EFFECT OF THERMAL OXIDATION ON THE CORROSION RESISTANCE OF CP-Ti

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Abstract
Commercially pure titanium (CP-Ti) was subjected to thermal oxidation at different temperatures and times for determining the optimum oxidation conditions to obtain the optimum corrosion resistance. The phase constituents of the samples were determined by X-ray diffraction (XRD), the morphology of the surface was observed by SEM, and the corrosion behavior was investigated using immersion test by exposing the samples in HCl solutions with a concentration of 37%. The results showed that Rutile TiO_2 layer was formed on the surface of CP-Ti after thermal oxidation and the thickness of the TiO_2 layer increased with the treating temperature. Meanwhile, it was found that the optimum corrosion resistance to HCl was obtained while oxidizing at 700℃ for 330min～500min.

Keywords: Thermal oxidation, CP-Ti, Corrosion resistance, X-ray diffraction

1 Introduction

Ti and its alloys are very attractive materials due to their various outstanding properties, such as high strength to weight ratio, good fatigue properties, excellent corrosion resistance, and good biocompatibility properties, etc [1-2]. Therefore, they have been widely used in aerospace, Marine, chemical, biological medicine, sports goods, etc [3-5]. However, they are of poor wear resistance and poor corrosion resistance in reducing acid, which limits their practical application in some fields [6-10]. In recent years, a lot of surface modification methods have been used to improve surface properties [11-13] (i.e., hardness and wear) of Ti based alloys, such as electroplating, ion implantation, laser surface treatment, carburizing, carbonitriding, thermal oxidation, etc [14-16].Among those, thermal oxidation is an easiest and most environmental friendly technique that can be used to harden the surface of titanium and its alloys[17-18], and thus improve their poor wear and corrosion properties, due to the formation of a crystalline rutile oxide film on the surface [19-21].

The aim of this research is to determine the suitable thermal oxidation condition of CP-Ti to get the optimum corrosion resistance in HCl, and it is found oxidizing at 700℃ for 330min～500min is appropriate condition.

2 Experimental

CP-TA2 (grade-2) (chemical composition (wt. %): N: 0.01; C: 0.03; H: 0.01; Fe: 0.20; O: 0.18 and Ti: Balance) utilized in the present investigation was received as 90mm diameter hot forged bar. The CP-Ti samples with dimension of 10mm×10mm×5mm were cut from the bar, polished using various grades of SiC paper, 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 500℃~850℃ at various times (90min, 210min, 330mim, 500min, 600min) in a conventional muffle furnace under air atmosphere, followed by furnace cooling.

The phase constituents of untreated and thermally oxidized samples were determined by X-ray diffraction (XRD) (Dmax 2500) using Cu–Kα radiation. The morphology of the surface was observed by SEM (JSM6360LA).

Corrosion behavior was investigated using immersion test by exposing the samples in HCl solutions with a concentration of 37%. During the corrosion tests, the temperature of the solution was hold at 36.5℃. The results of the corrosion tests were evaluated by measuring the weight loss of the samples every 2hrs, with an accuracy of 0.1mg, and the samples were ultrasonically cleaned in deionized water and acetone, and then dried prior to measuring the weight.

3 Results and discussions

3.1 XRD analysis

The XRD patterns of CP-Ti samples untreated and thermally oxidized at various temperatures for 210min are given in **Fig. 1**. It can be seen that the XRD patterns of samples thermally oxidized at temperature range of 600-750℃ exhibit rutile TiO_2, and the intensity of rutile TiO_2 becomes stronger with the increase of treating temperature, which suggests that the thickness of the oxide layer increases with the treating temperature. And the samples untreated and thermally oxidized at 500℃ are only comprised of α-phase due to too little oxide to be detected.

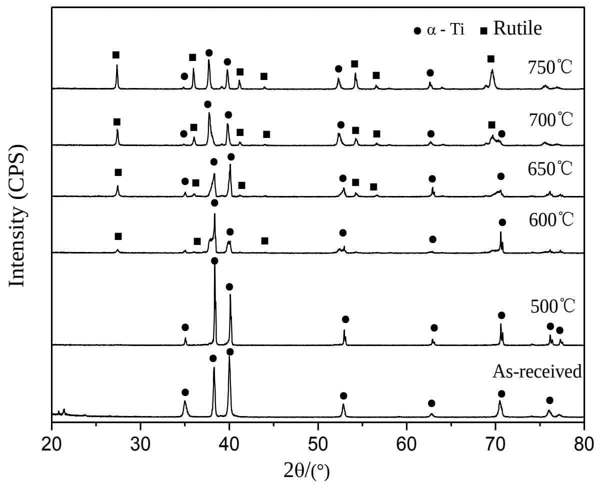

Fig. 1 XRD pattern of samples as-received and thermally oxidized at various temperatures for 210min

