Vacuum xxx (2016) 1–9

Contents lists available at ScienceDirect

Vacuum

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

Influence of anodizing time on morphology, structure and tribological properties of composite anodic films on titanium alloy

Liang Wu [a, *], Chen Wen [b], Gen Zhang [a], Jianhua Liu [c], Kun Ma [c]

[a] Chongqing University, School of Materials Science and Engineering, Chongqing 400030, China
[b] Beijing Spacecrafts, China Academy of Space Technology, Beijing, 100094, China
[c] Beihang University, School of Materials Science and Engineering, Beijing 100191, China

A R T I C L E I N F O

Article history:
Received 25 August 2016
Received in revised form
29 December 2016
Accepted 31 December 2016
Available online xxx

Keywords:
Composite anodic films
Anodizing time
Ti10V2Fe3Al
Tribological properties
Lubricating layer

A B S T R A C T

Composite anodic films containing polytetrafluoroethylene (PTFE) nanoparticles were fabricated on Ti10V2Fe3Al by anodic oxidation in an environmentally friendly electrolyte. The influence of anodizing time on the morphology, surface roughness and crystal structure of composite anodic films were studied by using field emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM) and Raman spectroscopy, respectively. The results show that composite anodic films had a surface full of tiny bumps and PTFE nanoparticles. The bumps grew bigger and aggregated into larger ones with increasing anodizing time until 30 min later. The tribological properties of the films were investigated by dry friction tests in terms of the friction coefficient, wear loss and the morphologies of worn surfaces. The results indicated the thickness of films and the amount of PTFE particles had a synergistic effect on anti-wear and anti-friction performance of composite anodic films. The certain thickness of films provided reliable source of wear debris. PTFE nanoparticles could lead to the formation of lubricating layer.

1. Introduction

Titanium and its alloys have been widely used in aerospace, automotive, chemical and biomedical industries because of their high strength-to-weight ratio, high melting point, good corrosion resistance and biocompatibility [1–6]. However, their unstable friction coefficient, severe abrasive and adhesive wear have on the other hand limited their applications [7,8]. Consequently, enormous efforts have been devoted to improve the tribological properties of the titanium alloys.

To this end, a number of surface treatments have been developed, such as anodic oxidation, micro-arc oxidation, plasma spray, plasma immersion implantation, laser beam treatments, thermal oxidation, electroplating, thermal spray, and so on [9,10]. Among these technologies, anodic oxidation is widely applied owing to its low cost and simple operation. In particular, composite anodizing is an effective approach to offer attractive combinations of good wear and corrosion resistance as well as other mechanical properties for aluminum and titanium alloys [12–23]. So they have been studied increasingly.

In recent years, many investigations of composite oxidation films with nanoparticles had been taken on aluminum alloys firstly [12–16]. Zubillaga et al. fabricated anodic alumina films containing polyaniline and TiO_2 or ZrO_2 nanoparticles on an AA2024 aluminum alloy to improve its corrosion resistance [12]. Escobar et al. formed composite anodic films with PTFE nanoparticles on 1050 aluminum substrate to improve the tribological behavior [13]. Chen et al. prepared composite films with superfine Al_2O_3 and PTFE particles on AA2024 aluminium alloy, showing good anti-wear and self-lubricating properties [14]. Jin et al. added Fe micro-grains into the electrolyte to produce composite films which were much denser and harder and the wear resistance of aluminum was improved [15]. Vaezi et al. improved the wear resistance of the composite coatings by adding SiC nanoparticles in anodizing bath [16].

In the case of composite anodizing on titanium alloys [17–23], Aliofkhazraei et al. added Si_3N_4 and Al_2O_3 nanoparticles into electrolyte to generate composite films which improved wear resistance of titanium substrate [17]. A MoS_2-containing composite film on Ti6Al4V alloy was prepared by Mu et al., and it registered much lower friction coefficient and wear rate compared with the one without MoS_2 under dry sliding condition [19]. Li et al. studied composite anodic films containing SiC nanoparticles on Ti6Al4V alloy and the composite films show good anti-wear and anti-

* Corresponding author.
E-mail address: wuliang@cqu.edu.cn (L. Wu).

http://dx.doi.org/10.1016/j.vacuum.2016.12.047

corrosion properties [21]. Further, the effect of SiC nanoparticles concentration on tribological properties of composite films formed on Ti10V2Fe3Al alloy were investigated by Li et al. [22]. Zhu et al. fabricated a SiC/PTFE composite anodic film on Ti6Al4V alloy. SiC and PTFE nanoparticles had a favorable synergistic effect on tribological properties of the SiC/PTFE composite film [23].

The nanoparticles were incorporated mainly near the films surface and within cavities inside the films [12,14,17]. The properties of composite films were affected by different kinds of nanoparticles significantly. In a word, organic polymer nanoparticles such as PTFE [11,13,14,20,22] and hard ceramic nanoparticles such as SiC, Al_2O_3, Si_3N_4, ZrO_2 and etc. [12,16–19,21,23]can both significantly improve the tribological properties of composite films. The reason is that organic polymer nanoparticles have a self-lubrication property [24] and ceramic nanoparticles can improve the hardness of composite films [25]. Further, composite anodic films incorporating appropriate nanoparticles increase their tribological properties, meanwhile enhancing other properties such as corrosion resistance [12,21,26].

