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MICROSTRUCTURAL CHARACTERIZATION OF CYLINDRICAL $Fe_{1-x}Ni_x$ THIN FILMS

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Structural and microstructural characterization was performed on soft magnetic $Fe_{1-x}Ni_x$ thin films on copper and stainless steel cylindrical substrates. Thin films have been prepared using an electrodeposition device with uniform cylindrical deposition ability. Plating baths, containing nickel sulfate and iron sulfate, of variable Fe/Ni ion ratio in the electrolyte have been used in order to control the stoicheiometry. The microstructural characterization and composition analysis were performed using SEM. The structure of the alloys was investigated by X-ray diffraction. All samples have been submitted to thermal treatment at 450 ^{0}C at Ar atmosphere.

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Keywords: Thin films, Electrodeposition, Microstructural characterization

1. Introduction

There has been a great research interest in the development and characterization of FeNi thin films due to their operational capacity, economic interest and magnetic properties [1, 2]. FeNi alloys, of certain compositions, are preferable for high sensitivity applications since they exhibit high magnetic permeability at low intensity magnetic fields because of their low magnetic anisotropy and magnetoelastic energy [3]. A simple and inexpensive technique for the production of thin films is electrodeposition. It has been used successfully in the case of FeNi alloys for a wide range of concentrations of both elements [4]. The properties, the composition and the grain size of electrodeposited FeNi alloys are strongly dependent on the electrolyte composition and the deposition parameters [1,2]. One serious drawback of the electrodeposition process is the generation of internal stresses resulting in the formation of microcracks [4]. However, the internal stress level can be reduced by heat treatment or the addition of inhibitors [5]. Magnetic materials and their tailoring techniques towards the development of industrially applicable sensors play a significant role in engineering [6-9].

The objective of the present work has been focused on the development of soft magnetic $Fe_{1-x}Ni_x$ thin films, electrodeposited on copper and stainless steel cylindrical substrates, and on their structural and microstructural characterization [10,11]. The microstructural and composition analysis of the electrodeposited thin films were performed by Scanning Electron Microscopy, while the structural properties of the samples were investigated by X-Ray Diffraction.

2. Experimental

The electro-deposition device is illustrated in Fig. 1. The anode of the device was a 316L stainless steel tube while the cathode was first a conducting copper cylinder and then a S500 stainless steel cylinder. The voltage was supplied to the anode symmetrically in order to guarantee a uniform electric field throughout the electro-deposition process. A closed electric current feedback loop was used to control the amount of current in the solution.

The cathode surface was mechanically polished with successively finer grades of emery paper and then it was ultrasonically rinsed for 2 minutes in water. Finally, copper substrates were subjected to electrochemical cleaning, using phosphoric acid, for about 7 minutes.

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The effect of stoicheiometry on the material properties was investigated by preparing samples using several plating baths. All baths contained 0.05M $NiSO_46H_2O$ and 0.04M H_3BO_3 while the concentration of $FeSO_47H_2O$ was varied to achieve variable Ni/Fe ion ratios in the electrolyte. pH was adjusted to 3.0 by adding H_2SO_4 and the deposition temperature was kept at 25 ^oC.

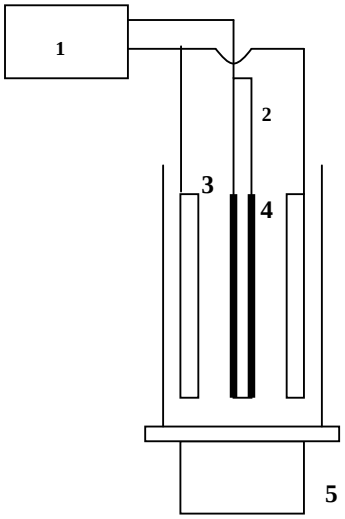

Fig. 1. The cylindrical electrodeposition device. (1) Pulsed current excitation. (2) Cathode Cu rod. (3) Cylindrical anode. (4) FeNi layer. (5) Magnetic steering.

The effect of deposition parameters on the material properties was investigated by varying the applied current density and the deposition time. The nickel-iron alloys were first deposited onto Cu cylindrical substrates. The deposition conditions and the results of the composition analysis of all the samples prepared are summarized in Tables 1 and 2. The metallic concentrations are in wt. %. Several attempts were also made to grow FeNi thin films on stainless steel cylinders as well.

