Computational Materials Science 147 (2018) 322–330

Contents lists available at ScienceDirect

Computational Materials Science

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

Editor's Choice

Effect of alloying elements on mechanical, electronic and magnetic properties of Fe_2B by first-principles investigations

Xiang Wei [a], Zhiguo Chen [a,b,c,*], Jue Zhong [a,*], Li Wang [b], Wei Yang [c], Yipeng Wang [c]

[a] Light Alloy Research Institute, Central South University, Changsha 410083, China
[b] Department of Materials Engineering, Hunan University of Humanities, Science and Technology, Loudi 417000, China
[c] School of Materials Science and Engineering, Central South University, Changsha 410083, China

ARTICLE INFO

Article history:
Received 26 September 2017
Received in revised form 31 January 2018
Accepted 1 February 2018

Keywords:
Fe_2B
Alloying
Mechanical properties
Electronic structure
Magnetic properties
First-principles calculations

ABSTRACT

First-principles calculations using density functional theory (DFT) were performed to explore the effect of common 3d elements M (M = Ti, V, Cr, Mn, Co, Ni and Cu) on the mechanical, electronic and magnetic properties of Fe_2B. A formula of $(Fe_{0.875},M_{0.125})_2B$ was used. Firstly, the negative cohesive energy and formation enthalpy suggest that all the compounds are thermodynamically stable. With the knowledge of calculated elastic constants, the moduli, the Pugh's modulus ratio G/B, the Poisson's ratio v and the hardness of Fe_2B and $(Fe_{0.875},M_{0.125})_2B$ were further predicted. Overall, with increasing atomic number, the moduli and hardness of the borides initially increase and then decrease. $(Fe_{0.875},Cr_{0.125})_2B$ possesses the largest bulk, shear and Young's modulus simultaneously, while $(Fe_{0.875},Mn_{0.125})_2B$ has the largest hardness. The G/B and v values indicate that all the alloying elements are able to enhance the ductility of the Fe_2B except Mn, but they do not change the nature of intrinsic brittleness of the Fe_2B. Combined with the electronic structures, we revealed that the mechanical properties of the borides are mostly determined by Fe—B and M—B bonds. Fe—Fe bonds in ⟨2 2 0⟩ and ⟨1 1 3⟩ orientations are both covalent bonding. It can also be predicted that all the alloying elements reduce the magnetic moments (Ms) of the Fe_2B mainly because the Ms of the substituted M atom is smaller than that of Fe atom.

1. Introduction

Fe_2B is a typical intermetallic compound which has been widely used in boriding layer and Fe-B alloys for achieving high hardness, excellent wear and corrosion resistance, etc [1–4]. During the boriding, alloying elements M (M = Ti, V, Cr, Mn, Co, Ni, Cu, Mo, W, etc.) can diffuse from the surface layer of substrate materials into the boriding layer, resulting in the formation of a $(Fe,M)_2B$ phase. Similarly, when the alloying elements M are added in Fe-B alloys, the alloyed $(Fe,M)_2B$ can also be formed. To date, numerous experimental researches suggested that the hardness and toughness of the Fe_2B are significantly affected by this alloying. Cr [5], Mn [6], Mo [7] and W [8] increase the toughness and/or hardness of the Fe_2B in the Fe-B alloys, and thus improving wear resistance. However, for the case of boriding, Balandin [9] reported that Cr plays a negative role on hardness while increasing toughness, whereas Üçisik [10] pointed out that Cr has a negative effect on toughness. Besides, it was found that Ni [11] and Cu [9] decrease the hardness, while Cu and Mn [10] increase the toughness. Therefore, it is meaningful to clarify the role of each alloying element in Fe_2B for designing $(Fe,M)_2B$ effectively, and thus achieving optimal alloying effects. On the other hand, Fe_2B is also a promising magnetic functional material due to its large magnetocrystalline anisotropy energy and saturation magnetization, high Curie temperature, low cost and non-toxic raw materials [12]. It was found that the partial substitutions of Fe with 3d transition metal elements greatly affect the magnetic properties of the Fe_2B. For example, compared with the Fe_2B without uniaxial magnetic anisotropy, the $(Fe_{1-x},Co_x)_2B$ with a certain value of x (0.1–0.5) shows a uniaxial magnetic anisotropy [13]. However, to the best of our knowledge, up to now the investigated alloying elements are limited to Mn [14], Co [13,15] and Ni [16], and some 5d elements that were added in $(Fe_{1-x},Co_x)_2B$ [13].

