EFFECT OF SODIUM TUNGSTATE ON THE PROPERTIES OF ELECTRODEPOSITED NANOCRYSTALLINE Ni-Fe-W FILMS

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Ni-Fe-W (Nickel-iron-tungsten) alloy thin films have been deposited by electrodeposition technique on copper substrates with different concentration of sodium tungstate in the bath to investigate the 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 B_s of the films were studied with the help of Vibrating Sample Magnetometer (VSM). The thickness of the films was measured by gravimetric technique. The deposits are found to be smooth, nanocrystalline and with good adherence to the substrate. Increase in tungstate concentration in the bath causes a decrease in Ni content and increase in W content of the films. All the films exhibit face centered cubic crystalline structure with the lattice parameter (a) nearly 3.64 Å. Among the different compositions, $Ni_{61}Fe_{25}W_{14}$ compounds exhibit good soft magnetic properties having magnetic flux density (B_s) 0.99 T and coercivity (H_c) 8 Oe, and are suitable for read/write heads in hard disc, sensors, MEMS and various electronic devices including high density recording media.

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1. Introduction

Electrodeposited alloys of iron group metals have been widely applied in industry, mainly as the materials for magnetic storage devices and electronics [1]. Mostly CoNiFe magnetic thin films have been analyzed, because of its potential applications in computer read/write heads [2,3] 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 magnetostriction. The coercivity and permeability of these films are in the order of 1 to 5 Oe and 500 to1000 [4] respectively. As iron is the most corrosion susceptible metal among the magnetic elements, corrosion is still a major issue in the development of a soft magnet with good chemical stability and high B_s. 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 [5]. Tungsten is a good additive candidate as it is highly corrosion resistant metal and also bears high mechanical strength. Very few research works [6-10] 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. This article summarizes the result of electrodeposition of Ni-Fe-W films deposited using sodium tungstate as the source of tungsten.

The effect of sodium tungstate on the properties of Ni-Fe-W deposits including elemental composition, magnetic properties, surface morphology and structure have been studied. We adapted the deposition based on ammonium citrate electrolytes, since the wide range of W deposited composition obtained with high deposit hardness, fine texture and smooth surface morphology [11]. As far as the authors knowledge go, the magnetic properties of Ni-Fe-W thin films in diammonium citrate bath are not available.

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. Ni-Fe-W 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 2.1. The thicknesses of the films were determined by gravimetric method with the help of single pan balance (Metler model having 0.00001g least count).

Table 2.1 Range of parameters and optimized data of bath compositions for NiFeW thin films depositions

S. No	Name of chemical and Parameters	Range g/l	Optimized data g/l
1	Nickel sulphate	30 - 120	60
2	Ferrous sulphate	15 - 60	30
3	Sodium tungstate	5 - 30	10
4	Diammonium citrate	30 - 110	70
5	Citric acid	5.5	5.5
6	Boric acid	10	10
7	pH value	3 – 8	8
8	Temperature	30 – 80 ^oC	75 ^oC
9	Current density	1 – 4 A/dm^2	1 A/dm^2

2.2 Determination of composition and characterization of NiFeW alloy deposits

The composition of the film was determined using the EDAX analyzer attachment in (JEOL 6390 model) Scanning Electron Microscope (SEM) 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 CuK_α 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

$$D = \frac{0.94\lambda}{\beta \cos\theta} \quad (1)$$

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

$$\beta = \frac{\lambda}{D \cos\theta} - \varepsilon \tan\theta \quad (2)$$

The dislocation density (δ) is evaluated from the relation

$$\delta = \frac{1}{D^2} \quad (3)$$

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

$$\frac{\text{Sin}^2\theta}{h^2 + k^2 + l^2} = \frac{\lambda^2}{4a^2} \quad (4)$$

