First Principle Calculation of Electronic Structure and Stabilities of TiC/Mg Composites Interfaces

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Abstract. The Millken charge of atom, charge density difference and electronic structures of TiC(111)/Mg(0001) with different stacking sequences were studied by the basis of the first-principles calculation method, and the Interfacial wettability and bond strength were evaluated by interfacial adhesion work. The results show that the C-CS(center site)-Mg interface, the C-TS(top site)-Mg interface and Ti-CS-Mg interface is almost no change and the Ti-TS-Mg interface change s into a new Ti-CS-Mg interface after geometry optimization. Compared with the original Ti-CS-Mg interface, the new Ti-CS-Mg interface has a similar ideal work of adhesion and interfacial distance. And the C-CS-Mg interface is the most stable owing to it has the greatest ideal work of adhesion (7.221 J/m²) and the smallest interfacial distance (1.39 Å). The C-CS-Mg and C-TS-Mg interfaces have both covalent bonds and ionic bonds. However, the Ti-CS-Mg interface only has metallic bond.

1. Introduction
In recent years, the magnesium alloy applied in the automotive industry, electronic communication and aerospace industry are common due to its excellent physical and mechanical behavior, such as low weight, great specific stiffness, great specific strength, good damping performance and excellent anti-electromagnetic interference ability, etc. [1]. However, the strength of magnesium composites is relatively low, that greatly limits its further application. According to the mechanism of particle strengthening the mechanical strength of the alloy can be significantly improved by adding reinforced particles. In addition, a large number of studies show that the interface has a significant impact on the properties of metal matrix composites. Therefore, studying interface is very important.

Nowadays, the first-principle calculation method has been widely used to calculate the electronic mechanism and related properties of materials, and a lot of achievements have been obtained in material microstructure simulation, atomic electronic structure analysis and so on [2]. In addition, many scholars have applied it to the study of the interface of metal matrix composites. For example, Mizuno et al. [3] used the first-principle calculation method to study the interface of Fe(001)/TiX(001) (X= C, N, O). The result shows that the atom of Fe/TiX interface is mainly bound by covalent bonds and a few ionic bonds, and when the interface atom is bound by Fe and X, the interfacial bond strength is the highest. Zhang et al. [4] used the first-principle calculation method to study eight staking sequences for Cu(111)/TiC(111) Interface and found that Ti-terminated interface has higher ideal work of adhesion and lower total energy than others. Li et al. [5] used the first-principle calculation method to study seven staking sequences for Mg/ZrB₂ Interface. The result shows that B-terminated interface is the most stable.
At present, it is a hot research topic to analyze the interface of metal matrix composites by using the first-principle calculation method. However, there is no report on the interface of TiC/Mg alloy. In this paper, the plane wave pseudopotential method based on the first-principles density functional theory (DFT) is used to analyze the ideal work of adhesion, the density of states (DOS), charge density difference and electronic structures of TiC(111)/Mg(0001).

2. Model and Theoretical Method

TiC is NaCl structure. The space group of it is Fm3m, and the lattice constant is 4.328 Å. However, Mg is hcp structure, and its primitive cell shape is parallel hexahedral, which is very different from TiC unit cell. So in order to construct a coherent interface, the TiC unit cell must be cut into parallel hexahedral along the (111) plane. In addition, TiC(111) plane is a polar surface that can be cut into different types of termination, and there are several different stacking positions in TiC(111)/Mg(0001) interface. Therefore, four different TiC(111)/Mg(0001) interfaces structure models (see figure 1) can be established to be analyzed by the first-principle calculation method in theory.

