First-principles study on the stability and electronic structure of Mg/ZrB₂ interfaces

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ABSTRACT The geometric optimizations, values of the ideal work of adhesion, interface energies and electronic structures of Mg(001)/ZrB₂(001) interfaces with different stacking sequences (top, center and bridge) were studied by the plane wave pseudopotential method based on the first-principles density functional theory (DFT). The results show that the B-terminated top-site (top1 and top2) interfaces have little change and the B-terminated bridge-site interface transforms into a new B-terminated center-site interface, and both the Zr-terminated top- and bridge-site interfaces transform into new Zr-terminated center-site interfaces after geometry optimizations. The bond lengths of Mg-B, interfacial distances and values of the ideal work of adhesion of the newly formed center-site interfaces and the optimized original center-site interfaces are close to each other. The B-terminated center-site interface is the most stable as it has the largest value of the ideal work of adhesion and the smallest interfacial distance. The values of the ideal work of adhesion of the sub-interface regions indicate that the interfaces can improve the bond strengths of the sub-interfaces in Mg side while weaken those in ZrB₂ side. The B-terminated (Zr-terminated) center-site interface has negative interface energy and can be formed spontaneously in B-rich (poor) environment. The B-terminated center- and top-site interfaces have both ionic bonds and covalent bonds which exhibit strong directionality in the B-terminated center-site interface. ZrB₂ particles are suitable to be used as effective nucleants to refine the grain size of Mg alloy or as reinforcements to prepare Mg matrix composites due to the strongly bonded Mg/ZrB₂ interfaces.

Keywords: Mg/ZrB₂ interface, density functional theory, ideal work of adhesion

INTRODUCTION

Nowadays, with the rapid development of industry, people become more and more interested in environment protection and energy savings. The light-weight materials applied in the automobile and aerospace industry are particularly important. Pure magnesium and magnesium alloys develop fast due to their excellent mechanical and physical properties, such as low density, high strength-to-weight

ratio, high stiffness, high damping capacity, good elastic modulus, good castability and unique biodegradability in the physiological environment [1–4]. However, their applications are limited by the poor high-temperature strength and creep resistance.

To improve the strength of magnesium alloy, it is a reliable way to refine the grain size using effective nucleants during the casting process. ZrB₂ nanoparticle are such effective nucleants and they are capable of inducing finer long-period stacking ordered phase (nano-LPSO-layer) formation due to the nano-surface effect and finally resulting in the formation of nanograins in magnesium alloys [5]. Also, it is a suitable way to improve the magnesium alloys' stiffness, elastic modulus and wear resistances by preparing particle reinforced magnesium matrix composites since ceramic particles have high strength, hardness and high-wearing features [6,7]. Compared with SiC and TiC particles, ZrB₂ particle reinforced magnesium-based composites fabricated by a direct melt-mixing method [8] have the best strength [9]. The stress transfers from Mg matrix to ZrB₂ reinforcement through the ZrB₂/Mg interface, and the micro-hardness, fatigue resistance and friction factor of the composites are directly affected by interface bonding [10,11].

Up to now, it is known that for effective heterogeneous nucleants in magnesium melt or effective reinforcements in particle reinforced magnesium matrix composites, the lattice mismatch and the chemical interaction play important roles in the overall interfacial energy [12]. And, the ZrB₂/Mg interface will seriously influence the nucleating in Mg melt [5] or the strength of the composites [13]. Hence, the main purpose of this work was to investigate the mechanism of interface bonding of Mg/ZrB₂ in atomic level and help to improve the mechanical properties of the material.

First-principles calculation is a powerful method to provide fundamental information at atomic or electronic level. Generally, (001) plane is a stable low index plane for

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hexagonal crystals. Mg(001) and ZrB₂(001) surfaces have been widely investigated [14,15], and the lattice constant of Mg(001) closely matches that of ZrB₂(001). Therefore, Mg(001)/ZrB₂(001) interface was proposed in this paper, and to better understand its interface bonding behavior, the geometric optimization, ideal work of adhesion, interface energy and electronic structure of the interface were obtained by the plane wave pseudopotential method based on the first-principles density functional theory (DFT).

