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Role of pH and current density in electrodeposited soft magnetic Co-Ni-Fe alloy thin films

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The influence of pH and current density on the structural and magnetic behavior of soft magnetic Co-Ni-Fe alloy thin films has been studied. The effect of pH and current density on the compositional, structural, and magnetic properties of the as-obtained films was investigated by EDX (energy dispersive analysis by X-rays), XRD (X-ray diffractometer) and VSM (vibrating sample magnetometer). The EDX results revealed that at the optimized deposition conditions, nickel content was low compared with cobalt and ferrous content. X-ray diffraction patterns revealed that the deposited films have polycrystalline nature with mixed (fcc-bcc) cubic structure and small crystallite size (<20 nm). The films prepared in optimized conditions exhibit high saturation magnetization ($4\pi M_s$ value above 2T) and low coercivity (below 160 A/m), which may be due to the reduced crystallite size.

Keywords: *Electrodeposition, Co-Ni-Fe alloy, structural properties, magnetic properties*

1. Introduction

Soft magnetic alloy thin films are usually prepared by means of electrodeposition. Electrochemical deposition of metals and alloys onto metallic substrates play an important role in several new technologies such as magnetic sensors, magnetic recording heads and microelectromechanical systems [1]. It is a very effective method because of its simplicity and low cost synthesis. The soft magnetic alloy thin films are utilized in thin film recording heads to meet the future trends in high-density magnetic recording. NiFe [2, 3], FeSiAl [4], CoTaZr, CoNbZr [5] and nanocrystalline FeTaN films [6, 7] are widely used in the read write heads. Recently, Co-Ni-Fe alloy thin films have received a great interest because of their possible applications in magnetic recording devices [8]. Thin-film magnetic recording heads fabricated by the electrodeposition are attractive because it is possible to produce precise structures, such as very narrow head gaps and tracks, which enables the area recording density to be higher and higher [9]. In general, Co-Ni-Fe alloys possess excellent, soft magnetic properties and in some cases, they exhibit a high magnetic moment and low coercivity [10–12]. Many research workers have dealt with the properties of Co-Ni-Fe alloy thin films deposited by electroplating method using organic additives such as saccharin and thiourea [13, 14]. However, Co-Ni-Fe alloy thin films with higher saturation magnetization and low coercivity, manufactured using an aqueous electrolytic bath without any organic additives have not been reported yet [10]. The solution pH and current density variations have an influence on the composition of the alloy [15]; the stability of the films can be improved by increasing the solution pH from 2.0 ±0.1 to 3.0 ±0.1 [16]. The objective of the present study is to obtain the Co-Ni-Fe alloy thin films prepared using solutions of changing pH at different current density values. The effect of pH and current density on struc-

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tural, compositional, morphological and magnetic properties of the films is studied and discussed.

2. Experimental details

The electrodeposition of soft magnetic Co-Ni-Fe alloy thin films was carried out galvanostatically in a three-electrode system, using Cu substrate as a working electrode, a graphite plate as a counter electrode, and a saturated calomel electrode (SCE) as a reference electrode. The substrates were washed previously in H_2SO_4 solution to remove any oxide formed. The electrolytic bath consisted of 0.085 M $CoSO_4$, 0.18 M $NiSO_4$, 0.04 M $FeSO_4$, 0.37 M H_3BO_3 and 0.30 M NH_4Cl without any organic additives. Ammonium chloride and boric acid were added as supporting electrolyte and pH buffer, respectively. All the solutions were prepared by dissolving the analytical reagent grade reagents (99.5 % purity, acquired from S.D Fine Chemicals, Mumbai, India) in de-ionized water. The electrochemical experiments were carried out at various current densities from 3.5 to 12.5 mA/cm^2, at various solution pH from 2.0 to 3.5 $\pm$0.1. The pH of the electrolytic bath was altered by adding an adequate amount of H_2SO_4 up to the required value using a digital pH meter. The deposition was carried out using a potentiostat/galvanostat (EG&G, Model 362, PAR, USA).

The film composition and morphological properties were determined by energy dispersive analysis with a X-ray set up attached to a scanning electron microscope (Philips, model XL 30). The structural properties of the films were investigated using a X-ray diffractometer (X'Pert PRO PANalytical, NETHERLAND) employing CuKα radiation with λ = 1.540 Å. The magnetic properties of the films were studied using Vibrating Sample Magnetometer (7404 Lakeshore, USA).

