Applied Surface Science 356 (2015) 135–141

Contents lists available at ScienceDirect

Applied Surface Science

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

Influences of urea and sodium nitrite on surface coating of plasma electrolytic oxidation

Shang-Chun Yeh[a], Dah-Shyang Tsai[a,*], Sheng-Yong Guan[a], Chen-Chia Chou[b]

[a] *Department of Chemical Engineering, National Taiwan University of Science and Technology, 43, Keelung Road, Section 4, Taipei 10607, Taiwan*
[b] *Department of Mechanical Engineering, National Taiwan University of Science and Technology, 43, Keelung Road, Section 4, Taipei 10607, Taiwan*

ARTICLE INFO

Article history:
Received 30 January 2015
Received in revised form 25 April 2015
Accepted 6 August 2015
Available online 10 August 2015

Keywords:
Plasma electrolytic oxidation
Urea
Sodium nitrite
Bipolar pulse current
Morphology
Aluminum alloy

ABSTRACT

Urea and sodium nitrite are generally viewed as nitridation additives in the electrolyte for plasma electrolytic oxidation (PEO) of aluminum alloys. We study the influences of these two convenient chemicals in presence of sodium aluminate and find very different effects on film growth. Urea addition enhances the nitrogen content of PEO layer, diminishes the layer thickness, increases the porosity, interferes with the α-alumina formation, and promotes precipitation in the electrolyte. Hence, the electrolytic urea content ought to be maintained less than 45 g dm^{-3}. On the other hand, sodium nitrite behaves like an oxidation additive, more than a nitridation additive. $NaNO_2$ addition effectively introduces nitrogen in the PEO layer at low concentration, yet the nitrogen content of oxide layer decreases with increasing $NaNO_2$ concentration. The effects of $NaNO_2$, such as increasing layer thickness, reducing porosity, promoting α-alumina formation are attributed to oxidation enhancement, not because of nitridation.

1. Introduction

The surface modification technique of plasma electrolytic oxidation (PEO) has proven valuable in growing ceramic layers to protect the lightweight metal surface, such as aluminum, magnesium, titanium alloys. Compared with its counterparts of vacuum-based plasma technology, the equipment of PEO costs less, and requires less effort to install. The resulting oxide layer, although complex in structure, bonds the substrate tightly and offers a combination of high wear resistance, corrosion resistance, mechanical strength, and thermal insulation at low energy expense [1–6]. The PEO coating technology does not involve chromium, and its water-based electrolyte is typically alkaline, less aggressive toward the environment. The oxide growth takes place on the anode with high-voltage polarization to generate localized electrical sparks and oxidative plasma in an envelope of vapor and gases surrounding the electrode. The spark durations appear on the time scale of millisecond [7]. And the densely populated sparks are micrometer in size, judging from the craters that electric breakdowns leave behind [8]. Being characterized with localized spark discharge and plasma, the PEO technique is also known as micro-arc oxidation, spark anodizing, or microplasma oxidation.

PEO coatings are typically performed with a pulsed current of bipolar waveform containing both anodic and cathodic components [9–11]. Compared with the unipolar mode, the bipolar current mode is reported to produce a relatively uniform layer of compact structure with less defects and pores [12,13]. Major growth-related events, such as charge-transfer reaction, melting, recrystallization, ion diffusion occur on the surface of the work piece when imposing the anodic component. However, the involved anodic reactions may or may not result in film growth. The overall current efficiency is estimated 10–30%, spent on the oxide layer formation [14]. For example, oxygen evolution reaction always consumes electricity, since the electrode potential goes up to several hundred volts during the anodic excursion to initiate plasma, well beyond the electrolysis potential of water. Yet only a fraction of the evolved oxygen takes part in oxide growth. Electrical discharge at the electrolyte/solid interface redirects the evolved oxygen, also the surrounding electrolyte, dissolved anion, into the oxide formation through plasma action. Therefore, research attention is focused on the plasma generated by those micro-arcs, which are confined in the porous structure. It is generally believed that those high-energy events, proceeding in the local vapor envelope, dominate the coating growth mechanism and grow the well-adhered layer [15]. The electron temperature at the arc center is reported to reach ∼16,000 K, with a low temperature ∼3500 K in the peripheral region, estimated with the optical emission spectra [8]. Meanwhile, the surrounding water is cold, maintained at low

