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Effect of pH on composition, structure and magnetic properties of electrodeposited Co-Ni alloys

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Abstract: Co-Ni alloy thin films were electrodeposited from sulfate baths at various solution pH values (1.5-5.5) ±0.1. The deposition kinetics of the films was studied using linear sweep voltametry (LSV). XRD studies exhibited fcc and hcp phases for Co-Ni alloys deposited at low and high pH ranges, respectively. EDAX studies showed that the cobalt content increased and nickel content decreased with increase in solution pH. The surface morphology of Co-Ni films were analyzed by scanning electron microscopy. It is found that the Co-Ni alloys synthesized at low pH exhibited soft magnetic properties and the films deposited at higher values revealed hard magnetic properties and the results are discussed.

1. Introduction

Iron group of metallic alloys are very important due to their industrial (electronics, computers, automotive and energy storage devices) and technological (space, rocketry) applications and also due to their suitable magnetic, mechanical, chemical and physical properties for device applications [1]. Cobalt-Nickel (Co-Ni) is one of the important metallic alloys widely used as recording head materials in computer hard drive industries [2], micro systems technology for manufacturing micro-actuators, micro-sensors and micro-inductors [3-7]. Electrodeposited Co-Ni alloys are widely used as active materials for oxygen evolution reaction [8] and the hydrogen evolution reaction [9] in water electrolysis.

There are few reports available on the electrodeposition of CoNi alloy thin films [10-14]. In the present work, Co-Ni films have been prepared by elecrodeposition technique due its low cost, easily maintainable equipment, easy control of film thickness and the method is also environmentally friendly. Even though several reports are available in the literature on electrodeposited CoNi alloys, there is lack of studies related to the growth parameters with the physical properties. The objective of the present work is to explore the effect of solution pH on electrochemical synthesis and properties of Co-Ni alloy thin films. The effect of solution pH on films composition, structure, morphology and magnetic properties of electrodeposited Co-Ni alloy films were studied and discussed.

2. Experimental details

Co-Ni alloy films were prepared by galvanostatic electrodeposition from a sulfate bath. The Co-Ni electrolytic solution consisted of 0.20 M $CoSO_4.7H_2O$, 0.18M $NiSO_4.6H_2O$, 0.4 M H_3BO_3 and 0.4 M NH_4Cl. All electrochemical experiments were performed in a three-electrode cell. Electrolyte solutions were prepared using analytical grade reagents (Merck) and double distilled water. Copper substrate was used as working electrode on which the films were deposited. The counter electrode and reference electrodes were graphite and Saturated Calomel Electrode (SCE), respectively. Prior

to deposition, copper substrates were polished mechanically with silicon carbide emery paper and chemically etched in 10% H_2SO_4 for 1 minute. After etching, the substrates were rinsed thoroughly in distilled water and degreased in acetone. The depositions were carried out at different pH values ranging from 1.5 to 5.5 ±0.1. The solution pH of the bath was adjusted to appropriate values by using H_2SO_4. The bath temperature during deposition was maintained at 30^0C. The current density and the deposition time were kept as 8.5 mA/cm^2 and 30 minutes, respectively.

After deposition, the samples were taken out of the bath, washed thoroughly in acetone and kept in a desiccator. The depositions were carried out in a Potentiostat [EG&G Model 362, USA] instrument. Thickness of the films was measured using gravimetric method and found to be in the range between 700 and 950 nm. It is found the there is no appreciable variation in film thickness for samples deposited under identical conditions. X-ray diffractometer system [Brucker Discover D8] using Cuk$_\alpha$ radiation with λ=1.5418 A^0 was used to identify the phases of Co-Ni alloy films. The composition and morphology of the films were analyzed using EDAX and scanning electron microscope, respectively. The magnetic properties of Co-Ni thin films were analyzed using a Vibrating Sample Magnetometer (VSM 7300, Lake Shore). A magnetic field of the order of 10 kOe was used to study the magnetic properties of the samples in vibrating sample magnetometer.

3. Results and Discussion

Linear sweep votlammetry curves for individual electrodeposition of Co, Ni and Co-Ni alloy are presented in Fig. 1.

