Applied Surface Science 359 (2015) 405–411

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Synchronised electrical monitoring and high speed video of bubble growth associated with individual discharges during plasma electrolytic oxidation

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ARTICLE INFO

Article history:
Received 11 July 2015
Received in revised form
22 September 2015
Accepted 18 October 2015
Available online 21 October 2015

Keywords:
Plasma electrolytic oxidation
Electrical discharges
Bubbles
High speed photography

ABSTRACT

Synchronised electrical current and high speed video information are presented from individual discharges on Al substrates during PEO processing. Exposure time was 8 μs and linear spatial resolution 9 μm. Image sequences were captured for periods of 2 s, during which the sample surface was illuminated with short duration flashes (revealing bubbles formed where the discharge reached the surface of the coating). Correlations were thus established between discharge current, light emission from the discharge channel and (externally-illuminated) dimensions of the bubble as it expanded and contracted. Bubbles reached radii of 500 μm, within periods of 100 μs, with peak growth velocity about 10 m/s. It is deduced that bubble growth occurs as a consequence of the progressive volatilisation of water (electrolyte), without substantial increases in either pressure or temperature within the bubble. Current continues to flow through the discharge as the bubble expands, and this growth (and the related increase in electrical resistance) is thought to be responsible for the current being cut off (soon after the point of maximum radius). A semi-quantitative audit is presented of the transformations between different forms of energy that take place during the lifetime of a discharge.

1. Introduction

The commercial significance of the plasma electrolytic oxidation (PEO) process continues to increase, but technical developments still depend largely on empirical experimentation. However, progress is being made on obtaining improved understanding of certain fundamental features - particularly the main characteristics of the individual discharges. For example, their duration (~30–300 μs), spatial distribution (many localised "cascades" that persist for at least several tens of ms), the "incubation" periods between individual discharges in a cascade (~0.1–1 ms), the peak discharge current (~10–100 mA), the discharge energy (~1–10 mJ) and the diameter of the core discharge channels (~10–50 μm) are all now fairly well established [1–7], although they exhibit some dependence on substrate type, electrolyte composition and imposed electrical conditions. Correlations have also been established [3,8,9] between external conditions, discharge characteristics and features of resultant coatings, including the growth rate, and a start has been made [7,10] on correlating the energetics of individual discharges with that of the process as a whole (with the ultimate aim of reducing the – often relatively high – rate of energy consumption).

There have also been extensive (time-averaged) spectrographic studies [1,3,11–16] of the discharges, aimed at establishing temperatures, charge densities and chemical compositions. There is now quite a lot of information available about these features, and the role of variables such as the frequency of the AC supply is now a little clearer. Some studies [8,17–20] have revealed that, under certain conditions, the discharges can become very "diffuse" ("soft" regime), and it has also been shown recently [21–23] that discharges can in some cases occur during the cathodic part of the cycle, with both of these types of change affecting the growth characteristics and microstructure of the resultant coatings. However, it has not really been possible so far to explain properly why the conditions concerned lead to these changes in discharge characteristics, and in general it is evident that current understanding of the process as a whole is still far from complete.

A feature that has been noted, and (to a limited extent) investigated, by a few researchers [5–7,14,24,25] is that gas bubbles (or "plasma bubbles") tend to form in the region where an individual

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http://dx.doi.org/10.1016/j.apsusc.2015.10.124
0169-4332/

discharge emerges into the electrolyte, apparently with a tendency to grow rapidly to a significant size (and then to shrink). Attempts have also been made [26] to explore how external introduction of (relatively large) gas bubbles can affect discharge formation. However, the phenomenon of bubble expansion from a discharge is clearly very different from that of external gas injection and indeed it also appears to be quite distinct from that of conventional electrolytic formation of gases (usually hydrogen and/or oxygen) at an electrode [27], which normally leads to escape of (relatively large) bubbles.

It has been speculated [5,7,25] that these discharge-linked bubbles, which apparently can rapidly oscillate in size, arise from pressure created as the hot plasma expands, and that this expansion leads to cooling, reduction in charge density, increase in electrical resistance, sharp curtailment of the discharge current and then collapse of the bubble. In fact, preliminary attempts have been made [5] to predict the bubble radius as a function of peak discharge current, although this model was based on several very crude exploratory assumptions, including neglect of the electrical resistance of the plasma, compared with that of the electrolyte (and also neglect of water volatilisation, viscous flow effects, etc.). The outcome was that the bubble radius was predicted to range up to about 30–40 μm, but there were few systematic experimental data available at the time for comparison. Hamdan et al. [25] did observe bubbles forming of up to several hundred microns in diameter (over periods of the order of 100 μs), although this was in heptane, rather than aqueous solution, and was under rather different conditions from those created during PEO. Vol'f et al. [24] did observe "vapor-plasma" bubbles forming under PEO-like conditions, and reported that their lifetime was about 200 μs, but did not draw any conclusions about gas pressures or mechanisms of growth.

