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 g l⁻¹ NaAlO₂, 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 g l⁻¹ NaAlO₂. A more concentrated electrolyte, containing 56 g l⁻¹ NaAlO₂, resulted in relatively compact, single-layered

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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.

Keywords: Plasma electrolytic oxidation, Aluminium, Current regime, Electrolyte concentration, Growth mechanisms.

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 800-20000 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 behaviour 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].

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 5 nm to 1 μ m. 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 has 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 occur at the pore bases, leading to growth of the inner layer, and type E, which penetrate the outer layer and lead 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 NaAlO₂, using a pulsed bipolar constant current regime. Coatings formed in 5 g l⁻¹ NaAlO₂ displayed a bi-layered structure, with large pores between the layers. In contrast, the coatings formed in 32 and 56 g l⁻¹ NaAlO₂ 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 have 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 ($60\text{ mm} \times 80\text{ mm}$) was used as cathode. The distance between the anode (specimens) and the cathode is $\sim 5\text{ cm}$. 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 NaAlO₂

Figure 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 NaAlO₂ 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 discussed in the Introduction. Some pancakes have an open pore at their centre. The cross-section reveals a bi-layered coating attached to the alloy substrate (Fig. 1(d)). Al-Cu-Fe-Mn constituent second phase particles are evident in the substrate as light features in the backscattered electron image, with sizes up to the order of 10 µm [25]. The alloy also contains fine strengthening precipitates that are developed during ageing, including T₁ (Al₂CuLi) and δ' (Al₃Li) phases, which are not resolved in the micrograph [26, 27]. No light regions are detected in the coating indicating that the constituent particles are oxidized and that the oxidized ions are dispersed in the coating due to the mixing and transport of molten coating material by the discharges. Similar observations were made for the behavior of constituent particles for coatings formed under the other conditions of

PEO employed in the present study and also in a previous study by other researchers on PEO of an AA 2219 aluminium alloy [28]. The previously mentioned large pores are clearly seen between the outer and inner layers of the coating. The inset shows a large pore at increased magnification, with a smaller open pore in the protruding outer layer. This coating has a poor wear resistance [12], possibly due to the presence of the large pores.

Figure 1(e) shows the surface of a coating formed after 1200 s in the absence of a negative pulse (the unipolar regime). The surface is also dominated by pancakes. However, open pores are not visible. Although a seemingly compact coating from the surface observation, there is a $\sim 15\text{ }\mu\text{m}$ wide gap between the outer and inner coating layers (see Fig. 1(f)), which is possibly formed by the connection together of large pores developed at an earlier stage of the PEO treatment. A similar gap has been found within coatings formed on a zirconium alloy in a dilute aluminate electrolyte, which seriously reduced the wear resistance [10]. Notably, the inner layer of the present coating is very thin, compared with the outer layer.

3.2 Coatings formed in $32\text{ g l}^{-1}\text{ NaAlO}_2$

The waveforms and coating morphologies resulting from PEO in $32\text{ g l}^{-1}\text{ NaAlO}_2$ under various current regimes are presented on the left-hand and right-hand sides of Fig. 2, respectively. The coating growth rate has been found to be significantly

increased with increase of the electrolyte concentration [12]. Hence, a shorter treatment time of 300 s has usually been employed for the coatings formed in this electrolyte. However, for the growth of a coating under very low positive and negative current densities of 0.066 and 0.048 A cm⁻², respectively, the time was increased to 900 s. The coating formed for 300 s at average positive and negative current densities of 0.22 and 0.13 A cm⁻², respectively, is single-layered (see the inset of Fig. 2(b)), the same as a coating formed for 480 s reported in previous work [12]. Its surface morphology shows irregularly-shaped solidification features with different sizes. Relatively few pancakes are present. Figure 2(d) shows the coating formed under a unipolar regime with the same positive current density of 0.22 A cm⁻². The coating morphologies, both in surface and cross-section views, are significantly changed by the omission of the negative pulse. The coating is thinner than the coating formed under the bipolar regime, i.e. ~ 18 μm, compared with ~25 μm. The porosity of coating is also increased, with some large pores being found in the cross-section. The coating surface is dominated by pancakes, similar to the coating formed in the dilute electrolyte. Figure 2(f) shows a coating formed under the unipolar regime with a higher positive current density of 0.42 A cm⁻². The thickness of the coating is increased to ~26 μm. However, the large pores are more evident in the coating cross-section. The coating surface is also dominated by pancakes, but with increased size. Figure 2(h) shows a coating formed for 900 s under a bipolar regime with very low positive and negative current densities, with a ratio of ~1.4. The coating is single-layered, with a thickness of ~ 25 μm. The surface features are finer than those

