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Time dependent statistics of plasma discharge parameters during bulk AC plasma electrolytic oxidation of aluminium

C.S. Dunleavy*, J.A. Curran, T.W. Clyne

Department of Materials Science & Metallurgy, Cambridge University, Pembroke Street, Cambridge CB2 3QZ, UK

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ABSTRACT

A method for the measurement of parameters of plasma discharge events during plasma electrolytic oxidation processing is detailed and applied to AC plasma electrolytic oxidation of aluminium. Data were obtained for processing durations from 2.5 to 40 min. Statistical distributions of plasma discharge parameters such as duration, peak current and charge transferred, are measured and presented as functions of processing duration. Event durations spanned 10–400 μs. Discharge currents were from <10 mA to more than 100 mA. Charge transfer by single events ranged from <1 μC to over 20 μC. The frequency of plasma discharges per unit time and area was determined throughout processing, falling from initial values in the range 300–350 mm^{-2} s^{-1} to fewer than 50 mm^{-2} s^{-1} after 1000 s of processing. A correlation between the upper bound of plasma electrical energy dissipation and the typical size of coating surface features (represented by coating roughness) is demonstrated. Quantitative relationships between discharge duration, peak current and the applied voltage are presented and compared to previously published data for a simpler, but less representative of coating deposition, experimental DC plasma electrolytic oxidation system. It is demonstrated that plasma electrolytic oxidation plasma discharge current is bounded by the applied voltage during processing.

1. Introduction

1.1. Properties and applications of plasma electrolytic oxide coatings

The surface modification technique known as plasma electrolytic oxidation (PEO), and alternately as micro-arc oxidation (MAO), may be used to produce oxide coatings on a variety of metallic substrates, including aluminium, magnesium and titanium. Oxide coatings are deposited on aluminium or magnesium for the purposes of protection against wear, corrosion, or both. Coatings on titanium have been investigated for potential applications relying on the biocompatibility or photo-activity of titania. The process involves high voltage electrolysis, leading to dielectric breakdown of the growing oxide coatings, which produces the many bright and short lived plasma discharges which are thought to be a crucial element of the coating formation mechanism.

Oxide coatings generated by PEO on aluminium generally contain a mixture of the α and γ phases of alumina, and when silicon containing additives are used, alumino-silicate phases including mullite [1–7]. Fractions of the α alumina phase as high as 40% by volume have been reported [5]. The presence of significant volume fractions of crystalline phases is generally regarded to explain the reported hardness of PEO coatings on aluminium, up to 16–25 GPa [1,2,5], and local elastic moduli from nano-indentation in the range 100–400 GPa [1,2,5]. Those elastic modulus values are local, and measurements of the elastic modulus of bulk coatings have reported much lower values in the range 10–50 GPa [5]. This combination of high hardness and low bulk stiffness is attractive for wear protection.

The much lower bulk coating stiffness, when compared to the local values from nano-indentation, is probably the result of relatively high levels of interconnected porosity, reported to be 20% by volume for alumina PEO coatings [8]. This porosity is related to commonly observed features of PEO coatings, including microcracks and residual pores from plasma discharges [3–5,7,9–12]. Owing to high porosity levels, when PEO coatings are used for corrosion protection, they are best used in conjunction with a secondary treatment such as painting or infiltration with a polymer to seal the porosity.

1.2. Background on the properties of PEO plasma discharges

The discharge events visible as bright “sparks” or “arcs” on the surface of substrates undergoing PEO processing are integral to the coating growth mechanism. Efforts to optimise the production of

* Corresponding author. Tel.: +44 7751877212.
E-mail address: csd30@cam.ac.uk (C.S. Dunleavy).

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oxide coatings by PEO have largely been limited to empirical studies of processing conditions, and comparatively little is known about the properties of the plasma discharges. There has been increasing interest in understanding the mechanisms which allow surfaces containing high temperature phases such as α-alumina to be fabricated under conditions of ambient temperature and pressure [13–26]. This manuscript describes the dynamic measurement of plasma discharge parameters during PEO processing. These plasma discharges create new coating material by providing a mechanism for mass transport through the oxide coating [27,28], circumventing diffusion limited growth rates. Additionally the heating effect of the discharges on existing coating material has been suggested to be important in the development of coating phase structures [1–7]. As such, any attempt to understand the microstructure and properties of PEO coatings must include a consideration of the plasma discharges which create and modify the coatings.

Plasma discharge durations of ~200 μs have been reported for Ni plated steel [29]. The present authors previously reported discharges through Al PEO coatings spanning the range from 10 to 160 μs [16,18]. Theoretical estimates of the duration required to cause observed local coating melting of an alumina PEO coating have been used to postulate a range from 250 to 3500 μs [6]. A range of plasma durations from 50 to 4000 μs has been reported for Mg PEO [13], though the longer discharge lifetimes in that work were measured using camera exposure times of 185 μs, and might have been overestimated due to recurring discharge events at the same spatial location. Discharges occurring in "cascades" with separations as short as 10–100 μs between events have been reported for Al [18], and the possibility of discharges recurring rapidly at the same site in any PEO process must be considered during any study of discharge duration. A recent study of Ti PEO processing reported discharge durations ranging from <10 μs up to 5 ms [19]. The same work demonstrated that discharge events were extinguished during cathodic polarisation of the sample in AC PEO processing, before recurring at the same location during subsequent periods of anodic polarisation. Such persistence was reported for periods ≤200 ms, spanning up to 20 cycles of positive and negative voltage.

