STRUCTURAL AND MAGNETIC PROPERTIES OF ELECTRODEPOSITED Ni-Fe-W THIN FILMS

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Thin films of Ni-Fe-W alloy have been deposited by electrodeposition technique on copper substrates with different concentration of diammonium citrate in the bath to investigate structural and magnetic properties of Ni-Fe-W compounds. The structural and surface morphology of the films were detected by using X-ray diffractogram (XRD) and Scanning Electron Microscope (SEM) respectively. The constituents in the films were determined by Energy Dispersive X-ray spectroscopy (EDAX) technique. The magnetic properties such as the coercivity H_c and saturation magnetization of the films were studied with the help of Vibrating Sample Magnetometer (VSM). The deposits are found to be smooth, nanocrystalline and with good adherence to the substrate. Increase in citrate concentration in the bath causes a decrease in Ni content and increase in W content of the films. Among the different compositions, $Ni_{61}Fe_{25}W_{14}$ compounds exhibit good soft magnetic properties and are suitable for read/write heads in hard disc, sensors and MEMS.

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1. Introduction

Mostly FeNiCo magnetic thin films have been analyzed, because of potential applications in computer read/write heads [1, 2] and also in microelectromechanical systems (MEMS). The thin films on the write heads are deposited mostly using electrodeposition technique. Electrodeposited Permalloy ($Ni_{80}Fe_{20}$) is the best known iron group thin films in computers and MEMS, because of its high magnetic saturation, low coercivity and low magnetization. The coercivity and permeability of these films are in the order of 1 to 5 Oe and 500 to1000 [3] respectively. Now the researchers show interest in electrodeposited alloys of W and Mo with iron group metals, because of their enhanced and specific magnetic, electrical, mechanical, thermal and corrosionless properties [4]. Very few research works [5, 6] are documented about the structural and composition of electrodeposited amorphous and crystalline iron group W alloys.

The electrodeposition conditions such as physical conditions (bath temperature, current density, deposition time) and chemical conditions (pH value, addition of complexing agent) determine the film microstructure (crystallite size, uniformity, and adherence) which in turn influence the physical and chemical properties of the films. The thin films of NiFeW prepared by Goltz [7] and Kharolamov [8] were porous and weak, since the concentration of relevant salts in ammonium salts, ammonium hydroxide and ions of the metals were limited by their solubility and the employed current densities were too high. Introduction of organic hydroxyl acids such as citrate, malate and tartrate into ammoniocal baths improve the faradic efficiency and solubility of the metal ions in the bath so that, hard and thin deposits of the alloy could be deposited at lower current densities. An organic hydroxyl acid together with NH_3 is a known complexing agent for the iron group metals. Tungsten alloy deposition can be developed in two ways based on the nickel iron pyrophosphates complexes [9] and citrate complexes [5]. We adapted the deposition based on citrate – ammonium electrolytes, since the wide range of W deposited composition obtained with high deposit hardness, fine texture and smooth surface morphology [10]. As far as the authors knowledge go, the magnetic properties of NiFeW thin films in diammonium citrate bath are not available. The effect of diammonium citrate on the properties of NiFeW deposits including elemental composition, magnetic properties, surface morphology and structure have been studied. This article summarizes the result of electrodeposition of NiFeW films deposited using diammonium citrate as complexing agent.

2. Experimental

2.1 Deposition of NiFeW thin films

Structural and magnetic properties of the thin films deposited on electrodeposition are decided by the concentration of the relevant salts and the parameters (pH, temperature, current density) of the chemical bath. NiFeW thin films were deposited using different concentrations of relevant salts and the conditions as shown in Table 2.1. All the reagent grade chemicals were dissolved in triply distilled water without any additive in order to keep the bath and system as simple as possible. Copper and stainless steel electrodes were degreased and slightly activated with 5% sulphuric acid (only for copper electrodes) and then rinsed with distilled water just before deposition. All the deposited films were inspected to have good properties (structure and magnetic properties) with the help of XRD, SEM and VSM. The optimal data of the chemical compositions and parameters are as shown in Table 1.

