Molecular Dynamics Study on the Interface Properties of the Ternary Boride Cladding Materials with Atomic Vacancy Defects

Junru Yang, Minglan Wang and Haitao Feng

ABSTRACT

In the paper, the interface models of Mo$_2$FeB$_2$(100)/$\alpha$-Fe (001) with different atomic vacancy defects are constructed. The formation energies of different atomic vacancy defects and the interface binding energies of the models are studied. The research results show that the formation energy of B atomic vacancy defect in the interface is the smallest and that of Fe atomic vacancy defect in the clad layer is the biggest. The interface binding energy of the model with B atomic vacancy defect in the interface is the biggest and that with Mo atomic vacancy defect in the interface is the smallest.

INTRODUCTION

Due to the preparation process, and other factors, the micro defects will be initiated in the interface of the ternary boride hard cladding materials [1]. Usually, these defects are atomic vacancy, interstitial atom, dislocation, atomic inclusions, and so on [2]. Up to now, many researchers have made studied the atomic vacancy defect influences on the material performance. S. Chandra et al. [3] studied the crack growth behavior in the aluminum with vacancies using molecular dynamics simulation method, the results showed that the stress concentration at the crack tip was changed because of the atomic vacancy defects, with the increase of atomic vacancy defects, the crack tip became blunt. Guo Lei et al. [4] used first-principle method to study the stability of Zn Vacancy in ZnSe, the result showed that single Zn vacancy defect structure was not easy to form because it was unstable in ZnSe. Xu Zhongfei [5] studied the defect formation energy of double Al or double Cu vacancy defects in AlCu3 structure with first-principles method, the results showed that double Cu vacancy defect was easier to form than double Al vacancy defect. Jia Lixia et al. [6] studied the interaction mechanism of He atom and the vacancy...
defect in Ti3SiC2 material with the first principles method, the result showed that Si Vacancy was easy to form, and it easily captured two He atoms to get VHe2 complex.

Ternary boride hard cladding material (5Cr2Ni08C/Q235) is a new cladding composite with good comprehensive properties. Its interface is composed of the hard phase (Mo2FeB2) and the binding phase (α-Fe). Because of fabrication technology, there are some defects in the interface. In the paper, based on the Mo2FeB2 (100)/α-Fe (001) models with different atomic vacancy defects, the atomic vacancy defect formation energy and corresponding interface binding energy are studied. The research results will be import to improve the interface properties of the material.

ESTABLISHMENT OF MO2FEB2 (100)/A-Fe (001) MODELS WITH ATOMIC VACANCY DEFECTS

The space group types of unit cells of Mo2FeB2 and α-Fe are P4/MBM and IM-3M separately. The lattice constant parameters of Mo2FeB2 are: \(a=b=5.807\,\text{Å}, c=3.412\,\text{Å}\), those parameters of α-Fe are \(a=b=c=2.8664\,\text{Å}\) [7,8]. Based on the above parameters, using the Molecular dynamics simulation software, the ideal Mo2FeB2 (100)/α-Fe (001) model without any defect is established, as shown in Fig.1. In fact, the interface model usually contains some atomic vacancies of Fe, B and Mo, which makes interface micro cracks to initiate easily near the atomic vacancy defect. Based on the ideal interface model, the interface models with Mo, B and Fe atomic vacancy defects are built respectively. The selected B atom in interface is removed from the ideal interface model to get the interface model with B atomic vacancy defect, as shown in Fig.2. Similarly, the interface models with Mo or Fe atomic vacancy defects are built respectively, as shown in Fig.3 and Fig.4. In the figures, “○”, “△” and “□” represents Mo, B and Fe atomic vacancy defect respectively.
Similarly, the Mo$_2$FeB$_2$ (100)/α-Fe (001) models with the atomic vacancy defects of Mo, B and Fe in the clad layer and the model with Fe atomic vacancy in the substrate are established respectively, as shown in Fig. 5, Fig.6, Fig.7 and Fig.8.

**CALCULATION OF THE ATOMIC VACANCY DEFECT FORMATION ENERGY**

All the calculations in this paper are performed based on the density function theory and using CASTEP software [9]. The correlation potential of exchange-correction function is corrected by the GGA-RPBE [10]. The cutoff energy of the atomic wave is set to be 300 eV. The grid number k point is set to be 4×4×8. The stable lattice structure is obtained by the BFGS optimization algorithm scheme [11]. When the system is optimized, the conditions for self-consistent convergence is set as the following: the final convergence value of the whole system energy is less than 1×10$^{-5}$ eV/atom, the stress on each atom is less than 0.03eV/Å, the stress deviation is less than 0.05GPa, and the allowance deviation is less than 10$^{-3}$ Å.

Firstly, it is performed to optimize the structure of the Mo$_2$FeB$_2$ (100)/α-Fe (001) model with B atomic vacancy defect in the interface. And then get the total energy of the interface model with the molecular dynamics simulation, namely $E_{total-IVB}=-1.66278317×10^4$ eV.

