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Interfacial stability, electronic structure and bond characteristics of Pt_3Zr (1 1 1)/Pt(1 1 1) interfaces: A first-principles study

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ABSTRACT

Interfacial behavior plays a crucial role in fracture toughness of the high-temperature materials. To explore the fracture toughness of Pt_3Zr/Pt, the surface energy, adsorption energy, interfacial energy, bond characteristics and electronic structure of Pt_3Zr(1 1 1)/Pt(1 1 1) interface are investigated by first-principles calculations. Four different interfacial models are considered in detail. The calculated adsorption energy shows that the atomic configuration in model 2 exhibits the strongest bonding energy at the interface. The calculated interfacial energy of model 2 (-6.066 J/m^2) is smaller than that of other models, indicating that this interface has strong interfacial stability in comparison with other models. It is concluded that the interfacial stability of those interfaces is derived from atomic arrangement and localized hybridization at the interface. In particular, the bonding state at the interface is contributed by Pt–Zr and Pt–Pt metallic bonds.

1. Introduction

For high-temperature structural materials, the operation temperature and strength must be considered. Among these materials, Pt-based alloys are promising candidates for high-temperature applications because of their excellent physical and mechanical properties such as high melting-point, high strength, excellent oxidation and corrosion resistances [1–6]. Some early studies have shown that the operation temperature of Pt–Zr alloys is much higher than that of Ni-based superalloys [7,8]. In particular, the melting-point of Pt_3Zr is about of 2523 K, which is larger than that of other Pt-based alloys. On the other hand, our previous work further found that the Pt_3Zr with cubic $L1_2$ structure shows high bulk modulus (275 GPa) and shear modulus (129 GPa) [9]. Therefore, these results indicated that the Pt_3Zr has attracted considerable attention in recent years.

For Pt_3Zr, however, the nature of fracture mechanism remains a big challenge because the first-principles calculations are not consistent with the experimental results [9,10]. Some experiments have reported that the Pt_3Zr exhibits the poor ductility and low fracture toughness at low temperature. Thus, the fracture behavior of this alloy may be related to other factors. It is worth noticing that the single phase Pt_3Zr is difficult to synthesize under ambient condition. Fairbank and Humphreys [11] have reported that the prepared Pt_3Zr sample includes the $L1_2$ ($AuCu_3$) and DO_{24} (Ni_3Ti) structures, and the Pt–12.8% Zr alloy has two different solid solutions such as α and β precipitates. Stalick and Waterstrat [10] have pointed out that the Pt-rich Pt–Zr alloy forms two different structures: Pt_3Zr with $L1_2$ structure and Pt solid solution. For these compounds, fracture behavior strongly depends on the interfacial microstructure between two phases. In other words, the interfacial structure plays an important role in fracture toughness because the interfacial feature determines the stress relaxation, the plastic deformation and the formation of crack. For Pt_3Zr, unfortunately, the atomic interaction at the interface is currently not entirely clear. Therefore, further research is necessary to understand the interfacial structure at atomic level.

As we known, the first-principles calculation is a powerful tool to study the interfacial information under the atomic level or even electronic level, which accurately estimate the adsorption strength, interfacial stability and fracture toughness and so on. In this present paper, the bulk properties, surface behavior, interfacial energy, bond characteristics and electronic structure of Pt_3Zr/Pt were investigated by first-principles approach. The purpose of this work is to reveal the interfacial relationship between Pt_3Zr and Pt solid solution.

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2. Computational method

All calculations were performed by using density functional theory (DFT), as implemented in the CASTEP code [12]. Exchange correlation functional was treated by the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) [13]. The interactions between ionic and valance electron were described by ultrasoft pseudopotential [14]. The electronic configurations of Pt atom and Zr atom were $5p^6 5d^9 6s^1$ and $4p^6 4d^2 5s^2$, respectively. The ground state was found by Kohn–Sham equation with the self consistent field (SCF) to carry out the electronic minimization, and the SCF convergence was less than 1.0×10^{-6} eV/atom. During the structural optimization, Forces on atoms were calculated through the Hellmann–Feynman theory as the partial derivatives of the free energy with respect to the atomic position. The force was smaller than 0.01 eV/Å and the total energy was lower than 10^{-6} eV/atom.

For bulk materials such as Pt, Zr and Pt_3Zr, the cutoff energy of plane wave was chosen at 400 eV. Integrations in the Brillouin zone were performed by using special *k*-points generated with $16 \times 16 \times 16$, $18 \times 18 \times 12$ and $16 \times 16 \times 16$ mesh grids for Pt, Zr and Pt_3Zr, respectively. For surfaces and interfaces, the cutoff energy of plane wave was chosen at 350 eV. Integrations in the Brillouin zone were performed by using special *k*-points generated with $6 \times 6 \times 4$ mesh grids. Those set of parameters were adopted based on the convergence test. Surfaces and interfaces were modeled by using the supercell approach with periodic boundary conditions.

3. Results and discussion

3.1. Bulk materials

To evaluate the interfacial properties, we firstly calculated and discussed the bulk properties of Pt, Zr and Pt_3Zr, respectively. The calculated lattice parameter, density, formation enthalpy, bulk modulus, shear modulus and Young's modulus of bulk Pt, Zr and Pt_3Zr are listed in Table 1. According to the first-principles calculations, the structural stability is measured by formation enthalpy. The equation is given by:

$$\Delta H(Pt_3Zr) = E^{bulk}_{Pt3Zr} - 3E_{Pt} - E_{Zr} \quad (1)$$

where E^{bulk}_{Pt3Zr}, E_{Pt} and E_{Zr} are the total energy of bulk Pt_3Zr, Pt with cubic structure and Zr with hexagonal structure at ground state, respectively.

