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Effect of boron vacancies on mechanical properties of ReB_2 from first-principles calculation

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ABSTRACT

The lattice parameters, vacancy formation energies, elastic properties, Vickers hardness and electronic structure of ReB_2 with lower concentration of boron vacancy are studied using first-principles approach. The lattice parameters and unit-cell volume of ReB_2 with boron vacancy rapidly decrease as boron vacancy concentration increase. The calculated vacancy formation energies show that the ReB_2 are more stable than that of system with boron vacancy. With increasing boron vacancy, the bulk modulus, shear modulus, Young modulus and Vickers hardness gradually decrease and the boron vacancy results in mechanical transition from brittleness to ductility, which are in good agreement with experimental results. The decreases of elastic modulus and Vickers hardness are originated from the weak hybridization between Re atoms and B atoms in boron vacancy region and forms the weak Re–B bonds and B–B covalent bonds.

1. Introduction

The introduction of light elements such as C, N and B into the interstitial sites of transition metal (TM) is expected to profound influence their chemical and physical properties because the structure and bond characteristic of TM are changed. Numerous investigations show that these transition metal borides (TMBs) all have high hardness, high bulk modulus, ultra-incompressible and exhibit a degree of metallic behavior et al. [1–9]. According to the feature of these TMBs, Kaner et al. [10] pointed out that the potential superhard TMB candidates should be meet two conditions: valence electron density and bond covalency. In particular, the shorter and directional covalent bonds must be considered as large as possible. Based on this principle, the ReB_2 as the bulk superhard material is synthesized and the measurement average hardness is about of 48 GPa [11,12]. Obviously, the ReB_2 is considered to be one of the most promising superhard materials.

However, we note that there is an apparent contradiction between the first-principles calculations and experiment because the theoretical results are failed to agree with the experiment. The theoretical calculations show that this boride has high bulk modulus (340–370 GPa) [13,14] and shear modulus (173 GPa) [15]. But the experimental results indicate that the ReB_2 has a maximum hardness of 49.9 GPa and a minimum hardness of 20.8 GPa with increasing applied load [8]. Unfortunately, not much is known on the detail of the relationship between hardness and applied load. It is well know that the physical properties of a material including elastic modulus, hardness and electric properties et al. are strongly affected by these defects such as vacancy, dislocation and grain boundary et al. In fact, the real sample has a large number of defects. Therefore, the hardness of these TMBs is related not only to the high valence electron density and covalent bonds but also to a degree of defect concentration. However, the relationship between defect and mechanical properties for TMBs has not been reported.

To understand the vacancy effect on the mechanical properties of TMBs, in this paper, we performed first-principles calculation to investigate the lattice parameters, vacancy formation energies, elastic modulus and electronic structure of ReB_2 with different concentrations of boron vacancy. Three different types of boron vacancy concentrations including 0.32 wt%, 0.65 wt% and 1.30 wt% are considered. The main purpose of this work is to reveal the nature of hardness for TMBs with the defects.

2. Computational details

The ReB_2 is a hexagonal structure with lattice parameters: $a = b = 2.900$ Å and $c = 7.478$ Å (space group: P63/mmc, No: 194) [16]. The Re atoms and B atoms occupy the 2c (0.3333, 0.6667, 0.2500) and 4f (0.3333, 0.6667, 0.5483) sites, respectively. To investigate the effect of the boron vacancy on the mechanical prop-

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erties of ReB_2, we have built up $2 \times 2 \times 2$ supercell containing 48 atoms for hexagonal phase by removing boron atoms from the inner of supercell. All calculations were performed using the CASTEP code [16]. The interaction between ions and electrons was described using the ultrasoft pseudopotential [17]. The exchange correlation functional was treated by local-density approximation (LDA) with Ceperley–Alder (CA) exchange correlation functional [18]. The plane wave kinetic-energy cutoff on the wave functions was 320 eV. To obtain full convergence in total energies and atomic forces, we applied the Monkhorst–Pack method [19] to sample using a Gaussian smearing methods with a width of 0.001 eV. The Brillouin zone was sampled with a $6 \times 6 \times 3$ Monkhorst grid for integrations in reciprocal space. During the structural optimization, no symmetry and no restriction were constrained for the unit-cell shape, volume and atomic positions. The structural relaxation was stopped until the total energy, the max force and the max displacement were within 1×10^{-5} eV/atom, 0.03 eV/Å, and 0.001 Å, respectively. In addition, the actual spacing for DOS calculations is less than 0.015 $Å^{-1}$.

3. Results and discussion

3.1. Structural information

In order to investigate the boron vacancy effect on phase stable and mechanical properties, the vacancy formation energies for ReB_2 with different boron vacancy concentrations are calculated and given by:

$$E_{vacan} = E_{vacan} - E_{bulk}^{ReB_2} + n\mu_B \quad (1)$$

where E_{vacan} is the total energy of ReB_2 with boron vacancy, $E_{bulk}^{ReB_2}$ is the total energy of ideal ReB_2. n and μ_B are the number of removed boron atom and chemical potential of boron atom, respectively. The chemical potential μ depends on the experimental conditions. For rhenium-rich region, $\mu_{Re} = E_{Re}(bulk)$, and for boron-rich conditions, $\mu_B = E_B(bulk)$, where $E_{Re}(bulk)$ and $E_B(bulk)$ are the total energies of Re atom and B atom in bulk Re and B system, respectively. In thermodynamics equilibrium for bulk system, the stable condition for ReB_2 satisfies the relation: $\Delta H(ReB_2) = \mu(ReB_2) - (\mu_{Re} + 2\mu_B)$, where $\Delta H(ReB_2)$ and $\mu(ReB_2)$ are the heat of formation and chemical potential for bulk ReB_2 system. The calculated heat of formation in bulk system is −1.797 eV compared with the other theoretical result about of −1.342 eV [13].

