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Letter

Cohesion properties of W-ZrC interfaces from first principles calculation

A B S T R A C T

Six interface models are constructed and used to find out the cohesion properties of W-ZrC interfaces through first principles calculations. It is revealed that interface orientation has an important effect on heat of formation and interface strength of W-ZrC interfaces, i.e., the W(110)-ZrC(111) interfaces with the Kurdjumov-Sachs (KS) relationship are not only energetically more favorable with more positive heats of formation, but also possess higher work of separation. Electronic structure calculations also show that the W-C bond fundamentally determines the magnitude of the interface cohesion between W and ZrC. The derived results are in good agreement with experimental observations in the literature, and could provide a deep understanding of cohesion properties of W-ZrC interfaces.

Keywords:
W-ZrC interface
Heat of formation
Interface strength
First principles calculation

1. Introduction

Tungsten (W) has been well regarded as a promising candidate of plasma facing materials (PFM) in fusion reactors due to its high melting point, low tritium inventory, high strength at elevated temperature, and low erosion rate against sputtering, etc. [1–4]. The main disadvantages of W, however, are its low-temperature embrittlement with relatively high DBTT (more than 673 K), recrystallization embrittlement, and irradiation embrittlement [5–8]. One of the effective approaches to increase the ductility of W is to add, in the W matrix, some dispersed second phases such as ZrC, TiC, HfC, La_2O_3, Y_2O_3, etc. [9–13]. Specifically, the addition of ZrC in W has raised great research interests as ZrC has high melting point, superior mechanical strength, low thermal conductivity, and coefficient of linear expansion, which are all comparable to those of W [11].

Regarding the W-ZrC system, there are already some experimental studies in the literature [9–15]. For instance, ZrC has been found to effectively improve mechanical properties of W [9,11,12], and the W-ZrC interface would have an orientation relationship of Kurdjumov-Sachs (KS), i.e., $(111)_{fcc}//(110)_{bcc}$ and $[1\bar{1}0]_{fcc}//[1\bar{1}1]_{bcc}$ [10]. Moreover, more W atoms would diffuse into the ZrC lattice to form the supersaturated (Zr, W)C solid solutions [9–11,14,16]. It is well believed that the cohesion of W-ZrC interface should play a very important role in the performance of various W-ZrC samples, while there is not any report about interface properties of W-ZrC in the literature.

By means of first principles calculations based on density functional theory [17,18], the present study is, therefore, dedicated to find out the heat of formation and interface strength of W-ZrC interfaces. Six possible interface models are first constructed between the ground-state structures of W (BCC) and ZrC (B1, rock-salt structure). The cohesion properties of these W/ZrC interfaces are then calculated and compared with each other. The derived results will be discussed extensively with experimental observations in the literature, and the fundamental mechanism will be revealed in terms of electronic structures, which could provide a deep understanding to various interface properties of W-ZrC.

2. Method of calculation

The present first-principles calculation is based on the well-established Vienna *ab initio* simulation package (VASP) with the projector-augmented wave (PAW) method [19]. The exchange and correlation items are described by local density approximation (LDA) [20], and the cutoff energy is 400 eV for plane-wave basis. In the present study, six interface structures are intentionally selected, i.e., W(100)/ZrC(100), ZrC(100)/W(100), W(110)/ZrC(100), ZrC(100)/W(110), W(110)/ZrC(111)-KS, and ZrC(111)/W(110)-KS, in which the first and second parts are overlayer and substrate, respectively, and KS refers to the Kurdjumov-Sachs relationship of $(111)_{ZrC}//(110)_W$ and $[1\bar{1}0]_{ZrC}//[1\bar{1}1]_W$ [21]. The optimized bulk lattice constants of the substrates and its crystal structures, i.e., 3.13 Å of BCC and 4.656 Å of the rock-salt structure (B1) are chosen for W- and ZrC-based interfaces, respectively. It should be pointed out that the above optimized lattice constants of W and ZrC are in good agreement with corresponding experimental values of 3.165 and 4.69 Å, respectively [6,22].

To achieve a nice lattice match, a 1×1 surface unit cell is selected for W(100)/ZrC(100) and ZrC(100)/W(100), 1×3 of W(110) and 1×4 of ZrC(100) are for W(110)/ZrC(100) and ZrC(100)/W(110), while 4×2 of W(110) and 3×3 of ZrC(111) for W(110)/ZrC(111)-KS and ZrC(111)/W(110)-KS, respectively. After the tests of the surface and vacuum layers, a vacuum layer of 20 Å is added to each interface, and the substrate layers are 6 and 4 for W(110)/ZrC(111)-KS and ZrC(111)/W(110)-KS, respectively,

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while 7 substrate layers for the remained four interfaces. A certain number of overlayers, i.e., (1,2,4,6) and (2,4,6), are added at the top of the substrate of W(110)/ZrC(111)-KS and ZrC(111)/W(110)-KS interfaces, respectively, while the number of overlayers (1–5) is added on the substrate of the other four interfaces. It should be noted that the above number of overlayers is chosen as a result of the symmetry of the surfaces and for the sake of comparison. As typical examples, Fig. 1 shows the interface models of ZrC(100)/W(100), ZrC(100)/W(110), and W(110)/ZrC(111)-KS. It should be noted that the interface layer of ZrC is intentionally selected to let more C atoms to form W-C bonds with the W atoms, as the W-C bond seems stronger than the W-Zr and Zr-C bonds (figures not shown).

