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SYNTHESIS AND CHARACTERIZATION OF NANO CRYSTALIINE Ni-Fe-W-S THIN FILMS IN DIAMMONIUM CITRATE BATH

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Nano crystalline Ni-Fe-W-S alloy thin films were deposited by electro deposition method on copper substrate with different temperatures in diammonium citrate bath. The structural, chemical composition, surface morphology and magnetic properties of the electro deposited Ni-Fe-W-S thin films were studied. The chemical compositions of the films were carried out by using Energy Dispersive X-ray spectroscopy (EDAX). The structural and morphology of the films were detected by using X-ray diffractometer (XRD) and Scanning Electron Microscope (SEM) respectively. The Mechanical properties of the films were analyzed by using Vickers Hardness Test (VHN).The magnetic properties of the electro deposited Ni-Fe-W-S thin films were studied by using Vibrating Sample Magnetometer (VSM). The deposits of Ni-Fe-W-S thin films were found to be smooth, nano crystalline, adherence to the substrate. All the electro deposited films exhibit FCC crystalline structure with crystalline size in the order of nano scale. The films obtained from higher bath temperature were found to have higher value of Hardness. Ni-Fe-W-S alloy thin films prepared at high temperature (80˚C) were found to have higher magnetization value (M_s) and magnetic flux density (B_s). Electro deposited Ni-Fe-W-S thin films exhibit good soft magnetic properties and are suitable for various electronic devices including high density recording media, magnetic actuators, magnetic shielding, and high performance transformer cores.

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1. Introduction

Electrodeposited nanocrystalline magnetic thin films have been developed due to their potential applications in power electronics, sensors, actuators, core material for writing elements in recording heads [1]. Magnetic thin films must have good adhesion, low stress, corrosion resistance with great magnetic properties [2]. Electro deposited Permalloy ($Ni_{80}Fe_{20}$) is the best known thin film alloy in magnetic thin film recording heads and MEMS applications [3]. The Ni-Fe alloys are the most versatile from all the known soft magnetic materials for magnetic storage, Because of their highest saturation flux density, lower coercivity and lower magnetostriction [4]. Due to their soft magnetic properties, Fe-Ni alloys have been used in industrial applications. Typical examples of applications that are based on the soft magnetic properties include read-write heads magnetic actuators, magnetic shielding, and high performance transformer cores [5]. The Ni-Fe alloys with composition close to 80% Ni are very much used for producing the magnetic recording heads. By adding other elements to these alloys ($Ni_{80}Fe_{20}$), the properties of these alloys can also be altered.

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Now the researchers show interest in electrodeposited alloys of W, Cr and Mo with nickel-iron metals [6-8], because of their enhanced and specific magnetic, electrical, mechanical, thermal and corrosion less properties. W is a good candidate as it is highly corrosion resistant metal and also bears high mechanical strength. Very few research works are documented about the structural and composition of electrodeposited crystalline NiFeW alloys [9-10].

The Low stress thin film alloys with improved magnetic properties are very much used in magnetic recording heads and MEMS [11].The best known stress reducing agents for nickel based electrodeposition are sulfur containing organic additives (saccharin, thiourea, benzene sulfonic acid etc). The electro deposition conditions such as physical conditions (bath temperature, current density, deposition time) and chemical conditions (pH value, addition of complexing agent) determine the microstructure (crystallite size, uniformity, and adherence) which in turn influence the physical and chemical properties of the films. This article summarizes the result of electro deposition of Ni-Fe-W-S films deposited using Thiourea as the source of Sulphur in Diammonium Citrate bath [12]. The effects of Thiourea on the properties of Ni-Fe-W-S deposits including elemental composition, magnetic properties, surface morphology and structure have been studied. So far, the magnetic properties of Ni-Fe-W-S thin films in citrate bath are not analyzed.

2. Experimental part

2.1 Electro deposition of NiFeWS thin films

NiFeWS thin films were electrodeposited on Copper substrate using relavant salts in Diammonium Citrate bath at different temperatures. The chemical composition and operating conditions of the electroplating path are as shown in table 1. A copper substrate of size (1.5 × 7.5 cm) as cathode and pure stainless steel of same size as anode were used for electro deposition of NiFeWS thin films. An adhesive tape was used to mask off all the substrate except the area on which the deposition of films was desired. All the reagent grade chemicals were dissolved in triply distilled water. Copper and stainless steel electrodes were degreased and slightly activated with 5% sulphuric acid and then rinsed with distilled water just before deposition. The pH of Solution was adjusted to 8 by adding few drops of ammonia solution. The films were galvanostically deposited on copper substrate by applying a constant current of 75 mA (1 A/ dm^2) for a period of 30 minutes. The structure and morphology of the NiFeWS thin films were studied with the help of XRD and SEM. The magnetic properties were studied by using VSM. The film composition was measured by Energy-dispersive X-ray Spectroscopy (EDAX).Hardness of the film was measured by Vickers Hardness Test (VHN).The thicknesses of the films were determined by cross sectional view of SEM images.

