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Impedance spectroscopy characterisation of PEO process and coatings on aluminium

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Abstract

Impedance spectroscopy is a comprehensive technique that operates with frequency response (FR) to provide useful information about both surface treatments and layers produced. In this paper, two FR types were obtained for the aluminium samples during treatment by plasma electrolytic oxidation (PEO). The first was obtained *in-situ* during PEO, using a frequency sweep of bipolar voltage pulses between 20 Hz and 20 kHz. The modulus and phase angle components of the frequency response were analysed as functions of voltage and treatment time. With increased frequency, the impedance modulus and phase angle were found to decrease from 10^4 to 10 Ω and from 0 to −80° respectively. The second FR was obtained using electrochemical impedance spectroscopy (EIS) of PEO coatings, at open-circuit potential. The samples were found to exhibit an active-capacitive load behaviour, whereby the impedance decreased from 10^6 to 10^2 Ω, and phase angle varied between −20° and −80° with the frequency increase. Both FRs show similar behaviour within the frequency range from 5 to 20 kHz. This approach allows estimations of the frequency response of the PEO microdischarges, to justify the optimal frequency for the pulsed bipolar PEO and also suggests concepts for feedback process control.

Keywords: Plasma electrolysis; Plasma electrolytic oxidation; Aluminium; Frequency response; Electrochemical impedance spectroscopy; Process optimisation and control

1. Introduction

Plasma electrolytic oxidation (PEO) is an emerging environmentally friendly technology for production of corrosion- and wear-resistant coatings on light metals [1]. New pulsed voltage techniques have recently been shown more effective than traditional DC and mains frequency AC approaches [2]. However, the problem of optimal frequency and pulse shape has not been thoroughly investigated yet. Moreover, such a complex process must be carefully monitored and controlled; this requires instant evaluation of the coating thickness, surface roughness and other properties. One of the process characteristics that could provide a justified solution for the problems is frequency response (FR) of the complex impedance of the system. This characteristic comprises two components, i.e. the impedance modulus and the phase angle, and could reveal characteristic frequencies at which the process would be effective. Furthermore, the FR could reveal an equivalent circuit with certain physical interpretation; this would help evaluate surface properties during the process. Within this research, two different frequency responses that correspond to the same surface were obtained by independent techniques. Firstly, an *in-situ* FR was obtained for the PEO process during the treatment. This frequency response must contain information about both the process and the treated surface. More details of the *in-situ* FR measurement can be found elsewhere [3]. Secondly, electrochemical impedance spectroscopy (EIS) was used to obtain the FR that relates mainly to surface properties. Comparison of the two FRs helps in identifying spectral features corresponding to the PEO process and to the surface layer.

2. Experimental

BS 6082 aluminium alloy samples 25 mm × 20 mm × 6 mm in size with a surface finish of $R_a \leq 0.2$ μm were used. The electrolyte was composed of 1 g/l KOH, 2 g/l $Na_2P_2O_7$, 2 g/l Na_2SiO_3. The PEO process was carried out at an ambient temperature in a 2-litre water-cooled stainless steel tank which also served as a counter-electrode.

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Table 1
Parameters of voltage pulses and the coating thickness

Treatment conditions	U_{av}=285 V, U_m=385 V		U_{av}=285 V, U_m=225 V	
Positive pulse amplitude (V)	587		462	
Positive pulse duty cycle (%) [a]	51		61	
Negative pulse amplitude (V)	57		5	
Negative pulse duty cycle (%) [a]	27		18	
Treatment time τ (min)	15	60	15	60
Coating thickness (μm)	30.1±2.4	44.7±3.4	2.2±0.4	1.3±0.5

[a] Both positive and negative pulses are centred within the corresponding half-period.

A bipolar pulse mode was set by an external waveform generator. The frequency f was logarithmically swept for 0.48 s from 20 Hz to 20 kHz. The pulse parameters were optimised to approximate closely an implied sine waveform. The waveform DC value (U_{av}) and the AC amplitude (U_m) were chosen as factors for the experimental design. The treatment time (τ) was used as the other factor. The factors were varied in the following ranges: U_{av}=225–285 V; U_m=225–465 V; τ=15–60 min to cover almost all PEO conditions. This paper discusses only the most characteristic conditions; the factor values and corresponding pulse parameters are indicated in Table 1.

The *in-situ* FR was obtained using the implied sine waves filtered out directly from the voltage and current waveforms at every frequency of interest. With the filtering procedure employed, the accurate and reliable measurements were possible within 50 Hz to 20 kHz frequency band. The modulus $|Z|$ was calculated as the ratio of effective voltage to current values. The phase angle θ was calculated as a phase shift between the filtered waveforms.

