Materials and Design 86 (2015) 259–265

Contents lists available at ScienceDirect

Materials and Design

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

Vacancy induced brittle-to-ductile transition of Nb_5Si_3 alloy from first-principles

Yong Pan [a], Yuanhua Lin [a,*], Hui Wang [b], Chunmei Zhang [a]

[a] School of Materials Science and Engineering, Southwest Petroleum University, Chengdu 610500, China
[b] National Key Laboratory for Nuclear Fuel and Materials, Nuclear Power Institute of China, Chengdu 610041, China

ARTICLE INFO

Article history:
Received 3 May 2015
Received in revised form 16 July 2015
Accepted 18 July 2015
Available online 23 July 2015

Keywords:
Transition metal silicides
Crystal defects
Brittle-to-ductile transition
First-principles calculations

ABSTRACT

The effect of vacancy on mechanical properties of α-Nb_5Si_3 is systematically investigated by first-principles calculations. Four different mono vacancies in this alloy are considered in detail. The vacancy formation energy, formation enthalpy, elastic modulus, hardness, B/G ratio, thermodynamic properties and electronic structure of α-Nb_5Si_3 with different vacancies are discussed. The calculated vacancy formation energies show that Nb vacancies are more stable than that of Si vacancies, and α-Nb_5Si_3 prefers to form the Nb_{-va2} vacancy. Those vacancies weaken the volume, shear deformation resistances and reduce the elastic stiffness. However, those vacancies result in brittle-to-ductile transition and α-Nb_5Si_3 with Si_{-va1} mono vacancy exhibits ductile behavior. The calculations of electronic structure reveal that these vacancies change the localized hybridization between Nb–Si and Nb–Nb atoms, which are the origin of brittle-to-ductile transition. Finally, we conclude that vacancy is beneficial for improving the ductility of Nb_5Si_3.

1. Introduction

Nb_5Si_3 alloy is promising as next generation ultrahigh-temperature material due to its high melting point (2515 °C), low density (7.16 g/cm^3), high-temperature strength and excellent oxidation resistance [1–8]. However, the low fracture toughness at room temperature and poor ductility are still the major drawbacks for practical application. For example, the tensile tests have demonstrated that this Nb_5Si_3 alloy exhibits cleavage fracture below 1197 °C [9]. The first-principles calculations have shown that the calculated B/G ratio of Nb_5Si_3 alloy is 1.53 [10], which is lower than 1.75, indicating that it is a brittle material. To overcome their shortages, a great deal of investigations have shown that alloying is a good method for improving the room-temperature ductility [11,12]. Recently, numerous experiments have reported that Nb solid solutions (Nb_{ss}) play an important role to improve the ductility in Nb_5Si_3 compound because metal Nb has high melting point (2472 °C) and good deformability. In addition, metal Ti additions to Nb–Si binary alloys can enhance the room-temperature flexural strength and fracture toughness [13]. Although metal Fe decreases the melting point of Nb_5Si_3, it enables this alloy to display super-plasticity bigger than 1400% at 1400 °C [14].

However, mechanical properties of structural materials are commonly controlled by atomic structure and atomic level behavior of defect. It must be mentioned that any real sample has various types of defects such as vacancy, impurity, dislocation and interface. Among those defects, the vacancy as native defect plays a crucial role in mechanical properties because the vacancy in crystal structure can constitute traps for impurities and influence the electrical and mechanical properties of structural materials. Nevertheless, the complexity of defect has made a comprehensive understanding of fracture mechanism to become very difficult. For Nb_5Si_3 alloy, although a variety of experiments have used to study the defect behavior, a deeper insight to vacancy mechanism has thus far remained elusive. Some fundamental questions should be answered: How does vacancy vary with structural stability in Nb_5Si_3? How does vacancy influence the mechanical properties? The answer to these questions is critical to improving the ductility of Nb_5Si_3.

In the present paper, we have presented the first-principles density functional theory (DFT) to study the vacancy on Nb_5Si_3. To explore the correlation between vacancy and brittle-to-ductile transition, the elastic modulus, thermodynamic properties and electronic structure are discussed in detail. We found that these vacancies are stable in Nb_5Si_3. Although vacancies weaken the volume and shear deformation resistances, they result in brittle-to-ductile transition. We predict that vacancy is a beneficial effect on ductile deformation of Nb_5Si_3.

2. Theoretical methods

2.1. Vacancy model

In order to study the effect of vacancy on mechanical properties of α-Nb_5Si_3, the crystal structure of α-Nb_5Si_3 should be firstly discussed, here. According to the literature, α-Nb_5Si_3 is known as a tetragonal structure with the space group *I4/mcm* structure (a = 6.557 Å and

* Corresponding author.
E-mail address: yhlin28@163.com (Y. Lin).

http://dx.doi.org/10.1016/j.matdes.2015.07.099
0264-1275/

$c = 11.860$ Å) [15]. It is observed that there are four formula units in a unit cell. Nb atoms occupy the 4*c* (0, 0, 0) and 16*l* (0.166, 0.666, 0.150) sites, and Si atoms locate at the sites 4*a* (0, 0, 0.250) and 8*h* (0.375, 0.875, 0), respectively. Therefore, we consider four different vacancies which include Nb_{-va1}, Nb_{-va2}, Si_{-va1} and Si_{-va2} in this paper. The structural model of Nb_5Si_3 with four different vacancy configurations is shown in Fig. 1(a).

