Sulfuric acid anodization of aluminium with subsequent modification of the film by anodic treatment in citric acid

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1. Introduction

It is well known that anodizing is the main process of corrosion protection of aluminum alloys. Two types of anodic oxide films can be formed during the anodization process of aluminum sample: barrier oxide films and porous anodic oxide films. Protective films for Al alloys formed by conventional sulfuric acid anodizing consist of a thin barrier layer at the metal-oxide interface and a thicker porous layer at the outer part. Because of the very thin barrier layer, less than 30 nm in sulfuric acid, the pores must be sealed in order to increase the corrosion resistance of the film.

2. Objective

Improvement of corrosion resistance through an anodizing process carried out in two stages in order to produce a porous film with thickened barrier film.

3. Experimental Techniques

3.1. Fabrication process

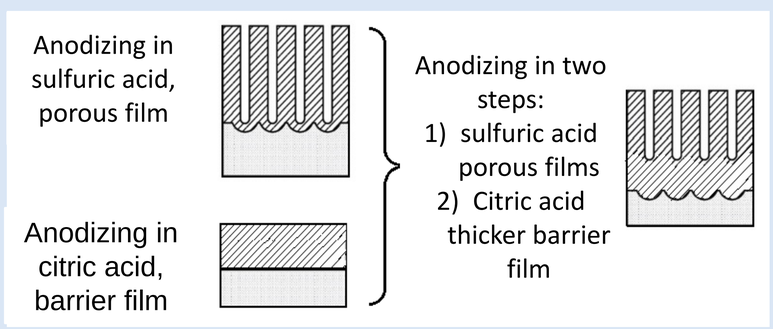

Fig 1.schematic sequence for a two step anodization process with thicker barrier film.

3.2. Materials and Methods

Material: AA1200 and AA2024
Electrolytes: H2SO4, 14% and citric acid, 0.05M
Tests: Galvanostatics under electrolyte agitation and temperature control; counter electrode: AA1200 .
Anodizing Process: The process consists of two steps:
1) Galvanostatic anodization in H2SO4.
2) Citric acid anodizing of the porous film sample previously formed in H2SO4.

Reference

1] H. Takahashi, M. Nagayama, The determination of the porosity of anodic oxide films on aluminium by the pore-filling method, Corros. Sci. 18 (1978) 911–925.

4. Results and discussion

anodizing voltage transients

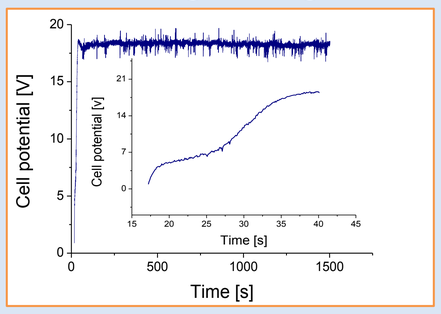

Fig.2: Galvanostatic anodization of Al in 14% H_2SO_4 (step 1).

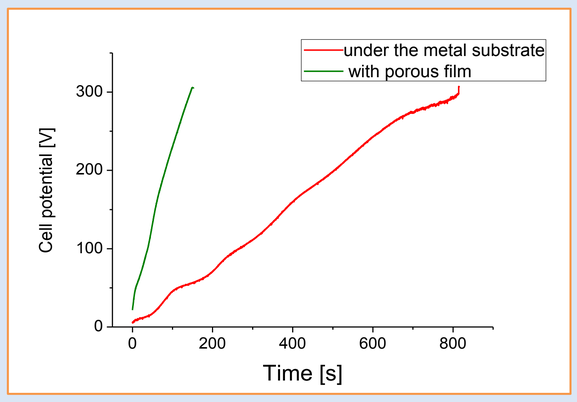

Fig.3: Galvanostatic anodization in Al citric acid in porous film and galvanostatic anodizing in Al citric acid (metal substrate).

