The Influence of "Light Green" Additive On the Anodizing of Aluminum In Sulfuric Acid

by T. Dimogerontakis & I. Tsangaraki-Kaplanoglou*

The effect of "Light Green" additive on the anodizing of pure aluminum in sulfuric acid was studied by electrochemical methods. The presence of this additive in the anodizing bath caused a decrease in the anodizing current density and the porosity of the resulting anodic film similar to that observed in phosphoric acid baths although reduced. However, the morphology of the oxide film and the degree of enrichment of both reactive species (additive and Al^{+3} ions) at the bottom of the pores seems mainly to be responsible for the extent of the effects of the additive.

Anodizing in acidic baths is the most widely used method for the corrosion protection and decoration of aluminum and its alloys. A porous oxide film is formed by this method, and consists of an outer layer containing a great number of hexagonally-shaped cells with a central pore perpendicular to the aluminum surface. An inner non-porous thin barrier layer is also included in the anodic film at the interface between the aluminum and the porous oxide.[1,2]

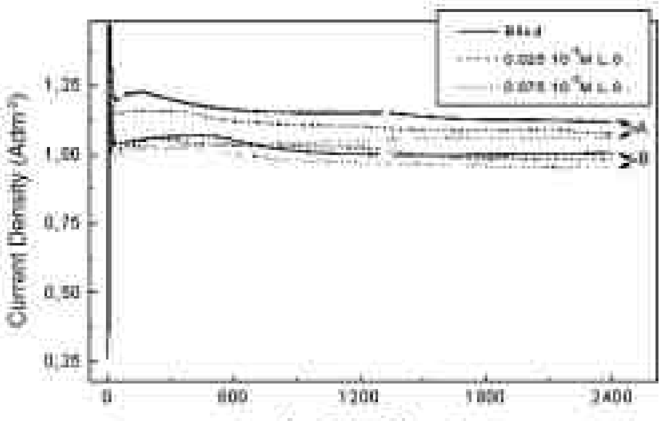

Fig. 1—Current density vs. time behavior during anodizing at 15V with the presence of Light Green at concentrations of 0.025 and 0.075x10^{-3} mol/L at 20°C (68°F) in a bath consisting of 170 g/L H_2SO_4 and $Al_2(SO_4)_3 \cdot 18H_2O$: (A) 5.0 g/L and (B) 0.5 g/L.

Nuts & Bolts: What This Paper Means to You

Under the microscope, an anodized coating consists of a great number of hexagonally-shaped cells with a central pore perpendicular to the aluminum surface. The use of sulfuric acid instead of phosphoric acid in anodizing baths produces thicker anodic oxide films with smaller diameter pores of greater depth, a less-desirable outcome. This work deals with the use of so-called "Light Green" additive which allows you to get a more desirable phosphoric bath-type structure out of a sulfuric acid bath.

The anodizing conditions (*i.e.*, choice of anodizing bath, anodizing voltage, anodizing temperature and time) influence the composition, mechanical properties and structural characteristics (*i.e.*, the size and structure of the pores) of the anodic oxide film. For example, the porous oxide layers have relatively narrow pores at lower voltages or deeper pores with longer anodization times. Prior studies have shown that the porosity increases with increasing temperature, but decreases with increasing voltage.[3] The diameter of the pores is independent of electrolyte concentrations below about 1.5 M.[4] On the other hand, the pore diameter is determined mainly by the acidic solution employed. The use of sulfuric acid instead of phosphoric acid in anodizing baths produces thicker anodic oxide films with smaller diameter pores of greater depth.

