

High-strength Copper Alloy and Its Composite Electrodeposition

張靜芳、李春穎、林招松、張舜長

E-mail: 9419520@mail.dyu.edu.tw

ABSTRACT

Copper has been widely used in industrial applications due to its excellent conducting properties both in thermal and electrical aspects. However, the inferiority in mechanical strength makes the scope of its application restricted. Therefore, improving the mechanical strength, while retaining the conducting properties, becomes an important research topic. During the last decades, most studies in the composite electroplating concentrated on the enhancement of the codeposition of alumina in copper matrix. The discussion on the relationship between the material property and microstructure of the composite coating is rarely seen in the literature. A closed electroplating system was fabricated in this thesis and an experimental study on the effect of process parameters for this alumina/copper codeposition was conducted. The field-emission scanning electron microscope (FE-SEM) and transmission electron microscope (TEM) were employed in the examination of the microstructure of the coating. On the other hands, X-ray diffraction (XRD), energy dispersive spectrometer (EDS) and hardness tester were used to study the correlation between the microstructure and mechanical properties. The results showed that the addition of cobalt or thallium ion in the electrolyte can increase the amount of codeposited alumina. Nevertheless, the codeposited alumina was only found near the surface of the coating instead of uniform distribution through the thickness. It is concluded that for the acid electrolyte of copper sulfide, the additive of TI or Co ion, pH of the solution and process parameters can used to tune the preferred orientation, defect of the microstructure and the hardness of the coating.

Keywords : Alumina, Composite Electroplating, Preferred Orientation

Table of Contents

目錄 封面內頁 頁碼 簽名頁 授權書 iii 中文摘要 v 英文摘要 vi 誌謝 vii 目錄 viii 圖目錄 xi 表目錄 xiii 第一章 緒論 1 1.1 前言 1
1.2 研究動機 2 1.3 本文架構 2 第二章 文獻探討 5 2.1 基本電鍍原理 5 2.2 複合電鍍共析機制 6 2.2.1 Guglielmi 二階段吸附機制 6 2.2.3 Foster 之動力式 7 2.2.3 增子昇及虫明克彥之研究 8 2.2.4 近年之共沈積機制 10 2.4 粉末共鍍含量分析 11 第三章 實驗方法 12 3.1 實驗設備 13 3.1.1 封閉式槽體 13 3.1.2 開放式槽體 18 3.2 鍍前處理 20 3.2.1 鍍液配置 20 3.2.2 氧化鋁粉前處理 22 3.2.3 陽極前處理 22 3.2.4 陰極前處理 23 3.2.4.1 銅基材前處理 23 3.2.4.2 不鏽鋼基材前處理 23 3.3 鍍層分析之各類試片製作 24 3.3.1 微硬度試驗與橫截面金相試片 24 3.3.2 掃描式電子顯微鏡試片製作 25 3.3.3 X 光射線繞射儀量測 28 3.3.4 顆粒共鍍量量測 28 3.3.5 穿透式電子顯微鏡試片製作 29 第四章 實驗結果 31 4.1 酸性硫酸銅 31 4.2 添加 $-Al_2O_3$ 對鍍層結構之影響 36 4.3 Co^{2+} 對複合鍍層之影響 39 4.3.1 Co^{2+} 對 $-Al_2O_3$ 共鍍量之影響 39 4.3.2 Co^{2+} 對鍍層硬度值之影響 41 4.3.3 Co^{2+} 對鍍層結構之影響 43 4.4 Tl^+ 對複合鍍層之影響 46 4.4.1 Tl^+ 對 $-Al_2O_3$ 共鍍量之影響 46 4.4.2 Tl^+ 對鍍層硬度值之影響 48 4.4.3 Tl^+ 對鍍層結構之影響 50 4.5 pH 對鍍層結構之影響 51 4.6 槽體對鍍層結構之影響 53 4.7 鍍層橫截面觀察 55 4.8 穿透式電子顯微鏡觀察鍍層微結構 57 第五章 結論 61 參考文獻 63 圖目錄 圖2.1 電鍍示意圖 5 圖2.2 Guglielmi 二階段吸附機制 7 圖2.3 現階段共沈積機制模型 9 圖3.1 本研究實驗規劃整體流程圖 12 圖3.2 封閉式複合電鍍裝置是意圖 15 圖3.3 開放式複合電鍍裝置是意圖 16 圖3.4 電解槽體示意圖 16 圖3.5 陽極壓克力蓋示意圖 17 圖3.6 陰極壓克力蓋示意圖 17 圖3.7 開放式複合電鍍裝置示意圖 19 圖3.8 SEI 觀察複合鍍層 27 圖3.9 橫截面TEM 試片製作流程圖 30 圖4.1 純銅電鍍鍍層金相圖, 1000X 33 圖4.2 純銅電鍍鍍層的表面形貌 34 圖4.3 電解槽不同角度放置示意圖制 35 圖4.4 銅及Cu- Al_2O_3 複合鍍層的XRD 圖 37 圖4.5 Cu- Al_2O_3 鍍層之表面形貌 38 圖4.6 Co^{2+} 添加量對顆粒共鍍之影響 40 圖4.7 銅鈷複合電鍍硬度值 41 圖4.8 複合鍍層金相圖, 1000X 42 圖4.9 添加 Co^{2+} 對鍍層優選方位的影響 44 圖4.10 橫截面TEM 照片 45 圖4.11 Tl^+ 添加量對顆粒共鍍量之影響 47 圖4.12 Tl^+ 添加量對鍍層硬度值之影響 48 圖4.13 添加 Tl^+ 後鍍層之表面形貌 49 圖4.14 添加 Tl^+ 對鍍層優選方位的影響 50 圖4.15 改變pH 值對鍍層優選方位的影響 52 圖4.16 槽體對鍍層優選方位的影響 54 圖4.17 以背向電子影像觀察鍍層橫截面 56 圖4.18 穿透式電子顯微鏡觀察鍍層微結構, 脈衝電鍍Cu-Co(0.5g/l) - Al_2O_3 , 脈衝週期: 1/2 鍍層微結構 58 圖4.19 穿透式電子顯微鏡觀察鍍層微結構, Cu- Co(0.5g/l)- Al_2O_3 -(N2 攪拌)鍍層微結 59 圖4.20 橫截面TEM 照片顯示氧化鋁粉吸附於鍍層表面 60 表目錄 表1.1 常用複合鍍層之金屬與材料微粒 4 表3.1 硫酸銅基本鍍液之組成 21 表3.2 銅鈷複合電鍍鍍液之組成 21 表3.3 銅鈹複合電鍍鍍液之組成 21 表3.4 複合鍍層之化學腐蝕液的組成 25 表4.1 純銅電鍍之操作條件 32 表4.2 Cu/ $-Al_2O_3$ 電鍍之操 36 表4.3 添加 Co^{2+} 之操作條件 39 表4.4 添加 Tl^+ 之操作條件 46

