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Adsorption of atomic oxygen on HfC and TaC (1 1 0) surface from first principles

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ABSTRACT

We investigated the initial adsorption of oxygen atom on the HfC (1 1 0) and TaC (1 1 0) surface using first principles. Both the carbides have the same crystal structure, a sodium–chloride structure. The (1 1 0) surfaces of the carbides were modeled with (2 × 1) supercells. Every supercell is composed of five atomic planes. Our results demonstrate that the preferred site for oxygen atom is the C–Hf bridge site and the Ta–Ta bridge site on the HfC (1 1 0) and TaC (1 1 0) surface, respectively. The adsorption sites are different from the one on the (1 0 0) surfaces of the carbides. For the carbides, the adsorption energies of oxygen on the (1 1 0) surfaces are larger than that on the (1 0 0) surfaces. There exists the C—O bond in O/HfC (1 1 0), while no C—O bond is found in O/TaC (1 1 0), indicating that the adsorption mechanism of atomic oxygen on the TaC (1 1 0) surface is different from that on the HfC (1 1 0) surface at initial adsorption stage.

1. Introduction

During a vehicle flying in atmosphere with hypersonic speed, its sharp leading edges and nose tips are subjected to very high temperatures. So it is necessary to choose high temperature materials as thermal protection materials. Thus, the materials can prevent the strength of the edges and nose tips from decreasing dramatically. The NaCl-type monocarbides of hafnium and tantalum (HfC, TaC) belong to the ultrahigh temperature materials due to their high melting points, high hardness, and high elastic modulus [1]. The carbides also have no phase transformation at high temperatures. Therefore, they are considered as the potential candidates for aerospace thermal protection materials. However, the problem for the applications of HfC and TaC is that they will undergo oxidation when they are exposed to oxidizing environments. So oxidation has become a bottleneck of developing ultrahigh temperature materials [2]. The oxidation of HfC and TaC usually occurs on surfaces at first. To clarify the interactions between oxygen and the surfaces of the carbides, researchers have done many experiments [3–6]. In these experiments, researchers found that there exists gaseous CO or CO_2, especially in the case of HfC. Then CO or CO_2 is desorbed from the substrate.

Besides the experiments, the density functional theory (DFT) has also been used to investigate the adsorption of atomic and molecular oxygen on the (1 0 0) surface of HfC and TaC. The results from DFT agree with the experiments [5–8]. For atomic oxygen, the results illustrate that the 3-fold hollow is the most favorable adsorption site on the HfC (1 0 0) surface, while the favorable site is the Ta-top site on the TaC (1 0 0) surface [9]. Souda et al. [10] also found that the preferential oxygen–metal bonds exist on the (1 0 0) surface of TaC, while the preferential oxygen–carbon bonds exist on the (1 0 0) surface of HfC. The oxygen–metal bonds can prevent the oxidation of TaC. The difference in the adsorption of oxygen is believed to be owed to the electronic structures of the carbides. For the adsorption of molecular oxygen, it is found that O_2 is bridging two metal atoms or is adsorbed on top of a metal atom [11]. Then O_2 is dissociated into atomic oxygen.

So far, researches have been mostly focused on the adsorption of oxygen on the nonpolar (1 0 0) surface of HfC and TaC. Comparing with the (1 0 0) surfaces, the (1 1 0) surfaces of the carbides are also nonpolar. How about the adsorption of oxygen on the HfC (1 1 0) and TaC (1 1 0) surface? In addition, the effect of atomic oxygen on ultrahigh temperature materials has not attracted much attention [2]. Whether or not the adsorption sites of atomic oxygen on the (1 1 0) surfaces are the same as that on the (1 0 0) surfaces at initial adsorption stage? In our research, we investigated the initial adsorption of atomic oxygen on the HfC (1 1 0) and TaC (1 1 0) surfaces from first principles.

2. Calculation methods

Our calculations were based on the density functional theory. All the calculations were performed with CASTEP code [12]. In the performance, the generalized gradient approximation (GGA) of the

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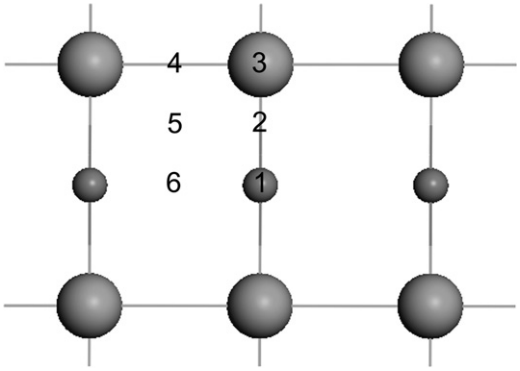

Fig. 1. The possible adsorption sites for oxygen atom on the HfC (1 1 0) and TaC (1 1 0) surface. The big spheres represent Hf or Ta atoms, while the small spheres represent C atoms. (1) Top-C; (2) M-C site, bridging one carbon and one metal atom; (3) top-M; (4) M-M site, bridging two metal atoms; (5) 4-fold hollow site, bridging two carbon and two metal atoms; (6) C–C bridge, bridging two carbon atoms.

revised Perdew–Burke–Ernzerhof functional (RPBE) [13] was used to treat the exchange-correlation potential. It has been indicated that RPBE can give a good description of adsorption [14].

We constructed the HfC (1 1 0) surface with the lattice parameters of bulk HfC reported in our previous work [15]. For TaC, we first optimized bulk TaC to obtain its stable structure. Then we used the lattice parameters of the structure to construct the TaC (1 1 0) surface. All the (1 1 0) surfaces were modeled by the slab approach. For the slabs, (2×1) supercells were used. Therefore, there are two metal and two carbon atoms in every (1 1 0) surface.

