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Early Stage of Oxidation on Titanium Surface by Reactive Molecular Dynamics Simulation

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Abstract: Understanding of metal oxidation is very critical to corrosion control, catalysis synthesis, and advanced materials engineering. Metal oxidation is a very complex phenomenon, with many different processes which are coupled and involved from the onset of reaction. In this work, the initial stage of oxidation on titanium surface was investigated in atomic scale by molecular dynamics (MD) simulations using a reactive force field (ReaxFF). We show that oxygen transport is the dominant process during the initial oxidation. Our simulation also demonstrate that a compressive stress was generated in the oxide layer which blocked the oxygen transport perpendicular to the Titanium (0001) surface and further prevented oxidation in the deeper layers. The mechanism of initial oxidation observed in this work can be also applicable to other self-limiting oxidation.

Keywords: Reactive force field, metal oxidation, self-limiting oxidation, Titanium (0001) surface, molecular dynamics simulation, compressive stress.

1 Introduction

As a material combining good mechanical strength and light weight [Chen, Fray and Farthing (2000); Plimpton (1995)], titanium is used in many technological areas such as aerospace, automotive industry, jewelry and medicine [Praveena and Nirmala (2017)]. It is well documented that biocompatibility and corrosion resistance properties, which are very important in such applications, is due to a thin passive film forming spontaneously on the surface of Ti when oxygen is present [Alves, Rossi, Ribeiro et al. (2017); Gemelli and Camargo (2007); Jaeggi, Parlinskawojtan, Kern et al. (2012)]. The passive film is normally a few nanometers thick and consists mainly of amorphous titanium dioxide [Pan, Thierry and Leygraf (1996)]. Nevertheless, the functionality of the oxide film depend on the chemical composition structure, morphology and mechanical conditions of the material [Gemelli and Camargo (2007)] Titanium oxide film produced from titanium surface has been the focus of experimental studies for many years. A great deal of

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experimental investigation has been performed to investigate oxide film using various experimental techniques such as vacuumS evaporated titanium oxidation [Babuji and Radhakrishna (1985)], DC plasma oxidation [Leng, Chen, Yang et al. (2003)], anodic oxidation [Wu, Liu, Wu et al. (2000)], micro-arc oxidation [Li, Kong, Kim et al. (2004)], thermal oxidation treatment [Dong and Bell (2000)], RF plasma oxidation [Valenciaalvarado, La Piedadbeneitez, Lopezcallejas et al. (2014)], and laser oxidation [Lavisse, Langlade, Berger et al. (2004)]. Many of these methods involve oxygen atoms under electric field to bombard the titanium surface to form an oxide film. However, mechanism on how electric field effect and intrinsic stress influence the transport of Oxygen atoms has not been clearly discussed. Moreover, studies concerning the early stage of oxidation are still very few. When the film thickness decreases to a nanometer scale, stress distributions are very crucial to the initial oxidation process. Therefore, the initial stage of titanium oxidation has been one of the most intensively studied topics, yet remains controversial. Understanding the initial oxidation behavior is also important for revealing and controlling the structure and properties of Titanium oxide films. In order to gain an atomic scale insight into the oxidation process, in this work, we simulate the oxidation of titanium by using molecular dynamics simulation under different electric field condition.

2 Computational details

In this paper, molecular dynamics simulations are performed using the “large-scale atomic/molecular massively parallelized simulator” (LAMMPS) code integrated with the Reactive Force-Field (ReaxFF) [Aktulga, Fogarty, Pandit et al. (2012); Plimpton (1995); Xia, Wang, Sun et al. (2016)]. ReaxFF is a generic bond order dependent force field that can simulate chemical reactions by introducing the dynamic bond-orders and partial charges of the atoms [Zheng, Li, Nie et al. (2017)]. The bonded interactions are bond-order-dependent, with the bond itself being calculated based on interatomic distance. In this method the forces are derived from the following energy expression [Ashraf and van Duin (2017)]:

$$\mathrm{E}_{system} = E_{bond} + E_{over} + E_{under} + E_{lp} + E_{val} + E_{vdWaals} + E_{coulomb} \tag{1}$$