3. Results and Discussion

3.1. Compositional analysis

The quantitative analysis of Co-Ni-Fe alloy thin films was carried out in order to determine the relationship between Co, Ni, Fe content at various solution pH and current density values. The composition analysis of Co-Ni-Fe alloy thin films was performed using energy dispersive analysis with a X-ray set up attached to a scanning electron microscope. The EDAX spectrum was taken at various points and the average composition was given with 5 % error. Fig. 1 shows the dependence of film composition on solution pH values in electrodeposited Co-Ni-Fe alloy thin films. It can be noticed that the content of cobalt increases from 55 to 60 % and the content of Fe increases from 21 to 30 % while increasing the pH value from 2.0 to 3.0; at higher pH values both of them slightly decrease. In contrast, the content of Ni decreases from 24 to 10 % at pH values from 2 to 3 and then gradually increases. Similar trend was noted for Co-Ni-Fe alloy thin films prepared using pulse-reverse electroplating method by Rasmussen *et al.* [17]. The composition of Co-Ni-Fe alloy thin films prepared at various current densities is shown in Fig. 2. It can be observed that the content of cobalt increases from 57 to 62 % while increasing current density value from 3.5 to 12.5 mA/cm^2. At the same time, the content of nickel decreases from 18 to 10 % and the content of Fe increase from 25 to 30 % up to the current density of 9.5 mA/cm^2. At higher current densities the tendency reverses: the content of Ni increases and the content of Fe decreases.

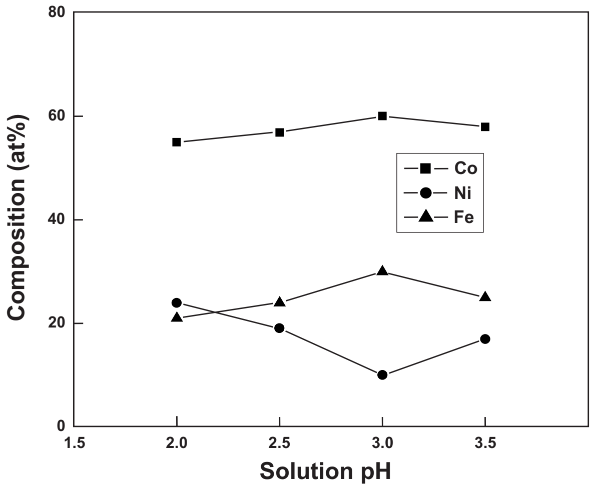

Fig. 1. Co, Ni, and Fe content in electrodeposited Co-Ni-Fe thin films as a function of various solution pH values.

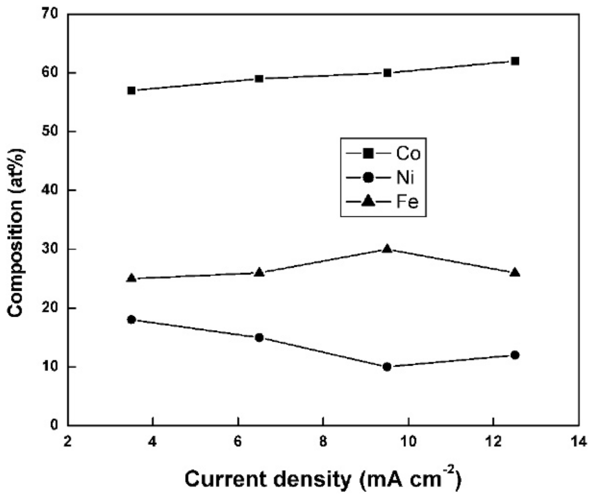

Fig. 2. Co, Ni, and Fe content in electrodeposited Co-Ni-Fe alloy obtained at various current densities.

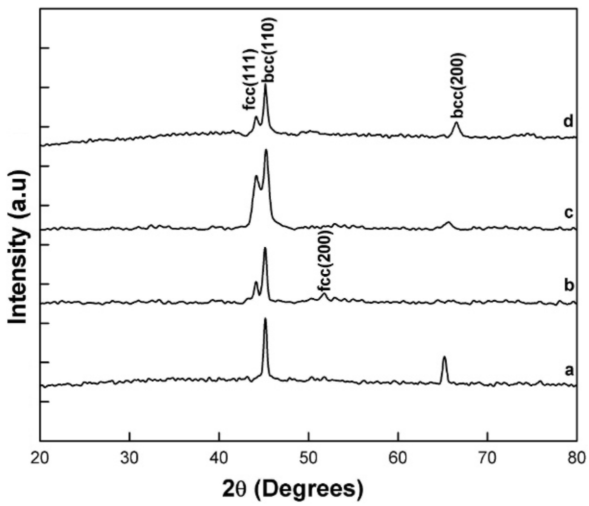

Fig. 3. XRD patterns of Co-Ni-Fe films electrodeposited at various solution pH values: a) 2.0 ±0.1 b) 2.5 ±0.1 c) 3.0 ±0.1 d) 3.5 ±0.1.

