An AIMD Study of Water on α-Uranium Surface

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Abstract. The ab-into molecular dynamics method (AIMD) was used to study the adsorption and dissociation of H_2O molecules on the surface of α-U (110). The adsorption and dissociation of H_2O molecules in different positions and different initial configurations were compared and analysed. For the case of dissociative adsorption, the radial distribution function (RDF) is analysed, and the bonding of U-O bond and U-H bond is studied.

Keywords: AIMD, Uranium, adsorption, dissociation.

1. Introduction

In the development and utilization of nuclear energy, uranium is a very important material. However, due to its high radioactivity and active chemical properties, the safe using, transportation and storage of uranium has always been a huge problem. The chemical property of uranium is very active, and it is easy to oxidize and corrode with oxidizing gases in the air in the environment, which will cause changes in its performance. When exposed to the air, an oxide layer will quickly form on the surface of uranium metal. The oxide on the surface will destroy the original surface structure and affect the chemical properties and reactivity of uranium. The surface corrosion of uranium metal starts from the adsorption and dissociation of active molecules on the surface. However, due to the very active chemical properties of uranium, the oxidation reaction on the surface proceeds very quickly, and it is difficult to observe the specific reaction details in the experiment. In order to study the reaction mechanism of uranium with water and oxygen, it is necessary to reveal the specific details of the process through theoretical research. Therefore, studying the surface reaction process and reaction mechanism of uranium metal has always been an important subject, which is not only of great significance in theoretical research, but also of important value in practical applications

The oxidative corrosion of uranium metal in the atmosphere is mainly caused by the oxidation reaction of H_2O and O_2. The corrosion of uranium metal by H_2O and O_2 is the interaction of U atoms with H_2O and O_2 molecules. The interaction is divided into two types, one It is the interaction of isolated U atoms with H_2O and O_2 molecules, and the other is the interaction of the entire U unit cell with H_2O and O_2. In recent years, the theoretical research on the corrosion of oxidizing gas on the surface of uranium has been continuously reported. Liang et al. [1] used laser ablation technology to generate isolated U atoms, and allowed the isolated uranium atoms to react with H_2O molecules in an inert gas atmosphere. Combining infrared spectroscopy and density functional theory calculations, the reaction products were carefully analyzed. Research. The results show that there are three reaction channels between isolated U atoms and H_2O molecules, and the reaction products are HUO(OH), H_2UO and H_2UO_2. Li et al. [2] used quantum chemistry calculations to study the interaction between U atoms and H_2O molecules, and clarified the reaction channels and intermediate states of the reaction process.

In fact, the reaction of oxidizing gas with uranium metal is a reaction with U atoms in the entire unit cell. Li et al. [3] used density functional theory to study the reaction of H_2O on the surface of uranium metal. The results showed that H_2O molecules would adsorb, diffuse and dissociate on the surface. The most stable structure of H_2O molecules on the surface of α-U (001) The type is a top adsorption structure parallel to the surface. Through density functional theory research, Huang et al. [4] found that H_2O molecules are more inclined to adsorb on the surface of α-U (001) with long bridge sites, which is different from Li Gan’s results. Huang et al. [5] also studied the adsorption of O_2

molecules and O atoms on the surface of α-U (001) by density functional theory. Huda et al. used density functional theory to study the dissociative adsorption of O_2 molecules on the γ-U (100) surface.

At present, the software that uses first-principles and molecular dynamics calculations is mainly VASP, CASTEP, etc. These softwares have an advantage when dealing with static systems, but they cannot handle calculations for large systems. The cp2k developed by Parrinello of the University of Zurich and his student Hutter can quickly calculate the dynamic response of a large system. In this paper, the first-principles molecular dynamics method is used to systematically study the adsorption and dissociation of O_2 and H_2O molecules on the surface of α-U (110), focusing on the radial distribution function, migration energy barrier and mean square distribution. function. The rest of this article is organized as follows. Section 2 introduces the calculation methods and models, Section 3 discusses the calculation results, and Section 4 summarizes the main conclusions.

2. Methodology

2.1. Computational Methods

According to the existing technical tools, CP2K software is used in the research process of this chapter. For the part of the valence electron wave function, the specific expansion is mainly carried out by mixing Gaussian and plane wave basis sets GPW and GAPW. In general, the initial temperature is set to 300 K and the NVT ensemble is adopted. Through the test, the cutoff energy is set to 600 eV. In order to speed up the calculation and avoid taking too much time, the H atom in H_2O is replaced with the D atom, and the time step is set to 1 fs. In the SCF iterative convergence, the OT method is selected, and the accuracy is 1.0×10-5 eV, and the Brillouin zone integration uses the Γ point approximation. After the introduction of the pseudopotential method, the nucleus and inner core electrons can be equivalent to the corresponding potential field, and in general, only the wave function needs to be analyzed. In the selection of the potential function, the 2s and 2p electrons of the O atom are used as the valence electrons, and the U atom uses the potential function which valence electron configuration is $6s^25d^{10}6p^67^{s2}5f^36d^1$. The remaining atoms are simulated by GTH pseudopotentials.