Table 1. Composition and operating conditions of the electroplating bath

S.No	Name of the chemical parameters	Data g/l
1.	Nickel sulphate	60
2.	Ferrous sulphate	30
3.	Sodium tungstate	10
4.	Thiourea	7.5
5.	Diammonium citrate	70
6.	Citric acid	5.5
7.	Boric acid	10
8.	pH value	8
9.	Temperature	28,40,60,80(˚C)
10.	Current density	1 A/dm^2

2.2 Characterization of NiFeWS alloy thin films

The chemical composition of the film was determined by using the EDAX analyzer attached in (JEOL 6390 model) Scanning Electron Microscope (SEM). Surface morphological studies were carried out with Scanning Electron micrographs. The structural analyses of the films were carried out using a computer controlled Shimadzu X-ray diffractometer employing Cu K_α radiation. The scanning was carried out using θ-2θ scan coupling mode, the rating begins with 30 Kv, 20 mA.

The crystalline size (D) were calculated using the Scherrer's formula from the full width half maximum (β) using the relation.

$$D = \frac{0.94\ 5\lambda}{\beta\ cos\theta} \tag{1}$$

The strain (ε) was calculated from the relation

$$\varepsilon = \frac{\beta\ cos\theta}{4} \tag{2}$$

The dislocation density (δ) was evaluated from the relation.

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

Magnetic properties (Coercivity, Magnetization, and retentivity) were studied using Vibrating Sample Magnetometer.

The Magnetic Flux density in the films are calculated in Tesla using the relation

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

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.

The squareness (S) was calculated from the relation

$$S = \frac{M_r}{M_s} \tag{5}$$

Where M_r is the Retentivity

3. Results and discussion

3.1 Composition of the deposits

The electrodeposited NiFeWS alloy films were smooth, uniform, adherent. The composition of the NiFeWS film from diammonium citrate was obtained from the EDAX analysis shown in Figure 1.The weight percentages of the films deposited with different temperature are tabulated as shown in Table 2.

