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Structural features and corrosion analysis of thermally oxidized titanium

Azadeh Ashrafizadeh*, Fakhreddin Ashrafizadeh

Department of Materials Engineering, Isfahan University of Technology, Isfahan, Iran

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ABSTRACT

Thermal oxidation process tends to improve surface characteristics of titanium alloys by thickening the native oxide film. In the present paper, the influence of short cycle thermal oxidation on corrosion behaviour of Ti–6Al–4V alloy is reported and the improvements are discussed in terms of process parameters. Oxidation treatments were carried out in the range 500–800 °C for 1-h cycles in muffle furnace under air atmosphere. Characterization of modified surface layers was made by X-ray diffraction, glow discharge optical spectroscopy and scanning electron microscopy. Evaluation of corrosion properties of the specimens by potentiodynamic polarization tests indicated that surface treated titanium had better corrosion resistance than untreated material. From the comparison of experimental findings, it is concluded that 600 °C is the appropriate oxidation temperature for improvement of corrosion resistance of the titanium alloy. This is different from the conditions suggested by previous researchers who optimized the process for wear resistance.

1. Introduction

Titanium and its alloys are used in a variety of applications due to such attractive properties as high strength-to-weight ratio, excellent corrosion resistance and good biocompatibility [1]. However, these materials have poor wear resistance [2–4] and, in some applications, their surface properties must be modified.

The high corrosion resistance of titanium under normal condition results from the formation of a native oxide film on the surface [5]. Although the oxide film has a dense structure, is stable and protects the metal in most environments, there are evidences that some conditions, as for example human body, can alter the stability of the passive film. The new passive layers form in milliseconds by reaction with the local environment, but metal ions are released in the process [6]. Sustained dissolution of underlying metal, after disruption of oxide film and the reformation of the passive oxide layer, leads to gradual consumption of the material [7].

Since the corrosion resistance of titanium is due to the passive oxide film, any surface treatment increasing the thickness and toughness of the oxide layer, will improve the surface characteristics of the metal. Thermal oxidation is one of these processes which tends to modify the surface properties of titanium by formation of a rather thick rutile titanium oxide on the surface in an oxidizing media [8–10]. In most previous investigations, thermal oxidation treatments were pointed at wear resistance and, for this purpose, rather high temperatures and long oxidation cycles have been practiced. Published results show that this process can significantly enhance the tribological behaviour of titanium alloys [1,3]. Such an increase in wear resistance relies on the thickness and load bearing of the surface layer. On the other hand, improvement in corrosion properties requires the oxide film to be crack free and very adherent to the base metal. In order to minimize the surface cracks and increase the adhesion of titanium oxide layer, short cycle thermal oxidation and slow cooling rates have been practiced in the present research. Characterization of the layers was carried out by structural examinations and analytical techniques. Corrosion behaviour was studied by potentiodynamic polarization tests and the improvements are presented in this paper and discussed in terms of processing parameters of the thermal oxidation.

2. Experimental

2.1. Thermal oxidation treatment

Ti–6Al–4V (IMI 318) supplied by Imperial Metal Industries Ltd. was used as the base material for this research. The alloy with nominal composition of 6%Al, 4%V, balanced Ti was received as 10 mm diameter rods. Cylindrical samples of 5 mm height were cut from the rod. Specimens were ground with SiC papers, polished, cleaned with acetone and then dried in hot air. Thermal oxidation treatments were carried out at 500, 600, 700 and 800 °C by a heating rate of 5 °C/min in a conventional muffle furnace under air atmosphere for 1 h followed by cooling in the furnace.

2.2. Characterization procedure

Low angle X-ray diffraction technique with Cu Kα radiation was used to study the crystalline structure and to identify the phases present in the surface layers. Scanning electron microscopy (SEM) and glow discharge optical spectroscopy (GDOS) were performed to examine the surface structure and surface depth profiles of the specimens, respectively. Hardness measurements were carried out by a Leitz microhardness tester under an indentation load of 200P.

