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Potentiostatic Electrochemical Preparation and Characterisation of Cobalt Containing Iron-Molybdenum Thin Film

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Abstract

Thin films of Cobalt containing Iron-Molybdenum of variable composition have been prepared by the electrochemical codeposition under the potentiostatic control to study their corrosion behaviour in sodium chloride, sulphuric acid and hydrochloric acid solutions. Thickness of different samples with different concentration of cobalt has been determined. Current-Voltage studies have been carried out for the construction of Tafel Plot to determine the corrosion rate and corrosion current. Grain size and stress on the thin film surface is also determined. The instrumental analysis of prepared samples has been done by SEM (Scanning Electron Microscope) and Energy Dispersive X-Ray Spectroscopy (EDAX analysis) for the morphological and structural studies while the elemental composition is determined by X-Ray Diffraction (XRD) studies of the prepared thin films.

Key words: Electro deposition, corrosion rate, Film-thickness, SEM, XRD, EDAX analysis.

Introduction

FeCo alloys have been extensively studied as soft magnetic materials. They have been used widely and commercially in magnetic sensors, magnetic recording head, motors, and generators in electric vehicles since it has high Curie temperature, high magnetization, high electric permeability and good thermal stability[1-3]. Electrodeposited Iron-group alloys are used widely in the field of microelectronics. Like, permalloy, a soft magnetic material with 80% Ni and 20 % Fe, is a commercially important material in dual performance magnetic heads[4]. FeCo falls under the category of materials that offer the possibility of a new generation of magnetic sensors, combining the advantages of non-contact sensing with high sensitivity[5]. Nowadays, in order to fabricate nanocrystalline metallic films, many deposition techniques are available, such as sputtering, molecular beam epitaxy, vacuum evaporation, sol-gel etc. But all

these methods require high precision process control, which demands higher capital cost and incurs huge material waste. As compared to different deposition methods for the metallic films, electrodeposition has always been a well accepted method, due to its relatively higher efficiency, easier control and lower cost[6-10]. In the present work Cobalt containing Iron-Molybdenum thin films have been electrodeposited from aqueous solution and the deposited thin films have been studied for its characaterisation.

Experiment

The chemical reagents used were Ferrous Sulphate, Cobalt Sulphate Heptahydrate, Molybdic acid and boric acid to act as a source of Co, Fe, Mo ions in the solution. All the reagents used were of analytical grade. The aqueous electroplating baths of these reagents were prepared in deionised water. Electrodeposition process is the simple and cost effective process which can be used in preparing thin film of FeCoMo ternary alloy. The electrochemical assembly consists of a conventional three-electrode assembly. The titanium electrode of surface area (1cm × 1cm) served as a counter electrode, saturated calomel electrode (SCE) was used as a reference electrode and a copper plate with surface area of (1cm × 1cm) was used as a working electrode. A copper wire is attached to one side of the titanium plate with the help of silver epoxy to ensure the conductivity of the electrode while rest of the portion at the backside of the titanium plate was covered by araldite for insulation.

The FeCoMo ternary alloy was potentiostatically electrodeposited at -1.00 V Vs SCE. The deposition of thin film was carried out for 30 minutes. For data acquisition transistor based power supply unit Model 613 (systronics electronics limited) and multimeters were used as per the circuit requirement for the measurement of current and potential during eletrodeposition. Three different solutions with varying concentration of cobalt were prepared by taking Ferrous Sulphate, Cobalt Sulphate Heptahydrate, Molybdic acid and boric acid, while one solution containing Ferrous Sulphate, Molybdic acid and H_3BO_3 were prepared. The pH of the solution was adjusted between 3-4. The electrodeposition process was carried out at room temperature. All the electrosynthesized samples were tested in 0.1 N HCl, 0.01 N HCl, 0.001 N HCl, 1 % NaCl, 0.01 % NaCl, 0.001 % NaCl, 0.1 N H_2SO_4, 0.01 N H_2SO_4 and 0.001 N H_2SO_4 to acquire the Current-Time data and Current-Voltage data. The SEM images and EDAX of the electrodeposited samples were obtained by SEM instrument model JEOL JSM 5600 while X ray diffraction pattern of the samples were obtained by X-ray diffractometer D8 Advance Bruker AXS.

