Full Length Article

First-principles study of adsorption and diffusion of oxygen on surfaces of TiN, ZrN and HfN

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ABSTRACT

Using first-principles calculations based on density functional theory, we systematically study the adsorption and diffusion behaviors of single oxygen (O) atom on the (0 0 1) surfaces of TiN, ZrN and HfN nitride coatings. The top of N site (top(N)) is the most energetic favorable site for O atom and followed by the hollow site for all the three nitrides. O atom tends to diffuse on the (0 0 1) surfaces of the nitrides from the top of transition metal top(TM) sites to a neighboring top(TM) sites by avoiding N sites. The adsorption of O on ZrN and HfN is more stable than that on TiN. Our findings could explain the experimental phenomenon that the oxide thickness of TiN is smaller than that of ZrN under the same oxidation conditions.

1. Introduction

Metal nitrides, especially TiN are widely used as protective coatings for cutting and forming tools due to their high hardness and wear resistance as well as good thermal stability and oxidation [1,2]. They are the main building blocks to design multicomponent hard coatings, including TiN, TiAlN, TiZrN, and HfAlN [3–6]. However, their service lifetime is greatly influenced by their adhesion to the substrate and the performance of coating materials [7–9]. During these applications, especially for cutting process, tools are always exposed to air at elevated temperature, which raises a high demand for the oxidation resistance of metal nitrides. The worn cutting tool will make tool surface oxidation and speed up the tool failure. Additionally, due to unavoidable contact with air components, nitride coatings contain considerable oxygen impurities [10].The oxidation between the coating surface and residual gas happens during and/or after deposition during [11].

The formation of surface oxides for hard coatings at different temperatures and oxygen pressures was investigated by ultra-high vacuum spectroscopic studies [12,13]. A microscopic model of the surface oxidation process was developed in the regime of early oxidation with elevated temperatures and pressures [14]. TiN coating started to oxidize at 500 °C and almost fully oxidized after 700 °C [15]. Chemical analysis of TiAlN and TiAlNO coatings indicated that oxygen is enriched at the surface region, and oxygen first chemisorbs self-limited at surface sites and some oxygen also dissolves in subsurface layers [11,16].

It is desirable to investigate this process from theoretical point of view because of the difficulty to observe the adsorption process of oxygen atom by experiments. The surface adsorption and diffusion mechanism have been widely investigated by using density functional theory (DFT) methods [17–19]. According to the oxygen diffusion on TiN(0 0 1), Holec et al. [20] found that the diffusion path of O on TiN(0 0 1) surface is between Ti sites. Janina [18] used four layers of slab to focus on the atomistic structure and stability of the TiN(0 0 1) surface during oxidizing atmosphere. They found that an ultrathin Ti oxide layer was formed while Ti vacancies are left behind at the metal/oxide interface.

Further understanding of oxygen absorption and diffusion process, as an onset stage of oxidation, is beneficial to better understanding of the mechanism of oxide growth, and thus further improving the oxidation resistance [21–24]. Therefore, the aim of this study is to extend the understanding of O atom adsorption and diffusion on TiN, ZrN and HfN surfaces, which have widely been studied to know the electronic structure and mechanical properties [17,19,25]. Here, we use DFT method to study the adsorption and diffusion behaviors of oxygen atoms on the (0 0 1) surfaces of the nitride coatings.

2. Computational methods

2.1. First-principles details

DFT-based first-principles calculations were carried out with the Vienna Ab-initio Simulation Package (VASP) [26–28] implemented using the generalized-gradient approximation (GGA) [29] and the projector augmented plane-wave (PAW) method [30]. Convergence tests with respect to the number of k points and the plane wave cut-off energies were performed, leading to the present setting of plane wave cutoff energy of 400 eV, and the Monkhorst-Pack methods of $9 \times 9 \times 9$ for bulk TiN, ZrN, HfN and $5 \times 5 \times 1$ for the slab case. These settings assure a total energy convergence of 0.001 eV/atom.

Adsorption energies E_{ads} of O atom on the surfaces of TiN, ZrN and HfN were calculated as follows:

$$E_{ads} = E_{total} - E_{slab} - E_{adsorbate} \qquad (1)$$

where E_{total} and E_{slab} are the total energies of the relaxed (0 0 1) nitride surface with and without O, respectively, and $E_{adsorbate}$ is the total energy of the free adsorbate in vacuum. Here $E_{adsorbate}$ is half of the total energy of an O_2 molecule, which was calculated by placing an O_2 molecule in a cubic box with dimension of $10 \times 10 \times 10$ Å. According to this definition, a negative value of E_{ads} indicates that the adsorption is exothermic (stable) with respect to a free oxygen molecule and a positive value indicates endothermic (unstable) reaction. The adsorption energy indicates the tendency of an adatom to stick onto a surface as used in Ref. [31], and it is also a comparable quantity related to the work of separation, which is used in the literature [32,33].