* Corresponding author. Tel.: +98 311 3915714; fax: +98 311 3912752.
E-mail address: aza_ashrafi62@yahoo.com (A. Ashrafizadeh).

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An electrochemical corrosion cell system (EG&G model 263A) was used for potentiodynamic corrosion tests in 0.9% NaCl. Graphite was employed as the counter electrode and saturated calomel electrode (SCE) as a reference electrode. Dynamic polarization curves were recorded at a potential scanning rate of 3 [mV s^{-1}] initiated at −250 below the open circuit potential and the atmosphere was open to air. Potentiodynamic polarization curves were determined at 37 ± 1 °C. The corrosion current densities were determined by Tafel extrapolation method.

3. Results and discussion

3.1. Composition and structure of the layers

The low angle XRD patterns for thermally oxidized titanium samples are presented in Fig. 1. It is observed that process temperature is the effective parameter to promote phase evolution of the surface layers. For the sample oxidized at 500 °C, only weak anatase peak at 25.4° can be depicted whereas with increasing temperature, rutile peaks were identified, too. At higher temperatures (700 and 800 °C) oxidized surfaces were principally consisted of rutile modification of TiO_2. As the X-ray penetration is beyond the thickness of the oxide layer, some peaks from alpha titanium were also detected in the XRD pattern. By increasing the temperature, the oxide layer became thicker and titanium peaks appeared with lower relative intensity and, finally, disappeared at the expense of rutile peaks.

Further examination of XRD patterns revealed that titanium peaks had a small shift from their original Bragg angles. These changes indicate variations in the lattice parameters of titanium substrate as the result of oxygen dissolution in the alloy. The lattice parameters (a and c) increased with increasing oxidation temperature and as is shown in Fig. 2, in all cases, the c/a ratio was increased along with hardness values after thermal oxidation. Alpha titanium is a hcp metal with c/a ratio less than the ideal value of a closed packed hexagonal [1] and the rather low hardness of the metal is related to this c/a ratio [11]. Diffusion of oxygen during thermal oxidation increased this ratio and enhanced surface hardness due to dissolution of oxygen in the titanium metal in addition to the formation of hard oxide layer on the surface. Higher temperatures caused fast diffusion rate leading to still higher hardness.

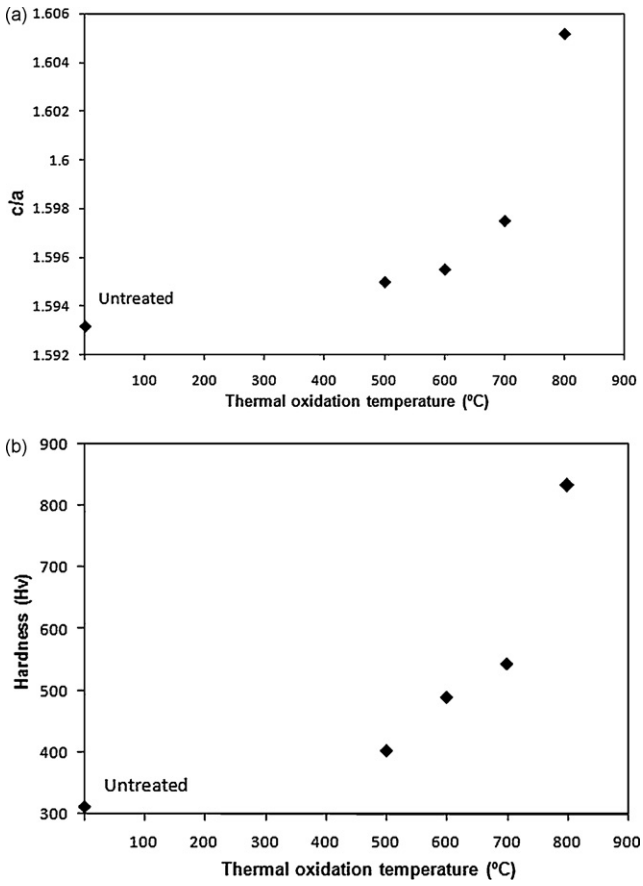

Fig. 2. Variation of (a) c/a ratio of titanium substrate versus treatment temperature; (b) hardness of treated specimens versus treatment temperature.

