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# Structural and Magnetic Properties of Ferrous Tungsten Phosphorous Thin Film

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**Abstract:** The magnetic films of Ferrous Tungsten Phosphorous (Fe-W-P) were prepared with urea as additive and phosphorous as precursors with varying concentrations were studied for different current densities. 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 out 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.
**Keywords:** Electrodeposition, Fe-W-P, EDAX, SEM, XRD, hardness.

## 1. Introduction

Ferromagnetic alloys based on iron group metals can be used for electronic components, transformers, memory devices etc.[1,2]. They possess high corrosion resistance and attractive magnetic parameters, such as high permeability, low hysteresis losses and other valuable technological properties. In ferromagnetic alloy plating, iron plating displays specific features of interest than Co and Ni such as (i) abundant availability of iron; (ii) welding of electrodeposited iron and plating of other metals on it with ease and (iii) superior drawing properties of iron in the soft state. The ferrous sulfate bath produces deposits that are smooth and normally light gray in color. An advantage is that it can be operated at room temperature.

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[3]. There are also some literary reports in the electrodeposition of Fe-W[4], Ni-Fe-W-P[5], Co-W-P[6] and Co-W[7] films.

In the present study, we investigated in detail the effects of various concentration of phosphorous 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.

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 sodium hypophosphate ($NaH_2PO_2.2H_2O$) 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 $cm^{-2}$. 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 indenter method. Adhesion of the films was tested by bend test and scratch test.

## 3. Result and Discussion

### 3.1. Thickness Study

**Table 1** summarizes the effect of various concentration of phosphorous 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.

### 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 for 45 minutes deposition time were subjected to XRD studies (Figure 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 Orthorhombic structure with $Fe_4P$ (021) plane[8] and Rhombohedral structure with $Fe_7W_6$ (0210) plane[9] predominantly. According to Noyan and Cohen[10], the XRD peaks of thin film and metal were shifted due to the stress of the film. Stress of the films were calculated from XRD data, using the formula,

Young's modulus = Stress / Strain (1)

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[11] when the concentration of urea was increased. Crystallite size of the deposits were calculated from XRD data using Debye-Scherrer formula

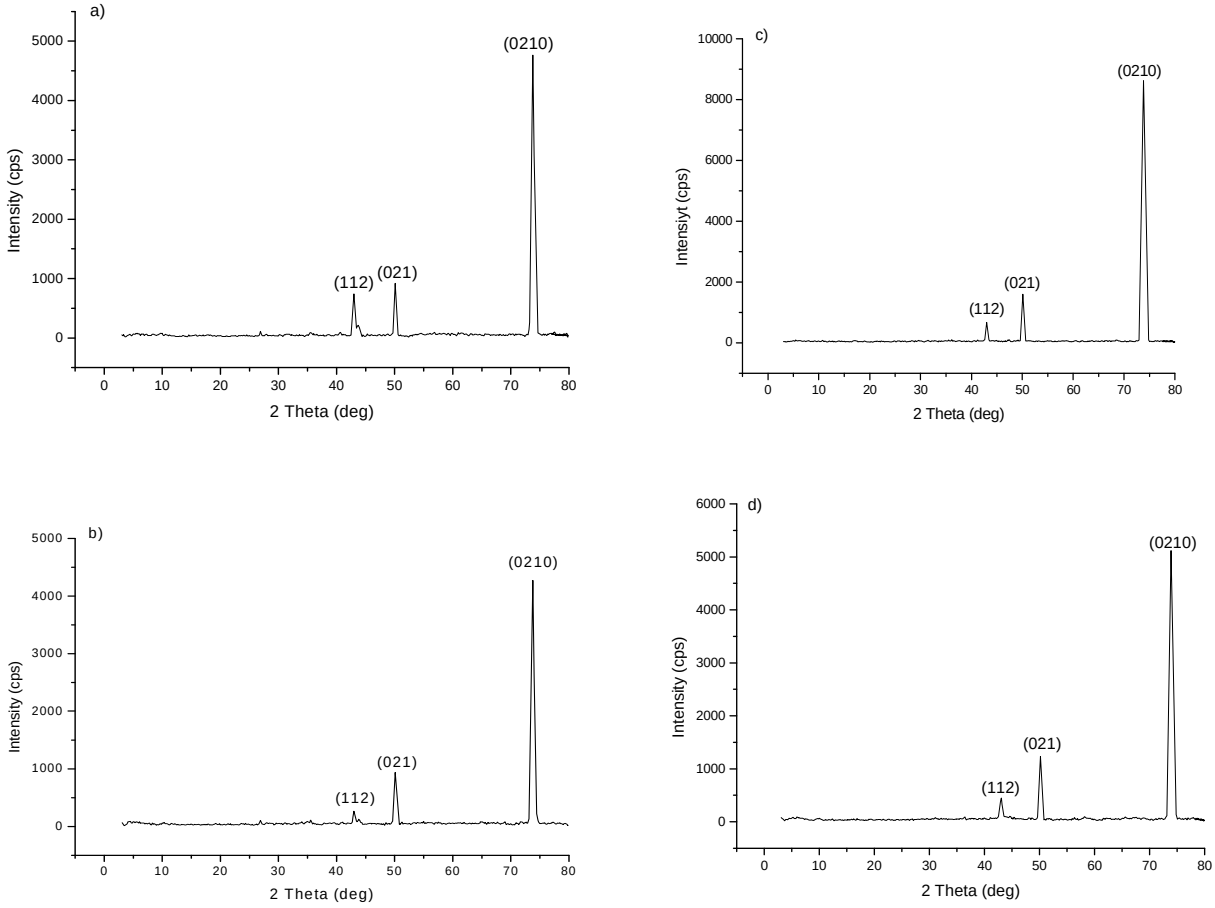
$$\text{Crystallite size} = 0.9\lambda/\beta \cos\theta \quad (2)$$