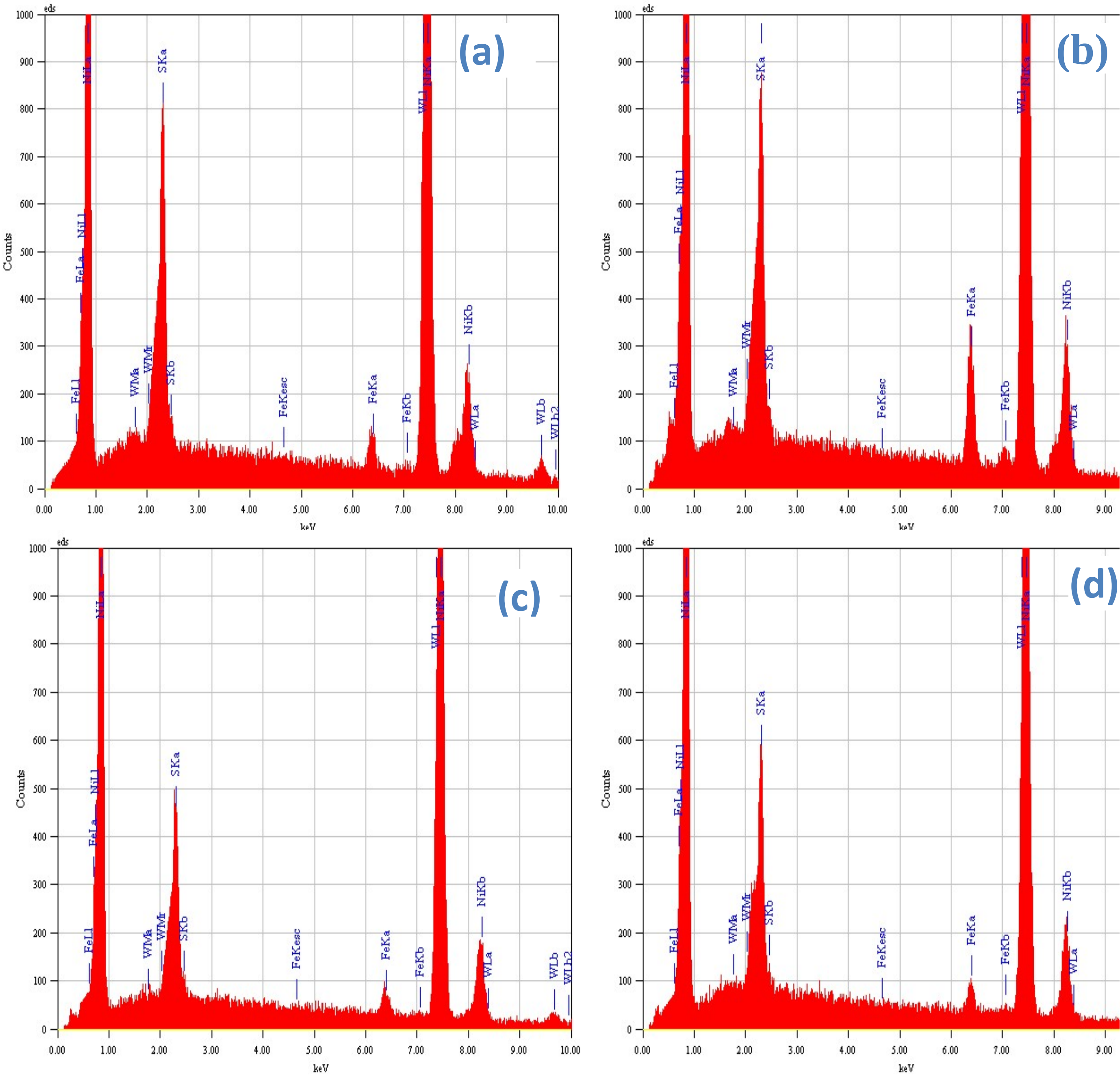


Fig. 1. EDAX Spectrum of Ni-Fe-W-S for different bath Temperatures (a) 28˚C (b) 40˚C (c) 60˚C (d) 80˚C