Table 1. Range of parameters and optimized data of bath compositions for NiFeW thin films depositions

S. No	Name of chemical and Parameters	Range mol/dm^3	Optimized data mol/dm^3
1	Nickel sulphate	0.1 – 0.4	0.2
2	Ferrous sulphate	0.05 – 0.15	0.1
3	Sodium tungstate	0.015 -0.075	0.03
4	Diammonium citrate	0.2 – 0.5	0.3
5	Citric acid	0.03	0.03
6	Boric acid	0.16	0.16
7	pH value	3 – 8	8
8	Temperature	30 -80 ^{o}C	75 ^{o}C
9	Current density	1 – 4 A/dm^2	1 A/dm^2

2.2 Determination of Composition and characterization of Ni-Fe-W alloy deposits

The composition of the film was determined using the EDAX analyzer attachment in JEOL 6390 scanning electron microscope and the surface morphologies of the films were observed with the SEM. The structural analysis of the films was carried out using a computer controlled Shimadzu X-ray diffractometer employing CuKα radiation. The scanning is carried out using θ - 2θ scan coupling mode, the rating being 30KV, 20mA. The particle size, lattice parameter, strain, lattice spacing and dislocation density values for the various films have been calculated using the following relations. The crystalline sizes (D) are calculated using the Scherrer's formula from the full width at half maximum (β) using the relation

$$D = \frac{0.94\lambda}{\beta \cos\theta} \tag{1}$$

The strain (ε) is calculated from the **β cosθ** vs **sinθ** plot using the relation

$$\beta = \frac{\lambda}{D \cos\theta} - \varepsilon \tan\theta \tag{2}$$

The dislocation density (δ) is evaluated from the relation

$$\delta = \frac{1}{D^2} \tag{3}$$

The lattice parameter (a) of the crystal is determined using the relation

$$\frac{\mathrm{Sin}^2\theta}{h^2 + k^2 + l^2} = \frac{\lambda^2}{4a^2} \tag{4}$$

Magnetic properties were studied using vibrating sample magnetometer. The magnetic flux density in the films are calculated in Tesla using the relation

$$B_s = \frac{4\pi M_S \rho}{m} \tag{5}$$

Where M_s is the saturation magnetization (emu), ρ is the density of the film (g/cc) and m is the mass of the film (g).

3. Results and discussion

3.1. Appearance and composition of the deposits

All the films deposited from the electroplating baths having different concentration of diammonium citrate, are smooth, uniform, adherent and gray in appearance. The compositions of thin films are obtained from the EDAX analysis (figure 1). The weight percentage and stochiometric formula of films deposited with different concentration of diammonium citrate are tabulated as shown in Table 2.

Table 2. Results of EDAX analysis

Film no	Citrate Concentration (mol/l)	Ni wt %	Fe wt %	W wt %	Stochiometric formula
1	0.2	67.5	25.5	7.0	$Ni_{30}Fe_{12}W$
2	0.3	61.2	24.5	14.3	$Ni_{14}Fe_6W$
3	0.4	61.3	24.5	14.2	$Ni_{14}Fe_6W$
4	0.5	54.5	27.3	18.2	Ni_9Fe_5W

