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Modulating the hardness and magnetic property of NiMnWP by an organosulphur additive for magnetic storage applications

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In this present investigation, we subjected a user friendly electrodeposition method to develop an NiMnWP thin film for magnetic storage devices .The key point of the research work is to enrich the mechanical and magnetic property by varying the deposition time, bath temperature and adding an organic additive. The NiMnWP magnetic thin film without and with thiourea of 2gm/l is developed and their characteristics were studied. The XRD peak confirms the presence of NiWP with an End centered monoclinic structure with the plane (820),(622) and manganese with (422) cubic plane. The crystallite size varies from 18.58 to 16.84 nm without thiourea and 19.83 to 12.33nm with thiourea. The hardness is found to be enhanced due to the addition of thiourea from 102 to 128, where as the other from 91.4 to 101.8.There is an considerable amount of enhancement in magnetization from 4.53 to 22.304×10^{-3} emu and retentivity from 1.2500 to 6.34×10^{-3}emu due to the addition of thiourea. From our experimental work analysis a better magnetic thin films were obtained, to be used in MEMS and magnetic storage devices.

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Keywords: Electrodeposition, Magnetic thin film, NiMnWP, Chloride-citrate bath, MEMS.

1. Introduction

Electrodeposition of a Nanostructured thin films is a flexible, simple and less-expensive method(1).The Morphological, Structural ,Mechanical and magnetic properties were controlled by the bath temperature, deposition time and the additives added(2).Several works have been reported in synthesizing magnetic (Ferromagnetic)thin films by electrodeposition and characterizing .NiMn in particular yields a enticing property since Nickel and Manganese show completely different classes of magnetic alignment ,making them to extend their applications in MEMS and magnetic storage devices.[1]Most of the earlier work have been done in sulphate based bath of NiMn, and very few on chloride based elements which might reduce polarization and increases efficiency of the cathode. No literature work has been recorded on further extension of NiMn to a tri or tetra compound so far.This makes the present work a very engrossing one .Tungsten and phosphorous were chosen as a third and fourth element since tungsten enhances the strength and hardness of the film and phosphorous gives a smooth and shining appearance to the film. In this present work a chloride-citrate bath of NiMnWP alloy is electrodeposited and the structural, Morphological, mechanical and magnetic properties are examined. Further a small proportion of an organosulphur compound thiourea is added to the bath and the change in the properties of NiMnWP without and with thiourea is observed.

2. Experimental procedure

2.1. Electrodeposition of NiMnWP magnetic thin films

A galvanoscopic technique was carried out to prepare a NiMnWP magnetic thin films from a chloride-citrate bath with thiourea as additive. Thiourea even though differ in properties with urea, they have similar structure except that the oxygen was replaced by sulphur atoms.

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2.2. Substrate arrangement

A nickel plate of 2x7cm area is taken as an anode and a copper plate of same dimension is taken as cathode. Both the electrodes were subjected to cleaning effect. The cathode is washed with 0.01N dilute sulphuric acid, followed by acetone wash and then with distilled water, where as Nickel plate is washed with acetone and then with hot double distilled water. Before subjecting to deposition the cathode plate is masked such that 2x5cm alone is exposed for deposition.

2.3. Bath preparation

The bath for electrodeposition is prepared by using the following analytical grade chemicals and double distilled water [11].

$NiCl_2.6H_2O$[Merck]	0.1M
$MnCl_2.H_2O$[Merck]	0.1M
Na_2WO_4[Sigma Alrich]	0.05M
H_3BO_3[Loba]	0.15M
NH_4Cl[Merck]	0.3M
$Na_3C_6H_5O_7$[Sigma Alrich]	0.3M
$NaPO_2H_2$[Loba]	0.2M
$CH_4(N_2S)$ [Merck]	2gm/Litre

Two set of solutions were prepared as without and with thiourea. In order to achieve an uniform suspension the solutions were prepared using magnetic stirrer at a rate of 200rpm for about 10 minutes. The PH of the solution is adjusted to 9 by adding a few drops of Sodium hydroxide.

2.4. Deposition process

The solution is taken in a beaker and the electrodes are fixed to obtain estimated coating area. A constant current density of $3mA/cm^2$ is applied through power supply. Here the bath temperature is varied to 35,45 and 55^0C whereas the deposition time is optimized to 15,30 and 45 minutes.