---

* Corresponding author.
E-mail address: dstsai@mail.ntust.edu.tw (D.-S. Tsai).

http://dx.doi.org/10.1016/j.apsusc.2015.08.043
0169-4332/© 2015 Elsevier B.V. All rights reserved.

temperature ~330 K. When the ceramic layer grows sufficiently thick, the micro-arcs become sparse due to a substantial ohmic resistance. And the scarcity of sparks suggests the end of modification process.

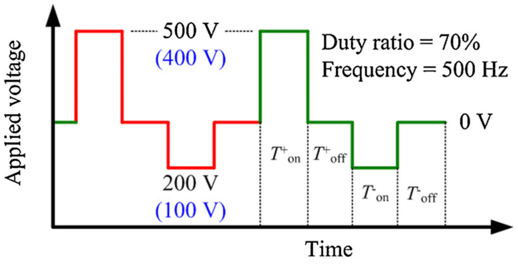
It is of interest to incorporate nitrogen into the surface coating of aluminum alloy via PEO. The nitrogen bond of covalent nature has the potential to raise the low thermal conductivity of oxide and other mechanical properties [16]. Most of aluminum nitride or oxynitride film syntheses have been done under high vacuum conditions [17]. And the only known electrochemical synthesis has been performed in the molten salt of LiCl–KCl–Li_3N under an argon atmosphere of the dry box, which is a different technology [18]. A few recent studies have reported that nitrogen can be incorporated in the PEO layer growth through additions of urea, sodium nitrate or nitrite in the aqueous electrolyte [19–21]. In this work, we study the electrolytic effects of urea and sodium nitrite on the PEO modification of 6061 aluminum alloy. Through comparison of surface features and phase variation with respect to electrolyte content, we report the dissimilar roles of urea and sodium nitrite.

2. Experimental

In this study, the 6061 substrates were sliced in form of 8.0 mm thick disk using a cylindrical bar of 30 mm in diameter (weight fraction: Fe 0.7%; Si 0.4–0.8%; Cu 0.15–0.40%; Mn 0.15%; Mg 0.8–1.2%; Cr 0.04–0.35%; Zn 0.25%; Ti 0.15%; balance Al). These samples were manually ground and polished in water with sandpapers of increasingly finer grain, starting from 400, 800, 1000, and finally 1500 grit. The ground samples were then degreased with acetone and rinsed with water. In each PEO experiment, one disk sample was electrically connected to a threaded stainless steel rod, and immersed in electrolyte. The electrical contact, along with a considerable section of the rod, was wrapped up with Teflon tape such that it would not make direct contact with the electrolyte. Only the 6061 surface, as the working electrode, was interfaced with the electrolyte during surface modification.

A DC supply of nominal power 10 kW (GX-100/1000, ADL GmbH) was connected with a personal computer to control the bipolar waveform being sent to the working electrode. The 6061 disk electrode was vertically placed at the central position surrounded by a counter electrode of stainless steel mesh which was ~13 cm in diameter. The electrolyte solution was 2.0 dm^3 in volume, cooled with circulating water. The conductivity and the pH value of electrolyte were measured with a benchtop meter (3107 Kit, JENCO). Most of surface modifications lasted for 5 min, counting from emergence of the micro-arcs, and only a small amount of water was lost due to electrolysis and evaporation. Some modifications persisted longer. The electrolyte was prepared with deionized water (resistivity 1 MΩ cm, RDI-20 RO water purifier), and calculated amounts of NaOH (reagent grade, Aldrich), $NaAlO_2$ (reagent grade, Aldrich), along with urea or sodium nitrite. The urea-containing electrolyte was denoted as electrolyte-I, the electrolyte of $NaNO_2$ was electrolyte-II. The electrolyte compositions were intentionally kept simple to examine the effects of urea and sodium nitrite.

