Effects of Chloride Bath Concentration on Structural and Magnetic Properties of Electroplated NiFeCr Thin Films

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ABSTRACT - *Electrodeposition of NiFeCr thin films have been successfully carried out from chloride bath at a constant current density (1 A/dm²) by varying the chloride bath concentration (0.1, 0.2, 0.3 and 0.4mol/lit). The surface morphology, microstructure and magnetic properties such as coercivity, saturation magnetization were investigated for electroplated NiFeCr thin films. The SEM micrographs of the electrodeposited films from the chloride bath concentration of 0.4 mol/lit have no micro cracks and also the films have more uniform surface morphology as compared with the film coated from lower concentration. The predominant peaks in X-ray diffraction pattern reveal the crystalline nature of the film and found to have BCC structure. From the VSM results of the electrodeposited NiFeCr thin films, the various magnetic analysis such as coercivity, saturation magnetization were calculated. The hardness and adhesion of the electroplated films with substrate were also investigated. Reasons for variation in magnetic properties and structural characteristics were discussed.*

Keywords--- NiFeCr films, Chloride bath, Microstructure, Coercivity, Saturationmagnetization and Adhesion.

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1. INRODUCTION

NiFe based thinfilms have immense applications in magnetic recording media, MEMS and NEMS etc.,High magnetic saturation with low coercivity, high permeability, zero magnetostriction and high electrical resistivity are the essential requirements for the field of MEMS and magnetic recording heads. The best known soft magnetic alloy for MEMS is NiFe based thin films because of its excellent soft magnetic nature[1-3].The Ni–Fe alloys with composition close to 80% Ni are very much used for producing the MEMS devices. Addition of alloying elements like Cr, W and Mo to NiFe alloys can reduce coercivity of the films and also improve corrosion resistance and other magnetic properties [4-9]. Cr is a good candidate as it is a highly corrosion resistant metal, chemically stable and also it have high melting point. The bath having Cr^{6+} ions are known to be toxic and carcinogenic substances. At room temperature it is difficult to synthesis the thin films from the aqueous solution which contains Cr^{6+} ions.

So that in this present work the solution containing trivalent chromium ions (Cr^{3+}) have been applied to an electrolyte for Cr electroplating [10-11]. Among the various physical and chemical deposition methods electrodeposition method is suitable for NiFe based thinfilms. The grain size and growth orientation are the dominant factors to decide the magnetic and mechanical properties of NiFe based thinfilms. These factors may be affected by current density, bath temperature and pH value etc. In the desired current density and bath temperature the NiFeCr films coated by varying the bath concentration have grain size is in the range of nano scale.

2. EXPERIMENTAL PART

In this study, the NiFeCr thin films are coated by varying the chloride bath concentration from 0.1 mol / lit to 0.4 mol / lit. The bath composition and working parameters of electrodeposited NiFeCr thin films are shown in the table

1. The NiFeCr thin films are electrodeposited from the chloride bath at temperature of30 ^{0}C with time period of 30 minutes. The pH value of the solution is maintained as 3. Both the anode and cathode (7.5 x 1.5 cm) are the aluminium substrates. The cathode substrate is covered with adhesive tape except the desired area of deposition. Before the electrodeposition, the substrates were polished with silicon carbide emery paper and degreased with 1M of NaOH for 5 minutes then rinsed with double distilled water and dried in air. The current density is 0.1 A/dm^2 for all the coated NifeCr thin films. The surface morphology and micro structure of the electrodeposited NiFeCr thin films were analysed with the Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD). Vibrating Sample Magnetometer (VSM) is used to analyze the magnetic properties. The compositions of the thinfilms were studied by using Energy-dispersive X-ray Spectroscopy (EDAX) analysis. Vickers hardness tester (VHN) is used to determine the hardness of the deposited film.

