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Investigation of organic additives on voltage rate in Aluminum hard-anodizing process

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ABSTRACT: Hard anodizing is a term that relates to the anodic coatings with high hardness and abrasion resistance. As has been pointed out in an article by researchers, these coatings are usually thicker than typical anodizing coating causes and in special circumstances to arise. The concentration of the oxide film layer in this process and therefore increases further. We also in the process electrolyte temperature are always kept low to reduce the rate of dissolution of the oxide film. In this project DC mode of Anodization used to study of voltage changes in different electrolyte consist of five types of organic additive.

Keywords: *DC mode; Hard-anodizing; Organic additive; Oxide layer; Voltage rate*

INTRODUCTION

Anodizing is commonly used to provide protection of aluminum alloys against corrosion and wear (Vijeesh and Prabhu, 2014). The process generates amorphous alumina films, classically consisting of a thin barrier region and a thicker porous region with linear pores extending from the barrier region to the film surface (Troeger and Starke, 2000, Liang, *et al.*, 2013). However, the presence of intermetallic particles in the alloy and the enrichment of alloying elements at the matrix just beneath the anodic film (Wang, *et al.*, 2011) can lead to modified pores, voids and occluded particles (Liu, *et al.*, 2015, Pakes, *et al.*, 2003, Bouchama, *et al.*, 2013, Sulka and Parkoła, 2007), and the efficiency of film growth can be reduced significantly by oxygen generation (Liu, *et al.*, 2015). Furthermore, alloying elements in solid-solution within the alloy matrix can be oxidized and incorporated into the alumina. The study of researchers showed that citric acid was the best additive. Voltage-time curves of anodic oxidation for high silicon aluminum alloy in different electrolytes conformed to the typical characteristic curve of aluminum anodic oxidation (Shang, *et al.*, 2016). One of the organic electrolytes is tartaric/sulfuric acid (TSA)

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anodizing, which is environmentally compliant and provides corrosion resistance properties, compatible with the requirements of the aerospace industry with appropriate paint adhesion (Costenaro, *et al.*, 2016). Salicylic acid, a well-studied contaminant of emerging concern, was also examined as target pollutant using the optimized 10 µm in length TNT films. As in the case of CAF, SA was also found to be stable in pH variations and furthermore it does not show significant photolysis (Arfanis, *et al.*, 2017). Researchers demonstrated the self-ordering behavior of porous alumina fabricated via etidronic acid solution, and the resulting nanostructures were investigated in details. Self-ordering of porous alumina is observed over a wide range of potential differences (at 165 V and 313 K in 4.2 M, at 205 V and 303 K in 1.0 M, and at 260 V and 298 K in 0.2 M), and the formation of OPA measuring 400-640 nm in cell diameter can be achieved. A hexagonal phosphorus-free distribution was formed in the OPA fabricated via two-step 1.0 M etidronic acid anodizing at 215 V and 298 K for 24 h and 120 min. The shape of this honeycomb nanostructure corresponds to the phosphorus distribution in the porous alumina (Takenaga, *et al.*, 2016). Using an oxalic acid-based electrolyte, with the addition of a relatively low amount of 0.4 % of HF in the anodizing bath found that these controllable macroscopic parameters affect the resulting micro-scaled structure that is formed in the AAO layer. Throughout the film thickness, a good compositional uniformity degree and a homogeneous morphology, for each of the chosen substrates. The most systematic study of the voltage–time behavior of the porous anodizing of aluminum in relation to the deposition condition's effects seems to be necessary to further exploit the structural/compositional properties of the samples that can be grown by the proposed simple procedure (Dhahri, *et al.*, 2016). Anodizing in concentrated selenic acid solution causes rapid fabrication of anodic porous alumina with a highly regular cell arrangement. The self-ordered anodic porous alumina formed by selenic acid anodizing under the most appropriate electrochemical conditions, a concentration of 3.0 M and an anodizing voltage of 46V possesses a Nano-porous structure with a cell size of 102 nm. Highly ordered convex nanostructures with diameters of approximately 20 nm and heights of approximately 40 nm were fabricated at the triple points by selenic acid anodizing and subsequent selective oxide dissolution and were surrounded by three adjacent hexagonal cells (Kikuchi, *et al.*, 2014).

