

平版印刷用鋁板電解粗化之研究

傅學名、傅家啟、鄧志堅

E-mail: 9015757@mail.dyu.edu.tw

摘要

本研究針對平版印刷用鋁板進行粗化製程，並藉由蝕孔形貌與微結構觀察以及表面性質分析，來了解鋁板經粗化之蝕孔衍生成長機構與差異。實驗中採用正弦波與方形波兩種交流電源波形以及使用硝酸系、鹽酸系電解液，並選用不同製程所生產之1050 鋁底材（CC 料與DC 料）。電解操作條件為電流密度15A/dm²、交流頻率50Hz、電解液溫度35 及30 秒~300 秒系列的粗化時間，粗化後鋁板浸漬於磷、鉻酸混合液中去除腐蝕膜，藉由量測表面粗糙度、蝕孔衍生數目與靜電容量進行表面性質分析，並利用SEM 觀察蝕孔形貌以及複製蝕孔內部結構之複製模，以期瞭解粗化過程對於蝕孔表面形貌、蝕孔內部衍生構造與表面性質的關係，實驗中又以TEM 解析含腐蝕膜試片之蝕孔微結構與腐蝕膜組織結構鑑定，並以EDS 半定量分析來鑑定腐蝕膜之組成。實驗結果顯示在硝酸液中含腐蝕膜的粗化表面所呈現高度的包旋表面，在鹽酸液中粗化鋁板則為具有許多坑洞的平坦的表面。另外由蝕孔橫截面的觀察，硝酸系的蝕孔特徵為半圓形蝕孔，鹽酸電解液之蝕孔特徵為不規則的半圓形蝕孔，蝕孔寬度較深度大且底部較為平坦。腐蝕膜組織皆為多孔非晶的氫氧化鋁，在硝酸電解液中腐蝕膜呈現層狀的結構且複製蝕孔曲率，顯示具有陽極膜的可能，在鹽酸電解液中腐蝕膜內部含有許多小孔洞，腐蝕膜的形成屬於沈積膜的形式。使用不同粗化電源波形於硝酸液電解粗化時，發現兩種波形所衍生的蝕孔皆為半圓形蝕孔，方波所衍生的蝕孔較為密集且隨粗化時間的增加，蝕孔發展因集中於包旋蝕孔，而使得粗化表面的蝕孔發展不如正弦波的發展均勻。由蝕孔橫截面觀察顯示，方形波所形成的腐蝕膜除層狀腐蝕膜外尚具有覆蓋形式之沈積膜。方形波的蝕孔朝向不均勻發展主要受方形波所提供的粗化電量較正弦波多以及腐蝕膜的沈積造成小型蝕孔被覆蓋，蝕孔的發展轉至包旋蝕孔或大型的圓形蝕孔所造成，因此粗化電量大，造成蝕孔尺寸發展過大，腐蝕膜的沈積造成蝕孔發展不均勻。對不同製程條件生產的1050 鋁板粗化行為探討發現DC 料與CC 料於硝酸電解液粗化時蝕孔的演進過程相近，所生成的基本蝕孔均為圓形蝕孔，並由於圓形蝕孔間的側向連結會有彎月型蝕孔的特徵，當蝕孔間產生二維方向的連結時則形成包旋蝕孔。雖然CC 料與DC 料皆為1050 系印刷用鋁板，但其製程方式不同，所表現出的粗化性質亦有所差異。DC 料在蝕孔的發展上演進較慢，使得表面粗糙度及蝕孔數量皆低於CC 料，同時其表面積增加率較低。由於平版印刷板擁有較高的印刷品質與強韌的耐印性，因此廣泛使用於印刷界。平版經由適當的粗化處理可有效地提升印刷品的解析力與印刷品質，本研究的結果可幫助業者作為日後平版印刷用鋁板粗化條件的參考與品質提升改善的基礎。

