



High speed video evidence for localised discharge cascades during plasma electrolytic oxidation



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ABSTRACT

Information is presented from high speed video imaging of the free surface of coatings being grown on aluminium substrates by PEO processing. The exposure time during image capture ranged down to 5.5 μ s, while the linear spatial resolution of the images ranged upwards from about 12 μ m. The area being viewed was about 2.4 mm², which was taken to be representative of the substrate area as a whole (~129 mm²). PEO processing was carried out at 50 Hz AC. The periods over which image sequences were captured was about 100 ms, covering several cycles of variation of the applied potential. This operation was repeated periodically while the coating thickness increased from a few microns to several tens of microns. During the imaging periods, it was typically observed that tens or hundreds of individual discharges were occurring, all of them readily distinguishable from the background light levels. Their duration was of the order of several tens of microseconds. It was noticeable that they tended to occur in “cascades” at particular locations, each sequence comprising tens or hundreds of individual discharges, with an “incubation” period between them of the order of several hundreds of microseconds. It seems likely that they all occurred during the positive (anodic) half-cycle, while the applied voltage was sufficiently high. An individual cascade tended to persist (at the same location) over several voltage cycles. As the coating became thicker, these characteristics broadly persisted, although individual discharges became longer-lived and more energetic. An attempt is made to relate these observations to the overall picture of how coating growth takes place during PEO processing, and also to the overall energy consumption.

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1. Introduction

While plasma electrolytic oxidation (PEO) formation of surface coatings is now a relatively well-established technique, which is in quite extensive commercial use, a large degree of uncertainty still surrounds the fundamentals of coating growth. Repeated formation of through-thickness electrical discharges is clearly central to the process, presumably providing channels through which oxygen in the electrolyte becomes exposed in some form to the metallic substrate, which then becomes oxidised so as to incrementally increase the coating thickness. This broad picture is consistent with the common observation that the coating growth rate remains approximately constant as the coating becomes thicker, although the individual discharges do tend to become more energetic and violent later in the process, often placing an upper limit on the attainable thickness.

There has been quite extensive spectrographic and electrical investigation [1–12] of the plasmas formed during these discharges, to estimate

their temperature and also the charge density and species concentrations within them. Most such spectra have represented aggregated data from a large number of individual discharges, so there has been little attention paid to variations in these characteristics between discharges or during the lifetime of a single discharge. Nevertheless, there is some evidence [5] that the core of a discharge, during the early part of its lifetime, may be hotter and have a higher charge density (and hence conductivity) than later, when the plasma is probably expanding as a bubble into the electrolyte surrounding the top of the core.

A point of particular interest relates to the duration of individual discharges. This has been estimated a number of times using high speed photography and other techniques. Some optical studies [13,14] have produced values ranging up to several tens of ms. Of course, it should be recognised that most PEO processing is carried out using an AC voltage source, commonly at a frequency of 50 Hz, in which case, assuming the discharges take place only during the anodic half-cycle, and depending on the exact waveform, the “window” within which a discharge can occur has a duration of only about 5–10 ms. In any event, it's now clear [5,6,11,15–18] that typical discharge durations actually range from several microseconds to a few hundred microseconds. This is illustrated, for example, by Fig. 1(a), which shows [5] electrical current pulses

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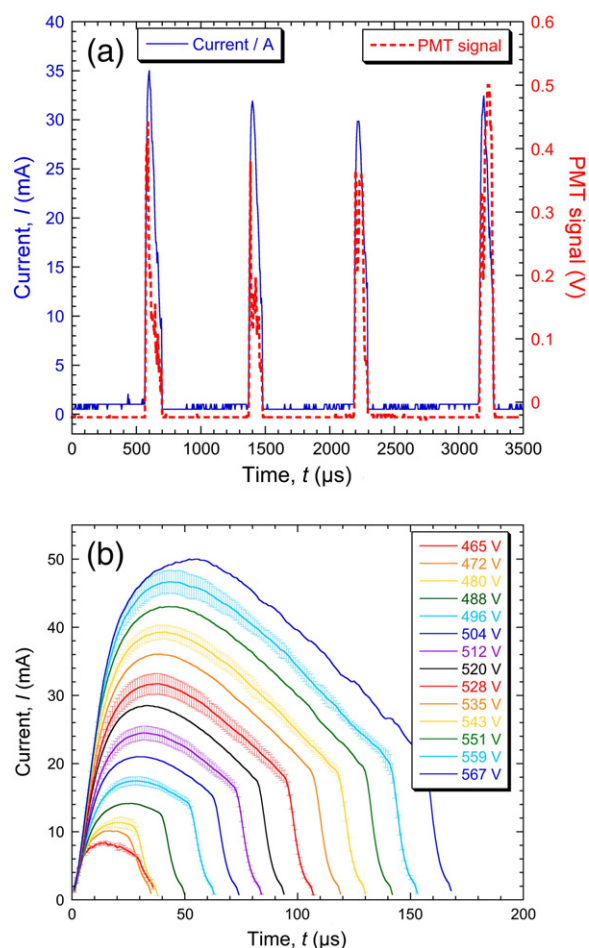


