First-principles calculations on FeWB bulk and FeWB(001)/\(\alpha\)-Fe (111) interface

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Abstract

FeWB bulk and FeWB(001)/\(\alpha\)-Fe(111) interface were studied by first-principles calculations. FeWB bulk bonding has the mixed characteristics of metallicity, covalency and ionicity, among which the metallicity is the most obvious. Such combination endows FeWB with promising toughness and excellent electrical conductivity. Adhesion work, \(W_{ad}\), was calculated for twelve different interfacial structures, taking into account four terminations of FeWB(001) and three stacking sequences. The B(Fe)-terminated center-site stacking interface is the most stable with the smallest interface distance and the largest \(W_{ad}\). Fe-B and W-B bond lengths at the interface are even shorter than those in FeWB bulk. By comparing the interface fracture work \(G\) with \(W_{ad}\), it is found that the interface fracture position has a certain occasionality, but it tends to occur in FeWB bulk. According to the results of density of states, we concluded the B(Fe)-terminated center-site stacking interface is a metallic/covalent mixing nature, while the combination of top-site stacking interface is mainly covalent bonds.

1. Introduction

Ternary transition metal borides, such as FeWB, WCoB and Mo\(_2\)FeB\(_2\), have been studied for years due to their high density, melting point, conductivity, excellent mechanical properties and thermal resistance [1–7]. Haschke et al [8] for the first time fabricated FeWB by mixing boride of tungsten with Fe powder, proved the thermal stability of Fe-W-B series compound, and obtained Fe-W-B ternary phase diagram. Leithe et al [9] further demonstrated the content range of stable FeWB phase at 1323 K, and defined the isothermal cross-sectional view at this temperature. Based on previous researches, Liu et al [3, 4] had prepared FeWB powder in batches by reactive synthesis technology, and confirmed excellent corrosion resistance of FeWB ternary compound by salt spray corrosion test.

With multiple advantages, FeWB is expected to be used as a coating material like other borides [10–12]. At present, some scholars have successfully applied it on the surface of \(\alpha\)-Fe matrix as a protective coating [13–16]. Eray Abakay et al [14] used FeB and FeW powder as raw materials to prepare FeWB coating on the steel surface by TIG welding. Wang et al [16] investigated the microstructure of FeWB/\(\alpha\)-Fe coating interface and found it has excellent wear resistance. However, the research on FeWB coating is basically limited to experimental preparation, and there is still a lack of in-depth study on the interface bonding mechanism, which has a crucial influence on the properties of coating composite. Understanding interface characteristics is a necessary step to improve the performance of coating material and realize its wide application. First-principles calculation with density functional theory (DFT) is a powerful method to provide fundamental information of interfaces between two solids at atom level or even at electron levels [17]. Shingo Tanaka et al [18] performed the first-principles calculations of the mechanical properties of alumina copper nano-coating interfaces and found that the O-terminated interface has a strong bonding comparable to the bulk Al\(_2\)O\(_3\), whereas the Al-terminated one has a weak bonding. Yang et al [19] found W-HCP-C structure is the most stable for WC/TiC interface by first-principles calculations. It provides guidance for the further promotion and application of wear-resistant coating material WC/TiC. Wang et al’s first-
Ternary boride FeWB has TiNiSi-type orthorhombic structure.

3.1. Stability, elastic properties and electronic structure of FeWB

3. Results and discussion

B3LYP or B3PW exchange correlation functionals

accuracy of GGA exchange correlation functional for the band gap of complex oxide materials is lower than that of

Cambridge Series Total Energy Package

principles calculation results on TiN(111)/ZrN(111) interface indicate that TiZrN₂ phase may be formed at the

interface [20], which provides theoretical support for the development of TiN/ZrN coatings.

Many achievements have been made in the study of coating interfaces by first-principles calculations. Therefore, we used first-principles calculations to systematically study FeWB/α-Fe interface. However, there are few studies on the calculation of boride interfaces that can be used for reference, and the research mainly focuses on boride phases [21–26]. Li et al [24] theoretically studied the chemical bonds, elastic properties and phase stability of TcB and the results indicated that the hexagonal wurtzite structure was more stable than NaCl, CsCl and WC structures. Chen et al [25] obtained the ground state elastic properties of TaB by DFT, the results suggested that TaB is a brittle material with a B/G ratio of 1.7 and has stronger compressibility along the B axis. The results of Wang et al [26] on the magnetic properties of Mo₂FeB₂ showed that the lattice parameters of antiferromagnetic (AF) phase are closer to the experimental data than those of nonmagnetic (NM) and ferromagnetic (FM) phases, and the energy of AF phase is the lowest, indicating that AF phase is the ground state. In addition, AF phase has the maximum enthalpy of formation which proves the maximum thermal stability.

In this study, the stability, elastic constants and electronic structure of FeWB bulk were systematically studied by first-principles calculations. Then the adhesion work, charge transfer and bonding characteristics of FeWB/α-Fe interface were researched, and the interface bonding strength and fracture toughness were obtained, thus clarifying the bonding mechanism of FeWB/α-Fe coating interface.

