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EFFECT OF PHOSPHOROUS ACID AND UREA ON THE FERROUS TUNGSTEN PHOSPHOROUS MAGNETIC THIN FILM

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The properties of hard magnetic Ferrous Tungsten Phosphorous (Fe-W-P) films electrodeposited in the presence of urea as additive and phosphorous as precursor with varying concentrations were studied for different current densities in order to get different thickness and uniform deposits. The magnetic saturation (M_s), retentivity (M_r) and coercivity (H_c) of the films were studied using vibrating sample magnetometer. Magnetic properties of the deposited films were increased with the increase of organic additive and phosphorous. 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 using scanning electron microscope (SEM). The magnetic properties and structural characteristics of the thin films deposited under various experimental conditions are discussed. Hardness and adhesion of the deposited thin films were also studied.

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Keywords: Electrodeposition, Fe-W-P, EDAX, SEM, XRD, Hardness

1 Introduction

The electrodeposition technique has become the dominant manufacturing technology in all new applications such as micro electromechanical system (MEMS) devices, nano electromechanical system (NEMS) devices, magnetic recording head and data storage media [1]. Ferromagnetic materials like Fe, Co and Ni play a vital role in the magnetic data storage. 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 P promotes the formation of the fully amorphous structure of Fe-based alloys and maintains high corrosion resistance [2]. There are also some literary reports in the electrodeposition of Ni-Fe-W-P [3], Co-W-P [4] and Co-W [5] films.

In the present study, we investigated in detail that the effects of various concentration of phosphorous and urea on the magnetic and structural properties of electrodeposited Fe-W-P thin film.

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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. A d.c current for electrodepostion has passed from a 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 buffed 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.

Electrodeposition of Fe-W-P magnetic thin film was plated from a bath contained 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 and ammonium sulphate $(NH_4)_2SO_4$ 0.3 M, with this composition 0.1 and 0.2 M of Phosphorous acid (H_3PO_3) and 2.5 g l^{-1} and 5 g l^{-1} of urea were added to this bath and their effect on the properties of Fe-W-P films was investigated with different current density like 20 mA cm^{-2}, 25 mA cm^{-2} and 30 mA cm^{-2} and 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. These tests are widely used in the field of electroplating.

3 Results and Discussion

3.1 Thickness Study

Table 1 summarizes the effect of various concentration of phosphorous acid and urea on the thickness and magnetic properties of Fe-W-P films obtained under different experimental conditions. The thickness of the film was increased with increase in urea and phosphorous as well as increases in current density. The magnetic properties of the thin films were increased with the increase of thickness.

Table 1. Effect of the thickness and magnetic properties of Fe-W-P films electrodeposited for different current densities with 0.1 M and 0.2 M of H_3PO_3.

S. No.	Bath additive		Current density (mA cm^{-2})	Thickness of deposit (μm)	Magnetic saturation (A/m)	Remanent polarization (A/m)	Coercivity (Oe)	Squareness
	H_3PO_3 (M)	Urea (g/l)						
1	0.1	0	20	3.2	9.269	0.934	1401	0.10
2			25	3.4	10.656	1.211	1548	0.11
3			30	3.8	12.604	1.578	1754	0.13
4		2.5	20	3.4	11.541	1.385	2009	0.12
5			25	3.6	13.834	2.075	2142	0.15
6			30	3.9	15.692	2.933	2219	0.19
7		5	20	3.7	18.543	3.370	2164	0.18
8			25	4.2	20.468	4.707	2258	0.23
9			30	4.5	23.223	6.130	2336	0.26
10	0.2	0	20	4.2	11.564	1.865	1648	0.16
11			25	4.4	13.762	2.754	1720	0.20
12			30	4.8	15.829	3.634	1819	0.23
13		2.5	20	4.7	21.214	4.667	2100	0.22
14			25	4.8	27.539	7.711	2189	0.28
15			30	4.9	32.437	11.114	2242	0.34
16		5	20	4.8	30.380	9.418	2272	0.31
17			25	5.1	37.732	12.829	2396	0.34
18			30	5.3	41.453	16.224	2421	0.39