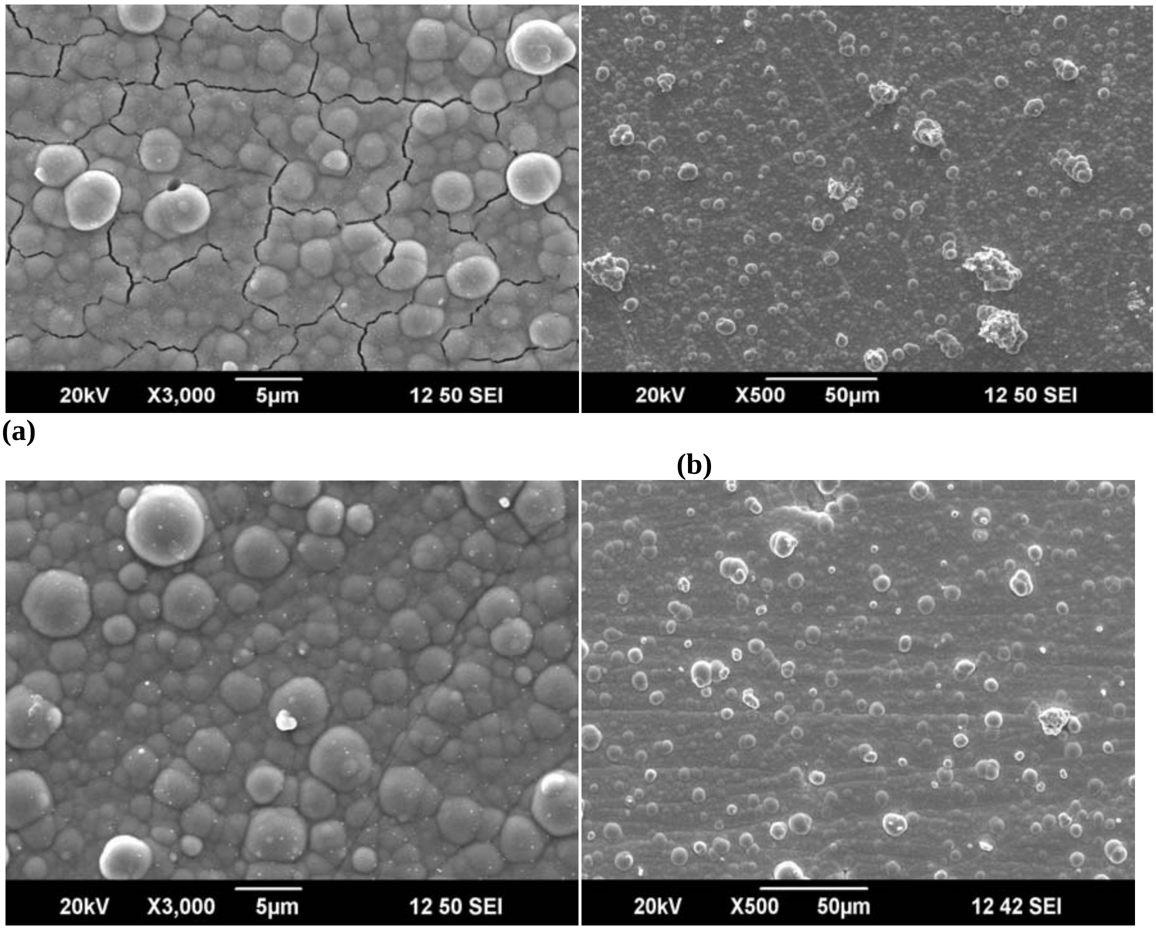
Table 2. Results of EDAX analysis

S.No	Temperature ˚C	Ni Wt%	Fe Wt%	W Wt%	S Wt%
1	28	89.15	3.07	0.43	7.35
2	40	85.81	8.02	0.70	5.45
3	60	90.03	4.50	0.5	4.97
4	80	90.76	4.43	0.73	4.06

EDAX result showed that the films obtained at higher temperature have low Sulphur content. So that the coercivity of films gets reduced and the magnetization values were increased. The lowest Sulphur content of 4.06wt% was obtained at temperature 80˚C in diammonium citrate 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.

3.2 Morphology of the deposits

The SEM images of electrodeposited NiFeWS thin films from diammonium citrate bath are shown in figure 2. The films obtained at low temperature have some micro cracks. This is due to the generation of internal stresses resulting in the formation of micro cracks. The film obtained from higher temperature (80˚c) of diammonium citrate bath having smaller crystallites and granular. The films obtained at higher temperature are crack free and grain boundaries can be seen among the crystal grains. This is due to uniform crystal orientation during electro deposition. Hence the film has low stress.



(a) **(b)**

(c) (d)

Fig. 2. SEM images for Electro deposited Ni-Fe-W-S thin film for different bath temperatures (a) 28˚C (b) 40˚C (c) 60˚C (d) 80˚C

3.3 X-ray diffraction of the deposits

Electrodeposited NiFeWS films from diammonium citrate bath were subjected to XRD studies. Films obtained from Diammonium Citrate bath at temperatures 28˚C, 40˚C, 60˚C and 80˚C were studied for their structural characteristics as shown in figure 3.