2. Methodology

Cambridge Series Total Energy Package (CASTEP) [27] code in the framework of DFT was used to calculate the total energy, elastic constants and electronic structure of materials. The interaction of ionic core and valence electrons were described with ultrasoft pseudopotentials. The generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) scheme was used to evaluate the exchange and correlation terms. The calculation accuracy of GGA exchange correlation functional for the band gap of complex oxide materials is lower than that of B3LYP or B3PW exchange correlation functionals [28, 29], but it is widely used in the calculation of borides. The self-consistent field (SCF) method was used to solve the Kohn-Sham equation [30] to achieve electron minimization and obtain the ground state. The SCF convergence threshold is set to 5.0 × 10⁻⁷ eV/atom.

By using Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm to achieve geometric optimization [31], the convergence tolerances were set as: energy 5.0 × 10⁻⁶ eV atom⁻¹, maximum force 0.01 eV/Å, maximum stress 0.02 GPa and maximum displacement 5.0 × 10⁻⁴ Å. Through the convergence test, the cut-off energy and k-points of FeWB bulk determined to be 450 eV and 13 × 7 × 7, respectively. The cut-off energy calculated by the interface is the same as FeWB bulk, while the k-point is set to 13 × 7 × 1. The effect of spin polarization was taken into account in the calculation. The valence electrons of Fe, W and B were 3d⁶4s², 5s²5p⁶5d⁶6s² and 2s²2p¹, respectively.

3. Results and discussion

3.1. Stability, elastic properties and electronic structure of FeWB

Ternary boride FeWB has TiNiSi-type orthorhombic structure [32], and its space group is Pnma with

a = 3.216 Å, b = 5.784 Å and c=6.740 Å (the original cell). FeWB structure contains four formulae per unit cell, as shown in figure 1.
The cohesive energy and enthalpy of formation can be used to describe the thermodynamic stability of FeWB. Calculation formulas can be expressed as:

\[
E_{coh}(\text{FeWB}) = \frac{E_{total} - nE_{Fe} - nE_{W} - nE_{B}}{3n} \quad (1)
\]

\[
\Delta H_{f}(\text{FeWB}) = E_{coh}(\text{FeWB}) - E_{coh}(\text{Fe}) - E_{coh}(\text{W}) - E_{coh}(\text{B}) \quad (2)
\]

where \(E_{total}\) is the total energy of FeWB unit cell, \(E_{coh}\) is the cohesive energy of FeWB; \(E_{coh}(\text{Fe}), E_{coh}(\text{W})\) and \(E_{coh}(\text{B})\) are the cohesive energy of Fe (Im-3m), W (Im-3m) and B (R-3m) bulk, respectively; \(n\) refers to the number of FeWB units contained in conventional cell; \(E_{Fe}, E_{W}\) and \(E_{B}\) are the atomic energy of Fe, W and B in isolation. The cohesive energy is a measure of the energy change of free atoms into compounds, and the enthalpy of formation represents the energy change during the conversion of simple substances into compounds. Therefore, if \(E_{coh}\) and \(\Delta H_{f}\) calculated by equations (1) and (2) are both negative values, it indicates the thermodynamically stable structure.

The computational details of pure elements and FeWB are shown in Table 1. The calculated optimum lattice parameters of bulk FeWB are \(a = 3.284\ \text{Å}, \ b = 5.765\ \text{Å}\) and \(c = 6.665\ \text{Å}\). Theoretically evaluated lattice parameters are in good agreement with experimental results [33], indicating the reliability of our calculations. Furthermore, the calculated results of \(E_{coh}\) and \(\Delta H_{f}\) proved the thermodynamic stability of FeWB.

Due to the symmetry between the stress tensor and the strain tensor, the non-zero independent elastic constants of the orthorhombic system are reduced to nine components, which are \(C_{11}, C_{22}, C_{33}, C_{44}, C_{55}, C_{66}, C_{12}, C_{13}, \) and \(C_{23}\). Necessary and sufficient Born criteria [36] regarding mechanical stability for an orthorhombic system are \(C_{ii} > 0\) and \(2C_{13} + C_{33} - 2C_{12} > 0\). The calculated elastic constants of FeWB are listed in Table 2, which meet the stability criteria. Combining the calculation of thermodynamic properties mentioned above, it is further confirmed that the ternary boride FeWB is stable.

Bulk and shear modulus of polycrystals can be calculated from \(C_{ij}\). There are two approximations for evaluating modulus: Voigt (V) and Reuss (R) methods. The average of these two estimation results is known as Voigt-Reuss-Hill (VRH) average, which is regarded as the best estimate for the theoretical value of
polycrystalline elastic modulus. The calculation formulas are as follows [37]:

$$B = \frac{1}{2}(B_V + B_R)$$  \hspace{1cm} (3)

$$G = \frac{1}{2}(G_V + G_R)$$  \hspace{1cm} (4)

The Young’s modulus and Poisson’s ratio can be calculated based on the above values by:

$$E = \frac{9BG}{3B + G}$$  \hspace{1cm} (5)

$$\nu = \frac{3B - 2G}{6B + 2G}$$  \hspace{1cm} (6)

where $B_V, B_R, G_V$ and $G_R$ are the Voigt and Reuss values for bulk and shear modulus, respectively. $E$ and $\nu$ refer to Young’s modulus and Poisson’s ratio, respectively. All calculated results are listed in table 2.