![Figure 1. Four different TiC(111)/Mg(0001) interfaces structure: (a) C-CS(center site)-Mg, (b) C-TS(top site)-Mg, (c) Ti-CS-Mg, (d) Ti-TS-Mg.](image)

In this work, all calculations were run by CASTEP, and the exchange and correlation effects was described by using the generalized gradient approximation (GGA) function of Perdew-Burke-Ernzerhof (PBE) [6], and the plane wave ultrasoft pseudopotential was used to express the interaction between ion and valence electrons. The pseudo-potentials based on the electronic configurations of 2p^3s^2 for Mg, 3d^24s^2 for Ti, and 2s^22p^2 for C. The plane-wave cutoff energy was selected as 380 eV. The Brillouin zone was sampled by using 9x9x1. The optimization of interface model was stopped when the change in energy was less than 1.0x10^-6 eV/atom, and the force on each atom was less than 0.03 eV/Å, the residual stress on the unit cell was less than 0.05 GPa. By using these parameters to optimize the structure of TiC and Mg, the lattice constant of TiC is a=4.332 Å, the lattice constant of Mg a=3.22 Å, c=5.17 Å, which is close to the results of Zhang [4] and Li [5]. It provides a reliable theoretical basis for subsequent interface analysis calculations.
3. Results and Discussion

3.1. Model Geometry
After optimization, four kind of the interfacial structure of TiC(111)/Mg(0001) has been changed. The interfacial atoms of C-CS-Mg, C-TS-Mg and Ti-CS-Mg interfaces only move along the direction perpendicular to interface, so that the interface distance is reduced. However, the interfacial atoms of Ti-TS-Mg interface not only move along the direction perpendicular to interface, but also slide along the direction parallel to interface, and form a new CS interface in figure 2. It has been shown that the interfacial atoms move along different directions in the interfacial structure, which is to minimize their reaching more stable position and interfacial energy [7]. Consequently, it can be see that the Ti-TS-Mg interface is unstable.

![Figure 2. Ti-TS-Mg interface before and after optimization.](image)

3.2. The Ideal Work of Adhesion
The ideal work of adhesion $W_{ad}$ is important that can describe the bond strength between the atoms at the interface. $W_{ad}$ can be calculated by the following formula [8]:

$$W_{ad} = \frac{(E_{TiC}^{slab} + E_{Mg}^{slab} - E_{TiC/Mg}^{total})}{A}$$

where $E_{TiC/Mg}^{total}$ is the total energy of TiC(111)/Mg(0001) interface, $E_{TiC}^{slab}$ and $E_{Mg}^{slab}$ are the total energies of individual TiC(111) and Mg(0001) slabs, respectively. $A$ is the interfacial area.

After optimization, the $d_0$ and $W_{ad}$ of C-TS-Mg interface are 2.07 Å and 4.220 J/m², respectively. However, compared with the C-TS-Mg interface, the $d_0$ of C-CS-Mg interface is smaller (1.39 Å) and the $W_{ad}$ is larger (7.221 J/m²). As it is well known, the greater the ideal work of adhesion of the interface is, the stronger the interface is, the better the wettability is, and the less easy the interface is to break. As for Ti-terminated interface, the interfacial distance is larger than that of the C-terminated interface, and the ideal work of adhesion is smaller, that shows the C-terminated interface is more stable than that of Ti-terminated interface. In addition, it is worth mentioning that, compared with the $W_{ad}$ (3.237 J/m²) and $d_0$ (2.56 Å) of Ti-CS-Mg interface, the new Ti-CS-Mg interface formed from the fully relaxed original TS has a slightly lower $W_{ad}$ (3.162 J/m²) and lower $d_0$ (2.51 Å). It is very close to each other.

