Surface & Coatings Technology 344 (2018) 680–688

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Influence of the Ti alloy substrate on the anodic oxidation in an environmentally-friendly electrolyte

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ARTICLE INFO

Keywords:
Titanium alloy
Anodic film
Microstructure
XPS
TEM

ABSTRACT

The influence of the Ti alloy substrate (α, β, α + β) on the anodic oxidation process was studied. The surface morphology, composition and crystalline structure were analyzed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). It was shown that the surface morphology and crystalline structure of anodic oxide films were considerably affected by the Ti alloy substrate. The surface morphologies of the oxide films retain their matrix microstructure characteristics. The oxide film on the residual β phase contains a trace amount of V, Zr, Mo element for TA15. Compared to the secondary α phase, the β phase has a higher degree of oxidation for TB6. The oxide film has the higher Al content on the secondary α phase, while the oxide film formed on β-phase has the higher V content. The XPS results show that the Al, Mo, V, Zr alloy elements of TA15 are involved in anodic oxidation and exist as Al_2O_3, MoO_3, V_2O_5, ZrO_2. Likewise, the Al, V alloy elements of TB6 are involved in anodic oxidation and exist as Al_2O_3, V_2O_5, but Fe element is not involved in anodic oxidation. The anodic oxide films are partly crystallized and mainly amorphous for the three kinds of titanium alloys. The TA15 anodic oxide film has the highest crystal content, and TB6 has the least.

1. Introduction

Anodic titanium oxide has attracted much attention due to its potential for widespread application in photocatalysts [1–4], biomaterials [5–7], besides its use in corrosion protection [8–10] and wear resistance [10,11]. The performance of oxide film strongly dependents on anodic parameters, such as the nature (concentration) of the electrolytes, the applied current density, the anodic forming voltage, the given temperature, the agitation speed and the ratio of the surface area of the cathode to anode [12–18]. In addition, the influence of the titanium alloy substrate on the morphology, composition, crystal structure and the property of the formed oxide film continues to be investigated, as there are many unresolved issues in this matter.

A number of studies have investigated the influence of the substrate on anodic oxidation. For instance, Matykina has shown that nanotubes were formed on the underlying α-phase matrix [19] and the main feature being the loss of the film formed on the β phase [20]. Also, Bai et al. showed that uniform anodization at both the α-phase and β-phase regions in a glycerol-based electrolyte [21]. Different anodization rates at different phases lead to different oxide structures on biphasic Ti6Al4V alloy [22,23]. Tsuchiya also revealed that anodization in aqueous electrolyte leads to the formation of two regions with different features on a biphasic alloy of $Ti_{29}Nb_{13}Ta_{4.6}Zr$ [24]. A report by Hanna Sopha [25] indicates that the Ti substrate plays an important influence in the ordering and growth of the nanotube layers. Further research is necessary to explain the specific influence on growth of the anodic oxide film, though several studies show interesting differences between the substrates.

TA15, TB6, TC4 are three typical titanium alloys widely used in aviation industry. TA15 is a near-α titanium alloy with high aluminium equivalent. TB6 is a near-β titanium alloy with high vanadium equivalent and TC4 is a α + β titanium alloy. In this study, different types of Ti alloys (TA15, TB6, TC4) in terms of morphology, roughness, crystalline structure and chemical composition, as well as their influence on the anodic oxidation process in an environmentally friendly electrolyte were investigated. Accordingly, the objective of the present work is to investigate the influence of the Ti alloy substrate (α, β, α + β) on the anodic oxidation process in an environmentally friendly electrolyte. The surface morphology, thickness and crystalline structure of the oxide film were evaluated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS).

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https://doi.org/10.1016/j.surfcoat.2018.04.001
Received 8 January 2018; Received in revised form 31 March 2018; Accepted 2 April 2018
Available online 03 April 2018
0257-8972/

Table 1
Chemical compositions (wt%) of TA15, TB6 and TC4.

Alloy	Al	Mo	V	Zr	Fe	O	C	H	Ti
TA15	5.5–7.0	0.5–2.0	0.8–2.5	1.5–2.5	≤0.25	≤0.15	≤0.08	≤0.015	Balance
TB6	2.6–3.4		9.0–11.0		1.6~2.2	≤0.13	≤0.05	≤0.0125	Balance
TC4	5.5–6.8		3.5–4.5		≤0.3	≤0.2	≤0.08	≤0.015	Balance