METHODOLOGY

Our calculations were carried out using the DFT with a plane-wave basis set as implemented in the Cambridge Sequential Total Energy Package (CASTEP) computer code [16,17]. The core electrons were treated with the ultrasoft pseudopotentials [18]. The generalized gradient approximation (GGA) function of Perdew-Burke-Ernzerhof (PBE) [19] was chosen to treat the exchange and correlation effects. In these calculations, the following basis sets were adopted: the 2p⁶ 3s² states of Mg were treated as valence states, while for Zr and B we used 4s² 4p⁶ 4d² 5s², and 2s² 2p¹, respectively. The plane wave basis set was truncated at a kinetic energy of 450 eV and the Brillouin zone of each bulk structure was sampled by a *k*-point mesh with a spacing of 0.03 nm⁻¹, as generated by the Monkhorst-Pack scheme [20]. The optimization of atomic positions and unit cell was stopped when the change in energy was less than 5×10⁻⁶ eV/atom, the force on each atom was less than 0.01 eV Å⁻¹, the residual stress on the unit cell was less than 0.02 GPa, and the displacements were less than 5×10⁻⁶ Å.

BULK AND SURFACE CALCULATIONS

Bulk properties

The calculations on bulk properties of Mg and ZrB₂ were firstly carried out by GGA (PBE) and LDA (CAPZ) [18]. Mg has a hexagonal crystal structure of space group *P63/mmc* (No. 194). The bulk ZrB₂ consists of alternating hexagonal layers of Zr atoms and B honeycomb layers with the

space group symmetry *P6/mmm* (No. 191). The calculated lattice parameters (*a*, *c*) and bulk modulus (*B*) of Mg and ZrB₂ are shown in Table 1. It can be seen that the lattice constants calculated by LDA (CAPZ) are rather smaller than the corresponding ones calculated by GGA which is consistent with the so called “LDA (CAPZ) over-binding effect” in the calculations of other systems [21]. The lattice constants calculated by GGA (PBE) are closer to the experimental results, and are also consistent with other calculated ones. For the bulk Mg, the calculated lattice constants are *a*=3.222 Å and *c*=5.170 Å, which are in good agreement with other theoretical results in [22,23] and the experimental results in [24]. For the bulk ZrB₂, the calculated lattice constants are *a*=3.168 Å and *c*=3.536 Å, which are in good agreement with other theoretical results in [25,26] and the experimental results in [27]. Therefore, the GGA (PBE) method was adopted in our calculations.

Surface properties

To make sure that both sides of the surface slabs of Mg(001) and ZrB₂(001) are thick enough to show the bulk-like interior, the convergence tests on Mg(001) and ZrB₂(001) surfaces with different thickness were carried out firstly. A vacuum region at least 15 Å thick was employed in the super cells [28]. The surface energies of Mg(001) and ZrB₂(001) surfaces were calculated using the method proposed by Boettger [29]. When a Mg(001) surface contains more than nine atomic layers, its surface energy converges to a fixed value 0.47 J m⁻², which is close to the result in [30]. The surface energy of a ZrB₂(001) surface containing more than six atomic layers converges well to a fixed value 3.88 J m⁻². It is worthwhile to mention that a ZrB₂(001) slab has Zr- and B-terminated surfaces at the top and the bottom sides, respectively. The surface energy calculated by the method of Boettger is the average value of the two stoichiometric terminated surfaces, namely $\sigma_s^{\text{ZrB}_2} = (\sigma_s^{\text{Zr}} + \sigma_s^{\text{B}})/2 = 3.88 \text{ J m}^{-2}$.

In order to calculate the surface energies of the B- and Zr-terminated ZrB₂(001) surfaces, the chemical potentials

Table 1 Bulk properties of Mg and ZrB₂ (the lattice constant *a*, *c* and bulk modulus *B*)