2.2. The H_2O-U model system

Uranium has three different crystal structures, namely α phase, β phase and γ phase, which are allotropes with each other. These three allotropes of uranium metal can be converted to each other at a certain temperature, and the conversion temperatures are 941K (α phase → β phase) and 1048K (β phase → γ phase). Therefore, uranium mainly exists in the α-phase structure at room temperature, and even if it is pressurized to 100 GPa, the uranium still remains in the α-phase. In the actual application of uranium, α-phase uranium is usually used in nuclear reactions, so the research object of this article is α-phase uranium (α-U). Existing studies usually study the (001) plane with the lowest energy. By analyzing the surface energy of each low-index crystal plane of α-U, Qu et al. [6] finds that the (001) plane is the most stable plane, while the (110) plane is the most stable plane. The energy is the highest, the activity is the strongest, and it is more likely to be oxidized and corroded. Therefore, studying the oxidation corrosion of (110) surface can better characterize its corrosion characteristics.

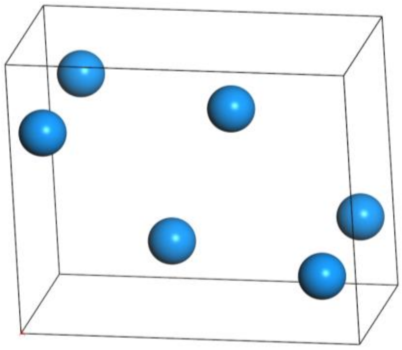

Figure 1. α-U unit cell.

The current research field often discusses the lowest energy (001) plane. After in-depth research on the surface energy of the α-U low-index crystal plane, Qu [6] indicates that the (001) plane is the most stable, but the (110) plane energy and activity The highest, easily corroded. In view of this, scientific exploration of the (110) surface is helpful to characterize its corrosion characteristics, so as to overcome various problems that may be faced in the practice stage, so that it has a more solid foundation for practical application. When studying the molecular reaction of H_2O and O_2 on the α-U (110) plane, it is first necessary to construct a p (4×2) slab model containing 6 layers of atoms, and a single slab unit cell has 24U atoms. In the calculation, the lower 3 layers of U atoms are fixed, and the upper 3 layers are released. Since adsorption tends to occur at high symmetry, we conducted studies on short-bridge sites, long-bridge sites, and hollow sites, respectively. Considering that the initial spatial state of H_2O molecules may affect the adsorption process, we calculated three H_2O molecules with initial configurations: <100>, <010>, <001> (the vector is the direction of the two H atoms).

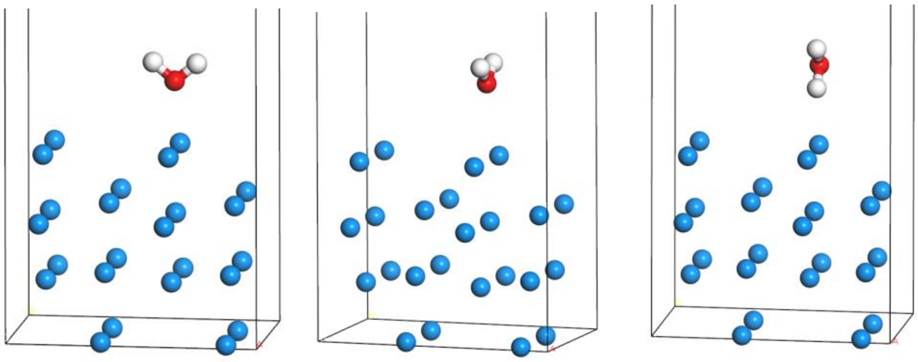

Figure 2. The three spatial configurations of H_2O at the short-bridge position: <100>, <010>, and <001>.

3. Results and discussion

In the calculation, we found something very interesting. H_2O dissociated and adsorbed only at the short bridge site, and it was related to the initial spatial configuration of H_2O. In the cave site and the long bridge site, only molecular adsorption of H_2O occurs. At the short bridge position, H_2O molecules in the <001> configuration are adsorbed, and H_2O molecules in the <100> and <010> configurations are dissociated and adsorbed.

When calculating the surface adsorption of water, one H_2O molecule with the oxygen end facing down is placed on the short bridge position, long bridge position and hole position of the U unit cell surface, and 1 OH and 1 H atom are generated after dissociation. While forming a U-OH bond and UH bond with adjacent U atoms. The H_2O molecule dissociates at about 0.26 ps at the short bridge position, and dissociates at about 1 ps at the other three positions, and the adsorption energy at the short bridge position is the smallest, -4.84 eV, indicating that the H_2O molecule is at the short bridge position. Dissociation adsorption is the easiest occurrence, and the adsorption is shown in Table 1. The dissociation of H_2O molecules in the three positions is similar, so Figure 3 and Figure 4 only shows the RDF of H_2O molecules at the short bridge position. In addition, it can be seen from the motion trajectory that OH and the bonded U atom move thermally at the equilibrium position, while H moves between the first and second layers of the unit cell surface, which indicates the U-OH bond Relatively stable, while UH bond is unstable

Table 1. Adsorption of H_2O.