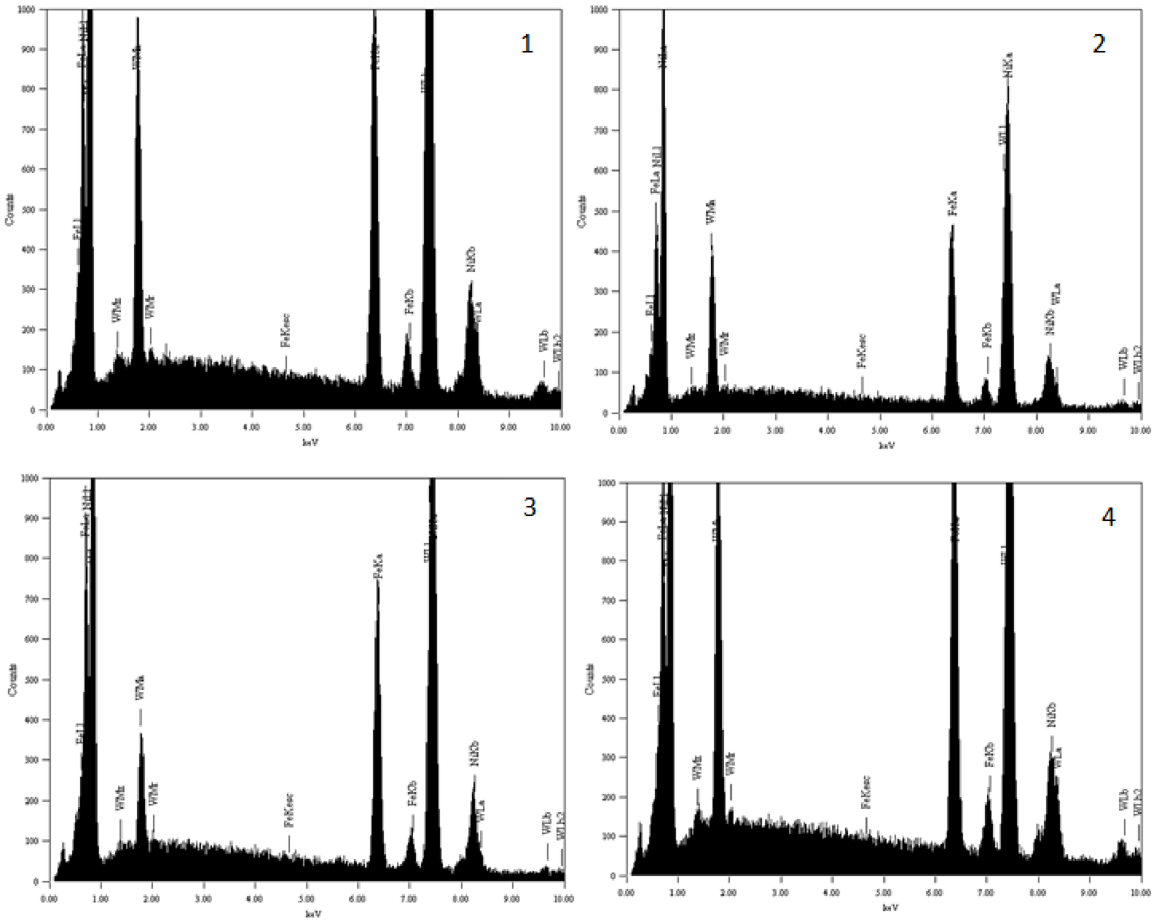

Fig. 1. EDAX spectrum for NiFeW thin film for various citrate concentrations
1) 0.2M 2) 0.3M 3) 0.4M 4) 0.5M

From the Table 3.1, it is observed that there is a decrease in Ni content and an increase in W content with the increase in citrate concentration from 0.2 to 0.5 M. However the iron content remains almost constant. At low citrate dosage, only W ions are complexed, as the dosage increases, the Ni and Fe ions are also complexed. Metals are more difficult to plate out from the complexed metal ions, due to high activation energies and low diffusivities to the cathode. It is usual to ignore the effect of ammonia on the composition of the films as it is a mild base which is used to adjust the pH of the solution.

3.2 Morphology of the deposits

The SEM micrographs of four representative thin films are shown in fig 2. The formation of thin films on the substrate is uniform in nature without any damage. The general serious drawback of the electrodeposition process is the generation of internal stresses resulting in the formation of micro cracks. But all the as plated thin films are crack free and grain boundaries can be seen among the crystal grains. Hence the films have low stress. From the figure 2, surface morphology is found to strongly depend on NiFeW film composition. That is NiFeW film crystallinity decreases with the increase in W content at higher citrate concentration.

