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Effect of thermal oxidation on the combined performances of TA2

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ABSTRACT

Thermal oxidation tends to improve the surface performance of titanium and its alloys by thickening the native passive oxide layer. In the present paper, investigation of thermal oxidation in a muffle furnace under air atmosphere for commercially pure titanium TA2 was carried out to determine the optimum thermal oxidation parameters by evaluating the wear and corrosion resistance. Characterization of modified surface layers was made by SEM examinations, X-ray diffraction analysis and surface hardness measurements. The results showed that the rutile TiO_2 layer was formed on the surface, and the thickness of the TiO_2 layer and the surface hardness increased with the treating temperature. Evaluation of wear and corrosion resistance indicated that the optimum thermal oxidation condition was 700°C for 3.5 hours.

KEYWORDS

TA2;
Thermal oxidation;
Corrosion resistance;
Wear resistance;
XRD.

INTRODUCTION

Titanium and its alloys have been widely used in aerospace, marine, chemical and bio-medical industries because of their high strength-to-weight ratio, biocompatibility and excellent corrosion resistance due to a stable, protective, strongly adherent oxide layer on the surface[1-3]. However, they have poor tribological properties and exhibit poor corrosion resistance in some environments, which restrict its wide application[4,5]. It was reported that many surface treatments could improve their wear and corrosion resistance by thickening and toughening the passive surface oxide layer on the surface, which includes anodizing, oxygen diffusion[6] C. Boettcher, Deep case hardening of titanium alloys with oxygen, Surf Eng (2000) (2), pp. 148–152. Full Text via CrossRef | View Record in Scopus Cited By in Scopus (12), ion implantation and thermal oxidation[6-9].

Among all these research methods, thermal oxidation is the simplest and most cost-effective technique, but selecting the appropriate parameters is very crucial, since the oxide layer produced at too high temperatures (above 800 °C) results in debonding and spalling due to the large lattice mismatch and the large difference in coefficient of thermal expansion between oxide and Titanium base metal, on the other hand, those produced at too low temperatures (below 550 °C) are not thick enough to significantly improve the tribological properties and corrosion resistance[10]. Thus, a need arises to find suitable thermal oxidation parameters that can produce adherent and thick enough layer of titanium oxide, preferably with rutile structure.

TA2 is the most popular Titanium metal in many kinds of applications, improving its combined performances by using a simple and cost-effective technique can further enlarge its wide application. Though there exist some literatures about thermal oxidation of Titanium and its alloys, the optimum condition for improving the combined performances of TA2 did not report yet.[10-12].

Therefore, the aim of the present study is focused on producing adherent and thick enough oxide layer on TA2 surface, which can provide the optimum combined performances. For this purpose, thermal oxidation was carried at different temperatures for the same timing of 3.5 hours in a muffle furnace under air atmosphere, the modified surface was characterized, and wear and corrosion behavior was evaluated.

EXPERIMENTAL

The material used for the investigation was TA2 (Grade-2 CP-Ti) (chemical composition in wt. %: N: 0.01; C: 0.03; H: 0.01; Fe: 0.20; O: 0.18 and Ti: Balance), received in the form of hot forged bar of 90-mm diameter. The specimens with dimension of 10mm×10mm×5mm were cut from the bar, prepared by grinding with 400-grit SiC paper and then ultrasonically cleaned in deionized water and acetone for 5 minutes, respectively, dried prior to thermal oxidation using a stream of cold compressed air. Thermal oxidation was carried out in the range of 500Ú~850ºC at the same duration of 3.5 hours in a conventional muffle furnace under air atmosphere, followed by furnace cooling.

Phase constituents of the samples were analyzed by Dmax 2500X-ray diffractometer, using Cu-$K_{á}$radiation, and the morphology of the surface was investigated by SEM (JSM6360LA). The microhardness was measured at the surface using a HVS-5Z microhardness tester under four different indentation loads, ranging from 300gf to 5000gf, applied for 15s. Each hardness value was determined by averaging at least 5 measurements.

Corrosion behavior was investigated using immersion test by exposing the samples to HCl solution with a concentration of 36~38%. During the corrosion test, the temperature of the solution was hold at 36.5ºC. The results of the corrosion test were evaluated by measuring the weight loss of the samples every 2 hours, with an accuracy of 0.1mg, and the samples were ultrasonically cleaned in deionized water and acetone, and then dried before measuring the weight.

