MORPHOLOGY AND CAPACITANCE OF AC ETCHED ALUMINUM FOILS UNDER VARIOUS ETCHING CONDITIONS

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ABSTRACT Alternating current (AC) etching of aluminum foil for low voltage capacitors in chlorine ion containing solution has been used to increase the surface area of aluminum foils for electrodes of capacitors. Numerous etching variables affect the etch pit morphology and in turn the capacitance of the foils. In this study, the effects of current waveform and frequency of aluminum foils have been studied. The grain boundaries and roll scratches were dominant nucleation sites of etching. For a given anodic charge of the same peak etching current, sinusoidal and triangular current waveforms gave rise to one capacitance peak and rectangular waveforms two peaks within the experimental frequency range of 1 to 50. The initial slope of triangular current wave form influenced etching behavior.

Keywords: *AC etching, capacitance, etch pit morphology, frequency, waveform, surface defects*

1. INTRODUCTION

The AC etching of high purity aluminum foil (>99.9%) has been used to increase the surface area of high purity aluminum foils(>99.9%) for low voltage electrolytic capacitor electrodes, whereas DC etching for high voltage capacitors. According to an AC etching model suggested by Dyer and Alwitt[1], anodic dissolution of aluminum takes place and etch pits of cubic shape are formed during anodic half-cycle of applied AC current, while reduction of H^+ during cathodic half-cycle causes pH rise, forming passive film on the cubic etch pits which were formed in the previous anodic half-cycle. Dyer and Alwitt's model suggests that the role of cathodic polarization during AC etching is to limit the growth of existing pits, so that, for a given anodic charge, a large total number of pits obtained. Lin and Hebert's work[2] suggests the role of cathodic polarization is more complex. They found that prior cathodic polarization increased pit densities on aluminum by a factor of 100 during the first 20ms of anodic polarization above the pit initiation potential, in 1N HCl at 65℃, and the average pit growth current densities. From this result, they suggest that the cathodic reaction might produce a species which participate in the initial stages of anodic dissolution.

The etch pit morphology and in turn the capacitance of the aluminum foil are influenced by numerous etching variables, which can be classified into three kinds of group. First, there are variables related to the applied current such as current density, amount of charge, frequency, waveform, etc. Second, variables related to electrolytic solution are HCl concentration, composition of additives, and solution temperature. Finally, variables related to aluminum foils such as microstructure, surface defects, etc. may be controlled by thermomechanical treatment. Studies have been made by many researchers including present authors[1-6] of the effects of these variables on AC etching.

This study lays emphasis on the effects of etching current waveform and surface structure of aluminum on capacitance and etch pit morphology of the etched aluminum foil.

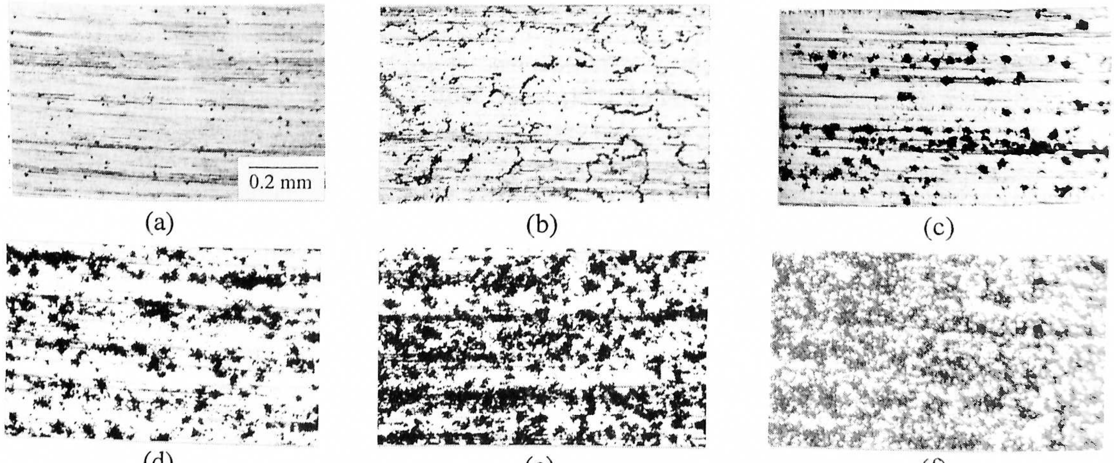
2. EXPERIMENTAL PROCEDURES

Aluminum foils of 99.9% in purity and 100μm in thickness were pretreated in 0.1M NaOH for 2 minutes at 30℃ and rinsed in distilled water. AC etching of the aluminum foils was performed in an electrolyte containing 1.5M HCl and some other additives such as 0.15M HNO_3, 0.2M H_3PO_4, 0.003M H_2SO_4, and 0.3M $AlCl_3$ at 30℃ unless otherwise specified. AC current was applied until total anodic charge reaches 54C/cm^2. AC currents with sinusoidal, triangular and rectangular waveforms were applied at a frequency range of 1 to 50Hz. AC currents of various triangular waveforms were also used to etch aluminum foils at 15Hz. Capacitance of etched aluminum foils was measured using a LCR meter after they were anodized to 22V in 150g/l ammonium adiphate solution.