		Mg			ZrB ₂		
		<i>a</i> (Å)	<i>c</i> (Å)	<i>B</i> (GPa)	<i>a</i> (Å)	<i>c</i> (Å)	<i>B</i> (GPa)
This work	GGA(PBE)	3.222	5.170	36.3	GGA(PBE)	3.168	3.536
	LDA(CAPZ)	3.160	5.074	38.0	LDA(CAPZ)	3.128	3.484
Others	GGA [22]	3.209	5.188	35.4	LDA [25]	3.170	3.533
	GGA [23]	3.21	5.202	34.0	GGA [26]	3.170	3.548
	Exp. [24]	3.209	5.211	35.4	Exp. [27]	3.1652	3.5242
							215 [26]

of bulk ZrB_2 ($\mu_{\text{ZrB}_2}^{\text{bulk}}$) and B atom ($\mu_{\text{B}}^{\text{slab}}$) in the surface slab should be considered [31], and the corresponding process can be found in [15,32]. The calculated formation heat $\Delta H_f^0(\text{ZrB}_2)$ of bulk ZrB_2 at 0 K in our work is -3.108 eV, which is very close to -3.019 eV in [15]. In B-rich environment, when the Zr- and B-terminations contain more than seven atomic layers, their surface energies respectively converge to the fixed values of 4.66 and 3.12 J m^{-2} . The surface energies of $\text{ZrB}_2(001)$ surface with seven atomic layers are also shown as the function of chemical potential $\mu_{\text{B}}^{\text{slab}} - \mu_{\text{B}}^{\text{bulk}}$ in Fig. 1. From Fig. 1, the B-termination has smaller surface energies than the Zr-terminations in the range of -0.4 to 0 eV, meaning that the B-termination is more stable than the Zr-terminations in B-rich environment. In the range of -1.5 to -0.4 eV, the stabilities of the B- and Zr-terminations increase as the opposite-side. At the same time, it can be found that the average surface energy of the two different nonstoichiometric terminations is $(4.66+3.12)/2=3.89$ J m^{-2} , which agrees with the previous average surface energy 3.88 J m^{-2} calculated by the method of Boettger. Finally, nine atomic layers for Mg(001) surface and seven atomic layers for $\text{ZrB}_2(001)$ surface were reasonably adopted to build the interface models.

INTERFACE

Model geometry

Both the Zr-terminated and B-terminated $\text{ZrB}_2(001)$ surfaces were employed in building the Mg/ ZrB_2 interface models, and the possible positions of Mg atoms in Mg(001) surface on $\text{ZrB}_2(001)$ surface were considered in the calcu-

Figure 1 The relation between $\text{ZrB}_2(001)$ surface energies and the difference of B chemical potential ($\mu_{\text{B}}^{\text{slab}} - \mu_{\text{B}}^{\text{bulk}}$)

lations. When the interfacial Mg atoms directly sit above Zr or B atoms in ZrB_2 slab, it is named as Zr-terminated top-site interface (see Fig. 2a) or B-terminated top-site interface, respectively. Due to the special sites of Zr atoms in the second layer of B-terminated ZrB_2 slab, there are two top sites for Mg atoms. One is that Mg atoms in the second layer of Mg slab locate on the top of B atoms in the first layer of ZrB_2 slab, and the other is that Mg atoms in the second layer of Mg slab sit on the top of Zr atoms in the second layer of ZrB_2 slab, namely B-terminated top1- and top2-site interfaces (see Figs 2d and e), respectively. If the interfacial Mg atoms locate on the top of B or Zr atoms in the second layer of ZrB_2 slab, they are named as Zr- or B-terminated center-site interface (see Figs 2b and f). When the interfa-

Figure 2 Seven stacking sequences for Mg/ ZrB_2 interface models: (a) Zr-terminated top-site, (b) Zr-terminated center-site, (c) Zr-terminated bridge-site, (d) B-terminated top1-site, (e) B-terminated top2-site, (f) B-terminated center-site, and (g) B-terminated bridge-site.

cial Mg atoms locate in the middle of the interfacial Zr or B atoms of Zr- or B- terminated ZrB_2 slab, they are presented as Zr- or B- terminated bridge-site interface (see Figs 2c and g). Consequently, seven different Mg/ ZrB_2 interfacial structures have been investigated, as shown in Fig. 2. The crystal lattice parameters of these interface models are defined as the average of those of Mg(001) and ZrB_2 (001) slabs to minimize the lattice mismatch. The lattice mismatches, 0.85% for Mg(001) slab and 0.83% for ZrB_2 (001) slab, are less than 5%. During the calculations, a vacuum layer of 15 Å thick has been used to avoid interactions in Mg/ ZrB_2 interface models.

