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Effect of current density on electrodeposited cobalt ferrous tungsten phosphorus magnetic thin films

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ABSTRACT

The properties of Co-Fe-W-P magnetic thin films electrodeposited in the presence of sodium hypophosphite as a precursor with varying concentrations were studied with respect to thickness of the films. Films were electrodeposited in various current densities in order to get different thickness and uniform deposits. Vibrating sample magnetometer studies indicate the magnetic saturation (M_s), retentivity (M_r) and coercivity (H_c) of these films. Crystallite size and dislocation density of Co-Fe-W-P thin films were calculated by X-ray diffraction studies. Surface morphology analysis was carried out by using Scanning Electron Microscope. Percentages of elemental analysis of Co-Fe-W-P thin films were obtained by using energy dispersive X-ray analysis. Hardness and adhesion of the films were also studied. Difference in magnetic properties and structural characteristics are discussed.
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1. Introduction

The technique used is Electro deposition which is more interesting and ready to use because films can be deposited in any desired shape and at room temperature and pressure in very less expensive [1]. The ferromagnetic metals (such as Fe, Ni and Co) and their alloys have been attracting due to their magnetic and magneto-astrictive properties resulting in an enormous applications. For e. g.: data storage devices and magneto-astrictive sensors. Among these, alloys form of iron and cobalt play interesting role in magnetic properties, cobalt, when alloyed with iron increases the magnetic saturation. The alloys of Co-Fe used in electromagnets, beam-focusing lenses for electron microscopes, air craft motors, generators and transformers [2]. As iron is the most corrosion affected metal among the magnetic elements, corrosion is still a major problem in the development of a magnet with good chemical stability and high Bs. Now the research, show interest in electro deposition alloys of W (tungsten) with iron group metals, because of their highly magnetic, electrical, mechanical, thermal and corrosion less properties [3]. The Co based hard magnetic films are developing a major role because of their potential applications in electromagnetic-actuated micro electromechanical system (MEMS) [4–6].

The good additive agent tungsten is added, because of its highly corrosion resistant and also with stand high mechanical strength. Very few research works [7–11] are experimented about the structured and composition of electrodeposited amorphous and crystalline iron group W alloys. The various compositions of Co-W-P films may exhibit a unique properties and can be used as coatings in electronics and automobile industries, rocketry and space technology [12].

The crystal structure, grain size, morphology and magnetic properties were investigated when Co-Fe-P alloy films were co-deposited from NaH_2PO_2 containing solutions on copper substrates [13]. In order to fill up nano sized pores, the grain size of metal or alloy should be small. If the electroforming of MEMS or similar micro devices is of concern, the electrodeposits should be crack free and their surface should have low roughness [14]. The formation of Fe-based alloys, maintain a high corrosion resistance because of the addition of Phosphorous [15]. There are various literary reports in the electro deposition of Fe-W [16], and Fe-W-P [17,18] films.

In the present study, we investigated in detail the effects of different current density on the magnetic and structural properties of electrodeposited Co-Fe-W-P thin films.

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2. Experimental

2.1. Synthesis and deposition

A copper substrate of size 1.5 × 5 cm as cathode and stainless steel plate is used as anode for galvano static electro deposition method. Current for electro deposition was passed from a d.c regulated power supply. Analytical grade chemicals were used to prepare bath solution. An adhesive tape was used as mask for all the substrate except the area on which deposition of film desired. The copper electrode was buffed for removing scratches by using mechanical polishing wheel with a buffing cloth containing aluminium oxide abrasive. After buffing the substrates were cleaned by concentrated H_2SO_4 or acetone. Before electro deposition, these substrates were cleaned in an alkaline electro cleaning bath and the substrates were rinsed in distilled water. The electro deposition was done with different current density.