which consists of different partial contributions: bond energies (E_{bond}), energy penalties for over-coordination (E_{over}) and (optionally) stabilize under-coordination of atoms ($E_{over}\ and\ E_{under}$), lone-pair energies (E_{lp}), valence angle energies (E_{val}), and the terms to handle non-bonded van der Waals ($E_{vdWaals}$) and coulomb ($E_{coulomb}$) interaction energies [Huygh, Bogaerts, Duin et al. (2014)]. The force field parameters used in this work were developed by Ashraf C et al. [Huygh, Bogaerts, Duin et al. (2014)] which provides accurate description of the interatomic interactions among the Ti and O atoms. To further verify the accuracy of the ReaxFF in describing the interatomic interactions in Ti-O systems, we compare the adsorption energy for an oxygen adadtom on various sites of Ti (101) surface and the formation energy of an oxygen atom in the different interstitial sites in bulk Ti obtained from ReaxFF with those from first principles DFT calculations as shown in Fig. 1 and Fig. 2 respectively.

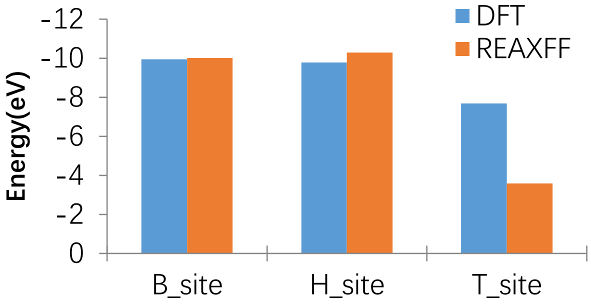


Figure 1: Oxygen adsorption energies per O atom in various configuration on Titanium (0001) surface

The ReaxFF MD and the DFT results on the adsorption energies are compared in Fig. 1. Although the absolute values of the adsorption energy from both calculations are not exactly the same, the relative stability of the adsorption site predict by the ReaxFF MD calculations agrees well with that of the DFT result. This comparison suggests that the ReaxFF can give a good description of reactions occurring at the titanium surface.

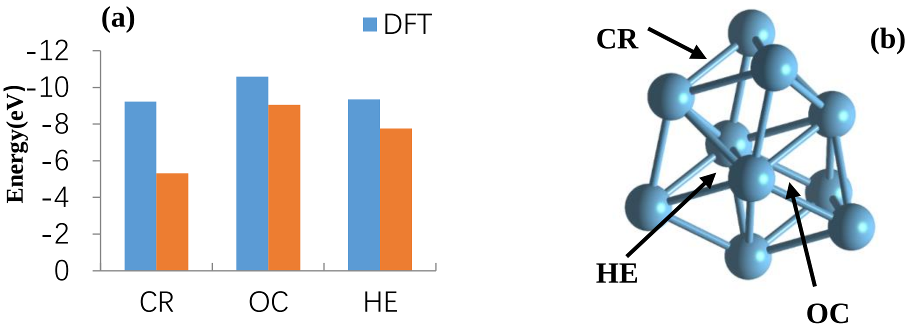


Figure 2: Formation energies calculated with ReaxFF MD and DFT for the different interstitial oxygen sites located in the titanium. (a) formation energies (b) interstitial sites

In Fig. 2 the formation energies of interstitial oxygen calculated with the ReaxFF MD and with DFT are compared. Octahedral center (OC) site, hexahedral center (HE) site and Ti-Ti bond center crowdion (CR) site as indicated in the right site of the figure represent different locations where an oxygen interstitial atom can occupy in bulk titanium. The relative stability of the interstitial sites obtained from the ReaxFF MD calculations also agrees with that from DFT calculations. However, ReaxFF MD result underestimates all formation energies compared to the DFT result [Huygh, Bogaerts, Duin et al. (2014)] pecially for CR site, for which the formation energy calculated with ReaxFF lies about

42% below the DFT value. Therefore, ReaxFF MD overestimates the significance of CR site in comparison with the OC and HE sites.