3. RESULTS

In order to locate etch pit initiation sites, AC sinusoidal current with a frequency of 1Hz was applied to the aluminum foil in 1M HCl solution at 30℃ under a peak current density of 3000A/m^2. Fig.1 shows that pitting starts at roll scratches and grain boundaries, and the pit density increases with increasing number of cycles.

Fig.2 shows SEM micrographs of the surface of aluminum foil etched under AC sinusoidal current with an anodic peak current density of 3000A/m^2 . The pit size at 1Hz looks larger than that at 5Hz. However, pitting is increasingly localized on weak points like grain boundaries and roll scratches with increasing frequency of AC current.



(a) (b) (c)

(d) (e) (f)

Fig.1 Etch pits formed on surface of rolled aluminum foil etched in 1M HCl solution under 1Hz sinusoidal waveform for (a)5cycles (b)15cycles (c)30cycles (d)60cycles (e)100cycles and (f)200cycles.

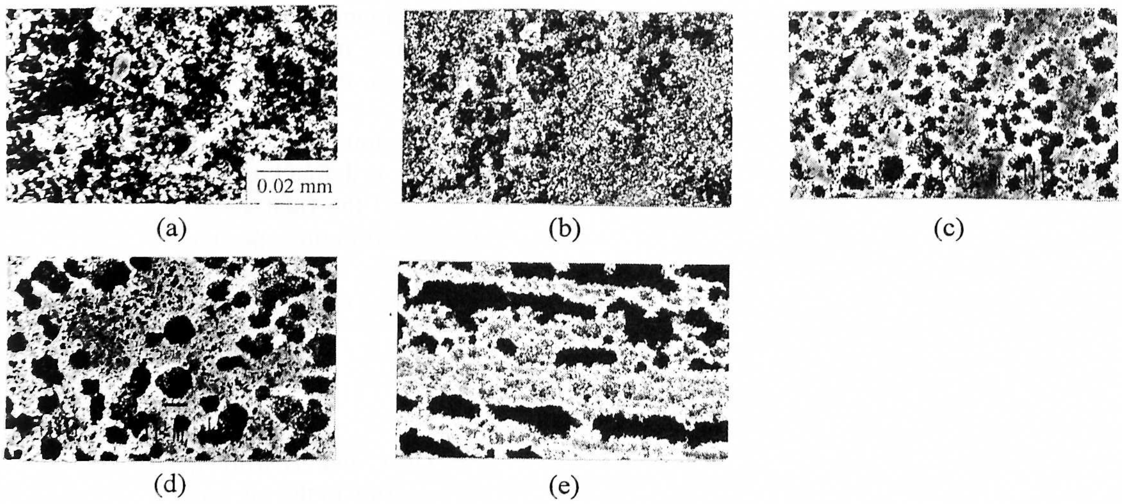
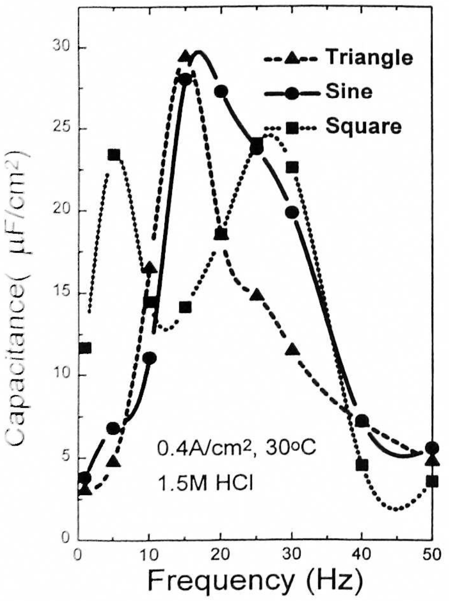


Fig.2 SEM micrographs showing etching morphology of aluminum foils etched in 1.5M HCl solution at 30℃ under AC sinusoidal currents of 50C/㎠ charge with (a)1Hz (b)5Hz (c)15Hz (d)25Hz and (e)40Hz up to a charge of 50C/㎠.

Fig.3 shows the effects of the frequency and waveform of applied AC current on capacitance of etched aluminum foils. It can be seen that a maximum capacitance was obtained at about 15Hz for triangular and sinusoidal waveforms and two capacitance peaks were obtained for rectangular waveforms.