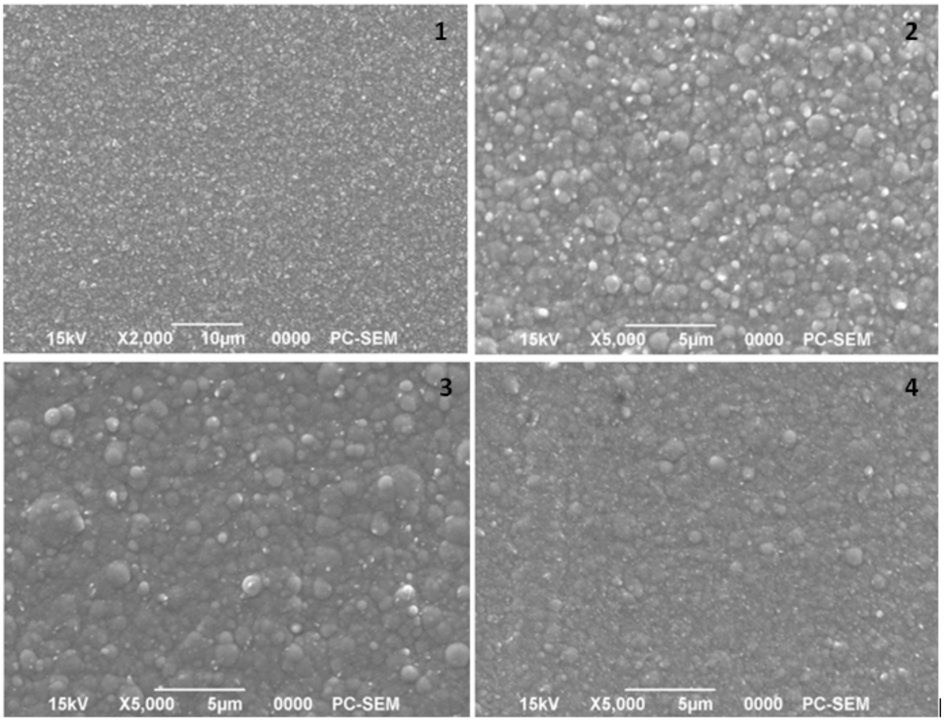

Fig. 2 SEM images of NiFeW thin films deposited using various citrate concentrations
1) 0.2M 2) 0.3M 3) 0.4M 4) 0.5M

3.3 X ray diffraction of the deposits

X-ray diffraction pattern for NiFeW thin films deposited using different concentration of diammonium citrate is shown in figure 3. The presence of sharp peaks in XRD pattern reveals that the films are crystalline in nature. The peaks corresponding to (111), (200) and (220) reflections were observed in all films. There is decrease in (111) peak intensity and increase in width of the XRD pattern with increase in W content in the film. All the films exhibited face centered cubic structure and the lattice parameter 'a' of each film was calculated using the relation (5) and the values are tabulated as shown in Table 3. The crystalline size decreases with increase in citrate concentration.

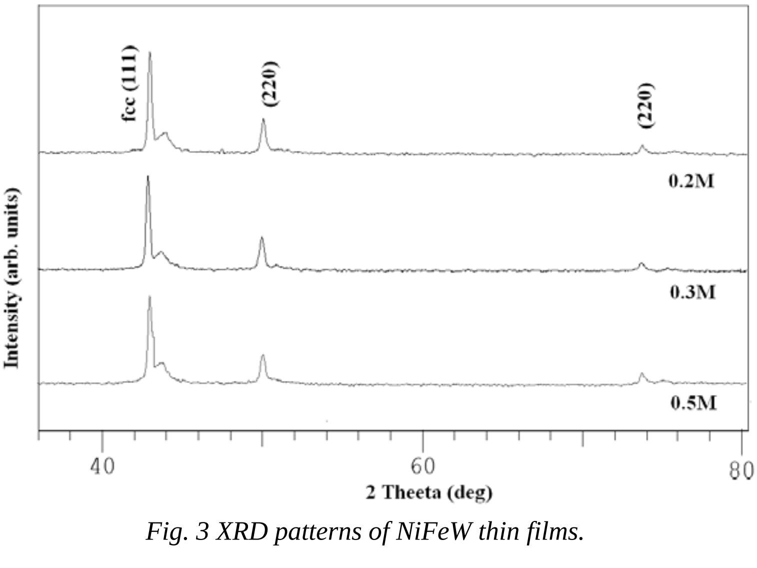

Fig. 3 XRD patterns of NiFeW thin films.

