



Recent advances in energy efficient PEO processing of aluminium alloys



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Abstract: Plasma electrolytic oxidation (PEO) coatings developed under voltage-controlled mode on various commercial wrought, gravity cast and rheocast aluminium alloys were discussed with respect to enhancement of their tribological and corrosion performance and minimization of the PEO energy consumption. It is demonstrated that use of conventional porous anodic film precursors reduces the PEO energy consumption by up to 50%. The wear of 6082 alloy with PEO coatings with added α -Al₂O₃ particles is two times lower compared with electrolytic hard chrome. The long-term corrosion resistance of the PEO-coated A356 rheocast alloy is enhanced via use of a precursor and hydrophobic post-treatment.

Key words: aluminium; anodizing; plasma electrolytic oxidation; wear; corrosion

1 Introduction

1.1 Fundamentals of PEO process

Plasma electrolytic oxidation (PEO) is variously known as micro-arc oxidation (MAO) [1], spark anodizing [2], anodic oxidation under spark discharge [3] and electrochemical microplasma process [4,5]. This terminology reflects several basic facts of PEO: 1) it is an oxidation process that occurs in aqueous electrolytes on the anode; 2) PEO initiates as conventional anodizing with growth of a barrier oxide film; 3) as the film thickness and hence the voltage increase, the dielectric breakdown of the film and ionization of the oxide material and accompanying gas (i.e., generation of plasma) occur, which are manifested as numerous short-lived discharges. The growth of the oxide film continues inside the discharge channels under the high temperature and pressure, which enable generation of crystalline phases, comprising the oxides of the substrate elements and new insoluble compounds which consist of the substrate and electrolyte species [6]; the latter is formed as a result of the electrolyte thermolysis and plasma chemical reactions occurring at the discharge sites.

PEO processing is most commonly used for

aluminium [7], magnesium [8] and titanium alloys [9] but can be extended to any alloy that can be conventionally anodized, for instance, zirconium [10], tantalum [11] and niobium [12,13]. PEO coating can be generated by applying direct, alternating current, unipolar or bipolar pulsed current or voltage (Fig. 1(a)). The introduction of the negative pulse and a pause (“time off”) between the pulses facilitates quenching the microdischarges and prevents their transition into more powerful and destructive arc discharges. In aluminium alloys, the DC mode generates thinner coatings lacking the intermediate dense layer rich in α -Al₂O₃ [14], which is formed in AC and bipolar modes. The bipolar mode has the advantage of two DC power supplies separately controlling the positive and negative pulses so it is easy to vary the duty cycle and time off period between the pulses. From the industrial point of view, this mode of control permits achievement of higher power and frequencies up to several thousands Hz [15]. The PEO power supplies may differ with respect to the input signal control mode (Fig. 1(b)). There are some researches that use current as an input signal, in which the voltage increases in accordance with the increase of the coating resistance [16]. The other option is to input constant amplitude, peak-to-peak or rms voltage and limit the maximum current [17]. In this case, the current peak

