A comparative study of sodium hypophosphite and phosphorous acid on the Ferrous Tungsten Phosphorous thin films

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The magnetic film of Ferrous Tungsten Phosphorous (Fe-W-P) were prepared with NaH_2PO_2 and H_3PO_3 by electrodeposition method for current density of 30 mA cm^{-2} and 45 minutes deposition time. The magnetic saturation (M_s), retentivity (M_r) and coercivity (H_c) of the films were studied using vibrating sample magnetometer. The retentivity (M_r) and the magnetic saturation (M_s) of the deposited films increased with the increase of organic additive. The crystallite size and stress of the deposited thin films were calculated using X-ray diffraction (XRD) studies. Percentages of elemental analysis of Fe-W-P films were obtained using energy dispersive X-ray analysis (EDAX). Surface morphology analysis was carried out using scanning electron microscope (SEM). The magnetic properties and structural characteristics of Fe-W-P thin films with NaH_2PO_2 and Fe-W-P thin films with H_3PO_3 are discussed.

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1. Introduction

The current trends towards miniaturization, cost competitiveness and high performance packaging, electrodeposition has become the dominant manufacturing technology in many new applications and remains firmly established in others such as micro electromechanical system (MEMS) devices, nano electromechanical system(NEMS) devices, magnetic recording head and data storage media [1-3]. Ferromagnetic materials like Fe, Co and Ni play a vital role in the magnetic data storage. Among other methods of plating, iron plating displays specific features of interest due to welding of electrodeposited iron and plating of other metals on it with ease.

Ferrous–tungsten coating is considerably cheaper than those of nickel and cobalt and is characterized by higher physicochemical properties in comparison with pure iron. The introduction of tungsten into metal deposits allows for a significant improvement of the properties of the obtained coatings, increasing their hardness, corrosion stability, and heat resistance. It is found that tungsten-containing alloys obtained through the galvanic method exceed pure metals of the iron group in corrosion stability due to the tungsten inertia and the lower porosity of the coatings. An iron–tungsten alloy has a higher wear resistance than pure iron. Fe–W alloys are used in both mechanics and micromechanics. The addition of phosphorous promotes the formation of the structure of Fe-based alloys and maintains high corrosion resistance [4]. There are also some literary reports in the electrodeposition of Fe-W [5], Ni-Fe-W-P [6], Co-W-P [7] and Fe-W-P [8-9] films.

In the present study, we investigated in detail the effects of phosphorous from sodium hypophosphate and phosphorous acid and urea on the magnetic and structural properties of electrodeposited Fe-W-P thin film.

2. Experimental

2.1. Synthesis and deposition

A copper substrate of size 1.5 x 5 cm as cathode and stainless steel plate is used as anode for galvanostatic electrodeposition method. Current for electrodepostion 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 aluminum oxide abrasive. After buffing the substrates were cleaned by con H_2SO_4 or acetone. Before electrodeposition, these substrates were cleaned in an alkaline electro cleaning bath then the substrates were rinsed in distilled water. The electrodeposion was done with different concentration of urea and phosphorous.

Fe-W-P films were electrodeposited on copper substrate from a single bath containing ferrous sulphate ($FeSO_4.7H_2O$) 0.1 M, sodium tungstate ($Na_2WO_4.2H_2O$) 0.05 M, tri sodium citrate ($Na_3C_6H_5O_7.2H_2O$) 0.3 M, boric acid (H_3BO_3) 0.16 M, ammonium sulphate $(NH_4)_2SO_4$ 0.3 M, sodium hypophosphite ($NaH_2PO_2.2H_2O$) 0.2 M. Hereafter the above bath composition will be referred to as bath A**.** Then 2.5 g l^{-1} and 5 g l^{-1} of urea were added in this bath.

Fe-W-P films were electrodeposited on copper substrate from a single bath containing ferrous sulphate

($FeSO_4.7H_2O$) 0.1 M, sodium tungstate ($Na_2WO_4.2H_2O$) 0.05 M, tri sodium citrate ($Na_3C_6H_5O_7.2H_2O$) 0.3 M, boric acid (H_3BO_3) 0.16 M, ammonium sulphate ($(NH_4)_2SO_4$ 0.3 M, phosphorous acid (H_3PO_3) 0.2 M. Hereafter the above bath composition will be referred to as bath B. Then 2.5 g l^{-1} and 5 g l^{-1} of urea were added in this bath.

The effect of organic additive and phosphorous on the properties of Fe-W-P films was investigated at current density of 30 mA cm^{-2} with 45 minutes deposition time. The pH value was fixed at 8.0 for all the electrodeposition 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 crystallite size and stress of the deposited Fe-W-P film has been calculated from the XRD data. Percentage of elemental analysis of Fe-W-P film was obtained using EDAX. Hardness of the deposited thin film was obtained using Vickers hardness tester through diamond intender 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 phosphorous and urea on the thickness and magnetic properties of Fe-W-P films. The thickness of the film was increased with increase in urea for both phosphorous contents. The magnetic properties of the thin films were increased with the increase of thickness. The thickness of the film at bath B in the absence of urea was 4.8 µm, it was higher than thickness of the film at bath A with 5 g/l urea.