With sulfuric acid anodizing, the porous oxide film grows linearly with time. The growth rate is dependent on the current density, while the growth efficiency, in terms of thickness versus charge, is independent of the current density.[5] Under the same anodizing conditions, it was found that the growth rate of the oxide layer in sulfuric acid was about twice as fast as that in phosphoric acid.[4] Consequently, the morphology of the porous anodic oxide film on aluminum anodized in phosphoric acid is fundamentally different from that formed in sulfuric acid, which has finer features. Based on data in the literature,[6] oxide films formed at 20V for 20 min have pore diameters in the range of 12 to 15 nm (0.47 to 0.59 μ-in.) when formed in sulfuric acid versus 30 to 33 nm (1.18 to 1.30 μ-in.) for phosphoric acid. The oxide films produced in these different anodizing baths, also have different amount of anions incorporated into the oxide film with typical levels being 6 to 8% for phosphates and 12 to 14% for sulfates.[7]

Some triphenylmethane dyes have already been studied as additives in electrolytic treatments of aluminum.[8,9] It has also been found[10,11] that the sulfonated triphenylmethane acid dye "Light Green" added to a phosphoric anodizing acid bath concentrates at the bottom of the pores under the influence of the applied electric field. It also interacts with Al^{+3} cations, inhibiting their movement into the electrolyte bulk. This results in a reduction of field-assisted dissolution and of the direct ejection of Al^{+3} cations into solution

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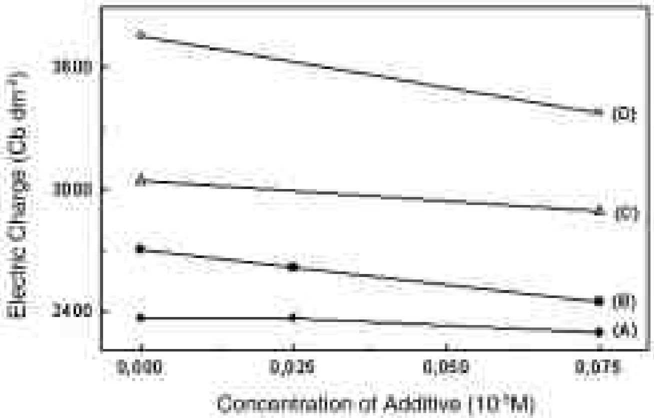

Fig. 2—Consumed electric charge vs. concentration of Light Green for anodizing at 15V in:
(A) 170 g/L H_2SO_4, 0.5 g/L $Al_2(SO_4)_3 \cdot 18H_2O$ at 20°C (68°F);
(B) 170 g/L H_2SO_4, 5.0 g/L $Al_2(SO_4)_3 \cdot 18H_2O$ at 20°C (68°F);
(C) 147 g/L H_2SO_4, 0.5 g/L $Al_2(SO_4)_3 \cdot 18H_2O$ at 25°C (77°F), and
(D) 170 g/L H_2SO_4, 0.5 g/L $Al_2(SO_4)_3 \cdot 18H_2O$ at 25°C (77°F).

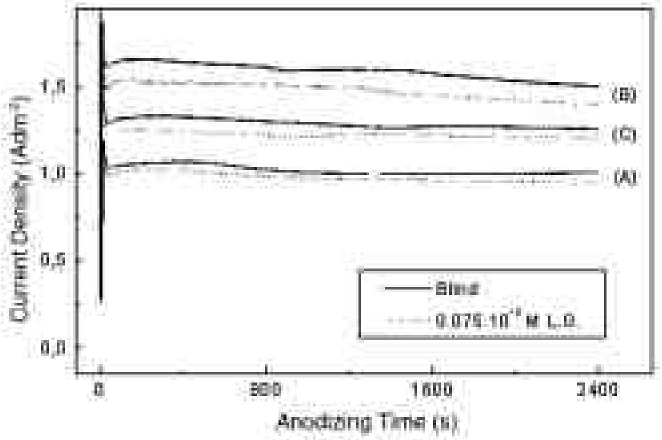

Fig. 3—Current density vs. time during anodizing at 15V in the presence of 0.075x10^{-3} M Light Green in:
(A) 170 g/L H_2SO_4, 0.5 g/L $Al_2(SO_4)_3 \cdot 18H_2O$ at 20°C (68°F);
(B) 170 g/L H_2SO_4, 0.5 g/L $Al_2(SO_4)_3 \cdot 18H_2O$ at 25°C (77°F), and
(C) 147 g/L H_2SO_4, 0.5 g/L $Al_2(SO_4)_3 \cdot 18H_2O$ at 25°C (77°F).

causing a decrease in the rate of oxide film growth. Assuming that the additive results in a decrease in porosity and pore density as well as an increase in diameter of the cells, the additive mechanism can be explained as follows. According to the geometrical model of O'Sullivan and Wood,[12] a decrease in the local electric field at the bottom of the pore results in an alteration of the radius of curvature of the pore and cell base. These alterations cause the above-mentioned changes in the porosity and diameter of the cells.

