



Coloring the aluminum alloy surface in plasma electrolytic oxidation with the green pigment colloid



Jian-Mao Wang^a, Dah-Shyang Tsai^{a,*}, James T.J. Tsai^b, Chen-Chia Chou^c

^a Department of Chemical Engineering, National Taiwan University of Science and Technology, 43, Keelung Road, Section 4, Taipei 10607, Taiwan

^b Department of Materials Engineering, McGill University, 3610 University Street, Montreal, QC H3A 0C5, Canada

^c Department of Mechanical Engineering, National Taiwan University of Science and Technology, 43, Keelung Road, Section 4, Taipei 10607, Taiwan

ARTICLE INFO

Article history:

Received 5 August 2016

Revised 22 December 2016

Accepted in revised form 16 April 2017

Available online 22 April 2017

Keywords:

Plasma electrolytic oxidation

Green electrolyte

Chromium oxide pigment

Bipolar pulsed current

X-ray diffraction

Duty ratio

ABSTRACT

Chromium oxide pigment is a promising electrolyte additive to green the aluminum alloy surface with plasma electrolytic oxidation (PEO) because of its opacity, outdoor durability, and hardness. Initial coating efforts reveal that pigment and adsorbed dispersant, with extra negative charges, dramatically raise positive current and cause power fluctuations under the constant-voltage mode. Accordingly, research attention is redirected to a search of proper electrical parameters under constant current with a required amount of pigment and dispersant. The parameters for green coating involve; 92 mA cm⁻² in positive and negative current densities, 10–20% in duty ratio, 500 Hz in frequency, when the electrolyte is formulated with 10 g dm⁻³ pigment and 0.8 g dm⁻³ dispersant. Microstructure analysis shows that the resultant coating comprises two layers of different compositions; the top layer is a mixture of chromia and alumina, a dense layer underneath involves nearly 100% alumina. Phase analysis indicates that the aluminum oxide crystallizes in γ - and α -alumina both. A small amount of α -alumina exists in solid solution with chromium. Although the as-received pigment is oxygen deficient, similar to Cr₂O_{2.4} in crystal structure, the oxidative plasma of PEO converts it into stoichiometric Cr₂O₃.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Plasma electrolytic oxidation (PEO) has developed into a technique of industrial importance for surface protection of lightweight metals and alloys. In PEO, the valve metal surface is immersed in an aqueous electrolyte and subject to high-voltage polarization, strong enough to generate localized electrical breakdowns and oxidative plasma. These discrete micro-discharges induce multiple physical and chemical events, along with fast growth of the oxide coating. Hence the oxide layer thickness and the impedance of the electrolytic system increase with coating time [1–3]. It is generally agreed that the high-energy events, occurring in the short bursts of electrical discharge, dominate the growth mechanism of coating and its associated microstructure and properties. Therefore, PEO is also known as micro arc oxidation, spark anodizing, micro-plasma oxidation [4–6].

The aqueous electrolyte is commonly formulated with oxyanions of the desired transition metal or semi-metal, which diffuse and adsorb on the alloy surface. These adsorbed anions transform into oxide deposits via charge-transfer reactions during positive polarization [7,8]. And the deposition rate is accelerated in the high-energy electrical breakdown. Furthermore, the electrical discharges are transitory and the

localized high-temperature events are quenched right away. The crystal only grows for a brief moment. The resultant coating, hence, consists of many defective nanocrystals. When a coating of well-defined crystals is desired, researchers may introduce particles of chosen crystal in form of colloid, and include them through electrophoresis. The suspended particles may be viewed as another type of coating precursors.

Incorporation of α -alumina particles has been investigated in PEO treatment of several lightweight metals, including aluminum alloys [9, 10], magnesium alloys [11,12], and pure titanium [13,14]. Another popular inclusion is the zirconia powder of nanometer size, which have been employed to enhance the toughness and corrosion resistance of magnesium alloys and pure magnesium [15–19], aluminum [20,21], titanium alloys [22–26]. Particles of carbide and nitride can be incorporated too, but less studied in literature [27–30]. Addition of iron particles is suggested to enhance the microwave absorbing properties of PEO coating [31]. In these composite coatings, the bonding between particles and anion-derived oxide often occupies the research attention because of its significance on film adhesion [9,20,32–34]. Another issue, important but seldom discussed, is how to tune the pulsed electricity parameters in the presence of colloid. Evidently, the presence of colloidal particles interfere the surface plasma conditions.

