Computational Materials Science 146 (2018) 255–260

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Effects of ternary element additions on the generalized-stacking fault energy of Ti_5Si_3 in prismatic $\{1\bar{1}00\}[0001]$ slip system: A first-principles study

Cheng Wang [a], Zhuang Yang [a], Xin-Yu Xu [a], Hui-Yuan Wang [a,b,*], Min Zha [a], Feng Qiu [a], Qi-Chuan Jiang [a]

[a] Key Laboratory of Automobile Materials of Ministry of Education and Department of Materials Science and Engineering, Nanling Campus, Jilin University, No. 5988 Renmin Street, Changchun 130025, PR China

[b] International Center of Future Science, Jilin University, Changchun 130012, PR China

ARTICLE INFO

Article history:
Received 15 December 2017
Received in revised form 2 January 2018
Accepted 3 January 2018

Keywords:
Intermetallics
Brittleness and ductility
Electronic structure
Planar faults
Ab-initio calculations

ABSTRACT

A design map in regard to the generalized-stacking fault (GSF) energy is plotted for Ti_5Si_3 ($Ti_{60}Si_{36}$) alloying with 12 ternary elements in $\{1\bar{1}00\}[0001]$ slip system. Hereinto, alloying elements occupy preferable Ti sites near slip planes. The elements with a larger radius difference from Ti tend to reduce the GSF energies more dramatically. Moreover, the elements smaller than Ti are more prone to decreasing GSF energies than those larger than Ti. Accordingly, the addition of ternary elements, like Ni, Cu and Co, will lead to an obvious decrease in GSF energies by 18.0%, 16.7% and 13.4% respectively, and therefore may facilitate the initiation of prismatic stacking faults and furthermore enhance ductility. Note that the decline of GSF energies is attributed to the weakening covalent bonds between slip planes with the introduction of ternary elements. Our calculations provide a guide to experiments on the design of Ti_5Si_3 compounds with tailored properties.

1. Introduction

Ti_5Si_3 is being considered as a candidate material suitable for high-temperature applications due to its high melting point, low density, relatively high hardness, good oxidation and creep resistance [1]. Unfortunately, the development and application of Ti_5Si_3 have been severely restricted owing to its low fracture toughness at ambient temperature. The weaknesses can be attributed to the different types of chemical bonds along *c*- and *a*-axis. Moreover, the hexagonal $D8_8$ structure in Ti_5Si_3 leads to difficulties in the activation of slip systems and anisotropy of coefficient of thermal expansion (CTE) [2,3].

To tailor the mechanical properties of transition-metal silicides, element alloying is frequently adopted as a simple but effective way [4–6]. Using the nanoindentation method, Xu et al. [4] revealed that the plastic deformability of $(Mo_xCr_{1-x})_5Si_3$ films is significantly improved with increasing Cr contents. Moreover, Schneibel and Rawn [5] demonstrated that the additions of V, Cr and Hf reduce the CTE anisotropy of Ti_5Si_3 evidently, which is beneficial to the ductility enhancement. However, the effects and mechanisms of alloying elements on the ductility of Ti_5Si_3 are still unclear. For the purpose of material design, it is of great significance to find the proper alloying elements which may toughen Ti_5Si_3.

As an alternative to heuristic experiments, the first-principles calculation is always adopted to design silicides with proper ductility [7–10], as it provides valuable physical insight at low cost. In our previous work, we reported that the addition of V, Nb and Cr to Ti_5Si_3 can increase the ratio of bulk modulus to shear modulus (B/G) remarkably by first-principles calculation [7], indicating that the ductility can be enhanced according to Pugh's [11] theory.