Table 1. Effect of organic additive on the thickness and magnetic properties of the films.

S. No.	Fe-W-P film bath	Urea (g/l)	Thickness of deposit (µm)	Magnetic saturation (A/m)	Remanent polarization (A/m)	Coercivity (Oe)	Square ness
1	A	0	4.3	12.197	0.923	1744	0.08
2		2.5	4.4	25.154	3.153	1876	0.13
3		5	4.6	26.612	4.919	2272	0.18
4	B	0	4.8	15.829	3.634	1819	0.23
5		2.5	4.9	32.437	11.114	2242	0.34
6		5	5.3	41.453	16.224	2421	0.39

3.2. Structural analysis

Electrodeposited Fe-W-P films were obtained from the baths A and B contained 5.0 g 1^{-1} urea were subjected to XRD studies are shown in Fig. 1. The X-ray wavelength was used 1.5405 Å of Cu Kα radiation. The data obtained from the XRD pattern were compared with Joint committee for powder diffraction studies data and were found to have Rhombohedral structure with Fe_7W_6 (0210) plane [10] in both phosphorous contents and one more peak of Hexagonal structure with Fe_2P (312) plane[11] was obtained at bath B with urea. According to Noyan and Cohen [12], the XRD peaks of thin film and metal were shifted due of the stress of the film. Stress of the films were calculated from XRD data, using the formula,

$$\text{Young's modulus} = \text{Stress} / \text{Strain} \quad (1)$$

The results are shown in Table 2. Stress of the film was low when no urea in the bath concentration. The stress of the film increased and crystalline sizes of the film decreased [13] when the concentration of urea was increased in the bath. Crystallite size of the deposits were calculated from XRD data using Debye-Scherrer formula

$$\text{Crystallite size} = 0.9\lambda/\beta \cos\theta \quad (2)$$

Crystallite sizes were obtained in nano scale range.

Table 2. Effect of organic additive on the structural properties of the films.

Fe-W-P Film Bath	Urea (g/l)	Crystalline size (nm)	Stress (MPa)	Vicker Hardness (VHN)	Film Composition (at %)		
					Fe	W	P
A	0	27.40	631	168	85.00	13.20	1.80
	2.5	26.10	662	177	85.89	11.90	2.21
	5	25.54	675	192	86.30	10.80	2.90
B	0	27.93	619	192	87.64	10.20	2.16
	2.5	25.86	668	201	89.12	8.57	2.31
	5	25.79	670	219	89.74	7.04	3.22

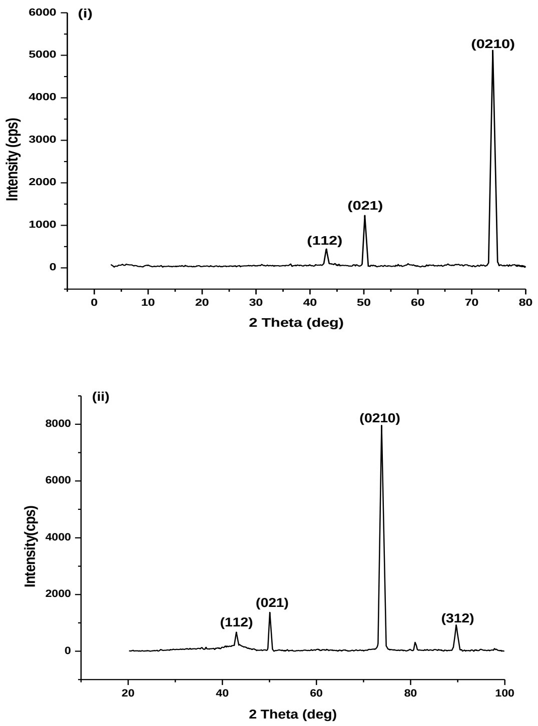
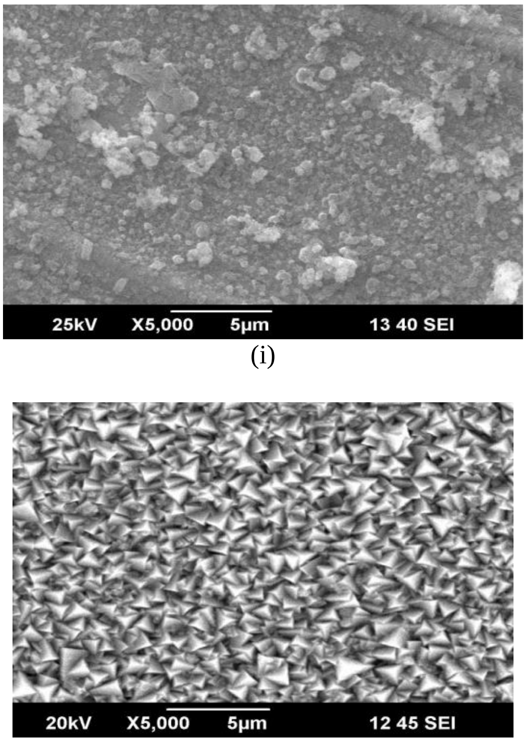


