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First principles study of nanoscale mechanism of oxygen adsorption on lanthanum zirconate surfaces

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HIGHLIGHTS

- O_2 adsorption on $La_2Zr_2O_7$ surfaces is investigated using ab initio calculations.
- The lowest adsorption energy site is 3-fold-FCC on (111) plane.
- (011) plane has the lowest surface free energy.

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ABSTRACT

Lanthanum zirconate ($La_2Zr_2O_7$) is a rare-earth pyrochlore material, which has been proposed as a promising thermal barrier coating (TBC) material due to its low thermal conductivity and high temperature phase stability. At elevated temperatures, degradation of $La_2Zr_2O_7$ may occur due to adsorption of oxygen (O_2) on $La_2Zr_2O_7$ surfaces. This paper investigates nanoscale mechanism of O_2 adsorption on $La_2Zr_2O_7$ coating surfaces using the density functional theory (DFT) calculations. $La_2Zr_2O_7$ surface energies on (001), (011) and (111) planes are calculated. The surface free energy of (011) plane is lower than those of (001) and (111) planes. On (001), (011) and (111) planes of $La_2Zr_2O_7$, the lowest adsorption energy occurs at 4-fold site, bridge site, and 3-fold-FCC site, respectively. Among all calculated cases, the lowest adsorption energy site is 3-fold-FCC on (111) plane, which is confirmed by the Bader charge transfer analyses. Charge density difference analyses show that the 3-fold-FCC site on (111) surface has the largest charge density, suggesting the strongest interaction between O_2 and $La_2Zr_2O_7$ surface.

1. Introduction

Thermal barrier coatings (TBCs), which comprise multiple ceramic and metallic coating layers, insulate blades or combustion components of gas turbine engine and improve energy efficiency and lifetime of engines [1]. $La_2Zr_2O_7$, a rare-earth based TBCs material, has recently become popular because of its desirable high-temperature thermal and physical properties. Compared with the current state-of-the-art TBCs 8 wt% Y_2O_3-stabilized ZrO_2 (YSZ), $La_2Zr_2O_7$ has the following advantages: a relatively low thermal conductivity, no phase transition, low sintering activity, and high chemical stability [2–5]. Interfacial damage in TBCs due to the oxidation has been widely investigated by experiment. Zhu et al. found that the oxidation process of bond coat and substrate significantly reduced the coating adherence, resulting in delamination at both the top coat/bond coat and bond coat/substrate interfaces, due to the adsorption of oxidizing gas and oxidation process [6]. Evans studied the oxidation induced failure of YSZ/MCrAlY TBC system [7]. The final spallation often occurred by buckling or release of strain energy within the TBC top coat and the thermally grown oxide (TGO) layer due to oxidation induced phase or volume change. In addition, advanced application of TBC materials requires understanding of the ideal material properties and mechanism of interaction between TBC materials and its environment. Specifically, an atomic-level investigation of TBC materials becomes essential. However, the pursuit of the nano-properties requires high precision nano-devices, which makes it particularly challenging to characterize the properties in nanoscale [8]. As a result of that, theoretical method becomes a feasible approach to investigate the gas adsorption mechanism in nanoscale.

Density functional theory (DFT) calculations were used in this paper to investigate the O_2 adsorption mechanism on $La_2Zr_2O_7$ surface. DFT is an alternative approach to finding the solution to

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the Schrödinger equation, which is the fundamental equation to describe the quantum behavior of atoms and molecules [9–11]. In our previous work, several thermal and mechanical properties of $La_2Zr_2O_7$ were calculated using DFT calculations, including specific heat, Young's modulus, thermal conductivity, coefficients of thermal expansion (CTE) [12,13]. In terms of gas adsorption process, Wallin et al. studied O and O_2 adsorption process on α-Al_2O_3 (0001) surface using the DFT method. Four atomic Al_2O_3 layers were built, and adsorption energies were calculated at various positions. Charge density was analyzed to interpret the adsorption mechanism. Atomic O was found to have strong interaction with the double layer Al-Al terminated surface, where O_2 molecules were found to easily dissociate on this surface [14]. Li et al. studied the oxygen adsorption process on Cr_2AlC (0001) surface. The surface energy, adsorption energy, bonding character, and electronic structure of Cr_2AlC (0001) surface with or without single O atom and molecular O_2 were investigated by the DFT calculations. The result showed that the O strongly bonded to the Al atom on the surface [15]. In addition, we have previously studied carbon dioxide adsorption process on $La_2Zr_2O_7$ surface using nano-scale slab models [16]. The results showed that (011) plane was the most thermodynamically stable plane due to its lowest surface energy.

Oxygen adsorption on TBC surface is the first step of the oxidation process. However, no previous study was found about the O_2 adsorption on $La_2Zr_2O_7$ surfaces. In this paper, the surface energies of $La_2Zr_2O_7$ (001), (011) and (111) planes are calculated. Then adsorption energies of O_2 on these planes are studied. The electronic density difference and charge transfer analyses are carried out to investigate the adsorption mechanisms of O_2 on $La_2Zr_2O_7$ surfaces.