Young’s modulus is often used to determine the stiffness of solid materials. The higher Young’s modulus is, the greater stiffness of material is, namely, the harder it is. The Young’s modulus of FeWB is only 199.81 GPa, less than MoAlB (351 GPa) [38] and Mo$_2$FeB$_2$ (378 GPa) [26], so its hardness is not prominent in ternary borides.

The theoretical hardness of FeWB can be given by the semi-empirical formula [39]:

$$H_V = 2(G^V / B^V)^{0.585} - 3$$  \hspace{1cm} (7)

where $H_V$ denotes the Vickers hardness. The hardness of FeWB calculated according to the formula is 6.25 GPa, which is in good agreement with the experimental results [13]. It can be found that although the hardness of FeWB is inferior to Fe$_2$B (19.0 GPa), Fe$_3$B (9.1 GPa) [40], MoAlB (11.6 GPa) [38] and other borides, it is still at a relatively high level.

Poisson’s ratio, $\nu$, can predict the stability of crystal systems against shear. The Poisson’s ratio of FeWB is 0.314, indicating that the shear resistance is moderate, which is consistent with the conclusion of the shear modulus of only 76.03 GPa. In addition, Poisson’s ratio is directly related to the failure mode of solids. The Poisson’s ratio of ductile materials is greater than 0.26, while that of brittle materials is less than 0.26 [41, 42]. Hence, FeWB is a typical ductile material. The ratio of the bulk modulus to the shear modulus, $B/G$, called Pugh ratio [43], is also frequently used to measure the brittleness or toughness of a solid. If $B/G > 1.75$, the material performance is toughness, otherwise brittleness. FeWB has a $B/G$ of 2.355, which again confirms that it is a ductile material, consistent with the result of Poisson’s ratio. Pettifor [44] proposed to describe the chemical bonding properties of materials in terms of the values of $(C_{12-C_{44}})$, which is called Cauchy pressure. The positive value of $(C_{12-C_{44}})$ indicates metallic bonding with strong toughness, whereas the negative value represents directional covalent bonding with great brittleness. The Cauchy pressure of FeWB is 67.78 GPa. Therefore, it can be inferred that the good toughness of FeWB originates from the metallic bonding.

Compression and shear anisotropy percentages are often used to describe the elastic anisotropy of polycrystalline solids, as shown in the formula below [45]:

$$A_B = \frac{B_V - B_R}{B_V + B_R} \times 100\%$$  \hspace{1cm} (8)

$$A_G = \frac{G_V - G_R}{G_V + G_R} \times 100\%$$  \hspace{1cm} (9)

where $A_B$ and $A_G$ are the percent anisotropy of compression and shear, respectively. When $A_B$ and $A_G$ are both zero, the crystal is completely isotropic. With the increase of $A_B$ and $A_G$ values, the degree of anisotropy of the crystal increases. The universal elastic anisotropy index ($A^U$) can reflect the contribution of both shear and volume [46]:

$$A^U = \frac{5}{2} \frac{G_V}{G_R} + \frac{B_V}{B_R} - 6 \geq 0$$  \hspace{1cm} (10)

The degree of anisotropy is also positively correlated with the value of $A^U$. The calculated values of $A_B, A_G$ and $A^U$ are 4.15%, 5.23% and 0.63, respectively. That is to say, FeWB has a low degree of elastic anisotropy, and shear anisotropy is slightly higher than compression. It indicates that FeWB has good comprehensive mechanical properties.

Charge density differences of FeWB is shown in figure 2. Figures 2(a) and (b) are cross-sectional views of (100) and (010) planes, respectively. The blue and yellow areas represent electrons lost and gained, respectively. As shown in figure 2(a), the simultaneous loss and gain of electrons around Fe atoms suggest that Fe acts as ‘bridge’ for bonding in FeWB. The lost electrons of Fe atoms transfer to B atoms, while the gained electrons of Fe atoms come from W atoms, indicating that Fe-B and Fe-W bonds show a certain ionic feature. The directionality of the charge transfer between Fe and B atoms reflects the obvious covalent characteristic of Fe-B bonding. Therefore, covalent/ionic hybrid bonds have formed between Fe and B atoms. The pale green area of charge dispersion distribution between Fe and W atoms is a manifestation of metallic characteristics, so Fe-W is a mixture of metallic and ionic
bonds. There is obvious charge transfer between W and B atoms as shown in figure 2(b), and the charge density is localized around the two atoms, reflecting the ionic characteristics of W-B bonds.