The configuration of pin-on-wheel, in dry sliding conditions, was used to evaluate the wear resistance, conducted on a MMW-1A Wear Test Machine under ambient condition (20±2ºC and 50%RH). In the wear test, 45 steel (nominal composition in wt.%, C: 0.45; Si: 0.30; Mn: 0.65; Cr≤0.25; Ni≤ 0.30 and Fe: Balance) in hardened and tempered condition with 4.8mm diameter was used as the counterpart pin, rotating at a speed of 30rpm on the surface of the tested samples with 35mm diameter and 5mm thickness. The coupling load was 15N, sliding time was 180min. During the test, the friction coefficient was continuously recorded.

RESULTS AND DISCUSSION

Surface morphology

Figure 1 presents the surface morphology of TA2 samples as-received and thermally oxidized at various temperatures. It can be seen that the surface is kept almost smooth with very little oxide on the surface at 500°C as shown in Figure 1 (b); it becomes much rougher after oxidizing at 650°C, due to the oxide lay is formed on the surface as shown in Figure 1 (c). Titanium oxide crystal with fine grain size can be clearly seen in Figure 1 (d) and (e). However the grain size of Titanium oxide crystal is getting much coarser in Figure 1 (f). It can be concluded that 700°C may be the optimum temperature for TA2 to conduct TO treatment, which can form evenly distributed Titanium oxide crystal with fine grain size.

XRD analysis

XRD patterns of as-received and thermally oxidized samples are shown in Figure 2. The samples as-received and thermally oxidized at 500°C are entirely comprised of hexagonal α-phase which may be due to that the oxide layer is too thin to be detected by XRD. The XRD patterns of samples thermally oxidized at temperature range of 600-750°C exhibit the presence of rutile TiO_2, and the intensity of the rutile TiO_2 become