2. Computational details

All calculations are conducted using DFT based plane wave method with the Vienna *ab initio* simulation package (VASP) [9,10,17–19]. Generalized gradient approximation (GGA) functional is used to simulate the adsorption process [20–22]. The standard potentials of the projector augmented wave (PAW) of GGA are used to describe the ion cores [23,24].

In terms of the atomistic structure model in nanoscale, $La_2Zr_2O_7$ is a rare-earth pyrochlore crystal. Pyrochlore is a cubic crystal structure (space group *Fd-3m*). The lanthanum (La) atoms occupy at 16d positions (1/2, 1/2, 1/2), and zirconium (Zr) atoms take 16c positions (0, 0, 0). There are two different oxygen (O) positions. The O atoms locate at 48 f positions (x, 1/8, 1/8), while O' atom occupy at 8b positions (3/8, 3/8, 3/8) [25]. The unit cell of $La_2Zr_2O_7$ in nanoscale has 16 La atoms, 16 Zr atoms and 56O atoms, where each octahedron contains one Zr atom and six O atoms. The relaxed lattice parameter of the $La_2Zr_2O_7$ conventional cell model is 1.0882 nm.

To study the adsorption on different planes, three surfaces on (001), (011) and (111) planes are cut from a $La_2Zr_2O_7$ unit cell. More than five layers of atoms are included in the slab models, as shown in Fig. 1. All surfaces are fully relaxed with two layers of atoms on the bottom fixed at a cut-off energy of 500 eV. The positions of unconstrained atoms are optimized until the force change between two steps is smaller than 0.03 eV/Å. All atom electrons are also relaxed until the band structure energy change and total free energy change between two steps are less than 1×10^{-4} eV. Discretized k mesh ($3 \times 3 \times 1$), generated by the Monkhorst-Pack method [26], is used in Brillouin zone for energy integration. Oxygen molecules are initially placed at a height of 1.2 Å above each surface.

The proposed O_2 molecule adsorption sites on each surface plane are shown in Fig. 2. Position A is the bridge site located

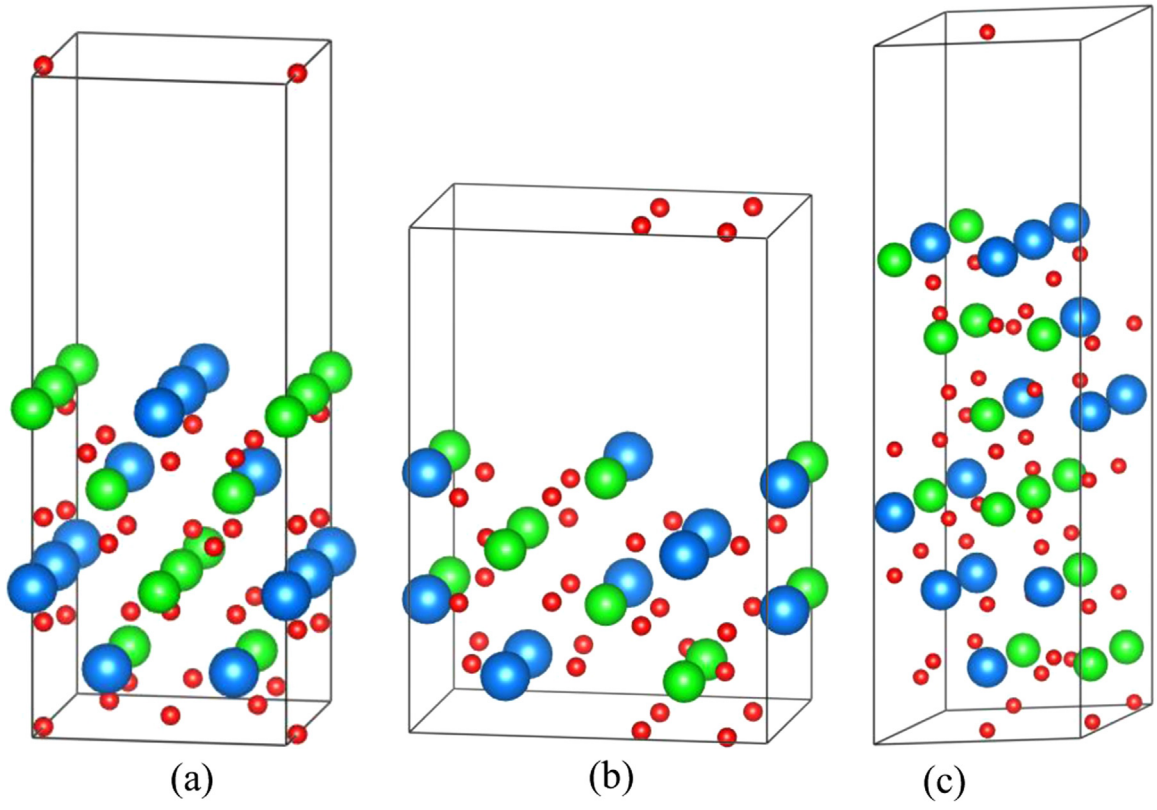

Fig. 1. Computational slab models of various $La_2Zr_2O_7$ planes: (a) (001) plane, (b) (011) plane, and (c) (111) plane. The blue, green, and red balls indicate La atoms, Zr atoms, and O atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)