Fig. 1. Examples of current–time characteristics from individual PEO discharges on small area samples, showing (a) data [5] for a sequence of current pulses, and for the associated light emission (obtained from a photomultiplier tube – PMT), and (b) averaged current–time relationships [17], plotted for various discharge initiation voltages (showing error bars for half of the curves).

associated with individual discharges in a small area sample (in parallel with the main specimen). Also shown are synchronised outputs from a photomultiplier focussed on the small sample, confirming that current and light emission pulses are from the same events. It can be seen that the periods between the discharges are in this case of the order of several hundred microseconds. It seems likely that, during some video studies (in which frame exposure times were of the order of several milliseconds), such sequences were misinterpreted as single discharge events.

The data [17] presented in Fig. 1(b) also fit into the picture that is emerging of the electrical characteristics of a discharge: it can be seen that the evolution of the current during its lifetime is consistent with the initial (Joule) heating causing a sharp increase in plasma temperature and charge density, allowing increased current flow, followed by a reduction as the plasma starts to expand into the electrolyte and then a sharp cut-off as the resistance of the current path rises and the discharge channel is quenched. It's probably at this point that there is violent ejection of molten oxide from the core of the channel, giving rise to characteristic “volcanic craters” on the free surface of the coating.

It has been speculated previously [5,17,18] that the extended discharge sequences, termed “cascades”, take place in localised regions. The idea behind this is that an individual discharge may leave a “damaged” microstructure along the core channel, constituting a low resistance path that is a favourable location for subsequent discharge initiation. It's not yet clear whether electrolyte enters the channel before

the next discharge occurs, and indeed there may be insufficient time for this to occur. There is also uncertainty about changes in charge distribution during this period. Such a sequence of discharges might be expected to continue in the same location until the associated oxidation has thickened the coating in the vicinity sufficiently for it to no longer constitute a “low resistance” pathway. Incidentally, while channels may or may not become filled with electrolyte between discharges, it's clear [19] that PEO coatings contain an extensive network of (fine) interconnected porosity (presumably formed as a consequence of the violent events during and after each discharge) and at least most of this is full of electrolyte during processing. This may be relevant to the initial establishment of a “new” location for a discharge cascade.

The above picture is consistent with many (mostly fairly recent) observations and measurements. However, no direct evidence has been presented hitherto to confirm that a cascade of discharges does in fact take place in a localised region. The information presented in this paper, obtained using a high speed, high resolution camera, is aimed in this direction. Furthermore, an attempt is made to relate the observed characteristics of individual discharges, and their spatial and temporal distributions, to reported information about macroscopic features, including rates of coating growth and overall energy requirements of the process [20].

2. Experimental procedures

2.1. Sample preparation

Coatings were produced on Al-6082 substrates, in the form of circular plates, with a diameter of 12.8 mm, mounted in resin. Coatings were prepared using a 10 kW Keronite™ 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 $25 (\pm 2)^\circ\text{C}$ by re-circulation through a heat exchanger, with a whistle pump agitating and aerating the electrolyte. The applied potential was nominally sinusoidal, with a frequency of 50 Hz. A constant capacitance condition was set, so as to achieve a current density of $15 (\pm 1) \text{ A dm}^{-2}$ after the initial transitory regime. The applied voltage was therefore not pre-determined, but the overall RMS value was in the range of 300–400 V during most of the process. Coatings were progressively grown and video sequences obtained periodically. The coating growth rate was $\sim 1 \mu\text{m min}^{-1}$.