3.2 The effect of thermal oxidation temperature on the corrosion resistance

Fig. 2 presents the weight loss of CP-Ti samples untreated and thermally oxidized at various temperatures for 210 min immersing in 37% HCl at room temperature. It indicates that untreated samples exhibit the worst corrosion resistance due to the continuous dissolution without the

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protection of rutile TiO_2, as shown in **Fig. 1**, and the total weight loss reaches 103.83g/m^2 after immersing corrosion 12 hours. And the trend of the weight loss for the sample thermally oxidized at 500℃ is similar as that for the untreated samples, namely corrosion resistance of the sample is almost not improved. Then corrosion resistance to HCl was gradually improved by oxidizing at 600 ℃ and 650 ℃. While for the samples oxidized at 700℃, 750℃ and 850℃, little weight loss, no more than 10g/m^2, is obtained after immersing corrosion for 12h, therefore, it can be concluded that the corrosion resistance of CP-Ti can be significantly improved by thermally oxidizing at temperature at 700℃ or higher. From the energy saving perspective, 700 ℃ is the optimal oxidizing temperature for improving corrosion resistance of CP-Ti.

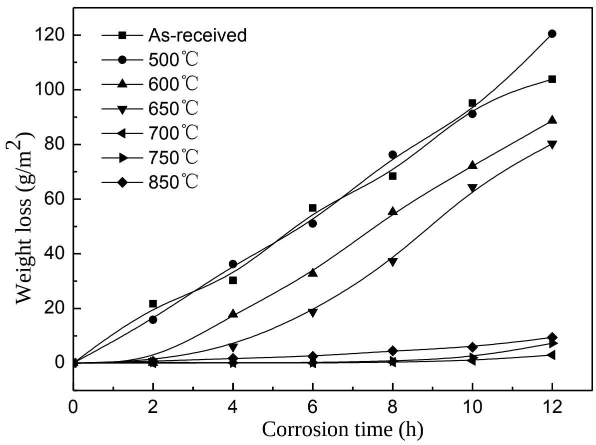
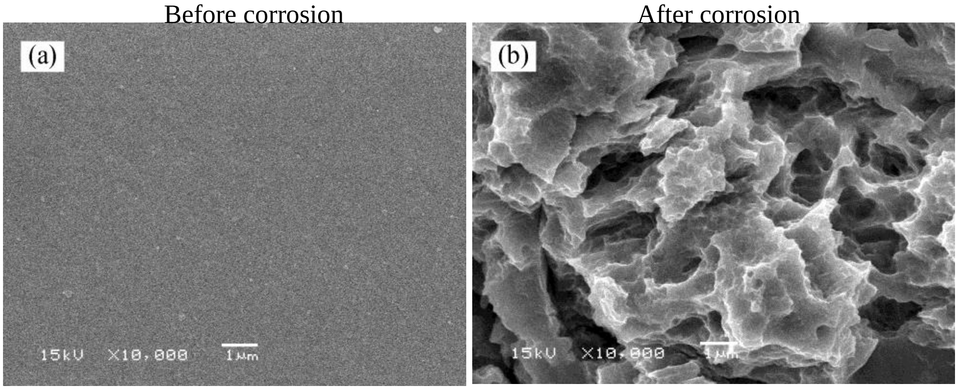


Fig. 2 The weight loss of CP-Ti immersing in 37% HCl vs. time for the samples untreated and thermally oxidized at various temperatures for 210min

SEM images of surface morphology of CP-Ti samples as-received and thermally oxidized before and after corroded in 37%HCl for 440min are shown in **Fig. 3**. It can be seen that the untreated sample appears large and deep holes after corrosion. Samples thermally oxidized at 500℃ still exist shallower holes after corrosion, which demonstrates that the protective effect of oxide film for the matrix is slight. The sample oxidized at 650 ℃ only has a few small holes in the surface after corrosion; while the surface of the sample treated at 700 ℃ has little change before and after corrosion and are still crystal particles, which is consistent with **Fig. 2**.