3.2. Structural studies

Co-Ni-Fe alloy thin films electrodeposited at various pH and current density values were subjected to X-ray diffraction analysis to examine their structural properties. X-ray diffraction patterns of Co-Ni-Fe alloy thin films electrodeposited at various pH values from 2 to 3.5 ±0.1 are shown in Fig. 3a–d. It can be observed in Fig. 3a, that the films deposited at lower pH values around 2.0 ±0.1, exhibit only the bcc structure with preferential orientation along

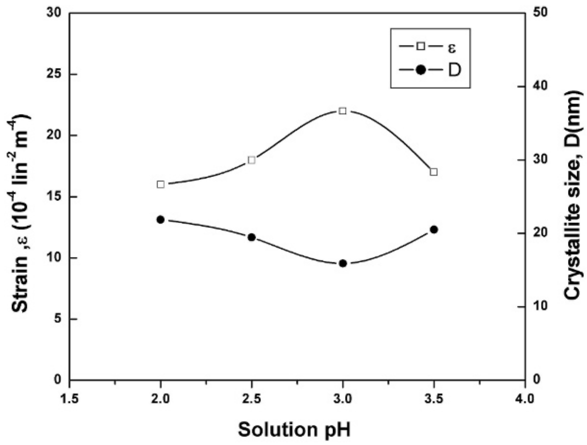

Fig. 4. Variation of crystallite size and strain of the films obtained at different solution pH values.

(110) plane and in a smaller degree along (200) plane. Further increase in the value of pH above 2.0 ±0.1 results in the formation of both bcc (110) and fcc (111) planes. The film prepared at the optimized pH value of 3.0 exhibits mixed fcc (111) and bcc (110) phases. This behavior may be due to the increase in Fe content compared to Ni content. If the pH value is increased above 3.0, the fcc (111) phase is found to decrease whereas the bcc (110) phase becomes more dominant. This may be due to the increase in Ni content and decrease in Fe content. For the structural characterization, thin films of approximately 900 nm thickness were used.

The crystallite sizes of the deposited films were calculated using FWHM data and the Debye-Scherrer formula

$$D = \frac{0.9\lambda}{\beta \cos \theta_B} \qquad (1)$$

where: λ is the wavelength of CuKα target (λ = 0.1540 nm), β is Full Width at Half Maximum of the peak in radians, θ_B is Bragg's diffraction angle at peak position in degrees. The variation of crystallite size and strain corresponding to the considered pH values are shown in Fig. 4. The crystallite size decreases from 22 nm as pH increases up to the optimized pH value of 3.0 ±0.1 and then it slightly increases to 16 nm for the highest pH. So, the decrease in crystallite size is observed at the occurrence of the mixed phase. However, the strain values show an exactly reciprocal pattern to that of crystallite size. Reduction of the crystallites size is responsible for an increase in the micro strains in magnetic alloys [18]. The fcc-bcc mixed phase formed, exhibits finer crystal structure compared to the crystal structure of bcc or fcc single phases [8]. The mixed fcc-bcc phase consisting of small crystallites possesses excellent magnetic properties which can be exploited for the core material for read write heads [19]. Fig. 5a–d shows X-ray diffraction patterns of Co-Ni-Fe thin films deposited at various current densities. Some new peaks emerge at bcc (200) and fcc (220) plane, when the current density during the film deposition increases above 6.5 mA/cm^2. As the current density increases, an increase in fcc (111) phase can be observed. At higher current density the fcc phase dominates. A transition of the film crystalline structure from bcc to fcc is associated with the increase in Ni content [20]. The bcc and fcc mixed phases of Co-Ni-Fe alloy are observed at the optimized value of current density equal to 9.5 mA/cm^2 as shown in Fig. 5. When the current density increases above 9.5 mA/cm^2, the cobalt and ferrous content in Co-Ni-Fe alloy thin films increase whereas nickel content decreases. Fig. 6. shows the variation of crystallite size and strain for the films deposited at different current densities. The effect of current density on crystallite size and strain shows the similar behavior as those observed with pH variation.