3.2 Surface analysis

3.2.1 Structural analysis

Electrodeposited Fe-W-P films were obtained from the baths maintained at 30 mA cm^{-2} current density in the absence of urea and the presence of urea with different concentration of phosphorous acid were subjected to XRD studies and are reported 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 [6] and Hexagonal structure with Fe_2P (312) plane [7] predominantly. The XRD peaks of thin film and metal were shifted due of the stress of the film [8]. Stress of the films were calculated from XRD data, using the formula,

$$\text{Young's modulus} = \text{Stress} / \text{Strain} \tag{1}$$

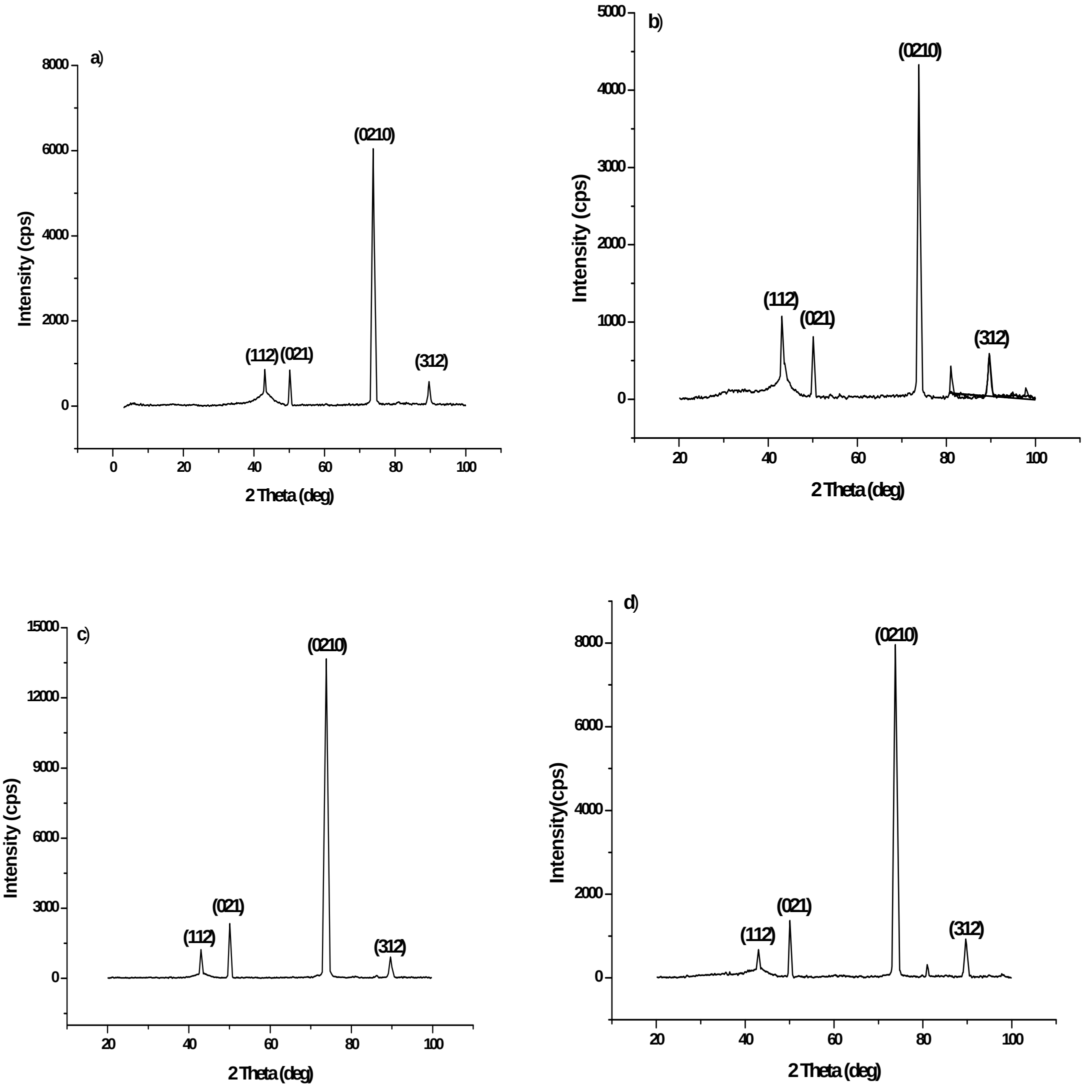

Fig.1. XRD images of Fe-W-P films electrodeposited at 30 mA cm^{-2} with 0.1 M H_3PO_3 (a) 2.5 gl^{-1} urea (b) 5.0 gl^{-1} urea and with 0.2 M H_3PO_3 (c) 2.5 gl^{-1} urea (d) 5.0 gl^{-1} urea

The results are shown in Table 2. Stress of the film was low when the bath was in lower concentration of urea. The stress of the film increased and crystalline sizes of the film decreased [9] when the concentration of urea is increased. Crystallite size of the deposits were calculated from XRD data using Debye-Scherrer formula

$$\text{Crystallite size} = 0.9\lambda/\beta \cos\theta \tag{2}$$

Crystallite sizes were obtained in the nano scale range.

3.2.2 Morphological observation

Electrodeposited Fe-W-P thin films were obtained from the baths maintained at 30 mA cm^{-2} current density in the absence of urea and the presence of urea with different concentration of phosphorous acid were subjected to SEM are reported 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 scans shown the crystalline sizes are decreased when the urea is increased which are accompanied with the XRD data reported in Table 2.