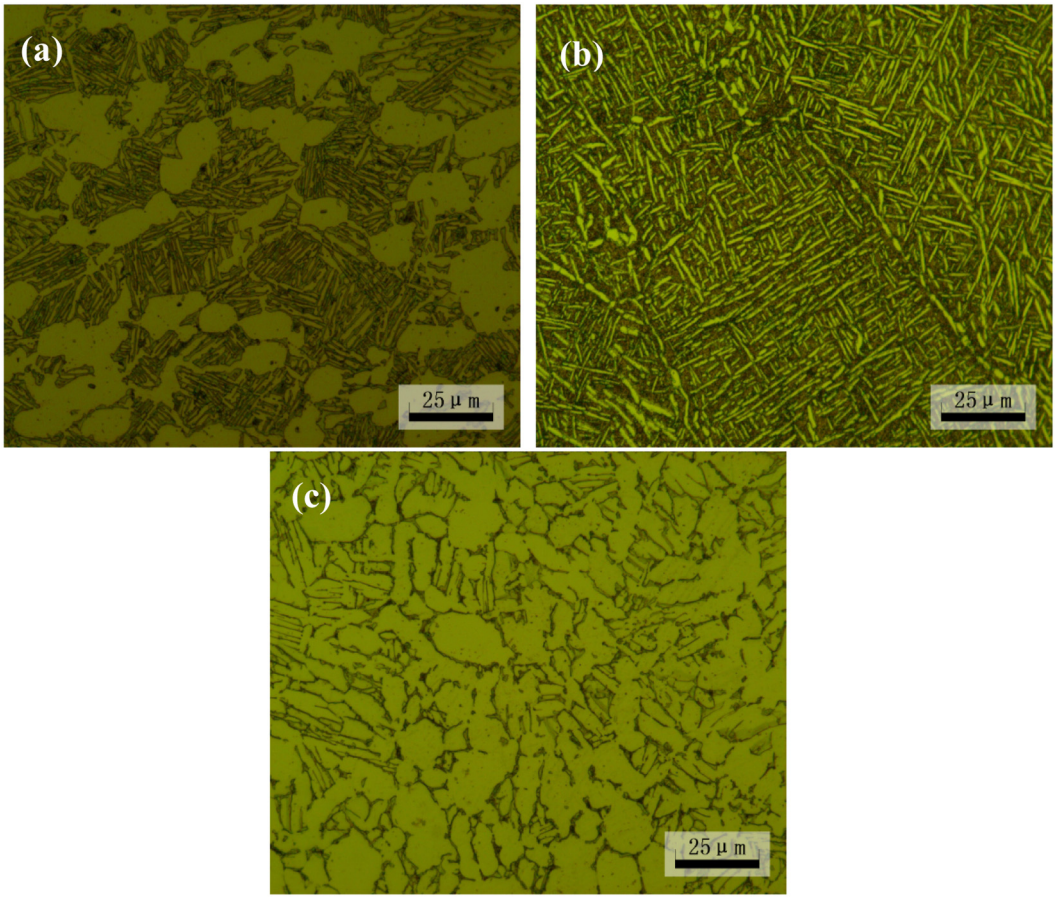

Fig. 1. Microstructures of (a)TA15, (b) TB6, (c) TC4.

2. Experimental

2.1. Materials and preparation

The nominal components and microstructures of the TA15, TB6 and TC4 (annealed, supplied by Baoti Group Inc., China) used in this work are shown in Table 1 and Fig. 1. Prior to pulse anodization, samples were abraded with silicon carbide (SiC) paper of successive grades from 200 to 2000 grit and further mechanically polished to mirror finish with a 1-μm diamond paste. All samples were ultrasonically cleaned in an ethanol solution, rinsed in deionized water and then activated in a mixed solution of H_2O_2 (5 g/L) + NaOH (10 g/L) for 10 min at 60 °C, which was the pretreatment procedure.

Anodic oxidation was processed using a homemade pulse power supply (WMY-IV). A periodical square wave with a current density of 5 A/dm^2 (amplitude), a frequency of 1.67 Hz and a duty ratio of 30% was used as shown in Fig. 2. The titanium alloy sample and a 1Cr18Ni9Ti stainless steel plate were used as the anode and cathode, respectively, and the ratio of their surface areas was < 0.5. During the treatment, the temperature of the electrolyte was kept constant at 15 ± 2 °C using a thermostat water bath, and the bubbles generated were eliminated using a magnetic stirrer. The electrolyte was composed

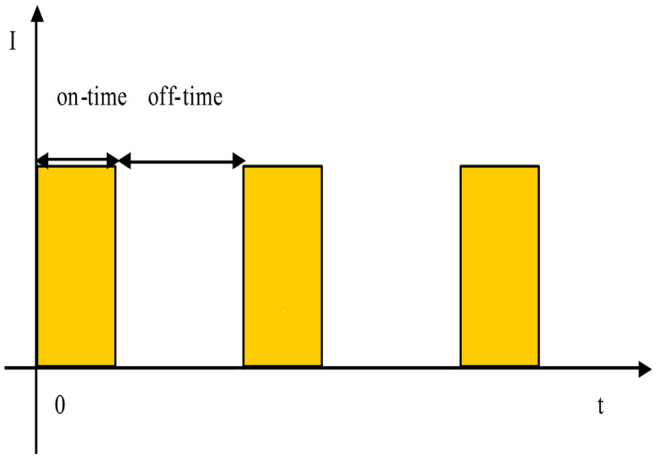

Fig. 2. The output mode of the power supply.

of 0.15 M sodium tartrate and the pH value is 7.4–7.6. The electrolyte is aqueous solution and it is free of strong acids and fluorides. The anodic oxidation process parameters were shown in Table 2. After the anodic