2.2. Computational details

The first-principles calculations were adopted by using density functional theory (DFT), as implemented in the CASTEP code [16]. All calculations were performed in a plane-wave basis, using the ultrasoft pseudopotential [17]. Exchange correlation functional was treated by the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) [18]. The electronic configurations of Nb and Si atoms were $4p^6 4d^4 5s^1$ and $3s^2 3p^2$, respectively. To ensure the total energy at ground state to be converged, a plane-wave basis set for electron wave function with cutoff energy of 360 eV was used. The Brillouin zone was sampled with $7 \times 7 \times 5$ mesh grids for integrations in reciprocal space. Total energy of a system was obtained by the density-mixing scheme in connection with the conjugate gradient technique. During the structural optimization, all atomic positions, lattice parameters and internal coordinates in a system were fully relaxed.

2.3. Theory

The formation energy of mono vacancy is studied in order to understand the stability of Nb_5Si_3 with vacancy. The vacancy formation energy (E_f) is calculated and given by:

$$E_f = E^M_{vacancy} - E^{total}_{perf} + \mu_M \tag{1}$$

where $E^M_{vacancy}$ and E^{total}_{perf} are the total energy of Nb_5Si_3 with M (M═Nb and Si) vacancy and Nb_5Si_3 perfect crystal in the same structure without defect. E_M (M═Nb and Si) is the chemical potential in pure crystal of each species. For niobium-rich region, $\mu_{Nb} = E_{Nb}$(bulk), while for silicon-rich region, $\mu_{Si} = E_{Si}$(bulk). Note that the E_{Nb}(bulk) and E_{Si}(bulk) are the total energy of Nb atom and Si atom in bulk Nb and Si system, respectively.

To estimate the thermodynamic stability of Nb_5Si_3 with vacancy, the formation enthalpy is calculated by:

$$\Delta H(Nb_mSi_n) = \frac{1}{m+n}(E_{total}(Nb_mSi_n) - mE_{Nb} - nE_{Si}) \tag{2}$$

where $E_{total}(Nb_mSi_n)$, E_{Nb} and E_{Si} are the total energy of Nb_mSi_n compound, pure Nb and Si atoms at ground state; *m* and *n* are the number of Nb and Si atoms of a system, respectively.

The mechanical properties of a solid are estimated by hardness and elastic modulus such as bulk modulus (B), shear modulus (G) and Young's modulus (E). Elastic stiffness constants (C_{ij}) were calculated by strain–stress method. For tetragonal structure, there are six independent elastic constants: C_{11}, C_{12}, C_{13}, C_{33}, C_{44} and C_{66}. The mechanical stability should be given by [19]:

$$C_{11}>0, C_{33}>0, C_{44}>0, C_{66}>0, C_{11}-C_{12}>0, C_{11}+C_{33}-2C_{13}>0, \tag{3}$$

$$2(C_{11}+C_{12})+C_{33}+4C_{13}>0.$$

From the calculated elastic constants, the bulk modulus and shear modulus were calculated according to the Voigt–Reuss–Hill (VRH) approximation method [20]. Therefore, the Young's modulus is obtained by:

$$E = \frac{9BG}{3B+G}. \tag{4}$$

Hardness of a solid indicates the elastic strain and plastic deformation resistance, which is an important mechanical parameter. In this paper, the theoretical hardness of Nb_5Si_3 is obtained by semi-empirical hard model [21]:

$$H_v = 2 \cdot \left(k^2 \cdot G\right)^{0.585} - 3 \tag{5}$$

where *k* represents the shear modulus vs bulk modulus and *G* is the shear modulus, respectively.

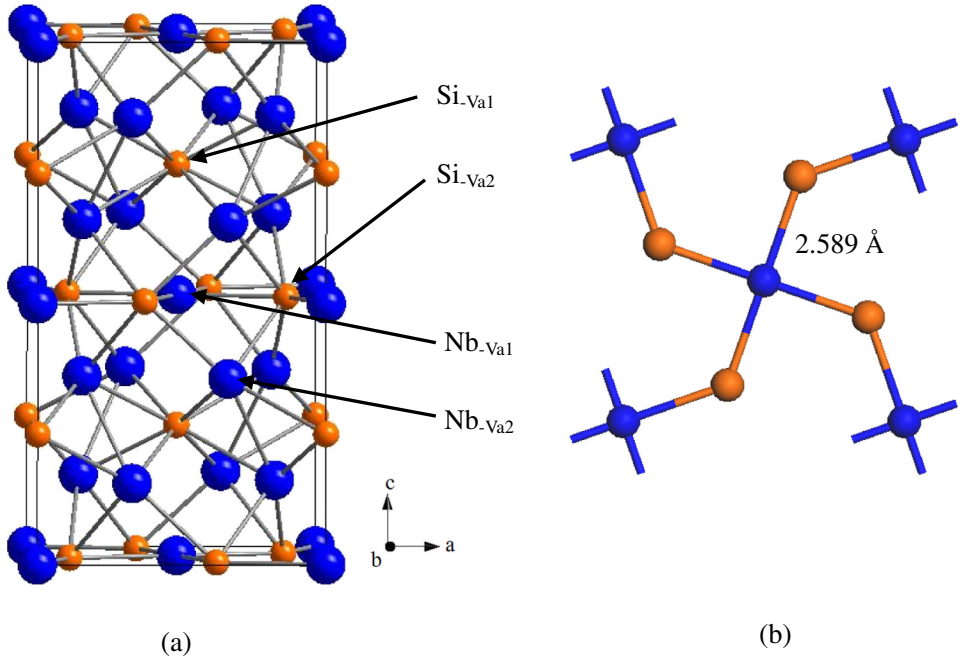

Fig. 1. (a) Crystal structure of Nb_5Si_3 with different vacancies, (b) the Nb–Si–Nb stacking order along the *b*-axis, the blue and orange spheres represent the Nb and Si atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)