2.2. High speed photography

The camera employed was a Photron Fastcam SA 1.1, with the acquisition rate set at 180,000 frames per second ($5.5 \mu\text{s}$ exposure time). The linear spatial resolution was $12 \mu\text{m}$ – i.e., an area of $144 \mu\text{m}^2$ per pixel. Typical images comprised 128×128 pixels, covering an area of 2.36 mm^2 . Sample surfaces were viewed through a glass window in the electrolyte tank. The distance between lens and sample was 50 cm. Image sequences were acquired after various PEO processing times, corresponding to coating thicknesses in the range of $5 \mu\text{m}$ to $60 \mu\text{m}$.

2.3. Data processing

Image acquisition periods involved accumulating 17,500 frames over about 100 ms. Individual frames (128×128 pixels) were 8-bit greyscale images, with pixel intensity values ranging from 0 to 255. These data were processed using the Photron FASTCAM viewer and the image processing software ImageJ. Superimpositions of a complete sequence ($\sim 17,500$ images) were produced by summing the pixel values of corresponding points in a sequence of images, which were then converted back into 8-bit greyscale images. Total intensity profiles were calculated by summing all the pixel values for each frame in a sequence. Maxima in light intensity of the summed images were found,

and circular regions of interest were defined, centred on these maxima. Intensity–time profiles from these circular regions were produced in a similar manner to the total intensity profiles. The volume viewer “Plugin” was used to create perspective views of frame sequences. For the perspective views, the contrast was reversed, with the transparency set so that low value pixels were transparent and high value pixels were opaque.

3. Video image characteristics

3.1. General characteristics

During examination of typical video footage, it rapidly became clear that there is a strong tendency, not only for discharge events (i.e., pulses of light emission) to occur in bursts comprising a sequence of events (at approximately regular intervals), but that each of these “cascades” was occurring in a highly localised region. This is illustrated by Fig. 2 (showing information about images obtained from a 50 μm thick coating), which clearly demonstrates that, during the period concerned (~ 100 ms), a series of discharges occurred at a particular location (and, at least in this case, nowhere else in the field of view). The

discharges apparently occurred only when the (anodic) applied potential was sufficiently high (>300 V for this case). Discharge durations were ~ 100 – 200 μs , separated by “incubation” periods of about 500–1000 μs . This is broadly consistent with previous observations – see Fig. 1. It certainly seems likely in view of these observations that “cascades” of this type, with these characteristic features, commonly occur at discrete locations.

3.2. Effect of coating thickness

Experiments of the type described above were carried out periodically as the coating thickness increased. It became clear that, while broadly similar behaviour was exhibited over a wide range of thickness, certain systematic differences were exhibited between “thin” (<10 μm) and “thick” (>20 μm) coatings. These are illustrated by Fig. 3, which shows corresponding information to that in Fig. 2, for a coating thickness of about 5 μm . It can be seen that, with such a thin coating, discharges occurred in several (4) locations within the viewed area, during the period concerned (~ 100 ms). As with the thicker coating, they were confined to the periods during which the applied (anodic) potential was sufficiently high. It seems clear that discharges can take place

