The effect of surface oxide film on etching in high purity aluminum foil

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Abstract A D.C. etching of a high purity aluminum foil for electrolytic capacitors, so-called tunnel etching`, was investigated. Two types of samples were prepared. One was pretreated by immersion in NaOH solution. The other was not pretreated, on which the oxide film was a thermal oxide film, which formed during annealing.

High density of tunnels developing perpendicular to the surface were obtained in the non-pretreated sample, while the density was low in the pretreated sample. In the pretreated sample, numerous pits formed, aligning in a channel shape. It is considered that the thermal oxide film depresses, the form of pits aligning in a channel shape and that there are sites to form tunnels in the thermal oxide film.

Keywords: *Aluminum foil, Tunnel etching, oxide film, pitting corrosion*

Introduction

Tunnel etching in high purity aluminum foil for electrolytic capacitors is formed by anodic dissolution of aluminum in a hot chloride solution. Tunnel etching is used for a process to make electrodes for aluminum electrolytic capacitors. A high density of the tunnels obtains a high capacitance for the aluminum capacitors. The tunnel extends along the (100) direction and a high density of the tunnel is performed by high cubicity aluminum. The geometric development of tunnels has been described earlier[1,2]. It has been reported that tunnels evolved from cubic etch pits, and that the tunnels had square cross sections with sides $\sim 1\,\mu$m and aspect ratios as high as 100:1.

Oxide films have been reported to affect tunnel etching in the early stages by B. J. Wiersma and K.R. Hebert[3]. In their study, a film on pretreated aluminum was described as inducing a high volume of pits during tunnel etching in the early stages. They supposed that a currentless oxidation process parallel to anodic dissolution produced a high volume of pits for pretreated aluminum. It was considered that a reaction between aluminum and water in the film, which was incorporated by the pretreatment, was the currentless oxidation. The reaction between aluminum and water is described as follows:

$$Al(metal) + 2H_2O(in\ oxide\ film) \rightarrow AlOOH(solid) + 3/2H_2$$

In this work, the objectives were to clarify the effect of an oxide film in the second stages during the tunnel etching. An observation of tunnels by scanning electron microscope was performed for a pretreated sample and a non-pretreated sample. The time for etching was 15sec. After the second stage etching, tunnels were developed perpendicular to the surface. For the pretreated sample and the non-pretreated sample, the density of tunnels and the weight loss during etching were investigated. Pits formed in a channel shape parallel to the surface were also observed, for the samples.

Experimental

Samples:

105 μ m-thick, 99.99%Al capacitor-grade foil was used for samples. The foil was a high cubicity type, so that a large proportion of the surface grains had (100) faces exposed.

Prior to etching experiments, the foil was pretreated by immersion for 30sec at room temperature in aqueous 1N NaOH. Then, the foil was rinsed in distilled water and dried by a dry spray. The apparent thicknesses, T, of the layers dissolved by pretreatment were calculated by the equation,

$$T=(Wb-Wa)/dA,$$

where Wb and Wa are the weights of the sample before and after dipping, d is the density for aluminum, 2.7g/cm^2,and A is the area of the sample immersed in NaOH solution.The apparent thickness calculated was 0.07 μ m as shown in Table 1.

Tunnel etching:

The samples were etched under the condition reported by Hibino et al.[4](Table 2). The etchant was 1mol/l HCl and 3mol/l H_2SO_4 solution, the temperature was 90℃ and the current density was 0.2A/cm^2. Tunnel features were studied by scanning electron microscopy(SEM). In order to investigate the density of tunnels perpendicular to the surface, after tunnel etching parts of the samples were polished electrically by 10V in the H_3PO_4 and CrO_3 solution and the surface layers which impede observation of perpendicular tunnels were removed.

Results and discussion

Pits aligning in channel shape parallel to a surface:

The surface SEM micrographs of the samples after the tunnel etching are shown in Fig.1. For the pretreated sample, some pits aligning in channel shape parallel to the surface were found. In contrast, for the non-pretreated sample, there were numerous pits aligning in channel shape parallel to the surface.

Here, one possible effect to vary a pit form, i.e. impurity elements in a surface, can be considered. Impurity elements in a surface were found to affect tunnel etching[5]. However, in this experiment, the layers dissolved by pretreatment were 0.1 μ m. The condensed layer of impurity elements is reported to be 1 μ m, and therefore the concentration of impurity elements of the pretreated sample was not a factor which could vary a pit form.