Electro deposition of Co-Fe-W-P magnetic thin film was plated from a bath containing cobalt sulphate ($CoSO_4{\cdot}7H_2O$) 0.1 M, ferrous sulphate ($FeSO_4{\cdot}7H_2O$) 0.1 M, sodium tungstate ($Na_2WO_4{\cdot}2H_2O$) 0.05 M, tri sodium citrate ($Na_3C_6H_5O_7{\cdot}2H_2O$) 0.3 M, boric acid ($H_3BO_3$) 0.16 M, and ammonium sulphate ($(NH_4)_2SO_4$) 0.3 M. To this solution varying composition of sodium hypophosphite (NaH_2PO_2) 0.1 M/0.2 M were added and their effect on the properties of Co-Fe-W-P films was investigated for different current density like 2.5 mA cm^{-2}, 5 mA cm^{-2} and 7.5 mA cm^{-2} and deposition time like 15, 30 and 45 min respectively. The pH value was fixed at 8.0 for all the electro deposition baths.

2.2. Characterization

The thickness of the deposited films was measured using digital micrometer (Mitutoyo, Japan). Magnetic properties of deposited films were studied with vibrating sample magnetometry. The structure and morphology of the magnetic films were studied using X-ray diffractometer (Rich Seifert, model 3000) and scanning electron microscope (JEOL) respectively. The crystalline size, strain and dislocation density of the deposited Co-Fe-W-P films has been calculated from the XRD data. Percentage of elemental analysis of Co-Fe-W-P film was obtained using EDAX. Hardness of the deposited thin film was obtained using Vickers Hardness tester through diamond indenter method. Adhesion of the films was tested by bend test and scratch test.

3. Results and discussion

3.1. Thickness study

Table 1 summarizes the effect of current density on the thickness and magnetic properties of the Co-Fe-W-P films electrodeposited for different current densities and different deposition times with 0.1 M and 0.2 M of NaH_2PO_2.

The thickness of the film was increased with increase in NaH_2PO_2 as well as increase in current density. The magnetic properties of the thin films were increased with increase of thickness.

3.2. Surface analysis

3.2.1. Structural analysis

Electrodeposited Co-Fe-W-P films were obtained from the baths maintained at 2.5 m A cm^{-2}, 5 m A cm^{-2} and 7.5 m A cm^{-2} current density for 45 min deposition time with different concentration of NaH_2PO_2 were subjected to XRD studies Fig. 1. The X-ray wavelength used was 1.5406 Å of Cu-K α radiation. The data obtained from the XRD pattern compared with the standard JCPDS data and were found to have cubic nature in Co_3Fe_7(1 1 0) (JCPDS card number 48-1816), CoP_3(4 1 1) (JCPDS card number 73-1239), Co_3Fe_7 (2 0 0) (JCPDS card number 50-0795) planes and have hexagonal structure in Co W (2 2 0) (JCPDS card number 65-3520) plane. The presence of sharp peaks in XRD pattern reveals that the films are crystalline in nature. Crystalline size of the deposits were calculated from XRD data using Debye- Scherrer formula

$$\text{Crystalline size (D)} = 0.945\,\lambda/\beta\cos\theta \quad (1)$$

Crystalline sizes were obtained in the nano scale range. The crystalline size decreases with increase in current density of various concentration of NaH_2PO_2. Strain of the films were calculated from XRD data, using the formula,

$$\text{Strain}\,(\varepsilon) = \beta\cos\theta/4 \quad (2)$$

Dislocation density is defined as the length of dislocation lines per unit volume of the crystal. The variation in lattice spacing leading to the variation in crystalline size may be the responsible for change in dislocation density [19].

$$\text{Dislocation density}(\delta) = 1/D^2 \quad (3)$$

The strain and dislocation density were increased and crystal sizes of the film is decreased when the concentration of NaH_2PO_2 is increased. The XRD peaks of thin film were shifted due to the strain and dislocation density of the film.

3.2.2. Morphological observation

Electrodeposited Co-Fe-W-P thin films were obtained from the baths maintained at 7.5 mA cm^{-2} current density for 45 min deposition time with different concentration of NaH_2PO_2 were subjected to SEM (Fig. 2). The crystallinity of Co-Fe-W-P film mainly depends on the amount of NaH_2PO_2 present in the bath. The surface scans shown the grain sizes are decreased when the concentration of NaH_2PO_2 in the bath was increased. As the grain size of Co-Fe-W-P thin films decreases, the magnetic properties increases.