First-principles calculation is a reliable and efficient approach in predicting mechanical, electronic and magnetic properties of various compounds and alloying systems [17–18]. For Fe_2B, Joyner [19], Li [20] and Ching [21] investigated its electronic structures and magnetic properties. Most recently, the effects of crystal form

* Corresponding authors at: Hunan University of Humanities, Science and Technology, Loudi 417000, China and Central South University, Changsha 410083, China (Z. Chen).
E-mail addresses: zgchen@mail.csu.edu.cn (Z. Chen), JZhong@mail.csu.edu.cn (J. Zhong).

https://doi.org/10.1016/j.commatsci.2018.02.001
0927-0256/

[22], pressure [23–24] and spin polarization of Fe atom [25] on structural, mechanical and electronic properties of the Fe_2B have been systematically studied. Besides, Deng [26] investigated the microscopic mechanism of the structural deformation of I4/mcm Fe_2B by calculating ideal strength values at large levels of strain. However, there are few works on alloyed $(Fe,M)_2B$ doped with 3d elements. Therefore, this work aims to close this gap in understanding by systematically exploring the effects of common 3d elements (Ti, V, Cr, Mn, Co, Ni and Cu) on the mechanical, electronic and magnetic properties of Fe_2B.

2. Computational details

In this work, a tetragonal Fe_2B crystal structure with I4/mcm space group was selected. There are 8 Fe atoms and 4B atoms in a unit cell. Both the Fe atoms and B atoms have only one equivalent lattice site, and they are Wyckoff position 8h and 4a, respectively. We replaced one Fe (fractional coordinate: (0.166, 0.334, 0.500)) with alloying elements M to form the alloyed broide $Fe_7M_1B_4$, namely $(Fe_{0.875},M_{0.125})_2B$. All calculations were conducted by the Vienna ab initio simulation package (VASP) base on density functional theory (DFT) [27]. The pseudo potentials generated by projector-augmented wave (PAW) method [28] were used to describe the interactions between valence electrons and ionic core. The valence electronic configurations of the elements used in this work are shown as follows: $2s^22p^1$ (B), $3d^34s^1$(Ti), $3d^44s^1$(V), $3d^34s^1$ (Cr), $3d^54s^2$ (Mn), $3d^74s^1$ (Fe), $3d^84s^1$ (Co), $3d^{10}$ (Ni) and $3d^{10}4s^1$ (Cu). The exchange-correlation effects were evaluated by the generalized gradient approximation (GGA) method in the scheme of Perdew-Burke-Ernzerhof (PBE) [29]. The Monhorst-Pack method was used to generate the k-points mesh in the Brillouin Zone (BZ). After extensive convergence tests, a plane-wave cutoff energy of 550 eV, as well as a $11 \times 11 \times 13$ k-points mesh were chosen for all calculations. The following convergence criterion were adopted: (1) the maximum energy change of electronic relaxation is lower than 1×10^{-7} eV/atom, (2) the maximum force acting on atoms is less than 0.001 eV/Å. Due to the fact that the ground state of Fe_2B is ferromagnetic, the spin polarization was considered for all calculations. Moreover, for Fe_2B, the initial Ms values of Fe atom and B atom are set to 2 and 0, respectively. For the $(Fe_{0.875},M_{0.125})_2B$, the initial Ms values of Fe atom and B atom are also set to 2 and 0, respectively, whereas the Ms value of alloying element M is set to −1, 0 and 1. It was found that the results calculated from three magnetic configurations are identical in alloyed Fe_2B. After the geometry optimization, the stress-strain approach was employed to calculate the elastic constants [30].

3. Results and discussions

3.1. Structure and stability

The equilibrium cell parameters of Fe_2B and its experimental and other theoretical results are shown in Table 1. These data indicate that the results calculated from ferromagnetic Fe_2B are more close to the experimental value because the ground state of Fe_2B is ferromagnetic. Moreover, the VASP-GGA-PBE method can increase the accuracy of the results. Compared to the experimental value of Fe_2B, the errors of calculated cell parameters a, c and volume are 1.14%, 0.40% and 2.65%, respectively, indicating that the calculation method used in this work is reliable.