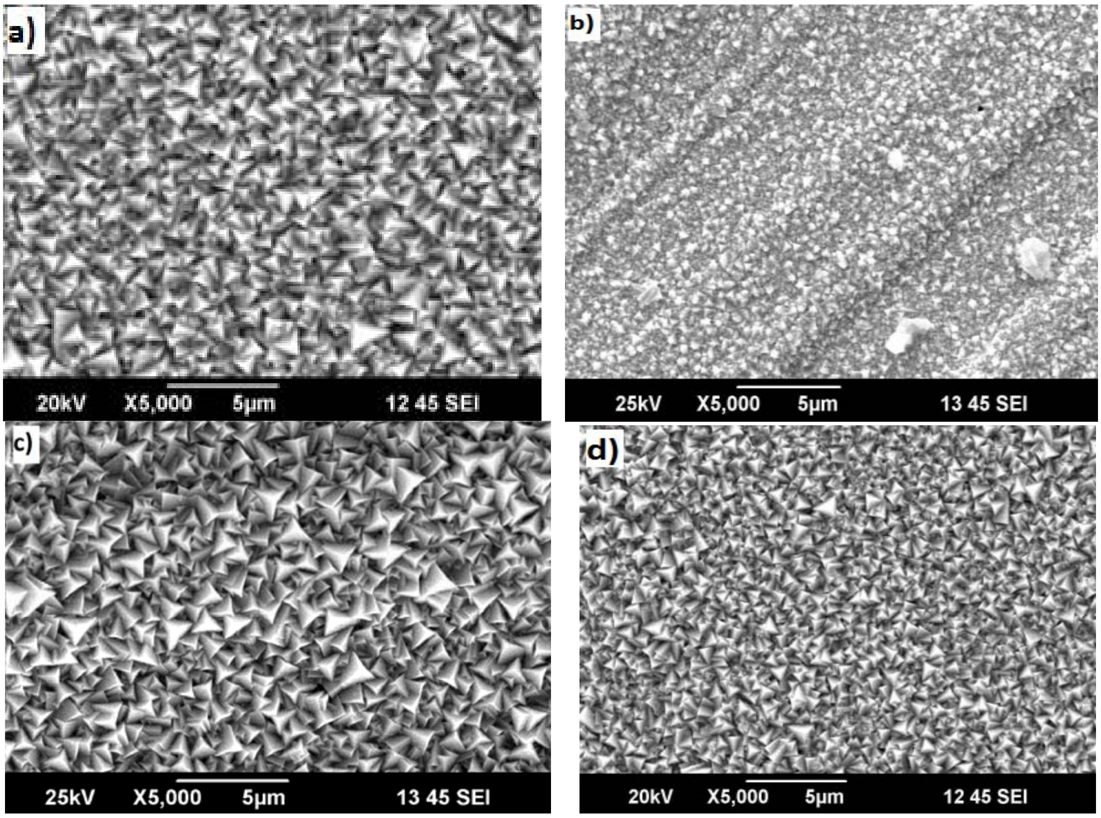

Fig.2. SEM images of Fe-W-P films electrodeposited at 30 mA cm^{-2} with 0.1 M H_3PO_3 (a) 2.5 gl^{-1}urea (b) 5.0 gl^{-1}urea and with 0.2 M H_3PO_3 (c) 2.5 gl^{-1}urea (d) 5.0 gl^{-1}urea

Table 2 - Crystalline size, hardness and composition of Fe-W-P films at 30 mA cm^{-2} current density.

H_3PO_3 (M)	Urea (g/l)	Crystalline size (nm)	Stress (MPa)	Vicker Hardness (VHN)	Film Composition (at %)		
					Fe	W	P
0.1	0	28.29	611	189	87.40	10.64	1.96
	2.5	27.84	621	197	88.96	8.82	2.22
	5	26.17	660	208	89.32	7.58	3.10
0.2	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

3.3 Mechanical Properties

Fe-W-P films, which were selected for XRD and SEM studies, were tested for their Vicker's hardness number. The results are shown in Table 1. Higher concentration of urea in the bath increased the hardness of the film. It was happened due to the stress present in the film. Adhesion of the film with the substrate was found to be good.

3.4 Elemental Analysis

Table 2 represents the results of EDAX. It was observed that all the films obtained from various baths had less than 4 % phosphorous. In the higher phosphorous acid content the films showed high magnetic properties. It was due to the addition of urea in the bath, which improved the crystalline structure of Fe-W-P films.

3.5 Magnetic Studies

The VSM images of Fe-W-P electrodeposited thin films obtained from the baths contained in the absence of urea and the presence of urea with different concentration of phosphorous acid are shown in Fig. 3. On increasing the urea from 0 to 5 g l^{-1} at 0.2 M H_3PO_3, the coercivity increased from 1819 Oe to 2421 Oe. The magnetic properties of the film are enhanced due to increase in urea. The electrodeposited films were uniform and bright. The morphology of the film was found to be poor when the absence of urea in the electrodeposition bath. The effect of phosphorous with urea was investigated. 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, 30 mA cm^{-2} current density with 0.2 M H_3PO_3 and 5.0 g l^{-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.