Table 1. Bath composition and operating conditions of the electrodeposition bath

Bath chemicals	**Temperature (^{0}C)**	**pH**	**Bath concentration (mol / lit)**
Nickel chloride	30	3	0.5
Ferric chloride			
Chromic chloride			
Boric acid			
Glycine			
Ammonium formate			

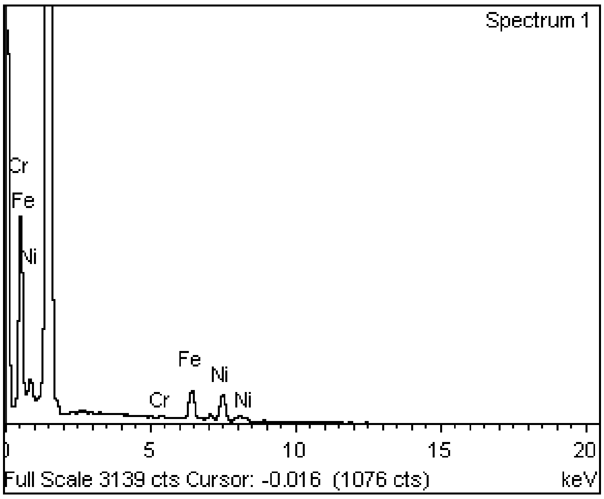
3. RESULTS AND DISCUSSION

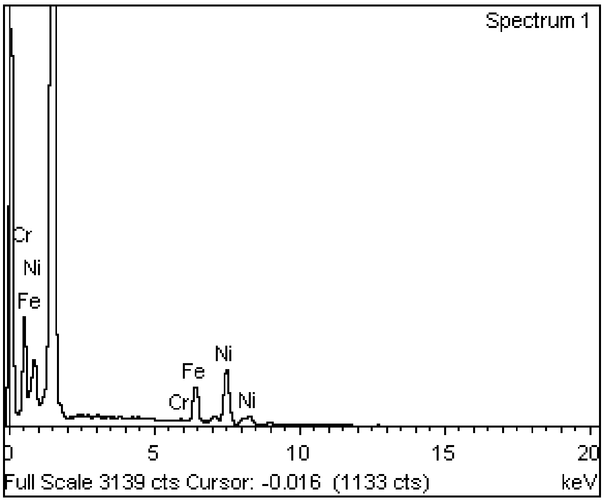
3. 1. Elemental composition of the NiFeCr thin films

The elemental composition (Ni, Fe and Cr) of each electrodeposited NiFeCr thin film was confirmed by the EDAX analysis and it is shown in Fig. 1. The atomic weight percentage of Cr content present in the films were 0.8, 0.17, 0.38 and 0.7 and Ni, Fe contents present in the films were shown in table 1. The atomic percent of Ni content present in the film increaseswith an increment of bath concentration and it was almost equal to 80 % at the concentration of 0.3 mol/lit. All the coated films have lower Cr content.

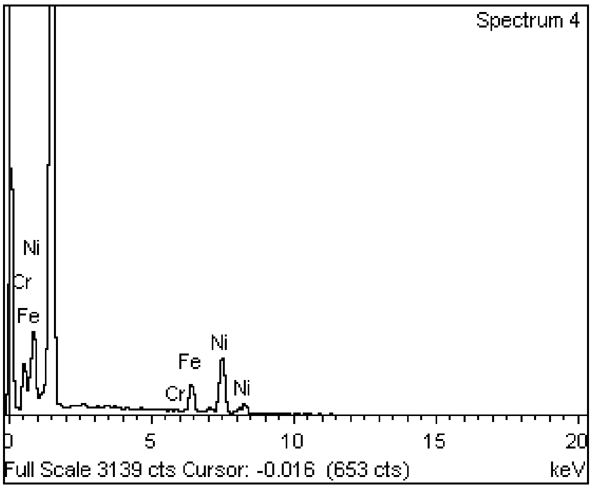
Table 1. EDAX analysis of NiFeCr thin films

