

磁場對奈米鎳磷合金之電催化活性研究

曹竣誠、李弘彬、李得勝

E-mail: 371963@mail.dyu.edu.tw

摘要

本論文使用二次陽極氧化法製備陽極氧化鋁膜，以陽極氧化鋁膜做為結構模板，結合電解沉積法製備鎳奈米線與鎳磷合金奈米線，同時電解沉積製備鎳平板和鎳磷合金平板。藉由場發射掃描式電子顯微鏡(FE-SEM)、穿透式電子顯微鏡(TEM)、震動樣品磁度儀(VSM)和X光繞射分析儀(XRD)對奈米線進行分析與觀察，獲得孔洞厚度為30 μm、直徑為70~80nm陽極氧化鋁膜後，電解沉積鎳奈米線與鎳磷合金奈米線，在以0.5M H₂SO₄酸性溶液中，進行有磁場與無磁場環境對平板與奈米線做電化學量測。研究結果顯示，在磁場與無磁場環境中，磁場有助於提升平板與奈米線的電催化活性；研究再藉由奈米效應增加比表面積，也有助於鎳奈米線與鎳磷合金奈米線對電催化活性的增加。

關鍵詞：鎳奈米線、鎳磷合金奈米線、電催化活性膜、氧化鋁膜

目錄

封面內頁 簽名頁 中文摘要... iii	Abstract... iv	致謝... v	目錄... vi	圖目錄... x	表目錄... xiii																	
第一章 緒論... 1	1.1 前言... 1	1.2 研究動機... 2																				
第二章 文獻探討... 3	2.1 電鍍基本原理... 3	2.2 合金電鍍之電解定律與電流效率... 5	2.3 電鍍液系統與操作參數對鍍層性質影響... 7	2.3.1 鎳電鍍液系統種類... 7	2.3.2 有機添加劑之影響... 8	2.3.3 鍍液pH值之影響... 9	2.4 鎳磷共鍍機制... 10	2.5 鎳磷合金電催化特性... 14	2.6 電催化活性機制... 15	2.7 陽極氧化鋁... 18	2.7.1 多孔氧化鋁... 18	2.7.2 氧化鋁形成化學式... 21	2.7.3 多孔氧化鋁的形成機制... 22	2.7.4 二次氧化法增加多孔氧化鋁孔洞規則性... 24	2.8 奈米材料之特性... 26	2.8.1 小尺寸效應... 26	2.8.2 表面效應... 27	2.8.3 量子及量子穿隧效應... 28	2.9 磁性材料與磁場作用力... 29	2.9.1 磁性材料... 29	2.9.2 勞倫茲力... 32	2.9.3 磁滯曲線... 33
第三章 實驗方法... 35	3.1 陽極氧化鋁的治具與設備... 37	3.2 陽極氧化技術... 39	3.3 鍍液的配置... 41	3.4 電鍍平板與奈米線製備... 43	3.5 電化學量測... 45	3.6 鍍層分析與結構觀察... 49	3.6.1 場發射掃描式電子顯微鏡(FE-SEM)... 49	3.6.2 XRD量測... 50	3.6.3 穿透式電子顯微鏡(TEM)... 50	3.6.4 震動樣品磁度儀(VSM)... 51												
第四章 實驗結果... 52	4.1 陽極氧化鋁膜表面形貌... 52	4.2 電解沉積鎳磷合金平板與奈米線... 54	4.3 鍍層XRD分析... 58	4.4 鍍層EDS成分分析... 60	4.5 鎳奈米線TEM觀察... 62	4.6 磁性分析... 64	4.7 磁場對電催化活性分析與觀察... 66	4.7.1 磁場對平板電催化活性分析... 66	4.7.2 磁場對奈米電催化活性分析... 69													
第五章 討論... 72	5.1 磁場對平板與奈米穩定性... 72	5.2 電催化活性氣泡觀測... 74	5.3 磁場對平板與奈米線電極電催化活性影響... 78																			
第六章 結論... 81	參考文獻... 82																					