Table 3. Lattice parameters of NiFeW thin films

Film Composition	2θ (deg)	D (Å)	lattice parameter (Å)	crystal size (nm)	Strain 10^{-4}	Dislocation density ($10^{14}/m^2$)
$Ni_{30}Fe_{12}W$	42.91	2.100	3.646	38.7	5	6.67
$Ni_{14}Fe_6W$	43.02	2.092	3.636	27.5	7	13.22
Ni_9Fe_5W	43.19	2.076	3.625	24.6	10	16.52

The FCC nature and other data of the thin films are similar to the results of electrodeposited NiFe alloys [11], NiW alloys [12] and NiFeW alloys [13]. The absence of diffraction peaks with the results [11-13] shows that there is no formation of new phases and a structure similar to a solid solution of W and Fe in Ni is formed under these conditions. The'd' spacing of NiFeW thin films are larger than pure Ni. It may be due to the compressed space around W atoms and the stretched space around the Ni atoms in the films. Hence this results in lattice distortion and imperfections in the films.

3.4 Magnetic properties of the deposits

The soft magnetic properties of the electrodeposited Ni-Fe-W films have been observed via in plane magnetic hysteresis loop using VSM in magnetic fields up to 0.5T oscillating at a frequency of 75 Hz at room temperature and are tabulated in Table 3.3.

Table 3. Soft magnetic properties of Ni-Fe-W deposits

Citrate Concentration	W content Wt%	B_s Tesla	H_c Oe	S
0.2	7	1.304	6.645	0.059
0.3	14	0.992	8.216	0.154
0.4	14	0.936	9.639	0.156
0.5	18	0.595	10.856	0.177

As the citrate concentration increases, saturation magnetic flux density B_s decreases but coercivity increases (figure 4). The presence of tungsten, a non magnetic alloying element, affects the saturation magnetization by means of dilution mechanism. The linear decrease of B_s with the tungsten content in the deposit supports this mechanism.

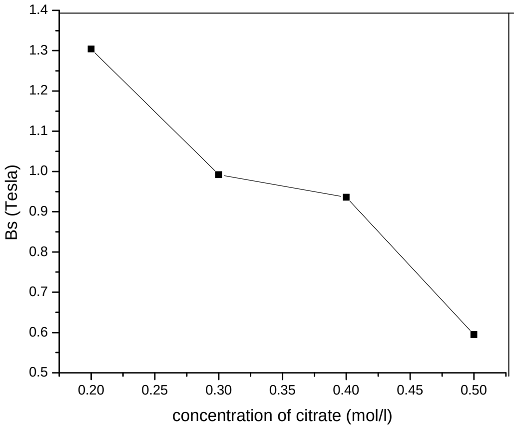

Fig. 4. Saturation flux density as a function of citrate concentration

The dependence of the saturation magnetization and coercivity on citrate concentration for Ni-Fe-W films is presented in figure 5. The coercivity has a minimum value for tungsten content around 7 wt%. The effect of film stress on H_c should be considered because soft magnetic properties of iron based films depend on film stress very sensitively [14] and the compressive stress lead to high H_c but the tensile stress reduced H_c. The XRD results show that (111) plane spacing of all deposited films up to 18 wt% tungsten is above 2.034 Å (that of pure nickel). This indicates that as tungsten content increases, the films may be under compressive stress and this leads to the increase in H_c.