Fig. 1 shows the specific contents of electrolyte-I, -II, and the parameters of bipolar pulse current. The as-prepared electrolyte-I had a pH value ~11.8, and an ion conductivity of ~16 mS cm^{-1}, measured at room temperature. As for the electrolyte-II, its pH value slightly increased with increasing $NaNO_2$ content, between 11.9 and 12.2, and the conductivity was 19–20 mS cm^{-1}. After modification, the pH value decreased slightly. The positive and negative voltage polarizations were set at +500 and −200 V in electrolyte-I; while those in electrolyte-II were +400 and −100 V. The frequency, defined as $(T^+_{on} + T^+_{off} + T^-_{on} + T^-_{off})^{-1}$, was 500 Hz. T^+_{on} and T^-_{on} were the duration periods of positive and negative pulses; respectively. T^+_{off} and T^-_{off} were the resting periods between the positive and negative pulses. The duty ratio, defined as $T^+_{on}/(T^+_{on} + T^+_{off} + T^-_{on} + T^-_{off})$, was set to be 70%.



Electrolyte-I	
$NaAlO_2$	8 g dm^{-3}
NaOH	2 g dm^{-3}
Urea	10 – 500 g dm^{-3}
Electrolyte-II	
$NaAlO_2$	8 g dm^{-3}
NaOH	2 g dm^{-3}
$NaNO_2$	0.1 – 1.3 g dm^{-3}

Fig. 1. Electrolyte compositions and the pulse waveform of power supply in this PEO study. Note the positive voltage is 500 V for electrolyte-I and 400 V for electrolyte-II.

Phase analysis of the PEO layers was performed with an X-ray diffractometer for thin film studies (D8 High Resolution Diffractometer, Bruker). The collected powder sample of electrolyte precipitate was dried at 120 °C overnight and analyzed using another diffractometer (D2 phraser, Bruker). Both were equipped with a copper Kα radiation source and nickel filter. Morphology of the PEO surface was examined with a scanning electron microscope (SEM, JSM-6500F JEOL), equipped with an energy dispersive spectrometer (EDS) for elemental analysis (INCA, Oxford). Accuracy of the EDS system was regularly checked with aluminum and copper Kα lines, low-energy inspection was done with the carbon Kα line. In calibration for the nitrogen analysis, three reference materials were used; including the pressed pellets of $NaNO_3$ (Aldrich), α-Al_2O_3 (Aldrich), 50 mol% $NaNO_3$ and balance Al_2O_3. The EDS composition was recorded as the average reading of five locations, ~200 × 300 μm^2 in area, randomly chosen on the surface. X-ray photoelectron spectra (XPS) were collected in a Thermo VG Scientific Theta Probe system under the high vacuum condition, ~5×10^{-9} mbar. The Al Kα 1486.6 eV line was the X-ray source and the Ag $3d_{5/2}$ line at 368.26 eV was the calibration reference. Surface cleaning was done by argon ion etching at the sample current 1 μA. The binding energy positions were determined through curve fitting with the mixed 30% Lorentzian and 70% Gaussian curves and Shirley baselines using the Avantage v3.2 software. The PEO modified surface was thoroughly washed with deionized water and acetone and vacuum dried before EDS and XPS analysis.

3. Results and discussion

We designate the PEO modified surface according to the electrolytic content of urea or sodium nitrite. For example, I-20U means the surface has experienced micro-arc oxidation in the electrolyte-I of 20 g dm^{-3} urea. Likewise, II-01N indicates the surface experienced micro-arc oxidation in the electrolyte-II of 0.1 g dm^{-3} sodium nitrite. We also note that the entire period that micro-arc can last is different for each electrolyte composition. The micro-arc period decreases with increasing urea content when performing PEO in the electrolyte-I.