

# Nucleation and Growth of the Etch Pits and Structure of the Etch Films of ac Etched Aluminum Foils.

吳恩育、林招松、李春穎

E-mail: 9224280@mail.dyu.edu.tw

## ABSTRACT

The aluminum foils for electrolytic capacitors were etched in hydrochloric acid (HCl) using a flow cell. The 25 Hz sinusoidal current waveform with a current density of 60 Apeak/dm<sup>2</sup>, generated via a precision function generator together with a power amplifier, was applied for electrolytic etching. In the meantime, the voltage-current relationship was recorded. The surface of the as-etched Al and the etched Al of which etch film had been removed was observed using scanning electron microscopy (SEM). The detailed morphology and microstructure of the pits and the etch films were characterized using cross-sectional transmission electron microscopy (TEM). In addition, the weight of the etch film and the dissolved Al was measured. Experimental results indicate that the pitted areas and the weight of the etch films and the dissolved Al decreased with increasing HCl concentration, leaving some areas remained unattacked up to 60 s of etching. Cross-sectional TEM further revealed that increasing HCl concentration not only reduced the thickness of the etch film covering the original surface of the Al foil, but also enhanced the propagation of the cubic pits into the Al substrate, forming more vertical-type cubic pits. Furthermore when the HCl concentration was increased, the pitting potential and dissolution time for each anodic half cycle decreased, whereas the induction time for the formation of the pit increased; thereby the effective charge imposed during each half cycle and the accumulated charge for the dissolution of the Al foil decreased with increasing HCl concentration. The longer induction time and shorter dissolution time for pitting in the HCl electrolyte of higher concentration correlate with the more areas that remained unattacked and the less amount of the dissolved Al. Sulfate anions were found to effectively inhibit the nucleation of the pits during the beginning of etching and enhance the formation of the vertical-type cubic pits. In the 0.8M HCl electrolyte, the pitting potential increased with increasing sulfate anions, whereas the dissolution time decreased and the induction time increased with increasing sulfate anions. Conversely, in the 3.2M HCl electrolyte, the pitting potential, the induction time and the dissolution time hardly changed with the electrolyte sulfate anion concentration. In general, the addition of the sulfate anions increased the effective charge imposed during each half cycle and the accumulated charge for the dissolution of the Al foil. The pitting behavior of the Al foil in the 0.8M HCl electrolyte containing 0.24M sodium chloride resembled that of the Al in the 0.8M HCl. Meanwhile, the Al foil etched in the 0.8M HCl electrolyte and in the 0.8M HCl and 2.4M NaCl electrolyte had similar pitting potential, dissolution time and induction time. The weight of the etch film and the dissolved Al in the 0.8M HCl and 2.4M NaCl electrolyte was in between these measured in the 0.8M HCl and 3.2M HCl electrolytes. Finally, the addition of NaCl increased the accumulated charge for the dissolution of the Al foil.

Keywords : electrolytic capacitors, electrolytic-etched aluminum foils, etch film, pitting potential, dissolution time

## Table of Contents

第一章 導論 .....	1	1.1 前言 .....	1	1.2 研究動機 .....	1
.....	2	第二章 文獻回顧 .....	3	2.1 鋁電解電容器之基本結構與原理 .....	3
.....	3	2.2 增加電解電容器靜電容量之方法 .....	4	2.3 鋁電解電容器中陰、陽極箔 .....	4
.....	4	2.3.1 陰極箔 .....	4	2.3.2 陽極箔 .....	5
鋁電解電容器擴面之方法 .....	5	2.4.1 物理方法 .....	6	2.4.2 化學方法 .....	6
.....	6	2.4.3 電解腐蝕 .....	6	2.5 前處理對鋁箔電蝕行為的影響 .....	7
.....	7	2.5.1 鹼洗 .....	7	2.5.2 酸洗 .....	7
.....	8	2.6 電蝕行為探討 .....	8	2.7 電化學方程式 .....	8
.....	9	2.8 鋁箔電蝕之進行機構 .....	9	2.9 交流電蝕之原理與機構 .....	9
.....	12	2.9.1 影響交流電蝕之因素 .....	12	2.10 直流電蝕之原理與機構 .....	12
.....	14	2.10.1 影響直流電蝕之因素 .....	15	2.11 鋁箔在含有氯離子溶液中的腐蝕型態 .....	15
.....	16	2.11.1 氯離子在鋁箔電蝕過程中的影響 .....	17	2.11.2 硫酸根離子在鋁箔電蝕過程中的影響 .....	17
.....	18	第三章 實驗方法 .....	19	3.1 鋁底材的種類 .....	19
.....	19	3.2 電化學腐蝕設備 .....	19	3.2.1 電流-電壓-時間量測 .....	19
.....	21	3.3 電蝕操作條件與程序 .....	26	3.3.1 實驗製程規劃 .....	26