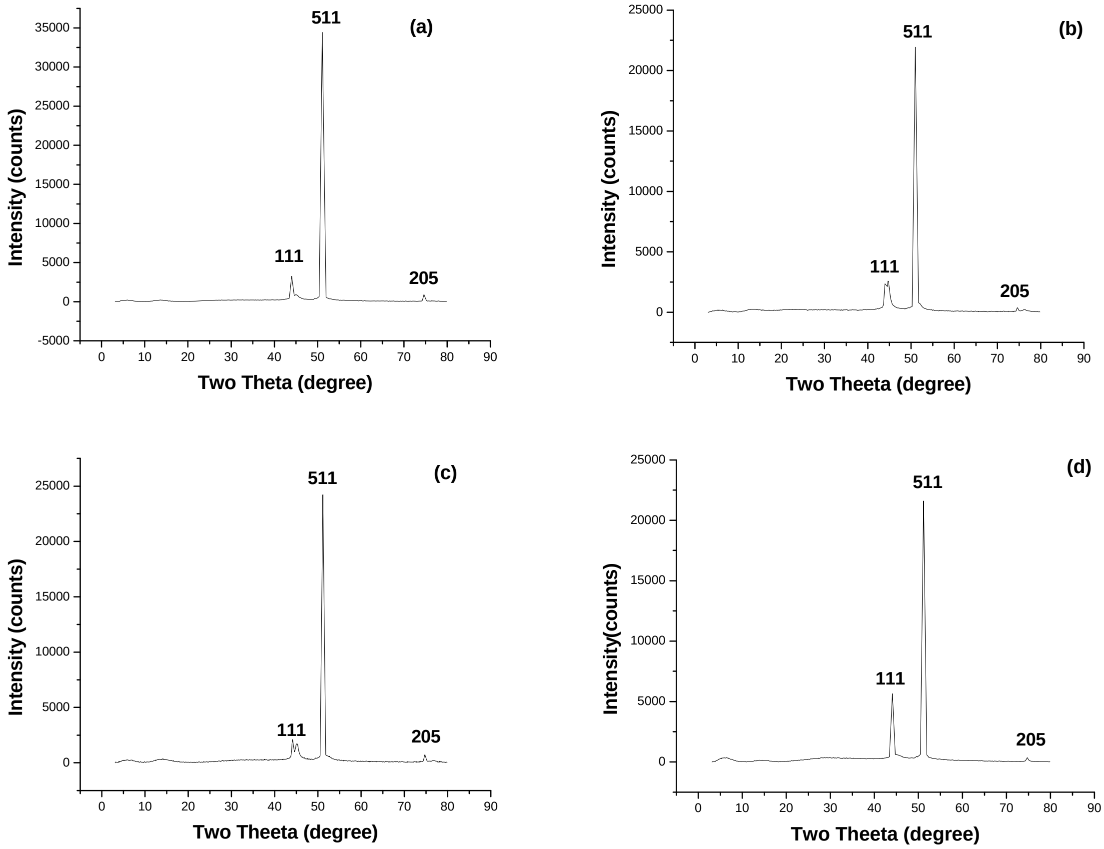


Fig. 3.XRD pattern for Electro deposited Ni-Fe-W-S thin film for different bath temperatures (a) 28˚C (b) 40˚C (c) 60˚C (d) 80˚C

The data obtained from the XRD pattern compared with the standard JCPDS data and were found to have simple cubic structure. The presence of sharp peaks in XRD pattern reveals that the films are crystalline in nature. The peaks corresponding to (111), (511) and (205) reflections were observed in all the films. The crystalline size decreases with increase in temperature of the bath. The crystal size of NiFeWS alloy films obtained from Diammonium Citrate bath are tabulated as shown in table 3. The dependence of crystalline size with diammonium citrate bath temperature is shown in figure4.

Table 3. Crystal size of NiFeWS alloy thin films

S.No	Bath Temperature ˚C	2 θ (deg)	d (A^0)	Lattice parameter a (A^0)	Crystalline size D nm	Strain 10^{-4}	Dislocation density(10^{14} / m^2)
1	28	51.03	1.7878	5.3645	33.99	10.705	8.6506
2	40	51.08	1.7888	5.3548	32.80	11.0951	9.2910
3	60	51.14	1.7844	5.3450	31.48	11.5614	10.0090
4	80	51.17	1.7843	5.3417	27.06	13.4470	13.6506

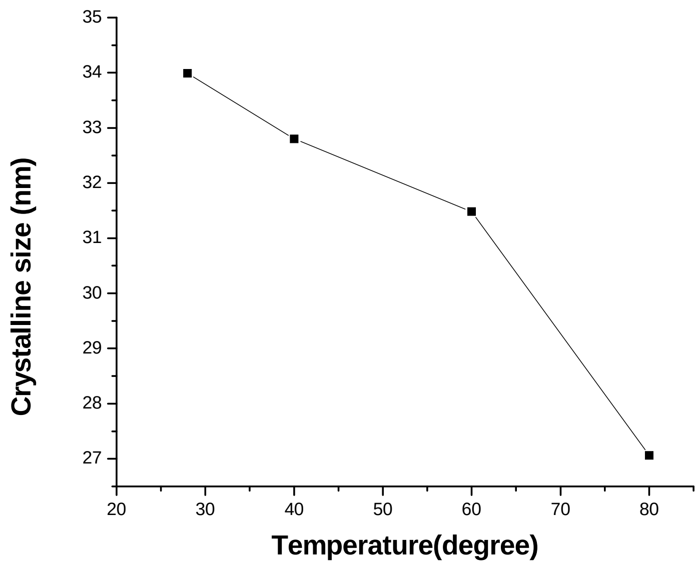


Fig. 4. Crystalline Size as a function of Bath temperature

Dislocation density is defined as the length of dislocation lines per unit volume of the crystal. It is found from table 3 the crystalline sizes are decrease while increasing the diammonium citrate bath temperature. It is also observed that dislocation density increases while increasing the diammonium citrate bath temperature. The variation in lattice spacing leading to the variation in crystallite size may be the responsible for change in dislocation density.

3.4 Mechanical Properties

Adhesion of the film with the substrate is tested by bend test and scratch test. It showed that the film is having good adhesion with the substrate. Hardness of the films was examined using a Vickers hardness tester by the diamond intender method. The results are tabulated and shown in table 4. The results show that the hardness increases with increasing bath temperature. This is may be due to lower stress associated with electrodeposited Ni-Fe-W-S film in diammonium citrate bath. The dependence of Vickers hardness and Bath temperature is shown fig 5.