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

$$B_s = \frac{4\pi M_S \rho}{m} \quad (5)$$

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

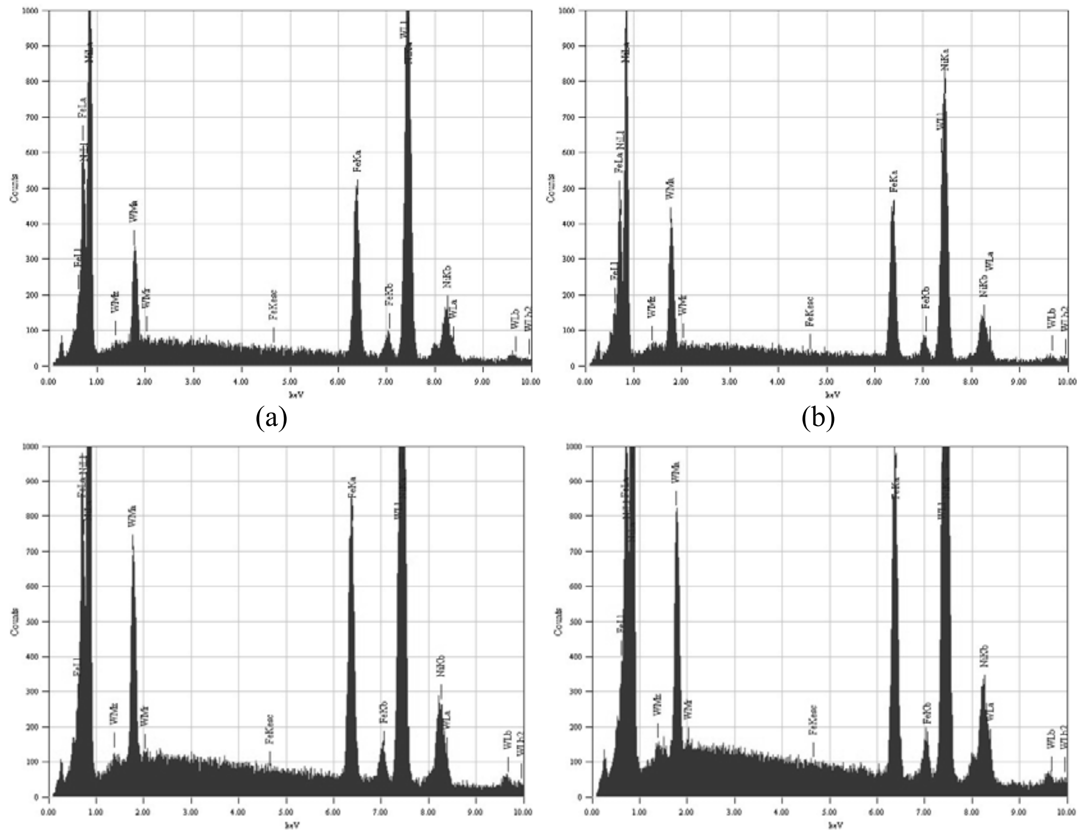
3.1. Appearance and composition of the deposits

All the films deposited from the electroplating baths having different concentration of sodium tungstate, are smooth, uniform, adherent and gray in appearance. The compositions of thin films are obtained from the EDAX analysis (fig 1). The weight percentage and stochiometric formula of films deposited with different concentration of sodium tungstate are tabulated as shown in Table 3.1.

Table 3.1 Results of EDAX analysis

Film no	Tungstate Concentration (g/l)	Ni wt %	Fe wt %	W wt %	Stochiometric formula
1	5.0	68.5	22.5	9.0	$Ni_{24}Fe_8W$
2	10.0	61.2	24.5	14.3	$Ni_{14}Fe_6W$
3	20.0	65.8	22.4	11.8	$Ni_{18}Fe_6W$
4	30.0	66.0	22.0	12.0	$Ni_{17}Fe_6W$

From the Table 3.1, it is observed that the tungsten content increases in conjunction with a decrease of nickel content with the increase in tungstate concentration from 5-30 g/l. However the iron content remains almost constant for all the films. At low tungstate 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. The highest tungsten content of 14 wt% is obtained at 10 g/l concentration of tungstate in the bath. 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.

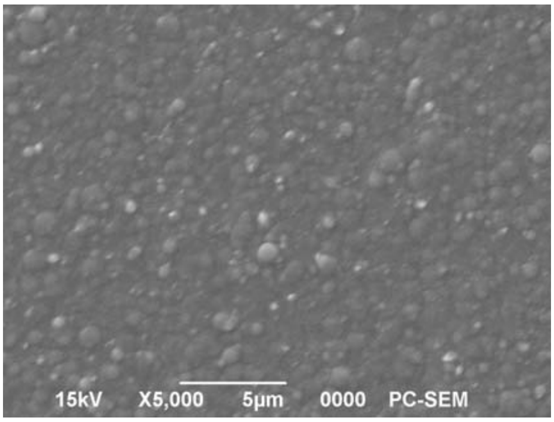


(a) (b) (c) (d)