It is well known that the geometrical characteristics of the porous anodic oxide films, *i.e.*, cell and pore diameter and barrier layer thickness , are directly dependent on anodizing conditions. Thus, it is important for many applications (metal matrix composites, selective membranes and microelectrodes) that by using this additive it is possible to change the cell diameter without altering any other geometrical characteristics of the film.

It is therefore of interest to compare the Light Green additive effect on the current density and porosity of an anodic film grown in a sulfuric acid bath (narrow pores) with that from a phosphoric acid bath (wider pores). The Light Green additive effect from a phosphoric acid bath has already been studied by the authors.[10, 11] In the present work then, a comparative study of the influence of Light Green dye in sulfuric and phosphoric acid anodizing solutions was made. In addition, the role of anodizing temperature, as well as sulfuric acid and aluminum sulfate concentration was investigated.

Experimental

Specimens of pure aluminium (99.96%), suitably pretreated, were used.[10] Anodizations were performed potentiostatically at 15V in solutions containing sulfuric acid (145 and 170 g/L) and hydrated aluminium sulfate (0.5 and 5 g/L). A thermostated cell was used with a stainless steel cathode and magnetic stirring. A DC power supply was used, and was controlled by a computer, while the variation of the current with time was recorded in a computer using a multimeter. The Light Green dye was used as an additive at concentrations of 0.025x10^{-3} and 0.075x10^{-3} mol/L. The latter concentration was close to the solubility limit of the dye in the anodizing conditions under study.

The anodized specimens were galvanostatically re-anodized at a current density of 1.0 mA/cm^2 (0.1 A/dm^2; 0.93 A/ft^2) in a solution of 0.5M H_3BO_3 and 0.05M $Na_2B_4O_7$ (pH 7.4) at 20 ± 0.5°C (68 ± 0.9°F) using a convenient cell with a working electrode area of 3.14 cm^2 (0.49 in^2). The corresponding voltage / time curves were obtained with a multimeter. The porosity of the anodized specimens was calculated from the above curves.[10,11,13] The linear correlation coefficients (R^2) of these curves were not less than 0.99. The increase in the slope of these curves was indicative of a decrease in porosity.

Results & Discussion

Figure 1 shows the current density / time transients during anodizing at a constant voltage of 15V in sulfuric acid containing 0.5 and 5.0 g/L $Al_2(SO_4)_3 \cdot 18H_2O$ with and without Light Green dye in concentrations of 0.025x10^{-3} and 0.075x10^{-3} mol/L. It can be seen that after the first stage (barrier layer formation) and during the second stage (pore initiation) the slope of the current density decreased as the concentration of Light Green dye increased.[1,10,11] However, the addition of Light Green to the bath caused a larger reduction in current density at the higher aluminum sulfate concentration. This became more evident as the concentration of the additive was increased.

The above results are more obvious in Fig. 2, where the electric charge passed during anodizing was calculated from the current density / time curves of Fig. 1. At 0.5 g/L $Al_2(SO_4)_3 \cdot 18H_2O$ (Fig. 2, curve A) the presence of 0.075x10^{-3} mol/L, Light Green dye caused a reduction in electric charge of about 3%, while at 5.0 g/L $Al_2(SO_4)_3 \cdot 18H_2O$ (Fig. 2, curve B), this reduction was 10%.

According to the literature,[1,4] a significant increase in current density occurs with increasing anodizing temperature or sulfuric acid concentration. This is also observed in Fig. 3. Further, the increase of anodizing temperature and sulfuric acid concentration enhanced the action of the Light Green dye. At 20°C (68°F), the presence of the additive reduced the consumed electric charge by about 3%, while at 25°C (77°F), the respective reduction was 10%. The increase of sulfuric acid concentration also enhanced the action of the additive. We calculated that the electric charge consumed was reduced by 5% with the presence of Light Green dye when the sulfuric acid concentration was 147 g/L. The reduction was 10% when the concentration of sulfuric acid was increased to 170 g/L.