參考文獻

- [1] M. M. Jaksic, "Advances in electrocatalysis for hydrogen evolution in the light of the Brewer – Engel valence-bond theory," *Int. J. Hydrogen Energy*, Vol. 12, 1987, pp.727-752.
- [2] 許臣翔, "微構型鎳磷合金電鍍及其於硫酸溶液中電催化活性研究", 大葉大學機械與自動化工程學系碩士論文, 2009年6月。
- [3] 馬振基, "奈米材料科技原理與應用", 全華圖書股份有限公司, 2007年10月。
- [4] 王世宗, "於檸檬酸浴中電鍍鎳磷合金及其電催化性質", 國立台灣大學材料科學與工程學研究所論文, 2006年6月。
- [5] 吳瑞文, "鎳磷合金電鍍層之內應力與磨耗研究", 大葉大學機械工程研究所碩士論文, 2008年6月。
- [6] 楊文呈, "壓花輪模具鎳磷合金電鍍製程", 大葉大學機械工程學系碩士論文, 2006年6月。
- [7] 張允誠、胡如南、向榮, "電鍍手冊(上冊)", 第二版, 國防工業出版社, 北京, 1997年。
- [8] 蘇葵陽、張良謙, "實用電鍍理論與實際", 復文書局, 1986。
- [9] N. K. Dirjal, et.al, Plat. "The Role of Electroless Plating Bath Constituents in the Catalytic Oxidation of the Hypophosphite Ion," *Plating and Surface Finishing*, Vol. 85, 1998, pp.74-77
- [10] J. L. Carbajal and R. E. White, "Electrochemical Production and Corrosion Testing of Amorphous Ni-P," *J. Electrochem Soc.*, Vol. 135, 1988, pp.2952-2957
- [11] M. Ratzker, D. S. Lashmore and K. W. Pratt, "Electrodeposition and Corrosion Performance of Nickel-Phosphorus Amorphous Alloys," *Plating and Surface Finishing*, Vol. 76, September 1986, pp.74-82
- [12] E. Toth-Kafar, I. Bakonyi, A. Solyom, J. Hering and G. Konczos, "Preparation and Characterization of Electrodeposited Amorphous Ni-P Alloys," *Surface and Coating Technology*, Vol. 31, 1987, pp.31-43
- [13] R. Rajnarayan and M. N. Mungole, "Electrodeposition of Ni-P Alloy Coatings," *Surface Technology*, Vol. 24, 1985, pp.233-239
- [14] J. Crousier, Z. Hanane and J-P. Crousier, "Electrodeposition of Ni-P Amorphous Alloys A Multilayer Structure," *Thin Solid Films*, Vol. 248, 1994, pp.51-56
- [15] 鄧伊浚, "電鍍鎳鈷與鎳鐵合金組織與機械性質之研究", 大葉大學機械工程研究所碩士論文, 2003年6月。