The interface structures were optimized within a fixed cell volume due to that the ideal work of adhesion is not very sensitive to the lattice distortions [33,34]. All atoms in the interface models are allowed to relax in the three directions, and the relaxed interface structures are shown in Fig. 3. After optimization, the interfacial atoms of Zr-terminated center-site interface only move along the direction perpendicular to the interface. The interfacial atoms of Zr-terminated top- and bridge-site interfaces glide along the direction perpendicular to the interfaces with parallel movements and form “new” center-site interfaces. The interfacial atoms of B-terminated top2- and center-site interfaces mainly move along the directions perpendicular to

the interfaces. The interfacial atoms of B-terminated top1-interface move along not only the direction perpendicular to the interface but also the direction parallel to the interface. As for the B-terminated bridge-site interface, it will change into a “new” center-site interface structure with the perpendicular movements of the interfacial atoms, which is similar to those of the Zr-terminated bridge- and top-site interfaces. As it is well known, the interfacial atoms in an interface mode move along different directions to achieve their more stable positions and the minimum total energy of the interface [35]. It means that the Zr-terminated center-site interface is more stable than the Zr-terminated bridge- and top-site interfaces, whereas the B-terminated top- and center-site interfaces are more stable than the B-terminated bridge-site interface.

Work of adhesion and interfacial energy

The ideal work of adhesion W_{ad} is defined as the bond energy needed to separate an interface into two free slabs. Although the ideal work of adhesion is lower than the actual mechanical work to separate an interface due to neglect of the interfacial plasticity and diffused degrees of freedom [36], it is still an important and convenient factor to predict the mechanical properties and the chemical bonding strength of an interface [37,38]. W_{ad} is calculated by the

Figure 3 Schematic illustration of the interfacial atomic sites in the interfacial structures. The left are the original states and the right are the relaxed interfaces. (a) Zr-terminated top-site, (b) Zr-terminated center-site, (c) Zr-terminated bridge-site, (d) and (e) B-terminated top-sites, (f) B-terminated center-site and (g) B-terminated bridge-site.

following equation:

$$W_{\text{ad}} = -[E_{\text{Mg/ZrB}_2} - E_{\text{Mg}} - E_{\text{ZrB}_2}]/A, \quad (4)$$

where $E_{\text{Mg/ZrB}_2}$ is the total energy of Mg/ZrB₂ supercell in vacuum, E_{Mg} (E_{ZrB_2}) is the total energy when ZrB₂ (Mg) side in the interface model is replaced by a vacuum, and A is the area of Mg/ZrB₂ interface. The ideal work of adhesion gives the direct information regarding the strength and bonding of the interface.

The interfacial distances d_{int} , bond lengths d_{bond} of Mg–Zr for Zr termination and Mg–B for B termination and ideal work of adhesion W_{ad} are summarized in Table 2. It shows that the initial Zr-terminated top-site and bridge-site interfaces will change into a new stacking sequence during the geometric optimization, as is same to the initial Zr-terminated center-site interface. However, compared with the ideal work of adhesion of the fully relaxed original center-site interface which is 2.632 J m^{−2}, the “new” center-site interfaces formed from the fully relaxed top-site and bridge-site interfaces respectively have a slightly higher W_{ad} (2.650 J m^{−2}) and a lower W_{ad} (2.629 J m^{−2}). The “new” and fully relaxed original Zr-terminated center-site and interfaces have almost the equal interface distances d_{int} and bond lengths d_{bond} of Mg–Zr. W_{ad} of the B-terminated top1- and top2-sites are 2.775 and 2.740 J m^{−2}, respectively, very close to each other, although these two top-site stacking sequences have a little difference. W_{ad} of the B-terminated center-site interface (3.808 J m^{−2}) is slightly lower than that of the B-terminated bridge-site interface (3.823 J m^{−2}) and, however, both these values are significantly much higher than those of Al/ZrB₂ interface (2.01 J m^{−2}) [39] and Mg/Al₄C₃ interface (1.968 J m^{−2}) [40]. The interface distances d_{int} of the B-terminated center-site and bridge-site interfaces are 1.720 and 1.714 Å, respectively. The bond lengths of B–Mg for the B-terminated center-site interface (2.533 Å) and the “new” center-site interface (2.524 Å) are close to that of B–Zr (2.544 Å) in bulk ZrB₂. The B-terminated center-site interface (see Fig. 2f) shows that the interfacial Mg atomic position in the B-terminated center-site interface is very close to Zr atoms of bulk ZrB₂, and this correspondingly results in the increased W_{ad} . This phenomenon also occurs in SiC/Ti [41], W/WC [42] and SiC/TiC [43] interfaces. Overall, after geometry optimization, the Zr-terminated top-, center- and bridge-site interfaces transform into the “new” center-site interfaces which almost have the same properties such as the atomic structure, interface distance d_{int} , bond length d_{bond} and ideal work of adhesion W_{ad} . In a similar way, the B-terminated center- and bridge-site interfaces transform into the “new” center-site interfaces with nearly the same properties. Generally, the smaller the