Though composite anodic films containing different incorporated nanoparticles have been formed and tribological properties of them have been improved, the synergistic effect between the thickness of films and the amount of PTFE particles have been reported seldom before. Besides, the effects of increasing anodizing time on the thickness of composite films and the amount of PTFE particles is paid little attention. The thickness of composite films and the amount of PTFE particles affect the tribological properties of composite films dramatically [22]. Furthermore, environmental protection is an increasingly severe issue, and our laboratory applies environmentally friendly electrolytes accordingly.

In this study, PTFE nanoparticles were incorporated into the anodic oxide films on the surface of titanium alloy Ti10V2Fe3Al for better tribological properties. The morphology, composition, structure and roughness of composite films formed at different anodizing time were investigated by SEM, EDS, Raman spectroscopy and AFM, respectively. The abrasive wear behavior of composite films formed at different anodizing time was evaluated and lubrication mechanism was put forward.

2. Experimental

2.1. Materials

A titanium alloy Ti10V2Fe3Al forged block was cut into $50 \times 25 \times 2$ mm and $10 \times 10 \times 3$ mm sheets. The nominal chemical composition of Ti10V2Fe3Al were shown in Table 1.

2.2. Preparation of composite anodic films

Prior to anodizing, samples were abraded with silicon carbide (SiC) papers of successive grades from 200 to 2000 grits and further mechanically polished to mirror finish with diamond paste of 1 μm. All samples were then ultrasonically cleaned in ethanol solution, degreased in alkaline solution, rinsed in de-ionized water. The temperature of electrolyte was kept at about15 °C using a thermostatic water bath. The electrolyte was stirred during the anodic oxidation process. A 1Cr18Ni9Ti stainless steel plate was used as cathode. A pulse galvanostatic power supply (PGPS, WMY-IV, 708th research institute of Astronautics, China) was used. The pulse of the power supply was unidirectional and exhibited a square wave. Anodizing was carried out at a constant current density of 5A/dm^2 in 30 g/L neutral sodium tartrate electrolyte with 10 ml/L PTFE latex. This electrolyte is an environmental friendly electrolyte without containing any hydrofluoric acid, fluoride or strong acid. The hydrofluoric acid and fluoride are harmful to the environment due to their high toxicity and complexity of their disposal process.

The PTFE aqueous dispersion contained 60 wt% PTFE nanoparticles of about 100 nm in size. The fabrication conditions were studied in detail previously [27–29]. The frequency and duty ratio were 1.3 Hz and 25%, respectively. And surface area ratio of cathode to anode was 4:1. Because this experiment is under constant current operation, the value of voltage is fluctuant during anodizing process. The samples were anodized at different times, being 5, 10, 20, 30 and 60 min, respectively.

2.3. Morphology and phase composition

The morphology, roughness and composition of the anodized samples were examined by using field emission scanning electron microscopy (FE-SEM, XL30S, FEI, USA) equipped with EDS analyzer and atomic force microscope (AFM, Dimension icon, Veeco, USA). The crystal structure characterization was carried out by using Raman spectroscope (Yvon Jobin Horiba-HR 800, He-Ne laser without filter, 650 nm).

2.4. Tribological tests

The tribological test was performed using a ball-on-disc rotating wear tester (UMT, UMT-2MT, CETR, USA). A Si_3N_4 ceramic ball with a diameter of 2 mm and surface roughness of about 0.01 μm was employed as the counterpart. All the tests were performed at a load of 100 g with a rotation diameter of 4 mm and rotating velocity of 100 rpm under ambient conditions. The friction coefficient curves and sliding times were recorded with computer. There were three parallel samples in each group and each parallel sample was tested for 30 min.

Morphologies of the worn surface after the tribological tests were examined by field emission scanning electron microscopy (FE-SEM, XL30S, FEI, USA). The composition of worn surfaces was measured using the EDS attached to the SEM. The wear loss of each sample was measured by electronic analytical balance (EAB, FA2104, Shanghai-LP, China). The precision of analytical balance used for wear loss measurements is 0.0001 g.

3. Results and discussion

3.1. Morphology and composition of composite anodic films

Fig. 1 shows the evolution of surface morphologies of composite anodic films formed in sodium tartrate electrolyte with PTFE latex addition. After anodizing for 5 min, the surface of titanium alloy is covered with a layer of oxide film uniformly, where lots of tiny bumps are clearly visible. Fig. 1b shows that the PTFE particles aggregate preferentially near the cracks of the anodic films. At 10 min, the bumps become larger. More cracks are formed on the surface with PTFE particles. Asquith et al. proposed that there was a tensile region at the interface of substrate and oxide films, and the tensile residual stress field would help drive crack [30]. The presence of cracks on the films was probably related to the tensile residual stress field. After 20 min, the surface is completely covered with dense composite films. The size of bulges and the fluctuation of the surface become larger. The surface of composite anodic films is divided into many plates due to the presence of cracks. The cracks

Table 1
Nominal chemical composition of Ti10V2Fe3Al (wt%) titanium alloy.

V	Fe	Al	C	N	O	Ti
10.100	2.100	3.100	<0.050	<0.050	<0.130	balance