Fig. 7 shows a typical scanning electron micrograph of Co-Ni-Fe alloy thin films prepared at optimized current density (9.5 mA/cm^2) and pH value (3.0 ±0.1) of the electrolytic bath. The morphology of the films was studied employing a scanning electron microscope. A typical morphology comprises very small sized and uniformly distributed grains.

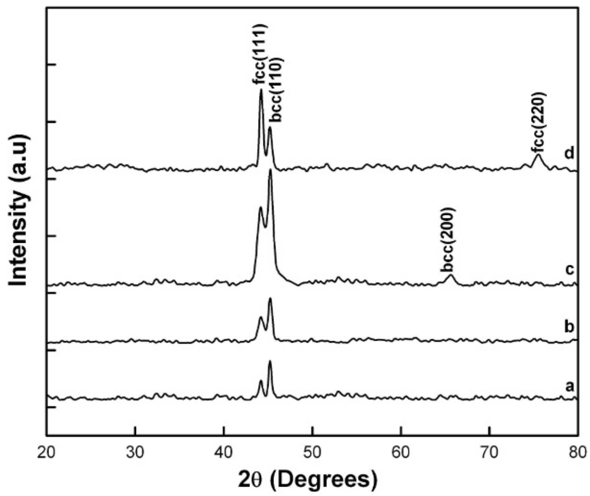

Fig. 5. XRD patterns of Co-Ni-Fe films electrodeposited at various current densities a) 3.5 mA cm^{-2} b) 6.5 mA cm^{-2} c) 9.5 mA cm^{-2} d) 12.5 mA cm^{-2}.

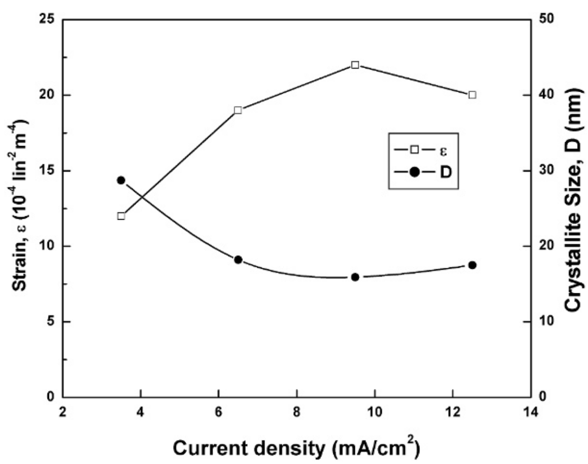

Fig. 6. Variation of crystallite size and strain in the films obtained at different current density values.

3.3. Magnetic Properties

Co-Ni-Fe alloy thin films prepared at various solution pH values from 2.0 ±0.1 to 3.5 ±0.1 and current density values from 3.5 to 12.5 mA/cm^2 were subjected to vibrating sample magnetometer tests to study their magnetic properties. Soft magnetic thin films are characterized by low value of coercivity (Hc), i.e. the critical field strength needed to reverse the direction of magnetization. Actually, reducing Hc of the soft magnetic Co-Ni-Fe thin film is important for magnetic recording purposes. Fig. 8. shows the variation of coercivity (in plane) with current density for Co-Ni-Fe alloy thin films obtained at different pH values. It can be observed that the value of coercivity decreases while increasing the current density value from 3.5 to 9.5 mA/cm^2 afterwards it slightly increases. The value of coercivity attains its minimum value of 154 A/m at the optimized current density value of 9.5 mA/cm^2 and pH value of 3.0 ±0.1. The considerable decrease in Hc

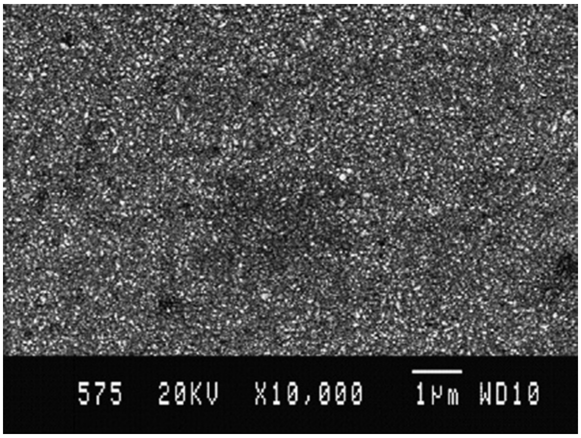

Fig. 7. Typical scanning electron micrograph of CoNiFe alloy thin films electrodeposited at optimized pH (3.0 ±0.1) and current density (9.5 mA/cm^2).