Information about discharge current levels is sparse, in part because it is much harder to obtain, and in part because, unlike optical monitoring, there is usually some unavoidable perturbation of the system being investigated. Discharge currents of 52 and 70 mA were reported for Ni plated steel [29]. Recent works by the present authors reported values spanning the range 4–75 mA [16,18].

The apparent radii of discharges were estimated from Ti processing to range from 35 to 185 μm [30], and 90 to 440 μm [31]. Data from the latter study were presented as apparent areas, and have been converted, assuming circular discharges, for comparison. Discharge areas have been reported from Al PEO, which, if again assumed to be circular, would indicate discharge radii in the approximate range of 100–300 μm [6]. Radii spanning the range from 35 to 500 μm are reported from PEO of Zircaloy-2 [14]. Apparent discharge areas reported by for PEO of Ta would suggest a range from 90 to 300 μm [32], when converted to radii assuming circular discharges. Literature data on discharge plasma size are reasonably consistent, and span a range from tens to hundreds of microns, for a wide variety of substrate types.

Plasma discharge event rates in the range 10^2–10^3 mm^{-2} s^{-1} were reported from optical studies of PEO on Mg with 185 μs exposure times [13]. Discharge rates reported for PEO of Ti rose from 5 mm^{-2} s^{-1} during early processing, to as high as 30 mm^{-2} s^{-1} after 800 s [30]. This study applied optical imaging with 10 ms exposure durations, as did a study of Ti PEO processing [31] which indicated a different trend. The study reported spatial densities in cm^{-2}, which may be used as the basis for an estimate of discharge rates by dividing by the camera shutter speed of 10 ms, if it assumed that no plasma discharges repeat at the same location within the exposure. Such estimates, based on the more recent study [31], suggest initial rates of 230 mm^{-2} s^{-1}, falling to 30 mm^{-2} s^{-1} after 120 s of processing, then remaining constant till the end of processing after 1800 s. A similar trend is estimated based on reported plasma spatial number densities for PEO on Ta [32], with initial rates of 230 mm^{-2} s^{-1} falling to 50 mm^{-2} s^{-1} by 300 s of processing, and remaining almost constant to the end of processing after 2700 s.

Estimates of plasma discharge temperature have been made from optical emission spectroscopy. Temperatures have been estimated to lie in a lower range of 3000–7000 K from some emissions, typically associated more with components from the electrolyte, whereas other emissions, typically from substrate elements or singly/doubly ionised species suggest higher temperatures in the range 10,000–30,000 K [18,20–24,31,32]. Corresponding electron density estimates span from 10^{15} cm^{-3} to 10^{17} cm^{-3}. The very different values are often attributed to the existence of different 'types' or 'modes' of plasma discharge, or a hot core and cooler periphery. However since all optical emission data has been accumulated across many thousands of plasma discharges, it has not been possible to be sure what the cause of these widely varying values of temperature and electron density might be.

The present work builds on previous studies by the authors, which have predominantly focused on Low Power DC Testing of coatings pre-deposited using an AC PEO process [16,18], hereafter abbreviated to LPDCT. Some limited data relating to discharges captured during in situ monitoring of Full Power AC PEO processing have previously been published [18], hereafter abbreviated to FPAC. In previous work, the FPAC data covered a range from 19 to 21 min into processing. The present study extends that range to provide PEO discharge parameter data from the application of FPAC to an AC PEO process from 2.5 to 40 min of coating deposition.

Descriptions of the FPAC methodology for obtaining PEO discharge event data from full scale PEO coating deposition, and the present limitations of this method, are presented in this Section 2. PEO discharge rates (mm^{-2} s^{-1}) are presented as a function of processing duration in Section 3.2. The time-dependent statistical distributions of important discharge parameters presented in Section 3.3 constitute a comprehensive set of PEO data, with the potential for providing important insights into the processes which create these functional oxide surfaces. A comparison of coating surface features and the upper bound of plasma discharge energy dissipation is presented in Section 3.4.

The authors have previously published data from LPDCT which suggested the existence of correlations between PEO discharge parameters such as the voltage at initiation, V_{init}, the peak current reached during the discharge, I_{peak}, and the discharge event duration, t_{event} [16]. In Sections 3.5–3.7, the existence of the same relationships is confirmed for data from FPAC, and comparisons are made to relationships previously observed for discharges during LPDCT. In this paper it is shown that the upper bound of discharge event I_{peak} values is constrained by the applied voltage during processing, which has important implications for understanding and controlling practical, industrial PEO coating deposition processes.

2. Experimental procedures

2.1. PEO processing

Experiments were performed in a 10 kW 50 Hz AC unit, described in a previous publication [18]. The electrolyte used was a commercially-available solution of approximate composition 1–2 g l^{-1} KOH, 3–5 g l^{-1} Na_2SiO_3 and 3–5 g l^{-1} $Na_4P_2O_7$. The conductivity of the electrolyte was 5.1 ± 0.1 mS and the pH was 10.9 ± 0.1. The samples were composed of a small area, A_{sm},