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Effects of current density on microstructure and properties of plasma electrolytic oxidation ceramic coatings formed on 6063 aluminum alloy

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Abstract: Plasma electrolytic oxidation (PEO) ceramic coatings were fabricated in a silicate-based electrolyte with the addition of potassium fluorozirconate (K_2ZrF_6) on 6063 aluminum alloy, and the effects of current density on microstructure and properties of the PEO coatings were studied. It was found that pore density of the coatings decreased with increasing the current density. The tribological and hardness tests suggested that the ceramic coating produced under the current density of 15 A/dm^2 showed the best mechanical property, which matched well with the phase analysis. Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curves proved that the coating obtained under 15 A/dm^2 displayed the best anti-corrosion property, which was directly connected with morphologies of coatings.

Key words: 6063 aluminum alloy; ceramic coating; plasma electrolytic oxidation (PEO); current density; microstructure; mechanical property

1 Introduction

Aluminum and its alloys are widely used in fields of automotive and aerospace industries because of their excellent properties, their high specific strength, quite good formability and lightweight [1]. However, their disadvantages, such as low hardness, low wear resistance and difficulty to lubricate, have seriously limited their extensive applications. On the other hand, aluminum alloys are susceptible to corrosion, especially intergranular and pitting corrosions caused by intermetallic constituent particles, which also greatly restricted their extensive usage [2].

Plasma electrolytic oxidation (PEO), also referred to as micro-arc oxidation (MAO) [3], micro-arc discharge oxidation (MDO) [4], has attracted recent attention as a relatively new surface modification technique of light alloys such as aluminum, magnesium, titanium and their alloys [5−7]. The plasma electrolytic treatment can produce a ceramic coating on aluminum alloys to enhance their wear resistance [8] and anti-corrosion properties [9]. The process of PEO is carried out at voltages higher than the breakdown voltage of the gas layer enshrouding the anode. Since the substrate alloy is connected to positive pole of the rectifier as anode, the gas layer consists of oxygen. The coating formed on the substrate alloy, which is of crystalline or amorphous phases, formed at breakdown sites, usually contains constituent species derived from the substrate and the applied electrolytes. Specifically, when the dielectric gas layer completely covers the anode surface, electrical resistance of the electrochemical circuit surges and the process continues providing that the applied voltage is higher than that of the breakdown voltage of the gas layer. Applying such voltages leads to the formation of electrical discharges through which electric current could pass gas layer. Many researchers have addressed that the properties of PEO coating depend on electrolytes [10], electrochemical parameters [11,12] and type of power source [13]. To obtain desired coatings, many investigations on the influence factors of PEO process have been done in recent years.

It has been demonstrated that ZrO_2 coating could provide a longer term protection to magnesium alloys compared with the traditional PEO coatings [14,15].

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However, the effect of current density on ZrO_2-containing PEO coatings has not been well studied. In this investigation, the objective was to study the most superior current density for PEO coatings on structure, tribological and anti-corrosion properties. A silicate-based electrolyte with the addition of K_2ZrF_6 was applied to producing ZrO_2-containing ceramic PEO coatings on the aluminum alloy substrate. Results showed that the increase of current density increased the wear resistance and corrosion resistance of aluminum alloy substrate in a certain scope.

2 Experimental

The material used in this study was 6063 aluminum alloy, its chemical composition is shown in Table 1. Oblong specimens with dimensions of 30 mm × 29 mm× 3 mm were used as substrate. The surfaces of specimens were ground by alumina waterproof abrasive paper up to 1800 grit and ultrasonically cleaned in pure ethanol for degreasing, then cleaned by distilled water and dried in ambient air in prior to PEO process. PEO process was carried out using a bipolar pulsed DC power source, a stainless steel vessel was used as the electrolytes container, a cooling system and a stirring system to keep temperature below 303 K. The cylindrical barrel with electrolytes was served as the negative electrode which was made of stainless steel. In order to ensure proper electrical contact, a threaded hole of 2 mm in diameter was made on the center of the sample and a thin aluminum rod with external threading was screwed to the sample. The electrolyte was an aqueous solution of $NaSiO_3$ (10 g/L), KOH (1 g/L) and K_2ZrF_6 (2 g/L) in 1 L distilled water. The detailed parameters and corresponding labels are shown in Table 2. All coated samples were rinsed in distilled water thoroughly after the PEO treatment immediately and dried in hot air.

Table 1 Chemical composition of 6063 aluminum alloy (mass fraction, %)

Si	Cu	Mn	Fe	Mg	Zn	Cr	Ti	Al
0.2−0.6	0.1	0.1	0.35	0.45−0.9	0.1	0.1	0.1	Bal.

Table 2 Plasma electrolytic oxidation parameters and corresponding labels of coated specimens

No.	Current density/ ($A \cdot dm^{-2}$)	Time/min	Duty cycle/%	Frequency/ HZ
S1	5	18	75	140
S2	10	18	75	140
S3	15	18	75	140
S4	20	18	75	140

Surface and cross-sectional morphologies of coatings were investigated by scanning electron microscopy (SEM, ISM−6510) with gold-sputtering. Some specimens were cross sectioned, mounted in epoxy and polished for the cross-section image. Thicknesses of coatings were studied by eddy current-based thickness gauge (Time Group Inc). Thickness measurements were made at 10 different locations and 4 scans were made for assessment of roughness on all specimens. Surface roughness measurements were carried out with a Hommel profilometer. Phase composition of coatings and bare alloy were studied by X-ray diffraction (XRD, Digaku D/max−2500) using Cu K_α radiation at 40 kV and 100 mA between 2θ values of 20° and 80° with a step length of 0.02° at a scanning rate of 1(°)/min. Data were analyzed with MDI Jade 5.0 software.

The tribological properties of the coatings were performed on a WTM−2E ball-on-disk tribometer with a rotational speed of 336 r/min. Coatings were served as the disc, and the counterpart was Si_3N_4 ceramic ball (4 mm in diameter, HV 1550 in hardness). The abrasion loss was measured after 35 min friction measurement with an electronic direct reading balance (LJBROR L−200, readability 0.01 mg). The hardnesses of coatings were evaluated by using an HMV-IT microhardness tester with Vikers under a load of 0.2 kg.

Electrochemical tests were carried out using a CorrTest AC potentiostat/frequency response analyzer (electrochemical workstation, CS350) system to evaluate the corrosion behavior of PEO coated specimens and bare alloy. A typical three-electrode-system, which consisted of a saturated calomel electrode (SCE) as a reference electrode, a platinum mesh counter electrode and the PEO coated specimens as working electrode (1 cm^2 exposed area). The electrochemical tests were carried out in 0.59 mol/L NaCl aqueous solution with pH of 7 approximately. Potentiodynamic polarization test was carried out over a potential range from −1.2 V to −0.2 V for PEO coatings and bare alloy after 2 h of immersion in 0.59 mol/L NaCl. Electrochemical impedance spectroscopy (EIS) tests were conducted in the frequency range of 10^5 Hz to 10^{-1} Hz on PEO coatings exposed to the corrosive electrolyte for 2 h. A 10 mV peak-to-peak amplitude of AC potential signal was selected after achieving a relatively much stabilized open circuit potential. The CorShow and ZSimpWin were used to deal with the data of potentiodynamic polarization and EIS measurements, respectively. Under each testing condition, potentiodynamic polarization and EIS measurements were repeated 3 times at least in order to guarantee the reliability and reproducibility.