AC ELECTROGRAINING OF ALUMINUM PLATES USING DIFFERENT CURRENT WAVEFORMS

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ABSTRACT

THE MECHANISMS OF ETCH PIT NUCLEATION AND GROWTH, AND ETCH FILM FORMATION WERE STUDIED VIA THE MICROSTRUCTURAL CHARACTERIZATION AND SURFACE PROPERTY MEASUREMENT ON THE ELECTRO -GRAINED 1050 ALUMINUM LITHOGRAPHIC PRINTING PLATES. SEVERAL PARAMETERS OF AC ELECTROGR -AINING WERE STUDIED, INCLUDING THE FREQUENCY, WAVEFORM, AND THE CHARGE AND DENSITY PEAK RATIO OF ANODIC HALF CYCLE TO CATHODIC HALF CYCLE OF THE AC CURRENT. ONE OF THE TWO SAM -PLES PREPARED AT EACH ELECTROGRAINING BATCH, WAS IMMERSED IN PHOSPHORIC/CHROMIC ACID TO REMOVED THE ETCH FILM SO AS TO MEASURE THE SURFACE ROUGHNESS AND CAPACITANCE OF THE AL P -LATE, AND THE WEIGHT OF DISSOLVED AL AND ETCH FILM. IN ADDITION, THE MORPHOLOGY OF THE ETCH PIT WAS CHARACTERIZED USING SCANNING ELECTRON MICROSCOPY (SEM). THE OTHER SAMPLE WAS RESERVED FOR PLANE-VIEW SEM AND CROSS-SECTIONAL TRANSMISSION ELECTRON MICROSCOPY (TEM) OB SERIATION FOR CHARACTERIZING THE MICROSTRUCTURE AND COMPOSITION OF THE ETCH FILM. WHEN ELECTROGRAINED USING SINUSOIDAL AC CURRENT WITH FREQUENCY OF 1 HZ, THE AL PLATE WA -S DOTTED WITH RELATIVELY LARGE ETCH PITS. CONVERSELY, THE AL PLATE WAS UNIFORMLY GRAINED AT 50 HZ, LEADING TO THE FORMATION OF RELATIVELY FINE ETCH PITS. AS ELECTROGRAINING FREQ -UENCY WAS INCREASED TO 250 HZ, THE AL PLATE WAS NON-UNIFORMLY GRAINED; THAT IS, THE AREA DOTTED WITH STRIPE-LIKE PITS COEXISTED WITH THE AREA THAT REMAINED UNATTACKED.GENERALLY, AS ELECTROGRAINING FREQUENCY INCREASED, THE WEIGHT OF THE DISSOLVED AL AND THE ETCH FILM DECREASED, AND EACH LAYER OF THE LAYERED ETCH FILM BECAME THINNER. ALTHOUGH NO DISCERNIB -LE DIFFERENCE WAS MADE BETWEEN THE SINUSOIDAL AND SQUARE WAVEFORMS AS FOR HOW THE ELECTR -OGRAINING FREQUENCY AFFECTED THE GRAINING BEHAVIORS OF THE AL PLATE, THE STRUCTURE OF THE ETCH FILMS DIFFERED WITH THE CURRENT WAVEFORM.FOR EXAMPLE, THE ETCH FILM EXHIBITED A LAYE -RED STRUCTURE WHEN THE SINUSOIDAL WAVEFORM WAS USED. HOWEVER, THE MOUTH OF THE LAYERED E -TCH FILM FORMED USING THE SQUARE WAVEFORM WAS FURTHER FILLED WITH ETCH PRODUCTS. WITH INCREASING THE CHARGE RATIO OF ANODIC TO CATHODIC HALF CYCLE, THE ETCH PITS FORMED IN NITRIC ACID BECAME BIGGER, RESULTING IN A NON-UNIFORMLY GRAINED SURFACE. THE WEIGHT OF THE DISSOLVED AL INCREASED AND THAT OF THE ETCH