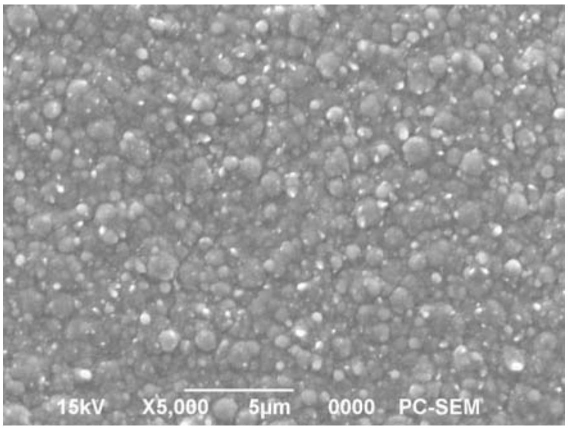
Fig 1. EDAX spectrum for Ni-Fe-W thin film for various tungstate concentrations
a) 5g/l b) 10g/l c) 20g/l d) 30g/l

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 fig 2, surface morphology is found to be strongly depending on Ni-Fe-W film composition. That is Ni-Fe-W film crystallinity decreases with the increase in W content at higher tungstate concentration. The thicknesses of the films measured with SEM instrument are around 500 nm which is equal to the data from the gravimetric technique.



(a)



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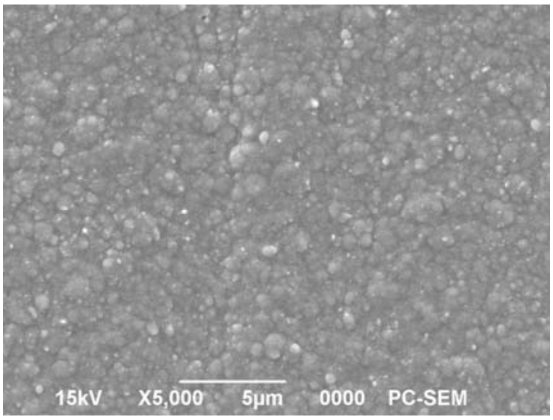

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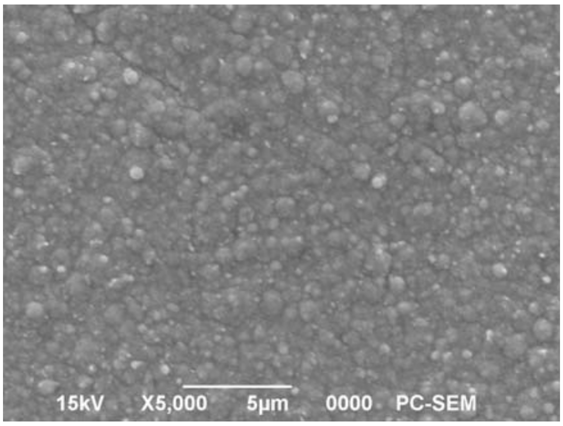

(d)

Fig 2. SEM images of Ni-Fe-W thin films deposited using various tungstate concentrations a) 5 g/l b) 10 g/l c) 20 g/ d) 30 g/l

3.3 X ray diffraction of the deposits

X-ray diffraction pattern for Ni-Fe-W thin films deposited using different concentration of sodium tungstate 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. All the films exhibited face centered cubic structure and the lattice parameter ‘a’ of each film was calculated using the relation (4) and the values are tabulated as shown in Table 3.2. The crystallite size increases with increase in tungstate concentration in the bath.