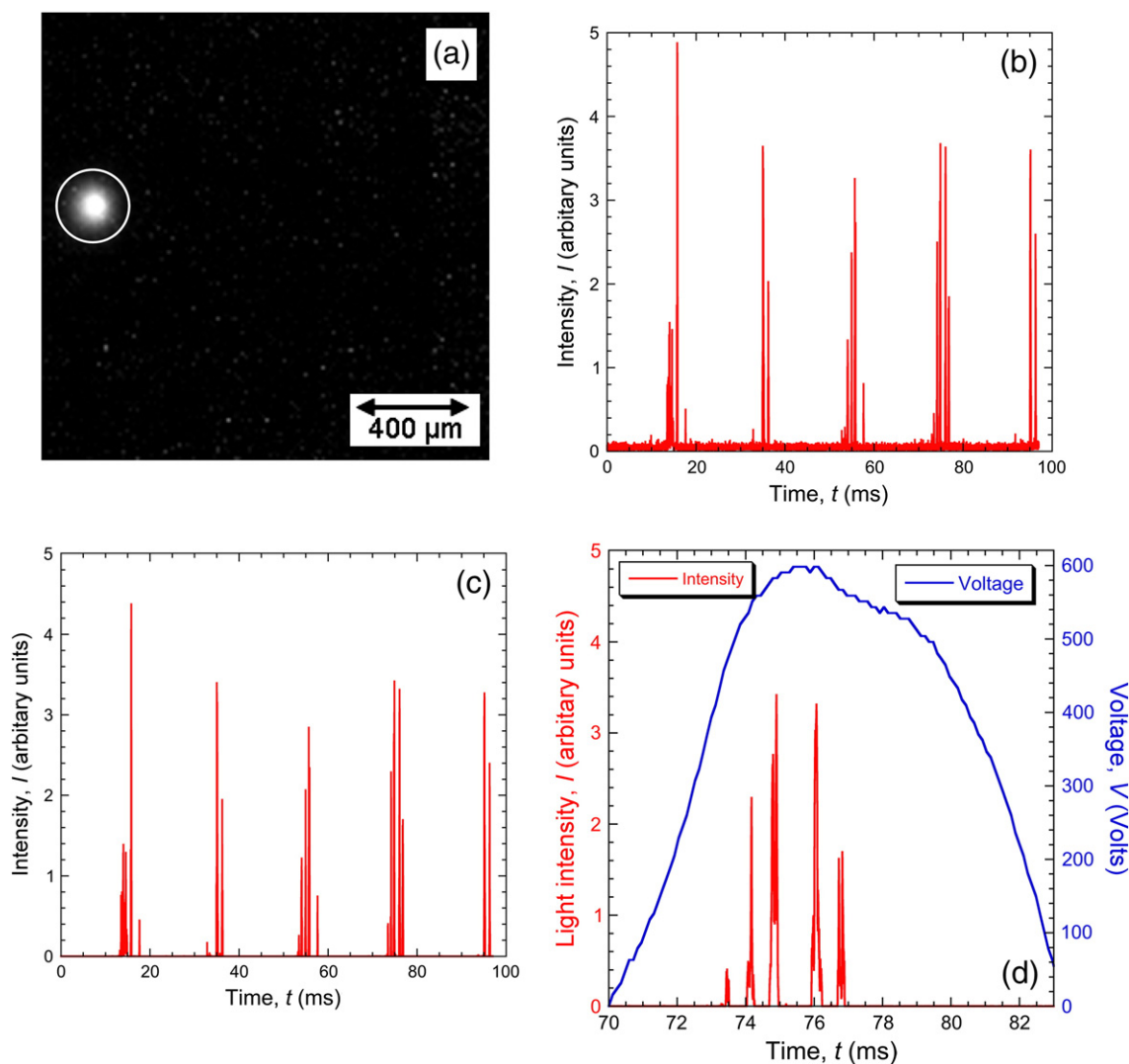


Fig. 2. Information relating to a sequence of 17,500 images (exposure time ~ 5.5 μs , pixel side length 12 μm) from a PEO coating ~ 50 μm in thickness, showing (a) a superimposition of the complete sequence, (b) total summed light intensity for each frame, as a function of time, (c) as for (b), but taken only from the bright area (circle of 288 μm diameter) in (a), and (d) higher resolution plot of part of (c), approximately covering an anodic half-cycle, with a typical measured voltage profile [5] during such a period superimposed.