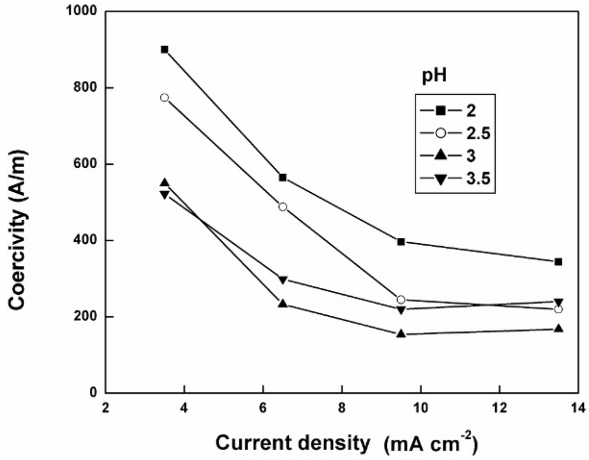

Fig. 8. Dependence of coercivity of electrodeposited Co-Ni-Fe alloy thin films on current density and solution pH.

may be due to the transition from a single bcc structure to the fcc/bcc-phase mixture. Co-Ni-Fe film with an extremely low value of Hc is composed of mixed fcc-bcc phases consisting of very fine crystallites [19]. The variations of saturation magnetization and remanence with respect to current density are shown in Fig. 9. It can be seen that the values of saturation magnetization and remanence increase while increasing the current density values and attain the maximum values for the films prepared at the optimized current density of 9.5 mA/cm^2, thereafter both the saturation magnetization and the remanence slightly decrease. The variations of saturation magnetization and remanence with solution pH values are shown in Fig. 10. It is observed that the values of saturation magnetization and remanence increase while increasing the solution pH values and attain their maximum values for the films prepared at optimized pH value of 3.0, thereafter both the saturation magnetization and the remanence slightly decrease. The increase in the value of saturation magnetization may be due to the increase in Fe content in the films prepared at various values of current density and solution pH which is illustrated in the compositional analysis. Moreover, the film deposited at pH value of 3 exhibits a low coercivity (Hc = 154 A/m) and high saturation magnetization ($4\pi M_s$ = 2.09 T). Similar variations of coercivity with solution pH and current density values have been reported earlier [15, 21].

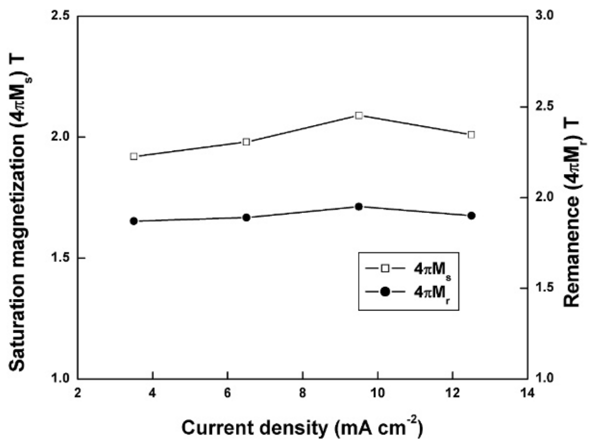

Fig. 9. Variation of saturation magnetization and remanance of Co-Ni-Fe films obtained at different current density values.

