Cathodic discharges during high frequency plasma electrolytic oxidation

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ABSTRACT

Using small area electrical data logging, high speed photography, sample mass gain monitoring, gas evolution measurement and microstructural examination, a study has been made of the formation and effect of cathodic discharges during PEO of Al substrates. Discharge formation during the cathodic half-cycle is promoted by high frequency, thick coatings and high pH. They form (under constant current conditions) when the voltage during cathodic polarization reaches a value (~250 V in the work described here) sufficient to cause dielectric breakdown across thin residual oxide layers on the substrate. This occurs when the normal cathodic process of proton flow through electrolyte channels in the coating can no longer deliver the required current. Cathodic discharges tend to carry higher currents, and emit more light, than anodic ones. Gas evolution rates during PEO are well above the Faraday yield level. This is due to water entering discharge plasmas, breaking down into ionized species and failing to recombine completely during subsequent collapse and quenching. It is reported here that rates of gas evolution rise as discharges start to take place in the cathodic part of the cycle, as well as in the anodic part. Rates of substrate oxidation (coating growth), however, drop off, rather than rise, when cathodic discharges start. Evidence is presented here suggesting that this is associated with their highly energetic nature, causing substantial amounts of oxide to be expelled into the electrolyte during cathodic discharges. This is also apparent in the coating microstructure, where recent cathodic discharge sites are identifiable as large, highly porous regions.

1. Introduction

Interest in Plasma Electrolytic Oxidation (PEO) continues to grow, and the technical attractions of the process are well established, but the mechanisms of oxide growth remain quite poorly understood. The key to improved understanding certainly lies in detailed study of the individual discharges, and indeed considerable progress has been made recently as a result of such investigations [1–8]. It's now clear that discharges have a strong tendency to occur in sequences ("cascades") at particular locations, with each discharge being of relatively short duration (few tens to few hundred μs), but the periods between them are somewhat longer (several hundred μs to a few ms) and the cascades can persist over many cycles of the applied potential. It's also clear that the process exhibits low energy efficiency [7,9,10], with relatively large amounts of electrical energy (~1 mJ) being absorbed during a discharge, each of which results in the creation of only a small amount of oxide (< 1 ng). Most of the injected energy eventually goes into heating of the electrolyte (via expansion of a gas bubble centred on the discharge site [10]), with little or no scope for subsequent recovery. (A small amount of energy is carried away in the form of evolved gas.) However, this high rate of energy absorption is not necessarily inherent

in the process and further improvements in understanding of how each discharge arises may lead to technological and economic benefits. Some efforts have been made in the direction of measures to reduce energy absorption during the process, such as the suggestion of Zhang et al. [11,12] that a grid counter-electrode should be located close to the surface of the substrate, but these have not so far been formulated within a well-defined theoretical framework or been widely adopted.

An issue that is receiving increasing attention concerns the significance of the cathodic part of the cycle. It's been clear for some time [13] that PEO coatings produced using AC are in general of superior quality (harder and denser, for example) than those produced under corresponding (anodic) DC conditions. It's also been shown that coating quality is improved if the cathodic voltage is raised [14] or if the ratio of cathodic current to anodic current is increased [15]. What actually happens during the cathodic half-cycle is less clear. It's certainly the case that, at least under most conditions, discharges predominantly occur during the anodic half-cycle, although current does flow in both half-cycles.

However, discharges have been observed in the cathodic part of the cycle under some conditions, usually after the coating has become relatively thick. Rakoch et al. [16] reported that such discharges are

favoured by more acidic electrolytes, relating this to the rapid acceleration of protons (towards the substrate) during the cathodic part of the cycle, bombarding the thin film of oxide on the substrate and hence making it more likely that it will undergo dielectric breakdown. On the other hand, Sah et al. [17] reported that cathodic discharges tend to occur in strongly alkaline (silicate) electrolytes, and can improve the coating quality. Nominé et al. [18–20] reported that high pH, and also high supply frequency and greater coating thickness, favour cathodic discharges.

It is not immediately clear whether having a high H^+ ion concentration is in fact expected to promote or inhibit cathode discharges. Certainly the argument of Rakoch et al. [16] does not explain the observation that they tend to occur with relatively thick coatings. Possibly a useful approach is to recognize that, when there is a high H^+ ion concentration, and only a short column of electrolyte above the thin oxide layer on the substrate (i.e. a thin coating), then plenty of H^+ ions reach the layer (during the cathodic part of the cycle), pick up electrons that are coming through the layer and form H_2 gas. However, a shortage of H^+ ions (high pH), a long distance through the electrolyte column (thick coating) and a short cathodic period (high frequency) are all likely to make this process more difficult, causing the current carried by the H^+ ions to fall, the voltage to rise (in order to maintain the current at the set value) and, when a sufficiently high field is thus created across the oxide layer, to cause dielectric breakdown. This explanation does not appear to have been put forward previously, although it should be recognized that the exact outcome is likely to depend on the details of the electrical circuitry.