The total and partial density of states (DOS) of FeWB are shown in figure 3, where the dashed line corresponding to 0 eV represents the Fermi energy level $E_F$. An obvious feature of TDOS is that the spin-up and
spin-up or -down, there is a large DOS value at the Fermi level, indicating that FeWB has a strong metallic property and superior electrical conductivity, which is consistent with the prediction given by the Cauchy pressure calculation results. In addition, it is worth to note that the spin-up DOS value of Fe atoms at the Fermi level is zero, which is a typical performance of semi-metallic properties. This conclusion is consistent with the observation that Fe atoms simultaneously gain and lose electrons in the charge density differences. B atoms contribute surface area and factor 2 indicates that there are two identical surfaces of the slab.

To be specific, the spin-up valence DOS can be divided into three main regions: (1) from −10 to −7 eV with mainly B-s states, partly W-d and a small amount of Fe-d states, indicating the hybridization between W-d, Fe-d and B-s states (2) from −6 to −2.5 eV with strong hybridization between Fe-d, W-d and B-p states, especially around −4.5 eV, reflecting covalent features, and (3) from −2 eV to $E_F = 0$ eV with mainly W-d states, which contribute the metallic feature of FeWB. The bonding properties reflected by spin-down DOS are basically the same as the spin-up, except that the spin-down metallic properties are mainly contributed by Fe-d states.

Analysis of charge density differences and DOS revealed that there is no B-B bond in FeWB. Mainly because: (1) the large atomic distance between B-B (3.355 Å); (2) the low B content in FeWB (4.3%). B-B bond plays an important role in the hardness of transition metal boride compounds [34, 47]. Low B content results in less B-B covalent bonds, so the dominant role in FeWB is a mixture of strong metallic and ionic bonds. The bonding characteristics of FeWB are beneficial to the transmission of electrons, causing FeWB to exhibit metallicity, but has poor resistance to dislocation movement and shear deformation, which is not conducive to the realization of high hardness.

3.2. FeWB/α-Fe Interface

3.2.1. Surface

In general, the interface is usually formed between the close-packed planes of two phases. The close-packed plane of FeWB is (001) plane, while that of α-Fe is (110) plane. However, the mismatch between FeWB (001) and α-Fe (110) is very large, reaching 8.7%. Excessive mismatch will cause greater interfacial stress, which is not conducive to the stability of the interface. After lattice mismatch calculation, the mismatch between FeWB (001) and α-Fe (111) is the smallest among α-Fe low-index planes, only 2.3%. Hence, the FeWB(001)/α-Fe(111) interface was established in our research.

Before constructing FeWB/α-Fe interface, it is necessary to determine the smallest atomic layer of FeWB (001) and α-Fe(111) that can reflect the bulk properties. Therefore, the surface energy convergence calculations were performed. FeWB(001) is a polar surface, and three kinds of terminal atoms Fe, W and B needed to be considered. Meanwhile, due to the subsequent atomic layer of B atom might be Fe or W, so the B-terminated has two cases: B(Fe) and B(W) (bracket means the type of atomic subsurface layer of B-terminated FeWB (001)). The surface energies of Fe ($\gamma_{\alpha-Fe}$) and FeWB ($\gamma_{\alpha-FeWB}$) can be expressed as follows:

$$\gamma_{\alpha-Fe} = \frac{E_{\text{total}}^{\text{bulk}} - N_x E_{\alpha-Fe} \mu_{\alpha-Fe}}{2A_j}$$

$$\gamma_{\alpha-FeWB} = \frac{E_{\text{total}}^{\text{bulk}} - N_{FeWB} E_{FeWB} - N_x E_x}{2A_j}$$

where $E_{\text{total}}^{\text{bulk}}$ denotes total energy of slabs, $E_{\alpha-Fe}^{\text{bulk}}$ and $E_{FeWB}^{\text{bulk}}$ denote energies of α-Fe and FeWB bulk, $N_x$ and $E_x$ represent the number of redundant ($X = \text{Fe, W, B}$) atoms and isolation atomic energies, respectively. $A_j$ represents surface area and factor 2 indicates that there are two identical surfaces of the slab.

Table 3 lists the surface energies of α-Fe(111) and FeWB(001) with four terminations under different number of layers. For α-Fe(111), the surface energy of nine atomic layers converges to 3.284 J m$^{-2}$. For Fe and B(Fe) terminated FeWB(001), the surface energy of four atomic layers can reach convergence, while W and B(W) terminated converge at five layers. The surface energy convergence values of the four terminations are all around 3.210 J m$^{-2}$. Therefore, 9-layer α-Fe(111), 4-layer Fe/B(Fe)-terminated FeWB(001) and 5-layer W/B(W)-terminated FeWB(001) are sufficient for the interface models. The free surfaces of FeWB and α-Fe slabs are separated by 15 Å vacuum layer to eliminate the interaction caused by periodicity.