3.3. Electronic Structure Analysis
So as to probe the interfacial bond between TiC and Mg, the charge density difference of C-CS-Mg and C-TS-Mg and Ti-CS-Mg interfaces were calculated and shown in figure 3a and 3b. As for the C-terminated interface, it can be seen that the interfacial Mg atoms lost the charges, and the charges are transferred to the interfacial C atoms to form covalent and ionic bonds in the interfacial region. At the interfacial region, the charge accumulation is formed, and the charge accumulation of the CS interface is more obvious, which shows that the bond strength of the CS-CS-Mg interface is better than the bond strength of the C-TS-Mg interface. In addition, as can be seen from figures 3d and 3e, there are three C atoms surrounding each Mg atom to form bonds in the CS interface, while each Mg directly sits under a C atom to form bonds in the TS interface. Therefore, the CS interfacial region has more charges than...
TS interfacial region, which means the bond strength of CS interface is higher and it is more stable. Moreover, distributed charges of the CS interface are very obvious directionality, that shows that the covalent bonds are very strong between Mg and C atoms. As for the Ti-terminated interface, the charge density difference of the interfacial Mg atoms is the same as that of the interior Mg atoms, which means there mainly exists metallic bonds between Mg and Ti atoms.

![Figure 3](image)

**Figure 3.** Electron density difference for the TiC(111)/Mg(0001) interfaces: (a) C-CS-Mg, (b) C-TS-Mg, (c) Ti-CS-Mg, (d) the cross section of C-TS-Mg interface, (e) the cross section of C-CS-Mg interface.

| Model     | Sites   | Species | s     | p     | d     | Total   | Charge (e) |
|-----------|---------|---------|-------|-------|-------|---------|------------|
| C-TS-Mg   | Interface | Mg     | 0.76  | 6.84  | 0.00  | 7.61    | 0.39       |
|           | Interface | C      | 1.60  | 3.19  | 0.00  | 4.79    | -0.79      |
|           | 2nd layer | Ti     | 2.43  | 6.55  | 2.62  | 11.60   | 0.40       |
| C-CS-Mg   | Interface | Mg     | 0.59  | 6.65  | 0.00  | 7.24    | 0.76       |
|           | Interface | C      | 1.63  | 3.28  | 0.00  | 4.91    | -0.91      |
|           | 2nd layer | Ti     | 2.45  | 6.56  | 2.62  | 11.63   | 0.37       |
| Ti-CS-Mg  | Interface | Mg     | 0.88  | 7.10  | 0.00  | 7.98    | 0.02       |
|           | Inside    | Mg     | 0.88  | 7.12  | 0.00  | 8.00    | 0.00       |

As can be seen from table 1, for C-terminated interfaces, the Milliken charge of the interfacial C atom in the TS interface (-0.79 e) is higher than that of the internal C atom. It obtains 0.40 e electrons from the Ti atom in the second layer and 0.39 electrons from the interfacial Mg atom. While the Milliken charge of the interfacial C atom in the CS interface is larger than that of the interfacial C atom in the TS interface, and it obtains 0.37 e electrons from the Ti atom of the second layer and 0.76 e electrons from the interfacial Mg atom. That is to say, the covalent bonds between Mg and C atoms in
the CS interface is stronger than that between Mg and C in the TS interface. As for the Ti-CS-Mg interface, the Milliken charge of the interfacial Mg atoms is substantially the same as that of the internal Mg atoms, exhibiting the metallic bonds strongly formed in the Ti-CS-Mg interface.

The atom Mulliken analysis of TiC/Mg interfaces is also consistent with the analysis of its charge density difference. The interfacial bond strength of the Ti-terminated interface is lower than that of C-terminated interface, and the interfacial bond strength of C-CS-Mg interface is the strongest.

4. Conclusions
The ideal work of adhesion, electronic structure and bond characteristics of the TiC(111)/Mg(0001) interface were studied by the first-principle calculation method. After optimization, the Ti-TS-Mg interface cannot exist stably after optimization, and it is transformed into a new Ti-CS-Mg interface. Simultaneously, the $d_0$ and the $W_{ad}$ of the new Ti-CS-Mg interface are the same as that of original interface. The C-CS-Mg interface has the greatest ideal work of adhesion, which shows that it is the most stable structure. The analysis of charge density difference and Milliken charge of atom reveal that the bonds of C-terminated interface are mainly covalent bonds and ionic bonds with a small amount metallic bonds, while the bonds of Ti-terminated interface are mainly metallic bonds.

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