For elastic modulus, the bulk modulus (B) and shear modulus (G) were calculated according to the Voigt–Reuss–Hill (VRH) approximation method [15]. Therefore, the Young's modulus (E) is obtained by:

$$E = \frac{9BG}{3B + G} \quad (2)$$

To the best of our knowledge, Pt is known as a cubic structure in the Fm-3m (No.: 225) symmetry, with lattice parameter, a = 3.924 Å [16,17]. Zr in a hexagonal structure (group space: P63/mmc, No.: 194), with lattice parameters a = 3.234 Å and c = 5.168 Å [18]. Pt_3Zr belongs to the cubic structure (group space: Pm-3m, No.: 221), with lattice parameter, a = 3.990 Å [11]. As listed in Table 1, the calculated lattice parameters of Pt, Zr and Pt_3Zr are in good agreement with the previous experimental data and theoretical results [11,16–18]. Moreover, the calculated formation enthalpy of Pt_3Zr (−7.271 eV/atom) is lower than that of Pt and Zr, indicating that the former is more thermodynamic stable than the latter. On the other hand, the calculated bulk modulus, shear modulus and Young's modulus of Pt_3Zr are 232 GPa, 105 GPa and 274 GPa, respectively. Although the bulk modulus of Pt_3Zr is slightly lower than that of Pt, the shear modulus and Young's modulus of Pt_3Zr are obviously larger than that of Pt. Therefore, it is concluded that alloying can improve the Pt's shear deformation resistance and enhance the elastic stiffness.

Fig. 1 shows the calculated density of states (DOS) of Pt, Zr and Pt_3Zr, respectively, and the black vertical dashed of DOS represents the Fermi level (E_F). It can be seen that the DOS profile of Pt_3Zr is contributed by Pt-5*d* state and Zr-4*d* state, implying that the strong hybridization between Pt atom and Zr atom, forming the Pt–Zr metallic bond along the *d*–*d* direction. In addition, the calculated bond length of Pt–Zr bond is 2.867 Å, which is in excellent agreement with our previous theoretical result (2.814 Å) [9].

Table 1
Calculated lattice parameters, *a*- and *c*-axis (Å), density, ρ (g/cm^{-3}), formation enthalpies, ΔH (eV/atom), bulk modulus, B (GPa), shear modulus, G (GPa) and Young's modulus, E (GPa) of Pt, Zr and Pt_3Zr, respectively.

Phase	Method	*a*	*c*	ρ	ΔH	*B*	*G*	*E*
Pt	GGA	3.998		20.27	−5.904	258	57	159
	Exp[a]	3.924				261		
	GGA[b]	3.985				265	53	
Zr	GGA	3.230	5.173	6.48	−6.967	92	35	93
	GGA[c]	3.234	5.168					
Pt_3Zr	GGA	4.055		16.85	−7.271	232	105	274
	Exp[d]	3.990						

[a] Ref. [16].
[b] Ref. [17].
[c] Ref. [18].
[d] Ref. [11].

3.2. Interfacial properties

Based on the lattice mismatch, the obtained lattice parameter of $Pt_3Zr(1\,1\,1)$ surface (a = 5.643 Å) is close to the supercell of Pt(1 1 1) surface (a = 5.549 Å), and the lattice mismatch of $Pt_3Zr(1\,1\,1)$/Pt (1 1 1) interface is about of 1.66%. Therefore, the $Pt_3Zr(1\,1\,1)$ and Pt(1 1 1) surfaces are adopted in order to investigate the interfacial properties between Pt_3Zr and Pt solid solution. According to the structural feature of surface, two main classes of (1 1 1) surface terminations ($Pt_3Zr(1\,1\,1)$ and Pt(1 1 1)) were considered in this paper. All atoms at surfaces and interfaces were relaxed during the geometry optimization. Thus, the interlayer relaxations for both surface terminations were converged when the number of atomic layer is more than seven. Four different interfacial models of $Pt_3Zr(1\,1\,1)$/Pt (1 1 1) interface are shown in Fig. 2.

Before estimating the interfacial properties of $Pt_3Zr(1\,1\,1)$/Pt (1 1 1) interface, the surface structures of $Pt_3Zr(1\,1\,1)$ (see Fig. 2 (a) and (c)) and Pt(1 1 1) (see Fig. 2(a) and (b)) were firstly studied. To obtain the stable surface structure, the surface energy of Pt_3Zr (1 1 1) and Pt(1 1 1) should be calculated. In this section, the convergence test of $Pt_3Zr(1\,1\,1)$ and Pt(1 1 1) surfaces was performed by first-principles calculations. The surface energy of $Pt_3Zr(1\,1\,1)$ and Pt(1 1 1) can be given by:

$$E^{Pt}_{sur} = \frac{E^{Pt(1\,1\,1)}_{slab} - N_{Pt}E^{bulk}_{Pt}}{2A_s} \quad (3)$$

$$E^{Pt_3Zr}_{sur} = \frac{E^{Pt3Zr(1\,1\,1)}_{slab} - N_{Pt3Zr}E^{bulk}_{Pt3Zr}}{2A_s} \quad (4)$$

where $E^{Pt(1\,1\,1)}_{slab}$ and $E^{Pt3Zr(1\,1\,1)}_{slab}$ are the total energy of the Pt(1 1 1) and $Pt_3Zr(1\,1\,1)$ surfaces. E^{bulk}_{Pt} and E^{bulk}_{Pt3Zr} are the total energy per atom in a bulk material. A_s is the corresponding surface area.