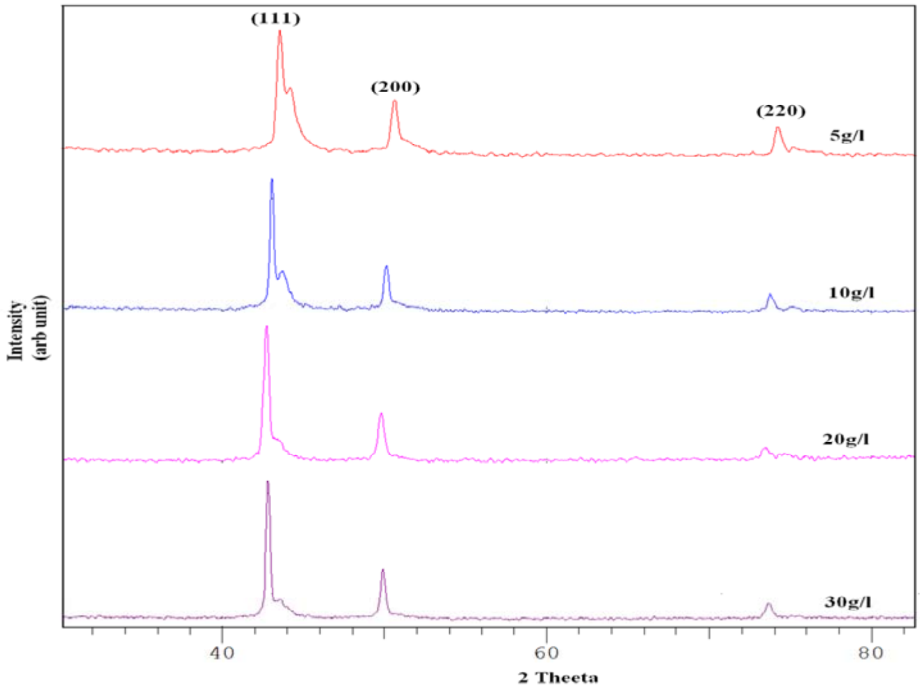

Fig 3. XRD patterns of Ni-Fe-W thin films.

Table 3.2 Lattice parameters of Ni-Fe-W thin films

Film Composition	2θ (deg)	d (Å)	lattice parameter a (Å)	crystal size D (nm)	Strain 10^{-4}	Dislocation density ($10^{14}/m^2$)
$Ni_{24}Fe_8W$	43.53	2.077	3.584	18.7	13	28.59
$Ni_{14}Fe_6W$	43.02	2.100	3.636	27.5	07	13.22
$Ni_{18}Fe_6W$	42.67	2.117	3.657	22.7	11	19.41
$Ni_{17}Fe_6W$	42.78	2.111	3.648	32.1	08	9.68

The FCC nature and other data of the thin films are similar to the results of electrodeposited NiFe alloys [12], NiW alloys [13] and Ni-Fe-W alloys [14]. The absence of new diffraction peaks with the results [12-14] 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 lattice spacing of Ni-Fe-W thin films is larger than pure Nickel (2.034Å). 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 3.3 Soft magnetic properties of NiFeW deposits

Tungstate Concentration (g/l)	W content (Wt %)	B_s (Tesla)	H_c (Oe)	S
5.0	9.0	1.286	10.207	0.138
10.0	14.3	0.992	8.216	0.154
20.0	11.8	1.122	6.995	0.101
30.0	12.0	1.152	6.045	0.103

As the tungstate concentration increases, saturation magnetic flux density B_s decreases and then increases (Fig 4a). 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 4b).

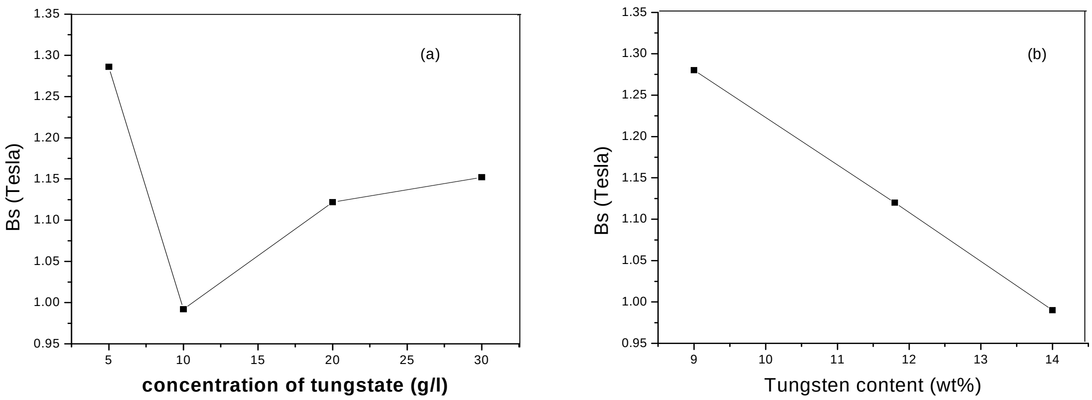

Fig 4. Saturation magnetic flux density as a function of (a) tungstate concentration and (b) tungsten content of the film

The dependence of the coercivity on tungstate concentration for Ni-Fe-W films is presented in Fig 5. Low coercivity value obtained at high tungstate concentration may be due to decrease in strain and dislocation density of the Ni-Fe-W films. Decrease in H_c with increase in tungstate concentration is caused by relaxation of lattice distortion. 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 [15] and the compressive stress lead to high H_c but the tensile stress reduced H_c. This indicates that as tungstate concentration in the bath increases, the films may be under tensile stress and this leads to the decrease in coercivity H_c. The squareness value $S = M_r/M_s$ decreases from 0.138 to 0.101 as the tungstate concentration increases.