Result and Discussion

Simultaneous discharging of two or more than two ionic species from the electroplating solution is essential for their codeposition. There is a wide difference in the deposition potential of Iron, Cobalt, and Molybdenum. Therefore, to obtain common deposition potential for these ionic species, the Current-Voltage behaviour of solutions having different compositions has been studied. The result shown in fig.1 indicates that the codeposition of these ions is possible at -1.00 V Vs SCE. The thin film of FeCoMo ternary was electrosynthesised potentiostatically by application

of requisite potential. During electrodeposition process it was found that the value of current was initially high which gradually decreases with time and after few minutes current value becomes nearly constant (Fig. 2). This can be attributed to the change in the surface condition of the working electrode as the electrodeposition process proceeds. The area under the Current–Time curve is used for estimating the thickness of the electrodeposited thin film.

The thickness of thin film prepared from the electroplating solution containing Fe (0.1M) + Mo (0.01M) is lesser than the thickness of thin film prepared from the electrolytic solution containing Fe (0.1M) + Mo (0.01M) + Co (0.02M) and Fe (0.1M) + Mo (0.01M) + Co (0.05M). These two bath composition in turn results in the formation of electrodeposit with nearly same thickness while thickness of electrodeposited thin film from the electrolytic solution of composition Fe (0.1M) + Mo (0.01M) + Co (0.10M) was found to be more than that of other samples. This indicates that the film thickness increases along with the increase in concentration of cobalt in the electrolytic bath. Boric acid plays an important role in all the electrolytic solutions. It has a significant role in the morphology and compositional characteristics of the finally deposited alloy. After electrosynthesis of CoFeMo ternary alloy, all the samples were subjected to the testing in NaCl, H_2SO_4, HCl solutions of different concentration for the study of their electrochemical parameters. The Current-Voltage response of the electrodeposits was used to construct the Tafel-Plot (Fig. 3). The plateau observed in the cathodic polarisation and anodic polarisation curve could be associated with accelerated passivation process. These Tafel Plots in turn were used to determine the corrosion rate in milli inches per year (mpy) and corrosion current respectively by using following expression

$$CR\ (mpy) = \frac{0.13 \times I_{corr} \times E_w}{F \times d \times A}$$

Similarly, electrochemical variations of current with respect to potential were determined for the thin films prepared from solutions having Fe (0.1M) + Mo (0.01M). These electrodeposits were also tested in NaCl, H_2SO_4, HCl solutions of same concentration as it was used in the testing of Cobalt containing Iron-Molybdenum thin films. After comparing the corrosion characteristics of CoFeMo thin films with the data of FeMo thin films, it can be said conclusively that the corrosion rate was comparatively lesser in former than in the latter thin films. This can be attributed to the inclusion of Cobalt in the electrodeposits. The corrosion rate also decreases with increase in the dilution of NaCl, H_2SO_4, HCl solutions. Similarly, corrosion rate was also found to decrease along with the increase in amount of cobalt in the electroplating solutions. These results clearly indicate that the percentage atomic weight of the cobalt in the electrodeposited thin film increases along with increase in its concentration in the bath (Fig. 4). The SEM images (Fig. 5-6) of all the prepared samples were studied which shows homogeneity and uniformity in the electrodeposits. EDAX of all the samples were taken along with SEM images, which clearly reveals the peaks of Iron, Cobalt and Molybdenum. This indicates the inclusion of these three ions in the electrodeposits (Fig. 7). Moreover, the EDAX analysis of thin film containing Fe-Mo alloy shows their corresponding peak indicative

of the inclusion of Iron and Molybdenum in the respective samples. The structural studies were carried out by XRD diffraction pattern. A representative X-ray diffraction pattern is shown in Fig. 8. The electrodeposited samples were mounted on a flat stage and scanned from $2\theta = 10^0$ to $2\theta = 70^0$ in stepsize of 0.02 having a count rate of 9 seconds. The peaks obtained in the XRD were compared with that of the reference pattern in JCPS card standard peaks. The XRD data was indexed successfully for the determination of crystal structure. The crystal was found to have a cubical structure. Scherer's equation is used for estimating the grain size which ranges between 25-50 nm. Williamson's Hall plot is drawn from the XRD data, a representative of which is shown in fig. 9. The microstrain is calculated for all the samples, this clearly indicates that samples may result in different values of lattice strain. Lattice strain in FeMoCo thin films arises due to the excess volume of grain boundaries dislocations.