Note that the generalized-stacking-fault (GSF) energy, first introduced by Vitek [12], interprets the macroscopical ductility properties based on the density functional theory calculation [13]. The nucleation [13,14] and mobility [15] energies of dislocations are related to GSF energies. A reduced GSF energy implies an increased probability to form stacking faults on corresponding slip planes, thereby enhancing the deformation ability of compounds. It was found that the substitution of Si by Mg or Al in $MoSi_2$ can reduce the GSF energy effectively, which is particularly beneficial to the ductility enhancement [9]. Meanwhile, Du et al. [16] also demonstrated that the Nb, Tc and Ta elements may improve the

* Corresponding author at: Key Laboratory of Automobile Materials of Ministry of Education and Department of Materials Science and Engineering, Nanling Campus, Jilin University, No. 5988 Renmin Street, Changchun 130025, PR China; International Center of Future Science, Jilin University, Changchun 130012, PR China.
E-mail address: wanghuiyuan@jlu.edu.cn (H.-Y. Wang).

https://doi.org/10.1016/j.commatsci.2018.01.008
0927-0256/

ductility of $MoSi_2$ based on results of GSF energies. In addition, the ductility properties of Mg-based binary alloys [17] and Mg–Zn–Ca alloys [18] have also been successfully evaluated by considering the probability of dislocation emission. Unfortunately, few investigations have been reported so far on studying effects of element additions on the GSF energy in Ti_5Si_3, which has great significance in predicting the ductility of Ti_5Si_3 compounds. Besides, there is still no standard to evaluate the substitution effects of alloying elements on Ti_5Si_3.

More recently, Kishida et al. [3] quantitatively studied the deformation behavior of Ti_5Si_3 single-crystal under compression at above 1300 °C. It was reported that the critical resolved shear stress (CRSS) for $\{1\bar{1}00\}[0001]$ prismatic slip is considerably lower than that for $\{2\bar{1}\bar{1}2\}1/3 < 2\bar{1}\bar{1}\bar{3} >$ pyramidal slip but is comparable to that for $\{2\bar{1}\bar{1}8\} < 8\bar{4}\bar{4}3 >$ twinning [3]. Thus the $\{1\bar{1}00\}[0001]$ slip system has the highest probability to operate under deformation. In this regard, a first-principles calculation is employed in this work to investigate the impact of common ternary element additions (Ni, Co, Fe, Cr, Cu, Mn, V, Al, Nb, Zr, Sc and Y) on the GSF energies of Ti_5Si_3 in the prismatic $\{1\bar{1}00\}[0001]$ slip system. The alloying elements were selected out according to the deviation of atomic radii and electron configurations from Ti. The purpose of this work is to provide a guide to experiments by predicting which alloying elements are likely to enhance the ductility without adversely affecting the advantageous physical properties of Ti_5Si_3 at microalloying levels.

2. Computational details

The energy calculation in this work was performed in the Cambridge Sequential Total Energy Package code (CASTEP) [19] based on density-functional theory (DFT), in which the Perdew-Burke-Ernzerhof (PBE) [20] version of the generalized gradient approximation (GGA) was employed as an exchange correlation functional. The plane-wave basis cutoff was set as 350 eV. The k-point mesh was generated by a Monkhorst Pack grid [21] and set within $4 \times 4 \times 6$ and $2 \times 3 \times 1$ for the calculation of formation enthalpy and GSF energy, respectively. Geometry optimization was performed until the total energy changed within 5×10^{-6} eV/atom and the maximum force converged to 0.01 eV/Å. All results were relevant for $T = 0$ K. Additionally, the spin-polarized calculation was performed for Mn, Fe, Co and Ni alloying in this study.

2.1. Formation enthalpy

To study the substitution sites of alloying elements in Ti_5Si_3, one substituted atom was added in a 16-atom unit cell ($Ti_{10}Si_6$), as shown in Fig. 1. Hereinto, Ti_5Si_3 possesses a $D8_8$ hexagonal structure with a space group of $P6_3/mcm$. There are two Ti sites and one Si site: Ti^{4d} at (0.333, 0.667, 0), Ti^{6g} at (0.240, 0, 0.250) and Si at (0.615, 0, 0.250). This configuration forms an ABAC stacking sequence along the c direction. Full relaxations were carried out on both crystal volumes and atomic sites in this case. The lattice parameters for Ti_5Si_3 in our calculation (a = 7.4669 Å, c = 5.1316 Å) are extremely close to the experimental results (a = 7.4529 Å, c = 5.1449 Å) [5].