MATERIALS AND METHOD

The materials comprised 99.99 % aluminum and AA 1050 alloy sheets of 0.3 and 1 mm thickness, respectively. The alloy was in the T3 condition, i.e. solution-treated, cold worked and naturally aged. The nominal composition of the alloy in wt.% is 3.8-4.9% Cu, 1.2-1.8% Mg, 0.3-0.9% Mn, 0.5% max. Si, 0.5% max. Fe, 0.25% max. Zn, 0.15% max. Ti, 0.1% max. Cr, 0.15% other elements, bal. Al. The AA 2024-T3 alloy typically contains Al_2CuMg, Al_2Cu and Al-Cu-Fe-Mn-(Si) intermetallic particles, of size in the range 0.1- 10 µm, rod-shaped AlCu-Mn dispersoids with lengths of a few hundred nanometers, and Al_2Cu grain boundary precipitates. Specimens of dimensions 3.0×1.5 cm were cut from the sheets. The aluminum specimens were then electropolished at 20 V for 3 min in 60% perchloric acid/ethanol (20/80 by vol.) at 278 K followed by rinsing in ethanol and then deionized water, and drying in a cool air stream. The alloy specimens were etched for 60 s in10 wt %NaOH at 333 K, desmutted in 30 vol % nitric acid at room temperature for 30 s, rinsed in deionized water and dried in a cool air stream. The technological process of preparing anodic layers comprised materials pre-treatment, anodic oxidation and hole sealing post-treatment. In order to prepare excellent anodic oxide films, pretreatment was a key step to remove impurities, oil stain and natural oxide film on alloy surface. The pretreatment of samples included mechanical polishing, deoil, caustic wash, acidic wash and bright dipping. Sulfuric acid with fixed concentration was used as dominant component of anodizing electrolyte, while anodizing temperature, time and current density was identified. Three kinds of organic acids were chosen as additives of anodizing electrolyte and their effect on the oxide films' quality and growth were discussed. Processing parameters for anodic oxidation were 170 $g{\bullet}L^{-1}$ of H_2SO_4, 20°C of temperature, 25 min of time and 1.5 $A{\bullet}dm^{-2}$ of current density.

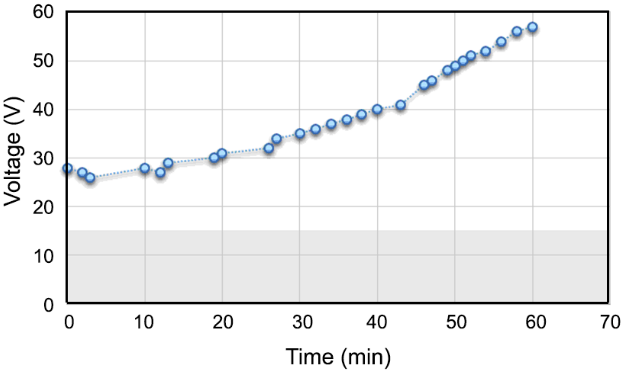

Fig. 1. petential rate profile for aodizing of Aluminum alloy in tartaric acid additive

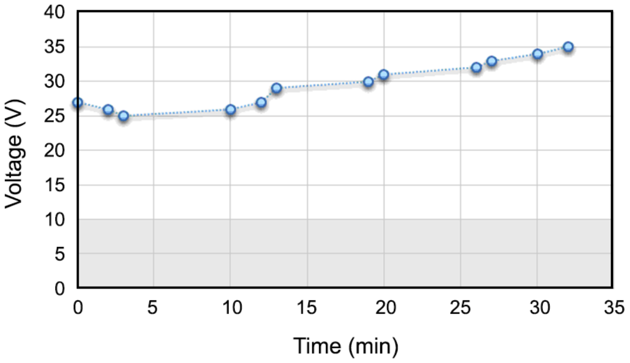

Fig. 3. petential rate profile for aodizing of Aluminum alloy in etidronic acid additive

RESULTS AND DISCUSSION

Constant current density of 3.5 ampere per square decimeter for hard anodizing aluminum samples will apply. Fig. 1 to 6 show how the gradual increase in the voltage of solutions with different additives. Hard anodizing often with the DC voltage applied at low temperatures is carried out. For aluminum alloys seemed significant amount of alloying element, the use of AC and pulse currents is recommended to reduce the likelihood of combustion. Anodizing with higher voltage AC current needs and required approximately 50% more effective flow of DC (Vijeesh and Prabhu, 2014). It also produces flawless coatings with thicknesses up with methods AC problem. Hydrogen gas emissions on the piece and produce hydrogen sulfide (the returns to Anodic, reduced hardness and reduced abrasion resistance of the other disadvantages of AC to DC. As in all time- Voltage curves for different solutions can be seen, the voltage curves in a special solution at different times good compliance. Minor difference can be attributed to slight variations electrolyte temperature and machine error. The potential difference of oxide coating solutions is reduced. The production of nitric acid and dissolved aluminum ion Al accelerating and that such differences it has with other additives.

This fact has caused constant current density and grown in the same conditions of temperature coating solution containing salicylic acid etidronic and have lower curves. At a fixed current density of 1.5 A•dm^{-2}, voltage-time curves for high silicon aluminum alloy in four kinds of electrolytes conformed to the typical characteristic curve of aluminum anodic oxidation, as shown in Fig. 3. The curves were divided into three stages. The ab stage was the formation of barrier layer and the voltage rose sharply. The formation of porous layer was in bc stage and the voltage dropped. The thickness of porous layer increased stably after point c, while voltage was basically unchanged. Thus, the shapes of voltage-time curves of three kinds of electrolyte with additives were identical with that of sulfuric acid electrolyte, indicating that additives did not change the anodic oxidation process.