From Fig. 4, it can be seen that changing anodizing conditions in the absence of Light Green affected the slope of the voltage / time curves derived from the galvanostatic re-anodizations. This implies corresponding changes in porosity. For instance, the increased temperature caused a significant decrease of the slope, corresponding to a significant increase of porosity. On the other hand, altering the sulfuric acid concentration and/or the aluminum sulfate concentration seemed to cause a small change in slope. These results are consistent with the literature.

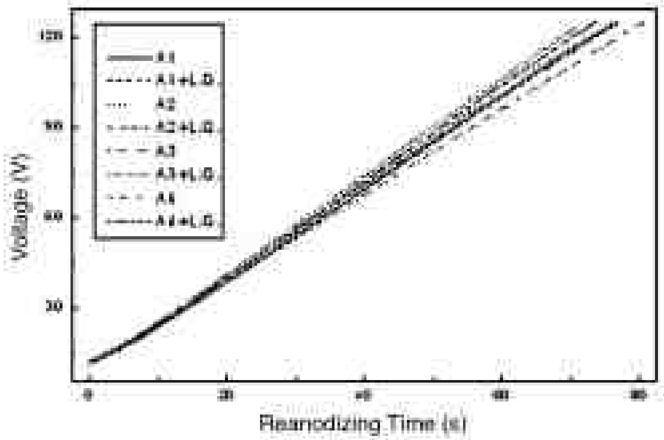

Fig. 4—Voltage Ð time curves during galvanostatic re-anodizing with 1 mA/dm^2 in 0.5 M H_3BO_3, 0.05 M $Na_2B_4O_7$ at 20 ± 0.5°C (68 ± 0.9°F) of specimens previously anodized at 15V in the presence of 0.075x10^{-3} M Light Green in:
(A1) 170 g/L H_2SO_4, 5.0 g/L $Al_2(SO_4)_3{\cdot}18H_2O$ at 20°C (68°F);
(A2) 170 g/L H_2SO_4, 0.5 g/L $Al_2(SO_4)_3{\cdot}18H_2O$ at 20°C (68°F);
(A3) 170 g/L H_2SO_4, 0.5 g/L $Al_2(SO_4)_3{\cdot}18H_2O$ at 25°C (77°F);
(A4) 147 g/L H_2SO_4, 0.5 g/L $Al_2(SO_4)_3{\cdot}18H_2O$ at 25°C (77°F).

With the addition of Light Green into the anodizing baths, a small decrease in porosity was observed, which became more intense at the higher anodizing temperature (25°C; 77°F).

Conclusions

Sulfonated triphenylmethane acid dye "Light Green," used as an additive in sulfuric acid anodizing baths reduced the current density and porosity of the resulting porous anodic films. The action of the additive was enhanced at higher concentrations in the anodizing bath, although the concentration was restricted by its lower solubility in the sulfuric bath, as compared to the phosphoric acid bath. The increase of anodizing temperature, aluminum sulfate and sulfuric acid concentration enhanced the action of the Light Green dye.

When compared with the effects in phosphoric acid baths however, the effect of this additive seemed to be reduced in sulfuric acid baths with low aluminum sulfate concentration. In addition, the effect of Light Green was significantly inhibited as porous oxide films grew in thickness and hence as the pores deepened. In the case of sulfuric acid anodizing the ratio of depth to pore diameter was unfavorable for the additive (aspect ratio too high), although the increase of sulfate content seemed to show an effect when compared with corresponding increase in phosphate content. The oxide film morphology and thickness seems to affect strongly the action of Light Green.

By increasing the concentration of the additive and the aluminum sulfate, the degree of enrichment of both reactive species (additive and Al^{+3} ions) at the bottom of the pores seemed to play an important role in indicating the extent of the action of the additive. The effect depended on parameters such as anodizing voltage, temperature, anodizing time and bath composition.

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