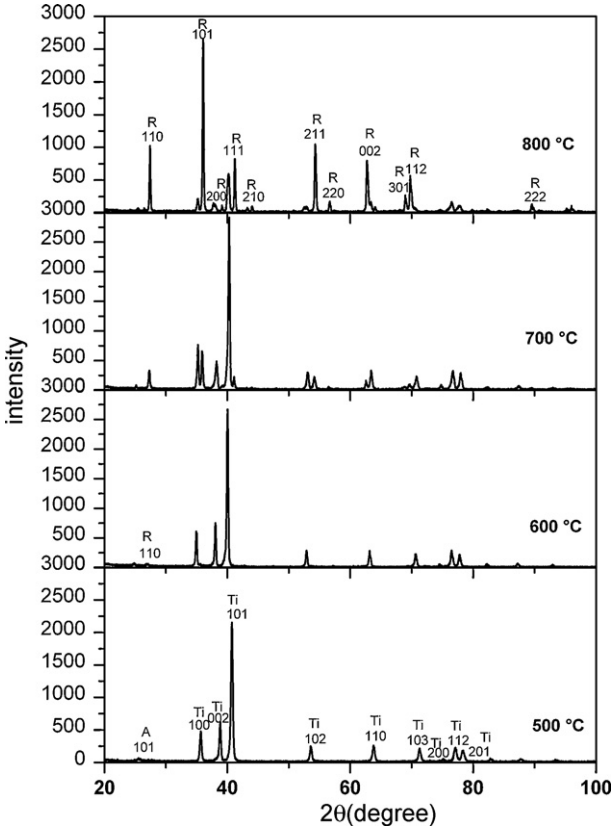

Fig. 1. XRD patterns of thermally oxidized titanium (A: anatase, R: rutile).

Typical results of GDOS in Fig. 3 confirm the diffusion of oxygen in titanium alloy substrate. It is established that thermal oxidation treatment provides titanium with an oxygen diffusion zone beneath the oxide layer. It is observed that at 700 and 800 °C, there is a relatively flat region before abrupt decrease of the oxygen concentration. This region contains a large amount of oxygen and corresponds to the surface oxide layer. Concentration of oxy-

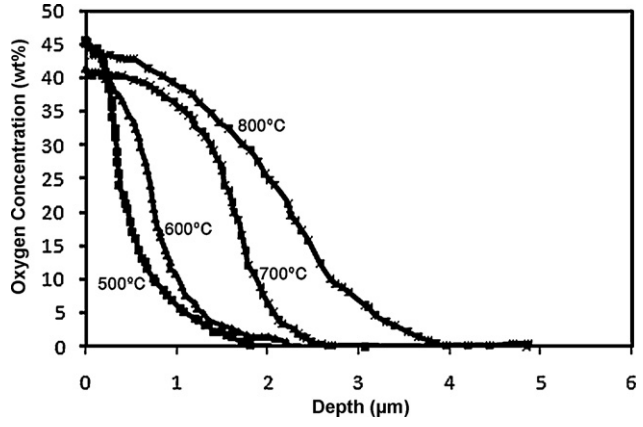

Fig. 3. GDOS concentration–depth profiles of oxygen.