FILM DECREASED WITH THE CHARGE RATIO. CONVERSELY, A RELATIVELY THICK SINGLE-LAYERED ETCH FILM FORMED WHEN THE CHARGE RATIO OF CATHODIC TO ANODIC HALF CYCLE WAS INCREASED. WHEN ELECTROGRAINED IN HYDROCHLORIC ACID, THE ATTACK OF THE AL PLATE CHANGED FROM GRAINING TO ETCHING AS THE CHARGE RATIO OF ANODIC TO CATHODIC HALF CYCLE WAS INCREASED, LEADING TO THE FORMATION OF COARSE SQUARE ETCH PITS. RELATIVELY LARGE HEMISPHERICAL PITS WHICH BASES WERE COVERED WITH A THIN ETCH FILM WERE OBSERVED AS THE CHARGE RATIO EXCEEDED 10. SIMILARLY, THE GRAINING CHANGED FROM UNIFORM TO NON-UNIFORM AS THE CHARGE OF THE CATHODIC HALF CYCLE INCREASED. MEANWHILE, THE ETCH FILM DISPLAYED A LAYERED STRUCTURE WITH MICORVOIDS RESIDING ALONG THE LAYER BOUNDARY. IN STEAD OF ELECTROGRAINING, THE AL PLATE DISSOLVED UNIFORMLY INTO THE ELECTROLYTE WHEN D -ECREASING THE CATHODIC DENSITY PEAK WHILE KEPT THE ANODIC DENSITY PEAK CONSTANT. MEANWHIL -E, THE ETCH FILM EXHIBITED A SINGLE LAYERED STRUCTURE, WHICH TENDED TO PEEL OFF THE AL SU -BSTRATE. A THIN OXIDE FILM WAS OBSERVED TO BE ADHERENT TO THE AL SUBSTRATE THAT REMAINED UNATTACKED. CONVERSELY, THE POPULATION DENSITY OF THE HEMISPHERICAL PITS DECREASED WITH DECREASING ANODIC DENSITY PEAK WHILE KEPT THE CATHODIC DENSITY PEAK CONSTANT. MOREOVER, THE ETCH PIT WAS ENTIRELY FILLED WITH ETCH PRODUCT.

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REFERENCES

1.H. TERRYN, AND J. VEREECKEN AND G. E. THOMPSON, "AC ELECTROGRAINING OF ALUMINUM", TRANS. IMF, VOL.66, 1988, PP. 116-121. 2.C. S. LIN,C. C. CHANG AND S.H. HSIEH, "PIT GROWTH OF 1050 ALUMINUM PLATES ELECTROGRAIN -ED IN A NITRIC ACID,"JOURNAL OF THE ELECTROCHEMICAL SOCIETY, VOL.147, NO.10, OCTOBER 2000, PP3647-3653. 3.C. S. LIN,C. C. CHANG AND H.M.FU,"AC ELECTROGRAINING OF ALUMINUM PLATES IN A HYDROCHL -ORIC ACID,"MATERIALS CHEMISTRY AND PHYSICS, 68, 2001, PP 217-224. 4.C. S. LIN AND H.M.FU, "ETCH FILM AND PIT STRUCTURE OF AA1050 ALUMINUM PLATES ELECTROGR -AINED IN NITRIC AND HYDROCHLORIC AICDS,"JOURNAL OF THE ELECTROCHEMICAL SOCIETY, VOL. 148, NO. 3, MARCH 2001, PP 240-246. 5.H. SAKAKI, A. SHIRAI AND A.OHASHI, "AC ELECTROLYTICALLY GRAINING ALUMINUM SUPPORT FOR MAKING A LITHOGRAPHIC PLATE AND PRESSENSITIZED LITHOGRAPHIC PRINTING PLATE," US PATENT 4301229,1981. 6.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. 