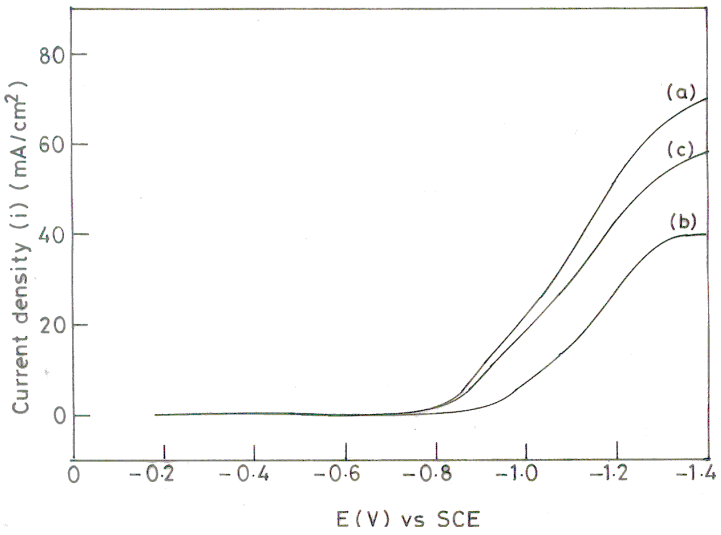

Figure1. Linear Sweep Voltammetry (LSV) behaviour of individual electrodeposition of (a) Co, (b) Ni and (c) Co-Ni alloy films.

Fig. 1 shows that the electrodeposition of Co, Ni and Co-Ni alloy takes place at potential more negative than -0.8V vs SCE. The electrodeposition of Co-Ni alloy based on the iron group of metals unavoidably exhibit a phenomenon known as “anomalous codeposition” [15]. It is observed from Fig. 1 that cobalt and Co-Ni alloy showed a fast deposition rate, revealed by the larger values of current than Ni. Fan and Piron [16] have studied the deposition kinetics of Co-Ni alloys and reported that cobalt deposition is intrinsically faster than nickel. X-ray diffraction patterns recorded for Co-Ni alloy thin films electrodeposited at various solution pH values from 1.5 to 5.5 is shown in Fig. 2.