Moreover, three stacking sequences were considered, namely top-site, center-site and hollow-site. The top-site refers to interfacial atoms of FeWB right above the atom of α-Fe slab, the center-site indicates the interfacial atoms of FeWB slab reside a bridge site on the first layer of α-Fe, and the hollow-site refers to the atoms of FeWB layer placed on the top of the second α-Fe layer. Therefore, considering different stackings and terminations, there are altogether twelve different interface configurations. Taking B(W)-terminated surface as an example, the interface models of three different stacking methods are shown in figure 4.
3.2.2. Adhesion work

Adhesion work, $W_{\text{ad}}$, is an important physical quantity of reaction interface strength and stability, which can be defined as the reversible energy required to separate the interface into two free surfaces. It can be calculated according to the following formula:

$$W_{\text{ad}} = \frac{E_{\alpha-\text{Fe}} + E_{\text{FeWB}} - E_{\text{FeWB}/\alpha-\text{Fe}}}{A}$$

where $E_{\alpha-\text{Fe}}$, $E_{\text{FeWB}}$, and $E_{\text{FeWB}/\alpha-\text{Fe}}$ are the total energies of isolated $\alpha$-Fe(111) slab, FeWB(001) slab, and FeWB/$\alpha$-Fe interface, respectively. $A$ is the total interface area.

$W_{\text{ad}}$ can be calculated by two different methods [48]. The first method is to establish the interfaces structure under different interface distances $d_0$ (1.0-3.0 Å) and calculate the total energies in the unrelaxation condition. Then the relationship $W_{\text{ad}}$ versus interface distances can be obtained, which is called the universal binding energy relationship (UBER, as shown in figure 5). The peak point of the relationship curve corresponds to optimal interface distance point. In the second case, the interface configuration with optimal interfaces distances obtained by UBER is relaxed, and then $d_0$ and $W_{\text{ad}}$ of relaxed interface structures can be obtained. The difference between the two methods is whether the atomic positions near the interface are relaxed or not.

The calculated values of $W_{\text{ad}}$, the interfacial distance $d_0$ and separation change $\Delta d$ before and after relaxation are summarized in table 4. The results in table 4 indicate that before optimization, stacking sequence is the main

**Table 3.** Surface energy of FeWB(001) and $\alpha$-Fe(111).

| Surface energy (J m$^{-2}$) | W-terminated | Fe-terminated | B(W)-terminated | B(Fe)-terminated | $\alpha$-Fe |
|-----------------------------|--------------|--------------|-----------------|------------------|------------|
| 1                           | 4.389        | —            | 3.662           | —                | 4.293      |
| 2                           | —            | 3.745        | —               | 3.939            | 3.952      |
| 3                           | 3.401        | —            | 3.423           | —                | 3.483      |
| 4                           | —            | 3.215        | —               | 3.210            | 3.472      |
| 5                           | 3.189        | —            | 3.204           | —                | 3.361      |
| 6                           | —            | 3.212        | —               | 3.205            | 3.322      |
| 7                           | 3.210        | —            | 3.216           | —                | 3.298      |
| 8                           | —            | 3.210        | —               | 3.210            | 3.290      |
| 9                           | 3.213        | —            | 3.215           | —                | 3.284      |
| 10                          | —            | 3.215        | —               | 3.213            | 3.282      |

**Figure 4.** B(W)-terminated interface: (a) Top-site, (b) Center-site and (c) Hollow-site. The spheres with pink, purple and blue represent B, W, and Fe atoms, respectively. The atomic radius of the planform increases from top to bottom. The dotted line is the interface segmentation point.
factor affecting $W_{ad}$ and the top-site has a lower $W_{ad}$ than other two stacking modes. After optimization, both termination and stacking sequence have great influence on $W_{ad}$ and $\Delta d$. $W_{ad}$ of B(Fe)-terminated interface after geometric optimization is higher than that of the other three terminations, suggesting that the interaction between $\alpha$-Fe and FeWB in B(Fe)-terminated interface is the strongest in all geometries. The interfacial separation changes of B(Fe)-terminal are also obvious, especially the center-site stacking interface (29.1%), suggesting that the interaction between $\alpha$-Fe and FeWB in this stacking interface is the strongest. It is not difficult to understand that interfacial Fe atoms of $\alpha$-Fe and interfacial W, B atoms of FeWB form the stacking of W-B-Fe layers at the interface, which is in line with the atomic arrangement of FeWB bulk. For all terminations, $W_{ad}$ of the center-site and hollow-site stackings are higher than that of the top-site. Termination atoms can interact with multiple nearest Fe atoms of $\alpha$-Fe surface if stacked in center-site or hollow-site. Whereas stacked in top-site, termination atoms can only interact with one Fe atom. As a result, atoms stacked in center-site or hollow-site have more opportunities to bond at the interface, and the stronger combination leads to the improved $W_{ad}$ of interface.