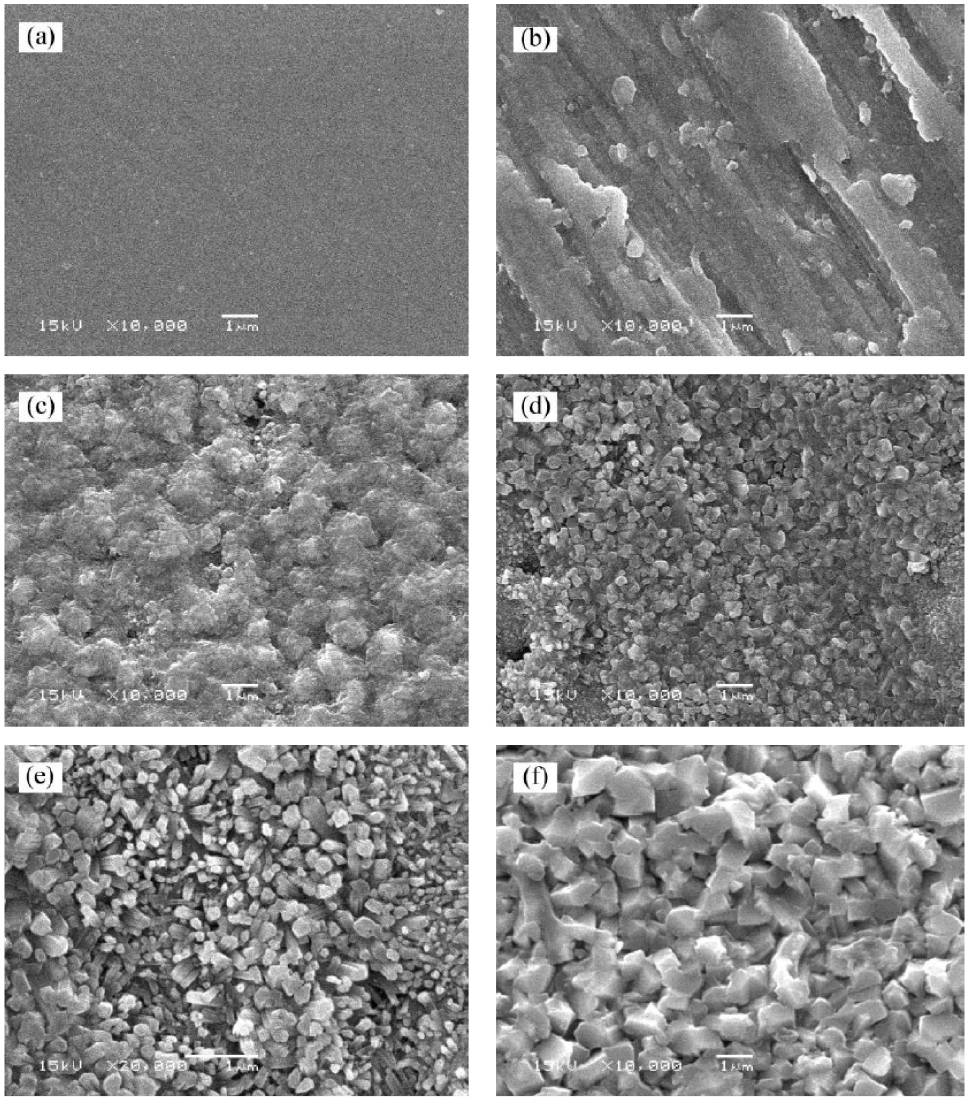

Figure 1 : SEM images of surface morphology of TA2 samples as-received and thermally oxidized at various temperatures for 210mins; (a) As-received (b) 500°C (c) 650°C (d) (e) 700°C (f) 750°C

stronger with the increase of treating temperature, this suggests that the thickness of the oxide layer increases with the treating temperature. Andα-Ti peaks are also observed after oxidation from 600-750°C, this is basically due to penetration of X-ray beyond the thin oxide layer. Further analysis revealed that diffraction angles of Ti peaks shifted slightly left from their original positions, probably caused by the dissolution of oxygen in the substrate zone. When the temperature increases to 850°C, the XRD pattern of samples shows rutile TiO_2 only, suggesting a oxide film thicker than the depth that Cu-Kαcan penetrate to was formed on the surface of the samples.

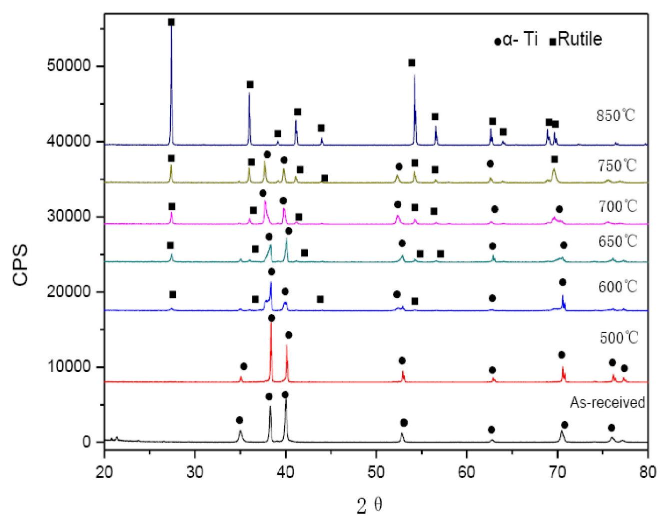

Figure 2 : XRD patterns of as-received and thermally oxidized for 210min at various temperatures

Microhardness

The hardness of untreated sample is 160HV, and the results of the surface hardness of the thermally oxidized samples are shown in Figure 3. The surface hardness for samples thermally oxidized from 500-600°C is almost kept constant at about 160HV, due to very thin oxide layers. When the treating temperature was getting higher, the surface hardness increased with the temperature. A dramatic increment of up to 500HV in surface hardness was achieved upon oxidizing at 750°C under indentation load of 300g. And on the oxidized surfaces, the decrease of hardness with increase of indentation load is due to the higher penetration depths of the heavier indenter.

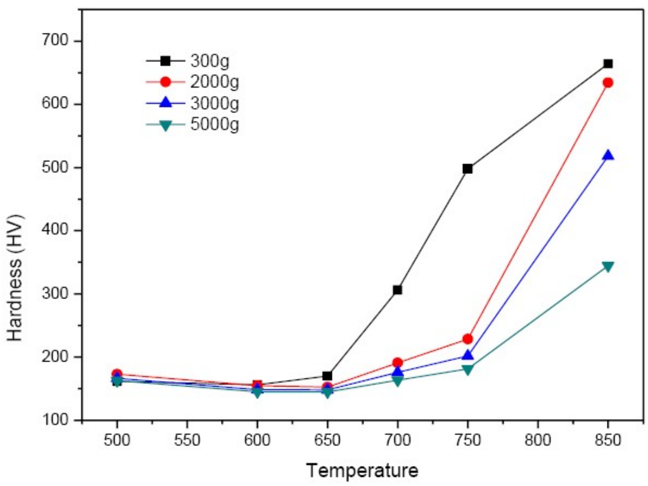

Figure 3 : The surface hardness-load profile of the specimens treated under various conditions

Corrosion behavior

The corrosion behavior of the samples as-received and thermally oxidized in 36~38% HCl at room temperature is shown in Figure 4. It indicates that untreated alloy exhibits the lowest corrosion resistance among the investigated samples due to the continuous dissolution; the total weight loss is 103.83g/m^2 after corroded for 12 hour. Thermally oxidized samples exhibit better corrosion resistance than untreated alloy, the total weight loss for samples oxidized at 700°C, 750°C, 850°C after corroded for 12 hour is 2.95 g/m^2, 7.24 g/m^2, 9.38 g/m^2, respectively. Little weight loss is obtained for the samples oxidized at 700°C.