To obtain the converged results, we examined the number of the slab layers, the vacuum gap between slabs, cutoff energy, and *k*-points. The converged results were obtained with the five-atomic-plane slabs, a 12 Å vacuum gap, a 370 eV cutoff energy for the plane wave basis set, and 12 *k*-points. The *k*-points were selected with the $6 \times 4 \times 1$ Monkhorst-Pack grid [16]. For the (1 1 0) surface consisting of five atomic planes, its three outermost planes were allowed to relaxed, while the other two planes were fixed. We provided six possible adsorption sites for atomic oxygen on the (1 1 0) surfaces of MC (Fig. 1). Here, MC means HfC or TaC. M represents Hf or Ta. The sites are as follows: top-C, M-C, top-M, M-M, 4-fold hollow site, and C–C bridge site. These sites were examined by optimizing geometric structure. In our calculation, we also examined the effects of spin polarization. Finally, we found that the energy of spin-polarized oxygen atom is different from that of non-spin polarized oxygen atom, while the effects of spin polarization on the structures and energies of clean and adsorption surfaces are not significant. So we did not consider the surfaces with the spin polarization. The convergence threshold for the maximum energy change, the maximum force, and the maximum displacement were specified 1.0×10^{-5} eV/atom, 0.03 eV/Å, and 0.001 Å, respectively. During our calculations, the self-consistent field convergence threshold was 5.0×10^{-7} eV/atom.

3. Results and discussion

3.1. Clean HfC (1 1 0) and TaC (1 1 0) surfaces

3.1.1. Geometric structure

The (1 1 0) surface slabs are composed of five atomic planes. Every atomic plane consists of equal amounts of metal atoms and C atoms, which is similar to the (1 0 0) surfaces of HfC and TaC, respectively. Before being optimized, the surfaces are named ideal (1 1 0) surfaces. The outermost atomic plane of every ideal (1 1 0) surface is defined as basal plane.

Table 1
Surface energies for the (1 1 0) and (1 0 0) surface of HfC and TaC.

	(1 1 0) Surface		(1 0 0) Surface
	eV/atom	eV/Å^2	eV/atom
HfC	1.71	0.22	0.38[a] 0.90[b] 0.52–0.70[c]
TaC	1.52	0.22	0.88[b] 0.52[c] 0.68[c]

[a] Ref. [15].
[b] Ref. [21].
[c] Ref. [22].

The (1 1 0) surface rumpling was calculated according to the formula reported by Kobayashi [17]. For the HfC (1 1 0) surface, our results show that there exists surface relaxation. The C atoms in the surface layer move outward and the Hf atoms inward with respect to the basal plane. The perpendicular C–Hf distance in the surface layer is 0.14 Å, yielding the rumpling of 8.4%. The HfC (1 1 0) surface rumpling is more than that of the HfC (1 0 0) surface. The rumpling of the HfC (1 0 0) surface is from 5.0% to 5.7% [17,18].

For the TaC (1 1 0) surface, the C atoms in surface still move outward and Ta atoms move inward, which results in the rumpling being up to 16.6%. The rumpling of TaC (1 1 0) surface still is more than the one of its (1 0 0) surface. The TaC (1 0 0) surface rumpling is from 10.3% to 10.6% [17,19]. As we know, the valence electron of Ta is more than Hf. This may result in the great repulsion force in the TaC (1 1 0) surface. Price et al. also consider that the great electric field results in the great rumpling of the TaC (1 1 0) surface [20]. Therefore, the rumpling of the TaC (1 1 0) surface is larger than the one of the HfC (1 1 0) surface due to the great repulsion force.

3.1.2. Surface energy

The surface energy σ is calculated by the formula [21] as follows:

$$\sigma = \frac{(E_{\text{slab}} - NE_{\text{bulk}})}{(2 \times n)} \quad (1)$$

where E_{slab} is the total energy of the relaxed clean HfC (1 1 0) or TaC (1 1 0) surface slab. E_{bulk} is the energy of bulk HfC or TaC; N is the atomic plane number of the surface slab; n means the number of atoms in the outermost layer. In our (2×1) supercell surface model, there are two metal and two carbon atoms in the outermost layer. So, the number is four, i.e., $n = 4$. In the formula (1), we substituted area of surface for n. Then we obtained the surface energies in eV/Å^2.

The surface energies of the (1 1 0) surfaces are listed in Table 1. For the early transition metal carbides such as TiC, HfC and TaC, they share the same NaCl-type crystal structure. The order of their surface energy is (1 0 0) < (1 1 0) < (1 1 1). The stability of (1 1 0) surface is lower than the (1 0 0) surface. Our results agree with the order.

3.1.3. Density of states

Fig. 2 shows the total and partial density of states (DOS) for the outermost layer of the clean HfC (1 1 0) and TaC (1 1 0) surfaces. For the HfC (1 1 0) surface, the DOS is composed of two evident bands. The band ranging from −10 eV to −8 eV is dominated by C-2s orbital. The valence band ranging from −5 eV to Fermi level E_F is composed of C-p and Hf-d. The overlap between the C-p and the Hf-d orbitals is very large, indicating that there exists strong hybridization between the C-p and the Hf-d. Therefore, the strong covalence exits in C–Hf bond. The strong hybridization and covalence also exist in the HfC (1 0 0) surface [15], indicating that the interaction between C and Hf in the HfC (1 1 0) surface do not change greatly compared with the HfC (1 0 0) surface. However, the DOS of the HfC (1 1 0) surface at Fermi level E_F is larger than that of