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Characterizations of anodic oxide films formed on Ti6Al4V in the silicate electrolyte with sodium polyacrylate as an additive

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ABSTRACT

Anodic oxidation coatings were prepared on Ti6Al4V alloy in Na_2SiO_3-based electrolyte with sodium polyacrylate (PAAS) as an additive, to develop a route of making thicker films under 200 V. The addition of PAAS as an anion species in the anodic electrolyte increased the conductivity of the solutions, leading to the reduction in breakdown voltage and thus the more vigorous discharging process on the metal surface during anodization. With the addition of PAAS, more and bigger porous and thicker ceramic coatings were obtained as shown by scanning electron microscopy (SEM) and Image-pro Plus software; the addition of PAAS promoted the growth of robust rutile TiO_2 and/or Al_2TiO_5 in the anodic coatings; however, the excessive addition of PAAS resulted in the incorporation of more amorphous silicates in the thicker outer anodic films as shown from the EDS measurement, X-ray diffraction and Raman spectra. Therefore, the microhardness and adhesion of the anodic samples with PAAS at an appropriate concentration of 0.7 g/L improved by about 2 times and 4 times, respectively; their friction coefficient and wearing rate were also reduced to quite lower values compared to those for the anodic sample without PAAS addition.

1. Introduction

Since the naturally formed oxide film on Ti alloy surface is generally very thin passive film which is insufficient for corrosion protection in harsh environments and wear protection, many surface modification techniques including anodic oxidation, ion implantation, plasma spraying and so on have been applied in improving their abrasion, anticorrosion, and chemical resistance under some special conditions [1–3]. Among them, anodic oxidation has been popularly used due to its cost effective and easy operation, and the structure and performances of anodic coatings can be properly controlled depending on the type of the electrolyte, the compositions of the electrolyte, and the electric parameters to satisfy different requirements [4–6]. Besides, some additives added as a supplementary component in the anodic electrolytes have been proved playing an important role on the structures and properties of the anodic coatings. Tang et al. found that by adding $FeSO_4$ in the sodium phosphate electrolyte, the surface roughness of the anodic coatings increased, and thus their bonding strength adhered by epoxy was also greatly improved [7]. Li et al. reported that with the addition of ZrO_2 particles in sodium phosphate electrolyte, thicker anodic coatings with less cracks and pores could be formed exhibiting much better oxidation resistance and wear resistance [8]. Khanmohammadi et al. obtained pancake-like anodic coatings with great adhesion to the substrate when NaF was added in aluminate base electrolyte during micro-oxidation [9]. Wang et al. found that the addition of $NaAlO_2$ in Na_2SiO_3-$(NaPO_3)_6$ solution significantly promoted the growth of rutile TiO_2 during anodization; and thus more dense, uniform and thicker ceramic coatings were obtained with better anti-friction performances and more positive corrosion resistance [10]. In comparison, only a few papers reported on the improvement of anodic oxidation on titanium alloy by adding organic additives. Li et al. reported that when adding polymer additive PTFE into the electrolyte, the composite film exhibited much better anti-friction performance [11]. Chanmanee et al. found that the thickness, diameter and length of the titanium nanotubes could be adjusted by adding polyhydroxy alcohol into the NH_4F/NaF based electrolyte [12].

The demand for oxide films with high electrochemical stability used in the fields of solar cells and batteries has arisen much broader interests in developing various porous anodic composite films in some recent studies [13–15]. In our previous studies, we reported the influences of organic molecule on the pore formation and anti-abrasion of anodic films on Ti6Al4V under low voltage of 10 V, and found that the amino silane had a great effect on the structures and performances of anodic films formed in pure alkali and alkali-Na_2SiO_3 electrolytes, respectively [16,17]. However, the ceramic layers formed under low voltage were generally too thin to provide robust protection, while

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micro-arc anodization generally performed under very high voltage (above 400 V) was mostly considered an energy-intensive technique; thus in this study, we chose 200 V as the anodic voltage like the working voltage of industrial equipment, in an attempt to obtain anodic coatings with comparable performances. We investigated the effect of water-soluble polymer (PAAS) additive on the pore distribution and mechanical properties of ceramic coatings on Ti6Al4V formed in Na_2SiO_3 electrolytes. Their surface and cross-sectional images of these porous anodic coatings were recorded by scanning electron microscopy (SEM), their compositions and structures were analyzed by energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) and Raman spectra, respectively; and finally their mechanical performances were measured by microhardness, adhesion test and wearing test, respectively.

2. Experimental

2.1. Materials

Titanium alloy (Ti6Al4V) was used with dimensions of 15 mm × 10 mm × 2 mm as the substrate. The samples were ground using $200^{\#}$, $400^{\#}$, $800^{\#}$, $1000^{\#}$, $1500^{\#}$, $2000^{\#}$ grit silicon carbide papers to obtain smooth surface on the substrate, cleaned using distilled water and acetone, followed by pickling in a mixture of 0.9 mol/L HF and 3.0 mol/L HNO_3 solution, and at last washed thoroughly by distilled water and dried in warm air before use.

The main electrolyte chemical sodium silicate (AR, Na_2SiO_3) and the additive sodium polyacrylate (AR, PAAS) were supplied by Sinopharm Chemical Reagent Co., Ltd. China and used as received.

