Surface & Coatings Technology xxx (2013) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Thermal oxidation of titanium to improve corrosion resistance in boiling nitric acid medium

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ARTICLE INFO

Article history:
Received 17 April 2013
Accepted in revised form 4 July 2013
Available online xxxx

Keywords:
Titanium
Thermal oxidation
Nitric acid
Corrosion
Nano-rod structure
Roughness

ABSTRACT

Commercially pure titanium (Cp-Ti) is being used as structural material for fabrication of dissolver in the reprocessing of carbide fuel from fast breeder test reactor. Thermal oxidation of titanium is one of the most simple and feasible options to extend the life of such critical components. In the present study thermal oxidation of titanium has been carried out at 923 K for 96 h. The thermally oxidized Cp-Ti samples were characterized by SEM, XRD, microscratch test and profilometry. Corrosion studies were carried out in boiling nitric acid medium as per ASTM A262 practice-C test and three phase corrosion test and the results were compared with Cp-Ti and Ti–5Ta–1.8Nb alloy. ASTM A262 practice-C test revealed reproducible outstanding corrosion resistance of thermally oxidized Cp-Ti compared to Cp-Ti and Ti–5Ta–1.8Nb alloy. Three phase corrosion test results also indicated better corrosion resistance of thermally oxidized Cp-Ti. The protective thick rutile TiO_2 oxide layer with nano-rod structure formed on the surface improved the corrosion resistance of thermally oxidized Cp-Ti in boiling nitric acid as evident from SEM and XRD results. The hardness of thermally oxidized Cp-Ti sample was found to be 2.5 times higher than that of Cp-Ti and the surface roughness of the thermally oxidized Cp-Ti samples was found to be smooth before and after corrosion when compared to the as-polished surface. The corrosion resistance of the thermally oxidized Cp-Ti samples can be further improved by optimizing the parameters to achieve good adhesion strength. The paper highlights the results of the present investigation.

1. Introduction

Commercially pure titanium (Cp-Ti) and its alloys are widely used in chemical, nuclear, aerospace and biomedical applications due to their low density, excellent corrosion resistance, biocompatibility and mechanical properties. Based on R & D, titanium is being successfully used as dissolver in CORAL (COmpact Reprocessing facility for Advanced fuels in Lead cells) plant for the reprocessing of carbide fuel from fast breeder test reactor [1,2]. In order to extend the life of critical components made of titanium, simple and economical surface modification methods have been envisaged. Schutz et al. [3] reported that improved performance of Ti in heat exchanger applications could be achieved by thermal oxidation compared to that of anodizing or pickling. Anodized films on titanium can be easily removed by acid pickling, whereas thermal oxide films are more resistant to acid pickling and sand blasting or processing in caustic descaling bath has to be carried out in order to remove thermal oxide films [3]. It has been reported that the surface films formed by oxidation remained unchanged during immersion for 250 h, while anodized film thickness decreased after 20 h of immersion in 2% HCl at 343 K [4]. They reported that anodized film consisting of hydrated TiO_2 has higher solubility which results in rapid dissolution of the anodized film in comparison with unhydrated TiO_2 film formed by thermal oxidation [4]. Another advantage of thermal oxidation compared to anodizing or pickling is the significant reduction in hydrogen uptake [3]. Fukuzuka et al. [4] clearly showed that the hydrogen absorbed by thermally oxidized titanium is lower than that absorbed by as-polished and anodized titanium. This is because thermally oxidized film acts as a barrier for hydrogen permeation due to the low diffusion coefficient of hydrogen in the titanium oxide [4]. It is also reported that with an increase in the oxide film thickness the hydrogen absorption of titanium decreases significantly [3,4]. Therefore higher corrosion resistance and lower hydrogen uptake can be achieved by forming thicker oxide films. Thus the oxide film formed by thermal oxidation of titanium at higher temperatures and/or longer times can prevent corrosion and hydrogen absorption. Hence thermal oxidation of titanium is considered as one of the most simple, effective and feasible options to improve the corrosion resistance under a broad range of corrosive conditions. Many researchers have studied thermal oxidation of Ti to improve wear resistance [5–11] for tribological applications and to improve corrosion resistance [3–5,9–13] for chemical and biomedical applications. Earlier studies showed better corrosion resistance in simulated radioactive solution for thermally oxidized titanium treated at 873 K compared to those treated at 823 and 923 K [11]. The improvement of corrosion resistance by thermal oxidation

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http://dx.doi.org/10.1016/j.surfcoat.2013.07.010

has been reported by many researchers mainly focused on potentiodynamic polarization and impedance studies [12–15]. Jamesh et al. [15] carried out potentiodynamic polarization and electrochemical impedance spectroscopy studies on thermally oxidized Ti (923 K/48 h) in 0.1 and 4 M HCl and HNO_3 mediums. Their studies revealed that thermal oxidation method significantly improves the corrosion resistance of Cp-Ti in both HCl and HNO_3 mediums. However for practical applications, immersion studies exposing the coated samples, simulating the actual service conditions are the best methods to determine the corrosion resistance of coating/surface modified material. Accelerated immersion tests for measuring uniform corrosion from coupon weight loss are fundamental in corrosion engineering which produces results in a reasonable testing time [16]. Therefore in the present study ASTM A262 practice-C test has been employed to determine corrosion resistance. Titanium and its alloys usually undergo accelerated corrosion in condensate phase of nitric acid. Therefore three phase corrosion test has also been carried out which is more relevant for the practical application of titanium in nitric acid medium for reprocessing plant applications. The present paper deals with characterization and corrosion evaluation of thermally oxidized Cp-Ti in boiling nitric acid solution and the results are compared with other candidate materials like Cp-Ti and Ti–5Ta–1.8Nb alloy.