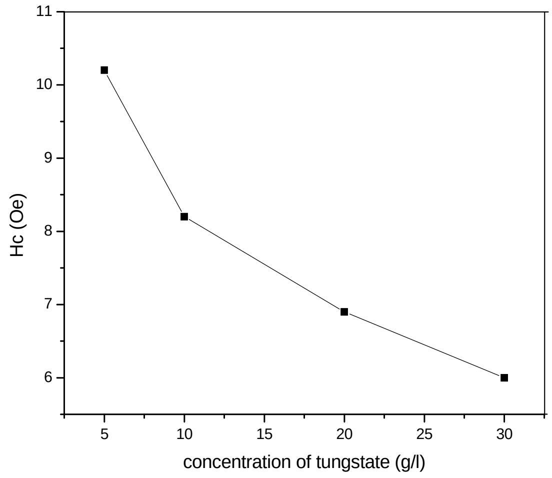

Fig 5. Coercivity as a function of tungstate concentration

Magnetic hysteresis loops measured parallel to the film plane of the Ni-Fe-W films for various tungstate concentrations are shown in figure 6. M-H curves obtained for 5g/l and 30g/l concentration of tungstate 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 high tungstate concentration. The corrosion resistance of tungsten alloys decreases with decrease in tungsten content in the alloy [16]. The sodium tungstate concentration of about 10 g/l in the citrate bath is optimized to obtain high tungsten content and good soft magnetic Ni-Fe-W films.

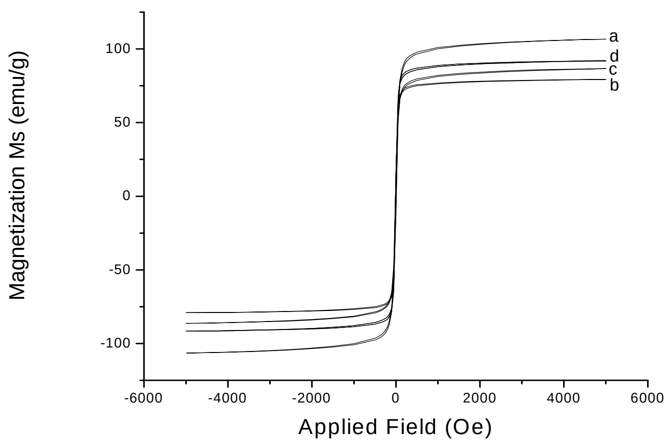

Fig 6. Magnetic hysteresis loops for tungstate concentration
a) 5 g/l b) 10 g/l c) 20 g/l d) 30 g/l

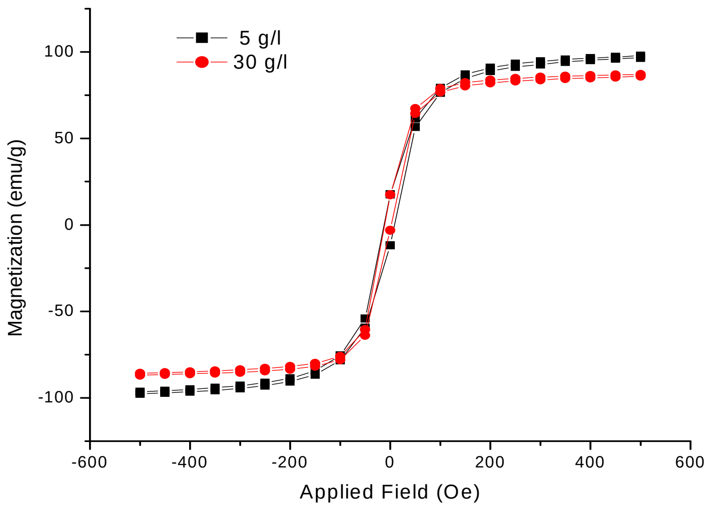

Fig 7. M-H curve for 5g/l and 30g/l tungstate concentration

4. Conclusion

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 sodium tungstate on the tungsten content, structural, morphological and magnetic properties of Ni-Fe-W alloy films has been studied. The tungsten content in the deposits increases and then levels off with increase in tungstate 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 nanocrystalline soft magnetic Ni-Fe-W electrodeposits with low coercivity and high saturation magnetization values was obtained at higher concentration of sodium tungstate ie.,30g/l in the electrolytic bath. However, high tungsten content $Ni_{61}Fe_{25}W_{14}$ film deposited at 10g/l tungstate concentration is the optimized material for read/write heads in hard disc, sensors, MEMS and various electronic devices.

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