S.No	Bath concentration (mol/lit)	Ni wt %	Fe wt %	Cr wt%
1	0.1	59.77	39.43	0.80
2	0.2	70.58	29.24	0.17
3	0.3	78.81	20.81	0.38
4	0.4	63.26	36.03	0.70

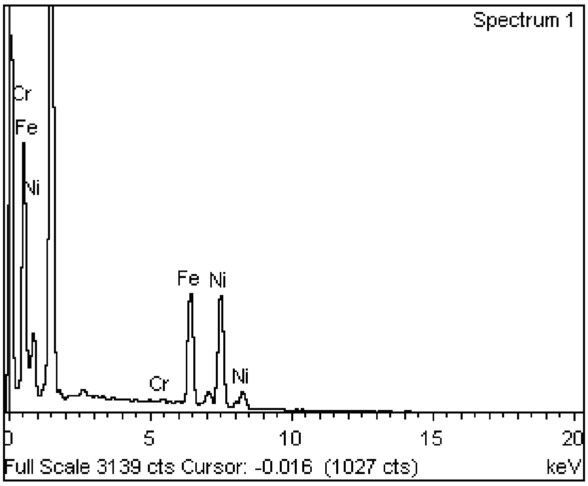




(a) **(b)**



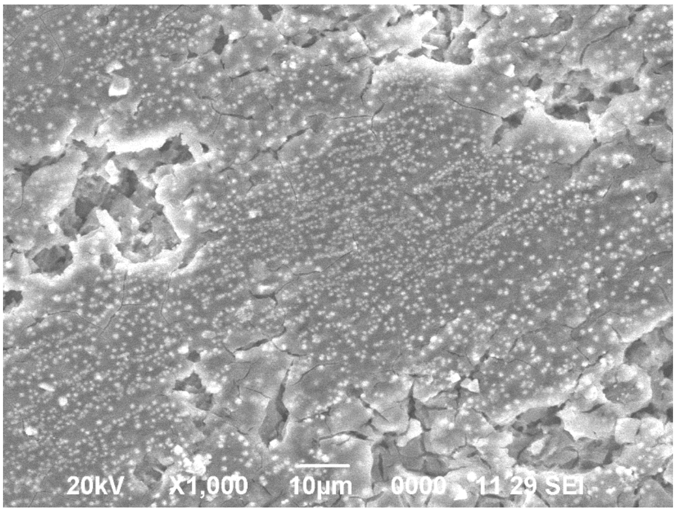
(c)

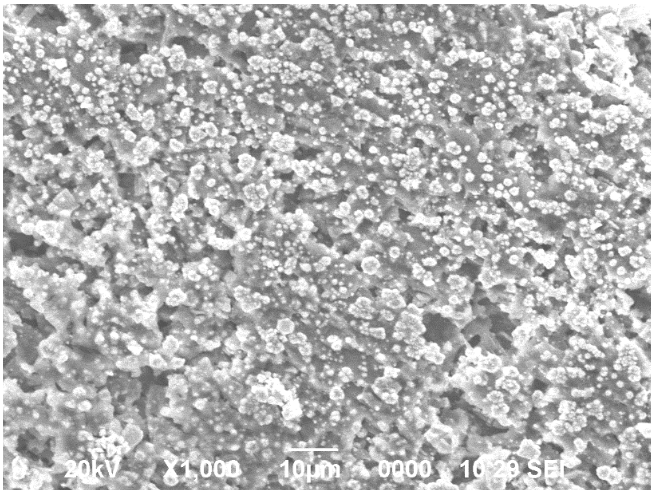


(d)