Table 4. Mechanical Properties of Electro deposited Ni-Fe-W-S thin film

S.No	Bath Temperature (˚C)	Crystalline size D nm	Vickers Hardness (VH)
1	28	33.99	126
2	40	32.80	147
3	60	31.48	163
4	80	27.06	225

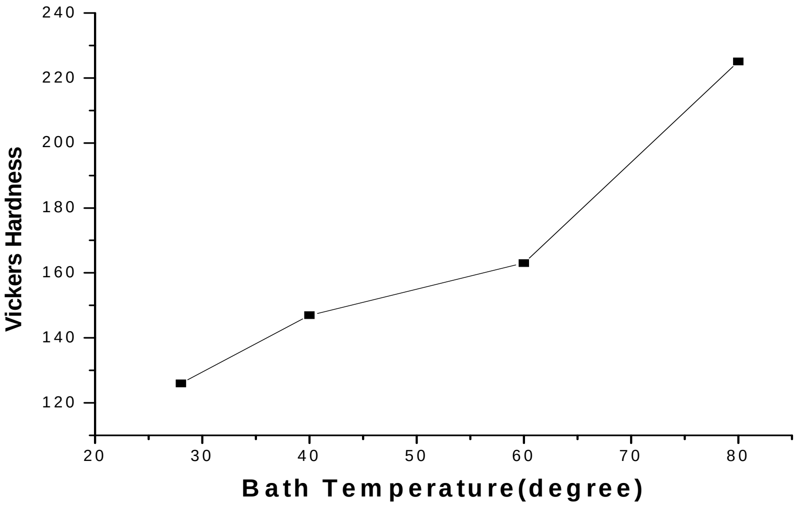


Fig 5. Vickers Hardness as a function of bath temperature.

3.5 Magnetic properties of the deposits

The crystalline nature of the material determines the magnetic properties of the materials. The saturation magnetization and coercivity are important parameters that determine the magnetic properties of soft magnetic materials [13-14].We have planned to examine the saturation magnetization, magnetic flux density and coercivity of electrodeposited NiFeWS alloy thin films from diammonium citrate bath. The magnetic properties of the electrodeposited NiFeWS films have been observed from VSM are tabulated as shown in table 5.

Table 5. Soft Magnetic Properties of Ni-Fe-W-S deposits

S.No	Bath Temperature (˚C)	Coercivity H_s (O_e)	Magnetization M_s (emu/cm^2)	Retentivity M_r (emu/cm^2)	Magnetic flux Density B_s (Tesla)	Squareness S
1	28	20.492	0.028519	0.47038×10^{-3}	1.3953	0.01649
2	40	46.588	0.067988	2.1315×10^{-3}	2.6078	0.03135
3	60	54.194	0.13205	5.1027×10^{-3}	4.5195	0.03864
4	80	69.259	0.17872	9.474×10^{-3}	5.6739	0.05301

The magnetic Hysteresis loops for NiFeWS alloy thin films prepared from diammonium citrate bath at temperatures 28˚C, 40˚C, 60˚C and 80 ˚C is shown in Fig. 6.