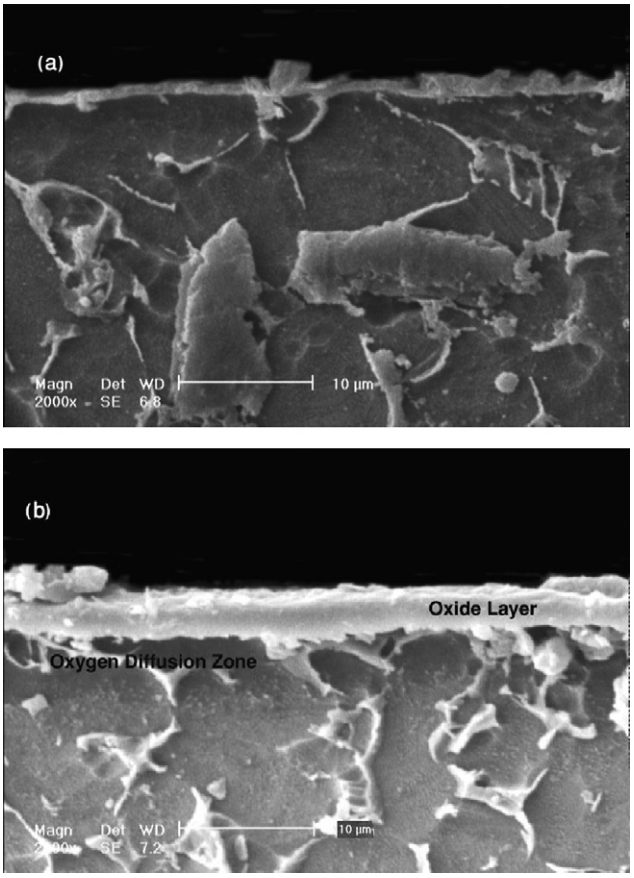

Fig. 4. SEM micrographs of treated titanium alloy: (a) thermally oxidized at 600 °C; (b) thermally oxidized at 800 °C.

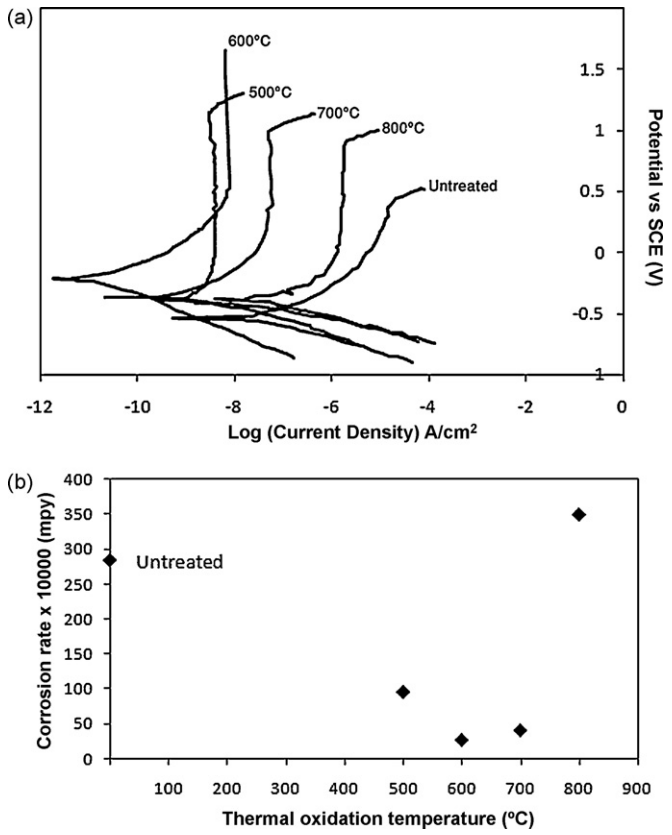

Fig. 5. (a) Potentiodynamic polarization curves in 0.9% NaCl solution; (b) corrosion rate of thermally oxidized titanium.

gen decreases gradually towards the depth of the specimen within the diffusion zone, showing that a smooth gradient has been produced by the diffusion of oxygen into titanium. The thickness of the oxide layer and the depth of oxygen diffusion zone increased with increasing temperature. Typical micrographs of the cross-section of the specimens that were oxidized at 600 and 800 °C are shown in Fig. 4. Oxide layers and oxygen diffusion zone can be compared in these micrographs. As will be discussed later, it is crucial to correlate the observed features of oxide layer with corrosion properties of the alloy.