Table 1. Testing of electrodeposited thin films in experimental solutions of different Concentrations

Electroplating Solution	Experimental solution H_2SO_4	Corrosion Rate (10^{-4} mpy)	Experimental solution HCl	Corrosion rate (10^{-4} mpy)	Experimental solution NaCl	Corrosion rate (in 10^{-4} mpy)
Fe(0.1M) +	0.1N H_2SO_4	4.94	0.1 N HCl	6.08	1% NaCl	4.40
Mo(0.01M)+	0.01N H_2SO_4	2.0	0.01N HCl	2.91	0.01% NaCl	3.42
C0(0.02M)	0.001NH_2SO_4	1.24	0.001N HCl	0.98	0.001% NaCl	2.47
Fe(0.1M) +	0.1N H_2SO_4	4.94	0.1N HCl	4.72	1% NaCl	4.94
Mo(0.01M)+	0.01N H_2SO_4	0.71	0.01N HCl	2.47	0.01% NaCl	2.47
C0(0.05M)	0.001N H_2SO_4	1.08	0.001N HCl	1.08	0.001% NaCl	1.45
Fe(0.1M) +	0.1N H_2SO_4	3.11	0.1 N HCl	2.71	1% NaCl	2.65
Mo(0.01M)+	0.01N H_2SO_4	0.73	0.01N HCl	1.96	0.01% NaCl	0.98
C0(0.10M)	0.001N H_2SO_4	0.65	0.001N HCl	0.70	0.001% NaCl	0.85
Fe(0.1M) +	0.1N H_2SO_4	10.75	0.1 N HCl	14.17	1% NaCl	8.54
Mo(0.01M)	0.01N H_2SO_4	3.90	0.01N HCl	8.94	0.01% NaCl	4.91
	0.001N H_2SO_4	1.59	0.001N HCl	1.59	0.001% NaCl	4.18