The B(Fe)-terminated center-site stacking interface (abbreviated as B(Fe)-C) model before and after optimization are shown in figure 6. The bond lengths of W-Fe and B-Fe in FeWB bulk are 2.721 and 2.208 Å, respectively. After optimization, the average distances of W-Fe and B-Fe at the interface are 2.545 and 2.173 Å,

### Table 4 Interface distance $d_0$ and $W_{ad}$ obtained with UBER and relaxed methods.

| Termination | Stacking | UBER       | Relaxed  |
|-------------|----------|------------|----------|
|             |          | $d_0$ (Å)  | $W_{ad}$ (J m$^{-2}$) | $d_{eq}$ (Å) | $\Delta d$ (%) | $W_{ad}'$ (J m$^{-2}$) |
| Fe-terminated | T-site  | ~2.100  | 2.641 | 1.818 | 13.4 | 3.813 |
|              | C-site  | ~1.500  | 3.534 | 1.404 | 6.4  | 4.921 |
|              | H-site  | ~1.700  | 3.792 | 1.558 | 8.4  | 4.686 |
| W-terminated | T-site  | ~2.200  | 2.694 | 2.314 | 9.7  | 2.392 |
|              | C-site  | ~1.600  | 4.976 | 1.816 | 13.5 | 4.772 |
|              | H-site  | ~1.500  | 4.256 | 1.579 | 5.3  | 4.012 |
| B(W)-terminated | T-site | ~1.500  | 2.269 | 1.608 | 7.2  | 3.027 |
|              | C-site  | ~1.600  | 3.398 | 1.396 | 12.8 | 5.481 |
|              | H-site  | ~1.700  | 3.421 | 1.410 | 19.4 | 5.077 |
| B(Fe)-terminated | T-site | ~1.900  | 3.450 | 1.704 | 5.3  | 5.938 |
|              | C-site  | ~1.600  | 3.354 | 1.134 | 29.1 | 6.920 |
|              | H-site  | ~1.500  | 3.975 | 1.218 | 18.8 | 6.549 |

Figure 5. Adhesion work ($W_{ad}$) of twelve interfaces at different distance.
especially the interface fracture toughness. According to Griffith's fracture theory, the fracture position has a certain occasionality. Unfortunately, to our knowledge, there is no experiment to verify this result. The interface bonding between coating and matrix directly affects the mechanical properties of composites, especially the interface fracture toughness. According to Griffith fracture theory [49], $G \approx 2\gamma$ can be used to calculate the fracture work of bulk materials on a specific crystal plane, where $G$ denotes the bulk materials’ fracture work and $\gamma$ is the surface energy. By comparing the value of $G$ and $W_{ab}$ the location of interface fracture can be judged. If $G > W_{ab}$, fracture occurs at the interface, otherwise fracture occurs in the bulk. The bulk fracture work of FeWB and $\alpha$-Fe are $G_{FeWB(001)} = 6.420 \text{ J m}^{-2}$ and $G_{\alpha-Fe(111)} = 6.568 \text{ J m}^{-2}$, respectively. It can be found that $W_{ad}$ of B(Fe)-C interface is slightly higher than $G_{FeWB(001)}$ and $G_{\alpha-Fe(111)}$, which means that cracks tend to initiate and propagate in FeWB bulk. Since the bond length of W-Fe and B-Fe at the interface is shorter than that of FeWB bulk, the interaction between interface atoms is stronger and fracture is less likely to occur at interface. Experimental results also confirmed this conclusion. Yang et al. [15] observed that after peeling off the coating, FeWB appeared on both coating side and $\alpha$-Fe matrix surface, that is to say, damage of the composite material occurred inside the coating rather than at the interface. However, these three values are very close, which means that the interface fracture position has a certain occasionality.

3.2.3. Electronic properties

Interface bonding characteristics are closely related to the mechanical properties of interface. According to the previous analysis, B(Fe)-C interface is the most stable, yielding the highest $W_{ad}$ among all models. In order to explore the difference in the properties of different interfaces, PDOS were calculated for B(Fe)-C and B(Fe)-T interfaces, as shown in figure 7.

For center-site stacking structure, PDOS of $\alpha$-Fe side atoms at the interface is very different from that of $\alpha$-Fe and FeWB bulk, but similar to Fe atom near the interface on FeWB side (Fe7 as shown in figure 6). That is to say, the bonding properties of Fe atoms at the interface are different from those in $\alpha$-Fe and FeWB bulks. There are obvious hybridizations between atoms on $\alpha$-Fe side and B(W) atoms on FeWB side. Specifically, peaks around $-8 \text{ eV}$ to $-6 \text{ eV}$ are caused by the hybridization between Fe2- $d$ and B1- $p$ states, while the peak at $-2 \text{ eV}$ is due to the interaction between Fe1- $d$ and W1- $d$ states. All of these formants indicate covalent bonding at the interface. The metallic characteristic of W atoms makes the interfacial Fe atoms have a higher metallicity than $\alpha$-Fe bulk, which can be seen from the larger DOS value at the Fermi level. Therefore, the bonding of center-site interface has covalent-metallic mixing properties. In addition, interface B atoms have strong non-locality, indicating that the effective carrier mass is small. That is to say, combination of FeWB/$\alpha$-Fe interface does not affect the performance of FeWB bulk, and the interface still inherits the excellent electrical conductivity of FeWB bulk.