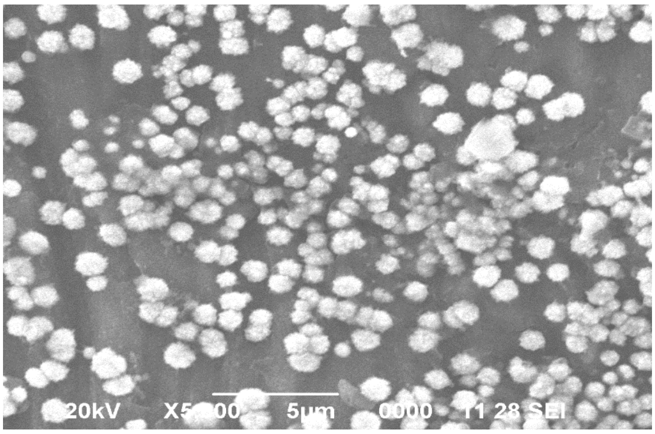
Fig.1 EDAX spectrums of NiFeCr films coated from chloride bath concentrations of (a)0.1 mol /lit (b) 0.2mol /lit (c) 0.3 mol /lit (d) 0.4 mol /lit

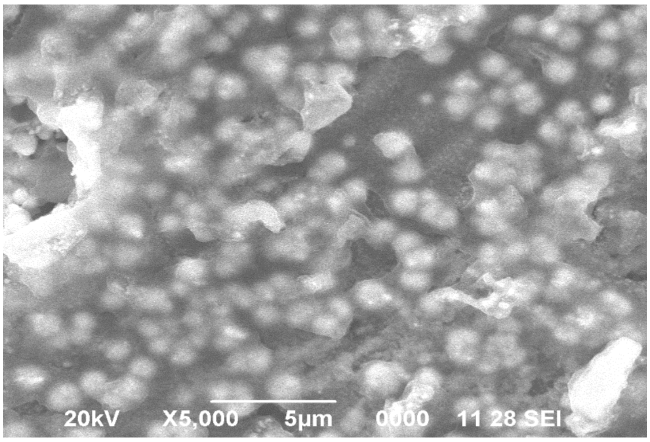
3.2. Surface morphology of the NiFeCr thin films





(a) **(b)**





(c) **(d)**

Fig. 2 SEM images of NiFeCr films coated from chloride bath concentrations of (a)0.1 mol /lit (b) 0.2mol /lit (c) 0.3 mol /lit (d) 0.4 mol /lit

Scanning electron micrographs of electrodeposited NiFeCr thin films are shown in Fig. 2. The NiFeCr films are obtained from different chloride bath concentration have no micro cracks. At a high bath concentration, the surface is uniform, bright and smooth. At a bath concentration of 0.3 mol / lit, the surface is granular and bright which indicates the ball like structure.

3.3.X - Ray diffraction analysis of the NiFeCr deposits

The X-ray diffraction pattern of electrodeposited NiFeCr films from chloride bath at different concentrations of 0.1, 0.2, 0.3 and 0.4mol/lit as shown in Fig. 3. The presence of sharp peaks in NiFeCr thin films indicates that the films were crystalline in nature. Crystalline size of the deposits were calculated from the XRD pattern using the Sherrorsformula. Calculated values from XRD pattern clearly show that the crystalline sizes of the NiFeCr thin films are in the nano scale. The effect of bath concentration on the structural properties of NiFeCr thin film deposited from chloride bath is shown in Table 2. The XRD patterns of NiFeCr films revealed the existence of BCC phase with (110), (200) and (211) diffraction peaks. The crystalline size decreases with the increase in bath concentration. The lowest crystalline size of 38 nm have been observed for NiFeCr thin film which is coated from bath concentration of 0.3 mol / lit.