.....26	3.3.2電化學腐蝕操作程序	.....30	3.4 微觀試片製備與觀察
.....32	3.4.1 掃描式電子顯微鏡試片製作與觀察	.....32	3.4.1.1 鋁箔橫截面的觀察
.....32	3.4.2 穿透式電子顯微鏡試片製作與觀察	.....32	3.5 重量變化量測
.....36	3.6 電流-電壓-時間量測	.....36	第四章 結果與討論
.....37	4.1鹽酸濃度的影響	.....37	4.1.1 含腐蝕膜之鋁箔表面形貌
.....37	4.1.2 去腐蝕膜之表面形貌	.....37	4.1.3 蝕孔橫截面TEM觀察
.....38	4.1.4 鋁箔溶蝕量與腐蝕膜重量	.....39	4.1.5 動態電流電壓實驗
.....39	4.2 於鹽酸中添加硫酸鈉的影響	.....41	4.2.1 含腐蝕膜之鋁箔表面形貌
.....41	4.2.2 去腐蝕膜之表面形貌	.....41	4.2.3 蝕孔橫截面TEM觀察
.....42	4.2.4 動態電流電壓實驗	.....42	4.3 純鹽酸中添加氯化鈉交流電蝕的影響
.....45	4.3.1 含腐蝕膜之鋁箔表面形貌	.....45	4.3.2 去腐蝕膜之表面形貌
.....46	4.3.3 蝕孔橫截面TEM觀察	.....46	4.3.4 鋁箔溶蝕量與腐蝕膜重量
.....46	4.3.5 動態電流電壓實驗	.....47	第五章 結論
.....115	第六章 展望	.....118	參考文獻
.....		.....119	

