



Influence of electrolyte ageing on the Plasma Electrolytic Oxidation of aluminium



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ABSTRACT

The chemical stability of the electrolyte in Plasma Electrolytic Oxidation (PEO) has been the subject of much systematic investigation. The present study reports on experimental results on the ageing of a usual PEO electrolyte and its effect on the oxidation of the Al2214 aluminium alloy. A solution of potassium hydroxide ($[\text{KOH}] = 1 \text{ g L}^{-1}$) and sodium silicate ($[\text{Na}_2\text{SiO}_3] = 1.65 \text{ g L}^{-1}$) diluted in deionised water was either aged by running a process during 8 h at most or not. Comparison between materials treated in either solution was made next. Cross-checked experimental results from analytical chemistry, plasma diagnostics and materials science clearly evidence the effect of ageing of the electrolyte on the PEO process behaviour. The transition from arc to "soft" regime occurs earlier (from 18 min to 13 min processing time) as the electrolyte gets older. The concomitant decrease in the electrolyte electrical conductivity (from 7.5 mS cm^{-1} to 6.8 mS cm^{-1}) is correlated with changes in the ionic species content in the electrolyte. Fast video-imaging (125 kfr/s) reveals that the micro-discharge characteristics are also sensitive since they become less numerous per area and unit time (from $220 \times 10^3 \text{ cm}^{-2} \text{ s}^{-1}$ to $120 \times 10^3 \text{ cm}^{-2} \text{ s}^{-1}$), exhibit shorter lifetime and have smaller sizes as the electrolyte ages. SEM observations of the as-grown coatings combined with roughness measures indicate a decrease in coating thickness (~20%) and roughness (~30%) while species from the electrolyte accumulate in the outer porous layer simultaneously with a gradual enrichment in $\alpha\text{-Al}_2\text{O}_3$ phase in the inner compact layer (from 36% to 43%). Finally, within the PEO conditions that were used, it is shown that the ageing phenomenon of the PEO electrolyte starts to influence the process after 2 h aged.

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1. Introduction

Plasma Electrolytic Oxidation (PEO) is a surface engineering process suitable for light weight metals (Al, Mg, Ti) and their alloys to form protective ceramic coatings [1]. Based on an electrochemical conversion of the metal surface, the rapid growth of the oxide layer takes place at potentials above the dielectric breakdown voltage of the insulating layer, leading thus to the development of numerous short-lived micro-discharges over the processed surface [2–4]. The resulting PEO coating exhibits improved surface performances in terms of adhesion, hardness, wear protection and corrosion resistance. As it uses diluted alkaline electrolytes, the PEO process complies with the present environmental and health regulations. Therefore it gains a growing interest in various industrial domains (transport, energy, medicine) to replace conventional chromic or sulphuric acid anodizing processes.

Researches devoted to improve the efficiency of the PEO process are abundant in the literature and one particular way consists in adjusting

the right chemical composition of the electrolyte [1]. Electrical conductivity and basicity of the PEO electrolytes are commonly adjusted by addition of alkaline reagents as potassium hydroxide (KOH) or sodium hydroxide (NaOH) which provide both enhanced growth rate and improved tribological behaviour of the oxide-like ceramic coatings (Al_2O_3 , MgO, and TiO_2) [5]. Furthermore, additives such as silicate (Na_2SiO_3) and aluminate (NaAlO_2) are widely used in order to reinforce the corrosion resistance and thermal barrier properties of Al and Mg oxides and their compounds [6–9]. The formation of stable products such as Mg_2SO_4 , MgAlO_4 , and $3(\text{AlO}_3) \cdot 2(\text{SiO}_2)$ that act as barrier layers prevents corrosion of alloys in the most corrosive environments. In recent years, thorough investigations have demonstrated the positive influence of new electrolyte additives (phosphate, fluoride, and borate) on the performance of PEO films formed on magnesium and aluminium alloys [10–14]. Some authors have proposed to incorporate suspended nano-particles (Al_2O_3 , ZrO_2 , TiO_2 , and TiC) in the electrolyte to reduce the porosity of the PEO oxide layer and to improve the wear resistance of the formed coatings [15–18].

Few works deal with the chemical stability of the PEO electrolytes with the effective ageing time over successive treatments. Ageing phenomena, which could affect the final layer characteristics, are usually neglected. From an industrial point of view, the issue of the chemical

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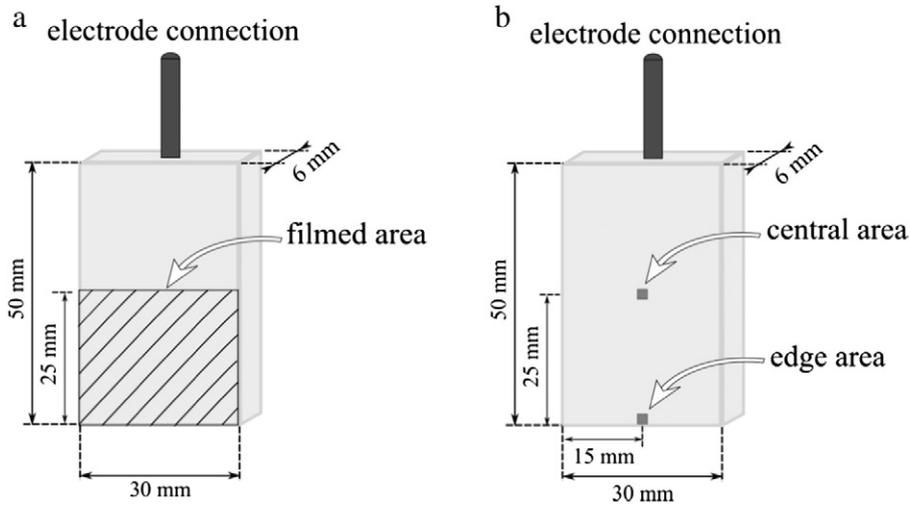