Table 2. Effects of bath concentration on structural properties of NiFeCr thin films

S.No	Bath concentration (mol/lit)	2θ (deg)	θ (deg)	Particle size, D (nm)	Strain (10^{-4})	Dislocation density ($10^{14}/m^2$)	d (A^0)	β (10^{-3}) (radian)
1	0.1	44.439	22.22	42.519	8.560	5.531	2.037	3.698
2	0.2	44.410	22.21	42.129	8.640	5.634	2.038	3.733
3	0.3	44.478	22.24	38.706	9.404	6.674	2.035	4.064
4	0.4	44.525	22.26	39.393	9.240	6.444	2.033	3.994

3.4. Mechanical properties of the deposits

Adhesion of the film with the Al substrate is tested by bend (bending the film with substrate to 180°) test and scratch test. This test shows that the have good adhesion with substrate. Hardness of the NiFeCr thin films were found to be about 93 VHN, 98VHN 140 VHN and 153 VHN for the chloride bath concentrations of 0.1, 0.2, 0.3 and 0.4mol/lit respectively. The film coated from high bath concentration has high hardness value.

Table 3. Micro hardness values of NiFeCr thin films

S.No	Bath concentration (mol/lit)	Vickers hardness(VHN)
1	0.1	93
2	0.2	98
3	0.3	140
4	0.4	153