## REFERENCES

- 楊邦朝,余忠,"低壓鋁箔交流腐蝕研究",電子元件與材料, Feb.1998, pp.9-12.
- 歐炳隆,朱俊悌,"電容器用電蝕鋁箔陰極箔研究",中國鋼鐵公司與國立中央大學建教合作期末報告,1997.
- 工業技術研究院技術簡介,固態/晶片型電容器製程,1998年6月
- 肖占文,"電容器鋁箔交流腐蝕擴面機理研究",電子科技大學,July 1999
- 涂肇嘉,"鋁箔電蝕反應之基礎研究及製程改進",行政院國家科學委員會專題研究計劃成果報告,1996.
- 黃志龍,"鋁電解電容器用低壓陽極箔電解腐蝕舉動之研究",中央大學機械工程研究所碩士論文,2000年6月
- 曾美貴,"鋁電解電容器用高壓陽極箔電解腐蝕舉動之研究",中央大學機械工程研究所碩士論文,2000年6月
- C. S. Lin, C. C. Chang and S.H. Hsieh, "Pit Growth of 1050 Aluminum Plates Electrograined in A Nitric Acid ", J. Electrochem. Soc., Vol. 147, No. 10,pp.3647-3653.
- C. S. Lin, C. C. Chang and H. M. Fu, "A-C Electrograining of Aluminum Plates in A Hydrochloric Acid ", Materials chemistry and physics, Vol. 68, No. 1-3, pp. 217-224.
- C. S. Lin and H. M. Fu, "Etch Film and Pit Structure of AA1050 Aluminum Plates Electrograined in Nitric and Hydrochloric Acids", Journal of The Electrochemical Society , Vol. 148, No. 3, in press.
- C. S. Lin and H. M. Fu, 2001, "Effect of AC Current Waveform on the Electrograining of Aluminum Plates I: Etch Film and Pit Morphology; II: Pit Growth and Surface Properties" submitted to Journal of The Electrochemical Society.
- C. K. Dyer and R. S.Alwitt, "Surface Changes during A. C. Etching of Aluminum," J. Electrochem. Soc., Vol.128, No.2,1981, pp. 300-315.
- H. Matsubara , H. Ucki and A. Jamada, "Observation of Chemical Etching Morphology of Aluminum Foil,"表面技術, Vol.45, 1994 , pp. 114-115.
- E. Suganuma and Y. Tanno, "Duplex Structure of Surface Films Formed on Aluminum during AC Etching in Hydrochloric Acid Solution," 表面技術, Vol.41, 1990 , pp. 702-703.
- E. Suganuma , Y. Tanno , T. Ito , A. Funakoshi and K. Matsuki, " Surface Films Formed on Aluminum during AC Etching in Hydrochloric Acid Solution,"表面技術, Vol.41, 1990 , pp. 1049-1053.
- Y. Tanns and E. Suganuma , "TEM Observation of Surface Films Formed on Aluminum under AC Etching in Hydrochloric Acid," 金屬表面技術, Vol.38, 1987 , pp. 492-493.
- K. Fukuoka and M. Kurahashi, "Effect of Indium on the Etching Phenomena for High Purity Aluminum Foil ,"住友輕金屬技報, Vol.34, 1993 , pp. 205-212.
- K. Fukuoka and M. Kurahashi, "Effect of Si -Precipitate on the Capacitor Cathode Foil ," 住友輕金屬技報, Vol.31, 1990 , pp. 238-245.
- H. Zhong and T. Oki, "The Effect of Hydrochloric Acid Concentration and Solution Temperature on the Characteristics of Al Foil during AC Etching under Potential Control," 表面技術, Vol.46, 1995 , pp. 270-275.
- E. Suganuma , Y. Tanno, I. Umetsu , A. Funakoshi and K. Matsuki ,"Factors Affecting the Formation of a porous Layer during AC Etching of Aluminum in HCL solution,"表面技術, Vol.42, 1991, pp. 928-932.
- 鄭陽助,陳秉琨,游建財,鄭智和,"電解電容器用之鋁箔交流電蝕之研究,"大同學報, 15期, 1985年, pp.109-113.
- K. Vu Quang ,F. Brindel , G. Laslaz and R. Buttoudin, "Pitting Mechanism of Aluminum in Hydrochloric Acid under Alternating Current," J. Electrochem. Soc., Vol. 130, 1983 , pp.1248-1305.
- H. Zhong ,R. Ichins, M. Okids and T. Oki, "The Effect of Frequency on the Characteristics of Al Foil during AC Etching under Potential Control," 表面技術, Vol.46, 1995 , pp. 739-744.
- R. S. Alwitt , T. R. Beck and K. Hebert, "Electrochemical Tunnel Growth in Aluminum,"NACE-9 Advances in Localized Corrosion, 1987 ,pp. 145-152.
- W. Lin, G. C. Tu, C. F. Lin and Y. M. Peng, "The Effect of Lead Impurity on the DC-Etching Behavior of Aluminum Foil for Electrolytic Capacitor Usage," Corrosion, Vol.38, 1996, pp.889-907.
- W. Lin, G. C. Tu, C. F. Lin and Y. M. Peng, "The Effect of Indium Impurity on the DC-Etching Behavior of Aluminum Foil for Electrolytic Capacitor Usage," Corrosion, Vol.39, 1997, pp.1531-1543.
- N. Osawa, K. Fukuoka and Z. Tanobe, "Mechanism of Pit Nucleation of Aluminum Foil for Electrolytic Capacitors during Etching Stage of D.C. Etching," 住友輕金屬技報, Vol.33, 1992 , pp. 166-172.
- A. Hibino, T. Oki, " Etching Behavior of Aluminum Foil in Hydrochloric Acid under Potentiostatic Conduction," 住友輕金屬技報, Vol.34, 1993 , pp. 199-204.
- J. Flis and L. Kowalczyk, "Effect of Sulphate Anions on Tunnel Etching of Aluminum,"Journal of Applied Electrochemistry, Vol.25,1995,pp.501-507.
- A. Hibino, M. Tamaki, Y. Watanabe and T. Oki, "The Effect Sulfuric Acid on Tunnel Etching of Aluminum in Hydrochloric Acid," 輕金屬, Vol.42, 1992 , pp. 440-445.
- E. Makino, K. Takeda, T. Sato, E. Suganuma, T. Ito and Y. Tanno, "Direct Current Etching of Aluminum in NaCl/NaNO<sub>3</sub> Mixed Electrolytes," 金屬表面技術, Vol.37, 1986 , pp. 163-168.
- N. Osawa,

