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Excessive oxygen evolution during plasma electrolytic oxidation of aluminium

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Abstract

The present study provides a detailed discussion of mechanisms underlying anomalous gas evolution and changes in electrolyte pH during Plasma Electrolytic Oxidation (PEO) of Al in alkaline solutions. This is important for process optimisation and control in deposition of wear and corrosion resistant PEO coatings, which currently attract significant interest. The oxidation was performed under galvanostatic conditions in the range of current densities from 400 to 1500 A m^{-2}, with concentration of aqueous alkaline electrolyte varied from 0.5 to 2 g l^{-1} KOH. Electrolyte pH was evaluated before and after each PEO treatment. The volume of anodic gas evolved during the process was also measured, with the composition of the gaseous products being subsequently analysed using a quadrupole mass spectrometer. It was proposed that, within the studied ranges of experimental parameters, the evolution excessive oxygen is primarily caused by peroxide decomposition due to the interaction with both hydroxyl ions and radicals at the discharge–electrolyte interface. The interaction with the ions also results in electrolyte acidification, although this process is likely to be contributed by water decomposition due to the ion bombardment from discharge.

Keywords: Plasma electrolytic oxidation; Aluminium; Excessive oxygen; OH radical; Electrolyte pH

1. Introduction

Plasma Electrolytic Oxidation (PEO) is an advanced high-voltage anodising process used for wear and corrosion protection of light weight metals, particularly of Al. When carried out in alkaline solutions, PEO of Al is usually accompanied with two phenomena that have not so far been explained satisfactory; these are anomalous gas evolution and acidification of the near-to-anode electrolyte volume [1–3]. The first of these results from the main side reaction which reduces dramatically the efficiency of the oxidation process and the second seems to be useful, since it causes a hydroxide precipitation from alkaline solutions on the anode [4,5], e.g.:

$$2[Al(OH)_4]^- + 2H^+ + (n-5)H_2O \rightarrow Al_2O_3 \cdot nH_2O \qquad (1)$$

In a similar way, amorphous gels of hydrated oxides can also be precipitated from silicate, tungstate and antimonite electrolytes. Morlidge et al. [4] explained this as being caused by local electrolyte acidification due to the following reaction of anodic oxidation:

$$2Al + 9H_2O \rightarrow Al_2O_3 + 6H_3O^+ + 6e \qquad (2)$$

However, Eq. (2) is valid for acidic and neutral solutions only, whereas for alkaline solutions the following reaction should be applicable:

$$2Al + 6OH^- \rightarrow Al_2O_3 + 3H_2O + 6e \qquad (3)$$

This would not lead to the acidification of the near-to-anode electrolyte. Indeed, our experiments [2] showed that during anodising in dilute alkaline solutions (0.5 to 2 g l^{-1} KOH) the electrolyte pH remains unchanged unless a plasma discharge occurs. This implies that discharge induced processes are likely to be responsible for the observed changes in the electrolyte solution. In this work, a more detailed quantitative study of anodic gas evolution and electrolyte acidification is therefore carried out, with further discussion given to the underlying mechanisms.

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2. Experimental

Rectangular coupons of total surface area 0.0012 m^2 made from a 6082 aluminium alloy (wt.%: 0.1 Cu, 0.3 Mg, 0.6 Si, 0.6 Fe, 0.7 Mn, 0.1 Zn, 0.25 Cr, Al balance) were mechanically polished to achieve surface finish of $R_a \approx 0.1$ μm, rinsed in water and dried. Then the samples were galvanostatically anodised with current density (i) set in the range from 450 to 1500 A m^{-2}. The treatment was carried out in a glass vessel equipped with a stainless steel ring cathode and a funnel to collect anodic gases. Further details of the experimental installation can be found elsewhere [2]. The alkaline electrolyte with concentration of KOH $C=0.5$ to 2.0 g l^{-1} was stirred and cooled by an external cooler to maintain the temperature below 30 °C. Electrolyte pH was measured before and after each experiment using a 211 Microprocessor pH meter (Hanna Instruments).

The rate of anodic gas evolution during PEO was measured according to the technique discussed in [2], with due account taken for its composition and humidity. The gas composition was evaluated using a Spectramass Data Quad Type DAQ 3.2 quadrupole mass spectrometer, whereby the mass channels corresponding to H_2, N, O, H_2O, N_2, O_2, Ar, and O_3 were monitored.