7.P. LAEVERS, H. TERRYN, J. VEREECKEN, B. KERNIG AND B. GRZEMBA, "THE INFLUENCE OF MANGA -NESE ON THE AC ELECTROLYTIC GRAINING OF ALUMINUM," CORROSION SCIENCE, VOL.38, NO.3, 1996, PP. 413-429. 8.G. J. MARSHALL AND J. A. WARD, "INFLUENCE OF MICROSTRUCTURE ON ELECTROGRAINING BEHAVIO - UR OF COMMERCIAL PURITY ALUMINUM USED FOR LITHOGRAPHIC PRINTING PLATES," MATERIALS SC -IENCE AND TECHNOLOGY, VOL.11, OCTOBER 1995, PP. 1015-1023. 9.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 SCI -ENCE, VOL.35, NOS.1-4, 1993, PP. 231-238. 10.H. TERRYN, J. VEREECKEN AND G. E. THOMPSON, "THE ELECTROGRAINING OF ALUMINUM IN HYDROC HLORIC ACID - . MORPHOLOGICAL APPEARANCE," CORROSION SCIENCE, VOL.32, NO.11, 1991, PP. 1159-1172. 11.H. TERRYN, J. VEREECKEN AND G. E. THOMPSON, "THE ELECTROGRAINING OF ALUMINUM IN HYDROC -HLORIC ACID -

. FORMATION OF ETCH PRODUCTS," CORROSION SCIENCE, VOL.32, NO.11, 1991, PP. 1173-1188. 12.P. LAEVERS, H. TERRYN, AND J. VEREECKEN, "COMPARISON OF THE A.C. ELECTROGRAINING OF AL -UMINUM IN HYDROCHLORIC AND NITRIC ACID," TRANS. INST. METAL FINISHING, VOL.70, NO.3, 1992, PP. 105-110. 13.J-C. HUANG,"THE TREND IN ALUMINUM TREATMENT TECHNOLOGY FOR LITHOGRAPHIC PRINTING PLATE APPLICATION," PROC. SYMP. ALUMINUM SURFACE TREAT. TECH., 1986, PP. 2-18. 14.A.J. DOWELL, " THE ALTERNATING CURRENT ETCHING OF ALUMINUM LITHOGRAPHIC SHEET," TRANS. IMF, VOL.57, 1979, PP. 138-144. 15.G. E. THOMPSON AND G. C. WOOD, "THE EFFECT OF ALTERNATING VOLTAGE ON ALUMINUM ELECTROD -ES IN HYDROCHLORIC ACID," CORROSION SCIENCE, VOL.18, 1978, PP. 721-746. 16.C. K. DYER AND R. S. ALWITT, "SURFACE CHANGES DURING A.C. ETCHING OF ALUMINUM," J. ELE -CTROCHEM. SOC., VOL.128, NO,2,1981, PP300-305. 17.A.J. DOWELL, "THE INFLUENCE OF METALLURGICAL FEATURES IN A.C. ETCHING

FOR LITHOPLATES ," TRANS. IMF. VOL.64, 1986, PP. 85-90. 18.M. P. AMOR AND J. BALL,"THE MECHANISM OF ELECTROGRAINING ALUMINUM SHEET IN NITRIC / BO -RIC ACID ELECTROLYTE," CORROSION SCIENCE, VOL. 40. NO.12, 1998, PP.2155-2172. 19.E. PLIEFKE, "PROCESS FOR THE ELECTROCHEMICAL GRAING OF ALUMINUM FOR USE AS PRINTING PL -ATE SUPPORTS," US PATENT 4671859,1987. 20.J. E. WALLS, "PROCESS FOR THE ALUMINUM SURFACE PREPARATION," US PATENT ,4502925,1985. 21.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. 22.R. GUMBINNER AND T-C. HUANG, "PROCESS FOR ELECTROLYTIC GRAINING OF ALUMINUM SHEET," US PATENT,4052275,1977. 23.M. C. LLOYD AND S. C. PARISH, "PROCESS FOR ELECTROLYTIC GRAINING OF ALUMINUM," US PATE -NT,3980539,1976. 