Wear test

Figure 5 is the friction coefficient curves of the samples as-received and thermally oxidized at various temperatures. It can be seen that the friction coefficient of as-received sample is much higher and unstable,

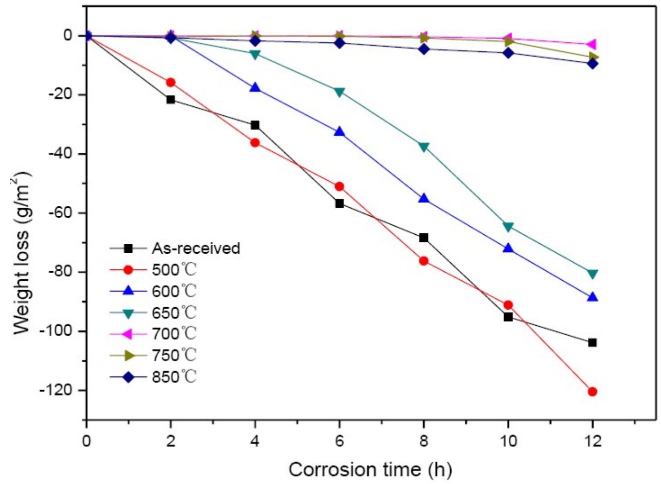

Figure 4 : The corrosion rate in 36~38% HCl of the samples as-received and thermally oxidized at various temperatures

which fluctuates greatly during the sliding cycles. On the other hand, the friction coefficient of the oxidized samples is reduced and become much more stable, among which the sample oxidized at 700°C is the most stable one, the average coefficient is 0.4.

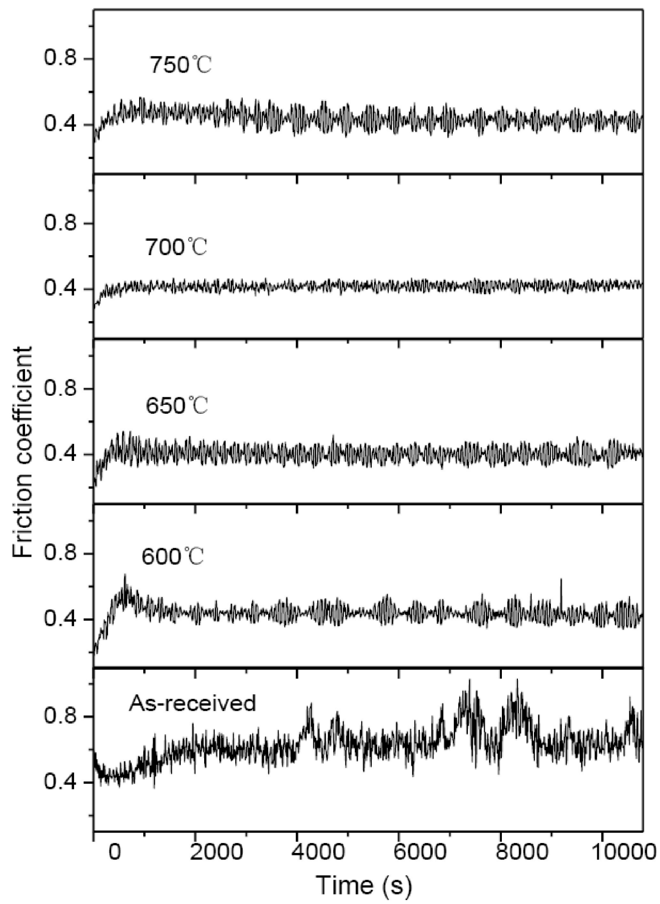

Figure 5 : Friction coefficient curves of the samples as-received and thermally oxidized at various temperatures

CONCLUSIONS

1) Rutile TiO_2 layer was formed on the surface of CP-Ti after thermal oxidation and the thickness of TiO_2 layer increased with the treating temperature.
2) The surface hardness was increased significantly when the treating temperature reached 700ºC and higher.
3) Thermally oxidized samples exhibited better corrosion resistance than untreated, and that oxidized at 700ºC showed the optimum corrosion resistance.
4) Thermally oxidized samples exhibited better wear resistance; the friction coefficient was reduced and become much more stable. The sample oxidized at 700ºC showed the best wear resistance, the friction coefficient was kept quite stable and the average value was 0.4.

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