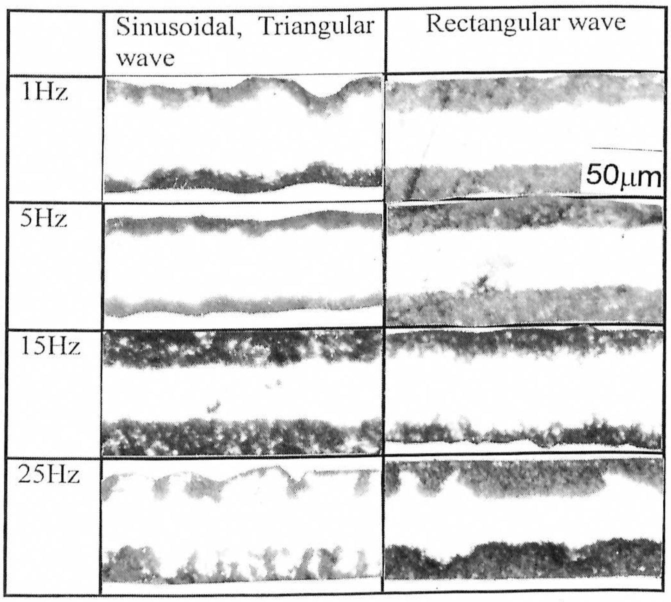


Fig.3 Capacitance of etched aluminum foils etched under various waveforms and frequencies of etching current.

Fig.4 Microstructures of cross sections of aluminum foils etched under various waveforms and frequencies of etching current.

Fig.4 shows microstructures of the cross sections of aluminum foils etched under various waveforms and frequencies of etching current. At low frequencies, macroetching took place and irregular etching occurred at high frequencies, resulting in an optimum etching at medium frequency.

In order to understand the effect of current waveform, various triangular waveforms were applied to the aluminum foils. The shape of triangular waveforms is defined by parameter S ($S=x/l$) in Fig.5. The initial slope of waveform is infinite at S=0 and the final slope of waveform is infinite at S=1. The effect of the shape of triangular current waveform on capacitance of the etched foils is shown in Fig.6. AC current of 15Hz and 0.3A/㎠ was applied up to 50C/㎠. Fig.6 demonstrates that capacitance of etched foils increases and decreases with increasing S value.

4.DISCUSSION

According to AC etching mechanism suggested by Dyer and Alwitt[1], the aluminum dissolutions takes place during anodic half cycle, and etch film forms in the pit wall due to local pH rise by hydrogen reduction during cathodic half cycle. A new etch pit is generated in a weak point of the etch film and repeated sequences of this kind give rise to multidirectional cube by cube pit propagation.

Lin and Hebert's study[2] suggests that the role of cathodic polarization is more complex. They found that prior cathodic polarization increased pit densities on aluminum and the average pit growth current densities. The rapid rise and subsequent drop of potential in the early stage of anodic half cycle in the galvanodynamic voltammetry polarization curves suggest that the breakdown of film takes place at a given anodic potential[3]. The potential is the breakdown potential of the film[6, 7]. Therefore, the electrical charge spent for anodic dissolution is smaller

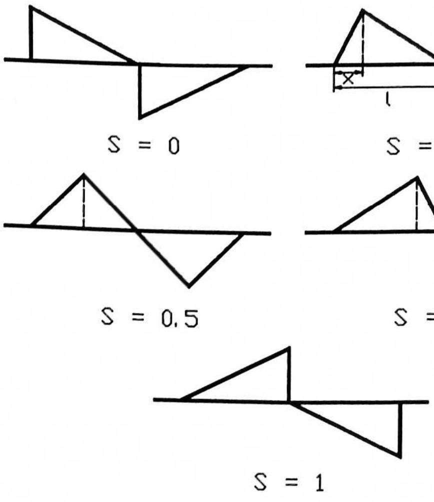


Fig.5 Various current waveforms.

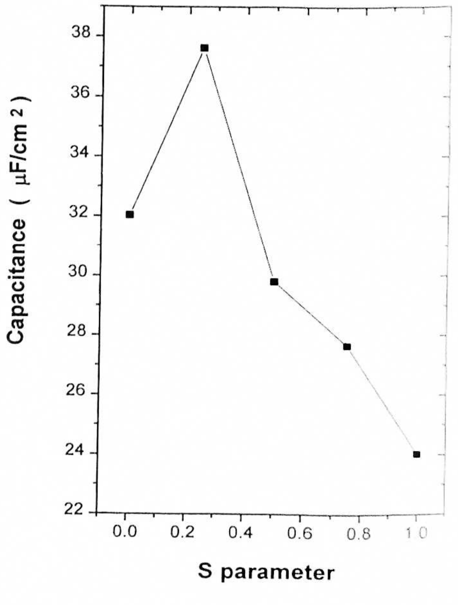


Fig.6 Effect of parameter S of asymmetrical triangular current waveform on capacitance.

