. However, the formation energy of the all Al doped systems is higher than that of pure system, which shows that the Al leads the \(\beta\)-Nb5Si3 unstable. The following discussion concentrates on the most preferential substituted stable systems: Ti-doped NbI site (Ti-Nb-Si), Cr-doped NbI site (Cr-Nb-Si), and Hf-doped NbII site (Hf-Nb-Si) systems.
Table 1  Impurity formation energy of doped β-Nb$_5$Si$_3$ system (Unit: eV)

<table>
<thead>
<tr>
<th>System</th>
<th>Doped site</th>
<th>Nb</th>
<th>Nb$^+$</th>
<th>Si</th>
<th>Si$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-doped β-Nb$_5$Si$_3$</td>
<td>–1.01</td>
<td>–0.80</td>
<td>1.71</td>
<td>1.59</td>
<td></td>
</tr>
<tr>
<td>Cr-doped β-Nb$_5$Si$_3$</td>
<td>–0.22</td>
<td>0.64</td>
<td>1.49</td>
<td>1.71</td>
<td></td>
</tr>
<tr>
<td>Al-doped β-Nb$_5$Si$_3$</td>
<td>0.21</td>
<td>0.69</td>
<td>0.24</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>Hf-doped β-Nb$_5$Si$_3$</td>
<td>0.14</td>
<td>–0.53</td>
<td>3.35</td>
<td>2.58</td>
<td></td>
</tr>
</tbody>
</table>

3.2. Lattice parameters

It is well known that the substitution of the atom does change the lattice parameters due to the differences in atom radius, electro-negativity, and other properties between different types of elements. The lattice parameters of β-Nb$_5$Si$_3$ systems before and after substitution are listed in Table 2. It is found that in contrast with pure β-Nb$_5$Si$_3$, the crystal lattice is relaxed along $a$ axis and $b$ axis in the Ti-Nb-Si system and is compressed along $c$ axis. In the Cr-Nb-Si system, the Cr atom shortens the length of $a$, $b$, and $c$ from 10.020 Å, 10.020 Å, 5.069 Å to 10.014 Å, 10.014 Å, 5.016 Å. In both of above-cited doped systems, the size of $a$ is consistent to the size of $b$ and the ratios of $c/a$ are lower than that of pure β-Nb$_5$Si$_3$. However, unlike in the Ti-, Cr-doped systems, $b$ axis extended less than $a$ axis in the Hf-Nb-Si system, which caused $a \neq b \neq c$. It indicates that the Hf atom transforms the crystal lattice of β-Nb$_5$Si$_3$ from tetragonal system to orthorhombic system.

Table 2  Lattice parameters of β-Nb$_5$Si$_3$ systems before and after substitution

<table>
<thead>
<tr>
<th>System</th>
<th>$a$/Å</th>
<th>$b$/Å</th>
<th>$c$/Å</th>
<th>$c/a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure β-Nb$_5$Si$_3$</td>
<td>10.020</td>
<td>10.020</td>
<td>5.069</td>
<td>0.505</td>
</tr>
<tr>
<td>Ti-Nb-Si</td>
<td>10.048</td>
<td>10.048</td>
<td>5.031</td>
<td>0.500</td>
</tr>
<tr>
<td>Cr-Nb-Si</td>
<td>10.014</td>
<td>10.014</td>
<td>5.016</td>
<td>0.500</td>
</tr>
<tr>
<td>Hf-Nb-Si</td>
<td>10.079</td>
<td>10.077</td>
<td>5.061</td>
<td>—</td>
</tr>
</tbody>
</table>

3.3. Total density of states

In order to analyze the principle of substitution further, the total densities of states (TDOS) of pure β-Nb$_5$Si$_3$ and the Ti-, Cr-, Hf-doped β-Nb$_5$Si$_3$ are calculated. Fig.2 compares the TDOS of pure β-Nb$_5$Si$_3$ with all doped systems. It can be realized that the TDOS of all systems are not zero at Fermi energy level sites, which means that the metallic bonds exist in the compound. And the pseudogaps of all systems appear near Fermi energy level sites, which suggest that the systems are stable. In Fig.2(a), below Fermi energy the sites of the main bonding peaks of Ti-Nb-Si system are –1.36 eV, –2.99 eV, –4.98 eV, and –7.99 eV, which are lower than those of pure β-Nb$_5$Si$_3$ (–1.33 eV, –2.99 eV, –4.95 eV, –7.96 eV). Therefore, the introduced Ti atom makes the bonding energy decline to lower energy level and reduces the energy of the whole system. As shown in Figs.2(b) and 2(c), the change of the TDOS of Cr-Nb-Si and Hf-Nb-Si systems is very similar to that of Ti-Nb-Si system. In addition, The TDOS of the three doped systems are higher than that of pure β-Nb$_5$Si$_3$ at Fermi energy level, which means that the doping of Ti, Cr, and Hf improves the conductivity of β-Nb$_5$Si$_3$ system.
3.4. Mechanical properties