of the previous specimens and pancakes are seldom found. The above results show that the bipolar regime favors the formation of single-layered coatings in 32 g l^{-1} NaAlO_2 . The unipolar regime decreased the homogeneity of the coating by the development of large pores, which are more evident when the positive current density is increased.

3.3 Coatings formed in 56 g l^{-1} NaAlO_2

During the PEO of the Al-Cu-Li alloy in 56 g l^{-1} NaAlO_2 , copious amounts of fine gas bubbles are evolved from the electrode surface, similar to the gas evolution seen during PEO in the 32 g l^{-1} NaAlO_2 electrolyte. However, the intensity of discharges in the 56 g l^{-1} NaAlO_2 is weaker and patches of soft sparking, similar to that observed in [10], are occasionally observed for both the unipolar and bipolar regimes. A treatment of 240 s has been applied to the Al-Cu-Li alloy for the PEO treatment in the 56 g l^{-1} NaAlO_2 electrolyte under both unipolar or bipolar regimes. Visual observation shows that the coatings formed under the unipolar (positive pulse) regime have a coarser surface. Figure 3 shows the waveforms and surface and cross-sectional morphology for a coating formed for 240 s under a unipolar regime with a positive current density of 0.25 A cm^{-2} . The coating surface is dominated by irregularly-shaped nodules and pancakes are absent. The inset in Fig. 3(c) shows dendrites in the nodules formed by solidification of molten coating material. Figure 3(d) shows that the coating is single-layered. The features of this coating are nearly the same as a coating formed for 240 s under a bipolar regime with average positive and negative current densities of

0.22 and 0.13 A cm⁻² [12]. The results show that the negative pulse had no obvious effect on the coating morphology, which is in contrast to the coatings formed in 5 and 32 g l⁻¹ NaAlO₂.

3.4 *Oxide yields under different conditions of PEO*

The oxide yields under the various conditions of PEO are presented in Table 1. The oxide yield for the coating formed under positive and negative current densities of 0.22 and 0.13 A cm⁻², respectively, in 5 g l⁻¹ NaAlO₂ is 34.5 µg C⁻¹. A coating formed in the same electrolyte with a positive current density only of 0.23 A cm⁻² formed with a lower yield of ~17.8 µg C⁻¹. When the concentration of the electrolyte was increased to 32 g l⁻¹, the yields for the coatings formed under different current regimes were raised to the range of ~64.2 – 138.0 µg C⁻¹, with the highest value for a coating formed under very low positive and negative current densities of 0.066 and 0.048 A cm⁻², respectively. It is also evident that the absence of a negative pulse in the waveforms resulted in reduced oxide yields, which decreased from ~121.2 to 75.8 µg C⁻¹. Simultaneously, an increase of the positive pulse for the unipolar regime seems to further reduce the yield, although this effect is not pronounced. The oxide yields for the coatings formed for 240 s in 56 g l⁻¹ NaAlO₂ under a bipolar regime [12] and the present unipolar regimes are quite high, namely ~217.8 and ~245. µg C⁻¹, respectively. This phenomenon differs from the behaviors in electrolytes of 5 and 32 g l⁻¹ NaAlO₂ and also contradicts the view in the literature that the negative pulse in a high

frequency bipolar regime allows three to five times enhancement of the coating growth rate [29].