Crystallite sizes were obtained in the nano scale range.

**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 $NaH_2PO_2.2H_2O$ and different concentration of urea at 45 minutes deposition time.

| S. No. | Bath additive | | Current density (mA $cm^{-2}$) | Thickness of deposit (µm) | Magnetic saturation (A/m) | Remanent polarization (A/m) | Coercivity (Oe) | Squareness |
|---|---|---|---|---|---|---|---|---|
| | Phosphorous (M) | Urea (g/l) | | | | | | |
| 1 | 0.1 | 0 | 20 | 3.0 | 1.977 | 0.099 | 1184 | 0.05 |
| 2 | | | 25 | 3.2 | 2.011 | 0.121 | 1210 | 0.06 |
| 3 | | | 30 | 3.8 | 2.492 | 0.181 | 1275 | 0.07 |
| 4 | | 2.5 | 20 | 3.1 | 5.137 | 0.357 | 1278 | 0.06 |
| 5 | | | 25 | 3.2 | 6.318 | 0.412 | 1314 | 0.07 |
| 6 | | | 30 | 3.9 | 7.097 | 0.538 | 1400 | 0.08 |
| 7 | | 5 | 20 | 3.5 | 6.431 | 0.450 | 1438 | 0.07 |
| 8 | | | 25 | 3.7 | 7.194 | 0.647 | 1559 | 0.09 |
| 9 | | | 30 | 4.0 | 8.143 | 0.799 | 1655 | 0.10 |
| 10 | 0.2 | 0 | 20 | 3.8 | 7.431 | 0.446 | 1552 | 0.06 |
| 11 | | | 25 | 3.9 | 10.987 | 0.769 | 1659 | 0.07 |
| 12 | | | 30 | 4.3 | 12.197 | 0.923 | 1744 | 0.08 |
| 13 | | 2.5 | 20 | 3.9 | 19.596 | 1.764 | 1658 | 0.09 |
| 14 | | | 25 | 4.0 | 21.458 | 2.360 | 1775 | 0.11 |
| 15 | | | 30 | 4.4 | 25.154 | 3.153 | 1876 | 0.13 |
| 16 | | 5 | 20 | 4.0 | 22.433 | 3.141 | 1995 | 0.14 |
| 17 | | | 25 | 4.2 | 24.581 | 3.933 | 2008 | 0.16 |
| 18 | | | 30 | 4.8 | 26.612 | 4.919 | 2272 | 0.18 |

**Figure 1.** XRD images of Fe-W-P films electrodeposited for 45 minutes at 30 mA $cm^{-2}$ with 0.1 M $NaH_2PO_2.2H_2O$ (a) 2.5 g $1^{-1}$ urea (b) 5.0 g $1^{-1}$ urea and with 0.2 M $NaH_2PO_2.2H_2O$ (c) 2.5 g $1^{-1}$ urea (d) 5.0 g $1^{-1}$ urea




### 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 for 45 minutes deposition time were subjected to SEM (Figure 2). The crystallinity of Fe-W-P film mainly depends on the amount of urea and phosphorous which are present in the bath. The film with low concentration of urea shows a crevice pattern (Figures 2(a), 2(c)). The films obtained from a bath maintained at higher urea shows crack due to stress of the film (Figures 2(b) and 2(d)). The surface scans shown the grain sizes are decreased when the urea is increased.