Table 1. Deposition conditions and approximate composition of samples on Cu substrates.

sample	$FeSO_47H_2O$ (M)	Current density (mA/cm^2)	Deposition time (min)	Fe (wt. %)	Ni (wt. %)
1	0.05	0.72	10	80	20
2	0.05	3.63	10	80	20
3	0.05	5.09	10	80	20
4	0.05	7.27	10	80	20
5	0.1	7.27	10	80	20
6	0.1	7.27	5	80	20
7	0.05	3.63	15	80	20
8	0.025	7.27	5	50	50
9	0.0125	7.27	5	30	70
10	0.00625	7.27	5	10	90
11	0.0268	7.27	5	50	50
12	0.016	7.27	5	40	60
13	0.01	7.27	5	30	70
14	0.0083	7.27	5	20	80
15	0.0071	7.27	5	15	85
16	0.05	7.27	5	65	35
17	0.2	7.27	5	90	10
18	0.4	7.27	5	95	5

As in the Cu substrate case, the plating bath contained 0.04M H_3BO_3 with variable $FeSO_47H_2O$ and $NiSO_47H_2O$ concentrations. pH was adjusted to 3.0 by adding H_2SO_4 and all experiments were conducted at 25 ^{0}C. The plating bath compositions and the deposition conditions are summarized in Table 2.

Table 2. Deposition conditions on stainless steel substrates.

Sample	***i***	***ii***	***iii***	***iv***	***v***	***vi***
$NiSO_46H_2O$ (M)	0,05	0,05	0,05	0,05	0,076	0,076
$FeSO_47H_2O$ (M)	0,05	0,05	0,02687	0,02687	-	-
Current Density (mA/cm^2)	3,63	7,27	7,27	5,09	14,54	7,27
Deposition Time (min)	10	10	5	3	10	10

3. Results

First, the optimum deposition conditions for the samples grown on copper substrates were established. It was observed that low current density (samples 1, 2) did not lead to a uniform deposition, while high current density and high deposition time (samples 3, 4, 5, 7) resulted in either cracking (Fig. 2) or black coating. The optimum deposition conditions, subsequently applied to all investigated samples, turned out to be 7.27 mA/cm^2 for 5 minutes (samples 6, 8-18) (Fig. 3).

Fig. 2. SEM image of sample 4.

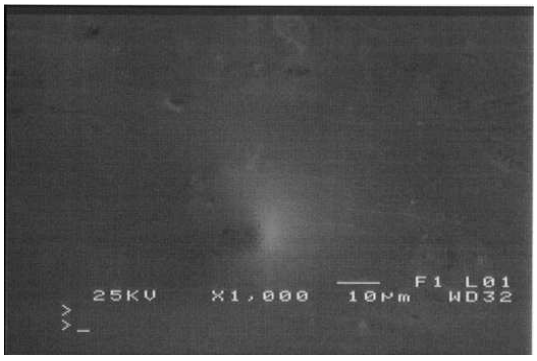

Fig. 3. SEM image of sample 10.

Scanning Electron Microscopy was used for the microstructural characterization and the composition analysis. The observation of sample 4, the thicker of all samples, revealed the presence of microcracks (Fig. 2) evenly distributed over the deposit thickness and oriented perpendicular to the surface deposit interface. The presence of microcracks is probably due to the growth of internal stresses during the electrodeposition process. Since all other samples were thinner than sample 4 and microcracks were not observed in any of them, it can be concluded that only thick deposits contain cracking. Increasing the ratio of iron to nitrate sulphate to 2:1 (sample 6), at optimum deposition conditions, resulted in a uniform coating (Fig. 3), while decreasing it to 0.5:1 (sample 8), a composition of approximately 50 wt% Ni and 50 wt% Fe was obtained. In Fig. 4, the induced anisotropy during the deposition process can be seen.

Based on the concentration analysis results summarized on Table 1, sample 11 was prepared under the presumption that the relationship in the region between 30 and 60 wt% Fe content is linear and the optimum 50-50 alloy was obtained with a 0.536 Fe/Ni ion ratio. This sample (Fig. 5) has a relatively smooth surface, smoother than that of sample 9 (Fig. 6), due to the relatively thin coating judging from the 30 wt% Cu content measured in the EDX analysis as well as by the lack of pores observed on sample 9 which are due to the formation of H_2.