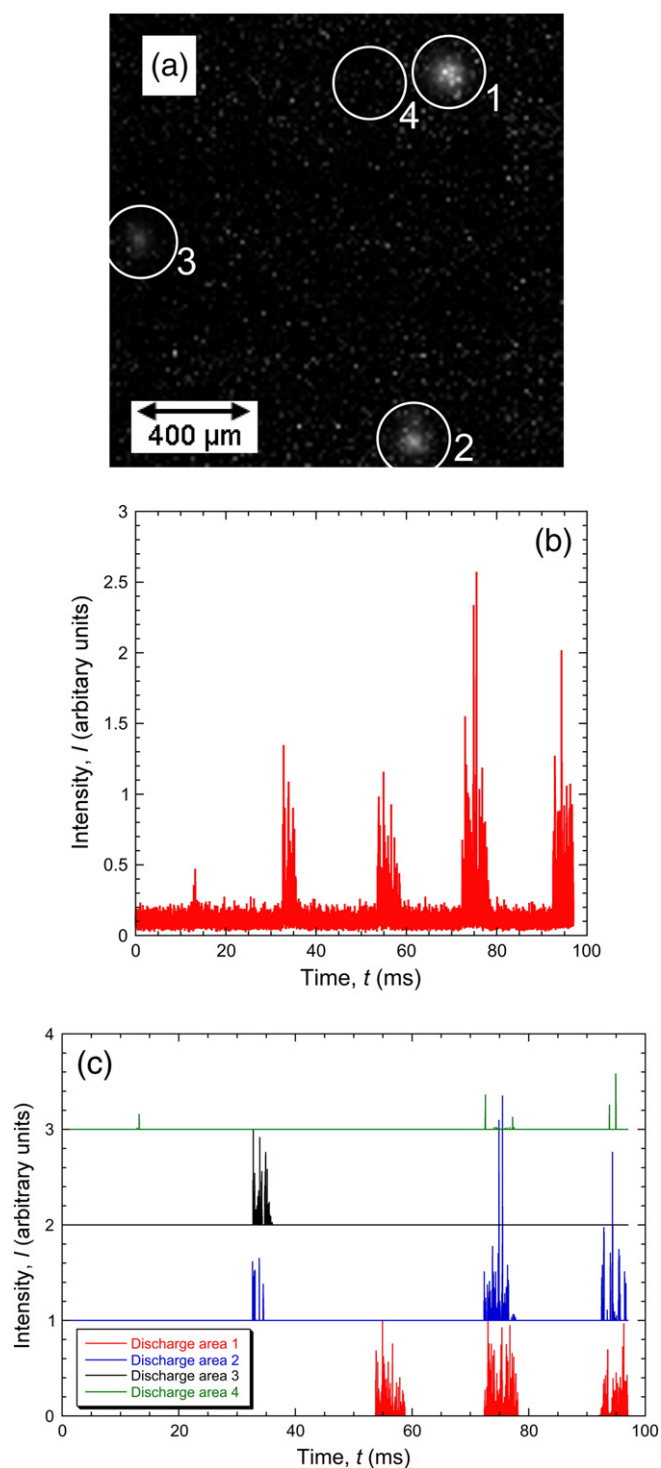


Fig. 3. Corresponding information to that of Fig. 2, from a PEO coating $\sim 5 \mu\text{m}$ in thickness, showing (a) a superimposition of all frames, (b) total summed light intensity for each frame, as a function of time, and (c) plots of summed intensity against time for light from the 4 circles ($288 \mu\text{m}$ in diameter) shown in (a).

simultaneously in different (nearby) locations, although it might be inferred that this becomes unlikely if they are very close: for example, discharges in location 4 appear to have been largely suppressed by being close to the (well-established) cascade taking place in location 1. This may be related to the charge distribution and equi-potential contours in the vicinity of a discharge. It's perhaps worth noting that the three "active" cascades in Fig. 3(a) are all about 1 mm apart. Of course, this can't be regarded as statistically significant, and in any event the area

from which charge may be flowing into a discharge probably becomes larger as the coating becomes thicker, but it may nevertheless be potentially of interest.

A further impression of the differences between discharge sequences taking place through thin and thick coatings can be obtained from Fig. 4(a) and (b). These two plots show perspective visualisations (with the contrast reversed), for thin and thick coatings, of a portion of the complete stack of (17,500) frames, covering a time period of about 8 ms (i.e., 1500 frames). In both cases, this captures part of a cascade (two for the thinner coating) occurring during an anodic half-cycle (which lasts about 10 ms). This confirms the strong tendency towards spatial localisation of individual cascades and also conveys an impression of the partially stochastic nature of these events. It's also clear that the individual discharges are less frequent and more intense when the coating is thicker – of course, this is a feature that is well-established for PEO and, indeed, is often apparent to the naked eye (although evidently it is not in fact discrete discharge events that are being observed in that case).