3.5 General relevance of the previous findings

In order to determine if the above observations are of more general relevance, PEO of the Al-Cu-Li alloy has been undertaken at a lower frequency of 100 Hz. The coatings obtained at the different conditions have been examined by SEM. Figure 4 (a) shows the current density waveforms recorded during the PEO treatment of the Al-Cu-Li alloy in the dilute aluminate electrolyte ($5 \text{ g l}^{-1} \text{ NaAlO}_2$) for 1200 s under constant average positive and negative current densities of 0.22 and 0.13 A cm^{-2} , respectively, with a frequency of 100 Hz. The waveforms are nearly the same as those observed at 1000 Hz (Fig. 1 (a)), showing little change during the PEO process. Figure 4(b) presents a cross-section of the coating after being a treatment of 1200 s. As found under the same current densities at 1000 Hz, the coating has a bi-layered structure, indicating that the frequency of the current waveform did not significantly change the coating structure in the dilute aluminate electrolyte.

The morphologies of the coatings formed in more concentrated electrolyte, $32 \text{ g l}^{-1} \text{ NaAlO}_2$, under bipolar (0.22 and -0.13 A cm^{-2}) and unipolar (0.22 A cm^{-2}) regimes at the frequency of 100 Hz, are presented in Fig. 5. The omission of the negative pulse leads to a thinner coating and the presence of large pores at the base of coating, as

shown by Fig. 5 (b). A comparison of the surface morphologies clearly indicates that more pancakes are found with the unipolar regime, as also observed at a frequency of 1000 Hz.

Additionally, a high purity aluminium substrate has been PEO-treated in 5 and 32 g l⁻¹ NaAlO₂, using the earlier frequency of 1000 Hz, to determine whether the alloy elements have a significant influence on the coating microstructure. Figure 6(a) shows the cross-section of the coating formed for 1200 s in 5 g l⁻¹ NaAlO₂, using average positive and negative current densities of 0.22 and -0.13 A cm⁻², respectively. The structure of the coating is similar to that of the coating formed under same conditions on Al-Cu-Li alloy (Fig.1 (d)), displaying two layers and large internal pores. The coatings formed in 32 g l⁻¹ NaAlO₂ under bipolar and unipolar regimes are presented in Fig. 6 (b) and (c), respectively. A homogenous, single-layered structure is found with the coating formed under the bipolar regime, while the omission of negative pulse leads to a thinner coating with long lateral pores at the coating base. Evidently, the alloying elements have little influence on the main features of the coating microstructures.

4. Discussion

4.1 Mechanism of formation of large pores

For the PEO of the Al-Cu-Li alloy under a frequency of 1000 Hz, large pores are

normally found in coatings formed in 5 and 32 g l⁻¹ NaAlO₂ under the bipolar and unipolar regimes respectively. The development and connection of such pores led to the formation of bi-layered coatings in the dilute electrolyte, whereas the pores were separated in coatings formed with 32 g l⁻¹ NaAlO₂. Similar observations are found following PEO of the Al-Cu-Li alloy under a lower frequency of 100 Hz and also for PEO of high purity aluminium at 1000 Hz. The generation of large pores within coatings is not unique to the PEO of the present Al-Cu-Li alloy in aluminate electrolytes, since similar pores have been found by other researchers following PEO of other types of Al alloys, such as 6061 [5,20] and 2214 [2] aluminium alloys in silicate electrolytes. The finding of similar pores in coatings on high purity aluminium suggests that the mechanism of pore generation is not dependent on the presence of alloying elements. Furthermore, our recent work shows that the large pores and a bi-layer structure exist in the PEO coating of a zirconium alloy [10]. In fact, such structures have also been found for the PEO of the present alloy in a dilute silicate electrolyte [4]. As mentioned previously, we have suggested that inner layer material is formed by type D discharges at the base of large pores, while type B or E discharges form pancakes at the coating surface.