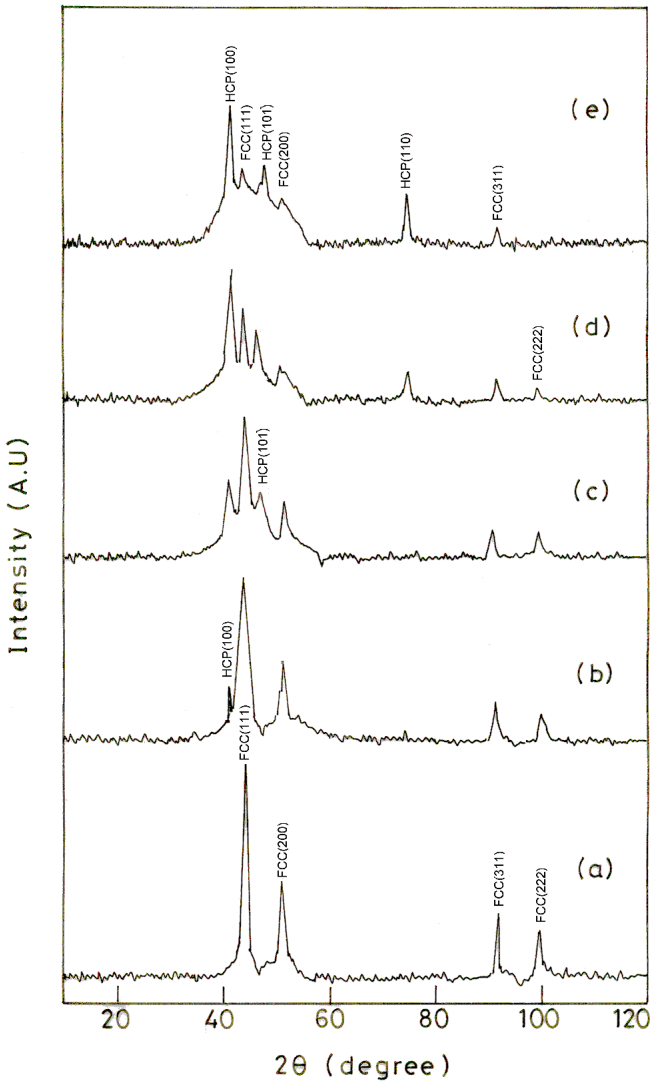

Figure 2.XRD patterns of electrodeposited Co-Ni alloy thin films deposited at different bath solution pH values (a) pH=1.5, (b) pH=2.5, (c) pH=3.5, (d) pH=4.5 and (e) pH=5.5.

It is observed from Fig. 2a the films deposited at pH value around 1.5 exhibits polycrystalline nature with fcc structure with preferential orientation along fcc (111) plane.
This particular Co-Ni electro deposit shows four peaks at 2θ values of 44.5º, 51º,91.5º and 99.5º corresponding to the reflections from (111),(200), (311) and (220) planes. The film deposited at pH 1.5 does not reveal any hcp phase. The occurrence of fcc structure for films deposited at 1.5 pH is in conformity with the results reported by Myung and Kobe [17].

However, Co-Ni alloy films deposited at other are found to possess a mixture of fcc and hcp phases. Figures 2(b), (c) and (d) exhibit additional peaks at 2θ values of 41º (pH=2.5), 47.5º (pH=3.5) and 75º (pH=4.5) corresponding to the reflection from hcp (100), hcp (101) and hcp (110) planes indicating the inclusion of Co-content in the Co-Ni films. For the Co-Ni alloy electrodeposited at a pH value 5.5, the face (222) peak has disappeared. The X-ray diffraction patterns of Co-Ni films are found to exhibit a mixture of cubic face and a hexagonal hip phase.Similar behavior was observed for Co-Ni deposits prepared using a cationic surfactant in the deposition bath [18]. It is evident that the intensities of face planes decreases and the intensities of hip planes increase with increasing the pH value from 1.5 to 5.5. The solution pH influences the crystal structure promoting a detestable face phase at low pH values and leading to a hip phase at higher pH values [19] The compositional

analysis of Co-Ni alloy electrodeposits were performed with an aim of determining the relationship between the pH values in the deposition bath and various properties of electrodeposited Co-Ni alloy thin films. The atomic percentage of cobalt and nickel present in the Co-Ni alloy films deposited at various pH values is depicted in Figure 3.

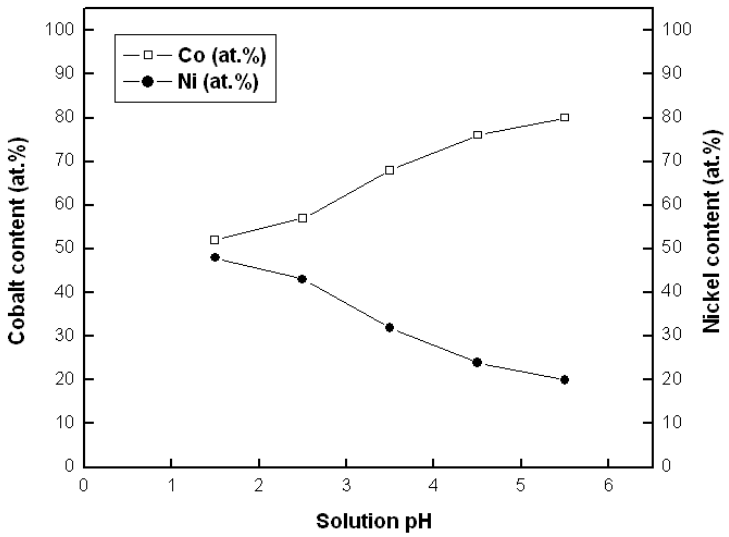

Figure 3. Variations of cobalt and nickel content (at %) of Co-Ni alloy thin films with solution pH in the deposition bath.