Fig. 1. XRD images of Fe-W-P films electrodeposited with 5.0 g 1^{-1} urea i) NaH_2PO_2 ii) H_3PO_3



(i)

(ii)

Fig. 2. SEM images of Fe-W-P films electrodeposited with 5.0 g 1^{-1} urea i) NaH_2PO_2 ii) H_3PO_3

3.3. Morphological observation

Electrodeposited Fe-W-P thin films were obtained from the baths A and B contained 5.0 g 1^{-1} urea were subjected to SEM as shown in Fig. 2. The crystallinity of Fe-W-P film mainly depends on the amount of urea and phosphorous which are present in the bath. The surface scan of the film shows from bath B with 5.0 g 1^{-1} urea had uniform grain size than the bath A with 5.0 g 1^{-1} urea.

3.4. Mechanical properties

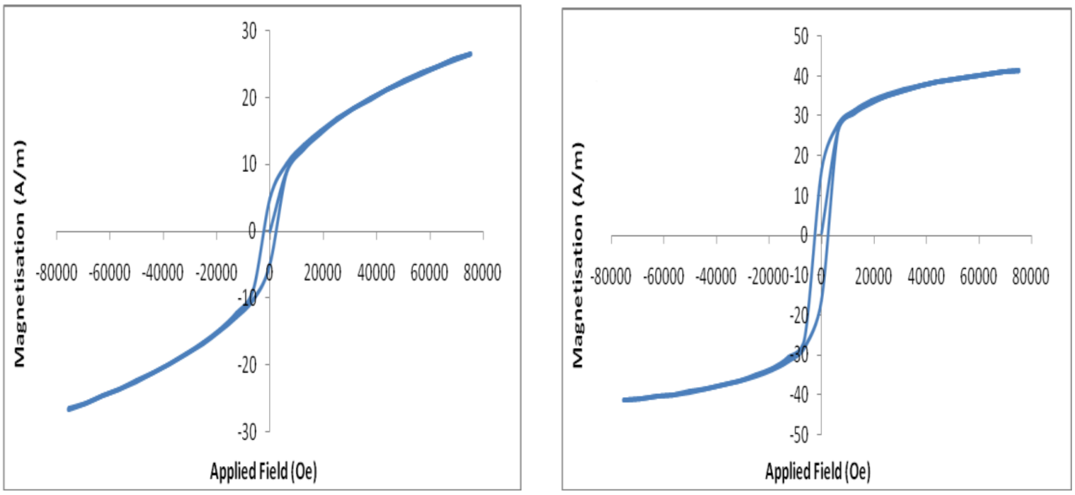
Fe-W-P films were tested for their Vickers hardness number are shown in Table 2. High concentration of urea in the bath B had higher hardness due to high stress present in the film. Adhesion of the film with the substrate was found to be good, it was observed from the scratch test.

3.5. Elemental analysis

Table 2 represents the results of EDAX. It was observed that the bath A with 5.0 g 1^{-1} urea had below 3% of phosphorous element than the bath B with 5.0 g 1^{-1} urea. In the higher phosphorous content of the films showed high magnetic properties. It was due to the addition of urea in the bath, which was improved the crystalline structure of Fe-W-P films.

3.6. Magnetic studies

The VSM images of Fe-W-P electrodeposited thin films obtained from the baths A and B contained 5.0 g 1^{-1} urea are shown in Fig. 3. On increasing the urea from 0 to 5 g l^{-1}, at bath B the coercivity increased from 1819 Oe to 2421 Oe however in bath A the coercivity increased from 1744 Oe to 2272 Oe. The coercivity range of soft magnetic material is less than 10 Oe. The coercivity values of these films maintain more than 1700 Oe. Therefore the above observable fact confirms that the Fe-W-P deposits are hard magnetic in nature. The magnetic properties of the film were enhanced due to increase in urea. The electrodeposited films were uniform and bright. With the increase in urea there was significant improvement in the thickness as well as magnetic properties of the film as shown in Table 1. Under the best conditions, at bath B with 5.0 g 1^{-1} urea the thickness of the film was found to be 5.3 µm with coercive and remanent values about 2421 Oe and 16.224 A/m respectively.



(i)

(ii)

Fig. 3. VSM images of Fe-W-P films electrodeposited with 5.0 g 1^{-1} urea i) NaH_2PO_2 ii) H_3PO_3

4. Conclusions

The Fe-W-P thin film from bath B with 5.0 g 1^{-1} urea having good hard magnetic properties than the Fe-W-P thin film from bath A with 5.0 g 1^{-1}urea. When the urea was increased the stress of the deposited thin film also increased. Higher hardness achieved from the film contained bath B at 5.0 g 1^{-1} urea. These films have good adhesion with the substrate and their crystalline sizes were in nano scale. High coercivity, remanent and Squareness values were observed as 2421 Oe, 16.224 A/m and 0.39 respectively at bath B with 5.0 g 1^{-1} urea. This Fe-W-P thin film from bath B with 5.0 g 1^{-1} urea has enhanced magnetic, structural and mechanical properties which can be used in magnetic data storage, MEMS and NEMS devices.

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