Diffusion energy and the minimum energy path (MEP) of O atom were obtained by the nudged elastic band (NEB) method [34,35]. This method is an efficient method to determine the MEP when both the initial and final minima are known. The diffusion behavior of a single O atom was investigated by determining the MEP and the saddle points along the pathways on the (0 0 1) surface. We used 3 images and the 2×2 surface supercell for the NEB calculations.

2.2. Surface model

Crystal structures of TiN, ZrN, and HfN are sodium chloride type with space group $Fm3m$ (No. 225). The most stable surface of this structure is the (0 0 1) based on the value of surface energy [31,36,37]. In the present work, the (0 0 1) surface was represented by the slab model. We used the optimized lattice constant to construct a 2×2 surface supercell with 5-layer slab (80 atoms) and vacuum space of 15 Å. During structural relaxations, three bottom layers were fixed in order to simulate a bulk environment, and others relaxed. There are four high symmetry sites on the (0 0 1) surface, as shown in Fig. 1. We put an O atom on each of the four sites as the initial configuration.

3. Results and discussion

3.1. Surface adsorption

To obtain equilibrium lattice parameters of TiN, ZrN, and HfN, first-principles calculated energy versus volume data points were fitted with the third-order Birch-Murnaghan state of equation [38]. The lattice parameters of the bulk TiN, ZrN, and HfN were calculated to be 4.247, 4.593, and 4.521 Å, respectively, which are in good agreement with the previous theoretical and experiment values, as shown in Table 1.

To study adsorption structures and energies of a single O atom on the (0 0 1) surface of nitride coatings, we consider the four adsorption sites for O atom, i.e., top(N), top(TM) (TM = Ti, Zr, Hf), bridge and hollow sites, as shown in Fig. 1. When O atom is on the bridge site, it is unstable because the single O atom will move towards the top(TM) site and bonds with TM atoms during the structural relaxations. Unlike the bridge site, O atom does not move to top(TM) site when it is on the hollow site, top(N) and top(TM) sites based on our calculations.

The adsorption energies and the corresponding adsorption configurations are shown in Table 2. In the results, the O atom is adsorbed at top(TM) site with adsorption energy of −3.21 eV, −3.32 eV and −3.77 eV on TiN(0 0 1), ZrN(0 0 1) and HfN(0 0 1) surface, respectively. Graciani et al. [47] present a detailed experimental and theoretical study of the oxidation of TiN(0 0 1) using a
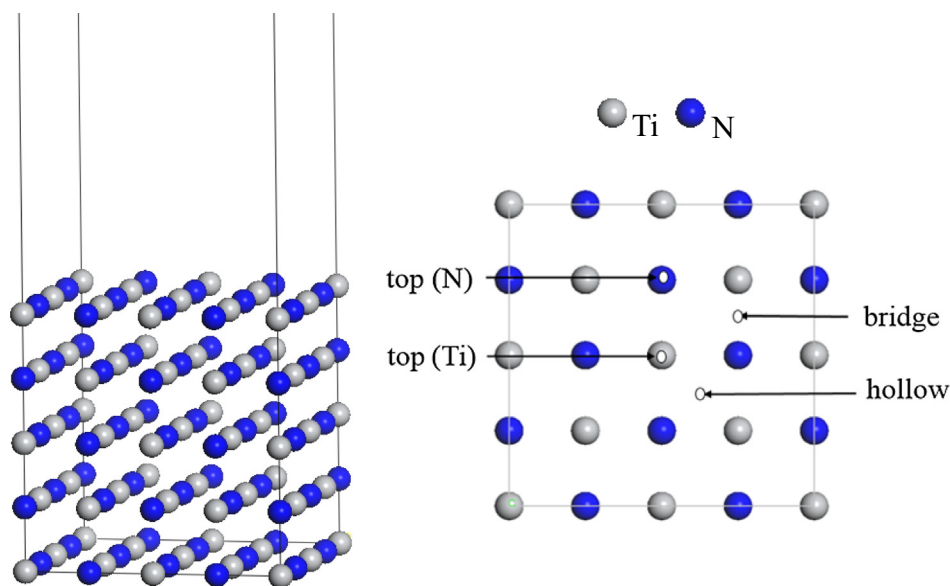

Fig. 1. The surface slab model (left panel) and surface adsorption sites (right panel) of TiN(0 0 1).