3.3. Mechanical properties

Hardness of Co-Fe-W-P films obtained from the current density 7.5 mA cm^{-2} with 0.1 M of NaH_2PO_2 and 0.2 M of NaH_2PO_2 were examined using a Vickers hardness tester by a diamond indenter method (Table 2). The hardness values were found to be 158 VHN and 165 VHN respectively. Hardness of the film increases gradually when the current density and the concentrations of NaH_2PO_2 increases. Adhesion of the film to the substrate was tested by bending test and scratch test. The tests showed that the films have good adhesion to the substrate. High hardness number also revealed that the films had good adhesion with the substrate. When the current density of Co-Fe-W-P films from the bath containing 0.1 M of NaH_2PO_2 and 0.2 M of NaH_2PO_2 was increased from 2.5 mA cm^{-2} to 7.5 mA cm^{-2}, the dislocation density increased. It leads to increase in yield strength and the material becomes harder.

3.4. Elemental analysis

Table 2 represents the results of EDAX. It was observed that all the films obtained from various baths had more than 3% of phosphorous element. In the higher phosphorous content, the films showed high magnetic properties with improved crystalline structure.

Table 1
Effect of current density on the thickness and magnetic properties of the Co-Fe-W-P films electrodeposited for different current densities and different deposition times with 0.1 M and 0.2 M of NaH_2PO_2.

S. No.	NaH_2PO_2 (M)	Current density (mA cm^{-2})	Deposition Time (min)	Thickness of deposit (μm)	Magnetic saturation (emu)	Remanent polarization (emu)	Coercivity (Oe)	Squareness
1		2.5	15	1.13	0.015	0.002	178.82	0.13
2			30	2.17	0.064	0.029	163.85	0.45
3			45	2.6	0.151	0.054	166.08	0.35
4		5	15	1.23	0.017	0.007	186.49	0.41
5			30	2.17	0.099	0.03	141.3	0.3
6	0.1		45	2.73	0.194	0.056	139.66	0.28
7		7.5	15	1.87	0.052	0.029	190.28	0.55
8			30	2.6	0.03	0.003	160.95	0.1
9			45	3.5	0.104	0.006	124.62	0.05
10		2.5	15	1.4	0.019	0.006	209.41	0.31
11			30	2.3	0.02	0.004	162.41	0.2
12			45	3.57	0.073	0.018	129.84	0.24
13		5	15	1.7	0.032	0.008	163.62	0.25
14			30	2.6	0.072	0.019	159.28	0.26
15	0.2		45	3.33	0.063	0.013	108.43	0.2
16		7.5	15	2.4	0.03	0.006	174.89	0.2
17			30	2.87	0.057	0.013	154.55	0.22
18			45	3.67	0.103	0.014	140.79	0.13