Nomine et al. [19] reported that cathodic discharges on Mg tend to be detrimental to the coating microstructure, although having a cathodic voltage is beneficial and they speculate that this relates to the associated charge redistribution somehow making the anodic discharges more effective. It's also worth noting that PEO coatings have been produced under conditions in which cathodic discharges predominate. For example, Stojadinovic et al. [21] reported cathodic PEO of Mo. Recognizing that coating creation (substrate oxidation) during PEO predominantly occurs during cooling of a plasma containing both substrate atoms or ions and oxidizing agents of some sort [8], it seems likely that this can take place as readily in a cathodic discharge as in an anodic one.

There have been relatively few studies of gas evolution during PEO processing. There is conflicting evidence regarding the composition of the evolved gas, with some reports that it is predominately oxygen [22,23], and others suggesting high concentrations of hydrogen [24]. It is, however, commonly reported [22–26] that the volume of gas liberated is considerably greater than the electrochemical Faraday yield, corresponding to electrolysis of water. This has also been reported for contact glow discharge electrolysis [27,28].

In any event, there are evidently several unanswered questions in this area. In practice, PEO processing is commonly carried out using AC supplies at 50 or 60 Hz, although higher frequencies are being increasingly employed. At low frequency, the cycle period is about 20 ms, which is sufficiently long to allow extended cascades during each (anodic) half-cycle - and indeed they commonly persist at the same location through a number of cycles. There is interest in how the process might change as the supply frequency is increased, such that the cycle period is no longer large compared with the inter-discharge period, or the discharge period itself, but there appears to have been little systematic work on this. Yao et al. [29,30] investigated the effect of cathodic pulses over a range of frequency, for PEO of titanium, observing some changes in the phases formed in the coatings, but did not explore any details of the discharges. There are several reports [3,31–33] that an increase in the supply frequency (with maximum values usually around 1.0–1.5 kHz) leads to a reduction in coating growth rates, as well as a coating microstructure that becomes finer and denser (so that high frequency might be regarded as beneficial in this respect). However, little information appears to be available about how

the nature of the (anodic and/or cathodic) discharges might change as the frequency becomes relatively high. The present paper is aimed at this area, as well as at effects on the coating microstructure.

2. Experimental procedures

2.1. Sample preparation and PEO processing

For high speed video, synchronised with electrical monitoring, the samples employed were Al-6082 substrates, in the form of 25.4 mm square section bars mounted in resin. A small piece of the bar was swaged to produce a wire of diameter 1 mm, which was mounted in the resin, adjacent to the bar. The wire and bar were connected to a pair of PVC-insulated twisted wires extending out of the tank, where a 100 Ω resistor connected the ends of the twisted wires. The set-up is described in detail in papers of Dunleavy et al. [1,6]. It allows the current though the small sample to be monitored, and this signal to be synchronised with high speed photography (and, at least in principle, with high speed spectral analysis).

Coatings were prepared using a 100 kW Keronite™ processing rig, with an electrolyte of a dilute aqueous solution of potassium hydroxide and sodium silicate (pH = 11.7), maintained at about 20 °C by re-circulation through a heat exchanger. The applied potential was square-wave and most of the work presented was carried out at either 50 Hz or 2.5 kHz. In all cases, the anodic and cathodic periods were equal, with no gap between them, so that the conditions are fully defined by the frequency. A constant current condition was set, so as to achieve a current density of 30 A dm^{-2}. The applied voltage was therefore not pre-determined, but adjusted by the power supply to maintain the appropriate current, which was about 2.0 A for these samples. Mass gain and microstructural observations were made on standard plates of Al-1050 with dimensions of 50 × 25 × 1.2 mm.

2.2. High speed video capture

The camera employed for synchronised current and video experiments was a Photron FastcamSA 1.1, with the acquisition rate set at 125,000 frames per second (8 μs exposure time). The linear spatial resolution was 9 μm - i.e. an area of 81 μm^2 per pixel. Typical images comprised 192 × 144 pixels, covering an area of 2.24 mm^2, which was large enough to view the entire cross section of the small area (1 mm diameter) wire. Sample surfaces were viewed through a glass window in the electrolyte tank. The set-up is fully described in a previous paper [10]. In the present work, no illumination was needed, since the images were created only by light emitted from the discharges. Image sequences were acquired after various PEO processing times, using different frequency waveforms. The high speed camera generated a TTL (Transistor-Transistor Logic) trigger signal (+5 V, 10 μs square wave) within 100 ns of the camera being activated. Since each frame corresponds to 8 μs, this 100 ns delay is considered negligible. The trigger signal was connected to one channel of a Picoscope, to initiate electrical recording.

Monitoring of the number of cathodic discharges occurring at various processing times was performed using a Phantom V12.1 camera, with an acquisition rate of 100,000 frames per second (10 μs exposure time). The linear spatial resolution was 34 μm – i.e. an area of 1156 μm^2 per pixel. Typical images comprised 160 × 160 pixels, covering an area of 30 mm^2 in the centre of the plates. Recordings were performed throughout processing, in sequences of 173 ms duration.

2.3. Monitoring of gas evolution and mass gains

Gas evolution is not routinely monitored during PEO processing, although, as outlined above, there have been a few studies. The gas produced is expected to be a mixture of H_2 and O_2, so storing large quantities is potentially hazardous. In addition, compositional analysis