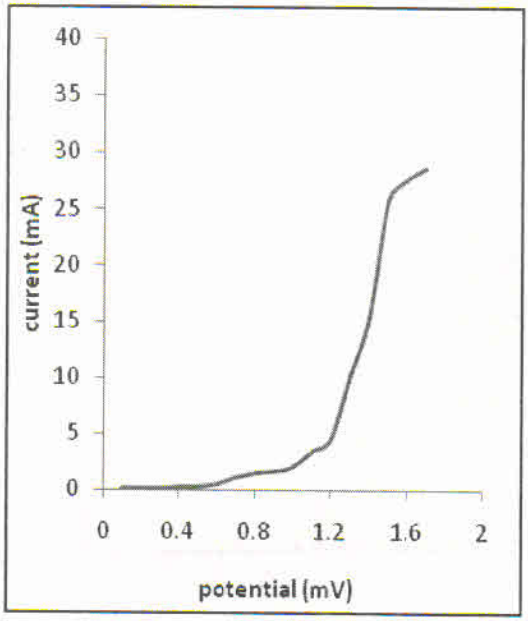

Fig. 1. Current Vs Potential

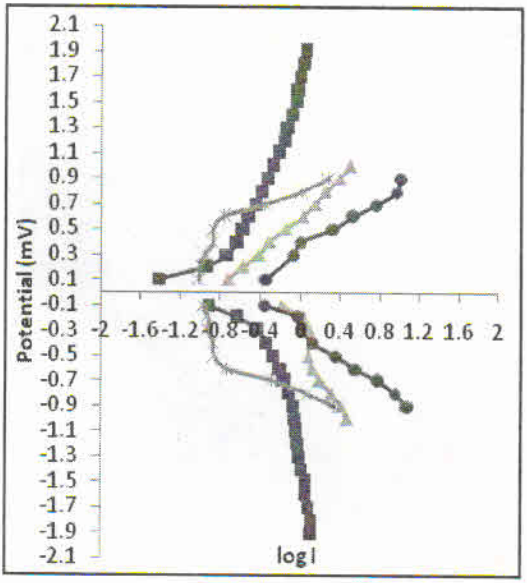

Fig. 3. A Representative Tafel Plot

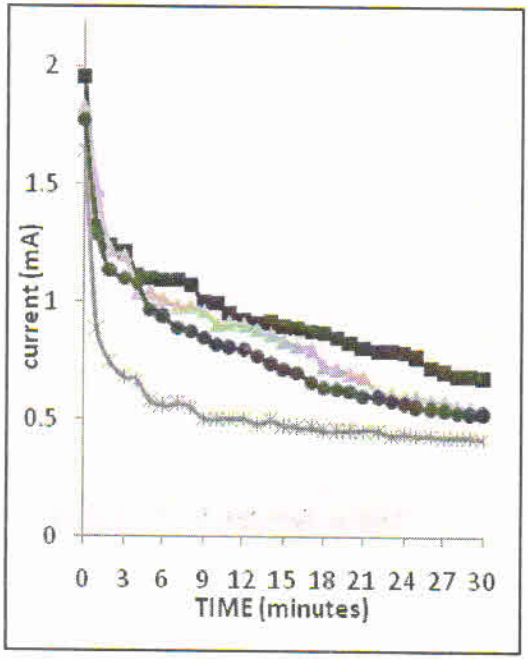

Fig. 2. Current Vs Time Graph

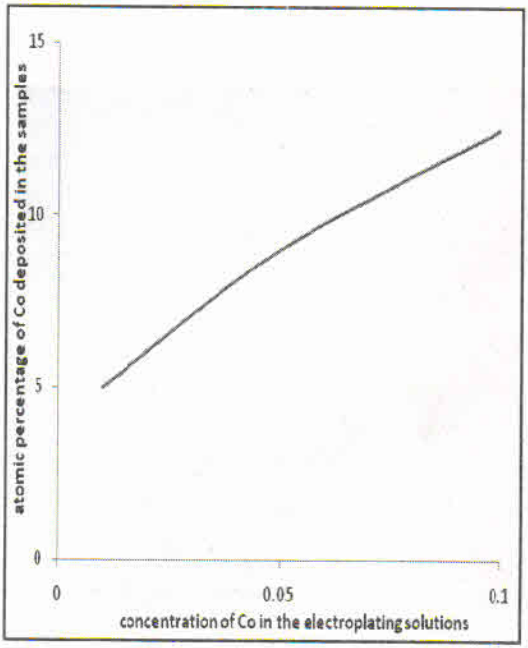

Fig. 4. Atomic Percentage of cobalt in electrodeposits Vs Cobalt concentration in electroplating solutions