The calculated lattice parameters, unit-cell volume, vacancy formation energies of ReB_2 as a function of boron vacancy concentration are listed in Table 1. It can be seen that the calculated lattice parameters of ideal ReB_2 are: $a = b = 2.870$ Å, $c = 7.398$ Å, which are in good agreement with the experimental data [4] and previous theoretical results [20], while a-axis and c-axis are underestimated by about of 1.0% and 0.5% in the case of LDA, respectively. Furthermore, the calculated a-axis and c-axis rapidly decrease as boron vacancy concentration increase. It is worth to note that the a-axis is smaller than that of ideal ReB_2 in contrast to the c-axis is bigger than that of ideal ReB_2 when boron vacancy is introduced in ReB_2 host structure. In addition, the c/a ratio increases from 2.578 to 2.604, indicating that the reduced rate for a-axis is more rapidly than that of c-axis. At the same time, the volumes of unit-cell decrease with increasing the boron vacancy concentration. There is no doubt that the boron vacancy can influence the variation of lattice parameters. However, the increase of c-axis indicates that the boron vacancy leads to the weak hybridization between Re atoms and B atoms along the z-direction and forms weak Re–B bonds.

Table 1
The calculated lattice parameters (in Å), c/a ratio, volume (in $Å^3$), vacancy formation energy (in eV/atom) of ReB_2 as a function of boron vacancy concentration corresponding to the ideal ReB_2.

	0			0.32	0.65	1.30
	Cal	Exp [4]	Theo [20]	Cal	Cal	Cal
a	2.870	2.900	2.875	2.866	2.855	2.841
b	2.870	2.900	2.875	2.866	2.855	2.841
c	7.398	7.479	7.421	7.407	7.406	7.402
c/a	2.578		2.581	2.584	2.594	2.604
V	52.78			52.63	52.27	51.74
E_{vacan}				0.227	0.454	0.911

On the other hand, there is a monotone relationship between the vacancy formation energy and the boron vacancy concentration. This is not surprising because it need enough energy when the boron atom at lattice point is removed. The general trend is, the higher the vacancy concentration, the more the vacancy formation energy. Although the high concentration of boron vacancy system is not stable compared with the ideal ReB_2, it is consistent with experimental phenomenon. For TMBs compounds, the recent experiment shows that the excess of boron powder changes the bond states and decreases the hardness [12]. The lower hardness for ReB_2 may originate from these defects. Namely, the average measured hardness of TMBs depends on the quality of sample.

The calculated lattice parameters (in Å), c/a ratio, volume (in $Å^3$), vacancy formation energy (in eV/atom) of ReB_2 as a function of boron vacancy concentration corresponding to the ideal ReB_2.

3.2. Mechanical properties

The elastic constants C_{ij}, bulk modulus B, shear modulus G, Young modulus E, Poisson's ratio υ and B/G ratio are essential for understanding the mechanical properties of a material. Although the hardness is different from the bulk modulus and shear modulus, the high hardness materials must have high bulk modulus and shear modulus. For example, the bulk modulus and shear modulus of diamond are 442 GPa [2] and 535 GPa [21], respectively. Therefore, the bulk modulus and shear modulus is the best indicator of the hardness for a solid.

For hexagonal system, there are six independent elastic constants: C_{11}, C_{12}, C_{13}, C_{33}, C_{44} and C_{66}.

The required of mechanical stability in a hexagonal system leads to the following restriction on the elastic constants [13]:

$$C_{11} > 0, C_{33} > 0, C_{44} > 0$$

$$C_{66} = (C_{11} - C_{12})/2 > 0, (C_{11} + C_{12})C_{33} - 2C_{13}^2) > 0 \quad (2)$$

Taking into account the structural symmetry, the polycrystalline bulk modulus and shear modulus in this paper are calculated by Voigt–Reuss–Hill approximation. The bulk modulus and shear modulus with Voigt approximation are given by [22]:

$$B_V = \frac{1}{9}[2(C_{11} + C_{12}) + 4C_{13} + C_{33}] \quad (3)$$

$$G_V = \frac{1}{30}(M + 12C_{44} + 12C_{66}) \quad (4)$$

$$M = C_{11} + C_{12} + 2C_{33} - 4C_{13}, C^2 = (C_{11} + C_{12})C_{33} - 2C_{13}^2 \quad (5)$$

The Reuss bulk modulus (B_R) and Reuss shear modulus (G_R) are defined as:

$$B_R = \frac{C^2}{M} \quad (6)$$

$$G_R = \frac{5}{2} \cdot \frac{C^2 C_{44} C_{66}}{3B_V C_{44} C_{66} + C^2(C_{44} + C_{66})} \quad (7)$$