The microstructure of the coatings is possibly affected by the transport mechanisms of species during the PEO process, which may be affected by the electrolyte concentration and pulse polarity. Under the strong electric fields during PEO, the ingress of electrolyte species (e.g. anions) and ejection of cations through the

discharge channels are possible. Unlike conventional thermal and anodic oxides, PEO-formed oxides grow discontinuously [9], with cycles of coating formation, dielectric breakdown with generation of discharge channels, and material deposition in the channels after the discharges terminate [30,31]. This model emphasizes the discharging behavior as the decisive role in coating formation. However, transport in the oxide bulk, such as occurs in anodizing or thermal oxidation, may also contribute to the coating growth. Of possible relevance, discharges often occupy only a small fraction of the coating surface in the later stages of PEO, although the coating continues to thicken.

The schematic diagram of Fig.7 shows the proposed mechanism of formation of large pores and a bi-layer structure in the present coatings. First, a barrier oxide film grows on the metal surface by conventional anodizing, with outward migration of Al^{3+} ions and inward migration of O^{2-} ions through the oxide [25]. Flaws are known to exist in anodic films on aluminium and electrical breakdown has been shown to be initiated at the locations of the flaws [32-35]. Figure 7(a) shows voids generated in the film, which are associated with the flaws and may contain oxygen gas. The generation of gas bubbles within amorphous alumina is commonly observed during anodizing of copper-containing aluminium alloys [36,37]. The gas bubbles expand as the film grows due to the plasticity of the alumina, with the gas eventually being released when the film ruptures. The barrier film thickens until dielectric breakdown occurs (Fig. 7(b)). A “B” type discharge occurs at the location of a void due to an enhanced

electric field at this site. When the discharge ends, electrolyte enters the open discharge channel or adjacent cracks caused by thermal stress during the cooling of the coating (Fig. 7(c)). Electrolyte components may also be drawn into the channel and the associated pore, either during or after the discharge event, by the strong electrical field ($\sim 10^6 \text{ V m}^{-1}$) [31]. However, the high temperature and high pressure ($\sim 10^2 \text{ MPa}$) in the discharge channel during the discharge event [1] will prevent the ingress of liquid electrolyte. Figure 7(d) shows a discharge that re-occurs in the same location, for instance due to the creation of a “damaged” microstructure that provides low-resistance pathways by the previous discharge [38]. The trapped electrolyte will be decomposed under the high temperature and pressure within the discharge channel and pore, generating gas within the pore. The gas evolution from PEO of a zirconium alloy has been shown to be as high as 16 times that of the expected Faradaic yield [6]. Most of the gas will be ejected into electrolyte through the discharge channel. However, an expansion of the pore may result from the gas pressure by plastic deformation of the heated oxide. Additionally, thermal decomposition of $\text{Al}(\text{OH})_4^-$ ions [12] results in deposition of Al_2O_3 on the pore wall (Fig. 7 (d)), the deposited amount depending on the electrolyte composition. After termination of the discharge, the temperature and pressure of the gas trapped in the large pore will be reduced. Liquid electrolyte is then able to enter the cavity. New discharges will initiate either at the same location or at other sites, leading to growth of the coating and formation of the coating structure shown in Fig. 7(e). The strong “B” type discharges may later be replaced by “E” type discharges, which were first proposed in [4] to account for the

formation of pancakes above large pores. In support of the model, it is evident that pancakes are dominant features of the coatings with large pores (see Fig. 1, 2(d) and 2(f)). The occurrence of type “D” discharges at the base of open or sealed pores is also possible, which may be assisted by the access of electrolyte following earlier discharges. It is evident from the proposed mechanism that the generation of large pores is associated with the occurrence and termination of the strong types of discharges, which may explain why the changing of frequencies from 1000 Hz to a lower 100 Hz does not affect the occurrence of pores in the PEO coatings. According to Dunleavy et al., the individual discharge events are believed to last ~ tens to hundreds μs [39]. The pulse-on time at the frequency of 1000 Hz is 200 μs , which is greater than or similar to the duration of the individual discharge events. Hence, the duration of individual discharge events may not be affected to a large extent by the change in the pulse-on time between 100 and 1000 Hz.