As observed from the figure, the cobalt content increased from 52 to 80 at% and the Ni-content decreased from 48 to 20 at% when the pH values in the deposition bath increased from 1.5 to 5.5. These results indicate that by suitably adjusting the solution pH in the deposition bath, various film compositions could be achieved in the electrodeposition process.

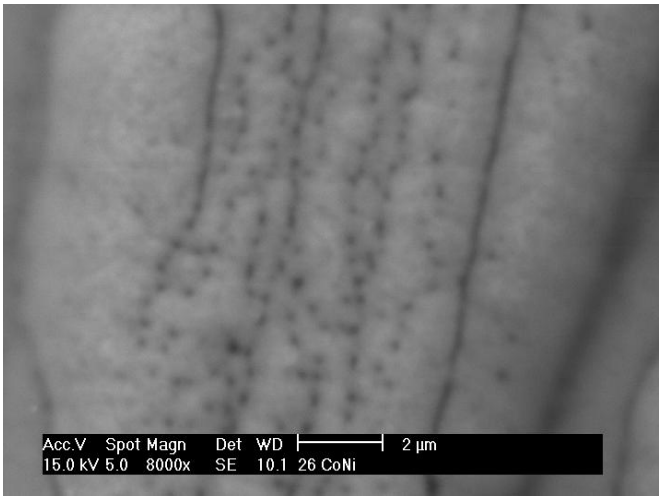

Fig.4a)

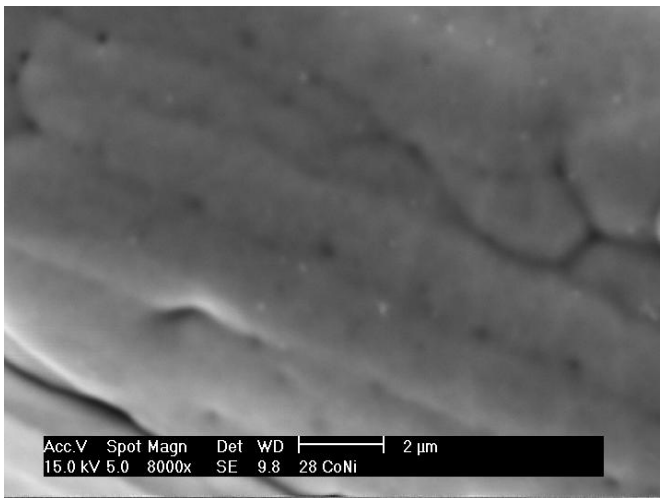

Fig.4b)

Figure 4. Scanning electron Micrograph of typical Co-Ni alloy thin films electrodeposited at various solution pH values: (a) 1.5 and (b) 3.5

Fig. 4 shows the scanning electron micrographs of Co-Ni electrodeposited onto precleaned copper substrates at solution pH values 1.5 and 3.5. Arrays of parallel layered surfaces are observed in the SEM picture (Fig.4a) for the film deposited at a solution pH 1.5 Small pores are also observed on the surface and fine grains are not observed in the micrograph. The presence of small pores in Fig.4a may be due to hydrogen evolution for films deposited at pH value of 1.5 due to the induced stress in the film [20]. Co-Ni alloy film prepared at solution pH 3.5 (Fig.4b) reveals comparatively a smooth surface and the number of pores is found to be reduced. Electrodeposited films usually possess residual stress which may arise due to the nature of the substrate, solution composition, current density etc during deposition. Moreover, the lattice mismatch of the substrate may result in a high intrinsic stress [21]. The pores and non-uniform nature of surface morphology may be mainly attributed to the residual stress in electrodeposited CoNi thin films. The magnetic properties of Co-Ni magnetic alloy thin films were studied using a vibrating sample magnetometer.

The magnetic properties, such as coercivity (H_C), saturation field (H_S), saturation magnetization (M_S) and remnant magnetization (M_r) were evaluated for films deposited between the pH values 1.5 and 5.5. The variation of coercivity (H_C) and saturation field (H_S) versus bath pH values were shown in Figure 5a.