- [16]陳黼澤, “ 鎳磷與鈷磷合金電鍍 ”, 國立台灣大學材料科學與工程學研究所碩士論文, 2005年7月。
- [17]D. Baudrand, “ Nickel Sulfamate Plating, Its Mystique and Practicality, ” *Metal Finishing.*, Vol. 94, 1996, pp.15-18 [18]T. Morikawa, T. Nakade, M. Yokoi, Y. Fukumoto and C. Iwakura, “ Electrodeposition of Ni-P Alloys From Ni-Citrate Bath, ” *Electrochimica Acta.*, Vol. 42, 1997, pp.115-118 [19]R. L. Zeller, III and U. Landau, “ Electrodeposition of Ni-P Amorphous Alloys, ” *J. Electrochem. Soc.*, Vol. 139, 1992, pp.3464-3469 [20]G. McMahon and U. Erb, “ Structural Transitions in Electroplated Ni-P Alloys, ” *J. Materials Science Letters.*, Vol. 8, 1989, pp.865-868 [21]M. M. V. Parente, O. R. Mattos, S. L. Diaz, P. Lima Neto and F. J. Fabbi Miranda, “ Electrochemical Characterization of Ni-P and Ni-Co-P Amorphous Alloy Deposits Obtained by Electrodeposition, ” *J. Applied Electrochemistry.*, Vol. 31, 2001, pp.677-683 [22]T. M. Harris and Q. D. Dang, “ The Mechanism of Phosphorus Incorporation during the Electrodeposition of Nickel-Phosphorus Alloys, ” *J. Electrochem. Soc.*, Vol. 140, 1993, pp.81-83 [23]Kawashima, Y. P. Lu, H. Habazaki, K. Asama and K. Hashimoto, “ Structure and Corrosion Behavior of Electro-Deposited Ni-P Alloys, ” *Corrosion Engineering*, Vol. 38, No 11, 1989, pp.643-653 [24]Brenner, “ Electrodeposition of Alloys, ” Academic Press, New York, Vol. II, 1963, p.457.
- [25]K. Masui, T. Nomura, S. Kwon and D. Chang, “ The Mechanism of Ni-P Alloy Deposition by Electroplating Method, ” *表面技術*, Vol. 43, 1992, pp.195-199.
- [26]T. Morikawa, M. Yokoi, S. Shiroma, S. Eguchi and E. Kousai, “ Electroplating of Ni-P Alloys from Ni-Citrate Bath, ” *表面技術*, Vol. 43, 1992, pp.353-354.
- [27]李鴻年、張紹恭、張炳乾、宋子玉, “ 實用電鍍工藝 ”, 第一版, 國防工業出版社, 北京, 1990年。
- [28]Paseka, “ Evolution of hydrogen and its sorption on remarkable active amorphous smooth Ni-P(x) electrodes, ” *Electrochim Acta.*, Vol. 40, 1995, pp.1633-1640 [29]W. K. Hu, Cao X. J., Wang F. P., Zhang Y. S. “ A Novel Cathode For alkaline Water Electrolysis, ” *International Journal of Hydrogen Energy.*, Vol. 22, 1997, pp.441-443 [30]D. S. Lashmore and J. F. Weinroth, “ Pulse Electrodeposition of Nickel-Phosphorus Metallic Glass Alloys, ” *Plating Surface Finishing.*, Vol. 69, 1982, pp.72-76 [31]G. Lu, P. Evans, “ G. Zangari, *J. Electrochem. Soc.*, Vol. 150, 2003, A551 [32]B. Borresen, G. Hangen, and R. Tunold, “ Hydrogen evolution on $Ru_xTi_{1-x}O_2$ in 0.5 M H_2SO_4 , ” *Electrochim Acta.*, Vol. 47, 2002, pp.1819-1827 [33]E. J. Kelly and H. R. Bronstein, *J. Electrochem. Soc.*, Vol. 131, 1984, p.2232 [34]B. E. Conway and B. V. Tilak, “ Behavior and Characterization of Kinetically Involved Chemisorbed Intermediates in Electrocatalysis of Gas Evolution Reactions, ” *Advances in Catalysis.*, Vol. 38, 1992, p.41 [35]A. Lasia, *Curr. Top. Electrochem*, Vol. 2, 1993, p.239 [36]E. R. Gonzalez, G. Tremiliosi-Filho, and M. J. De Giza, *ibid*, Vol. 2, 1993, p.167 [37]A. Lasia and A. Rami, J. “ Kinetics of hydrogen evolution on nickel electrodes, ” *Electroanal. Chem.*, Vol. 294, 1990, pp.123-141 [38]A. Lasia, “ Study of electrode activities towards the hydrogen evolution reaction by a.c. impedance spectroscopy, ” *Int. J. Hydrogen Energy.*, Vol. 18, 1993, pp.557-560 [39]J. P. O' Sullivan and G. C. Wood, “ The morphology and mechanism of formation of porous anodic films on aluminium, ” *Proc. Roy. Soc. Lond. A.*, 317, 1970, pp.511-543 [40]Hoar, T. P. and Yahalom, J. “ The initiation of Pores in anodic oxide films formed on aluminum in acid solutions, ” *J. Electrochem Soc.* 110, pp.612-614 [41]Dell' Oca, C. J. and Fleming, P. J. “ Initial Stages of Oxide Growth and Pore Initiation in the Porous Anodization of Aluminum, ” *J. Electrochem Soc.* 123, 1976, pp.1487-1493 [42]Keller, F., Hunter, M. S. and Robinson, D. L. “ Structural Features of Oxide Coatings on Aluminum, ” *J. Electro. Soc.* 100, 1953, pp.411-419 [43]S. Setoh and A. Miyata, *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, 1932, p.2772 [44]Masuda, H. and Fukuda, K. “ Ordered Metal Nanohole Arrays Made by a Two-Step Replication of Honeycomb Structures of Anodic Alumina, ” *Science*, 268, 1995, pp.1466-1468 [45]F. Li, L. Zhang, and R. M. Metzger, “ On the Growth of Highly Ordered Pores in Anodized Aluminum Oxide, ” *Chem. Mater.* Vol. 10, 1998, pp.2470-2480 [46]G. E. Thompson, “ Porous anodic alumina fabrication characterization and applications, ” *Thin Solid Films*, Vol. 297, 1997, pp.192-201 [47]H. Msuda and M. Satoh, “ Fabrication of Gold Nanodot Array Using Anodic Porous Alumina as an Evaporation Mask, ” *Jpn. J. Appl. Phys., Part 2* Vol. 35, 1996, pp.L126-L129 [48]Y. Kanamoria, K. Hane, H. Sai, H. Yugami, “ 100nm period silicon antireflection structures fabricated using a porous alumina membrane mask, ” *Appl. Phys. Lett.* Vol. 78, 2001.
- [49]白春禮, “ 奈米科技現在與未來 ”, 凡異出版社, pp.30-41。
- [50]張立德, “ Nanomaterials ”, 五南圖書出版社, pp.63-67。
- [51]RAO “ Elements of Engineering Electromagnetics Third Edition(林振漢譯) ”, 高立圖書有限公司, pp85-125。
- [52]L. C. Shen, and J. A. Kong “ Applied Electromagnetism Third Edition(吳清水&曾振東譯) ”, 全華科技圖書股份有限公司, 14-2-14-19。
- [53]蔡丕椿, 蔡明雄, 陳文照, 廖金喜, “ 材料科學與工程 ”, 全華科技圖書股份有限公司, 4-55-4-70。