



# Anodic dyeing of micro-arc oxidized aluminum with a cathodic pretreatment

Chun-Ming Chen<sup>\*</sup>, Hou-Jen Chu, Ju-Liang He

Department of Materials Science and Engineering, Feng Chia University, Taichung City 40724, Taiwan



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## ABSTRACT

Conventional anodized aluminum with diverse colors by surface dyeing has recently become widespread for consumer electronic appliances. Satisfactory performance, though, it failed to present good enough protection purpose. On the contrary, micro-arc oxidation (MAO) is a relatively new anodizing surface treatment to provide very high surface hardness and thus protection purpose but is incompatible with the dyeing process. In this study, we investigated a dyeing method for the MAO treated aluminum alloy by using a cathodic pretreatment to produce micropores over the MAO layer, as a result to absorb the anionic dye in a subsequent anodic treatment, thereby dyeing the MAO layer. The research results showed that the dyed MAO film achieved the optimal color saturation ( $L^* a^* b^*$ ) = (53.55, 1.17, -29.16) when the specimen was immersed in a blue dye to undergo a dyeing process with an applied anodic current of 1 A subsequent to the pretreatment at an applied cathodic voltage of 30 V. Additionally, red and green dyes were also demonstrated to be feasible. Mechanism to make the MAO layer dyeable is proposed.

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## 1. Introduction

Light alloys, composed mainly magnesium, aluminum, and titanium are characterized by high strength-to-weight ratio and are suitable for a wide variety of applications such as automotive, aerospace, and consumer electronics [1]. However, the relatively poor surface properties (e.g. poor corrosion resistance and low hardness) of light alloys have limited choices for surface finishing, where conventional anodizing is most often used to improve the surface properties by generating an oxide film over their surface through electrochemical routes. The grown oxide films, featuring highly regular nano-array porous structure with a good permeability are beneficial for the dye to infiltrate the capillary pores and color the workpiece surface [2–4] (shown in Fig. 1). Therefore, in recent years, conventional anodizing has been an important surface treatment technology in consumer electronics. However, these conventionally anodized films exhibit poor adhesion to a substrate, resulting in poor color durability [5]. On the other hand, micro-arc oxidation (MAO) or known as plasma electrolytic oxidation (PEO), based on a more aggressive anodic oxidation process where a high voltage is applied to a workpiece generating micro-arc discharge over the surface, has been technically well established. This can form a strongly adhered thick ceramic oxidation layer on the metal surface with ceramic

texture, higher hardness and superior corrosion resistance [6,7], as opposed to the conventional anodic oxidized layer.

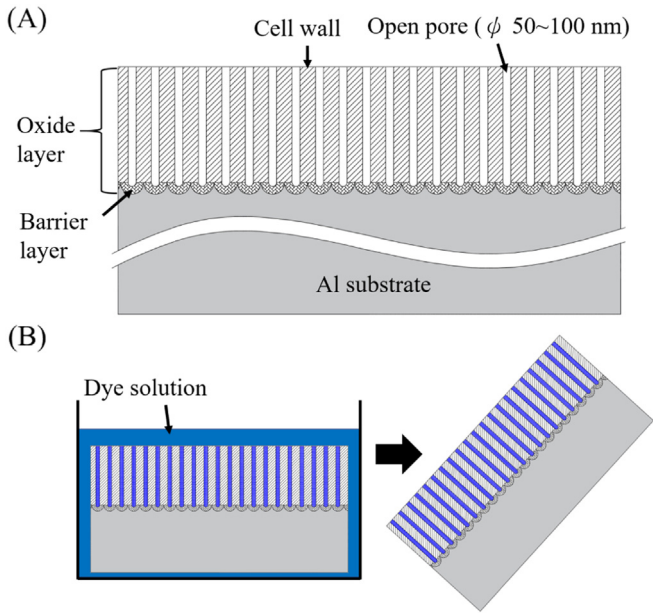
The MAO layers, differing greatly from the conventional anodized layer, are normally characterized by volcanic micrometer-scale pores. The size of these pores results in the failure of the dye to reside in the pores when coloring MAO treated workpieces using dye adsorption [8] (shown in Fig. 2). This gives a great barrier to the success of dyeing MAO films. Therefore, it may not be practically viable to change the color of a MAO film by applying a direct dyeing process. Recently, some studies have attempted to dye MAO films by adding inorganic colorants such as metal salts to the MAO electrolyte [9]. However, possible drawbacks of applying inorganic colorants to the MAO electrolyte may involve the interfering MAO process to affect MAO film adhesion [10] and environmental hazardous usage [11]. Alternatively, a thick electrophoretic deposition (EPD) process subsequent to MAO was developed for coloring MAO films and for the improved corrosion resistance [12–14]. This gives a polymeric coating over the top of the MAO layer, submerging the MAO layer and fading out its ceramic surface texture.