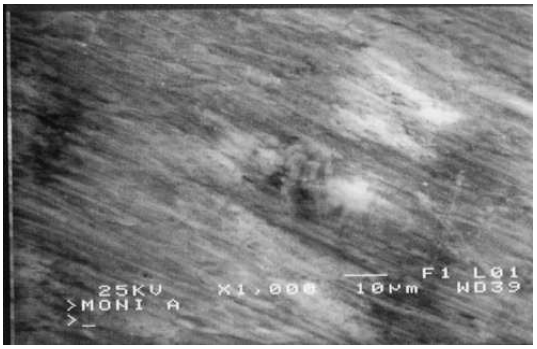

Fig. 4. SEM image of sample 6.

Fig. 5. SEM image of sample 11.

The deposition of FeNi films on stainless steel substrates was not successful because the substrate was not mirror finished (samples i-iv). Yet, Ni was easier deposited on this substrate (samples v-vi). Fig. 7 illustrates such a Ni-rich thin film the grains of which follow the grains of the stainless steel substrate. The composition analysis, for these samples, indicated high concentration of Ni, more than 90 Wt%.

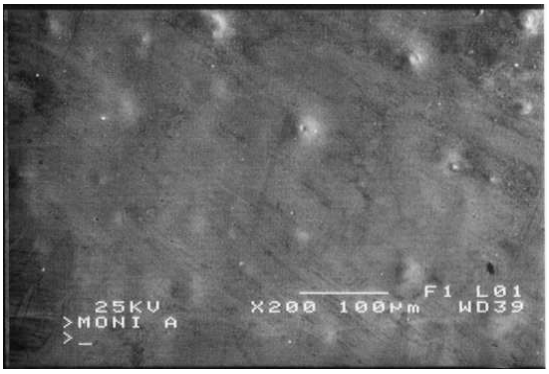

Fig. 6. SEM image of sample 9.

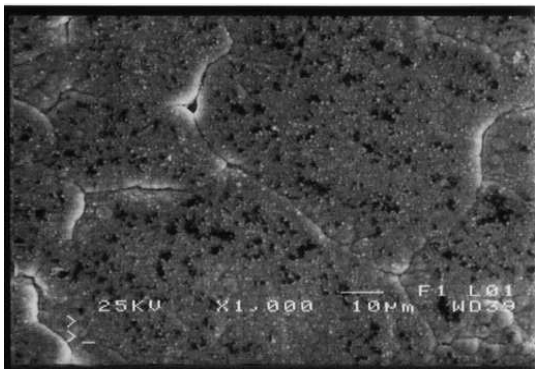

Fig. 7. SEM image of sample vi.

4. Discussion

Table 3 summarizes the results of the concentration analysis for the samples prepared at optimum conditions. The increase (decrease) of the wt% content of Fe (Ni) with increasing Fe:Ni ion ratio shows an exponential dependence (Fig. 8).

Table 3. Dependence of composition on Fe/Ni ion concentration.

sample	Fe/Ni	Fe (wt%)	Fe (mod)	Ni (wt%)	Ni (mod)
10	0.13	10	14.68	90	85.32
15	0.14	15	16.45	85	83.55
14	0.17	20	18.87	80	81.13
13	0.20	30	22.13	70	77.87
9	0.25	30	26.62	70	73.38
12	0.32	40	32.32	60	67.68
8	0.50	50	44.34	50	55.66
11	0.54	50	46.36	50	53.64
16	1.00	65	64.47	35	35.53
6	2.00	80	79.69	20	20.31
17	4.00	90	88.90	10	11.10
18	8.00	95	95.94	5	4.06

The Fe content increases rapidly with the Fe/Ni concentration (samples 9, 11, 12, 16, 6) but slows down for very high concentrations (samples 17, 18). A first attempt to model this dependence yielded the relationship:

$$y_{Ni} = 0.3e^{-5x} + 0.7e^{-35x} \times 100\%, \; y_{Fe} = 1 - y_{Ni},$$

where y_{Fe} and y_{Ni} are the wt% content of Fe and Ni respectively and x is the Fe/Ni concentration (Fig. 8).