Table 2 Interfacial distances d_{int} , bond lengths d_{bond} of Mg–B for the B terminations and Mg–Zr for the Zr terminations, and ideal work of adhesion W_{ad}

Termination	Stacking	d_{int} (Å)	d_{bond} (Å)	W_{ad} (J m ^{−2})
Zr	Top	2.650	3.194	2.650
	Center	2.632	3.215	2.632
	Bridge	2.590	3.214	2.629
B	Top1	2.277	2.295	2.775
	Top2	2.156	2.277	2.740
	Center	1.720	2.533	3.808
	Bridge	1.714	2.524	3.823

bond length is, the bigger W_{ad} is. From the model geometries above and the ideal work of adhesion, the B-terminated top1- and center-site interfaces and the Zr-terminated center-site interface have relatively stable structures, and therefore these three interfacial structures will be further investigated in the following.

In order to understand the interface effects, W_{ad} of another two interfacial regions, namely region-1 and region-2 shown in Fig. 2, were calculated and listed in Table 3. For comparison, W_{ad} of (001) surfaces of the bulk Mg and ZrB₂ were also calculated. From Table 3, one can see that Mg/ZrB₂ interface definitely affects the regions near the interface. The B-terminated center-site interface has great influence on region-1 and region-2, since W_{ad} of region-1 in Mg side is 1.422 J m^{−2}, which is much larger than 1.056 J m^{−2} of Mg(001), while that in region-2 in ZrB₂ side is 6.930 J m^{−2}, which is less than 8.072 J m^{−2} of ZrB₂(001). Similarly, Mg/ZrB₂ interfaces regarding to the B-terminated top-site and Zr-terminated center-site also can enhance W_{ad} of region-1 in Mg side but reduce that of region-2 in ZrB₂ side. That is to say, the interfaces can improve the bond strength of region-1 in Mg side while weaken the bond strength of region-2 in ZrB₂ side. However, the weakened bond strength of region-2 in ZrB₂ side is still much higher than that of region-1 in Mg side. This strongly proves that ZrB₂ particulates can be used to prepare Mg matrix composites with enhanced interfaces.

Although the calculations were performed at $T = 0$ K, it

Table 3 Ideal work of adhesion W_{ad} (J m^{−2}) of region-1 and region-2 for the Zr-terminated center-site interface and the B-terminated center- and top1-site interfaces

	B-top1	B-center	Zr-center	Mg	ZrB ₂
Region-1	1.298	1.422	1.268	1.056	8.072
Region-2	7.626	6.930	7.971		

has been confirmed that the calculated results are credible in solids at $T > 0$ K as detailed in [44], in which, it was revealed that the trends in interface stability are not significantly affected by temperature [45]. The interface energy γ_{int} is calculated by $\gamma_{\text{int}} = (\sigma_{\text{Mg}} + \sigma_{\text{ZrB}_2}) - W_{\text{ad}}$ [46], and the larger W_{ad} is, the smaller the interface energy is. From the calculated results in Fig. 4, in B-poor environment, the interface energies are 3.685, 2.652 and -0.372 J m $^{-2}$ for the B-terminated top1- and center-site interfaces and the Zr-terminated center-site interface, respectively. The Zr-terminated center-site interface has a negative interface energy of -0.732 J m $^{-2}$, indicating that it can spontaneously form the most stable interface structure in B-poor environment. In B-rich environment, the interface energies are 0.818, -0.215 and 2.485 J m $^{-2}$ for the B-terminated top1- and center-site interfaces and the Zr-terminated center-site interface, respectively. The B-terminated center-site interface also has negative interface energy, suggesting that it can spontaneously form the most stable interface structure in B-rich environment. However, the B-terminated top1-site interface is unstable even in very B-rich or B-poor chemical environments. Furthermore, the formation energy $\Delta H_f = E_{\text{MgB}_2}^{\text{bulk}} - 2E_{\text{B}}^{\text{bulk}} - 2E_{\text{Mg}}^{\text{bulk}}$ for the reaction $\text{Mg} + 2\text{B} \rightarrow \text{MgB}_2$ is -1.507 eV at 0 K, which is the same to [47], suggesting that the reaction product MgB_2 can easily form on Mg/ZrB_2 interfaces and play an important role in Mg/ZrB_2 interfacial behavior.