Despite the attractive overall performance of MAO films, the limited color options have imposed substantial restrictions on the application of light alloys to the protective casings of electronic products, for which a diverse range of surface colors is greatly desired by consumers. Given the availability of ceramic oxidation films with a diverse selection of uniform colors and excellent mechanical protection performance, the application of MAO technology may be rapidly promoted. This study aims to develop a simple and cost-effective method for applying a dyeing process directly to the MAO film with its surface retaining ceramic

Abbreviations: MAO, micro-arc oxidation; PEO, plasma electrolytic oxidation; EPD, electrophoretic deposition.

<sup>\*</sup> Corresponding author at: 100 Wenhwa Rd., Seatwen, Taichung City 40724, Taiwan.

E-mail addresses: [p9900093@fcu.edu.tw](mailto:p9900093@fcu.edu.tw) (C.-M. Chen), [jlhe@fcu.edu.tw](mailto:jlhe@fcu.edu.tw) (J.-L. He).

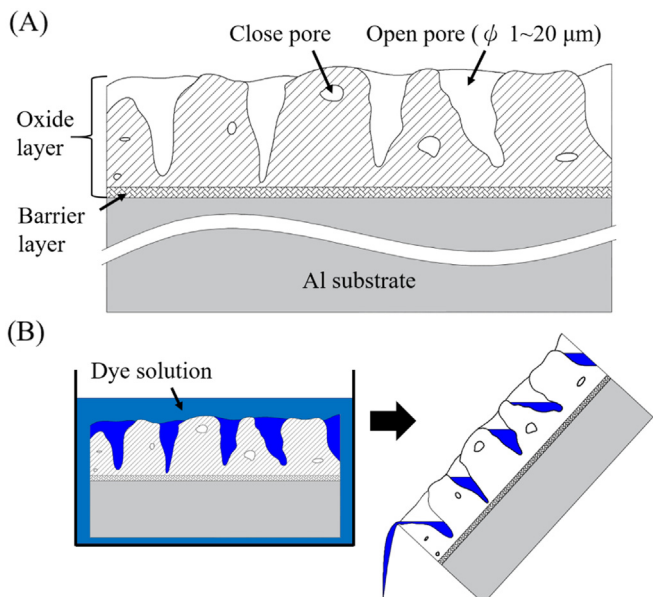


**Fig. 1.** (A) Schematic microstructure of a conventional anodized film and (B) mechanism of dyeing.

texture. The micro-arc treated aluminum workpieces were first cathodically applied in a pretreatment solution, followed by anodic treatment in the dye, which successfully enabled the MAO layer to be dyeable. Based on the microstructural and elemental composition change after dyeing process, dyeing mechanism is proposed.

## 2. Experimental procedures

As received MAO-treated 6061 aluminum alloy specimens which were prepared and supplied by a company, Techplasma Technology Co., LTD., from Taiwan who was used for this study. The specimens are visually white ( $L^* = 83.08$ ,  $a^* = -0.58$ ,  $b^* = 1.09$ ). The size of the specimens is  $80 \text{ mm} \times 50 \text{ mm} \times 1 \text{ mm}$ , and the thickness of MAO layer is approximately  $30 \mu\text{m}$ . Dyeing MAO specimens required two steps, we



**Fig. 2.** (A) Schematic microstructure of a MAO layer and (B) the reason to be undyeable.

named the steps “cathodic pretreatment” and “anodic dyeing”. Fig. 3(a) and (b) present respectively the schematic diagram of the equipment of cathodic pretreatment and anodic dyeing. The main material of tank was made of 304 stainless steel, and a DC power supply was selected. Table 1 lists the operating parameters for the whole dyeing sequences.