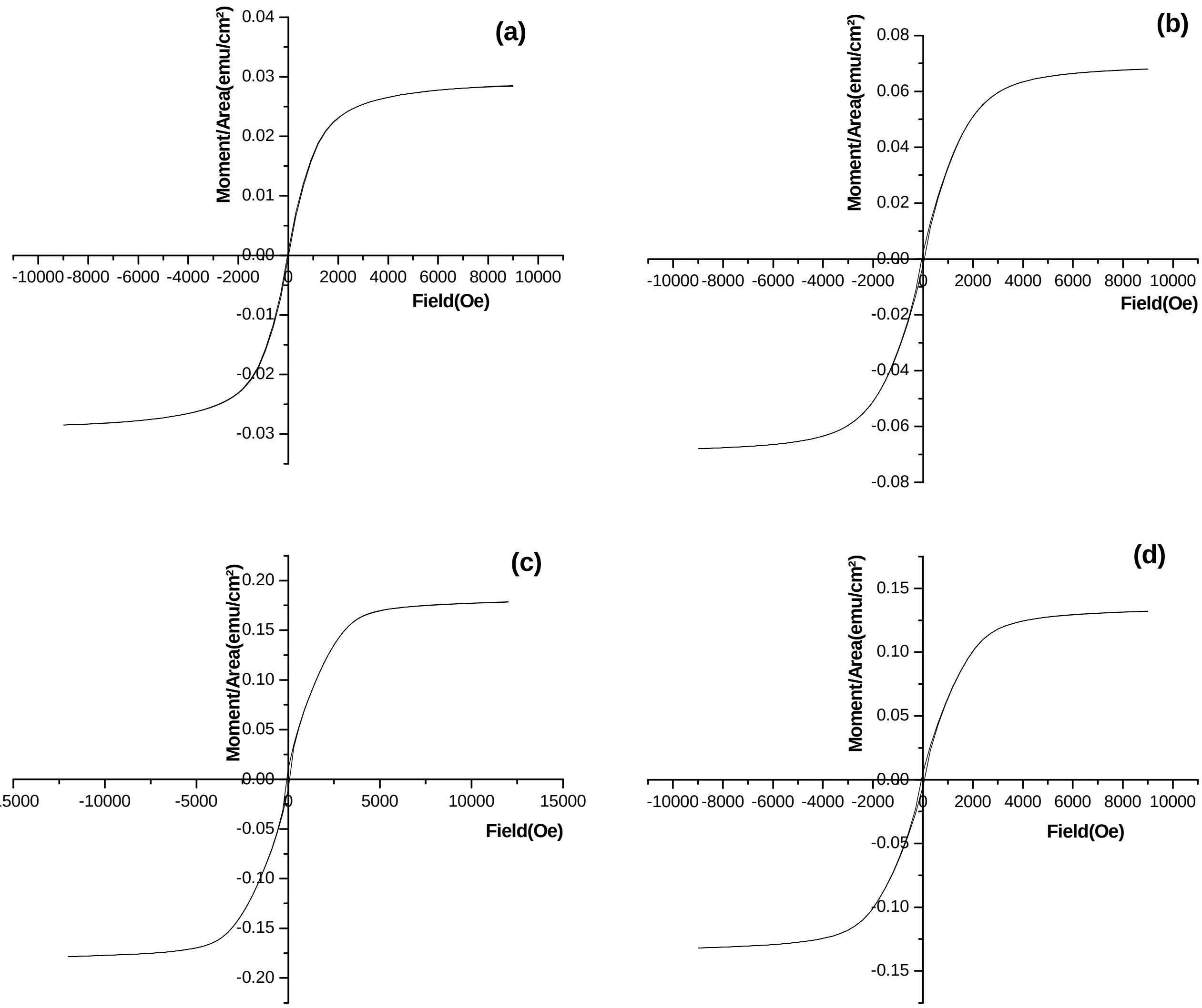


Fig. 6. Magnetic Hysteresis loops for Ni-Fe-W-S thin film for different bath temperatures (a) 28˚C (b) 40˚C (c) 60˚C (d) 80˚C.

The film coated under the temperature of 80˚c exhibits the higher magnetization and Magnetic flux density. It was observed that the magnetization increases from 0.028519 emu/cm^2 to 0.17872 emu/cm^2. From that we concluded the films prepared at higher temperature (80˚C) exhibits a higher value of saturation magnetization and magnetic flux density. The dependence of Magnetic flux density B_s, Saturation Magnetization M_s and bath temperature for electro deposited Ni-Fe-W-S films is shown in figure 7.