Electronic structure

The interface mechanical strength is closely related to the interfacial atomic bonding. In order to explore the interfacial bonding between Mg and ZrB_2 , the interfacial charge

Figure 4 The relation between Mg/ZrB_2 interface energies and B chemical potential difference $\mu_{\text{B}}^{\text{slab}} - \mu_{\text{B}}^{\text{bulk}}$.

density, charge density difference and layer-projected density of states of the B-terminated center-site and top1-site interfaces and the Zr-terminated center-site interface were calculated and shown in Fig. 5. One can see that the charges accumulated on the interfaces can form chemical bonds. The B-terminated center-site interface accumulates the largest amount of charges, while the Zr-terminated center-site interface accumulates the smallest ones. For the two B-terminated interfaces, the charge distributions between B and Mg atoms are directional, and simultaneously the B-terminated center-site interface has much stronger directional charge distribution, reflecting the covalent bonding feature. The B-terminated center-site interface has the strongest polar covalent bonds, causing the stronger interaction between Mg and B atoms near interface hence yielding the largest W_{ad} value.

Figure 5 The interfacial charge density of (a) B-terminated center-site, (b) B-terminated top1-site and (c) Zr-terminated center-site interfaces.

In Figs 6a and b, for the B-terminated center-site and top1- interfaces, the lost charges of interfacial Mg atoms transfer to the interfacial region and mix with the charges from interfacial B atoms, presenting the localized features and forming the covalent/ionic bonds at the interfaces. Simultaneously, Mg atoms in the center-site interface lose more charges than those in the top1-site interface, revealing the stronger ionic character. In addition, from Figs 6a and b, the charge accumulation in the B terminated center-site interface is lower than that in the B-terminated top1-site interface. However, from Figs 6d and e, it is worth noting that six identical B atoms distribute around each Mg atom to form bonds in the center-site interface, whereas four B atoms (one B atom directly sits under a Mg atom and other three identical B atoms distribute around the Mg atom) around each Mg atom form bonds in the top1-site interface. Consequently, the center-site interface actually obtains more charges than the top1-site interface, and the directivity of the distributed charges of the center-site interface is exceedingly distinct, exhibiting the covalent bonds strongly formed between Mg and B atoms. For the Zr-terminated center-site interface, the charge density difference of each interfacial Mg atom is almost the same as that of each interior Mg atom, implying the feature of metallic bonding as shown in Figs 6c and f. In addition, the

charges of interfacial Zr atoms and sub-interfacial B atoms rearrange slightly due to the interfacial influence.

To further study the bonding characteristics of Mg/ZrB₂ interfaces, the partial density of states (PDOSs) of the B-terminated center-, top1-site and Zr-terminated center-site interfaces are shown in Fig. 7, respectively. The PDOSs of interfacial Mg atoms of the B-terminated center-site interface and the B-terminated top1-site interface have new states in low energy region. The new state begins from -13.25 eV in the center-site interface, while it begins from -12.76 eV in the top1-site interface. Besides, there are overlaps in B and Mg layers of the interfaces. There exist nine major peaks at -11.556 , -10.732 , -6.63 , -5.88 , -5.03 , -3.83 , -2.98 , -2.08 and -1.2 eV for the center-site interface, however, only four major peaks at -10.096 , -3.25 , -2.12 and -0.67 eV in the top1-site interface. That is to say, the orbital hybridization of interfacial Mg and B atoms in the center-site interface is stronger than that in the top1-site interface, and it is also in accord with the previous analysis of charge density difference. For the B-terminated center-site interface, the DOS is not zero at the Fermi level and the PDOS of interfacial Mg layer slightly depletes, displaying the metallic and ionic features. Overall, the B-terminated interfaces mainly consist of covalent and ionic bonds with a small number of metallic bonds. For the Zr-terminated

Figure 6 Charge difference density: (a) B-terminated center-site, (b) B-terminated top1-site and (c) Zr-terminated center-site interfaces along (110) plane; (d) B-terminated center-site, (e) B-terminated top1-site and (f) Zr-terminated center-site interfaces along (001) plane $1.2 \text{ \AA}$ above the B atomic layer.

