Microstructure and mechanical properties evaluation of molybdenum disulfide-titania nanocomposite coatings grown by plasma electrolytic oxidation

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ABSTRACT

In this work, the molybdenum disulfide-titania (MoS_2-TiO_2) nanocomposite oxide coating on Ti-6Al-4V alloy was fabricated by plasma electrolytic oxidation (PEO) process. The MoS_2 particles with concentrations of 4 g/L was added into the electrolyte and three duty cycle values, 20%, 35% and 50% at a fixed frequency of 1000 Hz were used. We found that shorter activation time and lower breakdown voltage for the PEO reaction was achieved due to the addition of 4 g/L MoS_2 particles in the electrolyte. The oxygen rich, rutile and anatase nonstoichiometric TiO_2 phases were produced for all oxide coatings. In this work, the one-step PEO grown coatings consisting of MoS_2-TiO_2 nanocomposite structure with good adhesion, low coefficient of friction and low wear rate were achieved due to the lubricious effect of the 4 g/L MoS_2 particles in electrolyte under a duty cycle of 50%.

1. Introduction

Ti-6Al-4V alloy is characterized for its high strength-to-mass ratio and excellent anticorrosion property, which makes it be widely applied in the automotive, aerospace and biomedical field. However, the galling failure for this Ti-based alloy becomes a drawback during its application. Several surface engineering treatments have been employed to enhance its hardness and wear resistance, such as thermal oxidation [1], nitriding [2], laser surface alloying [2,3], hard coating [4], and plasma electrolytic oxidation [5–8]. Plasma electrolytic oxidation (PEO), or so-called micro-arc oxidation (MAO) process is an economical, efficient, and environmentally friendly technology to generate a functional oxide layer on light metals and alloys [9]. In order to further improve the performance of wear resistance and mechanical property of light metals, the PEO process with hard or lubricious particles, such as Si_3N_4 [10], ZrO_2 [11,12], Al_2O_3 [13] and MoS_2 [14,15], incorporated into the electrolyte has been studied in literature. However, only very limited data was reported on the incorporation of MoS_2 particles with the PEO process of Ti alloys. Mu and coworkers [14] reported that after adding 20 g/L

MoS_2 particles into the phosphate electrolyte and plasma electrolytic oxidized for 90 min, the tribological property of Ti-6Al-4V alloy can be greatly enhanced by the TiO_2/MoS_2 composite surface coating layer. However, the adhesion property of the PEO coating by the addition of MoS_2 particles was not revealed. And the relatively long plasma processing time, 90 min, also made this treatment be less economical and efficient. In this work, an attempt has been made to improve the adhesion and wear resistance of porous TiO_2 ceramic coating by adding lower amount of MoS_2 particles into the electrolyte of PEO process and using shorter processing time. The effects of MoS_2 particle concentration and duty cycles on the voltage-time behavior of PEO process, phase, microstructure, adhesion and tribological properties of PEO grown oxide layer were discussed.

2. Experimental procedure

Ti-6Al-4V alloy plates with dimensions of 20 mm × 20 mm × 2.0 mm were abraded with #1200 SiC paper, washed in distilled water, ultrasonically degreased in acetone and rinsed in alcohol. A direct current (DC) power supply unit connected to a pulse generator unit (SPIK 2000A, Melec, Germany) was employed for the PEO process. Three

duty cycles, 20%, 35%, and 50%, were selected and the frequency was fixed at 1000 Hz. The aqueous electrolyte solution contained 0.05 M K_3PO_4 and 0.01 M KOH. The molybdenum disulfide particles with average diameter of 500 nm were added into the PEO electrolyte in a concentration of 4 g/L to fabricate the MoS_2-TiO_2 nanocomposite coating on the surface of Ti-6Al-4V alloy. The electrolyte conductivities of aqueous electrolytes with and without MoS_2 particles were measured using a portable electrical conductivity meter (HANNA Instruments HI 991300 pH EC Electrical Conductivity) with automatic temperature compensation. A magnetic stirring system was used during PEO process to ensure the homogenous distribution of particles in the electrolyte. The PEO process was kept for 20 min at a constant current of 2.5 A. A maximum voltage of 400 V was set for PEO process. The reaction electrolyte was cooled down to room temperature using a water cooling system. After the PEO process, PEO grown coatings were cleaned with deionized water and air dried at room temperature. In this work, the PEO parameters and designation for each specimen are presented in Table 1. The phases of coatings were explored by a grazing incidence X-ray diffractometer (GIXRD, PANalytical, X'pert, Holland) with an incidence angle of 1°. Cu Kα radiation generated at 30 kV and 40 mA from a Cu target was used. The chemical composition of PEO grown coatings was analyzed with an energy dispersive spectrometer (EDS, XFlash 6/100, Bruker, Germany). The surface and cross-sectional morphologies of coatings were examined with a scanning electron microscope (SEM, S3400 N, Hitachi, Japan). The surface roughness of each coating was analyzed using a profilometer (Surfcorder ET3000, Kosaka Lab., Japan). A scratch test (Scratch Tester, J & L Tech. Co., Korea) with up to a maximum load of 50 N was adopted to evaluate the adhesion property of coatings. Furthermore, a Vickers microindentation test under 19.6 N load was used to determine the cohesive adhesion of PEO grown oxide layer on the Ti-6Al-4 V alloy substrate. The coefficient of friction of the coating was measured using a ball-on-disk wear tester (Tribometer, JLTB-02, J & L Tech. Co., Korea) to investigate the wear resistance of coatings against the 5 mm diameter high Cr steel ball. A normal load of 1 N was applied. The sliding speed was 83.9 mm/s with a wear track diameter of 8 mm. The sliding distance was 100 m for each test. The wear rate of each coating was determined based on the following equation [16]:

$$W_R = \frac{t\left(3t^2 + 4b^2\right)2\pi r}{6bF_n S} \tag{1}$$

where t is the depth of the wear track determined using a surface profilometer, b is the width of the wear track, r is the radius of the wear track, F_n is the normal load and S is the sliding distance.

3. Results and discussion

3.1. The breakdown voltage tendency

It is well-known that a thin oxide layer formed in the initial stage of PEO treatment and drastically increased the voltage. And then the point
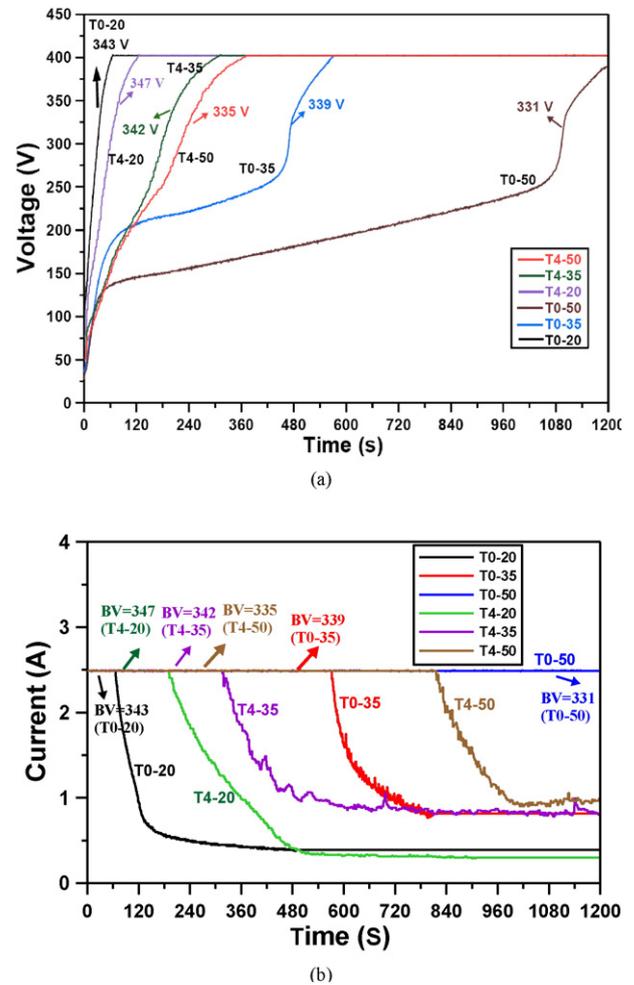

Fig. 1. The (a) voltage-time and (b) current-time curves for the PEO treatments.

plasma discharge occurred on the oxide surface when the voltage reached the breakdown potential. Fig. 1(a) and (b) show the voltage–time and current-time curves for the PEO processes of six samples. Arrows were inserted in the plots to indicate the breakdown voltages for point plasma reaction. In Fig. 1(a), for the PEO treatment with MoS2 additive, the slope of the voltage-time curve becomes steeper as the duty cycle decreased from 50% to 20%. Meanwhile, for the for the PEO treatment without MoS2 additive, the shape of the voltage-time curve changes from a steep curve to a ramp curve as the duty cycle increased from 20% to 50%. On the basis of results shown in Fig. 1(a), the maximum voltage of 400 V was reached after the activation of point plasma process. However, a time delay around 39 to 1102 s for plasma sparking was observed in Fig. 1 (a). A similar spontaneous decay of sparking

Table 1
Specimen designation, electrical conductivity of electrolyte and parameters for plasma electrolytic oxidation treatment (electrolyte containing 0.05 M K3PO4 and 0.01 M KOH, PEO treatment for 20 min at a constant current of 2.5 A and a maximum voltage of 400 V).

Specimen designation	T_{on} (µs)	T_{off} (µs)	Duty cycle (%)	MoS_2 concentration in electrolyte (g/L)	Electrolyte conductivity (mS/cm)	Breakdown voltage (V)	Time to reach breakdown voltage (s)
T0-20	200	800	20	0	14.45	343	39
T0-35	350	650	35			339	402
T0-50	500	500	50			331	1102
T4-20	200	800	20	4	14.75	347	77
T4-35	350	650	35			342	206
T4-50	500	500	50			335	248