4.2 Effect of electrical parameters and electrolyte concentration on coating formation

The present study shows that the electrical parameters (bipolar or unipolar) and electrolyte concentration have great influences on the coating microstructure. A unipolar regime with only positive current resulted in a gap in the coatings formed in 5 g l⁻¹ NaAlO₂ and large pores in those formed in 32 g l⁻¹ NaAlO₂. An increased positive current density produced larger pancakes and greater porosity with the latter electrolyte. The generation of the gap and the larger pores in the coating may indicate

more violent gas evolution within the internal of coating in these electrolytes in the absence of a negative pulse. Anions of the electrolyte components, such as OH^- , are drawn into the internal pores during the positive pulse and oxygen may be generated within the pores according to the equation: $4 \text{OH}^- \rightarrow \text{O}_2 \uparrow + 2\text{H}_2\text{O} + 4\text{e}^-$. An additional negative pulse may suppress the ingress of the anions, leading to less gas generation. However, the underlying reasons for the effect of negative pulse in these electrolytes requires further investigations.

The role of negative bias for the AC or pulsed bipolar regime PEO process is very complex and investigations are still on-going by various researchers. According to Yerokin et al. [17], the negative pulse may interrupt discharges, preventing the development of long lasting, large discharges, and liberate hydrogen, which provides a gas blanket that favours the establishment of a gas phase discharges during subsequent positive biasing. Discharges may also occur in the coating during the negative biasing. Recent work of Nomine et al. [40] on PEO of a magnesium alloy showed that although microdischarges may appear during the cathodic half-period, the oxide grows only during the anodic half-period. The use of a negative pulse slightly increased the present oxide yield in $5 \text{ g l}^{-1} \text{ NaAlO}_2$ and more significantly in $32 \text{ g l}^{-1} \text{ NaAlO}_2$. Surprisingly, a higher oxide yield was obtained in $56 \text{ g l}^{-1} \text{ NaAlO}_2$ with only the single positive pulse, which suggests that coating growth during negative cycles is unimportant.

The influence of the negative pulse on the coating microstructure formed in 32 g l^{-1} NaAlO_2 may be related to a modification of the discharge types during the PEO process. The single-layered coatings formed in this electrolyte under bipolar regimes show a significantly reduced numbers of pancake structures, which indicates that the strong discharges (types “E” and “B”) were greatly reduced, which is consistent with the findings of Hussein et al. [19]. The dominant discharges for the coating growth are possibly the “A” or “C” discharges, which occur on the coating surface or within the upper coating. Hussein et al. [19] reported that the plasma temperature of the B type discharges of a unipolar regime is higher than that under a bipolar regime. Hence, the single-layered coatings formed in 32 g l^{-1} NaAlO_2 may have experienced lower temperatures during PEO compared with the coatings featuring pancakes. The coatings formed on Al-Cu-Li alloy in 32 g l^{-1} NaAlO_2 under unipolar regimes appear of brownish red hue, the same as the coatings formed in 5 g l^{-1} under unipolar or bipolar regimes, while all the single-layered coatings formed in 32 g l^{-1} NaAlO_2 using bipolar regimes are blackish. A brownish red color of coatings formed on the same alloy in a dilute silicate electrolyte has been attributed to the formation of Cu_2O in the alloy [4]. A blackish color may indicate the presence of CuO , which is usually black. CuO is stable in air below 1050°C but transforms to Cu_2O at higher temperatures temperature [41]. The presence of CuO in single-layered coatings confirms the dominance of “A” or “C” discharges with the application of a negative pulse, which results in a lower temperature of the coating. The coatings formed in the 56 g l^{-1} NaAlO_2 appear white, which indicate that the oxides at the surface contain less of the

alloying element.