Before corrosion After corrosion



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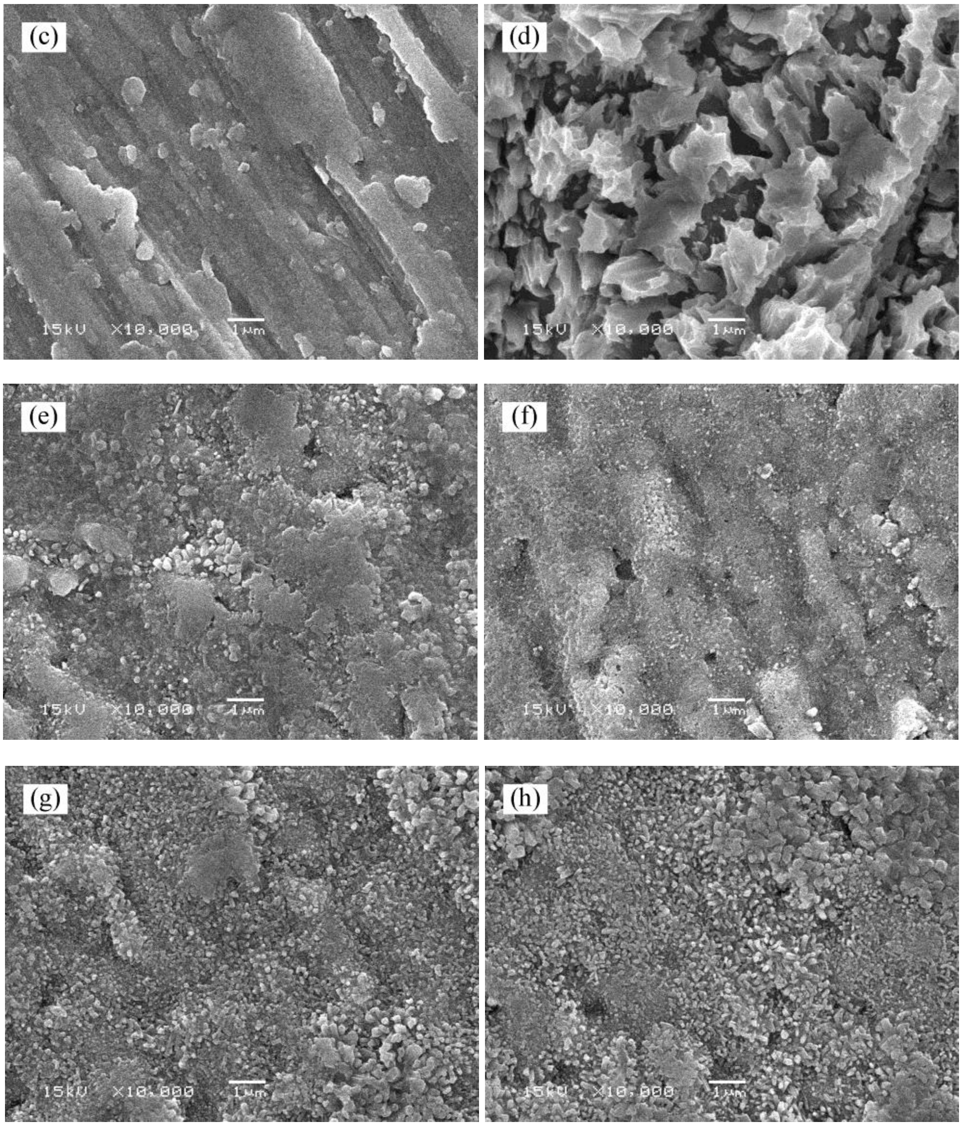

Fig. 3 SEM images of surface morphology of CP-Ti samples as-received andthermally oxidized before and after corrosion test: (a)(b) As-received;(c)(d) 500℃; (e)(f) 650℃; (g)(h) 700℃

3.3 The effect of thermal oxidation time on the corrosion resistance

Fig. 4 presents the weight loss of CP-Ti immersing in 37% HCl vs. time for the samples untreated and thermally oxidized at 700℃ for various times. It indicates that 330min and 500min oxidation brings about the best corrosion resistance to HCl, and the weight loss is less than $5g/m^2$. For the samples oxidized more than 600min, corrosion resistance turned to be worse. It can be concluded that corrosion resistance of thermally oxidized samples initially increases with oxidation time, and then turn to decrease with time after a critical duration.

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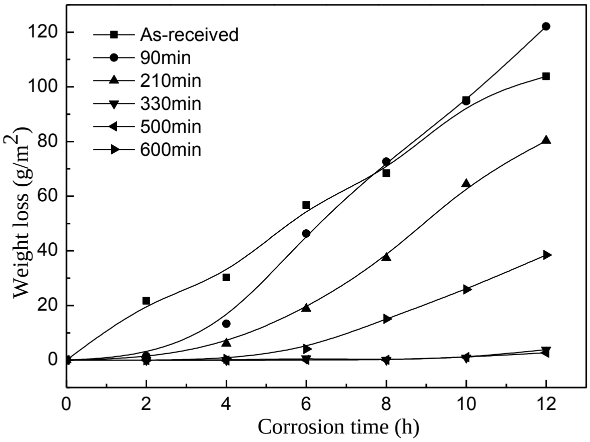

Fig. 4 The weight loss of CP-Ti immersing in 37% HCl vs. time for the samples untreated and thermally oxidized at 700℃ for various times

4 Conclusions

1) Rutile TiO_2 layer is formed on the surface of CP-Ti after thermal oxidation and the thickness of the TiO2 layer increases with the treating temperature.
2) 700℃ is optimal oxidizing temperature to improve the corrosion resistance of CP-Ti in 37% HCl.
3) The oxidizing duration range of 330min～500min is suitable to improve the corrosion resistance of CP-Ti in 37% HCl.

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