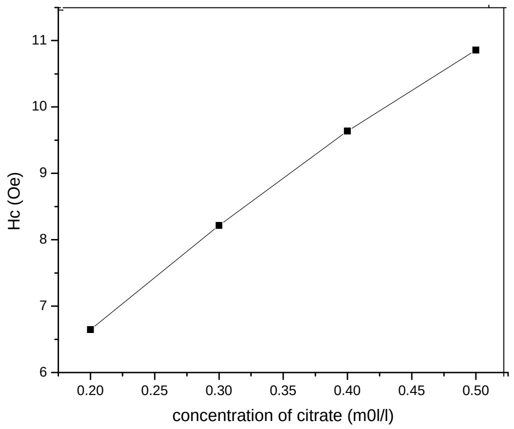

Fig. 5. Coercivity as a function of citrate concentration

The squareness value $S = M_r/M_s$ increases from 0.059 to 0.177 as the tungsten content increases. Magnetic hysteresis loops measured parallel to the film plane of the Ni-Fe-W films for various citrate concentrations are shown in figure 6. M-H curves obtained for 0.2M and 0.5M concentration are shown in figure 7. By analyzing the presented results it can be seen that the best soft magnetic properties have been obtained for the deposits electroplated from the bath containing low citrate concentration. The soft magnetic properties degrade as citrate concentration increases. Hence the diammonium citrate concentration of about 0.3M which is equal to the sum of the molar concentrations of nickel, iron, and tungsten ions is optimized to obtain high tungsten content and good soft magnetic Ni-Fe-W films.

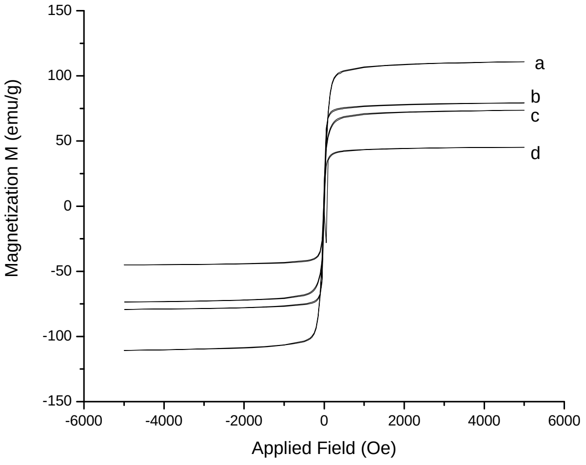

Fig. 6. Magnetic hysteresis loops for citrate concentration a) 0.2M b) 0.3M c) 0.4M d) 0.5M

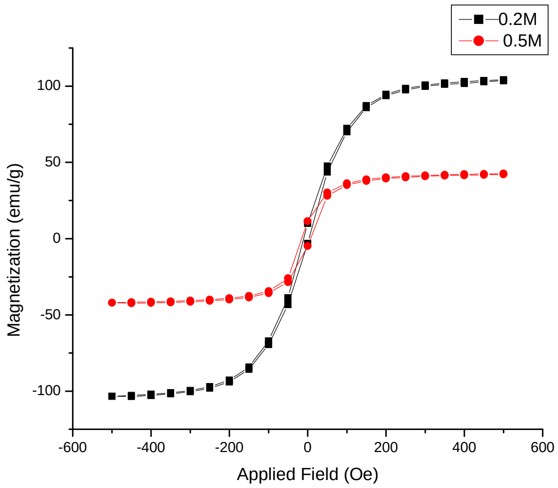

Fig. 7. M-H curve for 0.2M and 0.5M citrate concentration

4. Conclusions

Deposition of soft magnetic Ni-Fe-W alloy films from an ammoniacal citrate alkaline bath has been studied in an attempt to find the optimum conditions to obtain high tungsten content and better soft magnetic properties of the alloy. The effect of diammonium citrate on the tungsten content, structural, morphological and magnetic properties of Ni-Fe-W alloy films has been studied. The tungsten content in the deposit increases with increase in citrate concentration. SEM images showed low stress, crack free deposits which are granular in nature. The deposits are crystalline and the structure of the Ni-Fe-W films is that of highly deformed nickel. It is found that the concentration of diammonium citrate should be low to obtain nanocrystalline soft magnetic Ni-Fe-W electrodeposits with low coercivity and high saturation magnetization values. Deposit with 14 wt% tungsten electroplated from 0.3M citrate bath exhibits better soft magnetic properties of high saturation magnetic flux density $B_s = 0.99T$ and coercivity $H_c = 8$ Oe. These films can be used in various electronic devices including high density recording media.

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