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Influence of pulse currents on the nanostructure and color absorption ability of colored anodized aluminum

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ABSTRACT

Few investigations have been carried out on the influence of the variation of pulse current parameters on the anodized aluminum. The present paper deals with some experimental results regarding the influence of pulse current parameters on the nanostructure and color absorption ability of colored anodized aluminum. Under these conditions, the nanostructure and the color were found to be dependent on the duty cycles and frequencies. The Field Emission Scanning Electron Microscopy (FE-SEM) analysis showed that variation of the pulse current parameters changed and improved the distribution and uniformity of the pores within the anodic layer and consequently the quality of the final color.

1. Introduction

Anodization is an electrochemical process used to increase the thickness of the oxide layer on the surface of some metals such as aluminum [1–4]. Among anodizable metals, aluminum and aluminum alloys are of widespread interest, and are used because of their great commercial significance in industry and, more recently, in the field of nanotechnology [1,5]. Anodized aluminum articles show better properties compared to non-anodized aluminum, such as: high abrasive and wear resistance, high hardness and good corrosion resistance [6–10]. Depending on the electrolyte used for anodizing, two different types of oxide films are formed on the surface of aluminum: a non-porous oxide layer (Barrier layer) and a porous oxide film [5]. The porous oxide film is an appropriate surface for painting and coloring of aluminum [11–16]. Colored anodized aluminum is used in a wide variety of applications from architecture to airplane applications [15,16]. Also, colored anodized aluminum articles show better corrosion resistance [11].

Various methods for coloring anodized aluminum have been developed [11,16–20]. One of these methods includes the precipitation of various insoluble metal compounds inside the pores of the oxide layer (i.e. generally sulfuric acid anodized aluminum) [20]. This process consists of alternatively immersing the anodized surface in a concentrated solution of suitable metal salts until a sufficient amount of pigment is precipitated to achieve the desired color [20].

Anodization of aluminum can be categorized into two main groups: mild anodization (MA) and hard anodization (HA) [1]. The MA method produces straight and well-ordered nanopores but it is slow and can only be utilized for a narrow range of processing conditions. The HA process was originally developed in the surface finishing industry and has been widely used for various industrial applications. The current density of the HA process is usually one or two order of magnitude higher than MA process. So the rate of oxide film growth in HA is 25–35 times faster than MA process. However, hard anodizing produces an oxide film with disordered and non-uniform pore structure. Besides, this oxide film has many micrometer sized cracks. In order to overcome this problem, Lee et al. have suggested that a thin protective oxide film be created on the aluminum surface before performing HA process [1,21,22].

In most researches, direct current (MA, HA) is used for anodizing aluminum. The effects of direct current conditions and other parameters on the color and nanostructure of aluminum oxide film have been investigated. Most researchers have demonstrated that pulse currents have many advantages compared with direct currents such as: low energy consumption and good wear resistance [23–26]. Lee et al. suggested a new method for continuous structure engineering of nanopores based on pulse anodization [1,27–29]. Pulse anodization enables selective combination of the advantages of the MA and HA processes. Moreover, the reaction heat

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Table 1
Color processing performed in this work.

Color	Solution 1	T (°C)	Concentration	Solution 2	T (°C)	Concentration
Blue	$K_4[Fe(CN)_6]$	25	30 g/l	$FeCl_3$	25	30 g/l
Yellow	$Pb(CH_3COO)_2 \cdot 3H_2O$	25	40 g/l	$KMnO_4$	25	40 g/l

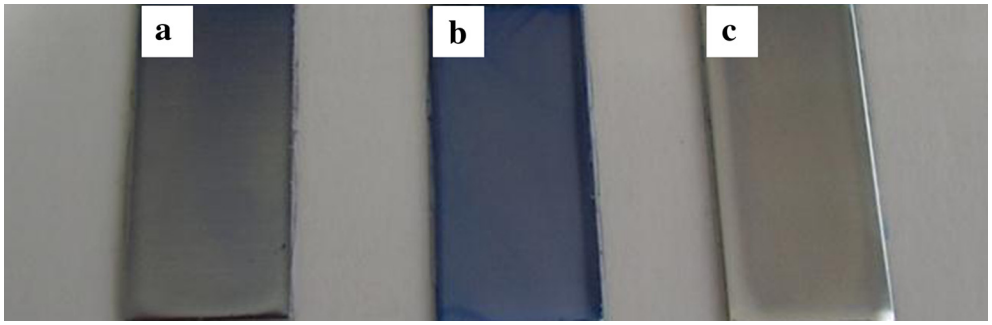

Fig. 1. The effect of anodizing temperature on the color variation of colored aluminum that formed by DC (20 mA/cm^2): (a) 5 °C (b) 25 °C (c) 55 °C. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

during HA-pulse can be efficiently dispersed during the subsequent MA-pulse, preventing the burning of the oxide film during anodization [1,27–29]. Recently, Chung et al. studied the effects of hybrid pulse anodization on the nanostructure of aluminum [30,31]. However, there are only a few investigations on the influence of pulse parameters on the nanostructure of anodized aluminum.

