



Key factors determining the development of two morphologies of plasma electrolytic coatings on an Al–Cu–Li alloy in aluminate electrolytes



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ABSTRACT

The porosity within plasma electrolytic oxidation (PEO) coatings strongly affects their properties, such as the wear resistance. Two typical types of coatings, i.e. bi-layered coatings with large internal pores, which show low wear resistance, and single-layered coatings with excellent wear performance, have been found following PEO of aluminium alloys under pulsed current regimes with an aluminate electrolyte. In this paper, the mechanisms of formation of the different coatings are investigated and discussed based on a thorough investigation of PEO of an Al–Cu–Li alloy using systematic variations of 1000 Hz pulsed current waveforms and electrolyte concentration. Both parameters have important roles in determining the structure of the resultant coatings. The coatings formed in a dilute electrolyte, containing $5 \text{ g l}^{-1} \text{ NaAlO}_2$, were bi-layered and contained both large pores and pancake structures irrespective of the application of a negative pulse. In contrast, the application of negative current pulse favored the formation of single-layered coatings that contained fewer pancake structures in an electrolyte $32 \text{ g l}^{-1} \text{ NaAlO}_2$. A more concentrated electrolyte, containing $56 \text{ g l}^{-1} \text{ NaAlO}_2$, resulted in relatively compact, single-layered coatings independently of a negative current pulse. Similar observations for the coating morphologies were made if the alloy was replaced by high purity aluminium and also for the alloy when the frequency was reduced to 100 Hz. Two different models for the growth of single- and bi-layered coatings are proposed.

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1. Introduction

In recent years, surface treatment of so called valve metals (Al, Mg, Ti, Zr, etc.) and their alloys by plasma electrolytic oxidation (PEO) has been of interest of materials scientists due to the environmentally-friendly nature of the electrolytes, a minimal requirement for surface pre-treatment and formation of coatings with improved corrosion and wear resistance [1–3]. This technique has evolved from traditional anodization, but operates under much higher voltages to maintain dielectric breakdown of the resultant oxide coatings [4–6].

Owing to the high voltages attained during the PEO processes, plasma discharges appear on the sample surface (the anode). The discharges usually first appear as fine sparks, which then turn to micro arcs or strong arcs as the treatment time is prolonged [2,7]. However, another type of plasma discharge, often termed “soft sparking”, has also been observed during PEO of aluminium [8,9] and zirconium [10] alloys. The high temperature of the plasma discharges, possibly in the range 800–20,000 K [1], induces complex physical and chemical processes, such as thermal and plasma chemical reactions, that accompany the electrochemical processes [1,11]. As an example,

non-Faradaic processes, such as plasma-assisted deposition of electrolyte species [12] and anomalous gas evolution [6,13,14] have been reported.

Although the PEO of valve metals, especially for Al and its alloys, has been intensively explored and a wealth of phenomenological information on the coatings, including the composition, morphology and structure, exists in literature, the growth mechanism of the coatings still remains somewhat unclear [4,15,16]. The microstructure and quality of PEO coatings are affected by many parameters, such as the electrical regime, the type and concentration of the electrolyte, and the composition of the substrate metal. Among these parameters, the influence of the electrical regime has been studied in detail. DC current regimes, which were mainly used in early studies, provide little control of the PEO process in comparison with AC and pulsed electrical regimes that provide greater scope for modifying the discharge behavior through changing the waveforms [1,17]. For instance, Yerokhin et al. have reported that bipolar current pulses in the kHz range are able to increase the coating growth rate on AA 2024 aluminium alloy, and reduce the thickness of the porous outer layer, compared with an AC process at 50 Hz [18]. In addition, the presence of a negative pulse in the waveform is beneficial to the coating quality on coatings on aluminium alloys by promoting a more homogeneous coating with reduced porosity, as indicated by Hussein et al. [19] and Mecuson et al. [8].

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Porosity is a general feature of PEO coatings, which affects the coating properties, such as wear resistance. Curran and Clyne [15] showed that a coating on an aluminium alloy contained ~20% porosity, with most pores having sizes in the range from 5 nm to 1 μm . The porosity was attributed to oxygen entrapment in molten alumina formed at electrical discharges. However, pores in the size range tens to hundreds of microns have also been occasionally found in the coatings on aluminium [2,4,5,20] or zirconium alloys [10], which may connect together to forming a long gap in the middle of the coatings [5,10,20]. These large pores, thought previously to be caused by gas generation [4], are seriously detrimental to the wear resistance of the coatings under high loads [10,12].

The microstructure and morphology of coatings are dependent on the microdischarges during the PEO process. Hussein et al. [21] proposed three types of discharge: types A or C, which occur at the oxide/electrolyte interface and within pores and cracks in the outer coating, respectively, and a strong discharge, type B, which occurs near the coating base. Types A or C result in coating material that contains relatively large amounts of electrolyte-derived species, while type B incorporates a relatively greater amount of substrate species [21]. Type B discharges are believed to form the pancake structures that are often observed in coatings on aluminium and zirconium alloys [4,5,6,10,22]. Cheng et al. [4] proposed two further discharges to account for a bi-layered coating containing large pores: type D, which occurs at the pore bases, leading to growth of the inner layer, and type E, which penetrates the outer layer and leads to large pores below pancakes. Type E discharges resemble type B discharges but do not affect the inner layer significantly.