On coloring the PEO coatings, several works have been reported in literature. Ammonium metavanadate, NH₄VO₃, is a popular precursor for a black coating on aluminum alloys [35–37]. Potassium

* Corresponding author.

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

permanganate, KMnO_4 , has been dissolved in the electrolyte to deliver brown color to magnesium alloys [38,39]. Sodium tungstate, NaWO_4 , in electrolyte also blackens the aluminum surface [40,41]. On the other hand, a group of oxide pigments are renowned coloring agents, yet they have not been exploited by researchers. For example, Cr_2O_3 is the main ingredient of color viridian, which is fade resistant under sunshine and rain. This green pigment is an ideal candidate to color aluminum alloys using PEO. Two colors are possible in the Cr_2O_3 - Al_2O_3 binary system. Al-doped chromia is green in color; while Cr-doped α -alumina is ruby red.

In this work, we explore the feasibility of coloring the 6061 aluminum alloy with a colloidal electrolyte of commercially available Cr_2O_3 pigment. The pigment addition is found to alter the plasma conditions and the growth behavior. Therefore, we optimize the electrical parameters of constant-current mode for PEO in colloid. Microstructure and color uniformity of the resulting green coating are also analyzed and discussed.

2. Materials and methods

The disk samples for PEO coating had been cut from a long 6061 aluminum rod. Each piece was 30 mm in diameter, 8 mm in thickness, with a threaded hole on its side. The surface was polished and cleansed thoroughly, $\sim 21.7 \text{ cm}^2$ in area [42]. For each experiment, one disk sample was tightly screwed to a steel rod, placed at the center of the electrolyte. The disk electrode was surrounded by a counter electrode of stainless steel mesh cylinder, 13 cm in diameter. We used a large glass beaker to accommodate the two electrodes, and an aqueous electrolyte of $\sim 2 \text{ dm}^3$ in volume. The electrolytic cell was cooled by circulating water. The 6061 disk electrode and the wire mesh electrode were electrically connected to a 10 kW DC power supply (GX-100/1000, ADL GmbH), which sent the bipolar pulsed current with a square waveform.

There were two steps involved in the coating procedure, as illustrated in Fig. 1. The first step was to grow a white barrier layer. The second step was to coat a green layer. Two types of electrical parameters, constant-voltage and constant-current modes, were implemented. The growth of barrier layer employed the constant-voltage mode. Most of the second steps, green coatings, were performed in the constant-current mode.

Electrical parameters of the first step included 500 Hz in frequency, 70% in duty ratio, 400 V positive and 100 V negative in polarization settings, abbreviated as 400 V (+)/100 V (-). The frequency was defined as $(T_{on}^+ + T_{off}^+ + T_{on}^- + T_{off}^-)^{-1}$, in which T_{on}^+ and T_{on}^- were the duration periods of positive and negative pulses; and T_{off}^+ and T_{off}^- were the resting periods between the positive and negative pulses. The duty ratio was $T_{on}^+ / (T_{on}^+ + T_{off}^+ + T_{on}^- + T_{off}^-)$, denoted as the fraction of oxidation time in the entire working period. Growth of the barrier layer was intended to establish a uniform oxide layer on the alloy surface, such that next pigment deposition entered the stage of micro arcs directly. The electrolyte for barrier layer growth did not contain

pigment, involving 4 g dm^{-3} NaAlO_2 and 1 g dm^{-3} NaOH . The conductivity was measured $\sim 10 \text{ mS cm}^{-1}$. Total PEO time was 5 min. Morphological features of the barrier layer are shown in Figs. S1 and S2 in the Appendix A Supplementary data.

The second step of green coating was carried out in an electrolyte containing pigment and NaAlO_2 , therefore, alumina and chromia were deposited concurrently. In the early phase of this study, several green coatings were done in the constant-voltage mode. The same electrical parameters were adopted just like the first step, that is, 400 V (+)/100 V (-), 500 Hz, and 70% duty ratio. The electrolyte was also the same electrolyte used in the first step, but supplemented with extra pigment colloid such that the electrolyte contained 25 g dm^{-3} chromia pigment (GN-M, Bayer Chemicals) with 2.0 g dm^{-3} Darvan C—N (Vanderbilt Minerals). The pigment colloid had been prepared through two-day ball milling with zirconia balls in a plastic jar.