2.2. Preparation of anodic coatings

A fresh electrolyte prepared by dissolving 50.0 g/L Na_2SiO_3 into deionized water was used for oxidation process. In order to study the difference of the structure and properties of the oxide film formed by the oxidation in the electrolyte containing different amount of additives, sodium polyacrylate (PAAS) was added to the electrolyte solution to prepare mixing electrolytes with PAAS at concentrations of 0, 0.5 g/L, 0.7 g/L and 0.9 g/L represented by $PAAS_0$, $PAAS_{0.5}$, $PAAS_{0.7}$, $PAAS_{0.9}$ as the corresponding test samples, respectively. After PAAS addition under stirring for 30 min, the conductivity of the electrolytes was recorded by using conductivity meter (DDS-11A, INESA Instrument Corp., China). The JJMF type pulse power source was used as the oxidation power supplier, and the graphite plate and the titanium alloy sample were used as the cathode and anode, respectively. The working voltage was kept at 200 V and the oxidation time was controlled at 20 min. During oxidation, the temperature of the electrolyte was always controlled under 35 °C. After 20 min treatment, the samples were cooled and rinsed thoroughly with distilled water, and finally they were dried in warm air before measurements.

2.3. Characterizations of oxidation ceramic coatings

The surface and cross-sectional morphologies of anodic samples were observed by using Cambridge Instrument S-360 SEM (England) equipped with Tracor Northern EDS detector at the working voltage of 20 kV and working distance of 10.5 mm, the relative element contents along the vertical direction of film thickness with a length of about 3.5 μm were also recorded. All the samples were sputtered by gold for 1 min before measurement. The average pore diameters and distributions were inspected and measured by using the Image-pro Plus software (Media Cybernetics, America) [18].

The coatings phase composition of the oxide film was investigated by X-ray diffraction (Rigaku DMAX-RB 12 kW, Japan). The solid target was copper target, the scanning angle from 10° to 80°, and the scanning speed was 0.02°/s. A micro-Raman spectrometer (LabRam-HR, French) was employed to study the normal temperature Raman spectra of ceramic coating. The excitation light was He-Ne with wavelength 632.8 nm and power 4.3 mW. The surface chemical composition of the oxide film was analyzed by X-ray photoelectron spectroscopy (ESCALab220i-XL, England). The excitation source was Al Ka X-ray, and the power was about 300 W.

The microhardness of the oxidized samples was tested by the microhardness instrument (HXD-100TMC), and three points were measured for each. In order to analyze the adhesion of the ceramic coatings, coating adhesion scratch tester (WS-2005) was used in this study. The tribological behavior of the Ti6Al4V alloy substrate and anodized samples was evaluated by a ball-on-disk reciprocating wear tester (WTM-2E). A GCr15 steel ball with a diameter of 3.0 mm was used as the counterpart. All the dry sliding was performed at a speed of 200 rpm.

3. Results and discussions

3.1. Surface and cross section morphology of the oxide films

The surface SEM images for the anodic films obtained in different electrolytes are shown in Fig. 1. The oxide film formed in base electrolyte in Fig. 1a is seen inhomogeneous having some particle aggregations in different areas, and these spherical particles with similar sizes (inserted picture) are evenly distributed in the smooth area. In contrast the ceramic coatings formed in the electrolyte with different additives ($PAAS_{0.5}$, $PAAS_{0.7}$ and $PAAS_{0.9}$) present a similar change of continuous surface dotted with pores in Fig. 1b, c and d, respectively, while their pore size and distribution are varied dependent on the amount of PAAS as shown correspondingly in Fig. 2B, C and D, respectively. When PAAS was added at 0.5 g/L in the electrolyte, the smooth platform around the pores can be identified clearly in an enlarged window (Fig. 1b) and the average pore size in diameter of 4 μm distributed at relatively regular interval from 3 μm to 6 μm is observed in Fig. 2B. With the addition of PAAS to 0.7 g/L, much more and larger pores are observed mostly in the range of 3 μm to 7 μm with a broader distribution on the anodic surface as shown in Fig. 2C. When the addition of PAAS was increased to 0.9 g/L, much larger pores with diameter above 7 μm were formed and the peak numbers in the range of 3 μm to 7 μm decreased while their total pore numbers do not show much increase in Fig. 2D (relative to those in Fig. 2C). Thus, the existence of PAAS promotes the formation of pores on the anodic coating, and much bigger pores can be formed with more PAAS additions. Nevertheless, the pore numbers may be irrelative to the amount of PAAS when PAAS was added above certain concentration since the statistical data trend of pore numbers goes relatively smooth at PAAS above 0.7 g/ L as shown in Fig. 2E.

The thickness of these oxide layers also varies depending on the amount of PAAS as shown in Fig. 3. The oxide layer with a thickness about 4 μm was obtained in the base electrolyte, while with the addition of PAAS, the thickness of oxide film increases from about 10 μm to 20 μm when PAAS was added from 0.5 g/ L to 0.9 g/L, respectively. In some previous studies, the structure and morphology of anodic films were reported greatly affected by the anodic voltage, the growing process was considered initiated at potentials above the breakdown voltage of the oxide film and moved rapidly across the anode surface, and the pore was formed through the molten oxide and gas bubbles throw out of discharge channels [19,20]. The existence of partially ionized PAAS increased the conductivity of the anodic electrolytes as shown in Table 1 [21]; under electric field, the ionized PAAS moves to anode, and at higher concentrations, more anionic species in the electrolyte absorbing on the oxide film subsequently result in a higher density of primary electrons introducing into the conduction band of the oxide. Consequently, the higher primary electron current density results in the critical value of the secondary electron current density reaching comparatively lower voltages and then film breakdown occurs