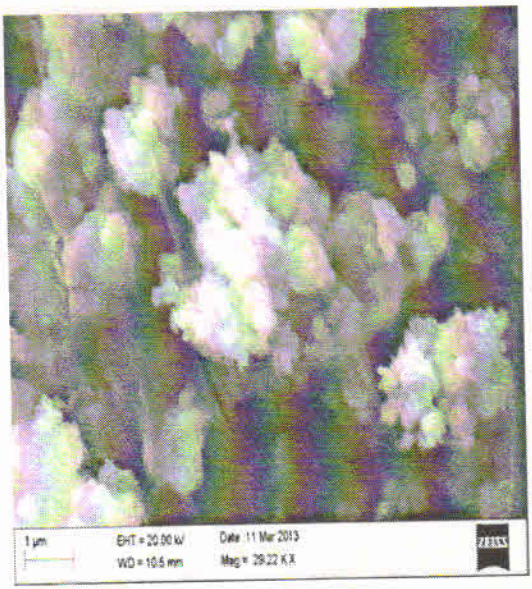

Fig. 5. SEM image of a FeCoMo sample

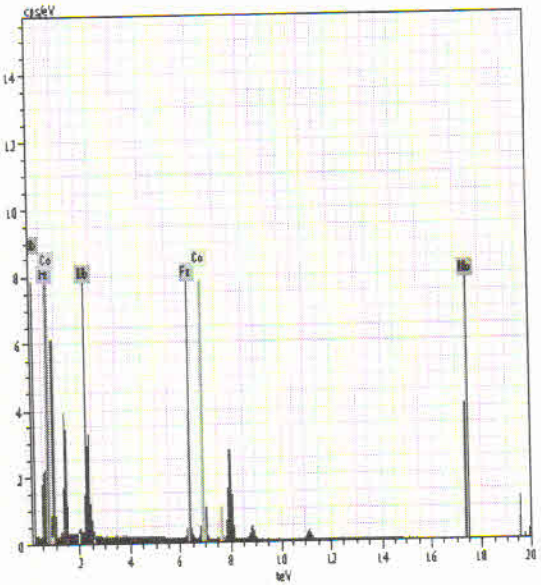

Fig. 7. EDAX of a FeCoMo sample

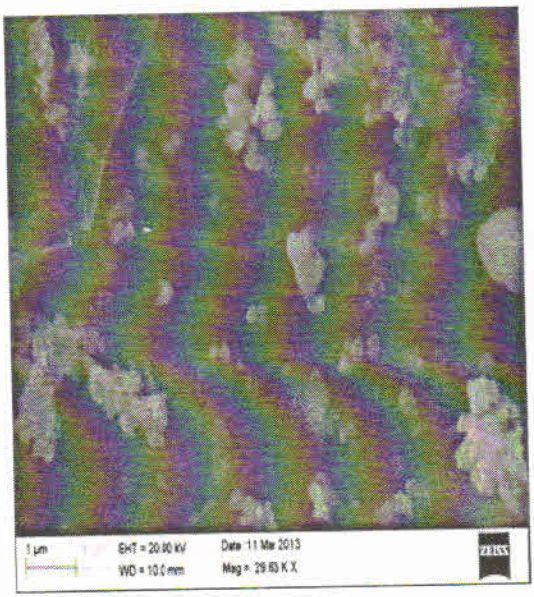

Fig. 6. SEM image of FeMo

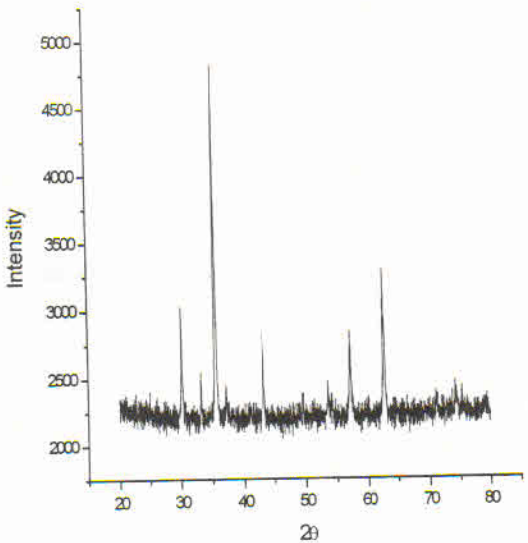

Fig. 8. XRD of a sample of FeCoMo alloy

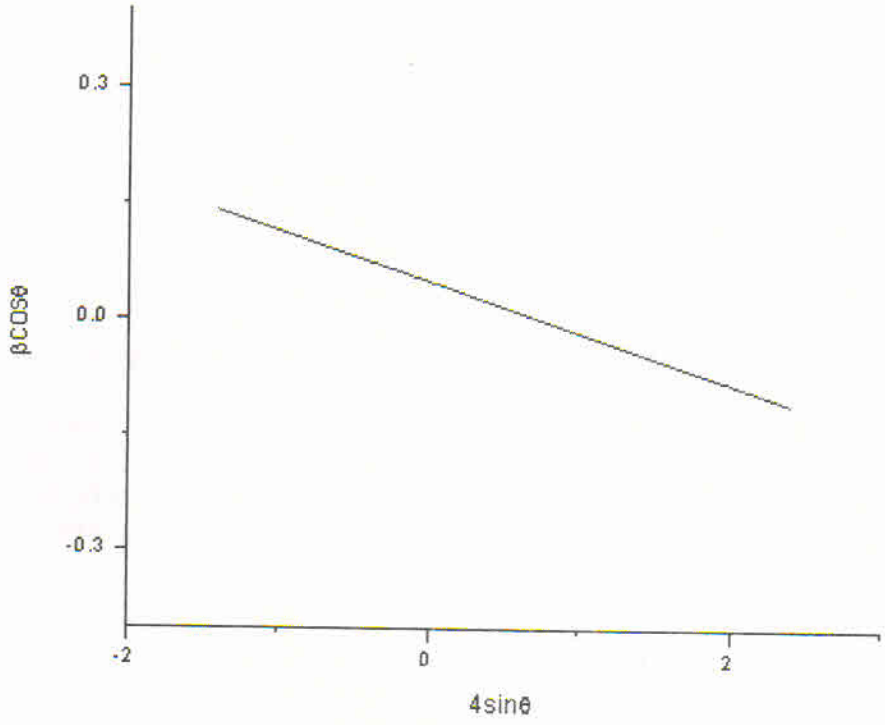

Fig. 9. A representative Williamson's Hall Plot

Conclusion

On the basis of current-voltage data derived from the cathodic and anodic polarisation Tafel Plot were constructed to calculate the corrosion rate. The corrosion rate of the samples was found to decrease with the increase in the concentration of cobalt in the electroplating solution. The corrosion rate also decreases with the increasing dilution of HCl, H_2SO_4 & NaCl solutions. The codeposition of Cobalt, Iron and Molybdenum at the common deposition potential is confirmed by XRD & EDAX of the samples. The XRD patterns recorded for the thin films shows polycrystalline nature with a cubical structure. The SEM images show that the deposited thin films are smooth and crack free with nanosized particle agglomerates. Several crystallites grouped together to form larger grains. Also, the grains tend to cover the substrate surface completely. The grain size is determined by Scherer equation. It lies between 25-50 nm, while the stress on the surface of thin film was calculated by Willaimsons Hall Plot.

Acknowledgement

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