Table 2 summarizes the equilibrium cell parameters of Fe_2B and $(Fe_{0.875},M_{0.125})_2B$. As can be seen, the alloying elements M induce the lattice distortion, the volume increase or decrease of Fe_2B. Moreover, it can be indicated from the lattice constants that the tetragonal Fe_2B transformed into monoclinic $(Fe_{0.875},M_{0.125})_2B$ (Note: it is a special monoclinic structure, where $a = b \neq c$, $\alpha = \beta = 90^\circ \neq \gamma$, whereas in monoclinic structure, $a \neq b \neq c$, $\alpha = \gamma = 90^\circ \neq \beta$ or $\alpha = \beta = 90^\circ \neq \gamma$.). These structural changes are mainly related to two factors. One is that due to the difference in atomic radius, the M atom can directly result in lattice distortion. The other factor is that the M—Fe (M—B) bond has a different bond length mainly caused by the difference in electronegativity and atomic radius when compared with Fe—Fe (Fe—B) bond. It is reasonable to deduce that these changes will greatly influence the mechanical properties of Fe_2B by changing the interactions of atoms.

The relative stability of Fe_2B and $(Fe_{0.875},M_{0.125})_2B$ were estimated by cohesive energy (E_c) and formation enthalpy (E_f), which are defined by Eqs. (1) and (2):

$$E_c((Fe_{1-x},M_x)_2B) = (E_{total}((Fe_{1-x},M_x)_2B,cell) - n(1-x)E_{iso}(Fe) - nxE_{iso}(M) - nE_{iso}(B))/n \quad (1)$$

$$E_f((Fe_{1-x},Mx)_2B) = (E_{total}((Fe_{1-x},M_x)_2B,cell) - n(1-x)E_{cry}(Fe) - nxE_{cry}(M) - nE_{cry}(B))/n \quad (2)$$

where E_{total} $(Fe_{1-x},M_x)_2B$ is the energy of the $(Fe_{1-x},M_x)_2B$ per unit cell; n is the number of $(Fe_{1-x},M_x)_2B$ unit formulas in a unit cell; E_{iso} (Fe), E_{iso} (M) and E_{iso} (B) are the energies of isolated Fe, alloying elements M and B, respectively; E_{cry} (Fe), E_{cry} (M) and E_{cry} (B) are the energies of bcc Fe, alloying elements M (bcc (Cr, Mo, W and V), fcc (Ni and Cu), hcp (Co and Ti) and α-Mn) and α-B per atom, respectively.

The calculated cohesive energy and formation enthalpy of Fe_2B and $(Fe_{0.875},M_{0.125})_2B$ are presented in Fig. 3. All the cohesive energies of the borides are negative, which indicates that they are stable from the view of cohesive energy. On the other hand, the formation enthalpy describes the thermodynamically stability of crystals. If the formation enthalpy is lower than zero, then the crystal is stable, otherwise it is metastable or unstable. Furthermore, a lower energy denotes a better stability. The formation enthalpy of Fe_2B is −0.6391 eV/f.u., which is comparable with the experimental value (−0.85 eV/f.u.) [33] and the theoretical value (−0.951 eV/f.u.) [32]. It can be seen from Fig. 1 that all the borides have negative formation enthalpy, suggesting that these compounds can exist stably. Thus, it is feasible to form all mentioned alloyed $(Fe_{1-x},M_x)_2B$ by partly substituting Fe atom with the alloying

Table 1
Cell parameters of the Fe_2B obtained from different methods.

Methods	Magnetic state	a = b (Å)	c (Å)	Volume (Å^3)	Reference
VASP-GGA-PBE	Ferromagnetic	5.052	4.232	108.012	This work
Experiment	Ferromagnetic	5.110	4.249	110.950	[31]
VASP-GGA-PBE	Ferromagnetic	5.056	4.232	108.183	[32]
VASP-GGA-PBE	Non-magnetic	4.9498	4.2026	102.964	[26]
CASTEP-GGA-PBE	Ferromagnetic	5.0123	4.209	105.743	[25]
CASTEP-GGA-PBE	Non-magnetic	4.890	4.222	100.957	[25]
CASTEP-GGA-PBE	Non-magnetic	4.838	4.208	98.488	[22]
CASTEP-LDA-CA-PZ	Non-magnetic	4.771	4.121	93.785	[22]