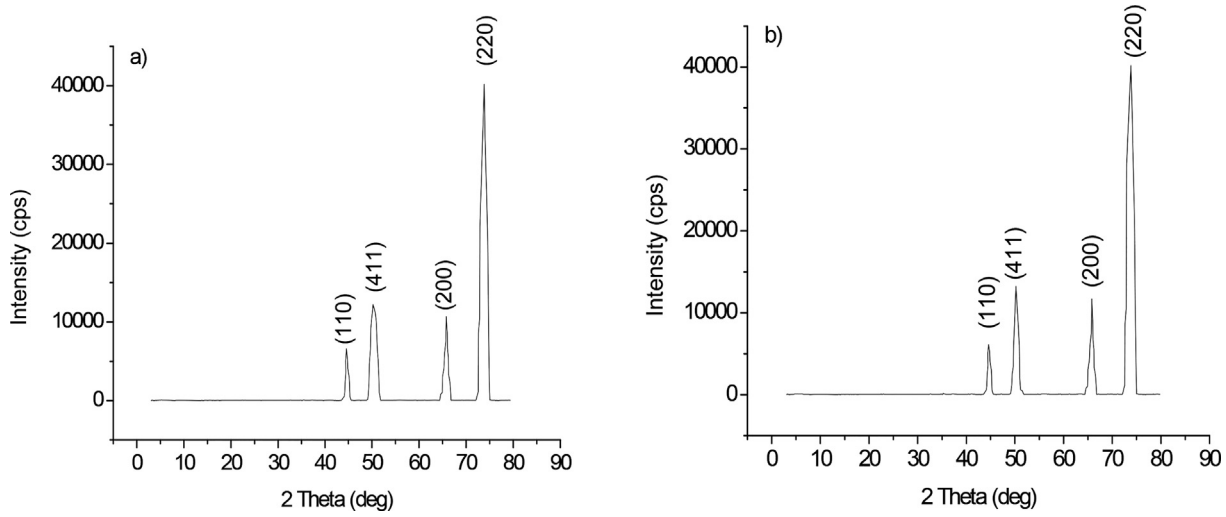


Fig. 1. XRD images of Co-Fe-W-P films electrodeposited at 7.5 mA cm^{-2} current density for 45 min deposition time with (a) 0.1 M of NaH_2PO_2 (b) 0.2 M of NaH_2PO_2.

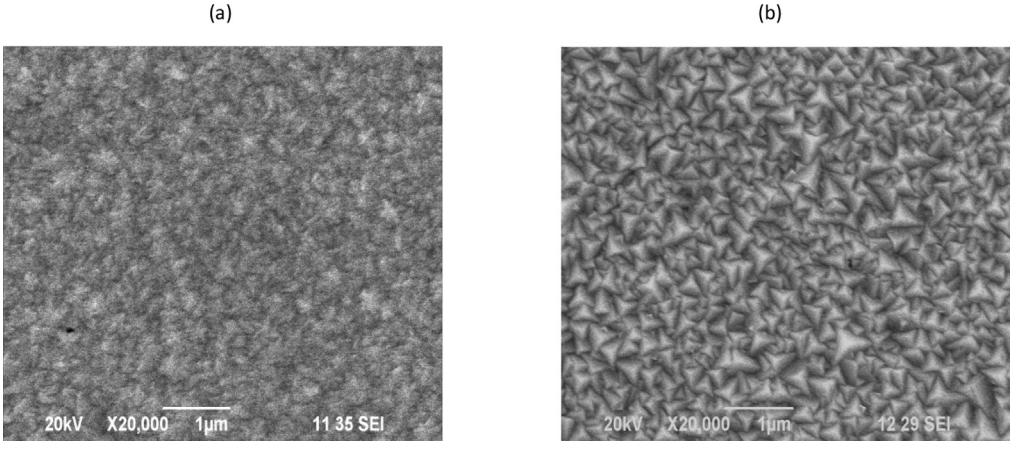


Fig. 2. SEM images of Co-Fe-W-P films electrodeposited at 7.5 mA cm^{-2} for 45 min deposition time with (a) 0.1 M NaH_2PO_2 (b) 0.2 M of NaH_2PO_2.

Table 2
Crystalline size, strain, dislocation density, hardness and composition of Co-Fe-W-P films at 45 min deposition time.

NaH_2PO_2 (M)	Current density (mA cm^{-2})	Crystalline size (nm)	Strain 10^{-4}	Dislocation Density ($10^{14}/m^2$)	Vicker Hardness Number (VHN)	Film Composition (at %)			
						Co	Fe	W	P
0.1	2.5	28.437	12.798	12.366	134	40.32	52.92	3.58	3.18
	5	27.371	13.296	13.348	148	40.68	51.78	4.16	3.38
	7.5	26.543	13.711	14.193	158	41.76	49.95	4.05	4.23
0.2	2.5	26.719	13.621	14.007	152	35.53	58.54	1.59	4.34
	5	25.317	14.375	15.601	159	41.15	51.49	2.21	5.16
	7.5	23.907	15.223	17.496	165	43.19	47.08	4.45	5.28