### 3.3. Mechanical properties

Fe-W-P films were tested for their Vickers hardness number (Table 2). Higher concentration of urea in the bath increased the hardness of the film due to the stress present in the film, which caused small cracks in the structure. 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 3 % phosphorous. In the higher phosphorous 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.

**Figure 2.** SEM images of Fe-W-P films electrodeposited for 45 mins at 30 mA $cm^{-2}$ with 0.1 M $NaH_2PO_2.2H_2O$ (a) 2.5 $g1^{-1}$ urea (b) 5.0 $g1^{-1}$urea and with 0.2 M $NaH_2PO_2.2H_2O$ (c) 2.5 $g1^{-1}$ urea (d) 5.0 $g1^{-1}$urea

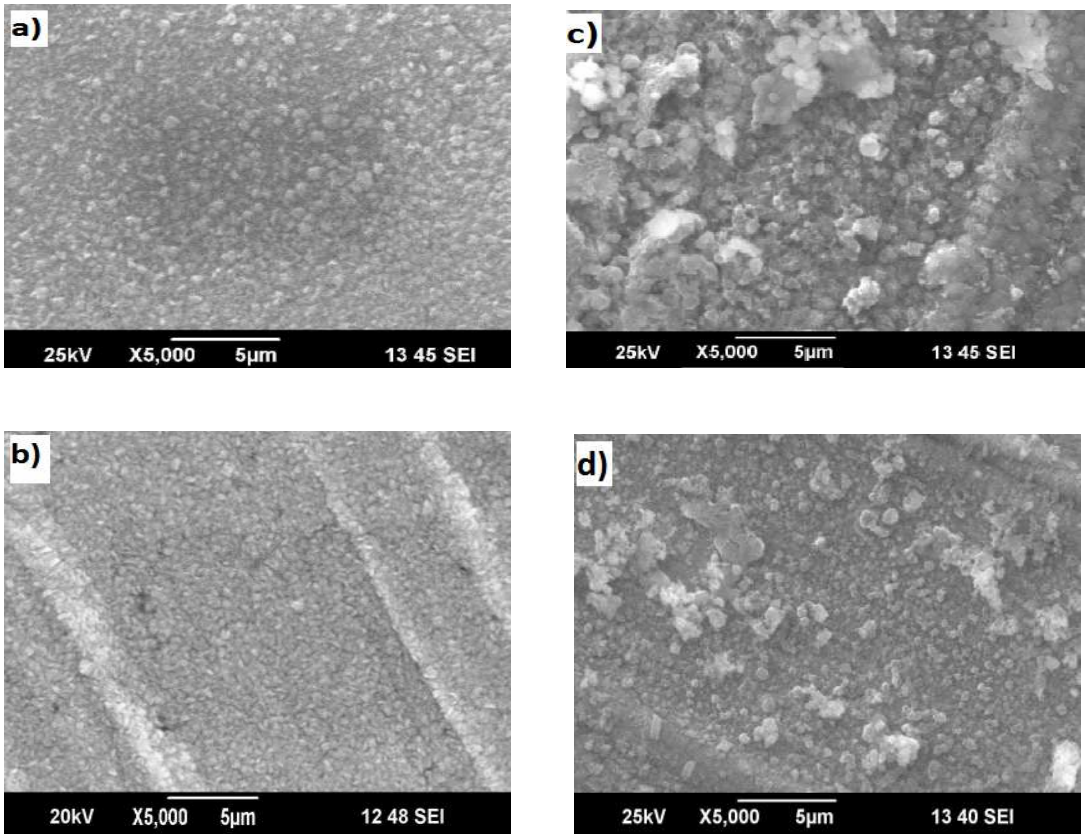



**Table 2.** Crystalline size, hardness and composition of Fe-W-P films at 30 mA $cm^{-2}$ current density for 45 minutes deposition time.