PDOS of top-site interface is similar with the center-site one. The main difference is that PDOS values of the interfacial Fe atoms at the Fermi level are not obvious, showing weak metallicity. This is related to the structural characteristics of the top-site stacking; interfacial Fe atoms are located directly above B atoms and the distance between them is relatively close, so it is easy to interact. While the interfacial Fe atoms and W atoms are far apart and it is difficult to form bonds. Therefore, the top-site interfacial Fe atoms of $\alpha$-Fe hardly form metallic bonds, respectively. The atomic distances of the interface are shorter than the bond lengths of W-Fe and B-Fe in FeWB bulk, indicating that interaction is formed at FeWB/$\alpha$-Fe interface, which is even stronger than the bond in FeWB bulk. In addition, it is found that the positions of FeWB side atoms change slightly after relaxation, while the arrangement of $\alpha$-Fe side atoms is extremely irregular, speculating that an amorphous region is formed at the interface. Unfortunately, to our knowledge, there is no experiment to verify this result.

The interface bonding between coating and matrix directly affects the mechanical properties of composites, especially the interface fracture toughness. According to Griffith fracture theory [49], $G \approx 2\gamma$ can be used to calculate the fracture work of bulk materials on a specific crystal plane, where $G$ denotes the bulk materials’ fracture work and $\gamma$ is the surface energy. By comparing the value of $G$ and $W_{ab}$ the location of interface fracture can be judged. If $G > W_{ab}$, fracture occurs at the interface, otherwise fracture occurs in the bulk. The bulk fracture work of FeWB and $\alpha$-Fe are $G_{FeWB(001)} = 6.420 \text{ J m}^{-2}$ and $G_{\alpha-Fe(111)} = 6.568 \text{ J m}^{-2}$, respectively. It can be found that $W_{ad}$ of B(Fe)-C interface is slightly higher than $G_{FeWB(001)}$ and $G_{\alpha-Fe(111)}$, which means that cracks tend to initiate and propagate in FeWB bulk. Since the bond length of W-Fe and B-Fe at the interface is shorter than that of FeWB bulk, the interaction between interface atoms is stronger and fracture is less likely to occur at interface. Experimental results also confirmed this conclusion. Yang et al. [15] observed that after peeling off the coating, FeWB appeared on both coating side and $\alpha$-Fe matrix surface, that is to say, damage of the composite material occurred inside the coating rather than at the interface. However, these three values are very close, which means that the interface fracture position has a certain occasionality.

![Figure 6. Schematic illustration of the site of interfacial atoms in B(Fe)-C interface structure without (left) and with (right) relaxation.](image-url)
but only form covalent bonds with B atoms of FeWB. Bonding strength of the atoms is weaker than the center-site, which explains why $W_{ad}$ of the top-site interface is smaller than that of the center-site interface.

4. Conclusions

In this work, first-principles calculations were employed to research FeWB bulk and FeWB(001)/$\alpha$-Fe(111) interface properties. For FeWB bulk, the structural stability, elastic constants and electronic properties have been studied. For FeWB(001)/$\alpha$-Fe(111) interface, a total of twelve interface models had been established, considering different terminations of surface (Fe-, W-, B(Fe)- and B(W)-terminated) and stacking sites (center-, hollow- and top-sites). The adhesion work, interface fracture toughness and bonding properties of FeWB/$\alpha$-Fe interface were investigated. The main results are as follows:

1. The bonding of FeWB can be seen as a mixture of metallic, covalent and ionic contributions, of which metallicity is the most obvious. Such bonding characteristics endow FeWB with excellent toughness and conductivity.

2. Compared with the other three terminations, B(Fe)-terminated interfaces are more stable. After optimization, B(Fe)-terminated center-site stacking structure has the smallest interface distance, which promotes the bonding of interface atoms, resulting in the largest $W_{ad}$.

3. Mechanical failure of the interface tends to occur in FeWB bulk, but the value of interface fracture work is close to the $W_{ad}$ of $\alpha$-Fe and FeWB, so the fracture location has a certain occasionality.

4. The bonding at B(Fe)-terminated center-site stacking interface has mixed covalent and metallic properties, while the top-site structure mainly exhibits covalent characteristic.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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References