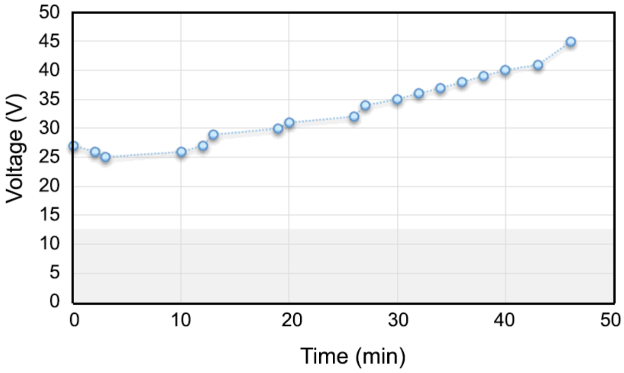

Fig. 2. petential rate profile for aodizing of Aluminum alloy in oxalic acid additive

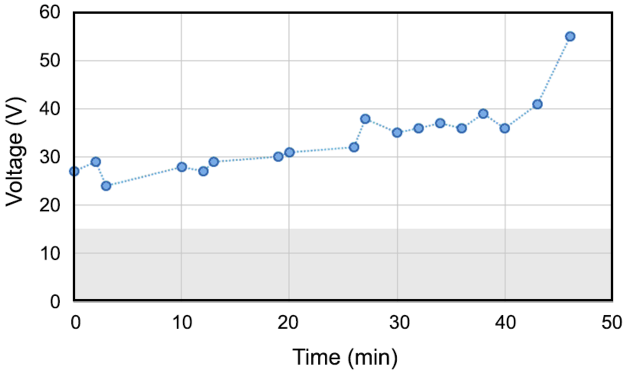

Fig. 4. petential rate profile for aodizing of Aluminum alloy in selenic acid additive

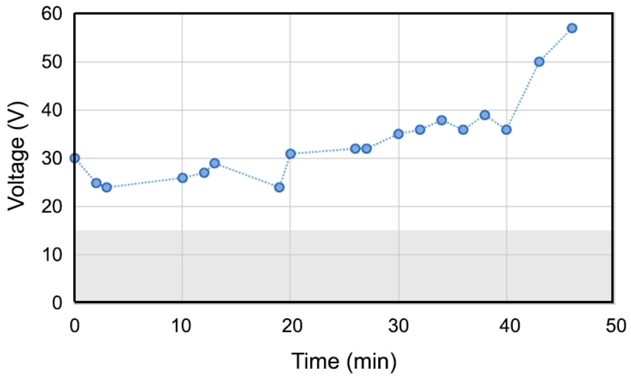

Fig. 5. petential rate profile for aodizing of Aluminum alloy in Salicylic acid additive

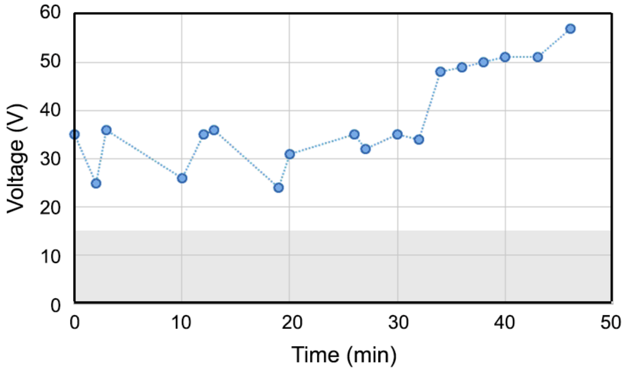

Fig. 6. petential rate profile for aodizing of Aluminum alloy in citric acid additive

Alkaline etching test (100 g•L^{-1} NaOH) was used to characterize the corrosion resistance of anodic oxidation film. Fig. 2 shows the influences of additives and their concentrations on corrosion resistance of anodic oxidation film. For the sample treated with 15 g•L^{-1} citric acid as additive, corrosion time got a maximum of 44 s. It is easy to understand that variations of corrosion time marched well with that of film weight.

CONCLUSIONS

Terms of the base alloy plays the most important factors affecting the formation rate in anodic oxide coating. The creation and growth of oxide layer in tartaric acid additives solution under a potential difference is less than oxalic acid solution. Increasing of nitric acid percent in solution decrease the potential of process and destroyed samples. Effect of etidronic acid in anodizing potential is in increasing of it and reduction of current density. Based on data of oxidation film weights and corrosion times, the optimal concentrations of additives were determined as follows: 15 g•L^{-1} of citric acid, 5 g•L^{-1} of oxalic acid, 5 g•L^{-1} of tartaric acid. Voltage-time curves for high silicon aluminum alloy in different electrolytes conformed to the typical characteristic curve of aluminum anodic oxidation. Formed in the mixed electrolyte of sulfuric acid and citric acid, the surface of anode oxide films exhibited advantages in smoothness, well distributed and excellent densification compared with the other films. EDS analysis and XRD pattern demonstrated the anodic oxide film contained Al and Si. The results of NSS test, potassium dichromate spot test and potentio-dynamic polarization indicated that citric acid was the most effective additive for enhancing corrosion resistance of anodic oxidation film for high silicon aluminum alloy.

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