3. Characterization of NiMnWP alloy thin films:

3.1. Structural studies

The Electrodeposited NiMnWP magnetic thin films from chloride-citrate bath 35,45 and 55^0C bath temperature an 15,30,45 minutes deposition time with and without thiourea is subjected to XRD studies by using Shimadzu XRD 6000-X-ray diffractometer and the corresponding graphs were shown in Fig 1.

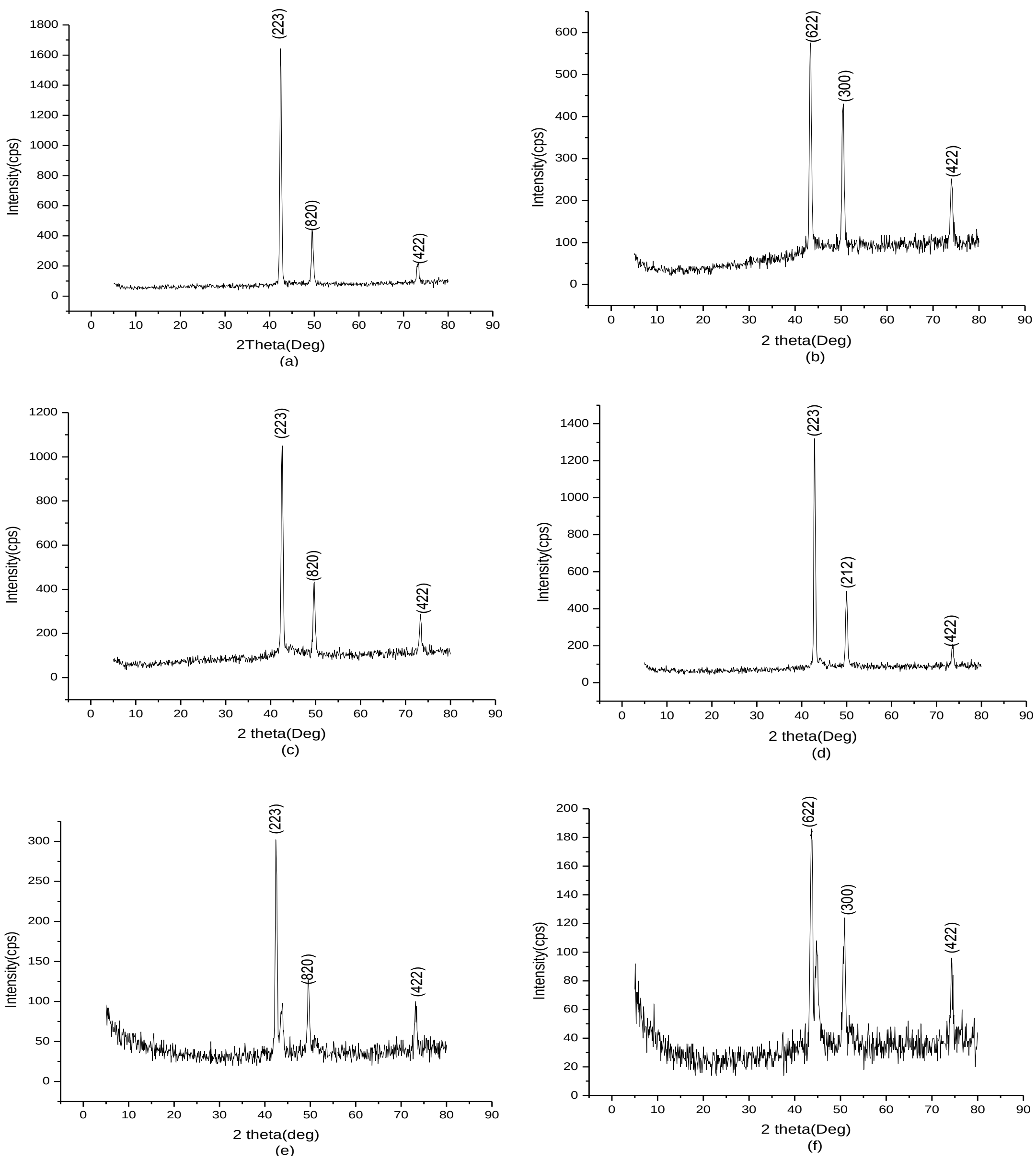


Fig. 1. XRD images for NiMnWP films electrodeposited at 55^{0}C for 15, 30, 45mins without thiourea (a,b,c) and with thiourea (d,e,f).