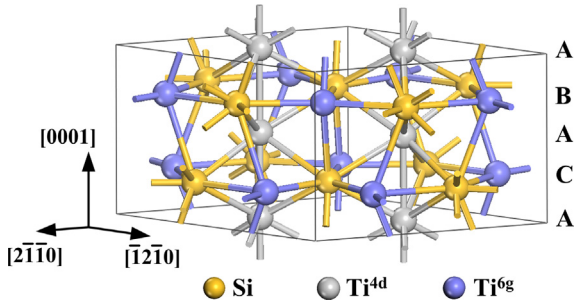

Fig. 1. The 16-atom unit cell of $Ti_{10}Si_6$. Light gray and blue spheres represent Ti atoms occupying Ti^{4d}- and Ti^{6g}-sites, respectively, and gold spheres stand for Si atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

We calculated the formation enthalpies for alloying elements occupying Ti^{4d} and Ti^{6g} sites, respectively. The formation enthalpy H_f is defined as [7]:

$$H_f = E_t - n_{Ti}E^{Ti}_{solid} - n_{Si}E^{Si}_{solid} - E^{Me}_{solid} \quad (1)$$

where E_t is the total energy of the compounds, n_{Ti} and n_{si} represent the total number of Ti and Si atoms, respectively, and E^{Ti}_{solid}, E^{Si}_{solid} and E^{Me}_{solid} correspond to the energies per Ti atom, Si atom and alloying element Me calculated in their most stable solid states.

2.2. GSF energy

The GSF energy γ_{GSF} is defined as the difference in total energies between two crystals with and without stacking faults [12], as shown in Formula (2). The stacking-fault vector u varies from 0.0**b** to 1.0**b** with a step of 0.1**b** for $\{1\bar{1}00\}[0001]$ system; here **b** is the corresponding Burgers vector.

$$\gamma_{GSF}(u) = \frac{E(u) - E_0}{A} \quad (2)$$

where E(u) is the total energy of the crystal with the fault vector u, E_0 represents the energy of the perfect lattice and A denotes the area of the fault plane. Moreover, the maximum energy on the γ_{GSF} curve is the unstable stacking-fault energy (γ_{us}), which denotes the lowest energy barrier for the initiation of stacking faults [13], whereas the local minimum indicates the intrinsic stacking-fault energy (γ_{is}) [22].

Fig. 2(a)–(c) illustrates the 96-atom model ($Ti_{60}Si_{36}$) used to calculate the GSF energy in the prismatic $\{1\bar{1}00\}[0001]$ slip system with increasing distortions, i.e. 0**b**, 0.3**b** and 0.5**b**. The slab is thick enough to eliminate the interaction between the top and bottom surfaces according to our test. Meanwhile, a large vacuum width of 15 Å was added to reduce the interaction between the periodically repeated slabs. The stacking planes along $[1\bar{1}00]$ were all named after the atomic types on corresponding layers, i.e. Si, Ti^{4d}, Ti^{6g} and Ti^{6g}-Si layers, respectively. Moreover, the slab models were terminated with Si layers, since the Si-terminated surfaces are more likely to expose because of a lower value of surface energy (Si-terminated: 2.15 J/m^2, Ti^{4d}-terminated: 3.00 J/m^2, Ti^{6g}Si-terminated: 2.24 J/m^2). In the calculation of GSF energies, all atoms were allowed to relax only along the $[1\bar{1}00]$ direction (***z***-axis), while were fixed in the [0001] (***x***-axis) and $[\bar{1}\bar{1}20]$ (***y***-axis) directions.

3. Results and discussion

3.1. Site occupancy of alloying elements

The formation enthalpy of $Ti_{10}Si_6$ systems with alloying elements occupying the Ti^{4d}- and Ti^{6g}-sites is calculated respectively, and is summarized against the symbol of elements in Fig. 3. Meanwhile, these element symbols on the horizontal axis are arranged in order of increasing atomic radius (see detailed information in Table 1) [23]. For Ti_9Si_6Me, the more negative the formation enthalpy is, the more stable the structure will be. Note that Zr (radius [23]: R = 1.57 Å), Sc (1.57 Å) and Y (1.77 Å) with larger