First-principles study of the effect of vacancies on the interface stability of 3C-SiC/Mg composites based on theoretical physical method

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Abstract. In this paper, the first principles calculation method based on theoretical physics method was used to optimize the structure of 3C-SiC(111)/Mg(0001) interface model with vacancies. The interface adhesion work, vacancy formation energy and electronic structure were calculated and analyzed. The results show that the interface adhesion work of 3C-SiC/Mg-V_{Mg-1}, 3C-SiC/Mg-V_{Mg-2}, 3C-SiC/Mg-V_{Mg-3} is greater than that of 3C-SiC/Mg interface, which indicates that Mg vacancy have a certain promoting effect on the interface bonding of 3C-SiC/Mg, and the interface adhesion work of 3C-SiC/Mg-V_{Mg-1} is the largest. Because after the presence of Mg vacancy, the number of wavelet peaks increases and the pseudo-energy gap increases, so that the covalent bond increases and the interface adhesion work increases. Their vacancy defect formation energies are not much different, which are 1.1057eV, 1.0584eV, 1.2299eV, respectively. After the presence of C vacancy and Si vacancy, the interface adhesion work of 3C-SiC-V_{C-1}/Mg, 3C-SiC-V_{C-3}/Mg, 3C-SiC-V_{Si-2}/Mg and 3C-SiC-V_{Si-4}/Mg is smaller than that of 3C-SiC/Mg, which indicates that C vacancy and Si vacancy have no effect on the interface bonding. Among them, the interface adhesion work of 3C-SiC-V_{C-1}/Mg is greater than that of 3C-SiC-V_{C-3}/Mg, and the interface adhesion work of 3C-SiC-V_{Si-4}/Mg is greater than that of 3C-SiC-V_{Si-2}/Mg. After the presence of vacancy, the number of small wave peaks in the density of states map becomes less, the distribution of the density of states near the Fermi level becomes narrower, the metallicity is enhanced, and the bond strength decreases. In terms of the formation energy of vacancy defects, the formation energy of 3C-SiC-V_{C-1}/Mg is less than that of 3C-SiC-V_{C-3}/Mg, and the formation energy of 3C-SiC-V_{Si-2}/Mg is less than that of 3C-SiC-V_{Si-4}/Mg.
1. Introduction
Magnesium-based composite materials combine the excellent characteristics of magnesium alloys with high specific strength, strong shock absorption performance, and good damping properties, as well as the fracture toughness, high temperature performance, wear resistance and corrosion resistance of the reinforcement. Magnesium-based composite material is a new material in the developing high-tech industry, which is widely used in the fields of aerospace, electronics, and automobiles[1-5].

In the process of preparing the material, the material will be affected by various factors such as the environment, leading to the generation of lattice defects. Atomic vacancy is one of the more easily generated lattice defects. The generation of vacancies will affect the nearby electronic structure, and the lack of atoms at the interface will cause the bonding of the cermet interface to change. Matsunaka et al.[6] studied the effect of O vacancies in MgO on the Ni/MgO interface. The results show that the structure of the interface does not change greatly due to the formation of O vacancies, but the formation of O vacancies leads to charge transfer, resulting in the mirror image between Mg ions and Ni induced ions. The adhesion work of the interface with vacancies is 15% higher than that of the intact interface. Zhukovskii and others[7] studied the effect of vacancy on the interface bonding of Ag/MgO composites by density functional theory. The results show that the formation of vacancies will affect the interface bonding of Ag/MgO composites, and the bonding energy of the interface with vacancy defects is greater than that of the intact interface. The electronic structure analysis of the interface after vacancy formation shows that there is charge transfer at the vacancy and the formation of ionic bonds. Dudiy et al.[8] used first-principles methods to study the effect of vacancies on the Ag/Ti(C,N) interface. Studies have shown that the presence of C vacancies and N vacancies will enhance the metallicity of the Ti atoms at the interface, so that the bonding of the interface will also increase.

The bonding characteristics of the magnesium-based composite interface is a current research hotspot. The effect of vacancies on the bonding of the 3C-SiC/Mg composite interface has not been reported. The first-principles calculation method can rely on software to analyze the interface of the composite material at the micro level. In this paper, the influence of Mg vacancies, C vacancies and Si vacancies on the interface bonding of 3C-SiC/Mg composites is studied by density functional theory.