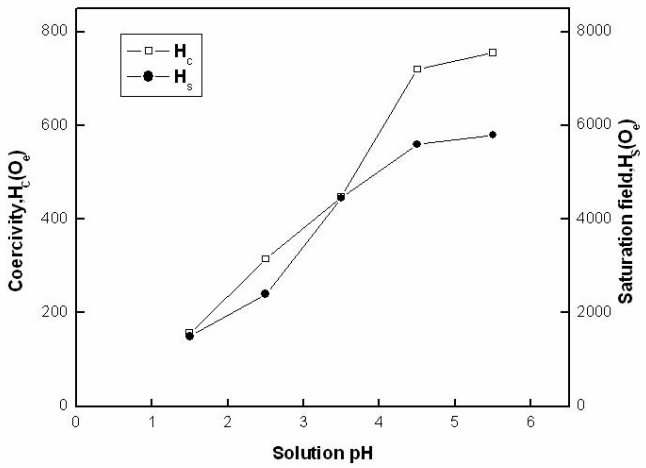

Figure 5a. Variation of coercivity (H_C) and saturation field (H_s) with solution pH in the deposition bath for Co-Ni alloy thin films.

It is observed that the coercivity increases from 160 O_e to 765 O_e and the saturation field from 1680 O_e to 5830 O_e when the pH in the bath solution increase from 1.5 to 5.5. It is interesting to note that the soft magnetic properties (small H_C, low H_S) are observed for films deposited in the low pH range (1.5 to 3.5) and the hard magnetic properties (higher values of H_C and H_S) for films deposited in the pH range 4.5 and 5.5. Our results are in conformity with the earlier report that Co and Co-Ni based alloys electrodeposited from low solution pH exhibited soft magnetic properties, whereas electrodeposits from higher solution pH revealed hard magnetic behavior [19]. Dependence of magnetic saturation (M_S) and remnant magnetization (M_r) on pH values in the deposition bath of Co-Ni thin films is shown in figure 5b.

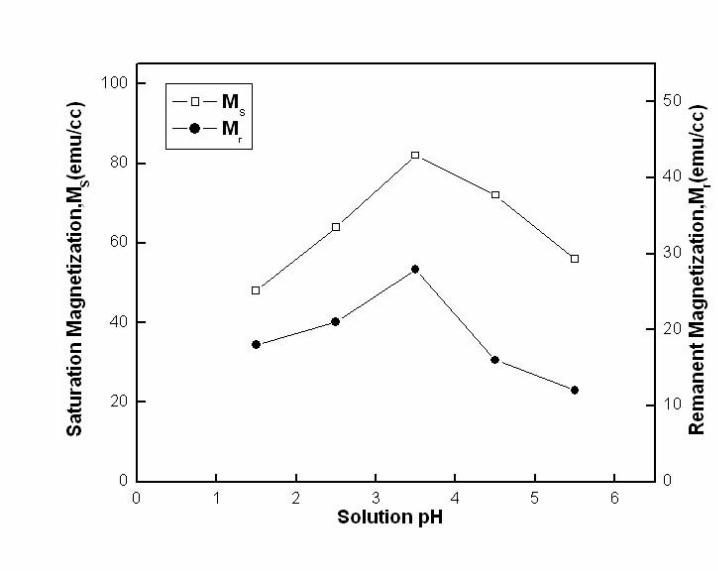

Figure 5b. Variation of saturation magnetization (M_S) and remnant magnetization (M_r) with solution pH in the deposition bath for Co-Ni alloy thin films.

Is observed that both M_s and M_r increase with the solution pH, reaches a maximum for the pH 3.5 and further decreases with the increase of pH. The above result indicates that the optimum pH value in the deposition bath to obtain CoNi films with hard magnetic properties is around 3.5±0.1. It has been reported that the hard magnetic properties are associated with hcp structures [22]. In our CoNi films, the increase of saturation magnetization (M_s) with solution pH from 1.5 to 3.5 may be due to the association of hard magnetic properties which is also evidenced by the observation of hcp phase in the X-ray diffraction results with increasing pH values. However, the decrease of saturation magnetization and remnant magnetization (M_r) at pH values 4.5 and 5.5 are not clearly understood and needs further detailed investigations.