With the same method, the following results can be obtained. The total energy of the ideal Mo$_2$FeB$_2$ (100)/α-Fe (001) model ($E_{total}$) is -1.67062140×10$^4$ eV, the system energy of Mo$_2$FeB$_2$ (100) supercell slab model (the left part after the lattice plane of α-Fe (001) deleted from Mo$_2$FeB$_2$ (100)/α-Fe (001) model) with B atom vacancy defect in the interface ($E_{Mo2FeB2(100)-IVB}$) is -9.70475987×10$^3$ eV, the total energy of the ideal Mo$_2$FeB$_2$ (100) supercell slab model ($E_{Mo2FeB2(100)}$) is -9.78310707×10$^3$ eV, the total energy of the ideal α-Fe(001) supercell slab model ($E_{α-Fe(001)}$)=-6.91921567×10$^3$ eV.
In the \( \text{Mo}_2\text{FeB}_2(100)/\alpha\text{-Fe}(001) \) models with \( Q(=\text{Mo, B, Fe}) \) atomic vacancy defects \( (V_Q) \), the original \( Q \) atomic potential energy \( (X_{VQ}) \) at atomic vacancy defect position is

\[
X_{VQ} = E_Y - E_{Y-VQ}
\]

(1)

Where, \( E_Y \) is the total energy of \( Y \) supercell slab model with fully relaxed, \( E_{Y-VQ} \) is the total energy of \( Y \) supercell slab model with \( Q \) atomic vacancy defect with fully relaxed.

Therefore, the original \( B \) atomic potential energy in the \( \text{Mo}_2\text{FeB}_2(100)/\alpha\text{-Fe}(001) \) model at the \( B \) atomic vacancy position in interface is

\[
X_{IVB} = \text{Mo}_2\text{FeB}_2(100) - \text{Mo}_2\text{FeB}_2(100)-IVB = -78.3472\text{eV}.
\]

The atomic vacancy defect formation energy can be calculated with the following equation [12].

\[
E_f = \left( E_{\text{interf-v}} + X_{VQ} - E_{\text{interf}} \right)/A
\]

(2)

Where \( E_f \) is the atomic vacancy defect formation energy, \( E_{\text{interf-v}} \) is the total energy of the \( \text{Mo}_2\text{FeB}_2(100)/\alpha\text{-Fe}(001) \) model with atomic vacancy defect in the interface, \( E_{\text{interf}} \) is the total energy of the ideal \( \text{Mo}_2\text{FeB}_2(100)/\alpha\text{-Fe}(001) \) model, \( A \) is the overlap area of interface, it can be gotten with the lattice constant parameters.

Let the atomic vacancy defect formation energy of the model with \( B \) atomic vacancy defect in the interface be \( E_{f-VI-B} \). The total energy of the model with \( B \) vacancy defect in the interface is \( E_{\text{interf-IVB}} \), then \( E_{\text{interf-IVB}} = E_{\text{total-IVB}} \). And \( E_{\text{interf}} = E_{\text{total}} \). Therefore, \( E_{f-IVB} \) can be calculate with Eq.(2), then \( E_{f-IVB} = 0.0342\text{J/m}^2 \).

Similarly, the following atomic vacancy defect formation energies \( (E_{f-V}) \) can be calculated. They are the atomic vacancy defect formation energies of the \( \text{Mo}_2\text{FeB}_2(100)/\alpha\text{-Fe}(001) \) model with Mo and Fe vacancy defects in interface, the energies of the model with Mo, B and Fe vacancy defects in the clad layer, and the energy with The results are as shown in table 1. In the table, \( V_{I-Mo} \) and \( V_{I-Fe} \) mean Mo and Fe vacancy defects in interface, \( V_{F-Mo} \), \( V_{F-B} \) and \( V_{F-Fe} \) mean Mo, B and Fe vacancy defects in the clad layer separately, and \( V_{J-Fe} \) means Fe vacancy defect in the substrate.

<table>
<thead>
<tr>
<th>Types of atomic vacancy defect</th>
<th>( V_{I-Mo} )</th>
<th>( V_{I-B} )</th>
<th>( V_{I-Fe} )</th>
<th>( V_{F-Mo} )</th>
<th>( V_{F-B} )</th>
<th>( V_{F-Fe} )</th>
<th>( V_{J-Fe} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic vacancy defect formation energy ( E_{f-V}(\text{J/m}^2) )</td>
<td>0.8085</td>
<td>0.0342</td>
<td>0.5550</td>
<td>0.2002</td>
<td>0.3351</td>
<td>0.9710</td>
<td>0.6208</td>
</tr>
</tbody>
</table>

The table 1 shows that the atomic vacancy defect formation energy of the model with \( B \) atomic vacancy defect in the interface is the smallest, namely \( E_{f-VI-B} = 0.0342\text{J/m}^2 \), and that with Fe vacancy defect in the clad layer is the biggest, namely \( E_{f-VF-Fe} = 0.9710\text{J/m}^2 \). Because the atomic vacancy defect formation energy is bigger, the formation of the atomic vacancy defect is more difficult. On the contrary, the atomic vacancy defect formation energy is smaller. The formation of the atomic vacancy defects is easier. Therefore, it is the easiest to form \( B \) atomic vacancy defect in interface, and the most difficult to form Fe atomic vacancy defect in the clad layer. It also explains that it is easy to initiate the micro-crack at \( B \) atomic vacancy defect position in the interface, and it is difficult to initiate the micro-crack at Fe atomic vacancy defect position in the clad layer.
CALCULATION OF THE INTERFACE BINDING ENERGY WITH ATOM VACANCY DEFECT