On the other hand, the oxide film on the non-pretreated sample was a thermal oxide film and differed from the film on the pretreated sample. The film on the non-pretreated sample formed at high temperature and its thickness was larger than that on the pretreated sample. The thicknesses of the films on the pretreated sample and the non-pretreated sample, calculated by ESCA data, were

23 Å and 43 Å, respectively(Table 2).

It has been reported that tunnel shape developing perpendicularly to the surface grew from a cubic pit in the initial stage[6]. High volume cubic pits have also been reported to form for a pretreated sample, which was immersed in 1N HCl at room temperature[3]. It was described that the geometric pit volume of the pretreated sample was $1.6\sim2.6\times10^{-7}cm^3/cm^2$, while that of the non-pretreated sample was $1.4\sim5.1\times10^{-8}cm^3/cm$. One possible hypothesis to explain pits in channel shape on the pretreated sample is that, the initial pits described by Wiersma et al. and Alwitt et al. form and align, and continuous channels result.

Development of tunnels perpendicular to a surface:

The surface SEM micrographs after electrical polishing are shown in Fig.2. The density of tunnel pits to count from the SEM micrographs is indicated in Fig.3. The density of tunnels of the pretreated sample was low, while that of the non-pretreated sample was high, which was twice as much as on the pretreated sample.

The weight loss after the electrical etching is shown in Fig.4. The loss of the non-pretreated sample was as much as that of the pretreated sample.

The amount of coulombs applied to the pretreated sample during tunnel etching was the same as that applied to the non-pretreated sample.

Therefore, it is supposed that some of the coulombs are consumed in forming the pits aligning in the shape of channels and that the other coulombs are consumed in forming tunnels perpendicular to the surface. The pitting potential for about half the number of tunnels was thought to be lower than that for pits aligning in the shape of channels. On the other hand, the pitting potential for the rest of the number of tunnels was thought to be higher than for pits aligning in the shape of channels. The density of the tunnels consequently decreases. It is thought that the thermal oxide film is needed to obtain a high density of perpendicular tunnels by depressing the pits, which are aligning in the channel shape parallel to the surface.

Conclusions

For samples of a high purity aluminum, which were pretreated and non-pretreated, tunnel etchings were investigated. The pretreatment was immersion in 1N NaOH solution at room temperature for 30sec. The features of the tunnel etchings are concluded to be as follows:

(1)The density of tunnels developing perpendicular to the surface is $1.6x10^6/cm^2$ in the pretreated sample, and is about twice that in the non-pretreated sample, which is $0.84x10^6/cm^2$.

(2)For the non-pretreated sample, numerous pits aligning in channel shape parallel to the surface were found, while for the pretreated sample, there were only a few pits aligning in channel shape parallel to the surface.

(3)The weight loss after a tunnel etching of the pretreated sample was $235x10^{-6}g/cm^2$, and was equal to that of the non-pretreated sample.

(4)A model for tunnel etching with a thermal oxide film is proposed as follows:

A site to nucleate for tunnels developing perpendicular to the surface is situated in defects in the thermal oxide film. The potential to nucleate for half of the tunnels is higher than that for pits aligning in channel shape. Therefore in the sample, the film which forms pits in channel shape decreases the density of tunnels.

References

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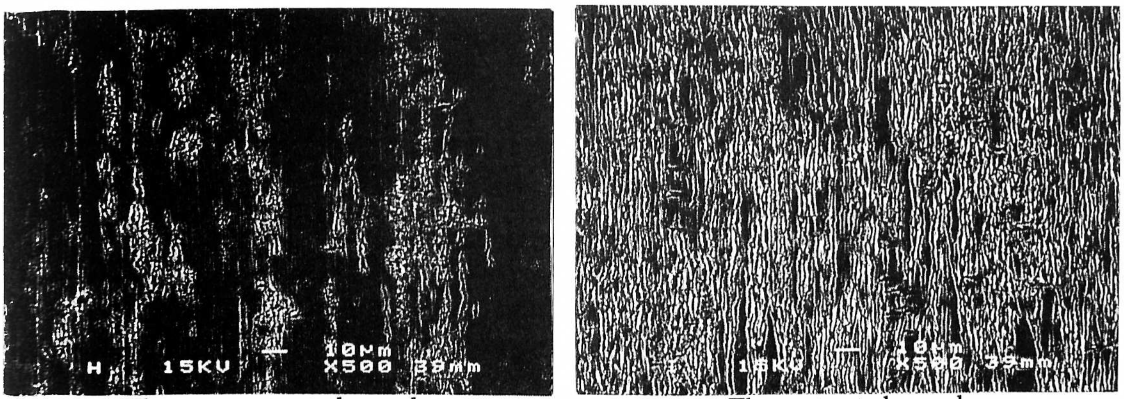
Table 1 The apparent thicknesses of the layer dissolved by pretreatment.

