

The Effect of Magnetic Field on the Electrocatalytic Activity of Nanocrystalline Ni-P Alloy

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ABSTRACT

In this thesis, a double anodic oxidation method was employed in the preparation of anodic aluminum oxide (AAO) template first. The Ni and Ni-P nanowires were then electrodeposited in the AAO templates, respectively. In the meantime, both the electrodeposited Ni and Ni-P plate electrodes were prepared for comparison. The fabricated nanowire specimens were examined and analyzed using field emission scanning electron microscope (FE-SEM), transmission electron microscope (TEM), vibrating sample magnetometer (VSM) and X-ray diffractometer (XRD), respectively. The AAO template had a thickness of 30?μm, through and well-spaced cylindrical holes of 70-80 nm in diameter. In 0.5M H₂SO₄ electrolyte, the effects of magnetic field on the electrocatalytic activity of these specimens were investigated. The measurement results showed that the effective increment in surface area of the electrode with nanowire configuration raised the electrocatalytic activity accordingly. Furthermore, with the application of external magnetic field, the Ni nanowire electrode demonstrated the most prominent enhancement in electrocatalytic activity comparing with its plate electrode counterpart.

Keywords : Ni nanowire、Ni-P nanowire、electrocatalytic activity、anodic aluminum oxide

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REFERENCES

- [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 Struture," 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 Foralkaline 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 RuxTi1-xO2 in 0.5 M H2SO4," 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 Giz, 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。