4. Conclusions

Co-Ni alloy films were electrodeposited from sulfate baths to investigate the dependence of the compositional, structural, morphological and magnetic properties with the solution pH in the deposition bath. XRD studies revealed that the solution pH influenced the crystal structure of Co-Ni electrodeposits, low pH promoting fcc structure with (111),(200), (311) and (220) planes and relatively higher pH promoting hcp structure with (100), (101) and (110) planes. EDAX studies showed that the cobalt content (at %) in the films increased and Ni- content in the films decreased gradually with increasing the pH in the solution bath. Surface morphological studies show a non-uniform surface with small pores in the electrodeposited Co-Ni thin films. The magnetic properties of the films are found to be influenced by solution pH in the deposition bath leading to soft magnetic properties at low pH and hard magnetic properties relatively at higher pH values.

Acknowledgments

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References

[1]. S.Djokic Stojan: The Electrochemical Society Vol.146 (1999) p.1824.

[2]. L.Shi, C.F.Sun , P.Gao , F.Zhou, W.M.Liu: Surface and Coatings Technology Vol.200 (2006) p.4870.

[3]. M.Duch, J.Esteve, E.Gomez, R.Perez-castillejos, E. Valles: Journal of Electrochemical Society Vol.149 (2002) p.C201-C208.

[4]. S.Armyanov: Electrochimica Acta. Vol.45 (2000) p.3323.

[5]. E.Gomez, E.Valles: Journal of .Applied Electrochemistry Vol.32 (2002) p.693.

[6]. E.Gomez, E.Valles: Journal of Applied Electrochemistry Vol.29 (1999) p.803.

[7]. E.Gomez, J.Ramirez , E.Valles: Journal of Applied Electrochemistry. Vol.28 (1998) p.71.

[8]. K.K.Lian, D.W.Kirk, S.J.Thorpe: The Electrochemical Society. Vol.142 (1995) p. 3704.

[9]. S.A.S.Machado, J.Tiengo, P.deLima veto, L.A.Avaca: Journal of Applied Electrochemistry Vol.26 (1996) p.431.

[10]. Liping Wang, Yan Gao, Qunji Xue, Huiwen Liu, Tao Xu: Applied Surface Science. Vol.242 (2005) p.326.

[11]. E.Gomez , S.Pane, E.Valles: Electrochimica Acta Vol.51 (2005) p.146.

[12]. D.J.Black Wood, Y.Y.Li, G.M.Chow: The Electrochemical Society Vol.149 (2002) p.D27 .

[13]. W.H.Safranek Properties of electrodeposited metals and alloys. New York ,London, 1974.

[14]. A.Bai, C.C.Hu :Electrochimica Acta Vol.47 (2002) p.3447.

[15]. A.Brenner: Electrodeposition of alloys Vol.I (1963) Academic Press, NewYork.

[16]. C.Fan, D.L.Piron: Electrochimica Acta Vol.41 (1996) p.1713.

[17]. N.V.Myung,K.Kobe: The Electrochemical Society Vol.148 (2001) p.C136.

[18]. E.Gomez , S.Pane, X.Alcobe, E.Valles :Electrochimica Acta Vol.51 (2006) p.5703.

[19]. N.V.Myung, D.Y.Park, M.Schwartz, K.Nobe, H.Yang, C.K.Yang, J.W.Judy :Sixth International Symposium on Magnetic Materials-Processes and Devices, Proceedings of Electrochemical Society (2000) p.29

[20]. S.D.Sartale, C.D.Lokhande: Ceramics Letters Vol.28 (2002) 467.

[21]. N.V.Myung, Y.D.Park, B.Y.Yoo, T.A.Sumodjo Paulo: Journal of Magnetism and Magnetic Materials Vol.265 (2003) p.189.