4. Inferred discharge characteristics

4.1. General characteristics

The development history of a discharge is envisaged to be broadly as shown in Fig. 5. It's still a little speculative to state that the initial breakdown occurs across a small insulating layer above the substrate (Fig. 5(a)), with the porosity within the rest of the coating being full of (conductive) electrolyte, although it does seem quite likely. There is also a degree of uncertainty surrounding the subsequent extension of the discharge through the thickness of the coating, current flow, Joule heating, bubble expansion, drop in charge carrier density, pinching off of the current, quenching and collapse of the channel (Fig. 5(b)–(f)). However, this is at least a plausible sequence and information of the type presented in this paper has the potential to assist in clarifying some of the details. The experimental outcomes described above do provide clear confirmation that discharges exhibit a strong tendency to occur in cascades, which take place in localised regions. The spatial resolution of these videos is not very high, but it is sufficient to be confident that successive discharges initiate and develop in locations that are favourable (constitute low electrical resistance paths) because of microstructural changes ("damage") that arose there during previous discharges.

The region from which light is emitted during a cascade appears to be of the order of several tens of microns in diameter, although there is evidence that it is smaller for thinner coatings than for thicker ones – see Fig. 4. This appears to be a consequence of the discharges themselves being larger (more energetic and longer-lived) with a thicker coating, rather than the location drifting around more in that case. These images suggest that each discharge in a cascade occurs at exactly the same location as previous ones in the sequence, at least within the available resolution. It's not surprising that the thickness of the coating has an effect on the details of how these discharges and cascades take place, but it seems likely that the sequence of events is similar across a wide range of thickness.

The nature of the microstructural "priming" of the site is not entirely clear, but it is presumably related to the formation of microcracks, porosity etc., that may or may not become filled with electrolyte before the next discharge. The characteristic time between discharges could be related to the flow of electrolyte into these regions, although it also seems likely that some redistribution of charge is required in the vicinity (in the electrolyte and coating) before conditions become established for a new discharge to initiate.

4.2. Oxidation associated with individual discharges

It's long been clear that for PEO, unlike conventional "electrochemical" processes such as electro-plating, it's not possible to

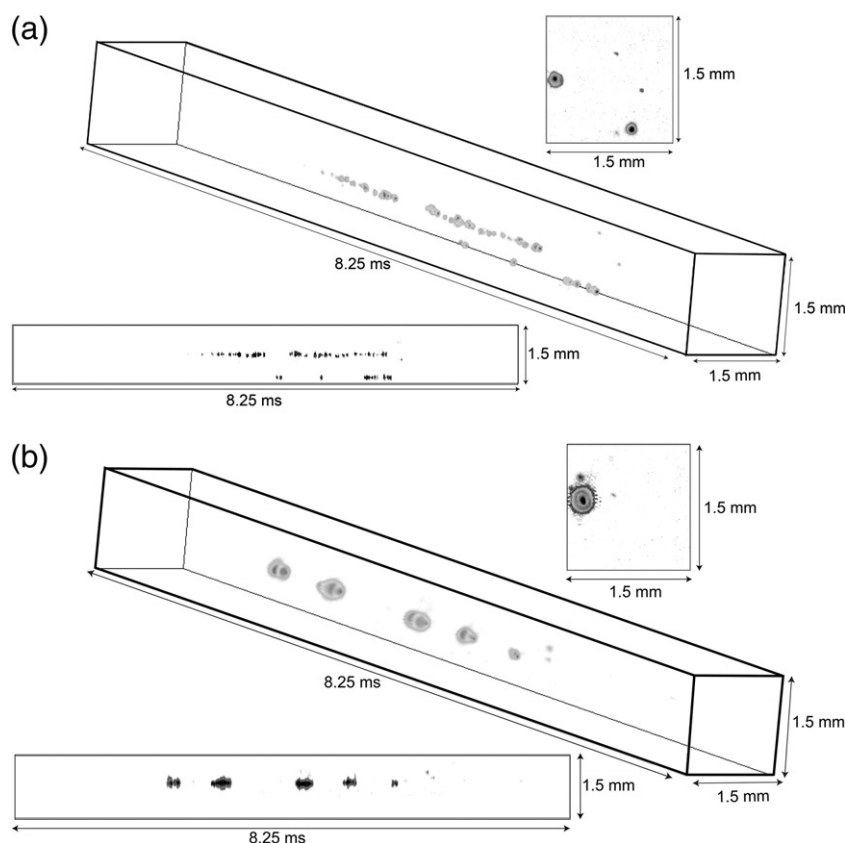


Fig. 4. 3-D perspective and 2-D projection views of a stack of images (with reversed contrast), representing periods of 8.25 ms duration, for coatings with approximate thicknesses of (a) 5 μm and (b) 50 μm .