關鍵詞：電解粗化；平版印刷板；半圓型蝕孔；方形蝕孔；電蝕；包旋蝕孔；彎月形蝕孔；腐蝕膜

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參考文獻

1. 西川泰久, "ALUMINUM SHEET FOR PRESENSITIZED PRINTING PLATE," 日本輕金屬學會第49 回研討 會論文集, 1996, PP. 44-51.
2. T. SUZUKI AND Y. HAYASHI, "ELECTROLYTIC ETCHING OF ALUMINUM STRIP FOR LITHOGRAPHIC PRINTING PLATES," 金屬表面技術, VOL. 30, NO. 10, 1979, PP. 541-546
3. H. TERRYN, AND J. VEREECKEN AND G. E. THOMPSON, "AC ELECTROGRAINING OF ALUMINUM", TRAN -S. IMF, VOL.66, 1988, PP. 116-121.
4. C. S. LIN, C. C. CHANG AND S.H. HSIEH, "PIT GROWTH OF 1050 ALUMINUM PLATES ELECTROGRAINED IN A NITRIC ACID," SUBMITTED TO JOURNAL OF THE ELECTROCHEMICAL SOCIETY.
5. C. S. LIN, C. C. CHANG AND H.M.FU, "A-C ELECTROGRAINING OF ALUMINUM PLATES IN A HYDROCHLORIC ACID," ACCEPTED, MATERIALS CHEMISTRY AND PHYSICS
6. H. SAKAKI, A. SHIRAI AND A. OHASHI, "AC ELECTROLYTICALLY GRAINING ALUMINUM SUPPORT FOR MAKING A LITHOGRAPHIC PLATE AND PRESENSITIZED LITHOGRAPHIC PRINTING PLATE," US PATENT 4301229, 1981.
7. B. KERNIG, B. GRZEMBA AND G. SCHARF, "AC GRAINING OF LITHOGRAPHIC SHEET IN HYDROCHLORIC ACID," TRANS. IMF, VOL. 70, NO. 4, 1992, PP. 190-194.
8. P. LAEVERS, H. TERRYN, J. 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.
9. G. J. MARSHALL AND J. A. WARD, "INFLUENCE OF MICROSTRUCTURE ON ELECTROGRAINING BEHAVIOR OF COMMERCIAL PURITY ALUMINUM USED FOR LITHOGRAPHIC PRINTING PLATES," MATERIALS SCIENCE AND TECHNOLOGY, VOL.11, OCTOBER 1995, PP. 1015-1023.
10. P. LAEVERS, 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.
11. H. TERRYN, J. VEREECKEN AND G. E. THOMPSON, "THE ELECTROGRAINING OF ALUMINUM IN HYDROCHLORIC ACID - MORPHOLOGICAL APPEARANCE," CORROSION SCIENCE, VOL.32, NO.11, 1991, PP. 1159-1172.
12. H. TERRYN, J. VEREECKEN AND G. E. THOMPSON, "THE ELECTROGRAINING OF ALUMINUM IN HYDROCHLORIC ACID - FORMATION OF ETCH PRODUCTS," CORROSION SCIENCE, VOL.32, NO.11, 1991, PP. 1173-1188.
13. P. LAEVERS, H. TERRYN, AND J. VEREECKEN, "COMPARISON OF THE A.C. ELECTROGRAINING OF ALUMINUM IN HYDROCHLORIC AND NITRIC ACID," TRANS. INST. METAL FINISHING, VOL.70, NO.3, 1992, PP. 105-110.
14. J.-C. HUANG, "THE TREND IN ALUMINUM TREATMENT TECHNOLOGY FOR LITHOGRAPHIC PRINTING PLATE APPLICATION," PROC. SYMP. ALUMINUM SURFACE TREAT. TECH., 1986, PP. 2-18.
15. A. J. DOWELL, "THE ALTERNATING CURRENT ETCHING OF ALUMINUM LITHOGRAPHIC SHEET," TRANS. IMF, VOL.57, 1979, PP. 138-144.
16. 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.
17. 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.
18. 羅福林, 李興才, 印刷工業概論, 印刷工業研究所, 1991.
19. A. J. DOWELL, "THE INFLUENCE OF METALLURGICAL FEATURES IN A.C. ETCHING FOR LITHOPLATES," TRANS. IMF. VOL.64, 1986, PP. 85-90.
20. M. P. AMOR AND J. BALL, "THE MECHANISM OF ELECTROGRAINING ALUMINUM SHEET IN NITRIC / BORIC ACID ELECTROLYTE," CORROSION SCIENCE, VOL. 40. NO.12, 1998, PP.2155-2172.
21. E. PLIEFKE, "PROCESS FOR THE ELECTROCHEMICAL GRAINING OF ALUMINUM FOR USE AS PRINTING PLATE SUPPORTS," US PATENT 4671859, 1987.
22. J. E. WALLS, "PROCESS FOR THE ALUMINUM SURFACE PREPARATION," US PATENT 4502925, 1985.
23. J. E. WALLS, R. L. DRAGON AND T. A. DUNDER, "ELECTROGRAINING OF ALUMINUM WITH HYDROGEN PEROXIDE AND NITRIC OR HYDROCHLORIC ACID," US PATENT, 4336113, 1982.
24. R. GUMBINER AND T.-C. HUANG, "PROCESS FOR ELECTROLYTIC GRAINING OF ALUMINUM SHEET," US PATENT 4052275, 1977.
25. M. C. LLOYD AND S. C. PARISH, "PROCESS FOR ELECTROLYTIC GRAINING OF ALUMINUM," US PATENT 3980539, 1976.
26. A. NISHINO AND T. KAKEI, "PROCESS FOR PRODUCTION ALUMINUM SUPPORT FOR PRINTING-PLATE," US PATENT 5045157, 1991.
27. K. AONO AND H. SAKAKI, "PROCESS FOR PREPARING POSITIVE-ACTING PHOTOSENSITIVE LITHOGRAPHIC ALUMINUM PRINTING PLATE PRECURSOR USING NITRIC ACID ELECTROLYTE FOR GRAINING," US PATENT 4824757, 1989.
28. K. FUKUOKA AND M. KURAHASHI, "EFFECT OF SI-PRECIPIRATE ON THE CAPACITANCE OF AC-ETCHING ALUMINUM ELECTROLYTIC CAPACITOR CATHODE FOIL," 住友輕金屬技報, VOL.31, NO.4, 1990, PP. 10-17.
29. 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.
30. Y. TANNO AND E. SUGANUMA, "RESIN REPLICA TECHNIQUE FOR SEM OBSERVATION OF PROGRESSIVE PITS PRODUCED DURING AC ETCHING OF ALUMINUM," 金屬表面技術, VOL.38, NO.8, 1987, PP. 31-32.
31. F. D. BOGAR AND R. T. FOLEY, "THE INFLUENCE OF CHLORIDE ION ON PITTING OF ALUMINUM," J. ELECTROCHEM. SOC., APRIL 1972, PP. 462-464.
32. A. NISHINO AND T. KAKEI, "PROCESS FOR PRODUCTION ALUMINUM SUPPORT OF A PRINTING PLATE," US PATENT 5141605, 1992.
33. O. GOBBETTI, "ELECTROCHEMICAL GRAINING OF ALUMINUM ON ALUMINUM ALLOY SURFACE," US PATENT 5064511, 1991.
34. JEN-CHI HUANG AND MT KISCO, "TWO STEP METHOD FOR ELECTROLYTICALLY GRAINING LITHOGRAPHIC METAL PLATES," US PATENT 4721552, 1988
35. W. M. MOORE, C. T. CHEN AND G. A. SHIRA, "A VOLTAMMETRIC INVESTIGATION OF AC CORROSION PHENOMENA AT AN ALUMINUM ELECTRODE IN HYDROCHLORIC ACID", CORROSION SCIENCE, VOL.40, 1984, 644-649.
36. K. SHIMIZU, K. KOBAYASHI, P.