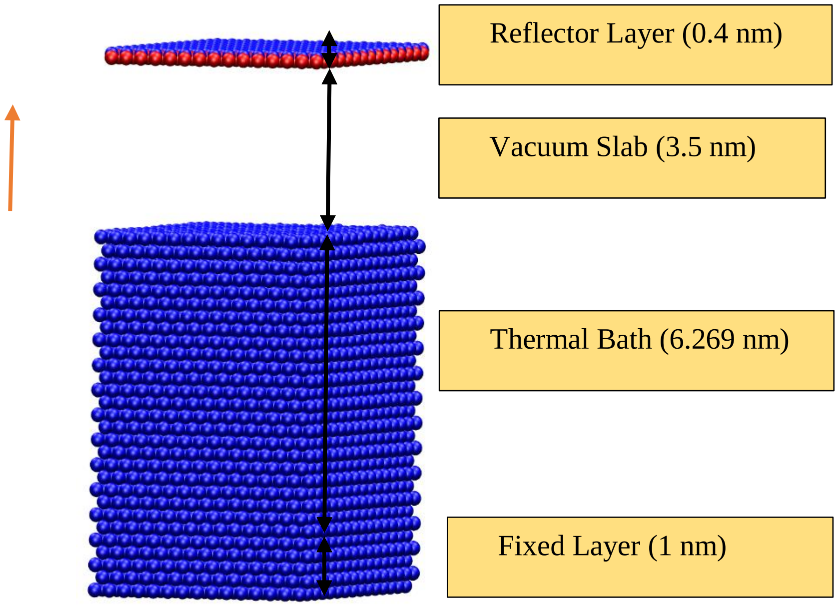


Figure 3: Side view of the simulation box. Red and yellow atoms are O atoms and Ti atoms, respectively

We also test the accuracy of the ReaxFF in describing the lattice parameters of Ti crystal. After relaxing at 300 K for 10 ps [Liu, Fan, Sun et al. (2016); Liu, Wang, Zhou et al. (2007); Sun, Dai, Song et al. (2014)], the hcp Ti crystal structure has lattice constants of a=0.2983 nm, c=0.4883 nm, which gives c/a=1.6371. These calculated values are close the experiment values of a=0.2949 nm, c=0.4677 nm and c/a=1.5860 [Liu, Wang, Zhou et al. (2007)] To perform the MD simulation, a thick slab of (0001) Ti containing 6957 atoms with the dimensions of 4.29 nm×4.29 nm×7.269 nm was set up. The simulation box was set to be 10.42 nm along z direction (the out-of-plane direction) to allow about 3.5 nm of free space (vacuum region) above the Ti (0001) surface for introducing oxygen atoms. Periodic boundary conditions were applied to all three directions.

Fig. 3 shows the simulation box used in the present simulation. In order to mimic a thick substrate, titanium atoms in the bottom 1 nm region of the simulation box were fixed. An oxygen reflection layer was also fixed at the top of the vacuum region so that oxidation can only occur at one surface (the non-fixed surface) of the Ti (0001) slab. Atoms in the region of about 6.6 nm above the fixed layer were kept at a constant oxidation temperature (300 K) during simulation to provide a thermal bath during the oxidation (Melro and Jensen (2017). The temperature of the moving atoms in the Ti (0001) slab was rescaled at every time step (0.5 fs) during simulation. Oxidation was proceeded by placing oxygen atoms one-by-one (shown as red balls) at the distance 2 nm above the Ti (0001) surface. In order to simulate the effect of electric field force on oxidation process, each oxygen atom is subjected to a constant electric field force and moves toward the titanium surface. The range of this force is determined by the anode voltage as shown in Tab. 1 [Li, Chen, Wang et al. (2016); Liu, Liu, Zhong et al. (2014)]. In order to compare the oxidation behavior with the previous ab initio calculations and the experimental results of surface reaction, we oxidized the surface by sequentially adding 100 oxygen atoms in to the vacuum region to study the evolution of the surface oxidation.

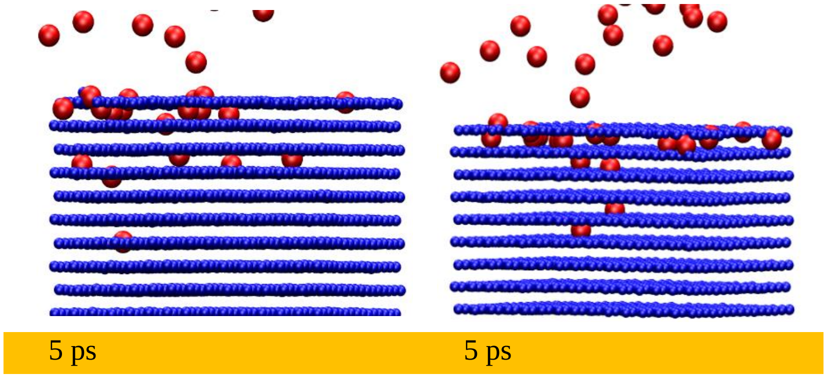
Table 1: The oxygen atom of force in reaction process