associate a given amount of “deposition” or “conversion” with a certain quantity of charge (via the Faraday constant). Indeed, the concept of the “efficiency” of a PEO process, in terms of comparing the energy consumed with the “minimum” energy required, is not a valid one (since, in principle, oxidation of the metal should release energy, rather than consume it). Nevertheless, there is considerable interest in evaluating the energy consumption per unit volume of coating produced, understanding its origins and, if possible, minimising its value.

Taking typical (order of magnitude) values, the rate of PEO growth is $\sim 1 \mu\text{m min}^{-1}$, i.e., $\sim 15 \text{ nm s}^{-1}$, over a wide range of coating thickness. Recognising that there is often an increase in volume as an oxide forms from its metal – the Pilling–Bedworth ratio for Al is about 1.28, that the oxide is quite porous and that there is often some “precipitation” from the electrolyte, the rate of consumption of the substrate might thus be $\sim 10 \text{ nm s}^{-1}$. A typical corresponding current density can be taken as $\sim 10 \text{ A dm}^{-2}$, occurring in the form of discrete discharges – each of which carries [5], say, a few hundred nC of charge, although it must be recognised that discharges vary considerably in intensity, even for a given coating thickness, and also tend to become more intense as the thickness increases. This current density therefore corresponds to about 10^9 discharges per m^2 per second, or about 10 discharges within 1 mm^2 in 10 ms. Recognising the crude nature of the estimate, this is broadly consistent with the observations presented here.

The substrate consumption rate of 10 nm s^{-1} corresponds to $10 \mu\text{m}^3 \text{ mm}^{-2} \text{ ms}^{-1}$, so one discharge consumes $\sim 10 \mu\text{m}^3$ of Al (creating $\sim 15 \mu\text{m}^3$ of coating). In terms of energy consumption, this represents $\sim 10^{13} \text{ J m}^{-3}$ of coating (since the energy of a discharge [5] is typically $\sim 100\text{--}200 \mu\text{J}$). This is broadly consistent with macroscopic electrical power consumption data. For example, Matykina et al. recently reported [20] very similar values (expressed as $\sim 3 \text{ kW h m}^{-2} \mu\text{m}^{-1}$)

obtained from external electrical measurements (current density and RMS voltage). They also showed that (relatively small) reductions in overall power consumption could be obtained by growing thicker “precursor” layers of porous alumina under conventional anodisation conditions – i.e., with no discharge formation.

An energy consumption rate of 10^{13} J m^{-3} of coating equates to $\sim 200,000 \text{ kJ mole}^{-1}$ of alumina produced. This is a high value, particularly when it’s recognised that the thermodynamic change in energy associated with the oxidation is $\sim 1500 \text{ kJ mole}^{-1}$ of alumina (and that it is negative, rather than positive!). There should thus be considerable scope for energy saving, provided that the mechanism of exposing the substrate to oxygen can somehow be made more efficient. A potentially promising direction for this is to reduce the energy of each discharge, possibly by limiting the voltage at which it is initiated.

5. Conclusions

The following conclusions can be drawn from this work, which has involved high speed video imaging of the free surface of Al samples during PEO processing at 50 Hz AC:

- Individual discharges (light emission events) tend to occur in sequences (“cascades”), with lifetimes from a few microseconds to several tens of microseconds and (“incubation”) periods between them from tens to hundreds of microseconds. They take place during parts of the anodic half-cycle where the applied potential is sufficiently high ($> \sim 300 \text{ V}$) and extend over at least several cycles.
- A particular cascade occurs in a well-defined physical location, with successive light emission events having similar radii and