2. Calculation method and model
The calculation in this paper is carried out under the Castep module of Materials Studio software[9], using plane wave super-soft pseudo-potentials, the choice of exchange correlation functional is GGA-PBE[10], BFGS is the optimization algorithm, and the convergence of the self-consistent iteration for energy calculation is $1.0\times10^{-6}$ eV/atom, the energy cut-off is 380eV, the maximum number of self-consistent iterations allowed for energy calculation is 100, the maximum force acting on the atom during geometric optimization should not exceed 0.03eV/Å, and the maximum stress should not exceed 0.05GPa. The maximum displacement should not exceed 0.001Å, and the K-points is $6\times6\times1$.

In this paper, the 3C-SiC(111) surface is stacked on the Mg(0001) surface, the number of layers of 3C-SiC(111) surface is 10, and the number of layers of Mg(0001) surface is 5. There are Mg vacancy, C vacancy, and Si vacancy in the 3C-SiC(111)/Mg(0001) interface model. The interface model is shown in the Fig 1.
Fig 1. 3C-SiC(111)/Mg(0001) interface structure model with different vacancy (a) 3C-SiC/Mg-V_{Mg-1}  (b) 3C-SiC/Mg-V_{Mg-2}  (c) 3C-SiC/Mg-V_{Mg-3}  (d) 3C-SiC-V_{C-1}/Mg  (e) 3C-SiC-V_{C-3}/Mg=(f) 3C-SiC-V_{Si-2}/Mg  (g) 3C-SiC-V_{Si-4}/Mg

3. Results and discussion

3.1. Ideal work of adhesion and vacancy formation energy

The vacancy structure model of 3C-SiC(111)/Mg(0001) interface was optimized, so that each atom of the model was fully relaxed, and the energy of the system can reach the lowest.

The formula for calculating the formation energy of vacancy defects on the interface is as follows:

\[ E_f = E_{\text{interface}-V} + X_V - E_{\text{interface}} \]  

where \( E_f \) is the formation energy of vacancy defect at the interface, \( E_{\text{interface}-V} \) is the total energy of the interface with vacancy defect, \( X_V \) is the chemical potential of the atom at the vacancy, and \( E_{\text{interface}} \) is the total energy of the interface without vacancy defect.

| Interface Model       | Total Energy(eV) | Wad(J/m²) | \( E_f \)(eV) |
|-----------------------|------------------|-----------|----------------|
| 3C-SiC/Mg             | -24724.95417     | 2.5834    | /              |
| 3C-SiC/Mg-V_{Mg-1}    | -23751.12032     | 3.0513    | 1.1057         |
| 3C-SiC/Mg-V_{Mg-2}    | -23751.16761     | 2.9574    | 1.0584         |
| 3C-SiC/Mg-V_{Mg-3}    | -23750.99614     | 2.9110    | 1.2299         |
| 3C-SiC-V_{C-1}/Mg     | -24568.42925     | 1.4372    | 2.8439         |
| 3C-SiC-V_{C-3}/Mg     | -24566.89300     | 1.3641    | 4.3802         |
| 3C-SiC-V_{Si-2}/Mg    | -24613.11644     | 1.6721    | 5.6956         |
| 3C-SiC-V_{Si-4}/Mg    | -24611.94278     | 2.5226    | 6.8693         |
The optimized calculation results of the interface structure with different vacancies are shown in the Table 1. It can be seen from the table that after the presence of Mg vacancy, the energy of the interface system is slightly reduced due to the occurrence of lattice distortion. The presence of Mg vacancy in the first, second and third layers makes the adhesion work (3.0513 J/m², 2.9574 J/m², 2.9110 J/m²) of the interface system greater than that (2.5834 J/m²) of the interface system without Mg vacancy. The adhesion work of 3C-SiC/Mg-V_{Mg-1} system is the largest. There are Mg vacancy in different positions at the interface, and the electronic structure is rearranged, which improves the wettability of the interface. The vacancy formation energy (1.2299 eV) of 3C-SiC/Mg-V_{Mg-3} is the largest among the three positions. The interface model with Mg vacancy in the third layer is the most difficult to form. The vacancy formation energy of 3C-SiC/Mg-V_{Mg-1} is not much different from the vacancy formation energy of 3C-SiC/Mg-V_{Mg-2}. The vacancy defects of the two are easier to form and the interface structure is easier to stabilize exist.

After the presence of C vacancy, due to the absence of C atom, the atoms near the C vacancy deviate from the original position, resulting in lattice distortion, and the energy of the system increases by 156.52 eV and 158.06 eV respectively. The presence of C vacancy in the first and third layers leads to the interfacial adhesion work of the system being 1.4372 J/m² and 1.3641 J/m². Compared with the ideal system without C vacancy (2.5834 J/m²), the interfacial adhesion work decreases significantly. It shows that the existence of C vacancy is not conducive to the interface bonding of 3C-SiC/Mg. In terms of vacancy formation energy, the vacancy formation energy of 3C-SiC-V_{C-3}/Mg is 1.5 times that of 3C-SiC-V_{C-1}/Mg. The interface model with C vacancy in the first layer is easier to form than the interface model with C vacancy in the third layer.