In anodizing with pulse currents (e.g. square pulse currents) three parameters are important and independently variable: the duration of pulse current (t_{on}), the time between pulses (t_{off}) and the current density of the pulses (i_c). The relation between t_{on} and t_{off} identifies two other parameters, frequency (F) = $1/t_{on} + t_{off}$ and duty cycle (T) = $t_{on}/t_{on} + t_{off}$ which are used for pulse currents [23,25].

In this study, the effects of square pulse currents (PC), performed under different duty cycle and frequency on the nanostructure and color of colored anodized aluminum were studied. The effects of anodizing and coloring temperature on the color of aluminum were also studied for the anodizing process with direct currents (DC) to estimate the optimum anodizing and coloring temperature for comparing PC and DC.

2. Experimental procedure

Commercial aluminum specimens were used in this investigation. Prior to anodizing, the samples were polished with abrasive paper up to No.3000 then annealed at 450 °C for 3 h to reduce internal stresses and increase the average grains size. Then the samples were electropolished in a 1:4 volume mixture of $HClO_4$ (68%) and C_2H_5OH (98%) at a constant voltage of 15 V for 2–3 min at 5 °C. After electropolishing, the samples were immersed in deionized water and immediately used for anodizing.

The anodizing process was carried out in a sulfuric acid solution containing 120 g/l H_2SO_4 at 15 ± 1 °C under agitation with a magnetic stirrer for 50 min. The anodizing process was performed with a maximum current density of 20 mA/cm^2 and minimum of zero (square pulse current), using different duty cycles (T) and frequencies (F). The pulse current was used only for the anodizing step. The cathode was an aluminum sheet similar to the samples. During the process a digital galvanometer, a common oscilloscope connected to a computer to control the current and also a refrigerator which controlled the temperature were used.

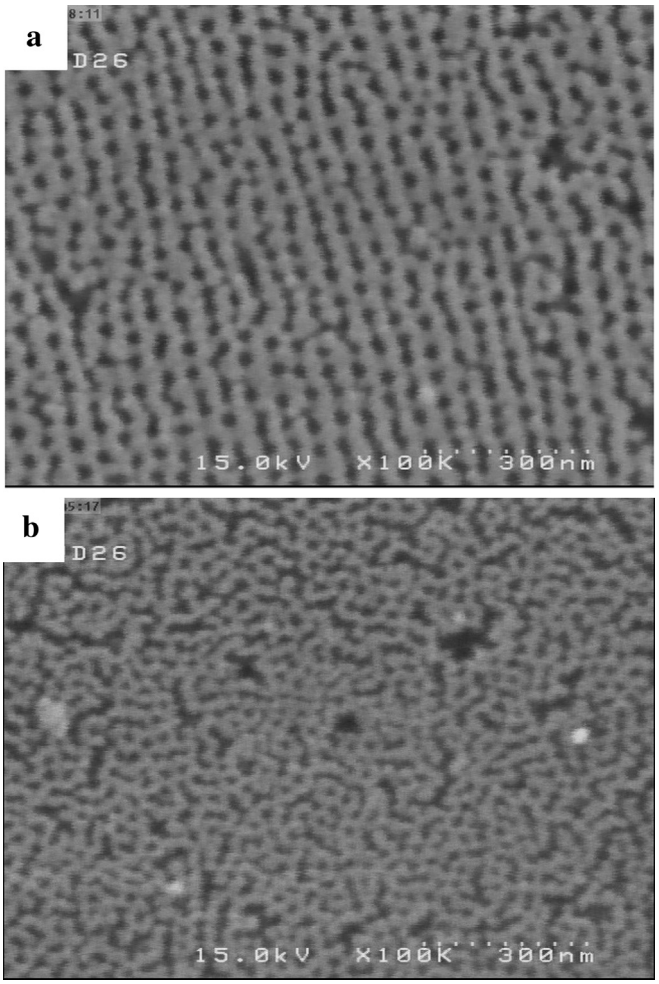

Fig. 2. FE-SEM micrographs of the anodic oxide layer formed at 55 °C by DC (20 mA/cm^2).