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Ab initio studies of Nb doping effect on the formation of oxygen vacancy in rutile TiO_2

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ABSTRACT

In this paper, the effect of Nb doping on the formation of O vacancies in rutile TiO_2 is studied by the use of *ab initio* density-functional calculations. The formation energies are calculated at different doping concentrations (C_{Nb}) and the corresponding electronic structures are analyzed. It is shown that the formation energy is mainly determined by the structural relaxation. As C_{Nb} increases, the formation energy first increases and then decreases with the maximum in vicinity of C_{Nb}=11.1 at%. The investigation of electronic structures shows that the distribution of excess electrons, which is affected by the doping concentration and the types of oxygen vacancy, determines the relaxation and formation energy of oxygen vacancy. Our calculated results indicate that the formation of oxygen vacancy in rutile TiO_2 can be most effectively suppressed by Nb doping in a large range of Nb doping concentration. This may be one of the reasons why the proper amount of Nb doping can improve the oxidation resistance of γ-TiAl.

1. Introduction

γ-TiAl alloy is one of the most widely investigated materials, due to its potential application in the aerospace and automotive industries. However, the poor oxidation resistance of γ-TiAl alloy at high temperature hinders its application [1–3]. Previous studies [1–8] have shown that the micro-structure of the oxide scale was a rather complex mixture of non-protective TiO_2 and potentially protective Al_2O_3. Thus, one of the most effective methods to enhance oxidation resistance is to suppress the growth of TiO_2 rutile and form a continuous protective Al_2O_3 scale. In the last few decades, a large number of experimental observations have shown that alloying can effectively improve the oxidation resistance of γ-TiAl by the addition of Nb, Cr, W, Mo, Si [1–5,9–15].

Among these elements, Nb, as a dopant with higher valence than Ti, was studied extensively. The experimental work by Chen et al. studied the oxidation of Ti–Al–Nb ternary intermetallic alloys and showed that their oxidation behavior was affected by both the Al content and the ratio of Ti-to-Nb [4]. The composition range with excellent oxidation resistance was for an Al content from 55 to 64 at%, and Ti-to-Nb ratio from 2 to 5. If the ratio of Ti-to-Nb was either too high or too low, the oxidation resistance was reduced dramatically [4]. Later, Yoshihara and Miura also studied the effect of Nb addition on oxidation behavior of γ-TiAl and found that the optimum content of Nb was in the vicinity of 10 at%. Furthermore, Nb was only found in rutile to substitute for Ti, while Nb was not found in alumina [1]. Roy et al. attributed the improved oxidation resistance of Nb-containing alloys to the reduction of the defect concentration in TiO_2, which slowed the diffusion of oxygen [5]. Recently, Lin et al. found that Nb substituted for Ti in TiO_2 as a cation with a valence of 5, and the doping by Nb decreased the oxygen vacancy concentration owing to the electroneutrality in the oxide, and thus to suppress TiO_2 growth [3].

TiO_2, as a functional material, has wide applications ranging from a substance for white pigment to photocatalysis and nanoscale electronic devices. The enhancement of its properties by metal-doping has been studied by experiment and theory [16–21]. As a material relating to the oxidation resistance of γ-TiAl, TiO_2 has not been theoretically studied, though a large number of experimental works have been carried out on this subject. To explain the effect of Nb on the suppression of oxygen vacancy formation in rutile TiO_2 from a theoretical view point, in this study, we carry out density functional theory (DFT) calculations to systematically investigate the electronic structures of Nb-doped TiO_2 with an oxygen vacancy.

2. Methodology and models

TiO_2 rutile belongs to the space group P42/mnm(136). In the rutile structure, each Ti is octahedrally coordinated with six

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oxygen atoms. And, four of the oxygen atoms combine with Ti by forming shorter bonds than those of the other two. Correspondingly, three Ti atoms combine with an oxygen atom through two short bonds and one long bond. α-NbO_2 is isostructural to rutile as well as having similar lattice parameters; $a=b=4.587$ Å, $c=2.954$ Å for TiO_2 [22], and $a=b=4.846$ Å, $c=3.032$ Å for NbO_2 [23]. It is possible to obtain solid solutions $Ti_{1-n}Nb_nO_2$ from TiO_2 and NbO_2 under certain processing conditions [24].

For pure TiO_2 rutile, we employed a $2\times2\times3$ supercell consisting of 24 Ti atoms and 48 O atoms. For the Nb-doped systems, the same size of supercell models is used, except n Ti atoms are replaced by Nb atoms with $n=4$, 8, 12, 16, 20, as shown in Fig. 1. The corresponding concentrations (C_{Nb}) of Nb are 5.6, 11.1, 16.7, 22.2, and 27.8 at%. To examine the different structures at a certain doping concentration, we define the doping energy as

$$E_{dope}=\frac{1}{n}[E_{Ti_{24-n}Nb_nO_{48}}+nE_{Ti}-nE_{Nb}-E_{perfect}] \quad (1)$$

where $E_{Ti_{24-n}Nb_nO_{48}}$ is the total energy of the Nb-doped TiO_2 in $2\times2\times3$ supercell ($n=0$, 4, 8, 12, 16, and 20, respectively). $E_{perfect}$, E_{Ti}, and E_{Nb}, are the total energy of the pure TiO_2 rutile with $2\times2\times3$ supercell, bulk Ti, and bulk Nb, respectively. And we employ the most stable structures as the doping models.