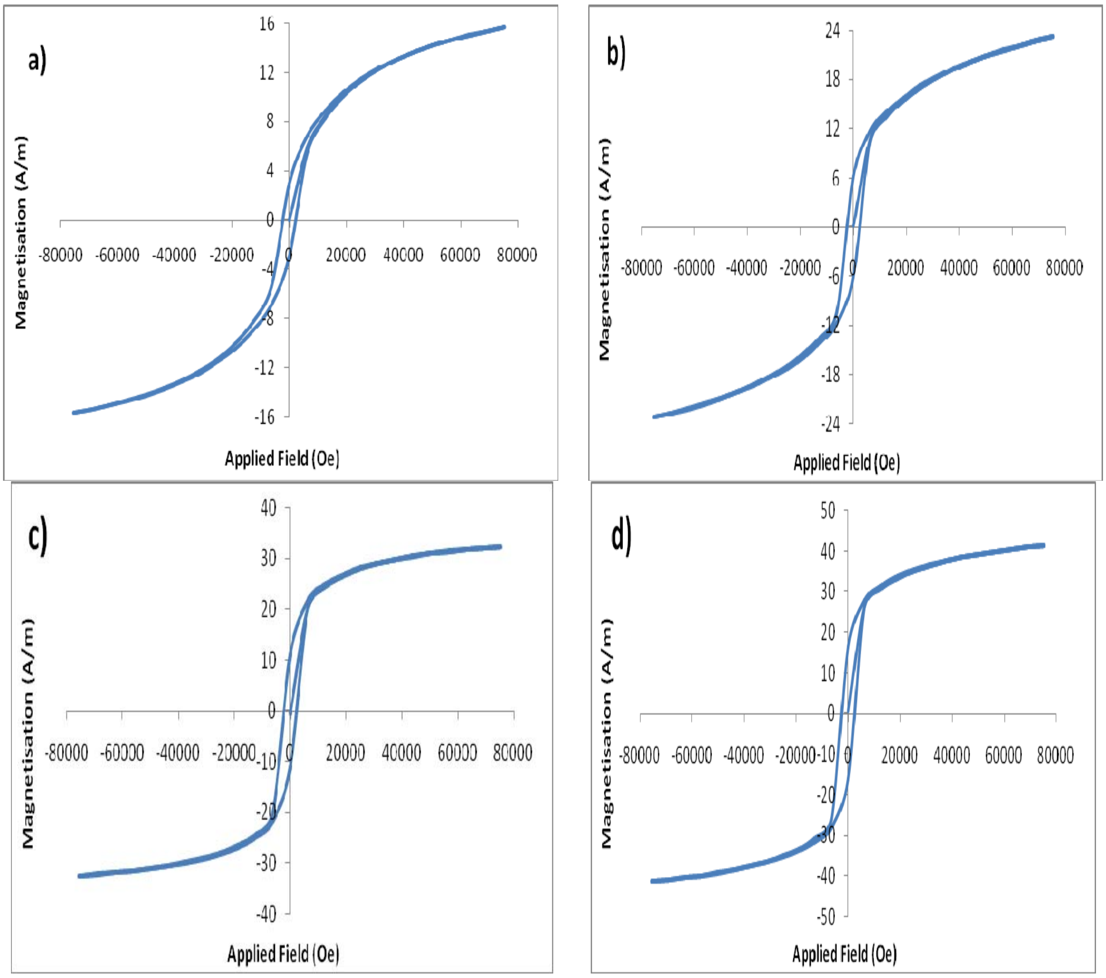

Fig.3- VSM images of Fe-W-P films electrodeposited at 30 mA cm^{-2} with 0.1 M H_3PO_3 (a) 2.5 gl^{-1}urea (b) 5.0 gl^{-1}urea and with 0.2 M H_3PO_3 (c) 2.5 gl^{-1}urea (d) 5.0 gl^{-1}urea

4. Conclusions

The Fe-W-P thin film having good hard magnetic properties can be electrodeposited from the higher concentration bath of urea. When the urea was increased the stress of the deposited thin film also increased, which is a cause for cracks in the thin film. Hardness of the film also increased at 5.0 g l^{-1}urea. Also these films have good adhesion with the substrate and their crystalline sizes are in nano scale. High coercivity, remanent and Squareness values achieved about 2421 Oe, 16.224 A/m and 0.39 respectively at 30 mA cm^{-2} current density with 0.2 M H_3PO_3 and 5.0 g l^{-1}urea. This Fe-W-P thin film has enhanced magnetic, structural and mechanical properties which can be used in MEMS devices and magnetic data storages.

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