REFERENCES

- [1]張允誠, 胡如南, 向榮, 1997, 電鍍手冊, 國防工業出版社 [2]曾貨梁, 陳均武等人編著, 1997, 電鍍工藝手冊, 機械工業出版社
- [3]L. P ' eter, A. Czira ' ki and L. Poga ' ny, 2001, " Microstructure and Giant Magnetoresistance of Electrodeposited Co-Cu/Cu Multilayers, " Journal of the Electrochemical Society, 14, 83, C168.
- [4]曾貨梁, 吳仲達, 陳鈞武, 呂佩仁, 秦月文, 1997, 電鍍工業手冊, 機械工業出版社 [5]N. Guglielmi, 1972, " Kinetics of the Deposition of Inert Particles from Electrolytic Baths, " Journal of the Electrochemical Society, 119, 1009.
- [6]J. Foster and B. Cameron, 1976, " The Effect of Current Density and Agitation on the Formation of Electrodeposited Composite Coatings, " Transactions of the Institute of Metal Finishing, 54, 178.
- [7]增子昇, 虫明克彥, 1977, " Electrodeposition of Ni-Al₂O₃ Composites on Rotating Cylinder Electrode, " 金屬表面技術, 28, 10, 534.
- [8]增子昇, 虫明克彥, 1980, " Deposition Kinetics of Alumina Particle During Electroplating of Nickel-Alumina Composites, " 金屬表面技術, 31, 10, 523.
- [9]增子昇, 虫明克彥, 1980, " Deposition Kinetics of Alumina Particle During Electroplating of Nickel-Alumina Composites, " 金屬表面技術, 31, 10, 541.
- [10]增子昇, 虫明克彥, 1985, " 分散型複合電鍍, " Denki Kagaku, 53, 1, 45.
- [11]J. P. Celis, J. R. Roos and C. Buelens, 1987, " A Mathematical Model for the Electrolytic Codeposition of Particles with a Metallic Matrix, " Journal of the Electrochemical Society, 134, 1402.
- [12]J. Fransaer, J. P. Celis and J. R. Roos, 1992, " Analysis of the Electrolytic Codeposition of Non-Brownian Particles with Metals, " Journal of the Electrochemical Society, 139, 413.
- [13]J. P. Celis, J. R. Roos and C. Buelens and J. Fransaer, 1991, " Mechanism of Electrolytic Composite Plating: Survey and Trends, " Transactions of the Institute of Metal Finishing, 69, 4, 133.
- [14]T. W. Tomaszewski, L. C. Tomaszewski and H. Brown, 1969, " Codeposition of Finely Dispersed Particles with Metals, " Plating, 1234.
- [15]J. R. Roos, J. P. Celis and J. A. Helsen, 1977, " Codeposition of Alpha- and Gamma-Alumina with Copper from Copper Sulphate Baths, " Transactions of the Institute of Metal Finishing, 55, 113.
- [16]E. S. Chen, G. R. Lakshiminarayanan, F. K. Sauter, 1971, " The Codeposition of Alumina and Titania with Copper, " Metallurgical Transactions, 2, 937.
- [17]G. Wu, N. Li, D. Zhou and K. Mitsuo, 2004, " Electrodeposited Co-Ni-Al₂O₃ Composite Coatings, " Surface and Coatings Technology, 176, 157.
- [18]V. V. Grinina and Y. M. Pokukarov, 1985, " Effect of Periodic Current on the Incorporation of Foreign Particles in Electrolytic Copper Deposits, " Insititute of Physical Chemistry, Academy of Sciences of the USSR, Nov., Russia.
- [19]李建成, 1987, " 銅/氧化鋁複合電鍍動力學之研究, " 碩士論文, 國立清華大學化學工程學系 [20]H. Hayashi, S. Izumi and I. Tari, 1993, " Codeposition of -Alumina Particles from Acid Copper Sulfate Bath, " Journal of the Electrochemical Society, 140, 2.
- [21]謝培煥, 2002, " 鎳-氧化鋁複合電鍍行為對鍍層性質之影響, " 碩士論文, 國立成功大學化學工程學系 [22]蔡梨暖, 2002, " 鈷銅合金電鍍之研究, 碩士論文, 大葉大學機械工程研究所 [23]C. S. Lin, C. Y. Lee, C. F. Chang, C. H. Chang, 2005, " Annealing Behavior of Electrodeposited Ni-TiO₂ Composite Coatings, " Surface and Coatings Technology, in press.