Table 3 presents the calculation results of elastic constants of the four systems. In the pure β-Nb$_5$Si$_3$, Ti-Nb$_5$Si$_3$, and Cr-Nb$_5$Si$_3$ systems with tetragonal symmetry (with six independent elastic constants: $c_{11}$, $c_{12}$, $c_{13}$, $c_{33}$, $c_{44}$, $c_{66}$), the terms with $c_{11} = c_{22}$, $c_{13} = c_{23}$, and $c_{44} = c_{55}$ are obtained. The Hf-Nb$_5$Si$_3$ system is of orthorhombic symmetry with nine independent elastic constants. The element Ti decreases the elastic constants $c_{11}$, $c_{12}$, and $c_{13}$ of Nb$_5$Si$_3$ system, and increases $c_{33}$, $c_{44}$, $c_{66}$. However, different from Ti-Nb$_5$Si$_3$ system, the constant $c_{66}$ of the Cr-Nb$_5$Si$_3$ system is less than that of pure β-Nb$_5$Si$_3$ system. In addition, the elastic constants except for $c_{13}$ are reduced by the doping of Hf. The calculated elastic constants allow us to obtain the macroscopic mechanical parameters of all systems, namely bulk modulus $K$, shear modulus $G$, and elastic modulus $E$.

Table 3 Calculation data of elastic constants, bulk modulus, shear modulus, and elastic modulus (Unit: GPa)

<table>
<thead>
<tr>
<th></th>
<th>Pure β-Nb$_5$Si$_3$</th>
<th>Ti-Nb$_5$Si$_3$</th>
<th>Cr-Nb$_5$Si$_3$</th>
<th>Hf-Nb$_5$Si$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_{11}$</td>
<td>359.58</td>
<td>350.10</td>
<td>356.05</td>
<td>344.65</td>
</tr>
<tr>
<td>$c_{12}$</td>
<td>359.58</td>
<td>350.10</td>
<td>356.05</td>
<td>337.96</td>
</tr>
<tr>
<td>$c_{13}$</td>
<td>308.86</td>
<td>315.05</td>
<td>324.87</td>
<td>296.98</td>
</tr>
<tr>
<td>$c_{44}$</td>
<td>84.16</td>
<td>87.55</td>
<td>90.70</td>
<td>69.09</td>
</tr>
<tr>
<td>$c_{55}$</td>
<td>84.16</td>
<td>87.55</td>
<td>90.70</td>
<td>52.93</td>
</tr>
<tr>
<td>$c_{66}$</td>
<td>129.37</td>
<td>130.00</td>
<td>126.98</td>
<td>126.82</td>
</tr>
<tr>
<td>$c_{12}$</td>
<td>127.03</td>
<td>122.96</td>
<td>123.47</td>
<td>126.56</td>
</tr>
<tr>
<td>$c_{13}$</td>
<td>107.26</td>
<td>104.00</td>
<td>106.02</td>
<td>108.46</td>
</tr>
<tr>
<td>$c_{23}$</td>
<td>107.26</td>
<td>104.00</td>
<td>106.02</td>
<td>107.01</td>
</tr>
<tr>
<td>$K$</td>
<td>190.13</td>
<td>186.35</td>
<td>189.78</td>
<td>184.85</td>
</tr>
<tr>
<td>$G$</td>
<td>105.30</td>
<td>106.64</td>
<td>108.44</td>
<td>92.27</td>
</tr>
<tr>
<td>$E$</td>
<td>266.67</td>
<td>268.67</td>
<td>273.27</td>
<td>237.32</td>
</tr>
</tbody>
</table>