[22]. M.Mirzamani, L.Romankiw , C.McGrath, J.Karasinski , J.Mahlke , N.C.Anderson: The Electrochemical Society Vol.135 (1988) p.2813.

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References

[1]. S.Djokic Stojan: The Electrochemical Society Vol.146 (1999) p.1824.
doi:10.1149/1.1391850

[2]. L.Shi, C.F.Sun, P.Gao, F.Zhou, W.M.Liu: Surface and Coatings Technology Vol.200 (2006) p.4870.
doi:10.1016/j.surfcoat.2005.04.037

[3]. M.Duch, J.Esteve, E.Gomez, R.Perez-castillejos, E. Valles: Journal of Electrochemical Society Vol.149 (2002) p.C201-C208.
doi:10.1149/1.1452116

[4]. S.Armyanov: Electrochimica Acta. Vol.45 (2000) p.3323.
doi:10.1016/S0013-4686(00)00408-4

[5]. E.Gomez, E.Valles: Journal of. Applied Electrochemistry Vol.32 (2002) p.693.
doi:10.1023/A:1020194532136

[6]. E.Gomez, E.Valles: Journal of Applied Electrochemistry Vol.29 (1999) p.803.
doi:10.1023/A:1003580302490

[7]. E.Gomez, J.Ramirez, E.Valles: Journal of Applied Electrochemistry. Vol.28 (1998) p.71.
doi:10.1023/A:1003201919054

[8]. K.K.Lian, D.W.Kirk, S.J.Thorpe: The Electrochemical Society. Vol.142 (1995) p. 3704.
doi:10.1149/1.2048402

[9]. S.A.S.Machado, J.Tiengo, P.deLima veto, L.A.Avaca: Journal of Applied Electrochemistry Vol.26 (1996) p.431.

[10]. Liping Wang, Yan Gao, Qunji Xue, Huiwen Liu, Tao Xu: Applied Surface Science.

Vol.242 (2005) p.326.
doi:10.1016/j.apsusc.2004.08.033

[11]. E.Gomez, S.Pane, E.Valles: Electrochimica Acta Vol.51 (2005) p.146.
doi:10.1016/j.electacta.2005.04.010

[12]. D.J.Black Wood, Y.Y.Li, G.M.Chow: The Electrochemical Society Vol.149 (2002) p.D27 .
doi:10.1149/1.1447223

[13]. W.H.Safranek Properties of electrodeposited metals and alloys. New York, London, 1974.

[14]. A.Bai, C.C.Hu :Electrochimica Acta Vol.47 (2002) p.3447.
doi:10.1016/S0013-4686(02)00281-5

[15]. A.Brenner: Electrodeposition of alloys Vol.I (1963) Academic Press, NewYork.

[16]. C.Fan, D.L.Piron: Electrochimica Acta Vol.41 (1996) p.1713.
doi:10.1016/0013-4686(95)00488-2

[17]. N.V.Myung,K.Kobe: The Electrochemical Society Vol.148 (2001) p.C136.
doi:10.1149/1.1345875

[18]. E.Gomez, S.Pane, X.Alcobe, E.Valles :Electrochimica Acta Vol.51 (2006) p.5703.
doi:10.1016/j.electacta.2006.03.003

[19]. N.V.Myung, D.Y.Park, M.Schwartz, K.Nobe, H.Yang, C.K.Yang, J.W.Judy :Sixth International Symposium on Magnetic Materials-Processes and Devices, Proceedings of Electrochemical Society (2000) p.29

[20]. S.D.Sartale, C.D.Lokhande: Ceramics Letters Vol.28 (2002) 467.
doi:10.1016/S0272-8842(01)00119-5

[21]. N.V.Myung, Y.D.Park, B.Y.Yoo, T.A.Sumodjo Paulo: Journal of Magnetism and Magnetic Materials Vol.265 (2003) p.189.
doi:10.1016/S0304-8853(03)00264-6

[22]. M.Mirzamani, L.Romankiw, C.McGrath, J.Karasinski, J.Mahlke, N.C.Anderson: The Electrochemical Society Vol.135 (1988) p.2813.
doi:10.1149/1.2095438