Due to the absence of Si atom, the atoms near the Si vacancy defect deviate from the original atomic center, resulting in lattice distortion, and the energy of the system increases by 111.83 eV and 113.01 eV, respectively. Compared with the ideal system without Si vacancy (2.5834 J/m²), the interfacial adhesion work of the system with Si vacancy in the second layer is 1.6721 J/m², which is significantly reduced. The interfacial adhesion work of the system with Si vacancy in the fourth layer is 2.5226 J/m². It shows that the existence of Si vacancy in the second layer is very unfavorable to the interface bonding of 3C-SiC/Mg, while the existence of Si vacancy in the fourth layer has little effect on the interface bonding of 3C-SiC/Mg. In terms of vacancy formation energy, the vacancy formation energy of 3C-SiC-V_{Si-2}/Mg and the vacancy formation energy of 3C-SiC-V_{Si-4}/Mg are 5.6956 eV and 6.8693 eV, respectively. The formation energy of Si vacancy is relatively large, and it is difficult to form. In contrast, the interface model of Si vacancy in the second layer is easier to form than the interface model of Si vacancy in the fourth layer.
3.2. Electronic structure analysis

Fig 2. Interface density of states (a) density of states of 3C-SiC/Mg and 3C-SiC/Mg-V_{Mg} (b) density of states of 3C-SiC/Mg and 3C-SiC/Mg-V_{C} (c) density of states of 3C-SiC/Mg and 3C-SiC/Mg-V_{Si}
Fig 2 shows the density of states at the interface. The dotted line is the density of states diagram of 3C-SiC(111)/Mg(0001) interface without vacancy, and the solid line is the density of states diagram of 3C-SiC(111)/Mg(0001) interface with Mg vacancy. It can be seen from the Fig 2(a) that the density of states of 3C-SiC(111)/Mg(0001) interface with Mg vacancy does not change greatly compared with the density of states of 3C-SiC(111)/Mg(0001) interface without vacancy, and the wavelet peaks of the density of states with Mg vacancy are increased. The DOS value of the solid-line density of states diagram at the Fermi level is not 0, which is lower than the ideal state. The lack of Mg atom leads to the weakening of the metalliclicity, and there are two adjacent peaks nearby, that is a obvious pseudo-energy gap, which can directly reflect the strength of the covalent bond of the system. After the presence of Mg vacancy, the pseudo-energy gap in the density of states diagram increases, the covalent bond of the system increases, and the interfacial adhesion work increases, which indicates that Mg vacancy is beneficial to the bonding of 3C-SiC(111)/Mg(0001) interface system. It can be seen from the Fig 2(b) and Fig 2(c) that the change of the density of states of 3C-SiC(111)/Mg(0001) interface with Si vacancy is similar to that with C vacancy. The peaks of the density of states decrease, and the number of wavelet peaks also decreases. The distribution of the density of states near the Fermi level narrows, and the bonding strength at the interface decreases, but the peak at the Fermi level is much larger than that in the ideal density of states. The metallicity is strongly enhanced. It shows that the presence of Si vacancy and C vacancy is not conducive to the combination of 3C-SiC(111)/Mg(0001) interface system.

4. Conclusion
In this paper, the effects of Si vacancy, C vacancy and Mg vacancy on the bonding properties of 3C-SiC(111)/Mg(0001) interface system were investigated by first principles. The conclusions are as follows.

(1) The interface adhesion work of 3C-SiC/V_{Mg-1}, 3C-SiC/V_{Mg-2}, 3C-SiC/V_{Mg-3} is all greater than the interface adhesion work of 3C-SiC/Mg, indicating that Mg vacancy is beneficial to interface bonding.

(2) The interfacial adhesion work of 3C-SiC-V_{C-1}/Mg and 3C-SiC-V_{C-3}/Mg is less than that of 3C-SiC/Mg, indicating that C vacancy are not conducive to interfacial bonding. The interface adhesion work of 3C-SiC-V_{C-1}/Mg is greater than the interface adhesion work of 3C-SiC-V_{C-3}/Mg.

(3) The interfacial adhesion work of 3C-SiC-V_{Si-2}/Mg and 3C-SiC-V_{Si-4}/Mg is less than that of 3C-SiC/Mg, indicating that Si vacancy is not conducive to interfacial bonding. The interface adhesion work of 3C-SiC-V_{Si-2}/Mg is less than the interface adhesion work of 3C-SiC-V_{Si-4}/Mg.

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