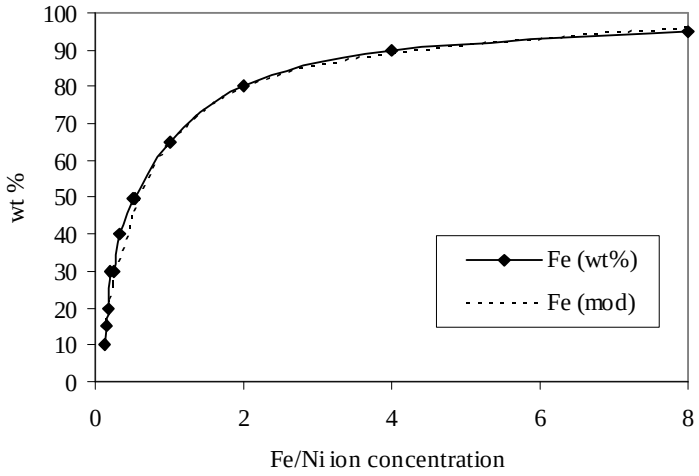

Fig. 8. Experimental (solid) and theoretical (dashed) curves for the Fe concentration vs the Fe/Ni ion content.

The structure of the alloys, as cast and after heat annealing at 450 ^{o}C for 1 h in Ar atmosphere, was determined using the X-ray diffraction technique with CuK_{α} radiation at 30mV. It is not so easy to distinguish between Cu and FeNi peaks because of the fact that the substrate was copper and we could not decrease the used voltage. After the heat treatment (Fig. 9) these peaks are better separated because of the crystallization of the alloys.

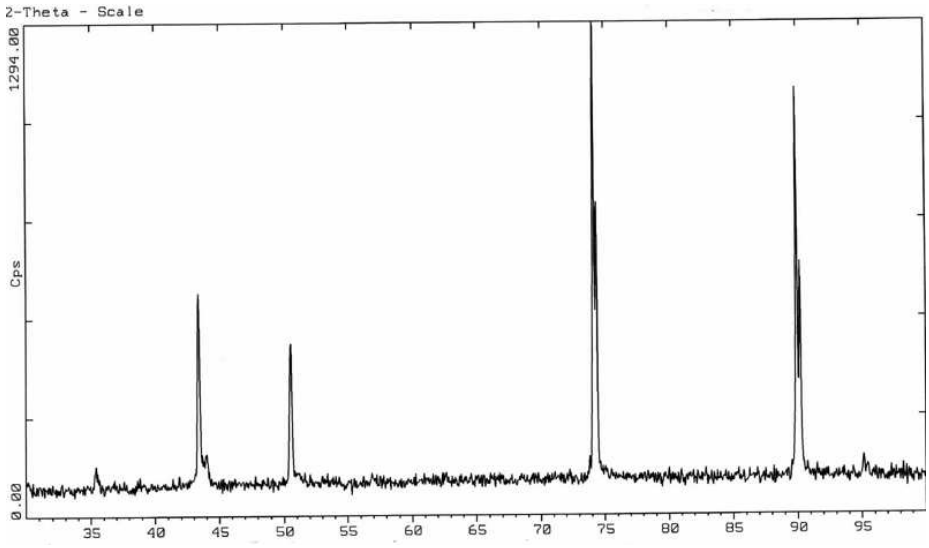

Fig. 8. XRD image of sample 12.

Because of the uniform cylindrical deposition ability of our electrodeposition device, the as-cast samples exhibited circumferential magnetoelastic anisotropy. After thermal treatment at 450 ^{0}C in Ar atmosphere internal stresses were partially removed as observed by AC magnetometry.

5. Conclusion

Soft magnetic $Fe_{1-x}Ni_x$ thin films have been electrodeposited on cylindrical copper substrates prepared in order to investigate their properties with respect to potential applications as sensors. The optimal deposition parameters and resulting has been established in order to obtain uniform coating and a smooth surface, suggestive of minimum internal stresses. Thermal treatment has also been used applied in order to improve on the crystallization of the alloys and further minimize internal stresses. Similar samples grown on stainless steel substrates failed to reproduce the same behavior.

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