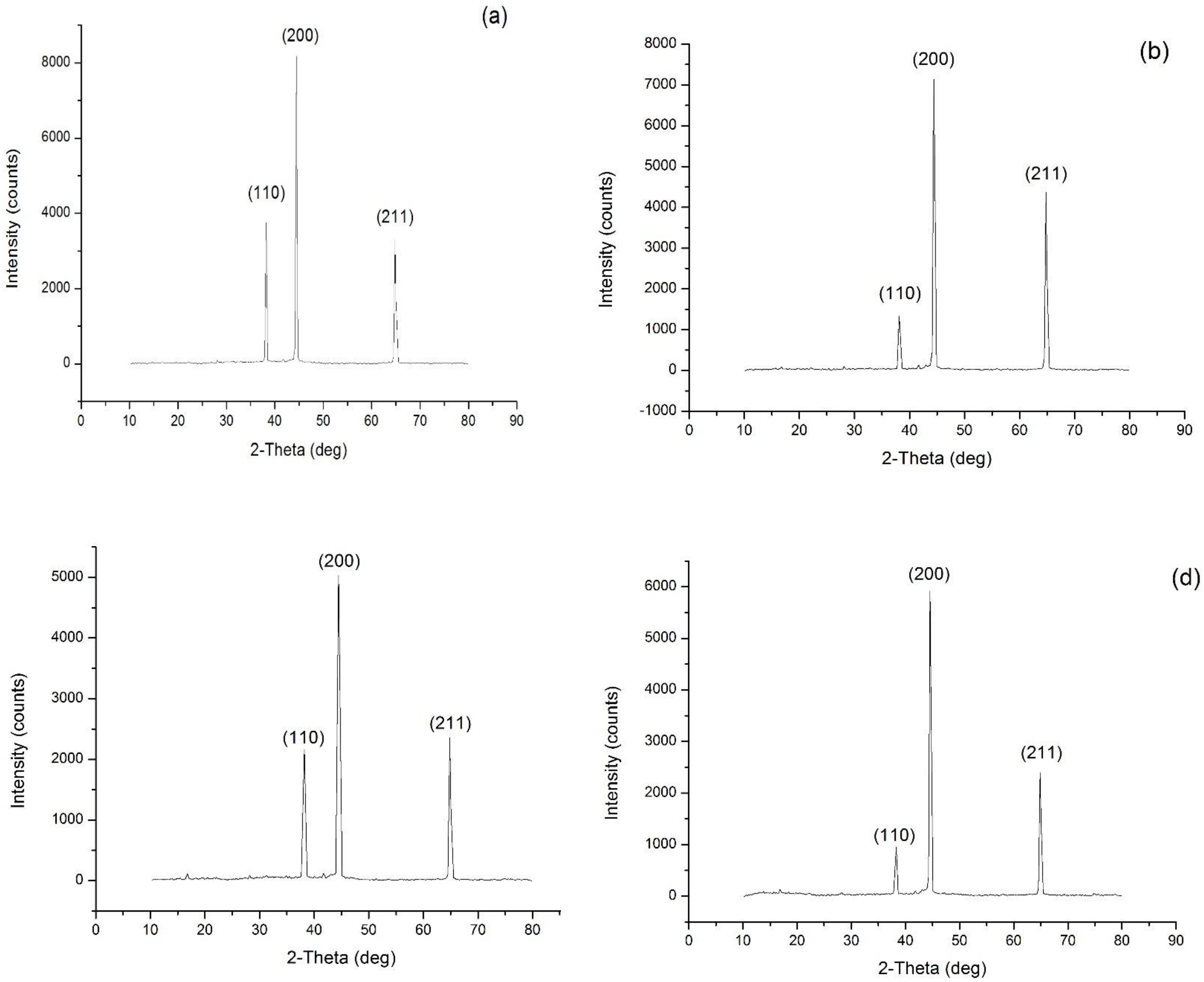


Fig. 3 XRD patterns of NiFeCr films coated from chloride bath concentrations of (a)0.1 mol /lit (b) 0.2mol /lit (c) 0.3 mol /lit (d) 0.4 mol /lit

3.5. Magnetic properties of the NiFeCr deposits

`Fig. 4 shows the hysteresis loop of NiFeCr alloy thin film deposited at different bath concentrations of 0.1, 0.2, 0.3 and 0.4mol/lit.The magnetic properties of NiFeCr films were observed from vibrating sample magnetometer and are tabulated as shown in Table 4.

The important parameters like crystalline size, bath temperature, bath concentration, pH value etc., have great impact on magnetic properties of electrodeposited NiFeCr alloy thin films. Grain size plays a major role to decide the magnetic properties of NiFe based thin films.

Generally single magnetic domains are easier to rotate when it is subjected to magnetic field instead of a larger domain. From XRD it was observed that, all the coated films have smaller crystalline size. Therefore, smaller grain size implies in smaller magnetic domains which are easy to rotate and in addition it decrease the coercivity. Maximum value of magnetization 5.942×10^{-3} emu/g with lower coercivity of NiFeCr thin films were obtained at the bath concentration of 0.3 mol /lit.