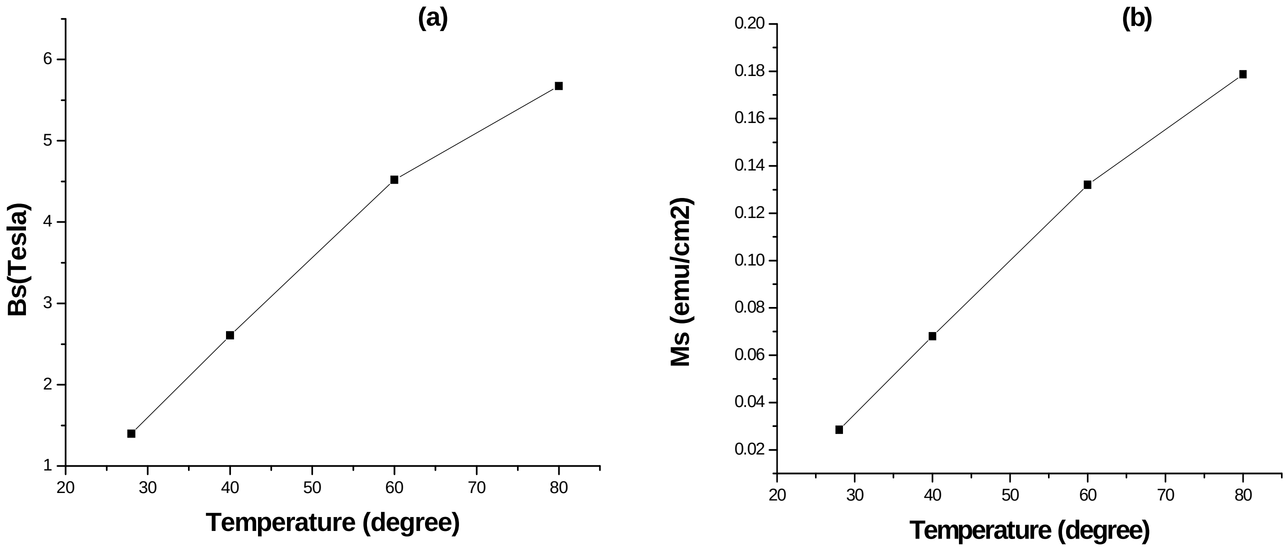


Fig. 7. Bath Temperature as a function of (a) Saturation Magnetic flux Density (b) Saturation Magnetization

The corresponding coercivity values of NiFeWS alloy thin films prepared from diammonium citrate bath at temperatures 28˚C, 40˚C, 60˚C and 80 ˚C is shown in table and it was found to be low value in the unit of oerstead.The effect of film stress on coercivity should be considered because soft magnetic properties of iron based films depends on film stress very sensitively and compressive stress lead to high coercivity but the tensile stress reduces coercivity. This indicates that as temperature of the bath increases the films may be under tensile stress and this leads to increase in saturation magnetization. Many factors contribute to the development of stress in electro deposits including film composition, natures of the substrate surface, bath composition, bath temperature, current density, and deposit thickness etc., The high initial intrinsic stress in the film is associated with lattice mismatch and with the grain size of the underlying substrate. But at high diammonium bath temperatures, the electro deposited film has low stress. This is due to uniform crystal orientation during electro deposition. The Squareness (S) increases from 0.01649 to 0.05301 as the bath temperature increases. The films obtained from 80˚C are having high saturation magnetization when compared to the films obtained from room temperature. Crystalline Permalloy has very low magnetostriction [4]. Due to this nano crystalline NiFeWS films have very low magnetostriction and the intrinsic anisotropy was simultaneously minimized with highest possible permeability. So that these films can be used for devices like magnetic recording heads. By analyzing the present results it can be seen that the best soft magnetic properties have been obtained for the electroplated nano crystalline films at high temperature diammonium citrate bath.

The NiFeWS thin films obtained from Diammonium citrate bath having enhanced magnetic properties (High saturation magnetization, High magnetic flux density, low remanent value) when it is compared to the films obtained from Trisodium citrate bath. The comparison of magnetic properties of NiFeWS nano crystalline thin films from Diammonium citrate bath and trisodium citrate bath is shown in table 6.

Table 6. Comparison of magnetic properties for NiFeWS thin films in different Citrate baths.

S.No	Name of the parameters	Trisodium citrate bath		Diammonium citrate bath	
1	Bath Temperature (˚C)	50	80	40	80
2	Coercivity H_s	372.10 (G)	338.66 (G)	46.588 (Oe)	69.259 (Oe)
3	Magnetization M_s (emu/cm^2)	0.016264	0.071102	0.067988	0.17872
4	Retentivity M_r (emu/cm^2)	0.0034	0.019821	0.0021315	0.009474
5	Magnetic flux Density B_s (Tesla)	0.45611	2.01112	2.6078	5.6739
6	Squareness S	0.2090	0.2788	0.03135	0.05301

From Table 6, It is found that the film obtained from diammonium citrate bath exhibits best soft magnetic properties when it is compared to trisodium citrate bath.

4. Conclusion

The nano crystalline NiFeWS alloy thin films were synthesized by electro deposition method in diammonium citrate bath. The crystalline size of NiFeWS thin films are in the order of nano scale. The films obtained from bath temperature of 80˚C have crystalline size around 27 nm. The films are smooth, uniform, adherent, low stress, crack free deposits from diammonium citrate bath. It is found that from Vickers Hardness Test, the film obtained from bath temperature of 80˚C having higher value of Hardness (225 VHN). The hardness of the film increases with increasing the bath temperature. The films obtained from bath temperature of 80˚C have high saturation magnetization and magnetic flux density with lower coercivity when compared to the films obtained from room temperature bath. The NiFeWS alloy thin films electrodeposited from 80˚C temperature of the bath has higher magnetization and Magnetic flux density value (0.17872emu/cm^2, 5.6739Tesla). We conclude that good soft magnetic property is observed in higher diammonium Citrate bath temperature (80˚C). The NiFeWS thin films obtained from Diammonium citrate bath having enhanced magnetic properties when it is compared to the films obtained from trisodium citrate bath. These films can be used in various electronic devices including high density recording media, magnetic actuators, magnetic shielding, magnetic writing heads high performance transformer cores and MEMS.

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