SKELDON, G. E. THOMPSON AND G.C. WOOD, "AN ATOMIC FORCE MICROSCOPY STUDY OF THE CORROSION AND FILMING BEHAVIOUR OF ALUMINUM", CORROSION SCIENC -E, VOL.39, NO.4, 1997, 701-718. 37. P. LAEVERS, A. HUBIN, H. TERRY AND J. VEREECKEN, "A WALL-JET ELECTRODE REACTOR AND ITS APPLICATION TO THE STUDY OF ELECTRODE REACTION MECHANISMS PART : STUDY OF THE MECHANISM OF THE A.C. ELECTROLYTIC GAINING OF ALUMINIUM IN HYDROCHLORIC ACID", JOURNAL OF APPLIED ELECTROCHEMISTRY, VOL.28, 1998, 387-396. 38. 森輝雄著, "PS版的歷史與將來", 1994. 39. 張進春, 林招松, "鋁板電解粗化之蝕孔形貌分析", 八七年中國材料科學學會年會論文集(D), PP. 21-24. 40. 張進春, 傅學明, 林招松, "平版印刷用1050 鋁板在鹽酸液中電解粗化", 八八年中國材料科學學會年會論文集, NO.880235. 41. 鮮祺振, "金屬腐蝕膜特性探討", 徐氏基金會, 1998, PP115-130 42. 張進春, "1050 鋁板電解粗化之研究", 大葉大學碩士論文, 1999, PP11-32.