Constant current was the preferred coating mode for the electrolyte with pigment. The constant-current mode used a different electrolyte formulation. The nominal electrolyte contained 4 g dm^{-3} NaAlO_2 and 0.375 g dm^{-3} NaOH , with 10 g dm^{-3} green pigment and 0.8 g dm^{-3} Darvan C—N. The dispersant concentration was referred as 8 wt% with respect to the pigment weight. The colloidal electrolyte conductivity was $\sim 4.2 \text{ mS cm}^{-1}$, and the pH value was 11.6. Due to the electrolyte difference, the growth of barrier layer and the green coating had to be performed separately. In studying the influences of duty ratio on coating microstructure, we varied duty ratio between 10% and 40%, meanwhile holding positive (I_+) and negative (I_-) currents at 2.0 A, $T_{on}^+ = T_{on}^-$, and frequency 500 Hz.

Dispersion of the green pigment in electrolyte was analyzed with the dynamic light scattering (DLS) technique (Zetasizer, Nano ZS, Malvern). The sample for DLS measurement was a 1/500 dilution of the electrolyte used in PEO, such that the solution was sufficiently transparent for laser light. Phase characterization of GN-M pigment was performed with an X-ray diffractometer for powder analysis (D2 Phaser, Bruker). Phase analysis of the PEO coating was done with another X-ray diffractometer for thin film study (D8 High Resolution X-ray Diffractometer, Bruker). The coating morphology was examined with a scanning electron microscope (SEM, JSM-6500F JEOL), equipped with an energy-dispersive spectrometer (EDS) for elemental analysis (INCA, Oxford). Microhardness of the coating was measured with 0.1 kgf loading force, using a Vickers hardness tester (DVK-1S Matsuzawa).

3. Results and discussion

3.1. Pigment and its dispersion

Homogeneous dispersion of pigment is a prerequisite to ensure a uniform coating in the electrolyte. Fig. 2a shows two DLS results of the pigment colloids dispersed with 8.0 and 5.0 wt% Darvan C—N, prepared as 1/500 dilution of the electrolyte formulation. The as-prepared sol was diluted right after ball milling and its size distribution was measured $\sim 10 \text{ min}$ later. The size distribution of 8.0 wt% is unimodal, showing one sharp peak only. The 8.0 wt% colloid is considered monodisperse, since its polydispersity index (PDI) is only 0.128. If PDI exceeds 0.2, it is considered polydisperse. The average particle size is estimated 351 nm, fairly close to the primary particle size, $\sim 300 \text{ nm}$, which was measured with electron microscopy and provided by Bayer Chemicals. One may question that 8.0 wt% dispersant could be too high, since a regular dispersant content is 3.0 wt% [43]. The content of 8.0 wt% has been chosen through a series of DLS measurements of four colloids. DLS results of the 1.0 and 5.0 wt% colloids display a bimodal distribution. On the other hand, the DLS results of 8.0 and 10.0 wt% have one peak only. Apparently, there are soft agglomerates in the pigment colloids of 1.0 and 5.0 wt%. For comparison purpose, the size distribution of 5.0 wt% is plotted in Fig. 2a. The major peak of 5.0 wt% is similar to, yet wider than, the peak of 8.0 wt%. Its minor peak is located in the range 3000–7000 nm, showing the evidence of agglomerates.

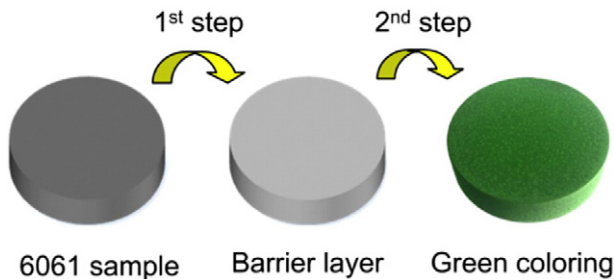


Fig. 1. Two stages of coloration with the green pigment. A white barrier layer is grown first, the green coating is then deposited. Both steps are performed with the PEO technique, though under different conditions.

Download English Version:

<https://daneshyari.com/en/article/5464565>

Download Persian Version:

<https://daneshyari.com/article/5464565>

[Daneshyari.com](https://daneshyari.com)