

# Ordered Oxygen Arrangement in Titanium Nanoparticles: *Ab Initio* Study

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## Abstract

We have used the density functional theory 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 modeling*

## 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]. The dissolution of oxygen in bulk titanium (up to 0.6 wt. %) has been shown recently [1] to improve its mechanical properties. Kyung-Ho Heo and co-authors [4] have shown the hardness and electrical resistivity of oxygen-doped bulk Ti to increase linearly with increasing oxygen concentration (500–7900 ppm O). The interaction of bulk and surface titanium with oxygen has been investigated for many years. It was shown by first-principles quantum-mechanical methods [3, 7–9] that the oxygen prefers to occupy an octahedral interstitial site in the bulk lattice. In addition, Henry *et al.* [9] have found three oxygen interstitial sites in titanium and quantified mechanisms for oxygen diffusion. Experimental results [10, 11] have indicated different oxidation levels of metallic titanium at different temperatures. At low temperature, the oxygen is initially adsorbed on the surface layer of Ti (0001) [10] and then diffuses into lower layers when the temperature increases [11].

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

## 2 Methods and approaches

First-principles calculations were performed using the generalized gradient approximation and allowing for spin polarization within the density functional theory by

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<http://www.ntse-2014.khb.ru/Proc/Chibisov.pdf>.

means of the ABINIT software package [12]. Pseudopotentials for Ti and O atoms were constructed using the program fhi98PP [13]. A special  $1 \times 1 \times 1$  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 with the size of approximately 19 Å. The atomic structure was relaxed in the calculations while the interatomic forces were less than 0.005 eV/Å. In addition, the Ti<sub>2</sub> dimer structure was calculated to validate the titanium pseudopotentials. The calculated Ti-Ti distance was 1.9055 Å that is slightly less than the experimental value of  $1.9422 \pm 0.0008$  Å [15].

### 3 Results and discussions

Experiments [16] have shown that the most stable titanium nanoparticle structures are the icosahedral clusters Ti<sub>13</sub>, Ti<sub>19</sub> and Ti<sub>55</sub>. We investigated the Ti<sub>13</sub> cluster here because larger clusters require considerable computing resources.

To study the interaction of the Ti<sub>13</sub> cluster with the oxygen, we considered two oxygen coverages, 0.05 and 1 monolayer (ML). The 0.05 ML coverage corresponds to one O atom on the Ti<sub>13</sub> surface whereas 1 ML corresponds to 20 oxygen atoms.

An average binding energy  $E_b$  of O atom on the Ti<sub>13</sub> surface is given by

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

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 energy of the Ti<sub>13</sub> cluster, and  $E^O$  is the energy of the O atom.

From Eq. (1), we obtain  $E_b = 12.01$  eV for the oxygen on the Ti<sub>13</sub> surface (Fig. 1), which is slightly higher than the energy of dissolved oxygen (11.85 eV) in bulk titanium. Therefore the titanium nanoparticles are more reactive to oxygen than the bulk titanium [17]. To characterize the dissolved oxygen in bulk titanium, one oxygen atom has been incorporated in the favorable octahedral site of the bulk lattice [3,7–9]. Hence our calculations demonstrate that, despite the transition from bulk titanium to the nanoscale (including Ti<sub>13</sub> clusters), the 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). Due to the similarity of the local atomic structures of the bulk and isolated Ti<sub>13</sub> clusters [18] and the coincidence of the Ti-O bonds, such a comparison is appropriate.

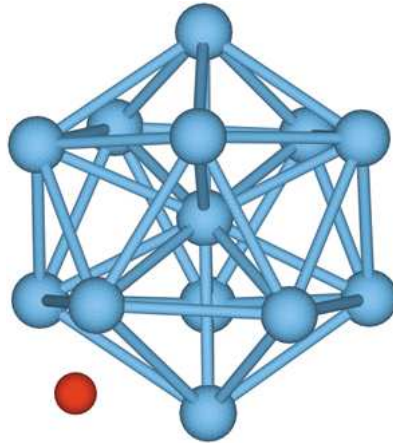


Figure 1: Position of one oxygen atom (red circle) adsorbed on the Ti<sub>13</sub> cluster (blue circles).

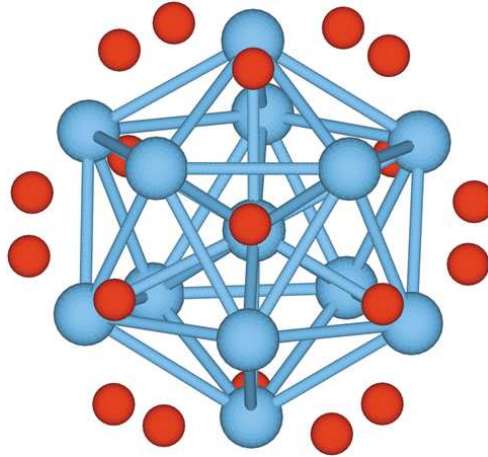


Figure 2: The  $\text{Ti}_{13}$  cluster structure (blue circles) with 20 adsorbed oxygen atoms (red circles).