Regardless of manipulated experimental condition, careful examination of the external surface of treated samples showed that little spallation has occurred in some areas of the specimen that was oxidized at 800 °C. Increasing process temperature accelerates the oxidation rate and, accordingly, thicker oxide layer and deeper oxygen diffusion zone is produced, but flaking and spallation occur. This phenomenon has been related to local cracking due to intrinsic and thermal effects during oxidation process [3]. Furthermore, the behaviour can be attributed to rutile structure; rutile is an oxygen deficient n-type semiconductor (TiO_{2-x}) [8] where at high temperatures, a progressively large number of vacancies are generated both on the surface and in the bulk of its lattice. This structure may cause scale growth by anion migration more than cation migration. It should be noticed that there is an important distinction between scale growths by these two species; cation migration leads to scale formation at the scale–gas interface whereas anion migration leads to scale formation at the metal–scale interface [12]. In the latter case, growth stresses are developed due to volume difference between the oxide and the metal. These stresses produce microcracks at the metal–oxide interface which may cause spallation of the surface layer. Such behaviour was not observed in specimens treated at lower temperatures.

3.2. Corrosion behaviour

Typical potentiodynamic polarization curves of as-received and treated titanium base alloy in 0.9% NaCl solution are shown in Fig. 5a. In all cases, the corrosion current density is very low, indicating the inherent corrosion resistance of titanium. Experimental data in Fig. 5 indicate that the corrosion characteristics of the specimens depend on the temperature of thermal oxidation. Effect of oxidation temperature on corrosion rate of as-received and treated titanium has been compared in Fig. 5b. The corrosion rate of specimens decreased as the temperature of thermal oxidation raised from 500 °C. Thermal oxidation process at these temperatures, not only shifted the corrosion potentials to more noble values, but also reduced the current density, significantly. Oxidized surfaces at 600 and 700 °C possess better corrosion resistance compared to the specimen that was treated at 500 °C. This behaviour is attributed to the formation of rutile which has good corrosion properties. It has been noted that anatase corrosion resistance is inferior in comparison to rutile [9] and, consistent with this, increasing the temperature from 500 to 700 °C, the corrosion resistance is improved due to both presence of rutile and thickening of the oxide layer.

At 800 °C, the surface of the specimen was covered by a thicker layer of rutile, nevertheless, the results of corrosion testing indicated a lower resistance. Based on SEM findings, formation of surface cracks and local spallation of the oxide layer are the probable reasons for lower corrosion resistance of this specimen. Structure of the oxide layer has a great influence on corrosion

behaviour of the substrate; a cracked oxide layer cannot separate titanium from the aggressive environment because cracks act as channels for corrosive media. Penetration of aggressive ions caused formation of galvanic cells at the metal–oxide interface and, since ceramics are generally electrochemically more noble than metals, TiO_2 act as cathode and the metal substrate as an anode. Thus, the exposed area anodically dissolved, then extended along the oxide–metal interface and, finally, led to the local flaking of the coating [5]. It is, therefore, concluded that a rutile film could be most effective in protecting titanium alloy against corrosive environment when it has a structure without cracks and pores.

Comparison of the results shows that the lowest corrosion rate belongs to the sample which is treated at 600 °C. The Tafel diagrams indicated that breakdown potential for thermal oxidation at 500, 700 and 800 °C is about 1 V, while for the specimen oxidized at 600 °C there is no breakdown up to 1.5 V. The oxide film produced under this condition was observed to be dense, free of cracks, very adherent to the substrate and with a smooth surface topography. Hence, thermal oxidation at 600 °C for a rather short cycle and slow cooling rate can be introduced as an appropriate surface treatment for improving the corrosion resistance of titanium alloy. The procedure is very simple and the properties of such layer are believed to be suitable for biomedical applications.

4. Conclusions

Thermal oxidation of titanium results in generation of TiO_2 on the surface which is accompanied with an oxygen diffusion zone. Corrosion behaviour of titanium alloy substrate can be significantly improved after short time thermal oxidation treatment when the oxide layer is dense and crack free. High temperatures and long cycles would decrease the corrosion resistance. In this research, 600 °C, short oxidation time and slow cooling rate were found as the appropriate conditions for improving the corrosion behaviour of Ti–6Al–4V alloy.

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