Table 3 also summarizes the elastic moduli obtained using Eqs.(2)-(6). There are some direct relationship between materials’ hardness and its elastic modulus and shear modulus[16]. In general, the higher the elastic modulus and shear modulus, the higher the hardness. From Table 3, the Ti and Cr improve the hardness of β-Nb$_5$Si$_3$ system, and in contrast, the Hf reduces the hardness of β-Nb$_5$Si$_3$. Therefore, the four systems are listed in descending order of hardness as follows: Cr-Nb$_5$Si$_3$ > Ti-Nb$_5$Si$_3$ > pure β-Nb$_5$Si$_3$ > Hf-Nb$_5$Si$_3$.

The room fracture toughness is one of the important mechanical properties of structural materials. According to the S. F. Pugh and J. Y. Wang’s discussion[17-18], there is a simple relationship that links empirically the plastic property of metals and intermetallics to the ratio of shear modulus to bulk modulus (Pugh’s ratio, $G/K$). If $G/K < 0.5$, the material behaves in the ductile manner, otherwise the material behaves in the brittle manner. The higher the $G/K$, the more the brittleness of material. Fig. 3 presents the Pugh’s ratios of the four systems. Pugh’s ratios are 0.572 and 0.571 for Ti- and Cr-doped systems respectively, which increases by about 3.06% because of Ti and Cr doping. The increments of Pugh’s ratios show that the Ti and Cr doping reduce the room temperature ductility of β-Nb$_5$Si$_3$ phase. However, the Pugh’s ratio of Hf-Nb$_5$Si$_3$ system is less than that of pure β-Nb$_5$Si$_3$, which indicates that Hf is beneficial to improve the room-temperature ductility of β-Nb$_5$Si$_3$ phase.

For all crystal structures, $K$, $G$, and $E$ of polycrystalline materials are estimated by the following equations (Voight approximation[15]):

\[
K = \frac{1}{9} (c_{11} + c_{22} + c_{33}) + \frac{2}{9} (c_{12} + c_{13} + c_{23})
\]

(2)

\[
G = \frac{1}{15} [(c_{11} + c_{22} + c_{33}) - (c_{12} + c_{13} + c_{23})] + \frac{1}{5} (c_{44} + c_{55} + c_{66})
\]

(3)

\[
E = 9KG / (3K + G)
\]

(4)

In the tetragonal system, there are six independent elastic constants ($c_{11} = c_{22}$, $c_{12} = c_{23}$, $c_{13} = c_{23}$, $c_{33}$, $c_{44} = c_{55}$, $c_{66}$). Therefore, the elastic modulus equation of tetragonal system can be written as

\[
K = \frac{1}{9} (2c_{11} + c_{33}) + \frac{2}{9} (c_{12} + 2c_{13})
\]

(5)

\[
G = \frac{1}{15} (2c_{11} + c_{33} - c_{12} - 2c_{13} + 6c_{44} + 3c_{66})
\]

(6)

4. Conclusions

A simple model from the first-principles calculations within the framework of DFT is used to study the effects of substitutional alloying element on the β-Nb$_5$Si$_3$, and the following conclusions are obtained:

(1) The impurity formation energy from first-principles calculations indicates that the atoms of alloying elements Ti, Cr, and Hf prefer to substitute the Nb$_5$Si$_3$.
Nb$_4$ and Nb$_{11}$ sites in $\beta$-Nb$_5$Si$_3$, respectively. The element Al induces the $\beta$-Nb$_5$Si$_3$ instable.

(2) Ti and Cr atoms decrease the $c/a$ ratio of crystal lattice and Hf atom transforms the crystal lattice of $\beta$-Nb$_5$Si$_3$ from tetragonal system to orthorhombic system.

(3) Ti, Cr, and Hf improve the conductivity of $\beta$-Nb$_5$Si$_3$ system.

(4) Ti and Cr increase the hardness and decrease the room temperature ductility of $\beta$-Nb$_5$Si$_3$. Contrarily, Hf decreases the hardness and increases the room temperature ductility. The four systems are listed in descending order of hardness as follows: Cr-Nb$_5$Si$_3$ $>$ Ti-Nb$_5$Si$_3$ $>$ pure $\beta$-Nb$_5$Si$_3$ $>$ Hf-Nb$_5$Si$_3$.

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