4. Conclusions

Soft magnetic Co-Ni-Fe alloy thin films were electrodeposited galvanostatically from sulfate electrolytic bath at various solution pH and current densities. The compositional analysis revealed that the content of Co and Fe increased and the content of Ni decreased up to pH value of 3.0 ±0.1, afterwards the trend was reversed. The same behavior exhibited the films prepared at various current densities, but the Co content increased even when the current density exceeded the optimized value of 9.5 mA/cm^2. X-ray diffraction patterns showed that the formation

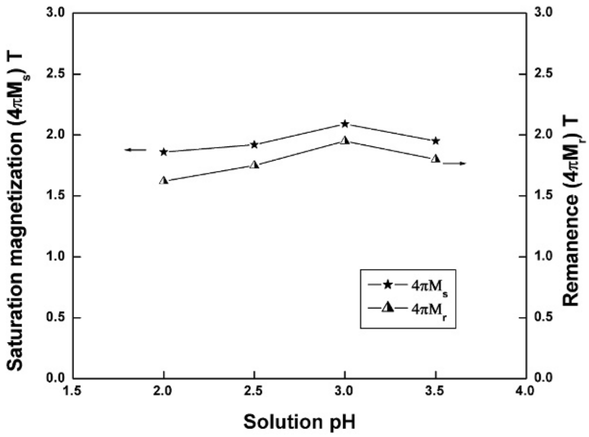

Fig. 10. Variation of saturation magnetization and remanance of Co-Ni-Fe films obtained at different solution pH values.

of mixed (bcc-fcc) phases consisting of very fine crystallites occurred at optimized pH and current density values. Co-Ni-Fe alloy thin films with high saturation magnetization ($4\pi M_s$) value of 2.09 T and low coercivity value (Hc) of 154 A/m were obtained under optimized conditions. The structure, composition of the films and their magnetic properties were strongly dependent upon both solution pH and current density values.

References

[1] JING-FENG L., ZHAO Z., JUN-YING Y., GENG-HUA Y., CHAO C., JIAN-QING Z., *T. Nonferr. Metal. Soc.*, 16 (2006), 659.
[2] ROBERTSON N., HIU H.L, TSANG C., *IEEE Trans. Magn.*, 33 (1997), 2818.
[3] JURY J., GEORGE P., JUDY J.H., *IEEE Trans. Magn.*, 35 (1999), 2508.
[4] KOHMOTO O., *IEEE Trans. Magn.*, 27 (1991), 3640.
[5] FUJIMORI H., KAZAMA N.S., HIROSE K., ZHANG J., MORITA H., SATO I., SUGAWARA H., *J. Appl. Phys.*, 55 (1984), 1769.
[6] HONG J., FURUKAWA A., SUNN N., WANG S.X., *IEEE Trans .Magn.*, 35 (1999), 2502.
[7] VARGA L., JIANG H., KLEMMER T.J., DOYLE W.D., *IEEE Trans.Magn.*, 34 (1998), 1441.
[8] OSAKA T., *Electrochim. Acta.*, 45 (2000), 3311.
[9] OSAKA T., TAKANO N., YOKOSHIMA T., *Surf. Coat. Tech.*, 169 (2003), 1.
[10] OSAKA T., TAKAI M., HAYASHI K., OHASHI K., SAITO M., YAMADA K., *Nature*, 392 (1998), 796.
[11] OSAKA T., TAKAI M., HAYASHI K., SOGAWA Y., OHASHI K., YASUE Y., SAITO M., YAMADA K., *IEEE Trans. Magn.*, 34 (1998), 1432.
[12] LIU X., ZANGARI G., *J. Appl. Phys.*, 90 (2001), 5247.
[13] NAKAMURA A, TAKAI M., HAYASHI K., OSAKA T., *J. Surf. Finn. Soc. Jpn.*, 47 (1996), 934.
[14] TAKAI M., HAYASHI K., AOYAGI M., OSAKA T., *J. Electochem. Soc.*, 144 (1997), L203.
[15] LIU X., EVANS P., ZANGARI G., *IEEE Trans. Magn.*, 36 (2000), 3479.
[16] ZHANG Y., IVEY D.G., *Mat. Sci. Eng. B.*, 140 (2007), 15.
[17] RASMUSSEN F.E., RAVINKILDE J.T., TANG P.T., HANSEN O., BOUWSTRA S., *Sensor. Actuat.*, A 92 (2001), 242.
[18] AMILS X., NAGUES J., SURINACH S., BARO M.D., MUNOZ J.S., *IEEE Trans. Magn.*, 34 (1998), 1129.
[19] OSAKA T., ASAHI T., KAWAJI J., YOKOSHIMA T., *Electrochim. Acta.*, 50 (2005), 4576.
[20] LIU X., ZANGARI G., SHAMSUZZOHA M., *J. Electochem. Soc.*, 150 (2003), C159.
[21] ATALAY F.E., KAYA H., ATALAY S., *J. Alloy Compd.*, 420 (2006), 9.

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