3. Results

Typical examples of cell voltage and anodic gas evolution under galvanostatic conditions of PEO are shown in Fig. 1. It is clear that the starting point (τ_o) of intense gas evolution coincides with the inflection in the voltage curve; the latter is typically associated with the onset of a plasma discharge on the anode surface. Prior to this point, much slower gas evolution is observed, corresponding to the conventional anodising that occurs with <100% current yield [2]. Fig. 2 illustrates the characteristic composition of anodic gas products. Regardless of current density and electrolyte concentration, the products comprise mainly oxygen (93 to 95 at.%), with hydrogen content not exceeding 2 to 3 at.%. Traces of nitrogen and water could also be identified. Nitrogen originated from residual air remaining in the pipelines of the experimental rig; its content did not vary much with the process parameters and reduced substantially with an increase in total volume of the anodic gas analysed. Hydrogen could either be a product of water decomposition on the spectrometer filament or can indeed be a genuine product of plasma electrolysis. At the moment there is no possibility to discriminate between these.

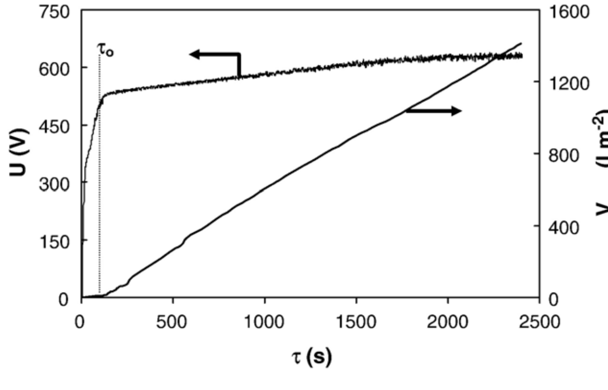

Fig. 1. Voltage and gas evolution curves versus PEO time at $i=935$ A m^{-2} and $C=1$ g l^{-1}.

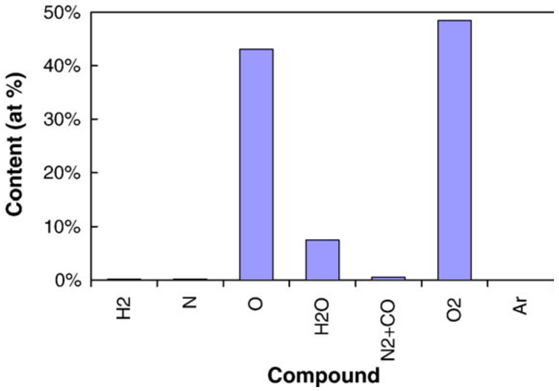

Fig. 2. Typical composition of anodic gas products in PEO of Al in diluted alkaline solutions.

Table 1 represents the data of oxygen evolution rate (r_{O_2}) during PEO, evaluated from the slopes of corresponding experimental curves, $r_{O_2} = \frac{dV}{d\tau}$ (here V is specific gas volume as shown in Fig. 1). The analysis of the gas evolution has shown that the decrease in current density leads to a corresponding decrease in both gas volume and evolution rate. At the same time, the electrolyte concentration does not affect these characteristics, except for the situations when plasma discharge stages could not be achieved, e.g. at $C \geq 2$ g l^{-1}; $i<1400$ A m^{-2} [2].

Effects of charge density and electrolyte concentration on the changes in electrolyte pH during PEO are shown in Fig. 3. Evidently, the plasma electrolysis leads to the solution acidification; the effect is similar to that observed during water treatment by a glow discharge [6,7]. Again, the only exception was observed for the conditions when plasma discharge stages could not be achieved throughout the treatment, e.g. at the experiment corresponding to $C=2$ g l^{-1} in Fig. 3b. In this case no change of electrolyte pH was found.

4. Discussion

As can be seen from Fig. 1, intense gas evolution commences after a certain 'incubation' period τ_o, corresponding

Table 1
Effect of process parameters on the rate of gas evolution and incubation characteristics of plasma discharge onset for PEO of Al in dilute alkaline solutions

$C=1$ g l^{-1}				
i (A m^{-2})	467	699	935	1407
r_{O_2} (ml m^{-2} s^{-1})	0.21	0.51	0.74	1.94
τ_o (s)	780	300	110	70
Q_o, (kC m^{-2})	364.26	209.7	102.85	98.49
$i=935$ A m^{-2}				
C (g l^{-1})	0.5	1.0	1.5	2.0
r_{O_2} (ml m^{-2} s^{-1})	0.8	0.74	0.8	0.05
τ_o (s)	80	110	300	No discharge
Q_o, (kC m^{-2})	74.8	102.85	280.5	–