Journal of Physics and Chemistry of Solids 123 (2018) 11–18

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs

First-principles calculation on the relationships of h-WC/γ-Fe interface

Zhijun Shi[a], Sha Liu[a], Yefei Zhou[a,b], Qingxiang Yang[a,*]

[a] State Key Laboratory of Metastable Materials Science & Technology, Yanshan University, Qinhuangdao 066004, PR China
[b] College of Mechanical Engineering, Yanshan University, Qinhuangdao 066004, PR China

ARTICLE INFO

Keywords:
h-WC/γ-Fe interface
First principles calculation
Adhesive work
Interfacial energy
Electronic property

ABSTRACT

The adhesive work, interfacial energy, charge density, charge density difference and layer-projected density of states (DOS) of h-WC(0001)/γ-Fe (111) interfaces were calculated by the first principles method. The structural stability of the interfaces was researched by the adhesive work and interfacial energy of h-WC(0001)/γ-Fe (111) interfaces. The interfacial electronic structures were analyzed by charge density and charge density difference, and the interface bonding characteristics were revealed by Mulliken charges and layer-projected DOS of the interface models. The results show that the work of adhesion for C-terminated HCP stacking interface structure is the largest (W_{ad} = 3.44 J/m^2), which indicates that the reversible work used to separate the C-HCP interface into two free surfaces is the largest in all interfaces. When $\Delta\mu_c$ changes from −0.37 eV to 0 eV, the interfacial energy of C-terminated HCP stacking interface structure is in the range of 1.186–1.588 J/m^2, while that of W-terminated HCP stacking interface structure is in the range of 1.142–1.541 J/m^2. When $-0.165\ eV<\Delta\mu_c<0$ eV, the interfacial energy of C-terminated HCP stacking interface is smaller than that of W-terminated one, which indicates the C-terminated HCP stacking interface is more stable. When $-0.37\ eV<\Delta\mu_c<-0.165$ eV, W-terminated HCP stacking interface turns to be more stable than C-terminated one. The total charge density of C-terminated HCP stacking interface is much larger than that of W-terminated one, and the degree of ionization of C-terminated HCP interface is also higher. The bonding of C-terminated HCP stacking interface is a mixture of covalent bond, ionic bond and metallic one, while that of W-terminated HCP stacking interface is a mixture of covalent bond and metallic one.

1. Introduction

Transition metal carbides are often used as hard strengthening phases to reinforce wear-resistant coatings, due to its excellent properties such as high hardness, high elastic modulus and high melting point [1–3]. In all of the transition metal carbides, tungsten carbide (WC) is one of the research hotspots because of its ultrahigh hardness.

Generally, wear resistant coatings can be divided into Co-based, Ni-based and Fe-based wear-resistant ones. At present, there are many reports about the experimental research of WC wear-resistant coatings. Yuan et al. [4] investigated the wear-resistance of WC-Co coatings sprayed by high velocity oxy-fuel (HVOF), and revealed that the addition of submicron-sized WC particles in Co-based coatings can improve their wear resistance obviously. Huang et al. [5] researched the abrasive wear behavior of WC-Ni coatings prepared by laser cladding, which show that the average microhardness of Ni-based cladding layers reach up to 650H < superscript > < /superscript > V and their wear resistance are 5–10 times higher than uncladding H13 tool steel. Zhang et al. [6] delved the microstructure and mechanical properties of WC-Fe coatings sintered by spark plasma sintering (SPS), which indicated that WC particles are homogeneously distributed in Fe matrix and WC coatings achieved good metallurgical integration with the substrate. The microhardness of the composite coating is about 2.4 times higher than that of Fe matrix (45# steel).

In recent years, because of the popular price, excellent corrosion resistance and well mechanical properties, the wear resistant coatings of austenitic stainless steel (γ-Fe based) have aroused people's concern in the industrial field [7]. Especially, the strength and wear resistance of the coatings can be further improved by particle reinforcement. Do Nascimento et al. [8] investigated the wear resistance of WC particles doped duplex stainless steel (γ-Fe/α-Fe) metal matrix composite coatings, and detected that WC particles can effectively strengthen the duplex stainless steel matrix and the interface between WC and substrate is well bonded. Meanwhile, the wear resistance of the coating has increased eightfold. Majumdar et al. [9] researched the mechanical properties of WC doped austenite (γ-Fe) stainless steel wear-resistant coatings prepared by laser cladding, which show that WC can improve the wear resistance of AlSl 304 stainless steel matrix effectively. The

* Corresponding author.
E-mail address: qxyang@ysu.edu.cn (Q. Yang).

https://doi.org/10.1016/j.jpcs.2018.07.007
Received 15 June 2018; Received in revised form 10 July 2018; Accepted 14 July 2018

above researches show that the performance and service life of WC reinforced austenite wear-resistance coatings are related to the interfacial relations of WC/γ-Fe interfaces. However, it is difficult to study the interface relationships between WC/γ-Fe by experimental methods. Especially, few reports about the related theoretical researches can be found.

Up to now, the first principles method based on the density functional theory (DFT) has attracted more and more attentions in the researches on material interface relationship [10]. Jin et al. [11] calculated the atomic structure, stability and electronic properties of WC/W interfaces by first principles method. The results indicate that the termination of the atomic layer of the surface model used to build the interface has an important influence on the stability of the interface, while the stacking of interface has a significant impact on the interfacial adhesive work. Yang et al. [12] researched the relationship and performance of $LaAlO_3$/austenite (γ-Fe) interface by first principles calculations, which revealed the LaO-doped C-terminated interface structure is the most stable interface with the largest adhesive work and the smallest interfacial distance. However, the interfacial relationships between WC/γ-Fe interfaces investigated by first principles method have not been reported.

