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Relationship between Si concentration and mechanical properties of Nb–Si compounds: A first-principles study

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ABSTRACT

The effect of chemical bonding on the mechanical properties of high-temperature materials remains a big challenge. In this paper, the relationship between Si concentration and mechanical properties for Nb–Si compounds was investigated by first-principles calculations. One previously unreported crystal structure of Nb_2Si with Ta_2Si-type structure was predicted. The elastic properties, hardness and chemical bonding of Nb–Si compounds were calculated in detail. The calculated formation enthalpy shows that Nb_5Si_3 is more stable than that of other Nb–Si compounds at the ground state. The obtained shear modulus, Young's modulus and hardness of Nb–Si compounds increase with increasing Si concentration. $NbSi_2$ exhibits the strongest shear deformation resistance and the biggest hardness among these Nb–Si compounds. It thus can be concluded that the variation of elastic properties depends not only on the Si concentration but also on the chemical bonding. With increasing Si concentration, Nb–Nb metallic bond is disappeared and Si–Si covalent bond is formed.

1. Introduction

Despite extensive studies carried out in the past decades, there are still many unresolved issues associated with the high-temperature materials, especially the nature of the mechanical properties. Among those mechanical properties, the shear deformation resistance and elastic stiffness play a crucial role in high-temperature environment because the shear modulus directly controls the dislocation motion of a solid and the Young's modulus indicates the degree of linear compression. Essentially, these elastic properties mainly depend on the cohesive force per volume, which is entirely determined by the localized electron density and chemical bonding. As we known, the bond strengths of covalent bond and ionic bond are much stronger than that of metallic bond. Thus, a large number of covalent bonds in a solid effectively improve the deformation resistance and enhance the elastic properties. However, the metallic bond plays an important role in all high-temperature materials [1–4]. This is why these materials have the low elastic properties. Therefore, the search for high-temperature material with the covalent bond is a topic of much interest.

Till now, C and Si are known as typical covalent elements. Obviously, the covalent bonds resist the deformation and prevent the propagation of dislocation. To explore the high-temperature materials, alloying additions such as C and Si are considered to be the most promising candidates because they are expect to have a larger number of covalent bonds and exhibit excellent mechanical properties [5–7]. Based on the design principle, Nb–Si based superalloys have received considerable attention for high-temperature application such as structural components in aircraft engines and rockets [8–12].

For Nb–Si compounds, early studies mainly focused on the structure and mechanical properties of Nb_5Si_3 and Nb_3Si [13,14]. Recently, Kashyap et al. [15] have attempted to study the microstructural and mechanical properties of suction cast Nb–Si binary alloys. The microstructure and mechanical properties of oxidation resistant suction cast Nb–Si–Al alloy have been reported [16]. Our previous work has shown that vacancy results in brittle-to-ductile transition for Nb_5Si_3 [17]. On the other hand, alloying additions effectively improve the mechanical properties of Nb–Si alloys [18,19]. With Ti addition, the room-temperature fracture toughness of Nb–Si binary alloys increases [20]. The addition of B in Nb–Si–Ti ternary alloy changes the morphological feature and restrains the crack propagation [21]. Actually, the mechanical properties of Nb–Si based superalloys mainly determined by the Si concentration because the Si–Si covalent bond obviously influences the resistance to deformation. Unfortunately, the effect of Si concentration on the mechanical properties of Nb–Si compounds and relevant mechanism are still unknown.

In the present paper, the formation enthalpy, elastic constants, elastic properties, hardness, electronic structure and chemical bonding of Nb–Si compounds were systematically calculated by using a first-principles approach. The structure and mechanical properties of Nb–Si compounds as a function of Si concentration were investigated in detail. We first found that Nb–Si compounds with high concentration of Si

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exhibit the strong shear deformation resistance and high elastic stiffness in comparison with the low concentration of Si. Although the resistance to volume deformation of $NbSi_2$ is weaker than that of Nb_5Si_3, $NbSi_2$ has the strongest shear modulus and the maximum Young's modulus among these Nb–Si compounds.

2. Theoretical methods

According to the Nb–Si binary phase diagram, the structures of Nb_3Si, Nb_5Si_3 and $NbSi_2$ are represented by the experimental determined cubic (space group *P*m-3n, No. 223) [22], tetragonal (space group *I*4/mcm, No. 140) [23] and hexagonal (space group *P*6222, No. 180) [24], respectively. It is worth noticing that Nb_5Si_3 has three different structures such as α-, β- and γ-phases [25,26]. Considering the structural stable at the ground state, we select the α-phase. For other Nb–Si compound such as Nb_2Si, there is not experimental structural parameter up to now. Here, the structure of Ta_2Si-type (space group *I*4/mcm, No. 140) for Nb_2Si is considered. The structural models of four different Nb–Si compounds are shown in Fig. 1.