The vacancy models ($Ti_{24-n}Nb_nO_{47}$) are simulated by removing one oxygen atom from the system ($Ti_{24-n}Nb_nO_{48}$). In the Nb doped TiO_2, different types of an oxygen vacancy at each doping concentration have been taken into consideration. For each oxygen atom, there are three metal atoms bonding with it. In the pure TiO_2, the bond lengths r_1 and r_2 are shorter than r_3. According to the different environments around the OXYGEN atoms, there are six main types of O vacancy as shown in Fig. 2. To study the effect of Nb doping on the formation of oxygen vacancy in TiO_2 rutile, we define the O vacancy formation energy as

$$E_{form}=E_{Ti_{24-n}Nb_nO_{47}}-E_{Ti_{24-n}Nb_nO_{48}}+\tfrac{1}{2}E_{O_2} \quad (2)$$

where $E_{Ti_{24-n}Nb_nO_{47}}$ is the total energy of the Nb-doped TiO_2 in $2\times2\times3$ supercell with an oxygen vacancy ($n=0$, 4, 8, 12, 16, and 20, respectively), and E_{O_2} is the total energy of a molecular oxygen.

All the calculated results were based on density functional theory (DFT) calculations, performed within the generalized gradient approximation (GGA) designed by Perdew and Wang (PW91) [25], as implemented in the Vienna *ab initio* simulation package (VASP) [26,27]. The projector augmented wave (PAW) method [28] is used to describe the ionic potentials, and the cutoff energy of the plane-wave basis set is 400 eV, after convergence tests. The integrations in the Brillouin Zone are performed on a grid of $(3\times3\times3)$ Monkhorst–Pack set [29] for the $2\times2\times3$ supercell. To obtain the equilibrium lattice parameters of the doped systems, the cell shape and the volume are relaxed. Only the positions of the atoms are relaxed, while the cell shape and volume are fixed when the system with an oxygen vacancy is being optimized. And atomic positions are relaxed until the

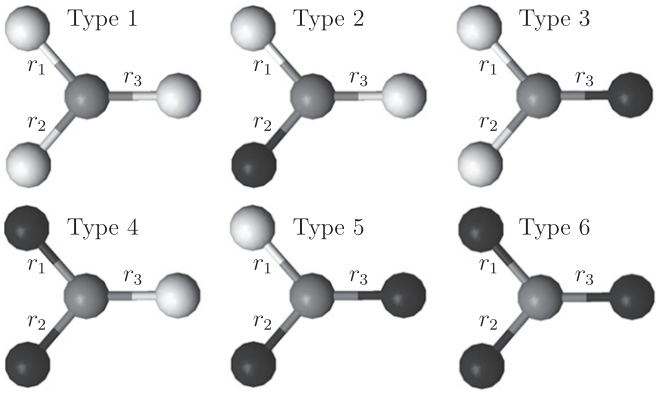

Fig. 2. The six main types of the oxygen vacancy, and r_i ($i=1$, 2, 3) are the distances between the O atom and its three nearest neighboring metal atoms. The white, gray and black balls represent the Ti, O and Nb atoms, respectively.

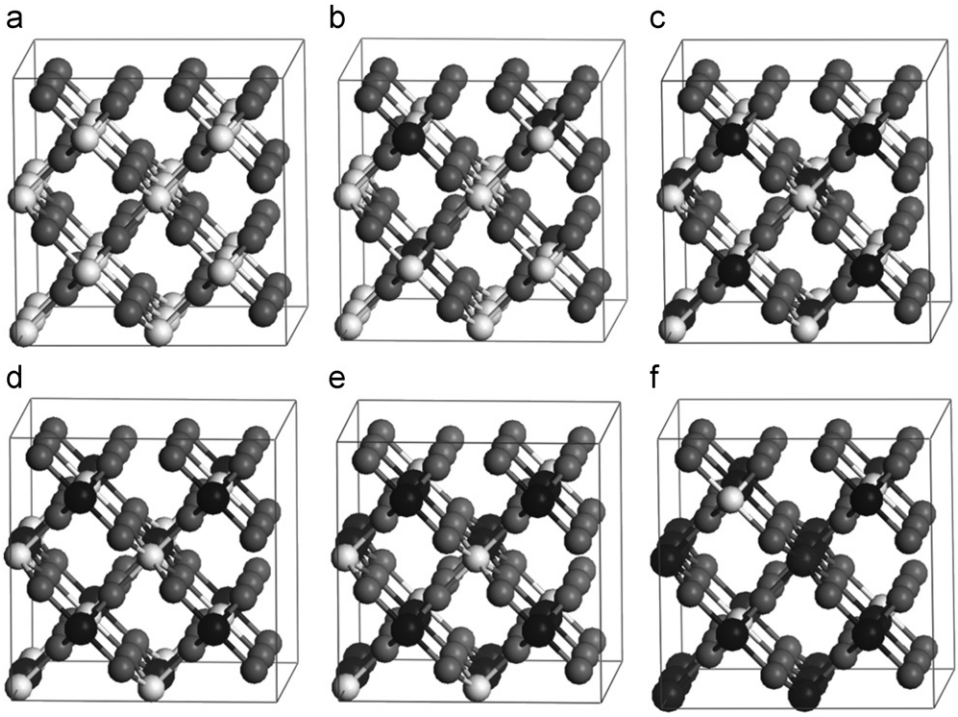

Fig. 1. The $2\times2\times3$ supercell models of TiO_2 rutile for the different doping concentration C_{Nb}: (a) 0.0 at%, (b) 5.6 at%, (c) 11.1 at%, (d) 16.7 at%, (e) 22.2 at%, and (f) 27.8 at%. The white, gray and black balls represent the Ti, O and Nb atoms, respectively.