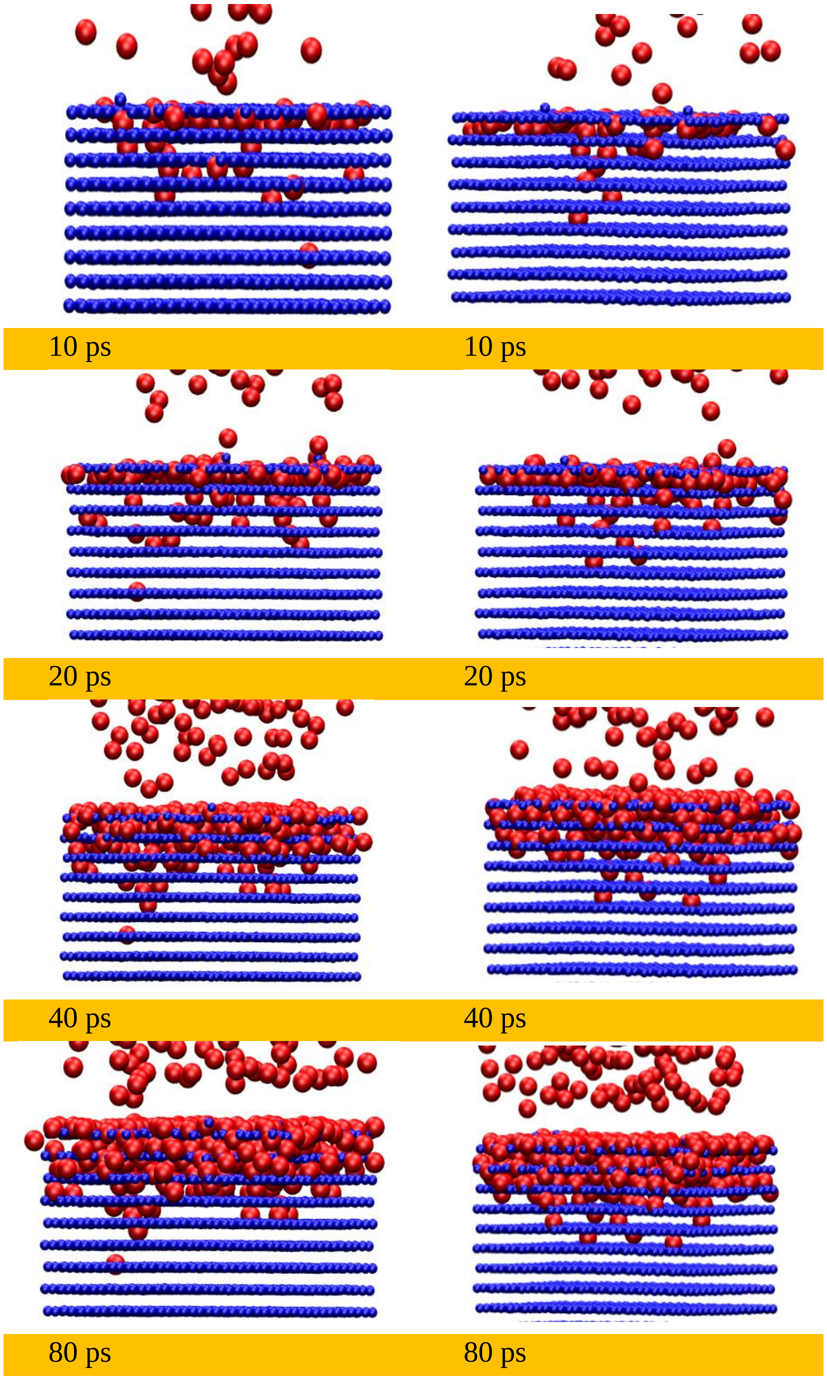
Name	Force-1	Force-2	Force-3	Force-4	Force-5
Electric field (V/cm)	5/4	10/4	20/4	30/4	40/4
Real force (eV/A)	0.57×10^{-6}	1.15×10^{-6}	2.3×10^{-6}	3.45×10^{-6}	4.6×10^{-6}

3 Results and discussion

Although titanium has been studied extensively for many decades, there are still a lot of debates regarding the fundamental oxidation mechanism of this material [Fang, Wen, Xu et al. (2017)]. It is important to obtain atomic scale information on the interaction of oxygen with titanium surface to gain better fundamental insights into which factors play an important role in the oxidation process.