The patterns obtained from XRD is compared with the standard JCPDS card-No 80-0146 for NiWP (820),(622) plane with End centered monoclinic structure and Card No-89-4857 for Mn(422) predominantly. The Strain and the dislocation density in the film calculated using the following formula were the main reason for the shifting of the plane,

$$\text{Strain } (\varepsilon) = \beta \cos\theta/4 \quad (1)$$

$$\text{Dislocation density } (\delta) = 1/D^2 \quad (2)$$

The crystallite size was calculated by the formula

$$\text{Crystallite size} = 0.945\ \lambda/\beta \cos\theta \quad (3)$$

where, λ corresponds to the X-ray wavelength of Cu K ∝ radiation.

The crystallite size decreases with increase in the temperature and it was found to be in nanoscale. Compared to the film without thiourea, it was found that due addition of thiourea leads to a very small crystallite size upto 12.3 nm. The strain and the dislocation density increase with increase in temperature.

2.2. Morphological studies

The SEM surface images of NIMnWP films capture by JSM 6390 Scanning Electron microscope for the 45mins deposition time at 35, 45, and 55^{0}C bath temperature are shown below.

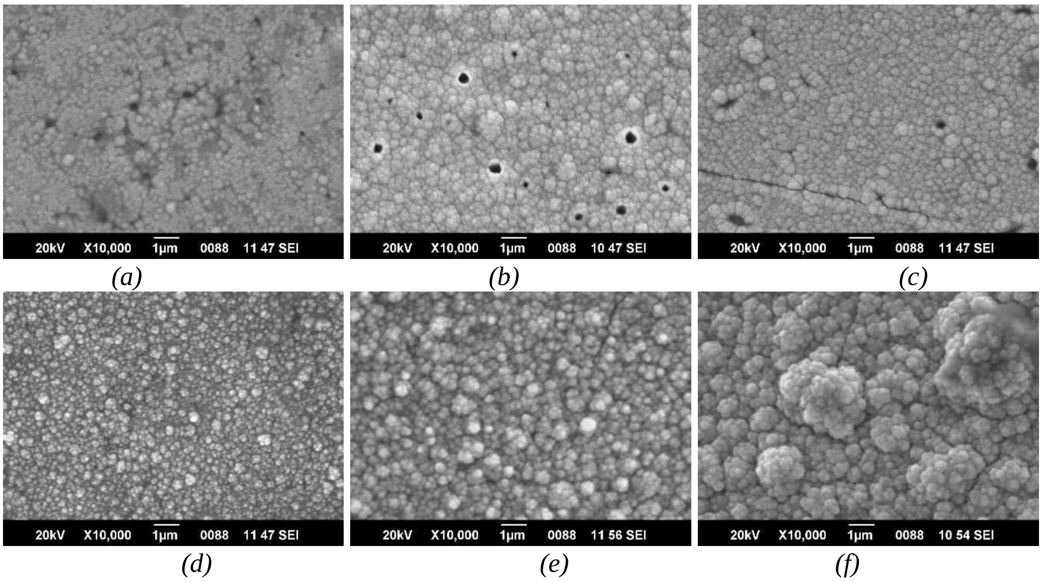


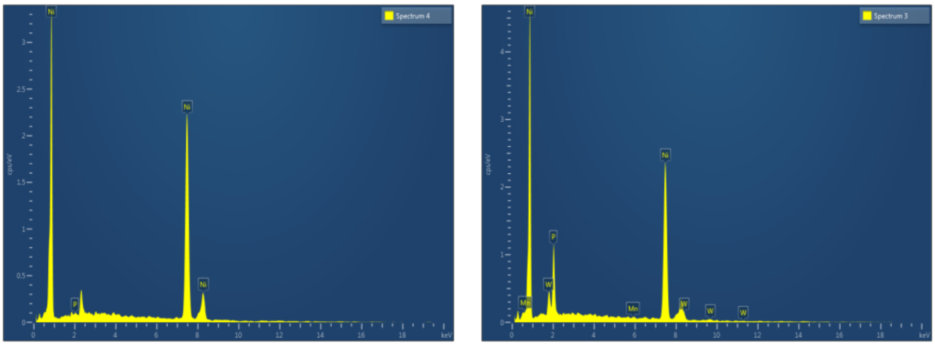
Fig. 2. SEM images for NiMnWP films electrodeposited at 55^{0}C for 15, 30, 45mins without thiourea (a,b,c) and with thiourea (d,e,f).

