Ordered oxygen arrangement in titanium nanoparticles: *Ab initio* study

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ABSTRACT

We have used density functional theory calculations to investigate the interaction of titanium nanoparticles with oxygen. We observed the energy-favorable site for oxygen atoms and investigated the atomic structure of the oxidized cluster.

Keywords: Nanoparticles; Metals and alloys; Oxidation; Simulation and modelling

1. Introduction

Titanium has a high corrosion resistance, a low thermal expansion, and a high mechanical strength [1, 2]. These properties make titanium and its alloys one of the most important structural materials for applications in aerospace vehicles, defense technology, and metal cutting.

The interaction of titanium with oxygen is an important scientific and technological problem [3] since its mechanical and electrical properties can be significantly modified [4-6]. Recently [1], it has been shown that the dissolution of oxygen in bulk titanium (up to 0.6 wt.%) improved its mechanical properties. Kyung-Ho Heo and co-authors [4] have shown that the hardness and electrical resistivity of oxygen-doped bulk Ti increased linearly with increasing oxygen concentration (500–7900 ppm O). The interaction of bulk and surface titanium with oxygen has been investigated for many years. With first-principles quantum-mechanical methods [3,7-9], it was shown that oxygen prefers to occupy an octahedral interstitial site in the bulk lattice. In addition, Henry et al. [9] found three oxygen interstitial sites in titanium, and

quantified mechanisms for oxygen diffusion. Experimental results [10,11] have indicated a different oxidation level of metallic titanium at different temperatures. At low temperature, oxygen initially adsorbs on the surface layer of Ti (0001) [10] and then diffuses into lower layers when the temperature increases [11].

It is still unclear how oxygen affects the atomic and electronic structures as well as the agglomeration processes of Ti nanoparticles. Thus, we have investigated oxygen adsorption on titanium nanoclusters and have calculated the binding energy as a function of oxygen concentration. Our results explain why oxygen adsorbs on faces of the icosahedral Ti_{13} cluster.

2. Methods and approaches

The first-principles calculations were performed with the generalized gradient approximation and spin polarization of density functional theory in the ABINIT software package [12]. Pseudopotentials for Ti and O atoms were constructed using the program fhi98PP [13]. A special 1×1×1 G-point in the Monkhorst-Pack grid [14] with a cutoff energy of 816.34 eV was used to simulate the Ti clusters. The simulation clusters were placed in a very large cubic cell, which had a size of approximately 19 Å. During the course of the calculations, the atomic structure was relaxed until the interatomic forces were less than 0.005 eV/Å. In addition, the Ti_2 dimer structure was calculated to validate the titanium pseudopotentials. The calculated Ti-Ti distance was 1.9055 Å, which is slightly less than the experimental value of 1.9422 ± 0.0008 Å [15].

3. Results and discussions

Experiments [16] have shown that the most stable titanium nanoparticle structures are icosahedral Ti_{13}, Ti_{19} and Ti_{55}. We investigated the Ti_{13} cluster here because the larger cluster sizes required considerable computing resources.

To study the interaction of the Ti_{13} cluster with oxygen we considered two oxygen coverages, 0.05 and 1 ML. The 0.05 ML coverage corresponds to one O atom on the Ti_{13} surface, whereas 1 ML corresponds to 20 oxygen atoms.

The average binding energy E_b of an O atom on the Ti_{13} surface is given by:

$$E_b = -\frac{1}{N_O}\left[E^{O/Ti} - \left(E^{Ti} + N_O E^{O}\right)\right] \qquad (1),$$

where N_O is the number of O atoms on the surface, $E^{O/Ti}$ is the total energy of the adsorbate-substrate system, E^{Ti} is the total energy of the clean Ti_{13} cluster, and E^{O} is the total energy of the O atom.

From Eq. 1, E_b=12.01 eV for oxygen on the Ti_{13} surface (Fig. 1), which is slightly higher than the energy of dissolved oxygen (11.85 eV) in bulk titanium. Thus, titanium nanoparticles are more reactive to oxygen than bulk titanium [17]. To characterize dissolved oxygen in bulk titanium, one oxygen atom was incorporated in the favorable octahedral site of the bulk lattice [3, 7-9]. Thus, our calculations have shown that, despite the transition from bulk titanium to the nanoscale (including Ti_{13} clusters), interacting O atoms are advantageously located in positions that correspond to "bulk" interstitial sites. These sites are certainly not octahedral (as in the bulk Ti), but because of the similarity of the local atomic structures of the bulk and isolated Ti_{13} clusters [18], and the coincidence of the Ti-O bonds, such a comparison is appropriate.

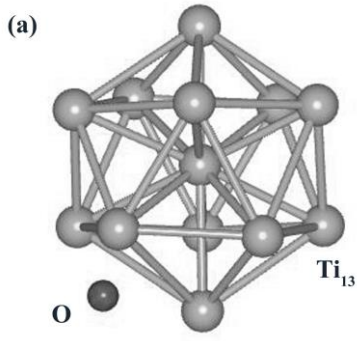

Fig. 1. The positions one oxygen atom adsorption on Ti_{13} cluster.

When the oxygen coverage is increased to one monolayer, *i.e.*, up to 20 atoms on the cluster surface (see Fig. 2), the oxygen binding energy reduces to 10.49 eV. The reduced binding energy indicates increased repulsive forces between the adsorbed oxygen atoms. In Fig. 2, it can be seen that all 20 oxygen atoms are located on each of the respective faces of the Ti_{13} icosahedron. The average Ti-O and O-O bond lengths are approximately 1.99 and 2.33 Å, respectively. However, when we allowed all the Ti atoms to relax in the cluster, it tends to form an oxide cluster where all the Ti-Ti bonds are broken. Thus, in this case, we have fixed the titanium atoms during the relaxation.

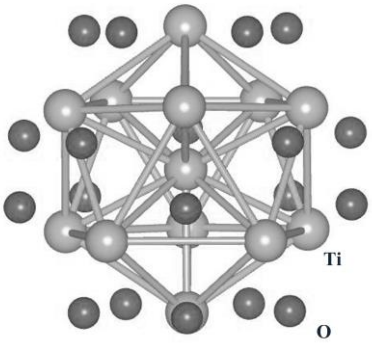

Fig. 3. The Ti_{13} cluster structure with 20 adsorbed oxygen atoms.

The results we obtained for the energetics and structural properties of oxygen adsorption on titanium nanoclusters are very important in understanding oxygen diffusion in nanostructured titanium materials. Specifically, the results will impact the design, production and application of these materials in aerospace and engineering.

4. Conclusions

In conclusion, we have used first-principles calculations to investigate the oxygen adsorption process on the stable Ti_{13} nanocluster. The atomic structure of the oxidized titanium clusters and the oxygen adsorption energy were studied in detail, for low and high O coverages on the Ti_{13} surface. The results indicate that titanium, during its interaction with oxygen, and for

both its bulk and nanoscale states, has O atoms advantageously located in the positions which correspond to "bulk" interstitial sites.

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