Pulsed unipolar and pulsed bipolar current regimes were used by Hussein et al. [19] to study discharges during PEO of aluminium by optical emission spectroscopy. Type B discharges, associated with high spikes in the plasma temperature, were significantly reduced under the bipolar regime. Further, Mecuson et al. [8] reported that “soft sparking” occurred when a higher negative charge was used under a pulsed bipolar regime. The “soft sparking”, which causes a change of optical emission and reductions in the microdischarge size and acoustic noise, normally occurs after a certain initial period of conventional PEO discharging behavior [8]. “Soft sparking”, which has been observed by many researchers [7,9,23,24], can improve the thickness and homogeneity of a coating [8]. The present authors also observed a transient form of “soft sparking” on zirconium alloys [6,10]. The sparking occurred in patches that moved across the electrode surface and filled large pores within the coating with material containing significant amounts of electrolyte species, hence improving the wear resistance of the coatings [10].

The electrolyte concentration also has a great influence on the morphology of the coatings. In a recent work [12], PEO of an Al–Cu–Li alloy was carried out in electrolytes containing 5, 32 and 56 g l^{-1} NaAlO_2 , using a pulsed bipolar constant current regime. Coatings formed in 5 g l^{-1} NaAlO_2 displayed a bi-layered structure, with large pores between the layers. In contrast, the coatings formed in 32 and 56 g l^{-1} NaAlO_2 were single-layered; the absence of large pores significantly improved the wear resistances. However, the underlying mechanism for the influence of the electrolyte concentration on the microstructure of the coatings was not explored.

The present paper examines the influence of current waveform (mostly using a frequency of 1000 Hz) and electrolyte concentration on the formation of bi-layered coatings, containing large internal pores, and of single-layered coatings, in which such pores are absent, during PEO of a commercial Al–Cu–Li aluminium alloy. The general relevance of the observations made for the Al–Cu–Li alloy treated at 1000 Hz has also been assessed by studies at a lower frequency of 100 Hz and also using a high purity aluminium substrate. Finally, the mechanisms of formation of such structures are proposed.

2. Experimental

A ~4 mm thick plate of 2A97Al–Cu–Li alloy (3.8% Cu, 1.5% Li, 0.3% Mn, 0.4% Mg, 0.5% Zn, 0.12% Zr, and 0.07% Ti, Al bal.: solution heat treated at 520 °C for 2 h, water quenched, then aged at 165 °C for 2 h, followed by cooling to ambient temperature) was cut into specimens with dimensions of 20 × 10 × 4 mm. Each specimen was connected to a copper wire and then masked in epoxy resin, leaving an exposed area of 2 cm^2 . The working area was ground to a 2000 grit SiC paper finish, degreased in ethanol, rinsed in distilled water and then dried in a stream of warm air. PEO was carried out in a 1 L glass vessel, equipped with magnetic-stirring and water-cooling. A stainless steel plate (60 mm × 80 mm) was used as cathode. The distance between the anode (specimens) and the cathode is ~5 cm. The power supplier was a 5 kW pulsed power source (MAO-5D, Pulsetech Electrical Co., Ltd., Chengdu, China).

The electrolytes used in this work are aqueous solutions containing 5, 32 and 56 g l^{-1} NaAlO_2 , each with the addition of 1 g l^{-1} KOH to adjust the pH. For preparation of the coatings in 32 and 56 g l^{-1} NaAlO_2 , either a pre-cursor coating or a short duration of higher current density was employed [12,25]. PEO was carried out under pulsed bipolar or unipolar constant current regimes to investigate the influence of negative pulse, using a frequency of 1000 Hz and a duty cycle of 20%. The negative and positive currents are provided by separate units of the power supply. An oscilloscope (Tektronix TDS 1002C-SC) was used to monitor the current waveforms during the PEO process. The average positive and negative current densities during PEO were obtained from integration of the waveforms recorded during the processes.

PEO of the Al–Cu–Li alloy has also been carried under 100 Hz to compare with the results obtained at 1000 Hz. Specimens were also prepared from a rolled plate, ~4.7 mm in thickness, of high purity aluminium (99.99 wt.%). The specimens were PEO-treated at 1000 Hz to investigate whether the coating microstructures generated were similar to those for the Al–Cu–Li alloy at the same frequency.

The thickness and surface or cross-sectional morphology of the coatings was determined by scanning electron microscopy (SEM, QUANTA FEG 250 or Nova NanoSEM 230, FEI, USA). In order to compare the oxide yields under different conditions of PEO, the coatings were chemically stripped from the substrates and weighed, and the ratios of the coating weights to the anodic charges passed during PEO were calculated. The coating stripping was carried out by immersing the specimen concentrated NaOH solution at room temperature, as described in [12]. The stripped coatings were washed in distilled water, dried at 100 °C for 3 h, and weighed to an accuracy of ± 0.1 mg. At least three specimens were used for the calculation of oxide yields.

3. Results

3.1. Coatings formed in 5 g l^{-1} NaAlO_2

Fig. 1 shows the current waveforms for the treatment of the Al–Cu–Li alloy under pulsed bipolar and unipolar regimes in 5 g l^{-1} NaAlO_2 and the associated coating morphologies in surface and cross-section views. The waveforms changed little during the whole PEO treatment time of 1200 s. The average positive and negative current densities for the pulsed bipolar regime are 0.22 and 0.13 A cm^{-2} , respectively, a ratio 1.69 [8]. The average positive current density for the unipolar regime is 0.23 A cm^{-2} , which is close to that of the bipolar regime. The cell potential-time responses for the coatings under pulsed bipolar regimes in the same electrolytes as those used in the present work have been described in our previous papers [12,25]. The application of the unipolar regime (single positive pulse) resulted in no obvious change to the positive cell potential-time response.

The coating surface after PEO of the alloy for 1200 s under the bipolar regime is dominated by pancake-like features (Fig. 1(c)), which are typical features of PEO coatings on aluminium and zirconium alloys, as

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