The first step of the experiment was cathodic pretreatment. There were three MAO specimens immersing in the NaCl solution and applying the three different condition of cathodic constant voltage, without pretreatment, 20 V, and 30 V. The obtained specimens were denoted as A1, A2, and A3. The second step, anodic dyeing was carried out by immersing the specimens into the dye solution (035 Blue (G) anionic-type dye, supplied by Yi-Hsuan Enterprise Co., LTD, Taiwan), delivering an anodic constant current (at 1 A) to all specimens to complete the dyeing process. The dyed specimen was washed with distilled water and air dried for further testing and material characterization works.

The crystalline structure of the MAO film at different treatment stage was analyzed by X-ray diffractometer (XRD, Rigaku MiniFlex 300) using the Cu K $\alpha$  radiation between  $2\theta$  values of  $20^\circ$  and  $80^\circ$  with a step of  $0.02^\circ$  at a scanning rate of  $5^\circ/\text{min}$ . The surface morphology of the MAO film was observed by using a variable vacuum scanning electron microscope (VVSEM, HITACHI S-3000N). In addition, the elemental composition of the MAO film was analyzed by an energy-dispersive X-ray spectrometer (EDS, HORIBA 7021H), and the color (chromatic value) of the dyed specimens was measured according to the CIELAB color scale using a spectrophotometer (X-Rite SP60).

## 3. Results and discussion

Fig. 4 shows the appearances of the specimen A1, A2, and A3, respectively after the dyeing process. It can be observed that specimen A1 (without cathodic pretreatment) present an undertone blue color, implicating a poor dyeing absorption. Specimen A2 pre-treated at an applied cathodic voltage of 20 V and a higher amount of the dye was adsorbed on the MAO film, leading to a deeper blue color. For specimen A3, with the cathodic pretreatment voltage increased to 30 V, allowing the adsorption of a greater amount of uniformly distributed dye, shows the deepest blue color. Table 2 lists the chromatic values of the dyed specimens. The dyed specimens A1, A2 and A3 have decrementally lower  $L^*$  and  $b^*$  values, indicating the gradual increase in the color saturation of the dyed oxide films.

Fig. 5 shows the XRD patterns of those aluminum specimens underwent different processing stages. From Fig. 5(B), (C) and (D), the MAO treated specimens mainly comprise of  $\gamma\text{-Al}_2\text{O}_3$  structure. The crystalline structure shows unobservable change subsequent to cathodic pretreatment and anodic dyeing, indicating that the crystal structure of the MAO layer was hardly affected by the cathodic pretreatment and anodic dyeing process. Moreover from Fig. 5(D), no corresponding peaks in the diffraction pattern for the dyed specimen can be ascribed to the dye layer, due probably to the very thin dye molecule adsorbed onto MAO layer surface from the dye solution and beyond the film thickness detection limit of the X-ray diffractometer.

Fig. 6 shows the surface morphology of aluminum specimens underwent MAO treated, cathodic pretreated, and anodically dyed, respectively. It can be observed that the surface of the MAO film is characterized by a typical porous morphology with a micropore diameter approximately at a micrometer-scale of  $1\text{--}20 \mu\text{m}$ . The surface morphology of the MAO layer following the cathodic pretreatment and anodic dyeing remains similar to that of the untreated MAO layer. This shows that the surface morphology of the MAO layer may very little be altered by cathodic pretreatment and anodic dyeing at the micrometer-scale. However, taking a closer look at those many pores in Fig. 6(C), there seemed to be very fine particles gathering around them and was speculated as the absorbed dyestuff.

Further intentional observation on a randomly selected area of the anodic dyed MAO layer surface was carried out. The result is shown in

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