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Mechanisms of oxidation of pure and Si-segregated α -Ti surfaces

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ABSTRACT

Using first-principles molecular dynamics, we identified the mechanisms of the oxidation of α -Ti surfaces. Si segregation was found to suppress α -case formation in Ti, which was also confirmed experimentally. Charge transfer from the metal atoms to the gas molecules drives the initial stages of oxidation on the pure and Si-segregated α -Ti (0001) surfaces, while during the later stages, oxidation proceeds via oxygen penetration into the slab. Growth of the oxide network was strongly dependent on the oxidation state of the surface Ti atoms. Oxide growth in the Si-segregated material was retarded with the formation of TiO_x ($0.5 \leq x \leq 1$) on the surface, which corresponds to the +1.5 oxidation state of the Ti atoms. The simulations and experiments clearly showed that Si reduces the ingress of oxygen into Ti, even at high temperatures. The primary and critical steps of identifying, understanding, and controlling the mechanisms of oxidation of Ti surfaces at high temperatures, as performed here, are expected to aid the design of new alloys with improved oxidation resistance.

1. Introduction

Titanium and its alloys are used for high-temperature components of jet engines owing to the superior combination of excellent mechanical properties with low density and good corrosion resistance [1,2]. Their high affinity for oxygen, particularly at elevated temperatures, severely limits their application above 650 °C [3,4]. Thus, it is necessary to reduce the diffusion of oxygen into Ti alloys to enable their use at higher temperatures. Considerable efforts have been made to improve the oxidation resistance of Ti alloys. Many researchers have investigated the influence of certain elements on the oxidation behavior of titanium-based alloys [5–14]. Experiments have shown that the addition of Si, Zr, Nb, and Hf to α -Ti increases the oxidation resistance, while Ga, Ge, and Sn have detrimental effects [13,14]. In particular, it was reported that the addition of Si lowers the oxidation rate of α -Ti [5,6,10]. Fig. 1 summarizes the parabolic rate constants derived from the mass gain during oxidation of commercially pure (CP) Ti and Ti–Si binary alloys in air or oxygen atmospheres, which were experimentally derived by several research groups [3,6,10,15,16,17]. It was confirmed that Si addition reduced the parabolic rate constant and effectively improved the oxidation resistance of Ti. The mechanisms behind the improved oxidation resistance of Ti by Si addition were proposed [6,10]. However, the role of Si is not yet well understood as it is difficult to analyze the chemical state and quantify the amount of Si

introduced into the oxide layer and at the oxide layer–Ti substrate interface. Recently, using density functional theory (DFT), we studied the oxidation of the Ti (0001) surface [18,19]. We varied the oxygen content and performed molecular dynamics (MD) simulations at 973 K. We observed a significant reduction in the oxygen penetration into the Ti slab in the presence of Si [19].

The oxidation of metals involves the nucleation of the oxide on the metallic surface, followed by the lateral growth of the nuclei, which eventually forms the oxide layer. In the case of pure Ti, growth of the oxide layer exhibits parabolic behavior at low temperatures, while at higher temperatures, it follows a linear law [20]. A critical feature of Ti oxidation is the formation of an oxygen-rich layer just beneath the oxide layer, commonly known as the α -case, where the oxygen atoms reside at the interstitial octahedral sites [21]. The formation of the α -case can lead to embrittlement and reduce the fatigue strength [22]. Adding alloying elements to the Ti matrix to enhance the oxidation resistance serves two purposes. First, the alloying elements should inhibit oxygen diffusion in the oxide layer, and second, they should suppress the formation of the α -case. The effect of the alloying elements on Ti oxidation was summarized by Dai et al. [20]. Although several studies of the high-temperature oxidation of Ti with added Si have been performed [5,6,10,23,24], the exact reason for the improved oxidation resistance with Si doping is still unclear. In our previous studies [18,19] we demonstrated the effect of Si on the oxidation of Ti; however, we did

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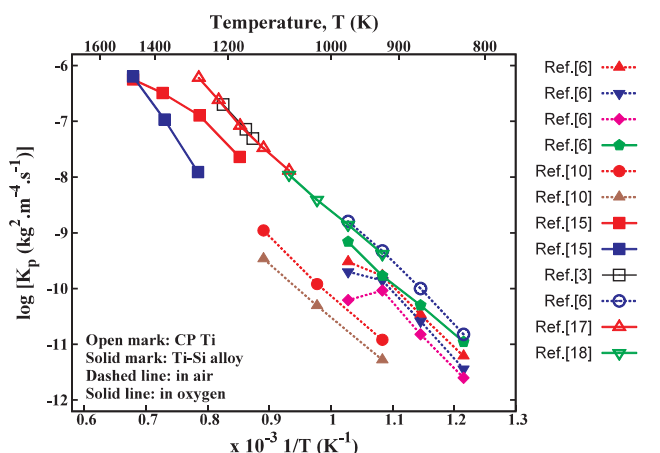


Fig. 1. Arrhenius plot of the oxidation rate constants (K_p) of CP Ti and Ti–Si alloys.

not focus on the kinetics of the oxidation. A detailed understanding of the factors driving the oxidation is essential to the design of Ti alloys with improved oxidation resistance.