2. Experimental details

2.1. Thermal oxidation of Ti

The nominal chemical composition of Cp-Ti and Ti–5Ta–1.8Nb alloy used in the present study is shown in Table 1. Cp-Ti samples 12 × 12 × 6 mm in size were ground with 80 grit SiC emery paper and then cleaned with acetone. Thermal oxidizing treatment was carried out at 923 K for 96 h. The β transus temperature for Ti, i.e., the temperature at which the hexagonal α phase is transformed on heating to cubic β phase is 1156 K. Thermal oxidation treatment above β transus temperature could disrupt the oxide layer formed during cooling because of phase transformations. Therefore thermal oxidation treatments were usually carried out below β transus temperature. Thermal oxidation treatments were carried out at 1073 K for only short times to avoid severe oxidation. Thermally oxidized samples exhibited higher corrosion protection when treated at 1073 K/24 h compared to 923 K/24 h and lower at 773 K/24 h [14]. However, in another study it is reported that the titanium oxide film formed above 1073 K does not seem protective as titanium gets severely oxidized with formation of a porous oxide film [4]. Therefore the temperature was chosen well below the beta transus temperature, i.e., 923 K. Thermal oxidation treatments at still lower temperatures need a much longer time to form a thick oxide layer. Four batches of thermally oxidized Cp-Ti samples were prepared for checking the reproducibility of thermal oxidation treatment and corrosion rate values. The first and fourth batch thermally oxidized Cp-Ti samples were characterized by SEM, XRD and microhardness to check the uniformity, structure and hardness of the oxide layer formed.

2.2. Microhardness

Microhardness values were obtained using SHIMADZU, model HMV-2 microhardness tester on the surface of Cp-Ti and thermally oxidized Cp-Ti samples. Microhardness measurements were made with a load of 980.7 mN (100 g) applied for 15 s on the first and fourth batch samples to check the reproducibility. Three readings were taken from the surface and its average values were calculated.

2.3. Corrosion tests

Cp-Ti and Ti–5Ta–1.8Nb alloy samples were polished with 600 grit emery paper while thermally oxidized Cp-Ti samples were tested without any surface preparation. The samples were cleaned with acetone and weighed before corrosion testing. ASTM A262 practice-C test [17] was carried out in 65% boiling nitric acid. The samples were suspended in boiling nitric acid using Teflon (PTFE) thread for a total period of 240 h. Every 48 h a fresh test solution was used and weight loss measurements were made. The corrosion rates in the individual periods were calculated using Eq. (1) [18].

$$\text{Corrosion rate (mm/year)} = \left(8.76 \times 10^4 \times \text{W}\right) / \left(\text{A} \times \text{D} \times \text{T}\right) \qquad (1)$$

Where:

T	time of exposure, h,
A	total surface area, cm^2,
W	weight loss, g, and
D	density of the sample, g/cm^3.

The average corrosion rate for five such test periods was calculated. The above mentioned corrosion tests were carried out on four batches of thermally oxidized Cp-Ti samples and the error was calculated. The details of corrosion test setup are described elsewhere [19,20].

Three phase corrosion test was carried out on thermally oxidized Cp-Ti in boiling 11.5 M nitric acid. The test was carried out by suspending samples in boiling liquid, vapor and condensate phases of nitric acid for 48 h. Weight losses of the samples were recorded and the test was repeated for five such 48 h periods with fresh test solution. The corrosion rates in the individual periods were calculated using Eq. (1) and the average corrosion rate for five such test periods was calculated. For comparison of the results, Cp-Ti and Ti–5Ta–1.8Nb alloy samples were also tested under similar conditions. The details of three phase corrosion test and experimental setup used are described elsewhere [21–23].

2.4. Surface morphology of attack

The surface morphologies of the thermally oxidized Cp-Ti samples were analyzed using scanning electron microscopy (SEM) (ESEM Philips XL-30) attached with EDX. SEM examination at high magnification was done using FE-SEM (FEI, Quanta 200F). SEM examination was also carried out after practice-C corrosion test to observe the changes in surface morphology. The SEM examination of three phase corrosion tested samples exposed to boiling liquid, vapor and condensate phases of nitric acid was also carried out using FE-SEM. AFM studies were also carried out before and after practice-C corrosion test to observe the changes in surface morphology. Triboindenter (TI-950, Hysitron-USA) attached with in-situ SPM was used for AFM studies. A Berkovich diamond tip was used for scanning.

2.5. XRD

XRD was carried out on first and fourth batch thermally oxidized Cp-Ti samples with a step size of 0.1 and with time per step as 7 s

Table 1
Nominal chemical composition of Cp-Ti and Ti–5Ta–1.8Nb alloy used in wt.%.

Material	Ti	Ta	Nb	Fe	O	N	C	H
CP-Ti	Balance	–	–	0.2	0.14	0.017	0.19	0.15
Ti–5Ta–1.8Nb	Balance	4.39	1.85	0.0263	501.5 ppm	47 ppm	125 ppm	9 ppm

Please cite this article as: A.R. Shankar, et al., Surf. Coat. Technol. (2013), http://dx.doi.org/10.1016/j.surfcoat.2013.07.010