In this paper, the interface structures and properties of h-WC and γ-Fe were researched by first principles method. The adhesive work, interface distance and interfacial energy changed with $\Delta\mu_c$ of h-WC/γ-Fe interface structures were calculated to analyze the stability of the interface structures with different termination and different stacking. The interfacial charge density and charge density difference calculated by first principles methods were used to perform the qualitative analysis of the interfacial electronic structures and bonding characteristics. Then, a semi-quantitative analysis of the interface bonding characteristics and bonding strength was carried out by the calculated interface mulliken charges. From the above researches, it can provide a theoretical foundation for the investigations of the bonding strength and stability between WC reinforcement phase and γ-Fe substrate in austenite.

2. Computational methods and models

All of the first principles calculations were performed by the Cambridge serial total energy package (CASTEP) module of the Materials Studio (based on the density functional theory (DFT) method) [13]. The local density approximation (LDA-CAPZ) method [14] and generalized gradient approximation (GGA-PBE) method [15] were used as exchange correlation functions. The kinetic energy cut-off value [16] used for plane wave expansion was set as 380 eV. The k-point sampling grids obtained by using monkhorst pack method were set to 8 × 8 × 8 and 8 × 8 × 1 for the bulk and all the slabs, respectively. The broyden-fletcher-goldfarb-shannon (BFGS) algorithm was applied to optimize structures. The convergence threshold of energy change during the optimization was set as 1.0×10^{-5} eV/atom and that of maximum force was set as 0.03 eV/Å.

The crystal structure of h-WC and γ-Fe is shown in Fig. 1. The h-WC structure used in this calculation belongs to P6-m2 space groups, while the γ-Fe structure belongs to Fm-3m space groups. Bulk models were all single unit cells. A vacuum layer of 15 E thickness was applied in all surface and interface models to reduce the interlayer atomic interaction of the orthogonal directions. To eliminate the dipole effect, the terminations of the atomic layer at the upper and lower surfaces of all models were set to be consistent.

Table 1
Calculated lattice constants, bulk modules and cohesive energies of the bulk WC compared with other references and experimental data.

System	Method	α (Å)	c (Å)	V_0 (Å^3)	B_0 (Gpa)	E_{coh} (eV)
WC	$GGA_{this\ work}$	2.91	2.84	20.97	386	16.69
	$LDA_{this\ work}$	2.88	2.80	20.19	424	17.83
	GGA[a]	2.92	2.84	20.98	375	16.67
	LDA-LCAO[b]	2.88	2.81	20.18	413	17.80
	Expt.	2.90[c]	2.83[c]	20.83	329[d],434[e]	16.70[f]

[a] Ref. [17].
[b] Ref. [18].
[c] Ref. [19].
[d] Ref. [22].
[e] Ref. [23,24].
[f] Ref. [18,20,21].

3. Results and discussion

3.1. Bulk property of h-WC and γ-Fe

Bulk properties included the lattice constants, elastic modulus and cohesive energy of h-WC were calculated by LDA-CAPZ and GGA-PBE method to evaluate the accuracy of the calculation method. The cohesive energy equation of h-WC is as follow:

$$E_{coh}^{WC} = E_{tot}^{WC} - E_{iso}^{W} - E_{iso}^{C} \quad (1)$$

where, E_{coh}^{WC} is the cohesive energy of h-WC bulk structure; E_{tot}^{WC} is the total energy of h-WC bulk structure; E_{iso}^{W} and E_{iso}^{C} is the energy of isolated W atom and C atom, respectively.

The calculated results comparing with other references are listed in Table 1. From it, the lattice constant of h-WC calculated by GGA method is a = 2.91 Å and c = 2.84 Å, which is close to the calculation values a = 2.92 Å and c = 2.84 Å of Ref. [17]. The lattice constant of LDA calculations is a = 2.88 Å and c = 2.80 Å, which is close to the calculation values a = 2.88 Å and c = 2.81 Å of Ref. [18]. GGA is more suitable for non-uniform system, while LDA is suitable for the calculation of uniform system. The calculated lattice constants obtained by the two methods were compared with the experimental ones in Ref. [19]. The results indicate that the value obtained by GGA method is 0.3% larger than that obtained by experimental one, while the value obtained by LDA method is 1.0% larger than that by the experimental one. The cohesive energy of h-WC calculated by GGA method is 16.69 eV, which is 0.1% smaller than that of the experimental one [18,20,21]. The cohesive energy of h-WC calculated by LDA method is 6.7% larger than that of the experimental one.

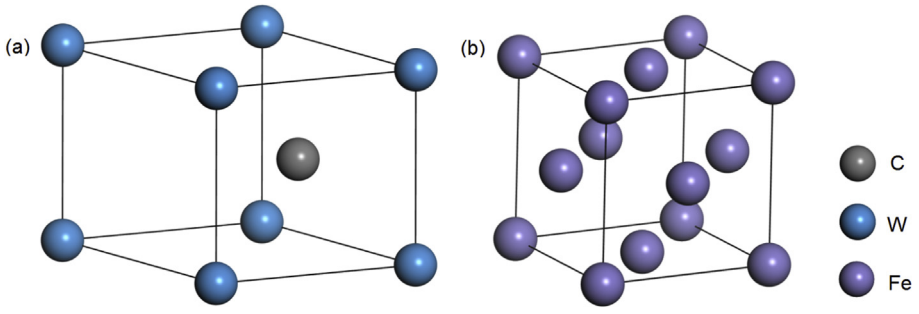

Fig. 1. Crystal structures. (a) h-WC, (b) γ-Fe.