The interface binding energy ($\gamma_{\text{int}}$) reflects the ability of interface resistance to crack propagation. The bigger the $\gamma_{\text{int}}$, the more stable the interface property, and the more difficult the initiation and propagation of the interface micro crack. Formula to calculate the interface binding energy is as follows [13].

$$\gamma_{\text{int}} = \frac{(E_Y + E_Z) - E_{\text{total}}}{A} \tag{3}$$

Where, $E_Y$ and $E_Z$ are the total energies of Y and Z supercell slab after the model is fully relaxed, $E_{\text{total}}$ is the total energy of Y/Z interface model with fully relaxed.

Therefore, interface binding energy of the Mo$_2$FeB$_2$ (100)/$\alpha$-Fe (001) model with B atomic vacancy defect in the interface ($\gamma_{\text{int-VI-B}}$) is

$$\gamma_{\text{int-VI-B}} = \frac{(E_{\text{Mo}_2\text{FeB}_2(100)}_{\text{IVB}} + E_{\text{Fe}(001)}) - E_{\text{total-IVB}}}{A}. \tag{4}$$

Then, with Eq.(4), $\gamma_{\text{int-VI-B}}$ is 3.760 J/m$^2$.

Similarly, the following interface binding energies with different atomic vacancy defects ($E_{\text{int-V}}$) can be calculated as shown in table 2. They are the interface binding energies of the Mo$_2$FeB$_2$(100)/$\alpha$-Fe(001) model with Mo and Fe atomic vacancy defects in interface, or those with Mo, B and Fe vacancy defects in the clad layer, and that with Fe vacancy defect in the substrate.

<table>
<thead>
<tr>
<th>Types of atomic vacancy defect</th>
<th>$V_{I,\text{Mo}}$</th>
<th>$V_{I,\text{B}}$</th>
<th>$V_{I,\text{Fe}}$</th>
<th>$V_{F,\text{Mo}}$</th>
<th>$V_{F,\text{B}}$</th>
<th>$V_{F,\text{Fe}}$</th>
<th>$V_{I,\text{Fe}}$</th>
<th>no</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interface binding energy $\gamma_{\text{int-V}}$ (J/m$^2$)</td>
<td>2.177</td>
<td>3.760</td>
<td>2.864</td>
<td>3.394</td>
<td>3.459</td>
<td>2.852</td>
<td>3.173</td>
<td>3.794</td>
</tr>
</tbody>
</table>

It is known from table 2 that the interface binding energy of the model with B atomic vacancy defect in interface is the biggest, namely $\gamma_{\text{int-VI-B}}=3.760$ J/m$^2$, and that with Mo atomic vacancy defect in interface has the smallest interface binding energy, namely $\gamma_{\text{int-VI-Mo}}=2.177$ J/m$^2$. Compared with the interface binding energy of the ideal Mo$_2$FeB$_2$ (100)/$\alpha$-Fe (001) model, all the interface binding energies of the model with atom vacancy defects are decreased, which means that existence of the atomic vacancy defects weakens the interface binding strength, and makes the interface binding property of the ternary boride hard cladding materials reduced. And the interface model with Mo atomic vacancy has the biggest influence on the interface binding energy of the material.

CONCLUSIONS

Based on the ideal Mo$_2$FeB$_2$ (100)/$\alpha$-Fe (001) model, the interface models with different the atomic vacancy defects are established. The conclusions are as follows.

1. The simulation calculation results of different atomic vacancy defect formation energies show that, the atomic vacancy defect formation energy of the
interface model with B atomic vacancy defect in interface is the smallest, and that with Fe vacancy defect in the clad layer is the biggest. Therefore, it is the easiest to form B atomic vacancy defect in the interface, while it is the most difficult to form Fe atomic vacancy defect in the clad layer.

(2) The calculation results of the interface binding energies of model with the different atomic vacancy defects show that, compared with the interface binding energy of the ideal $\text{Mo}_2\text{FeB}_2(100)/\alpha$-Fe (001) model, the interface binding energy of the model with Mo atomic vacancy defect in the interface has the largest reduction, which means that this interface model is the most unstable.

(3) Consider both the atomic vacancy defect formation energies and the interface binding energies, in the $\text{Mo}_2\text{FeB}_2(100)/\alpha$-Fe (001) model, the interface micro-crack is easiest to be initiated at Mo atomic vacancy position and to propagate to B atomic position in the interface.

ACKNOWLEDGEMENTS

This project is supported by the natural science foundation of Shandong Province (ZR2013EEM016), and postgraduate innovation fund project of Shandong University of Science and Technology (YC150210).

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