Figure 7 PDOS of (a) B-terminated center-site, (b) B-terminated top1-site and (c) Zr-terminated center-site Mg/ZrB₂ interfaces.

center-site interface, the PDOS of the interfacial Zr atoms moves to the right due to the influence of the interfacial Mg atoms, and some overlapped peaks of the PDOSs of the interfacial Mg and Zr atoms appear apparently near Fermi level with the charges depleting near Fermi level. Correspondingly, the Zr-terminated center-site interface has strong metallic bonds. These results indicate that the B-terminated center interface has stronger chemical bonds and stronger W_{ad} than other interfaces.

CONCLUSIONS

The geometric optimization, ideal work of adhesion, in-

terface energies and electronic structures of Mg(001)/ZrB₂(001) interface were studied by first-principles based on DFT. B- and Zr-terminations of ZrB₂(001) surface with different stacking sequences (top-, center- and bridge-sites) were considered. During the geometry optimization, the B-terminated bridge-site interface changes into the original B-terminated center-site interface, and the Zr-terminated top- and bridge-site interfaces transform into the original Zr-terminated center-site interface. The ideal work of adhesion of the B-terminated interfacial structures (four models in our work) are larger than those of the Zr-terminated interfacial structures (three models in our work).

The B-terminated center-site interface has the largest ideal work of adhesion, indicating that it is the most stable structure. In B-rich environment, the B-terminated center-site interface has negative interface energy and it can be formed spontaneously, and so can the Zr-terminated center-site interface in B-poor environment. The Mg/ZrB₂ interfaces can significantly enhance the ideal work of adhesion of Mg side and reduce that of ZrB₂ side near the interfaces. The analysis of electronic structure reveals that the bonds of the B-terminated center-site interface are mainly covalent, ionic and weak metallic, and the bonds of the Zr-terminated center-site interface are mainly metallic. In summary, theoretically it is a good choice to use ZrB₂ particulates as an effective nucleant to refine the grain size of Mg alloy during casting process or as reinforcements to prepare the magnesium matrix composites, which has been confirmed by other experimental work.

Received 11 December 2015; accepted 20 January 2016;
published online 29 January 2016

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Acknowledgments This work was supported by the National Natural Science Foundation of China (51171156) and the Fundamental Research Funds for the Central Universities (XDJK2014C008).

Author contributions Cheng N proposed the idea of this work. Li X, Li C, Shao D, Chen J, Wang P and Jia Z carried out the calculation. Li X and Hui Q wrote the manuscript. Cheng N, Hui Q, Chen Z and Li C revised it.

Conflict of interest The authors declare that they have no conflict of interest.

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Mg/ZrB₂界面稳定性和电子结构第一性原理研究

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摘要 本文采用平面波密度泛函理论研究了Mg(001)/ZrB₂(001)界面的分离功、界面能和电子结构。首先通过界面结构优化可知, B终端的顶位界面结构几乎不发生改变; 而B终端的桥位界面结构转变为B终端的中心位界面结构。另外, Zr终端的顶位界面结构和Zr终端的桥位结构都转变为Zr终端的中心位界面结构, 新形成的B终端中心界面结构中的Mg–B键的长度、界面距离、分离功与初始的B终端中心界面结构几乎相同。B终端中心位界面结构有最大的分离功, 同时有最小的界面距离, 因此B终端中心位界面结构是最稳定的界面结构。次界面位置的分离功表明Mg(001)/ZrB₂(001)界面增强了Mg端的结合强度, 削弱了ZrB₂端的结合强度。B终端中心位的界面结构和Zr终端中心界面可以自发形成是由于它们在富B和在贫B环境中分别有负的界面能。在B终端中心位和顶位界面结构中, 界面处有共价键和离子键形成, 而且B终端中心位界面结构的共价键方向性更强。结果表明, ZrB₂颗粒可以用来增强Mg合金。