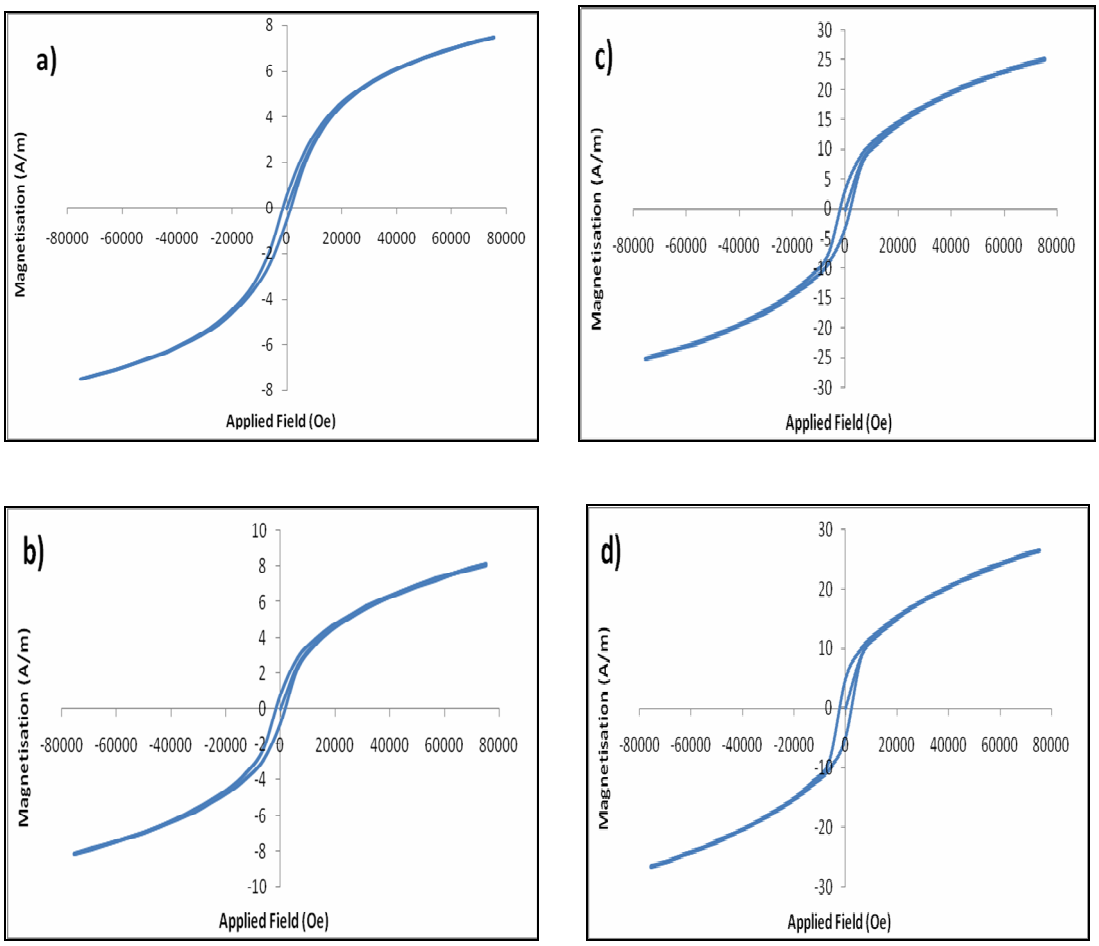
| Phosphorous (M) | Urea (g/l) | Crystalline size (nm) | Stress (MPa) | Vicker Hardness (VHN) | Film Composition (at %) | | |
|---|---|---|---|---|---|---|---|
| | | | | | Fe | W | P |
| 0.1 | 0 | 28.56 | 605 | 165 | 83.31 | 15.26 | 1.43 |
| | 2.5 | 27.66 | 624 | 171 | 84.51 | 13.49 | 2.00 |
| | 5 | 26.90 | 642 | 189 | 86.20 | 11.40 | 2.40 |
| 0.2 | 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 |

### 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 (Figure 3). On increasing the urea from 0 to 5 g $l^{-1}$ at 0.2 M $NaH_2PO_2.2H_2O$, the coercivity increased from 1744 Oe to 2272 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 and 45 minutes deposition time with 0.2 M $NaH_2PO_2.2H_2O$ and 5.0 g $1^{-1}$urea, the thickness of the film was found to be 4.8 µm with coercive and remanent values about 2272 Oe and 4.919 A/m respectively.

**Figure 3.** VSM images of Fe-W-P films electrodeposited for 45 minutes at 30 mA $cm^{-2}$ with 0.1 M $NaH_2PO_2.2H_2O$ (a) 2.5 g $1^{-1}$ urea (b) 5.0 g $1^{-1}$ urea and with 0.2 M $NaH_2PO_2.2H_2O$ (c) 2.5 g $1^{-1}$ urea (d) 5.0 g $1^{-1}$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 $1^{-1}$urea. Also these films have good adhesion with the substrate and their crystalline sizes are in nano scale. High coercivity, remanent and Squareness values were observed as 2272 Oe, 4.919 A/m and 0.18 respectively at 30 mA $cm^{-2}$ current density and 45 minutes deposition time with 0.2 M $NaH_2PO_2.2H_2O$ and 5.0 g $1^{-1}$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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