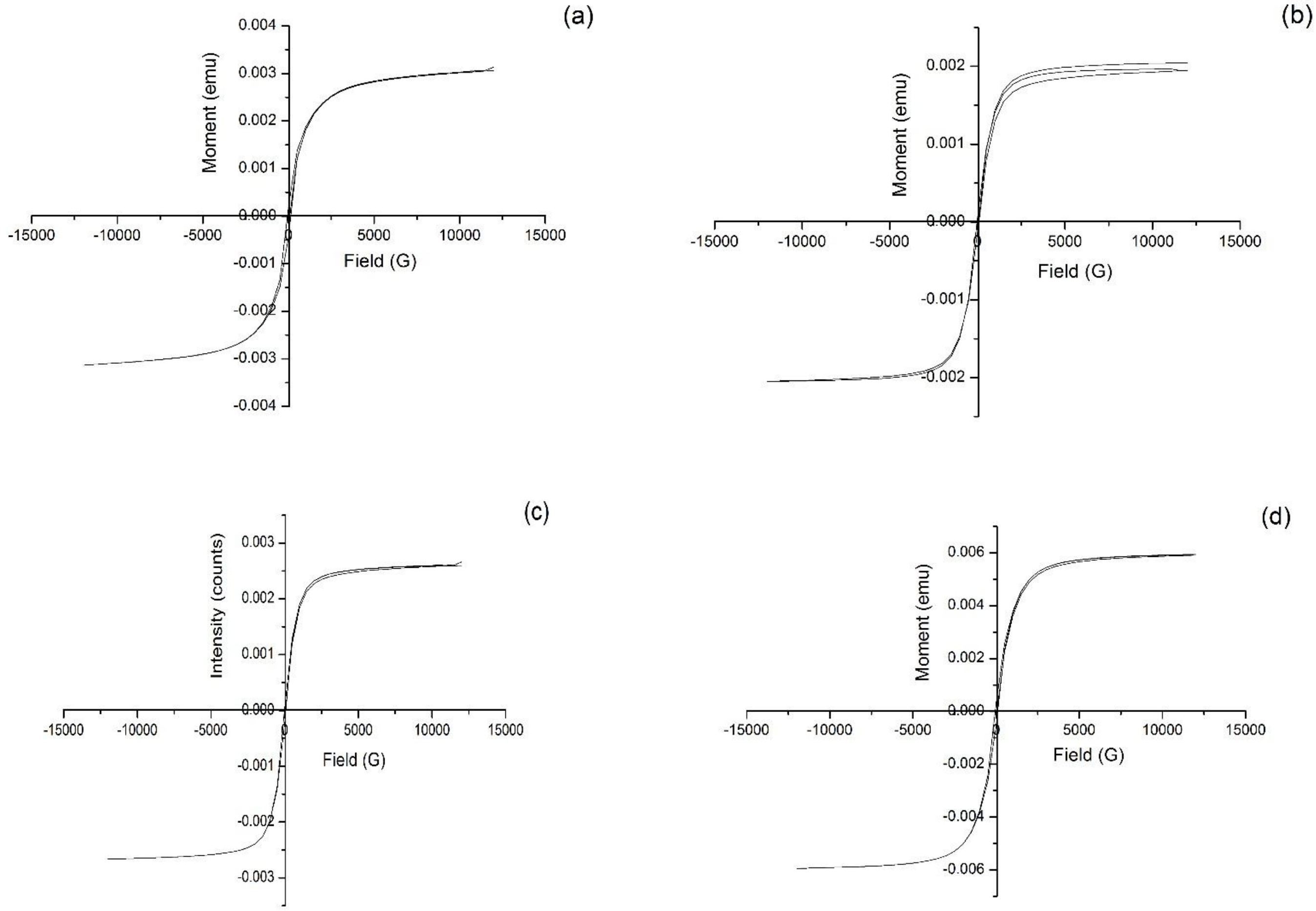


Fig. 3 VSM results of NiFeCr films coated from chloride bath concentrations of (a)0.1 mol /lit (b) 0.2mol /lit (c) 0.3 mol /lit (d) 0.4 mol /lit

Table 4. VSM results of NiFeCr thin films

Bath concentration (mol/lit)	Coercivity (G)	Magnetisation M_s 10^{-3} emu	Retentivity M_r 10^{-6}emu	Squareness S 10^{-3} (M_r/ M_s)
0.1	36.931	0.602	27.929	46.393
0.2	43.937	2.047	92.816	45.342
0.3	75.857	5.942	427.70	71.979
0.4	47.404	2. 266	137.05	51.470

4. CONCLUSIONS

In the present research work, NiFeCr films were electroplated from the chloride bath at 30°C. The effects of chloride bath concentrations on the structural, compositional, morphological and magnetic properties of NiFeCr thin films were analyzed. The electrodeposited NiFeCr thin film has body centered cubic structure. The crystalline size of the NiFeCr films was found to be in few tens of nano meter and decreased with the increase of chloride bath concentration. The Ni content present in the NiFeCr film increases with an increment of chloride bath concentration. The presence of Cr content are in low range for all the coated deposits. The deposits were uniform and granular coated from 0.3 mol / lit. The saturation magnetization was increased with the increment of bath concentration and high value of magnetization have been obtained for NiFeCr thin films coated from 0.3 mol / lit. The NiFeCr thin films have maximum value of hardness as 153 VHN was obtained at 0.4 mol / lit. It was concluded that, the NiFeCr thin films coated from the chloride bath concentration of 0.3 mol / lit exhibits the best soft magnetic nature which may be used well for the MEMS (Micro Electro Mechanical Systems) applications.

5. REFERENCES

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