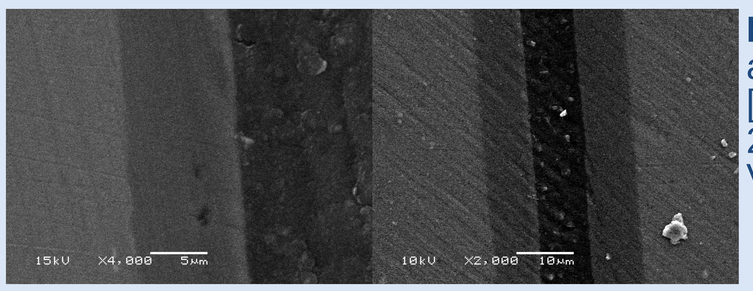

Fig.4: Cross section alloy AA2024: anodized in sulfuric acid for 25 min [9,75µm](right), anodized in two steps, 25 min in sulfuric acid and up to 300 Volt in citric acid [8,75µm](left)

Cross sections shows that the total film thickness is slightly reduced by the treatment in citric acid, indicating partial dissolution of the porous Al_2O_3 film formed in sulfuric acid. So to compare two films of the same thickness the following equation is used, which compares the final thickness of the two step film with the growth rate versus time for the sulfuric acid film.

$$t[min] = \frac{L[\mu m]}{0{,}37}$$

where t is the anodizing time in minutes and L the final thickness of the sulfuric acid film

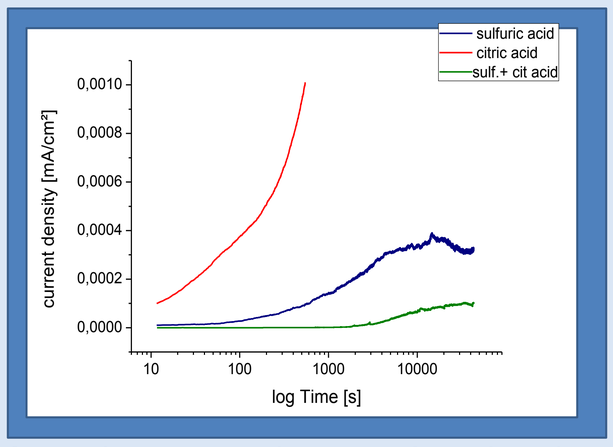

Fig.5: chronoamperiometry of coatings in AA2024 alloy in 0.1M NaCl, 30 mV above pite potential.

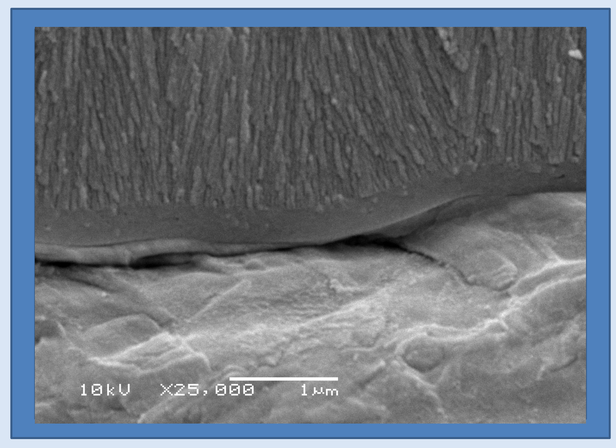

Fig.6: Barrier film formed in citric acid on Al anodized in sulfuric acid.

- The faster rise of the voltage in the second stage indicates that, in this case, a filling of the pores of the formed film in H2 SO4 occurs[1].
- The thickness of the barrier film formed at the metal / porous film interface is proportional to the final voltage applied in the second step
- The citric acid apparently partially dissolves the porous film formed in H2SO4.
- It can be clearly seen by means of microscopies that there is an increase in the thickness of the barrier film in the second step.
- In the chronoamperiometry the coating performed in two stages reaches the lowest current density, followed by the coating in sulfuric acid and, finally, the coating in citric acid, which reaches higher current density in the shortest time. This indicates that the thicker barrier film coating remains passive longer than the others.

Conclusions

- The study showed that it is possible to create a porous Al2O3 film with a 10 times thicker barrier film through a two-stage sulfuric / citric anodization process.
- The total oxide thickness remains constant, even where there are defects in the layer caused by copper precipitates.