Structure, total energy, elastic properties and electronic structure of Nb–Si compounds were calculated by using the density functional theory (DFT), as implemented in the CASTEP code [27]. To estimate the calculated results, the exchange correlation functional was treated by the generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) [28]. The ultrasoft pseudopotential [29] was used to describe the electronic exchange and correlation. The atomic 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 the ground state to be converged, a plane-wave basis set for electron wave function with cutoff energy of 400 eV was used. Integrations in the Brillouin zone were performed by using special *k*-points generated with 12 × 12 × 12, 14 × 14 × 14, 11 × 11 × 14, and 15 × 15 × 10 for Nb_3Si, Nb_2Si, Nb_5Si_3 and $NbSi_2$, respectively. The optimized atomic geometry was achieved through the minimizing Hellmann-Feynman forces acting on each atom until the

Table 1
Calculated elastic constants, C_{ij} (GPa) of Nb–Si compounds.

Phase	Method	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}
Nb_3Si	Cal	321	112			72	
	Theo[a]	290	151			78	
Nb_2Si	Cal	279	141	143	269	117	108
Nb_5Si_3	Cal	378	96	117	326	128	119
	Theo[a]	362	104	118	312	121	110
$NbSi_2$	Cal	355	67	74	440	133	

[a] Ref [25].

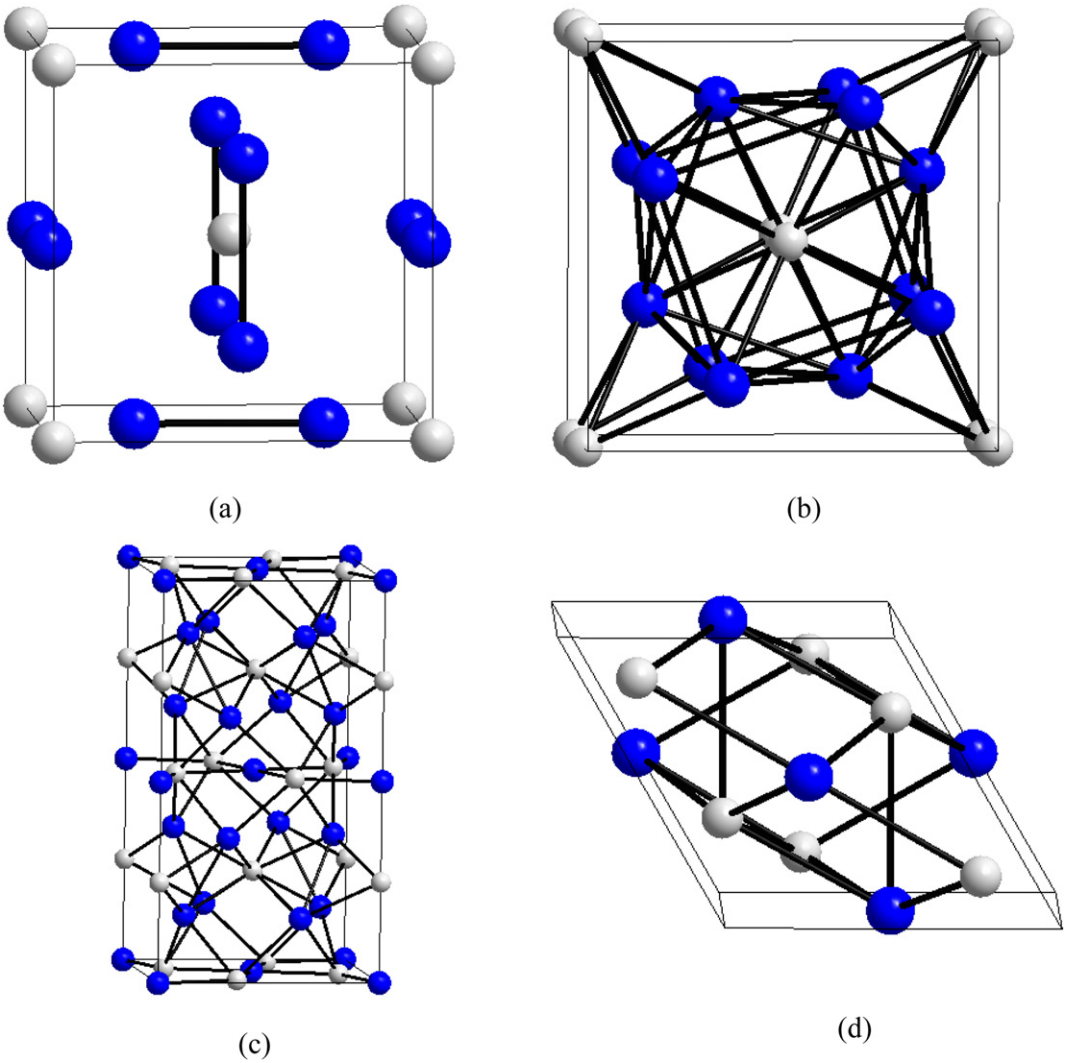

Fig. 1. Crystal structures of Nb–Si compounds, (a) Nb_3Si, (b) Nb_2Si, (c) Nb_5Si_3, (d) $NbSi_2$. The blue and gray spheres represent the Nb and Si atoms, respectively.