Orientation	short-bridge site	hollow site	long-bridge site
100	D	M	M
010	D	M	M
001	M	M	M

M = molecular adsorption, D =dissociation

Orientation = orientation of two hydrogen atoms

Combining the Figure 3 and Figure 4 to illustrate, H_2O molecules dissociate into OH and H atoms, and OH and U atoms on the surface form U-OH. The RDF is shown in Figure 3. The UO bond formation in the U-OH bond is similar to that of UO when O_2 is dissociated. In the short bridges, the first coordination layer is there is almost no density distribution between the second coordination layers, indicating that the UO bond is extremely stable. Combined with the analysis of dissociation adsorption time, adsorption energy and RDF function, it is verified that the H_2O molecule is more biased towards the dissociation and adsorption of short bridge sites.

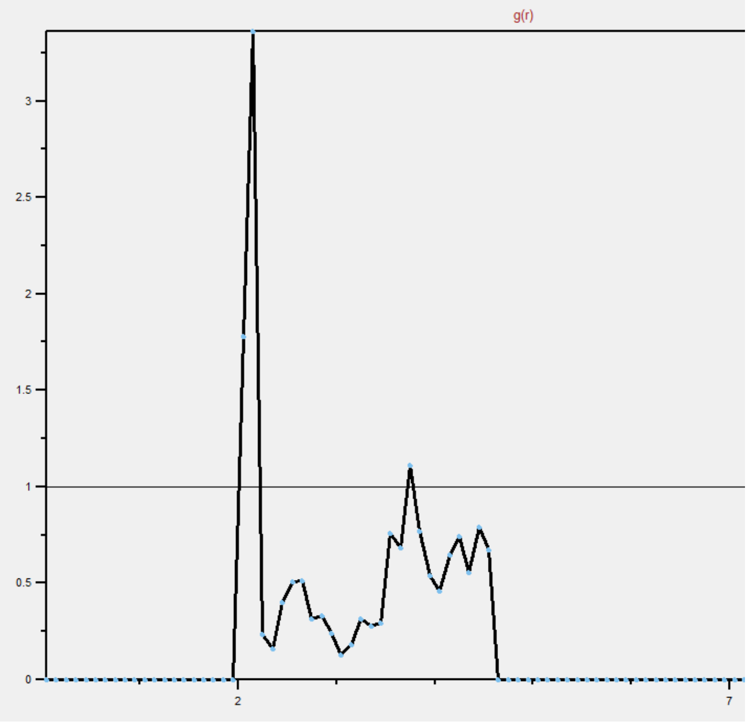

Figure 3. Short-bridge site <010> configuration O-U radial distribution function.

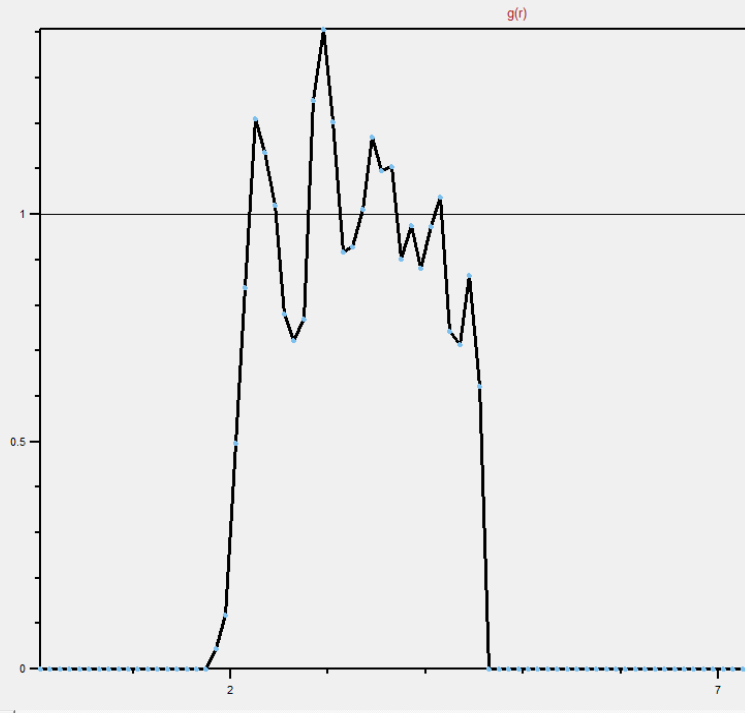

Figure 4. Short-bridge site <010> configuration H-U radial distribution function.

4. Conclusion

Through AIMD calculations, we found that H_2O molecules dissociated and adsorbed on the short bridge sites on the U surface, and all other positions were adsorbed by molecules. Moreover, in dissociative adsorption, both U-O and U-H bonds are not stable, and OH^- and H atoms keep moving on the surface of the U unit cell. Although this is the same as the DFT calculation result, from the perspective of molecular dynamics analysis, this result is problematic. We have done a more in-depth study on this problem and explored the cause and practical significance of the problem.

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