K. Fukuoka and Z. Tanobe, "The Etching Behavior of Pit Initiation and Tunnel Growth of Aluminum Foil for Electrolytic Capacitors during Early Stage of D.C. Etching," 住友輕金屬技報, Vol.32, 1991, pp. 124-131. 33. H. Terryn, and J. Vereecken and G. E. Thompson, "AC Electrograining of Aluminum", Trans. IMF, Vol.66,1988, pp. 116-121. 34. P.Laevens, H.Terryn, J. Vereecken and G. E. Thompson, "A Study of The Mechanism of A.C. Electrolytic Graining of Aluminum in Hydrochloric and Nitric Acid," Corrosion Science, Vol.35, Nos.1-4, 1993, pp. 231-238. 35. H. Terryn, J. Vereecken and G. E. Thompson, "The Electrograining of Aluminum in Hydrochloric Acid-I. Morphological Appearance," Corrosion Science, Vol.32, No.11, 1991, pp. 1159-1172. 36. Laevens, H. Terryn, and J. Vereecken, "Comparison of the A.C. Electrograining of Aluminum in Hydrochloric and Nitric Acid," Trans. IMF, Vol.70, No.3, 1992, pp. 105-110. 37. G. E. Thompson and G. C. Wood, "The Effect of Alternating Voltage on Aluminum Electrodes in Hydrochloric Acid," Corrosion Science, Vol. 18, 1978, pp. 721-746. 38. C. K. Dyer and R. S. Alwitt, "Surface Changes during A.C. Etching of Aluminum," J. Electrochem. Soc., Vol.128, No.2, 1981, pp.300-305. 39. 鋁質電解電容器產業專題, 詹文雄, 李克誠. 40. 吳昆祐, "鋁電解電容器用1000系陰極鋁箔之研究", 中央大學機械工程研究所碩士論文, 2000年6月. 41. 永田伊佐也, 鋁箔乾式電解電容器. 東京: 川竹????????株式會社, 1986. 42. 王守緒, 胡濤, 楊邦朝等. 低壓鋁箔腐蝕的鹼喜工藝. 電子元件與材料, 1997, 16(6), 50. 43. 世利修美, 田實孝介. ?????????前處理???NaOH洗滌???處理?檢討. 金屬表面技術, 1988, 39(12), 803. 44. 松木健三, 船越明, 管沼榮一, et al. 鹽酸溶液中????????交流????????前處理?影響. 金屬表面技術, 1986, 37(11), 655. 45. 火田知克. 電解????用陽極箔?製造方法. 特開平6-346260. 46. Wu X, Hebert K, et al. Development of surface impurity segregation during dissolution of aluminum. J Electrochem Soc, 1996, 143(1), 83. 47. Wu X, Asoka-kumar P, Lynn K G, et al. Detection of corrosion related defects in Aluminum using positron annihilation spectroscopy. J Electrochem Soc, 1994, 141(12), 3361. 48. 永田伊佐也, ?????乾式電解電容器, 日本蓄電器工業株式會社刊, chap.4, 171, (1985). 49. P. Laevens, H. Terryn, . Vereecken, B. Kernig and B. Grzemba, "The Influence of Manganese on The AC Electrolytic Graining of Aluminum," Corrosion Science, Vol.38, No.3, 1996, pp.413-429. 50. H. Terryn, J. Vereecken and G. E. Thompson, "The Electrograining of Aluminum in Hydrochloric Acid-II. Formation of Eath Products," Corrosion Science, Vol.32, No.11, 1991, pp. 1173-1188. 51. 日比野淳, 玉置充宏, 渡邊吉章, et al. ?????箔????????及???硫酸影響. 輕金屬, 1992, 42(8), 440. 52. Wu T I, Wu J K. Effect of sulfate ions on corrosion inhibition of AA 7075 aluminum alloy in sodium chloride solution. Corrosion, 1995, 51(3), 185. 53. Flis J, Kowalczyk L. Effect of sulphate anions on tunnel etching of aluminum. J Appl Electrochem, 1995, 25(5), 501. 54. M. S. Hunter, J. Electrochem. Soc. 117(1970)1215. 55. C. G. Dunn, R. B. Bolon, A. S. Alwan and A. W. Stirling, ibid. 118(1971)381. 56. C. E. Welch, Jr., US. Patent 3316164(1967). 57. M. T. Kosmynina and K. P. Bartashov, Zhur. Prikl. Khimii 6(1975)1476. 58. N. A. Hampson, N. Jackson and B. N. Stirrup, Surf. Technol. 5(1977)277. 59. H. Leckie and H. Uhlig, J. Electrochem. Soc., V.113, 1262(1966).