24.A.NISHINO AND T. KAKEI,"PROCESS FOR PRODUCTION ALUMINUM SUPPORT FOR PRINTING-PLATE, "US PATENT 5045157,1991. 25.K. AONO AND H. SAKAKI, "PROCESS FOR PREPARING POSITIVE-ACTING PHOTOSENSITIVE LITHOGRAP -HIC ALUMINUM PRINTING PLATE PRECURSOR USING NITRIC ACID ELECTROLYTE FOR GRAINING," US PATENT 4824757,1989. 26.F. D. BOGAR AND R. T. FOLEY, "THE INFLUENCE OF CHLORIDE ION ON PITTING OF ALUMINUM," J. ELECTROCHEM. SOC., APRIL 1972, PP. 462-464. 27.A.NISHINO AND T. KAKEI,"PROCESS FOR PRODUCTION ALUMINUM SUOOPRT OF A PRINTING PLATE," US PATENT 5141605,1992. 28.GOBBETTI, "ELECTROCHEMICAL GRAINING OF ALUMINUM ON ALUMINUM ALLOY SURFACE," US PATENT 5064511,1991. 29.JEN-CHI HUANG AND MT KISCO,"TWO STEP METHOD FOR ELECTROLYTICALLY GRAINING LITHOGRAPHIC METAL PLATES," US PATENT 4721552,1988 30.W. M. MOORE, C. T. CHEN AND G. A. SHIRA, "A VOLTAMMETRIC INVESTIGATION OF AC CORROSION PHENOMENA AT AN ALUMINIUM ELECTRODE IN HYDROCHLORIC ACID", CORROSION SCIENCE, VOL.40, 1984, 644-649. 31.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 SCIEN -CE, VOL.39, NO.4, 1997, 701-718. 32.P. LAEVERS, A. HUBIN, H. TERRYN AND J.VEREECKEN,"A WALL-JET ELECTRODE REACTOR AND ITS APPLICATION TO THE STUDY OF ELECTRODE REACTION MECHANISMS PART : STUDY OF THE MECHA -NISM OF THE A.C. ELECTROLYTIC GAINING OF ALUMINIUM IN HYDROCHLORIC ACID", JOURAL OF APPLIED ELECTROCHEMISTRY, VOL.28, 1998, 387-396. 33.K. FUKUOKA AND M. KURAHASHI, "EFFECT OF SI-PRECIPITATE ON THE CAPACITANCE OF AC-ETCHIN -G AL ELECTROLYTIC CAPACITOR CATHODE FOIL,"住友輕金屬技報, VOL.31, NO.4, 1990, PP. 10 -17. 34.Y. TANNO AND E. SUGANUMA, "RESIN REPLICA TECHNIQUE FOR SEM OBSERIATION OF PROGRESSIVE PITS PRODUCED DURING AC ETCHING OF ALUMINUM." 金屬表面 技術, VOL.38, NO.8, 1987, PP. 31 -32. 35.T. SUZUKI AND Y. HAYASHI, "ELECTROLYTIC ETCHING OF ALUMINUM STRIP FOR LITHOGRAPHIC PR -INTING PLATES," 金屬表面技術, VOL. 30, NO. 10, 1979, PP. 541-546 36.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. 37.森 輝雄著, "PS版的歷史與將來", 1994.PP. 9-14 38.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. 39.鮮祺振, "金屬腐蝕膜特性探討",徐氏基 金會,1998,PP115-130 40.羅福林,李興才,印刷工業概論,印刷工業研究所,1991. 41.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. 42.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.880235.43.張進春,"1050鋁板電解粗化之研究",大葉大學碩士論文,1999,PP11-32.44.傅學 明,李佳盈,林招松"平版印刷1050鋁板以方形波及正弦波電解粗化之研究",八九年中國材料 科學學會年會論文集 45.傅學明,"平版印 刷用鋁版電解粗化之研究",大葉大學碩士論文,2000,PP18-37.