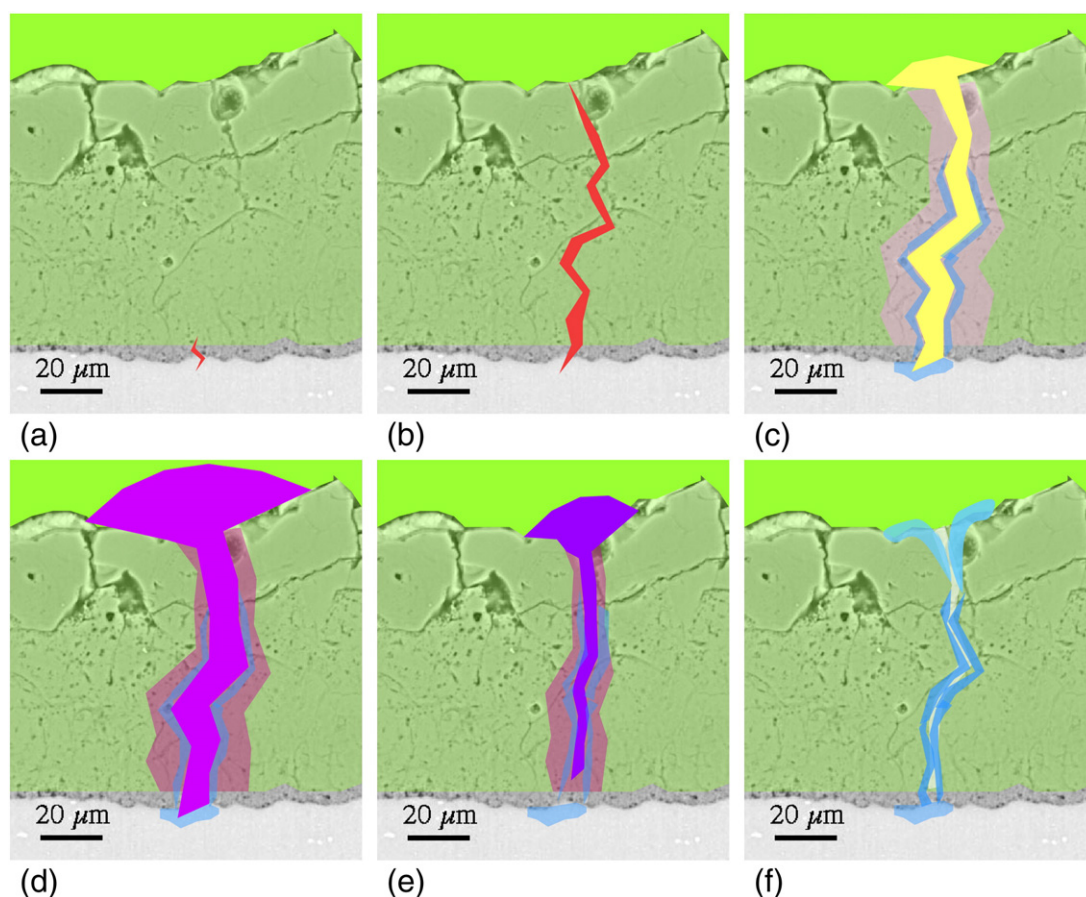


Fig. 5. Schematic depiction of the sequence of events during a single discharge, showing: (a) initial electrical breakdown, (b) development of the plasma channel through the coating thickness, (c) initial bubble growth and formation of oxide in the plasma, (d) bubble expansion and heating of region around discharge, (e) shrinkage and cooling as the plasma resistance rises, causing the current to fall, and (f) final quenching and expulsion of some liquefied oxide from the channel.

being centred on the same point (within the linear resolution of the images, which was 12 μm).

- (c) As the coating thickness increases, most of the characteristics remain qualitatively unaltered, but there is a tendency for the light emission to have a larger radius and greater intensity with thicker coatings. The diameter of the light-emitting region appears to vary from $\sim 50\text{ }\mu\text{m}$ for a thin (5 μm) coating to $\sim 150\text{ }\mu\text{m}$ for a thicker ($\sim 50\text{ }\mu\text{m}$) coating. It may be that these dimensions relate primarily to the gas bubble forming above the channel, rather than to its core within the coating. Discharge lifetimes, and incubation periods, also tend to increase as the thickness is raised.
- (d) An order of magnitude estimate is presented relating to substrate oxidation associated with individual discharges. It is noted that energy consumption during the process is relatively high. Improved understanding of discharge characteristics may point the way towards promising measures to reduce this.

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