The present findings show that increase of the electrolyte concentration greatly increased oxide yield of the anodic charge. This has been explained by an additional contribution to coating growth from plasma and thermally-assisted decomposition of the electrolyte [12]. It should be noted that the influence of electrolyte concentration is more decisive than the negative current pulse in determining the coating structure. Large pores were not eliminated by negative pulses in the dilute electrolytes, while in the highly concentrated electrolyte, such pulses had little effect on the oxide yields, morphology and microstructure. The absence of the pancakes in the coating formed in $56 \text{ g l}^{-1} \text{ NaAlO}_2$ under a unipolar positive current regime indicates that the coating formation is dominated by “A” or “C” type discharges. Hence, the electrolyte concentration plays an important role in determining the discharge types.

A schematic diagram is presented in Fig. 8 for the formation of single-layered coatings in a moderately or highly concentrated electrolyte. The main aluminium-bearing species in the electrolyte are $\text{Al}(\text{OH})_4^-$ ions [12,25]. Unlike the strong discharge types that occur during PEO in the dilute electrolyte or the moderately concentrated electrolyte in the absence of negative pulse, type “A” or “C” discharges are dominant, which decompose $\text{Al}(\text{OH})_4^-$ ions into Al_2O_3 , as suggested in [12]. For all the present coatings, the coating material (mostly alumina) originates from the oxidation of the alloy and the decomposition of electrolyte species. With

dilute electrolytes, relatively few $\text{Al}(\text{OH})_4^-$ ions are available to support the decomposition process, hence the coatings are mostly formed by oxidation of the alloy, leading to the low **oxide yield** in 5 g l^{-1} NaAlO_2 (Table 1). The increase of the electrolyte concentration significantly increased the **oxide yield**, even for coatings obtained without the assistance of a negative pulse, when type “B” or “E” discharges are dominant. However, type “A” or “C” discharges result in even higher **oxide yields** and a single-layered coating microstructure. The reason for the absence of large pores when the type “A” or “C” discharges occur may lie in the fact that fast deposition of alumina from electrolyte species becomes the main coating formation mechanism.

In our previous paper, it was proposed that the semiconducting nature of the PEO coatings formed on titanium or magnesium alloys favours the dominance of “A” or “C” discharges during PEO treatment of such alloys. The authors have conducted PEO of Ti-6Al-4V titanium alloy and AZ31 magnesium alloy using pulsed regimes similarly to the present study [42,43]. In accordance with the hypothesis here, the coatings on these alloys were single-layered and pancakes were absent from the coating surfaces. Extremely high growth rates, leading to the formation of $\sim 15\text{-}37 \text{ }\mu\text{m}$ -thick coatings after the first 60 s, have also been found for the PEO treatment of an AZ31 magnesium alloy in a silicate-hexametaphosphate electrolyte [43].

4.3 The occurrence of “soft sparking” and its effect on the coating microstructure

It is necessary to consider the relation of the present findings to the “soft sparking” regime that is mentioned in literature, since the regime can also drastically change the coating microstructure. In the work reported by Mecuson et al. in 2005 [2], AA 2214 aluminium alloy was PEO-treated in silicate electrolyte. Following an initial period of linear kinetics, the coating showed an enhanced growth rate when “soft sparking” commenced; the application of a sufficient negative current in the waveform has been considered to be necessary for the transition in the sparking regime to occur [8]. Before the occurrence of “soft sparking”, the coating displays a bi-layered structure, with large internal pores between the two layers [2], similar to the bi-layered coatings observed in the present study. However, the coating is transformed into a single-layered structure under the “soft sparking” regime [2]. The present authors’ previous findings with the PEO of a zirconium alloy also showed that a transient “soft sparking” regime can fill the large internal pores with materials that contain significant quantities of electrolyte-derived species [10]. From the “soft sparking” behaviors described in [8,10,44], it is suggested here that the “soft sparking” may merely indicate a transition of the discharge mode into a regime dominated by the type “A” and “C” discharges. In fact, weak discharges and transient “soft sparking” have been found for the PEO of the alloy in $56 \text{ g l}^{-1} \text{ NaAlO}_2$ under unipolar or bipolar current regimes, though no obvious voltage drop, which normally accompanies the “soft sparking” regime [7,9,10,23,24,44], has been found during the PEO process. The morphology of the coatings formed in $56 \text{ g l}^{-1} \text{ NaAlO}_2$ is consistent with the hypothesis that these coatings are formed by type “A” and “C” discharges. It is also