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 manifests increased repulsive forces between the adsorbed oxygen atoms. It can be seen in Fig. 2 that the oxygen atoms are located on each face of the  $\text{Ti}_{13}$  icosahedron. Average Ti-O and O-O bond lengths are approximately 1.99 and 2.33 Å, respectively. However, when we allow all Ti atoms to relax in the cluster, it tends to form an oxide cluster where all Ti-Ti bonds are broken. Thus, in this case, we have fixed the titanium atoms during the relaxation.

Our results regarding the energetics and structural properties of oxygen adsorption on titanium nanoclusters, are very important for understanding an 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  $\text{Ti}_{13}$  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  $\text{Ti}_{13}$  surface. The results indicate that titanium during its interaction with oxygen, for both bulk and nanoscale states, has O atoms advantageously located in the positions corresponding to “bulk” interstitial sites.

## References

- [1] A. K. M. Nurul Amin, *Titanium alloys — towards achieving enhanced properties for diversified applications*. InTech, Rijeka, 2012.
- [2] S.-Y. Wang, J.-Z. Yu, H. Mizuseki, J.-A. Yan, Y. Kawazoe and C.-Y. Wang, *J. Chem. Phys.* **120**, 8463 (2004).
- [3] G. Boureau, N. Capron and R. Tétot, *Scr. Mater.* **59**, 1255 (2008).
- [4] K.-H. Heo, N. R. Munirathnam, J.-W. Lim, M.-T. Le and G.-S. Choi, *Mater. Chem. Phys.* **112**, 923 (2008).

- [5] S. Firstov, V. Kulikovskiy, T. Rogul and R. Ctvrtlik, *Surf. Coat. Technol.* **206**, 3580 (2012).
- [6] S. J. Li, M. T. Jia, F. Prima, Y. L. Hao and R. Yang, *Scr. Mater.* **64**, 1015 (2011).
- [7] I. Lado-Tourino and F. Tsobnang, *Comp. Mater. Sci.* **32**, 13 (2005).
- [8] A. V. Ruban, V. I. Baykov, B. Johansson, V. V. Dmitriev and M. S. Blanter, *Phys. Rev. B* **82**, 134110 (2010).
- [9] H. H. Wu and D. R. Trinkle, *Phys. Rev. Lett.* **107**, 045504 (2011).
- [10] Y. Takakuwa, S. Ishidzuka, A. Yoshigoe, Y. Teraoka, Y. Yamauchi, Y. Mizuno, H. Tonda and T. Homma, *Appl. Surf. Sci.* **216**, 395 (2003).
- [11] Y. Takakuwa, S. Ishidzuka, A. Yoshigoe, Y. Teraoka, Y. Mizuno, H. Tonda and T. Homma, *Nucl. Instr. Meth. Phys. Res. B* **200**, 376 (2003).
- [12] X. Gonze, B. Amadon, P.-M. Anglade, J.-M. Beuken, F. Bottin, P. Boulanger, F. Bruneval, D. Caliste, R. Caracas, M. Cote, T. Deutsch, L. Genovese, Ph. Ghosez, M. Giantomassi, S. Goedecker, D.R. Hamann, P. Hermet, F. Jollet, G. Jomard, S. Leroux, M. Mancini, S. Mazevet, M. J. T. Oliveira, G. Onida, Y. Pouillon, T. Rangel, G.-M. Rignanese, D. Sangalli, R. Shaltaf, M. Torrent, M. J. Verstraete, G. Zerah and J. W. Zwanziger, *Comp. Phys. Comm.* **180**, 2582 (2009).
- [13] M. Fuchs and M. Scheffler, *Comp. Phys. Comm.* **119**, 67 (1999).
- [14] H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- [15] M. Doverstal, B. Lindgren, U. Sassenberg, C. A. Arrington and M. D. Morse, *J. Chem. Phys.* **97**, 7087 (1992).
- [16] L. Lian, C.-X. Su and P. B. Armentrout, *J. Chem. Phys.* **97**, 4048 (1992).
- [17] J. S. Golightly and A. W. Castleman, *J. Phys. Chem. B* **110**, 19979 (2006).
- [18] A. N. Chibisov, *Mater. Lett.* **104**, 91 (2013).