[1] Takagi K-I 2006 J. Solid State Chem. 179 2809–18
[2] Nishiyama K, Keino M, Furuyama Y, Sakaguchi T and Takagi K 2003 J. Alloy. Compd. 355 97–102
[3] Li C, Liu Y and Li J 2018 Mater. Res. Express 5 016517
[4] Li J, Li J, Li C and Liu Y 2014 Int. J. Refract. Met. Hard Mat. 46 80–3
[5] Zhang T et al 2019 Ceram. Int. 45 17536–44
[6] Zhou X P, Hu X B, Go B and Yan F 2008 Heat Treat. Mat. 33 73–5
[7] Hongwei Y, Jun L, Cheng L and Ying L 2018 Rare Metal Mat. Eng. 47 463–8
[8] Haschke H, Nowotny H and Benesovsky F 1966 Mon. Chem. 97 1459–68
[9] Leithe-Jasper A, Klesnar H, Rogl P, Komai M and Takagi K I 2000 J. Jpn. Inst. Met. 64 154–62
[10] Jiang J, Wang Y, Zhong Q, Zhou Q and Zhang L 2011 Surf. Coat. Technol. 206 473–8
[11] Khor K A, Yu L G and Thin Solid Films 548 232–7
[12] Campos I, Palomar M, Amador A, Ganem R and Martinez J 2006 Surf. Coat. Technol. 201 2438–42
[13] Santana R.A.C.d., Campos A R N, Prasad S and Leite V D 2007 Química Nova 30 360–5
[14] Abakay E, Kilince B, Sen S and Sen U 2014 Microstructural Examinations of Fe-W-B Base Hard-Faced Steel International Multidisciplinary Microscopy Congress pp 143–9
[15] Guo-Ping Y and Jun Li 2016 Guangzhou Chemical Industry 44 143–5
[16] Wang J, Pui H Z, Bi W B, Zhang X J and Wang M L 2018 Mater. Heat. Treat. 39 117–25
[17] Levy M 1979 Proc. Natl Acad. Sci. USA 76 4602–5
[18] Tanaka S, Yang R and Kohyama M 2004 MRS Proc. 843 T3.10
[19] Zhao X, Zhou Y, Liu S, Zhou Y, Zhao C, Wang C and Yang Q 2016 Surf. Coat. Technol. 305 200–7
[20] Wang S, Liu Z, Yang X, Fan X, Chen B, Zhang J and Li D 2018 Surf. Interface Anal. 50 321–7
[21] Wu J H and Yang G 2014 Comput. Mater. Sci. 82 86–91
[22] Zhao E, Meng J, Ma Y and Wu Z 2010 Phys. Chem. Chem. Phys. 12 13158–65
[23] Zhao E, Wang J, Meng J and Wu Z 2010 J. Comput. Chem. 31 1904–10
[24] Li J, Wang X, Liu K, Sun Y, Chen L and Yang H 2010 Physica B 405 4659–63
[25] Hai-Hua C, Yan B, Yan C, Guangfu J and Lingcang C 2012 J. Phys. Chem. Solids 73 1197–202
[26] Wang B, Liu Y, Ye J-W and Wang J 2013 Comput. Mater. Sci. 70 133–9
[27] Segal M, Lindan P, Probert M, Pickard C, Hasnip P, Clark S and Payne M 2002 J. Phys.-Cond. Matter 14 2717
[28] Egilits R I and Popov A I 2018 J. Solidi Chem. Soc. 22 459–68
[29] Egilits R I 2014 Int. J. Mod. Phys. B 28 1430009
[30] Kohn W and Sham L J 1965 Phys. Rev. 140 A1133
[31] Fischer T and Almlöf J 1992 J. Phys. Chem. 96 9768–74
[32] Raghavan V 2003 J. Phase Equilib. 24 5
[33] Kuz'ma Y, Krypyakevich P and Chepiga M 1968 J. Struct. Chem. 9 268–9
[34] Zhao C, Xiaolong J, Xiao B, Feng J, Xie X and Chen Y H 2013 Comput. Mater. Sci. 44 1056–64
[35] Rabe D 1998 Computational Materials Science - The Simulation of Materials Microstructures and Properties (USA: Wiley-VCH Verlag GmbH)
[36] Zhou Y, Yan P, Chong X and Feng J 2018 AIP Adv. 8 105132
[37] Hill T R 1952 Proceedings of Physical Society: Section A 65 337–47
[38] Ali M A, Hadi M, Hossain M M, Naqib S and Islam A K M 2017 Phys. Status Solidi B 254 201700010
[39] Chen X-Q, Niu H, Li D and Li Y 2011 Intermetallics 19 1275–81
[40] Li J-H, Wang W-L, Hu L and Wei B-B 2014 Intermetallics 46 211–21
[41] Frantsevich I N, Voronov F F and Bukuta S A 1983 Elastic Constants and Elastic Moduli of Metals and Insulators Handbook 60–180
[42] Vaidheeswaran G, Venkatakrishnan K, Svan A and Delin A 2007 J. Phys.-Cond. Matter 19 326214
[43] Pugh S 1954 Philosophical Magazine Series 6 823–43
[44] Pettifor D 1992 Mater. Sci. Technol. 8 345–9
[45] Vahlidiek F W and Mersol S A 1968 Anisotropy in Single-Crystal Refractory Compounds (US: Springer)
[46] Ranganathan S and Ostoj-Starzewski M 2008 Phys. Rev. Lett. 101 055504
[47] Zhang T, Yin H Q, Zhang C, Qu X H and Zheng Q J 2019 Chinese Phys. B 20 519–30
[48] Siegel D, Jr L and Adams J 2002 Surf. Sci. 498 321–36
[49] Jin N, Yang Y, Li J, Luo X, Huang B, Sun Q and Guo P 2014 J. Appl. Phys. 115 223714–223714