The EIS frequency response was obtained at the open circuit potential (OCP) in the same electrolyte using a Solartron SI 1260 gain-phase analyser. A saturated calomel electrode and a platinum plate were used as a reference and counter electrodes respectively. The surface area subjected to the analysis was 0.95 cm^2. The amplitude of the scanning sine waveform was 15 mV; the frequency was logarithmically swept from 10 Hz to 100 kHz.

Coating thickness and surface morphology were evaluated using an Elcometer eddy current gauge and a CamScan scanning electron microscope, respectively.

3. Results

For the selected experiments, the coating thickness and the surface morphology are shown in Table 1 and Fig. 1, respectively. The experiments were selected so that the PEO capabilities can be clearly seen, i.e. thick coatings obtained at U_{av}=285 V, U_m=385 V and thin coatings obtained at

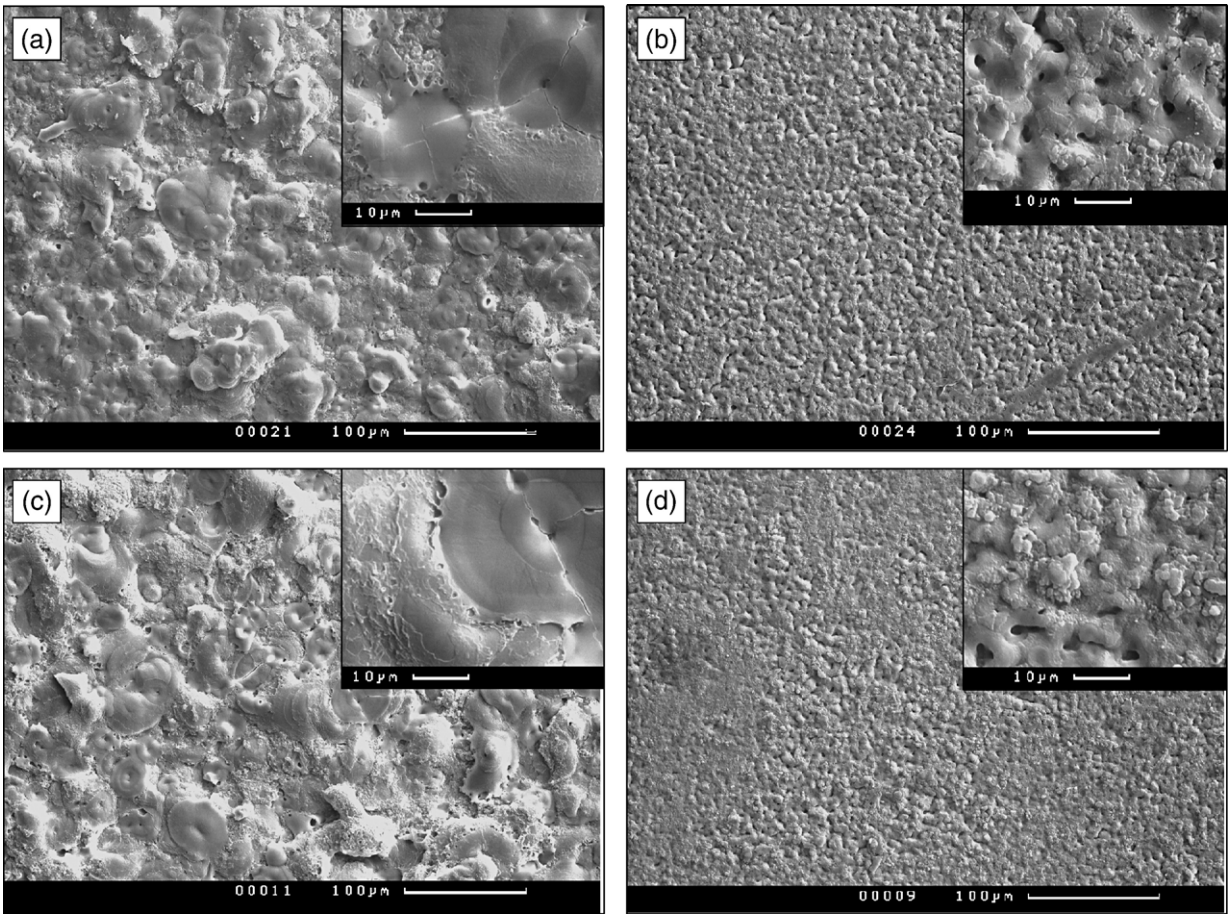

Fig. 1. SEM micrographs for samples treated at U_{av}=285 V, U_m=385 V (a, c) and U_{av}=285 V, U_m=225 V (b, d) for 15 (a, b) and 60 min (c, d).