noticed that the coatings formed in this study under the dominance of type “A” and “C” discharges reveal high growth rates, as observed during “soft sparking”. The observations of the discharge behavior during the PEO of the Al-Cu-Li alloy in 32 g l⁻¹ NaAlO₂ under the low positive and negative current densities of 0.066 and 0.048 A cm⁻², respectively, show that for most of the time the discharges were characterized by very tiny sparks, which is similar to the discharge behavior in a “soft sparking” regime [44]. The surface morphology of the coating (Fig.2 h) supports the formation of the coating primarily under the influence of “A” and “C” discharges.

In order to make a further exploration of the “soft sparking” phenomenon, PEO was carried out for longer times in a 32 g l⁻¹ NaAlO₂ under unipolar regime with an average positive current density of 0.22 A cm⁻² (the same as the waveforms in Fig.2 (c)). The results showed that “soft sparking” did appear after a relatively long time, usually after 1200 s, and lasted for ~ 60 s. The sparking was accompanied by a potential drop and is similar to that described for a zirconium alloy [10]. Figure 9 shows cross-sections of a coating formed for 1020 s, i.e. before the occurrence of “soft sparking”, and a coating formed for 1320 s, which includes a final period of 57 s with “soft sparking”. It is evident that the large pores have been filled with coating material, as observed also in [10]. Most unusually, the “soft sparking” occurred without a negative pulse. For the dilute electrolyte of 5 g l⁻¹ NaAlO₂, “soft sparking” has not been found with the PEO of the alloy for 3000 s under a bipolar regime with the average current densities of 0.22 and 0.13 A cm⁻², respectively. It is still unclear

precisely why “soft sparking” occurs in some PEO processes. However, it seems that this phenomenon may be affected by a range of factors, including the electrical regime, the electrolyte concentration and the coating microstructure. Further investigations are needed to have a better understanding of the phenomenon.

5. Conclusions

PEO of an Al-Cu-Li alloy has been carried out in 5, 32 and 56 g l⁻¹ NaAlO₂ under different electrical regimes at a constant frequency of 1000 Hz to investigate the influence of electrolyte concentration and electrical regimes on the coating formation mechanisms. The coatings revealed two typical morphologies, i.e., bi-layered coatings with large pores and single-layered coatings.

All the coatings formed in dilute electrolyte containing 5 g l⁻¹ NaAlO₂ are of a bi-layered nature, with large pores between the two layers. The coatings formed in 32 g l⁻¹ NaAlO₂ are single-layered under the bipolar regime. However, large pores appear in the coating cross-sections when unipolar regimes are employed. The coatings formed in 56 g l⁻¹ NaAlO₂ are always single-layered, irrespective of the electrical regimes. The above observations were also made for the Al-Cu-Li alloy treated at 100 Hz and for high purity aluminum treated at 1000 Hz, indicating that the findings for the alloy at 1000 Hz are of more general relevance, being relatively unaffected by the frequency or the presence of alloying elements.

The large pores in the cross-sections of the coatings are suggested to be caused by gas evolution during the strong types of “B” or “E” discharges. This hypothesis is supported by the observation that the surfaces of all coatings with large internal pores are dominated by pancake structures, which were formed by such discharges.

The single-layered coatings exhibit few or no pancake structures; it is suggested that type “A” or “C” discharges dominates the coating formation process. The type “A” or “C” discharges cause the decomposition of large amounts of electrolyte species, leading to significantly enhanced rate of coating formation.

The present study shows that the electrolyte concentration is a decisive factor in triggering the type “A” or “C” discharges. The application of a negative pulse also favors the “A” or “C” discharges in a less concentrated electrolyte containing 32 g l^{-1} NaAlO_2 .

The establishment of a transient “soft sparking” regime has been found on the Al-Cu-Li alloy, without the assistance of a negative pulse, in an electrolyte containing 32 g l^{-1} NaAlO_2 . It is proposed that the “soft sparking” is a discharging regime dominated by the type “A” and “C” discharges.