3.1 Structural properties




10 ps
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40 ps
40 ps
80 ps
80 ps

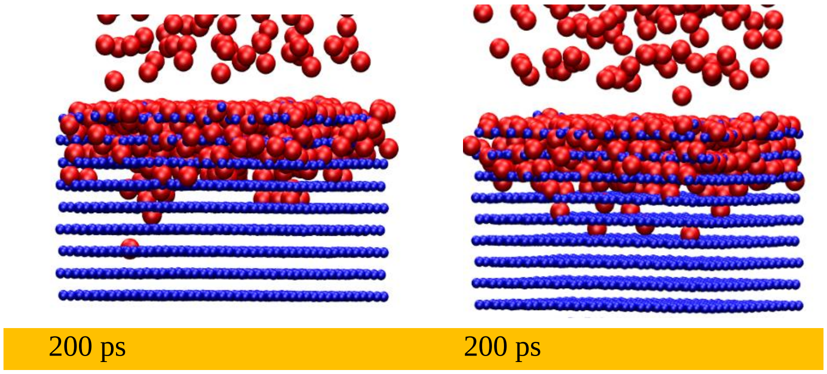

Figure 4: The evolution of atomistic structures during oxidation process under Force-1 and Force-5

Fig. 4 shows the typical snapshots of the oxidation reaction when the oxygen atoms were supplied at a constant force toward the relaxed Ti (0001) surface at 300 K. Our simulations show that for the low coverage the oxygen atoms prefer occupying both the surface layer and the seond layer. This calculated result agrees with the DFT results [Liu, Wang, Zhou et al. (2007)]. When the oxygen atoms dose was increased, the oxygen atoms were found mainly distributed into the second layer and the third layer, although a few adatoms are still left on the Ti (0001) surface. With the increase of oxidation time, the oxygen of the second layer and the third layer tends to be saturated and the coverage of surface oxygen atoms increases. Finally, the surface, second layer and the third layer of the Ti slab are all saturated with oxygen.

3.2 Oxidation time

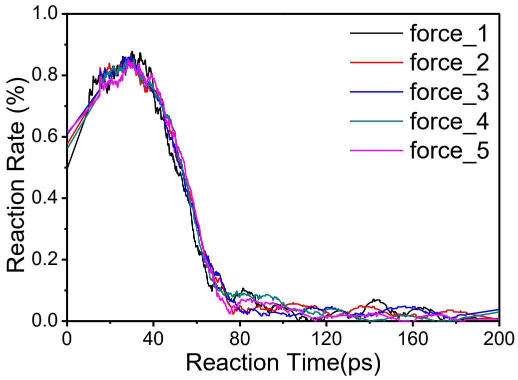

Figure 5: Reaction rate of oxidation process under different consist force

We found that the reaction kinetics is dependent on the position of oxygen atom on the Ti (0001) surface. Fig. 5 shows the oxidation process when the oxygen atoms were supplied with different force. The curves exhibit similar shape, all of which found three stages of early titanium oxidation. In the 1st stage, oxygen reaction rate increased with time. In the 2nd stage, oxygen then incorporated into the subsurface region and resulted in a reaction decrease and finally in the 3rd stage the reaction was very small which was caused by Ti-O layer formation. The oxygen-titanium reaction occurred very rapidly within 0.8 ps at all forces conditions. Therefore, it must be noted that the present simulations consider only very initial stage of the oxidation and exclude thermal diffusion of oxygen in a long time scale. However, the resulting atomic reaction rate of the oxygen atom is essentially the same for different applied forces. This result implies that the oxidation reaction on Ti (0001) surface is independent of applied forces.

3.3 Oxidation process

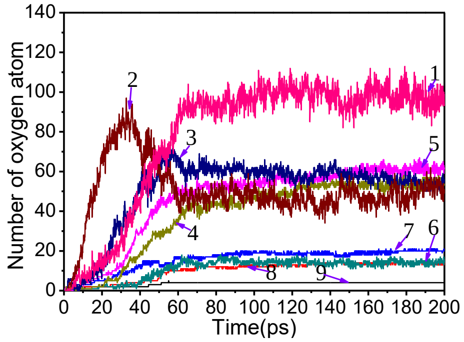

Figure 6: At top 9 layers, total oxygen atoms in each layer profile of the oxidized Titanium surface during oxidation process with 100 oxygen atoms in Vacuum Slab