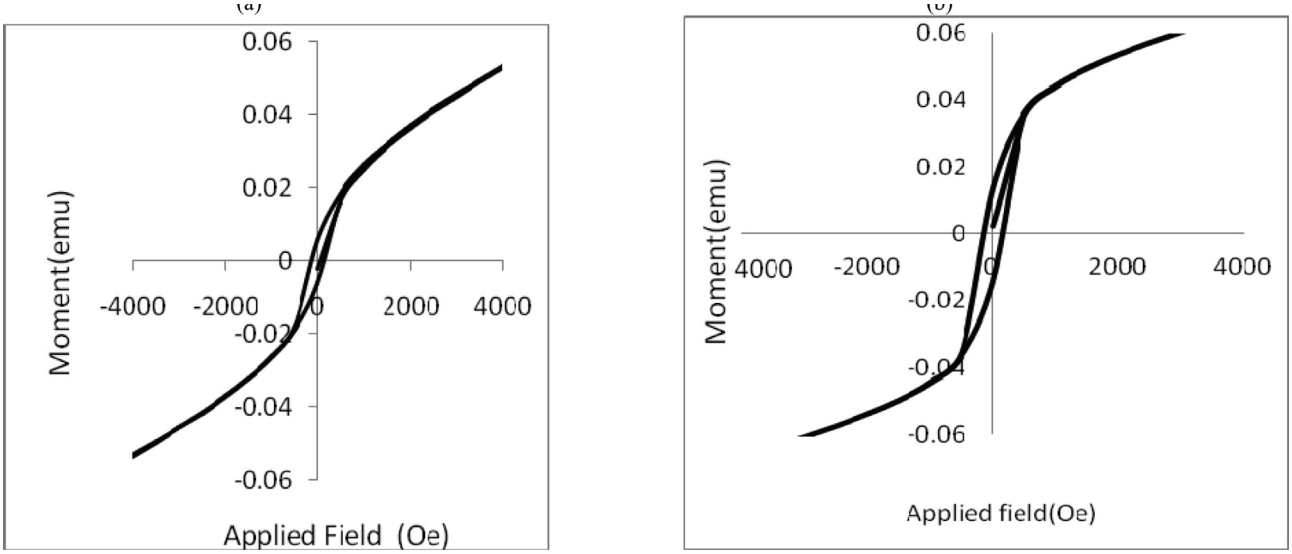


Fig. 3. VSM images of Co-Fe-W-P films electrodeposited at 7.5 mA cm^{-2} for 45 min deposition time with (a) 0.1 M NaH_2PO_2 (b) 0.2 M of NaH_2PO_2.

3.5. Magnetic studies

The VSM images of Co-Fe-W-P electrodeposited thin films obtained from the baths containing 0.1 M of NaH_2PO_2 and 0.2 M of NaH_2PO_2 at 7.5 mA cm^{-2} for 45 min deposition time are shown in Fig. 3. The coercivity range of soft magnetic material is less than 10 Oe. The coercivity values of Co-Fe-W-P films maintain more than 120 Oe. Therefore the above observable fact confirms that the Co-Fe-W-P deposits are hard magnetic in nature. The electrodeposited films were uniform and bright. With the increase in current density there was significant improvement in the thickness as well as magnetic properties of the film shown in Table 1. On increasing the phosphorous content, the remanent polarization, coercivity and squareness values increased from 0.006 emu to 0.014 emu, 124.62 Oe to 140.79 Oe and 0.05 to 0.13 respectively.

4. Conclusions

The nano crystalline Co-Fe-W-P thin films were synthesized by electrodeposition process. The films obtained from the bath containing 0.2 M of NaH_2PO_2 and the current density of 7.5 mA cm^{-2} having crystalline size around 23.907 nm and also having higher value of Hardness (165 VHN). The current density of the bath was increases from 2.5 mA cm^{-2} to 7.5 mA cm^{-2}, the strain, dislocation density and hardness of the film also increases. High remanent and squareness values were observed as 0.014 emu and 0.13 respectively in the films prepared at 7.5 mA cm^{-2} for 45 min deposition time with 0.2 M of NaH_2PO_2. These hard magnetic films can be used in various electronic devices including high density recording media, magnetic actuators, magnetic shielding, magnetic writing heads, high performance transformer cores and MEMS.

CRediT authorship contribution statement

T. Thangaraj: Supervision, Validation, Writing- review & editing. **T. Aruna Christy:** Supervision, Validation, Writing- review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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