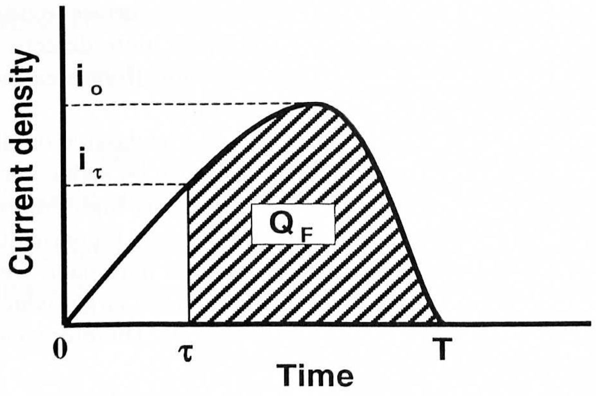


Fig.7 Definition of electrical charge spent for anodic dissolution in anodic half cycle.

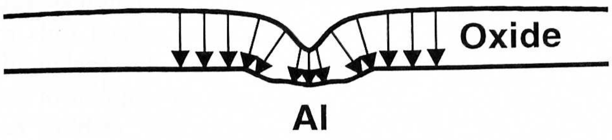


Fig.8 Weak point formation in roll scratch.

than the total electrical charge in the half cycle as shown in Fig. 7. The breakdown potential of the anodic film increases toward the noble direction and the ratio of induction time τ to half cycle period T increases with increasing frequency, because at high frequencies the anodic polarization speed is so high that the chlorine ion can not reach a concentration high enough to break the oxide film in the electrode-electrolyte interface[3].

Etching starts to take place at weak points of surface oxide film. Fig.1 shows that the weak points are related to grain boundaries and roll scratches of aluminum substrate. The impurity concentration is higher in the grain boundaries. Anodic oxide films have defects in the region of

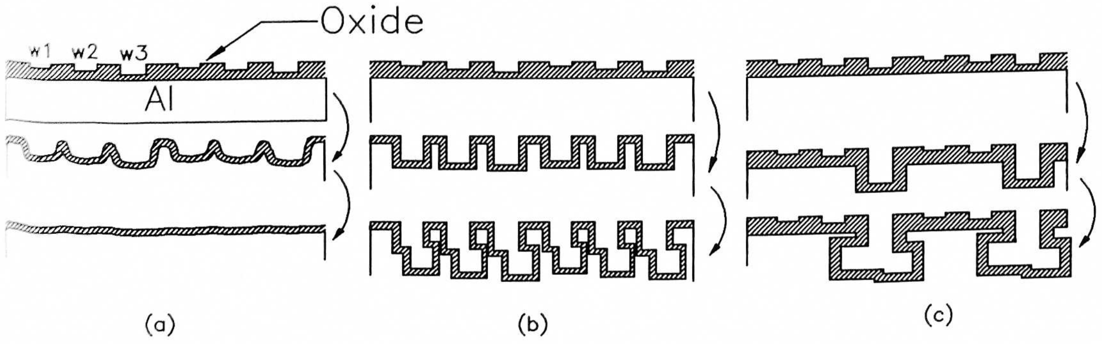


Fig.9 Etching morphologies depending on AC current frequencies.
(a) low frequency (b) medium frequency (c) high frequency

inclusion, in which breakdown of the oxide film starts. The surface oxide film on the grain boundary region of the aluminum substrate is expected to have more defects. The oxide thickness on roll scratches is expected to be thinner because the oxidation front area increases with time as shown in Fig. 8. Therefore, the roll scratches can be weak points.

In order for aluminum to develop deep pits during etching, the passive oxide film on the surface should be stable than the pit wall passive film, which should also be stable enough to resist general etching. When the chlorine ion activity in the etching solution is high enough to develop macro etching, deep etch pits will not be obtained and hence a capacitance increase due to etching will not be achieved. As schematically shown in Fig.9, aluminum foils may have weak points of various levels. At low frequencies, etching power is high and etch pits are large, which in turn make weak points of many levels be etched resulting in macroetching (Fig.9). Therefore, capacitance of the film is not much improved.

As the frequency increases, etching power and etch pit size decrease, and the thickness of passive film on etch pits increases. Therefore, etching occurs at weak points of lower level to form pits, which continue to grow into inside, resulting in increases in the surface area and capacitance(Fig.9).

When the frequency further increases, so that etching can take place at weak points of much lower level, current will be localized to them, resulting in formation of rough and irregular pits (Fig.9). Therefore, the surface area and hence capacitance of etched foils may decrease. Thus, a peak capacitance can be obtained at a medium frequency value. For rectangular waveform, the first peak capacitance was obtained at a lower frequency than for triangular or sinusoidal waveform. It implies that the initial slope of current waveforms influences etching behavior. This will be discussed elsewhere.

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