In each calculation, periodic boundary conditions are added in three directions of the unit cell, and the temperature-smearing method of Methfessel-Paxton [23] and tetrahedron method with Blöchl corrections [24] are used for relaxation and static calculations, respectively. After the test, the *k*-meshes of Monkhorst-Pack are selected, i.e., $13 \times 13 \times 1$, $11 \times 3 \times 1$, and $5 \times 5 \times 1$ for the relaxation of W(100)-ZrC(100), W(110)-ZrC(100), and W(110)-ZrC(111)-KS interfaces, respectively, while $17 \times 17 \times 1$, $13 \times 5 \times 1$, and $9 \times 9 \times 1$ for their static calculations [25]. The energy criteria of relaxation and static calculations are 0.01 and 0.001 meV, respectively.

3. Results and discussion

After a series of calculation, the heat of formation (ΔH_f) of the overlayers deposited at the substrate of the W-ZrC interfaces is first derived [26] as follows:

$$\Delta H_f = \frac{E_{tot} - E_{sub} - E_{ovl-b}}{N}, \quad (1)$$

where E_{tot}, E_{sub}, and E_{ovl-b} represent total energies of the W-ZrC interface, the substrate, and the corresponding bulk of the overlayers, respectively, and N is the number of the overlayer atoms. Fundamentally, the heat of formation of the overlayers could be defined as the energy change when the overlayer is put at the top of the substrate as a reference of its corresponding bulk, i.e., the positive ΔH_f means that the overlayer is energetically favorable to form bonding with the substrate, while the negative ΔH_f indicates that the overlayer does not wet the substrate [26].

The work of separation (W_{sep}) of each W-ZrC interface is then calculated according to the following formula [27,28]:

$$W_{sep} = \frac{E_W + E_{ZrC} - E_{tot}}{2A}, \quad (2)$$

where E_{ZrC} and E_W represent total energies of pure ZrC and W surface layers after removing the W and ZrC layers, respectively, and A is interface area of the W-ZrC interface. Physically, the work of separation (W_{sep}) is well regarded as the reversible work needed to separate the interface into two free surfaces, and therefore a direct measure of the interface bond strength, i.e., the bigger value of W_{sep} signifies a higher strength of interface cohesion.

Consequently, the obtained ΔH_f and W_{sep} values of various W-ZrC interfaces are summarized in Fig. 2. Several characteristics could be discerned from this figure. Firstly, interface orientation has an important effect on interface strength. Among the six W-ZrC interfaces, the two W(110)-ZrC(111)-KS interfaces have the highest interface strength, the two ZrC(100)-W(110) interfaces possess the lowest W_{sep} values, while the interface strength of the two ZrC(100)-W(100) interfaces is located between those of W(110)-ZrC(111)-KS and W(110)-ZrC(111)-KS interfaces.

Secondly, the W(110)/ZrC(111)-KS, ZrC(111)/W(110)-KS, and ZrC(100)/W(100) interfaces have positive heats of formation, suggesting that the overlayers of these three interfaces should be energetically favorable to form strong interface cohesion with their substrates. In other words, the W(110)/ZrC(111)-KS, ZrC(111)/W(110)-KS, and ZrC(100)/W(100) interfaces would be thermodynamically stable and could be formed in actual situations, which

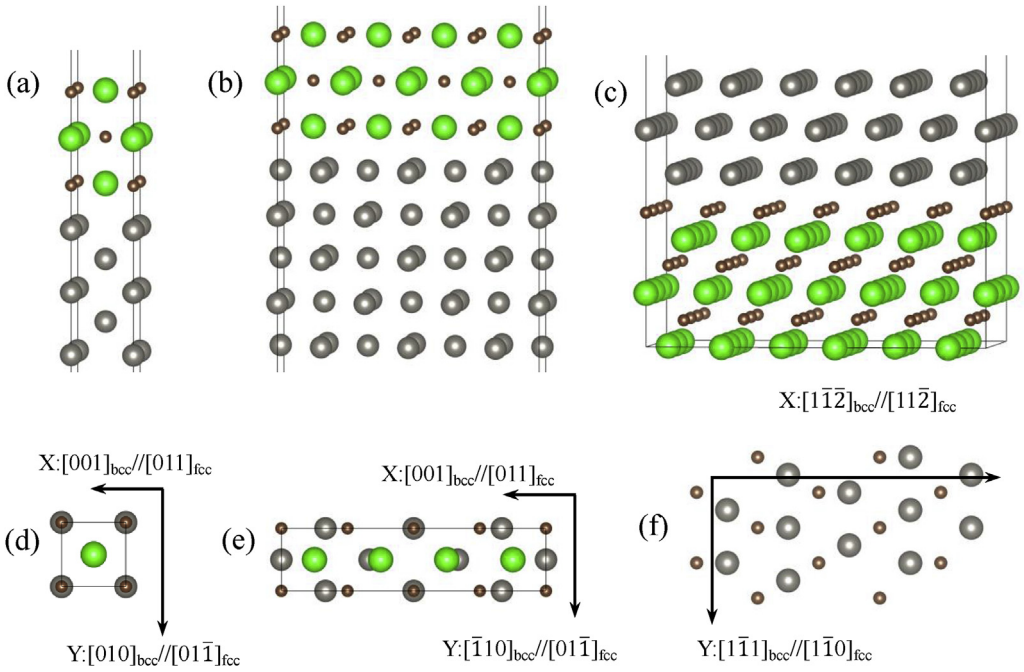

Fig. 1. Interface models of (a) ZrC(100)/W(100), (b) ZrC(100)/W(110), and (c) W(110)/ZrC(111)-KS. (d), (e), and (f) are top views of interfacial atoms of (a), (b) and (c), respectively. The green, gray and brown spheres represent Zr, W, and C atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)