DFT-based MD simulations can provide a comprehensive understanding of oxidation kinetics, allowing the identification of the processes driving the reaction and the design of an effective means of mitigating these reactions. Additionally, it is important to perform MD simulations that can mimic the experimental conditions under which the oxidation proceeds continuously. To study the effect of temperature, it is necessary to consider canonical systems. In the present study, we examined the oxidation of pure and Si-segregated α -Ti (0001) surfaces at high temperatures with the aim of understanding the mechanism(s) of Ti oxidation. We adopted a novel strategy to add oxygen molecules to the simulations, which mimics the increase in oxygen coverage on the surfaces, as well as the continuity of the reactions during experiments. Although our strategy is similar to that employed by Schneider and Ciacchi [25], there are significant differences; we studied canonical systems while they used a microcanonical ensemble. Moreover, Schneider and Ciacchi performed full atomic relaxation of their systems before placing oxygen molecules on the previously formed oxide layer. In our simulations, we did not perform atomic relaxation during any stage of the oxidation reaction, thus preserving the continuity of oxygen addition, as is the case under experimental conditions. Using our DFT-based simulations, we studied the dynamics of the oxide growth on pure and Si-segregated Ti surfaces. In addition, we studied the effect of Si addition on the α -case formation using both DFT and experiments. We were able to identify the mechanisms of oxide growth on the Ti surface and propose a structure for enhancing the high-temperature oxidation resistance of Ti alloys.

2. Methodology

2.1. DFT calculations

We performed DFT-based Born-Oppenheimer MD as implemented in the Vienna *Ab initio* Simulation Package (VASP) [26,27]. Projector-augmented wave (PAW) pseudopotentials [28,29] were used to describe the valence electron-nuclei interactions. The electronic wavefunction was expanded using a plane wave basis set with an energy cutoff of 500 eV. We used the Perdew-Burke-Ernzerhof (PBE) [30] exchange-correlation functional, while the Brillouin zone sampling was restricted to the Γ -point. The Verlet algorithm [31,32] was employed to propagate the ions and a time step of 1 fs was used to integrate the equations of motion. For the canonical ensemble simulations at 973 K, the Nosé thermostat [33] was used to maintain the selected temperature. An electrostatic correction was applied to remove the macroscopic

dipole along the z -direction of the supercell [34].

To study the oxidation reaction, we considered the α -Ti (0001) surface. The Ti (0001) surface was modeled using an asymmetric (4×4) slab with 11 layers, as shown in Fig. S1 of the supporting information (SI). For the Si-segregated surface, we considered a model with a Si concentration of 18.75 at.%, as shown in Fig. S2 of the SI. The slab models were validated in our previous study [19]. To mimic the oxidation of pure and Si-segregated Ti surfaces, we added oxygen molecules pseudo-randomly at a vertical distance of 2.5 Å above these surfaces. At time $t = 0$, we adsorbed four oxygen molecules onto the pure and Si-segregated Ti surfaces. Then, a constant temperature MD calculation at 973 K was performed for 10 ps. At $t = 10$ ps, we added four oxygen molecules to these surfaces and performed another 10 ps dynamic simulation at 973 K. For the pure Ti surface, we added four oxygen molecules every 10 ps until twenty oxygen molecules had been added to the system, as shown in Fig. S3(a)–(e). The interval of 10 ps was found to be sufficient, as we observed that the system equilibrated after 8 ps of MD. Thus, the MD simulations mimicked the actual process of adding oxygen to the surface along with the continuous reaction of oxygen molecules with the Ti surface, similar to the experimental conditions. For the Si-segregated surface, after $t = 20$ ps, the strategy to add oxygen molecules was modified, as explained later in Section 3. Adding four oxygen molecules at each interval corresponded to changing the coverage (θ) by half a monolayer (ML). As confirmed in our previous study [19], no oxygen penetration into the Ti slab was observed for $\theta \leq 0.5$ ML. Thus, a smaller change in θ would require longer simulations, while a larger change in θ led to computational complexities. Consequently, we decided to add four oxygen molecules every 10 ps.

2.2. Experimental procedures

We performed oxidation experiments using Ti-6Al-4V (64-0Si) and Ti-6Al-4V-0.34Si (64-0.3Si) alloys. A commercially available Ti-6Al-4V extra-low interstitial (ELI) forged bar was used as the 64-0Si alloy. The 64-0.3Si alloy ingot (70 mm \times 40 mm \times 25 mm) was prepared by non-consumable electrode Ar arc melting with the Ti-6Al-4V ELI forged bar and high-purity polycrystalline Si chips (9N) as raw materials. The ingot was subjected to forging in the β region at 1373 K and subsequent forging in the $\alpha + \beta$ region at 1173 K to produce a 14 \times 14 mm² square bar. Plates with a size of 12 \times 12 \times 2 mm³ were cut from the forged bars, and were used for the oxidation tests after mirror polishing and ultrasonic cleaning in ethanol and ultra-pure water. The plates were loaded into alumina boats (SSA-S #5B, Nikkato Co.) and placed in a muffle furnace (KBF828N, Koyo Thermo Systems Co., Ltd.) where they were heated in air at a rate of 1 K s⁻¹. We used an oxidation temperature of 973 K and an oxidation time of 24 h. After oxidation, we cooled the specimens in air.

We estimated the hardness and oxygen concentration distribution in the oxygen-dissolved layer (α -case) formed on the substrate side of the oxide-substrate interface. The hardness profile was evaluated using a Vickers micro-hardness tester (HM-102, Mitsutoyo Co.) under a 0.098 N load. The measurements were conducted at five positions for each point and the average value was calculated. To determine the oxygen concentration profile, we used a field-emission electron probe micro analyzer (FE-EPMA), where a calibration curve of oxygen concentration was used. The standard specimens used were Ti-6Al-4V-(0.13, 1.72, and 7.28 mass%)O alloys.

3. Results and discussion

3.1. Growth of oxide

We begin our discussion with the dynamic evolution of the oxide network on the Ti surfaces. To distinguish between the various oxygen molecules (atoms) added at different intervals, we will denote them as

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