It seems likely that a full understanding of how and why this sequence of events involving the "plasma bubble" takes place will be very helpful for optimization of the process as a whole. The literature presently contains little or no solid experimental evidence in this area, mainly because there has hitherto been no synchronised monitoring of electrical and optical (imaging) information. The current paper presents synchronised data of this type, together with a preliminary investigation of how energy is redistributed during bubble expansion and contraction.

2. Experimental procedures

2.1. Sample preparation

PEO coatings were produced on Al-6082 substrates, which were 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. This wire was mounted in the resin, adjacent to the bar. 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 depicted in Fig. 1(a).

Coatings were prepared using a 100 kW Keronite^{TM} processing rig and an electrolyte consisting primarily of a dilute aqueous solution of potassium hydroxide and sodium silicate. The electrolyte was maintained at a temperature of approximately 20 °C by re-circulation through a heat exchanger. The applied potential was nominally square-wave, with variable frequency, although the results presented here all relate to experiments carried out at 50 Hz. A constant current condition was set, so as to achieve a current density of 31 A dm^{-2}. The applied voltage was therefore not pre-determined, but adjusted by the power supply to maintain the appropriate current. The voltage was in the range 500–600 V during the process. A coating of thickness about 5 μm was created (by running the process for about 3 min) before the measurements were started.

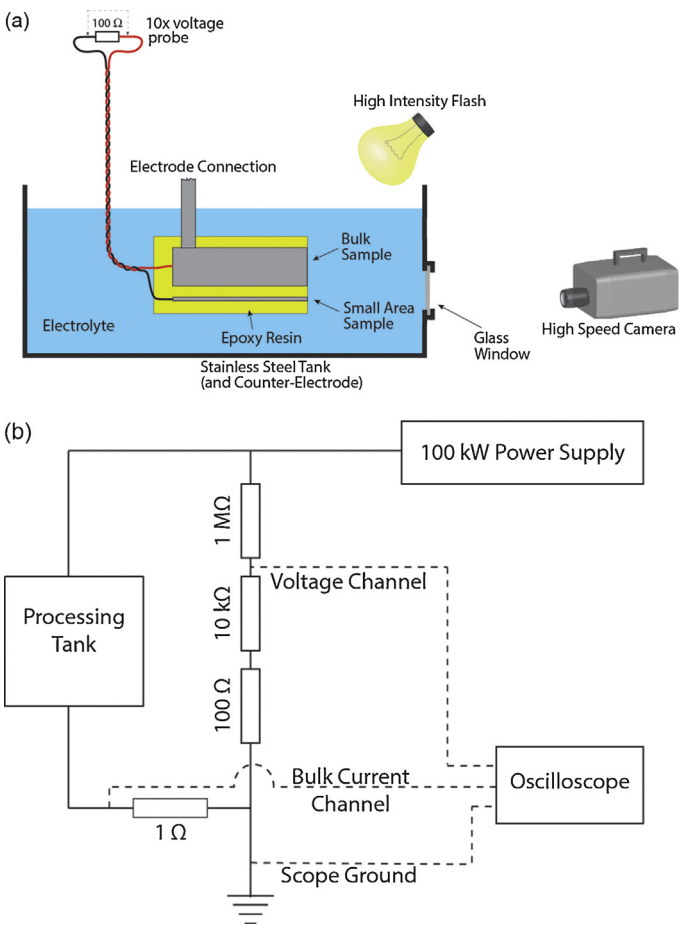

Fig. 1. Schematic representation of the experimental arrangement, showing (a) a depiction of the set-up and (b) a circuit diagram.

2.2. High speed video capture

The camera employed 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, as shown in Fig. 1(a). The distance between lens and sample was 500 mm. Image sequences were acquired after various PEO processing times, using different frequency waveforms. Due to the very high frame rates involved, it was necessary to illuminate the sample surface, in order to be able to see bubbles clearly. This was done using a high intensity flash (white light) source, which had a duration of approximately 10 ms. The maximum total record time of the camera (~2 s) was employed, since the flash was being triggered manually.

2.3. Small area current monitoring

The small area electrical monitoring technique is described in detail elsewhere [1,5,6]. The concept behind the methodology is that discharge events on a small area take place in much the same way as those on "normal" (larger) samples, but with a strong probability that, when a discharge occurs, it will be the only one taking place at that time. By monitoring the current flowing through the small area sample, the current–time profile of individual discharges can thus be obtained.