By analyzing the simulated oxide layer, initial oxidation behaviors at 300 K were studied. Fig. 6 shows the distributions of oxygen atoms in different layers as the function of oxidation time. The results show that the oxygen concentration in the 2nd layer increases sharply from 0 fs to 25 ps and then decreases quickly until about 60 ps when it becomes stabilizing. The slopes of the curves reflect the reaction rate, which indicate that oxidation rate was extremely high in the first 25 ps, especially at the 2nd layer. This result agrees with the results shown in Fig. 5. During early 25 ps, the oxygen concentration rise rapidly and reached a maximum, especially the change at second layer is much faster than that at the other layers. Our simulations suggest that oxygen go to the 2nd layer without adsorbed on the surface at initial stage of oxidation. After the first 25 ps, the oxygen concentration at the 2nd layer is saturate and we could observe that a lot of oxygen atoms start to accumulate on the first layer and generate a surface oxide layer. At the same time the number of oxygen atoms at deeper layer is less than the first layer because of oxidation was decelerating attributed to the compressive stress at the 2nd layer which block the diffusion of the oxygen atoms into the deeper layers as shown below.

3.4 Self-limiting oxidation

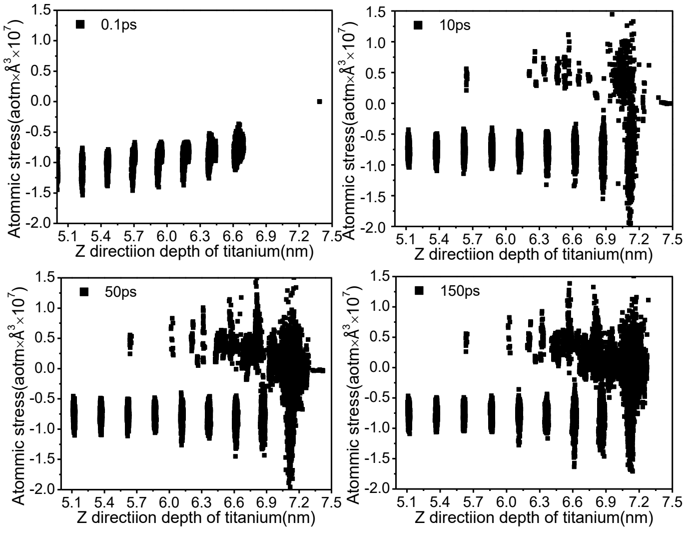

Figure 7: The corresponding *x* component stress distribution under different oxidation time

To unravel the oxygen atom transport mechanism during early stage of oxidation, compressive stress along *x*-*y* planar direction for different time ranging from 0.1 ps to 150 ps were calculated and shown in Fig. 7. Note that in the present work, the stress/atom is defined as the negative of the pressure tensor per atom. From 0.1 ps to 150 ps, the compressive stress in the surface region reached maximum at second layer then reduced at deeper layers. The maximum compression stress located at the region with the maximum oxygen concentration (Fig. 6). Indeed, the early stage of oxidation was almost completed within 80 ps. It was reported that one possible mechanism for ultrathin film oxidation is ballistic transport act as rather than the conventional dissolution-diffusion. This mechanism is supported by both experiment and simulations. Our present MD simulation results show that the accumulation of O atoms at top few surface layers during the initial stage of oxidation can generate compressive stress at the surface layers and further block O atom diffusion into deeper layers. The maximum compression stress located at the region where O concentration is at maximum. Due to the injection of O atoms, the oxide film turned to expand in parallel to the surface direction. But, as the lateral expansion was constrained by the titanium substrate, compression stress was generated in the oxide film. Such residual compressive stress in oxide film cause the so-called “self-limiting oxidation” since the barrier caused by compressive deformation is higher than the activation energy of oxygen diffusion and reaction. So the ballistic transport of O atoms at very early moment played dominant role during oxidation of titanium.

4 Conclusions

By performing a ReaxFF MD simulation study, the transport of O atoms was found to control the initial oxidation stage of titanium. Surface oxide layer is formed quickly within 2 ps of simulation time. Our simulation results also show that the oxidation reaction is independent of the initial applied forces. The O concentration accumulation was caused by the transport of O atoms into 2nd layer at the very beginning of oxidation (50 ps), leading to compressive stress of the surface layer which blocked the subsequent transport of O atoms. We believe that the mechanism discovered in this work can be applied to other self-limiting oxidation behaviors.

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