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Figure captions:

Figure 1. The waveforms (a, b) and surface (c, e) and cross-sectional (d, f) morphologies of coatings formed on the Al-Cu-Li alloy for 1200 s in 5 g l⁻¹ NaAlO₂ under different electrical regimes under bipolar and unipolar regimes.

Figure 2. The waveforms (a, c, e, g) and surface and cross-sectional morphologies (b, d, f, h) of coatings formed on the Al-Cu-Li alloy in 32 g l⁻¹ NaAlO₂ under different electrical regimes. Coatings in (b), (d) and (f) were formed for 300 s. The coating in (h) was formed for 1200 s.

Figure 3. The waveforms and surface and cross-sectional morphologies for a coating formed on the Al-Cu-Li alloy for 240 s in 56 g l⁻¹ NaAlO₂ under a unipolar regime with an average positive current of 0.25 A cm⁻². The inset in (c) is an enlargement of the nodules observed at lower magnification.

Figure 4. The waveforms and cross-sectional morphology for a coating formed on Al-Cu-Li alloy for 1200 s in 5 g l⁻¹ NaAlO₂ under average positive and negative current densities of 0.22 and 0.13 A cm⁻², respectively, with a frequency of 100 Hz.

Figure 5 Cross-sectional and surface morphologies for coatings formed on Al-Cu-Li alloy for 300 s in 32 g l⁻¹ NaAlO₂ under bipolar or unipolar regimes with the

frequency of 100 Hz.

Figure 6. Coatings formed on high purity aluminium in different electrolytes under different electrical regimes with a frequency of 1000 Hz. (a) A coating formed for 1200 s in 5 g l⁻¹ NaAlO₂ under a bipolar regime; (b) and (c) coatings formed in 32 g l⁻¹ NaAlO₂ for 300 s under bipolar and unipolar regimes, respectively. The insets are surface morphologies.

Figure 7. Schematic illustration of the formation of large pores in the PEO coatings. P₀ is the atmospheric pressure.

Figure 8. Schematic illustration of the formation of single-layered coatings.

Figure 9. Scanning electron micrographs of cross-sections of coatings formed on the Al-Cu-Li alloy in 32 g l⁻¹ NaAlO₂ under a unipolar regime with an average positive current density of 0.22 A cm⁻²: (a) a coating formed for 1020 s before the occurrence of “soft sparking”; (b) a coating formed for 1320 s, including a final “soft sparking” duration of 57 s.

Table caption:

Forming parameters and oxide yields (η) for the investigated conditions of PEO.

Table 1. Forming parameters and oxide yields (η) for the investigated conditions of PEO.

Electrolyte concentration (g l ⁻¹)	treatment time (s)	Average current densities (A cm ⁻²)		Weight of stripped coating (mg cm ⁻²)	η ($\mu\text{g C}^{-1}$)
		Positive	Negative		
5	1200	0.22	0.13	9.1 $\pm$ 1. 7	34.5 $\pm$ 6.4
5	1200	0.23	-	4.9 $\pm$ 0. 1	17.8 $\pm$ 0.4
32	300	0.22	0.13	8.0 $\pm$ 0. 6	121.2 $\pm$ 9.1
32	300	0.22	-	5.0 $\pm$ 0. 4	75.8 $\pm$ 6.1
32	300	0.42	-	8.1 $\pm$ 0. 9	64.2 $\pm$ 7.1
32	900	0.066	0.048	8.2 $\pm$ 0. 7	138.0 $\pm$ 11.7
56	240	0.22	0.13	11.5 $\pm$ 1. 0	217.8 $\pm$ 18.9
56	240	0.25	-	14.7 $\pm$ 4. 0	245.0 $\pm$ 66.7

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Graphical abstract

Coating with large pores

Single layered Coating

- Al(OH)_4^-
- Type A or C discharges
- Al_2O_3 derived from Al(OH)_4^-
- Al_2O_3 derived from the oxidation of substrate metal