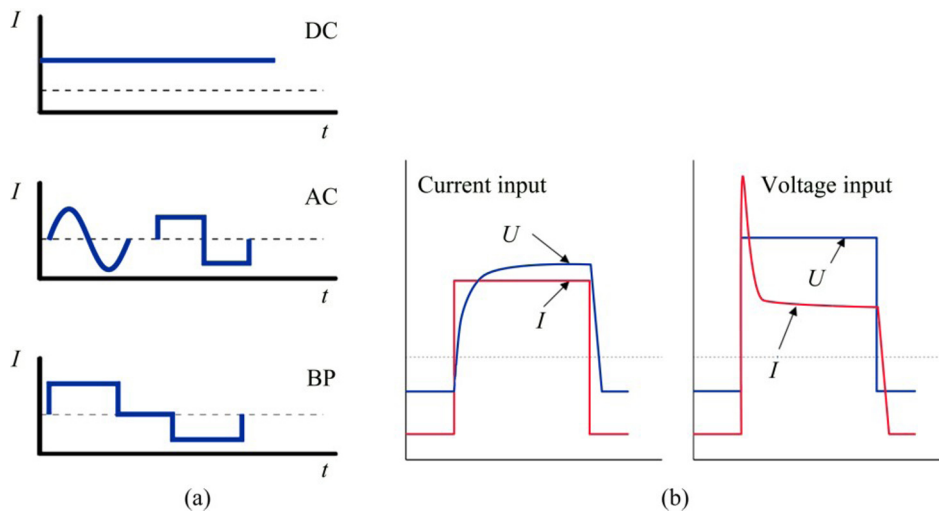


Fig. 1 Modes of PEO processing (a) and input signal control (b)

with the following current decay will be observed at the output as the impedance of the coating increases.

Table 1 summarizes the key characteristics of the coatings on aluminium alloys produced by PEO and conventional hard anodizing [15,18–21]. It is evident that PEO requires higher energy expenditure due to the considerably higher voltages and current densities applied. On the other hand, neutral and alkaline PEO electrolytes are environmentally friendly and easy to recycle compared with concentrated acids used in conventional anodizing.

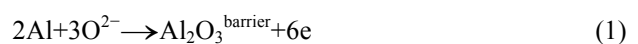
High temperature phases convey some exceptional properties to the PEO coatings on Al alloys [22,23], the most important properties are high hardness, thermal and wear resistance, associated with the presence of α - Al_2O_3 in the coating. Hard anodizing, on the other hand, generates amorphous alumina, its high thickness (compared with other conventional anodic alumina films) being the only reason for its relatively high hardness. PEO coating growth rate can be 2–3 times higher than that of hard anodizing. However, with respect to energy expenditure PEO coatings can be 20–30 times more costly than conventional anodizing. Currently PEO is commercially used for niche applications in aerospace, gas and oil industry, tools, heavy machinery and transport applications, and can be particularly attractive as a greener alternative for the applications seeking to substitute heavy materials (e.g., steels) by lightweight ones with equivalent performance and, in case of transport applications, to reduce the mass and fuel consumption and CO_2 emission. A further input (design and optimisation of PEO process parameters), is needed; however, in order to increase the energy efficiency of the PEO process and make it economically viable for mass production applications.

Table 1 Comparative characteristics of conventional anodizing and PEO of Al [15,18–22]

Characteristic	Conventional anodizing	PEO
Voltage/V	15–160	300–600
Current density/ ($\text{mA}\cdot\text{cm}^{-2}$)	≤ 50	100–500
Electrolyte	Acid	Dilute neutral or alkaline
Substrate pretreatment	Critical	Not too important
Temperature control	Precise	20–50 °C
Thickness/mm	5–50	50–150
Growth rate/($\text{m}\cdot\text{min}^{-1}$)	≤ 1 –1.5	2–5
Microhardness (HV)	≤ 500	1400–1700
Wear/($\text{mm}^3\cdot\text{N}\cdot\text{m}^{-1}$)	$(3\text{--}6)\times 10^{-4}$	$(0.33\text{--}3.3)\times 10^{-7}$
Dry friction coefficient	0.35	0.17–0.32
Fatigue limit (10^7 cycles)/MPa	100–210	160–270
Salt spray (ASTM B117)/h	300–1000	2000–7000
Energy consumption/ ($\text{kW}\cdot\text{h}\cdot\text{m}^{-2}\cdot\text{m}^{-1}$)	0.1–0.5	3–26.7

In order to understand why PEO needs more energy than conventional anodizing, one must look at the processes consuming energy in both cases. Porous and barrier anodic films can be grown in acid (e.g., chromic, sulphuric, oxalic, phosphoric and their mixtures) and alkaline (e.g., ammonium pentaborate, sodium phosphate) solutions, respectively. The followings are the processes involved in conventional porous film growth in acids.

A barrier film formation:



Dissolution of some of the barrier alumina regions:

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