Sample	Pretreatment condition	Apparent thickness
Non-pretreated	Not immersed	0 μ m
Pretreated	Immersed 1N NaOH at room temperature for 30sec	0.07 μ m

Table 2 The condition of tunnel etching.

Etchant	1mol/l HCl 3mol/l H_2SO_4
Temperature	90℃
Time	15sec
Current density	0.2A/cm^2

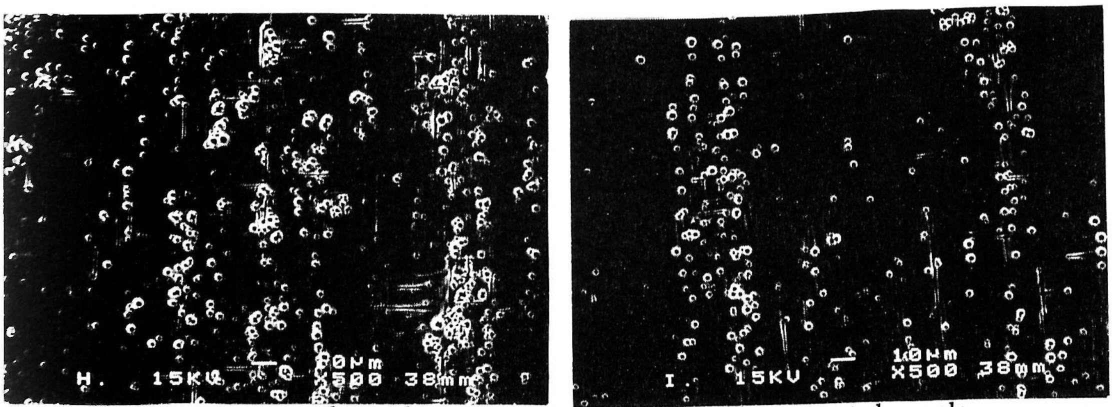


The non-pretreated sample The pretreated sample

Fig.1 The surface SEM micrographs of the samples after the tunnel etching.

Table 3 The thicknesses of the oxide films on the samples.

Sample	Thickness
Not pretreated	43 Å
Pretreated	23 Å



The non-pretreated sample The pretreated sample

Fig.2 The surface SEM micrographs after electrical polishing of the tunnel-etched samples.

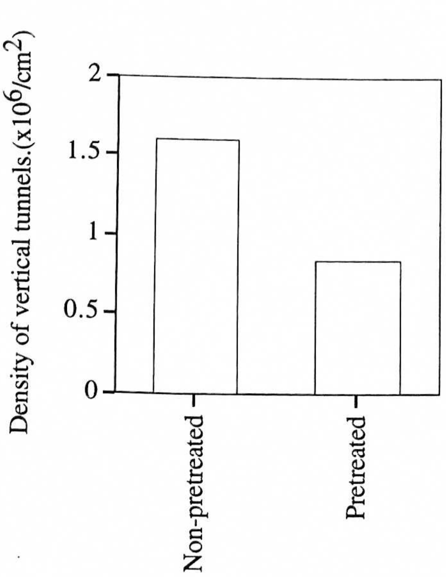


Fig.3 The density of perpendicular tunnels.

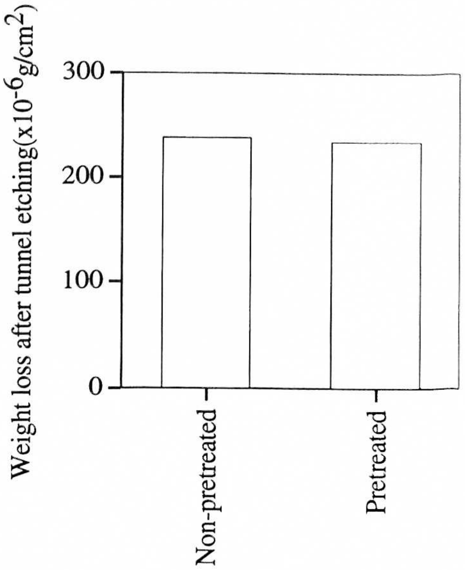


Fig. 4 The weight loss after tunnel etching.