Fig. 1. Schematic representation of the processed sample showing (a) the area filmed by fast video imaging and (b) the localisation of the investigated central and edge area (2 mm × 2 mm).

stability of the electrolyte is of crucial importance in order to guarantee the highest reproducibility of the sought-after properties with the minimum process intervention. Regarding conventional anodizing processes such as chromic acid anodizing (CAA) or sulfuric acid anodizing (SAA), ageing of the treatment baths (cleaning, sealing, painting) is controlled empirically by manufacturers who limit the drifts in chemical composition by continuously renewing and tuning the content of chemical reagents. In a recent paper Terleeve et al. [19] evidenced the variations in the elemental composition of a silicate–alkaline electrolyte characteristics with ageing time (mainly a decrease in concentration of OH⁻ and Si⁴⁺ and increase in Al³⁺), expressed in terms of accumulated charge quantity flowing through the investigated electrolyte. Their findings revealed that such variations in the electrolyte have a substantial influence on the PEO coating characteristics such as a decrease in the coating thickness and a substantial increase in the degree of aggregation of electrolyte components (Si, Na, and K) at the top most surface of the oxide layer.

However, researches on the ageing of the PEO electrolyte are scarce. In this context, the aims of the present study are mainly to confirm such previous results and to correlate variations of both the electrolyte state and the PEO layer characteristics with the micro-discharge behaviour as the electrolyte gets aged. For this purpose, an experimental investigation of the electrolyte ageing during the PEO treatment of an aluminium

alloy is reported. The selected electrolyte consists in a standard PEO electrolyte containing sodium silicate Na₂SiO₃ and potassium hydroxide KOH diluted in deionised water. The ageing process in the electrolyte has been evidenced by taking into account several criteria based on the process monitoring data (voltage– and current–time responses), the electrolyte chemistry (conductivity and ionic species content), the micro-discharges behaviour (density, spatial distribution, size and lifetime) and the material characterisation (layer morphology, roughness, thickness, element composition and alumina phase content). Finally, we shall discuss on correlation between the formation process of the oxide ceramic layer and the characteristics of the micro-discharges appearing at the surface of the processed sample in relation with the ageing process in the PEO electrolyte.

2. Experimental procedure

The experimental set-up consists basically of a 25 L electrolysis tank filled with the electrolyte. Rectangular samples of dimensions 50 mm × 30 mm × 6 mm (see Fig. 1) made of commercial 2214 grade aluminium alloy were used as substrate in this study (content in weight %, 3.9–5 Cu, 0.5–1.2 Mg, 0.4–1.2 Mn, 0.5–1.2 Si, 0.5 Fe, 0.5 Ti, 0.25 Zn, Al as balance). Prior to process, all the samples were ground down to 1200 SiC paper, ultrasonically degreased in acetone, dried in warm air, and then immersed in the electrolyte tank. The sample (anode) is located between two titanium counter-electrode plates (cathodes), of size 200 mm × 200 mm × 1 mm. The gap between each counter-electrode and the sample is set at 55 mm. Therefore, the active electrode area to electrolyte volume ratio is about 1.6 × 10⁻³ cm⁻¹. A cooling device allows the electrolyte temperature to be kept in the range of [15–25 °C]. All the PEO treatments carried out in this study were conducted using a bipolar pulsed current generator working at 100 Hz within the so-called “soft-regime” corresponding to electrical conditions that are reported in detail in Ref. [3]. Within such a regime, the anodic (Q_p) to

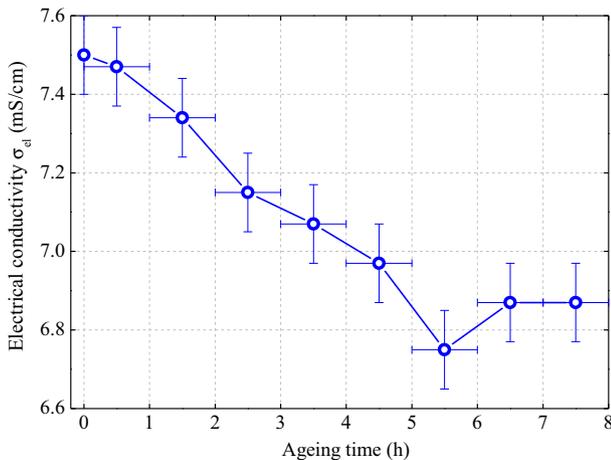


Fig. 2. Variation of the electrical conductivity σ_{el} as a function of the ageing time of the electrolyte.

Table 1

Sodium, potassium, silicon and aluminium ionic species content into a 1 g L⁻¹ KOH–1.65 g L⁻¹ Na₂SiO₃ PEO electrolyte after 1, 3 and 8 h effective processing duration.

Ageing time h	Na g L ⁻¹	K g L ⁻¹	Si g L ⁻¹	Al g L ⁻¹
1	0.120	0.549	0.385	0.007
3	0.120	0.539	0.367	0.015
8	0.116	0.505	0.317	0.047

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