The surface grain structure of the deposits without thiourea is found to be clear without cracks and with some pin holes. Images of NiMnWP with thiourea of about 2gm/l shows a clear grain size, crack free and no pinholes were observed compared to the previous one. A nano flower structure was observed for 55^{0}C. From the table 2, it was clear that as the deposition time increases the crystallite size decreases and the dislocation density and strain increases.

Table 1. Elemental composition of the NiMnWP magnetic thin films at 45mins.

Additive	Bath Temperature ^{0}C	Elemental composition (%)				Crystallite size (nm)	Strain 10^{-2}m	Dislocation Density 10^{14}
		Ni	Mn	W	P			
Without Thiourea	35	70.14	1.61	1.59	26.66	18.58	10.74	28.96
	45	78.75	1.18	2.02	18.05	18.33	10.89	29.76
	55	80.34	0.58	2.02	18.05	16.84	11.8	35.26
With Thiourea 2gm/l	35	99.12	0.83	0.01	0.03	19.83	10.02	25.4
	45	99.39	0.23	0.01	0.37	17.24	11.50	33.6
	55	99.71	0.0	0.29	0.00	12.33	16.35	65.7

As the bath temperature increases the percentage of Nickel increases whereas Manganese tungsten and Phosphorous decreases



(a) (b)

Fig. 3. EDAX graph for 45 mins deposition at 55^0C (a)with thiourea 2gm/l (b) without thiourea.

2.3. Hardness Studies

The hardness of the sample were measured using Shimadzu HMV-2T micro hardness tester. From above table it was clear that compared to the blank sample the harness of the samples with the film is found to be higher. Moreover films with thiourea have higher hardness than the one without thiourea. The following plot clearly reveals the above statement.Scratch and bend test confirms the Adhesion of the film was good.

Table 2. Thickness and Vicker Hardness Number without and with films at different temperature at 45 mins deposition time.

Additive	Bath temperature(^{0}C)	Deposition time(sec)	Thickness (µm)	Hardness number of the sample	
			Sample with film	Blank sample	Sample with film
Without Thiourea	35	15	2.12		91.4
		30	2.16		93.6
		45	2.19		96.56
	45	15	2.32		95.7
		30	2.38		98
		45	2.49		100.5
	55	15	2.55		99.7
		30	2.64		100.5
		45	2.77		101.8
With thiourea 2gm/l	35	15	2.99	86.6	102
		30	3.17		105.5
		45	3.45		106
	45	15	3.59		110.1
		30	3.78		112
		45	3.99		115
	55	15	4.05		119
		30	4.32		123.4
		45	4.73		128

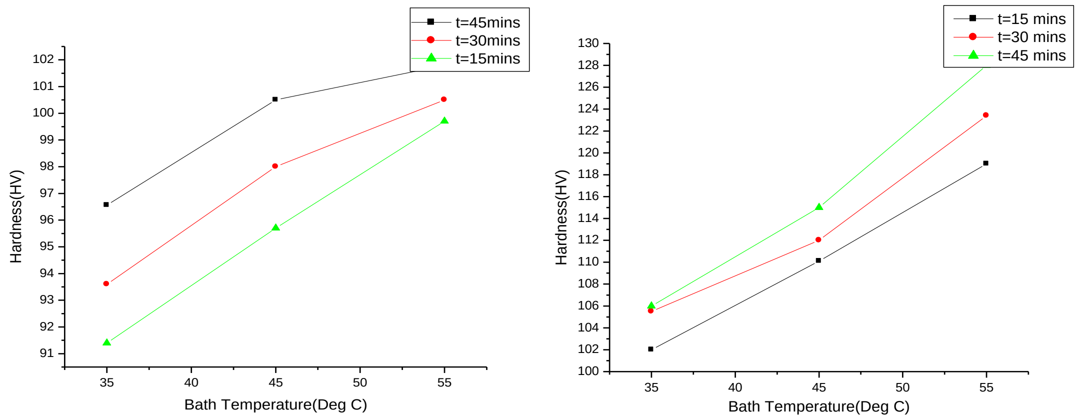
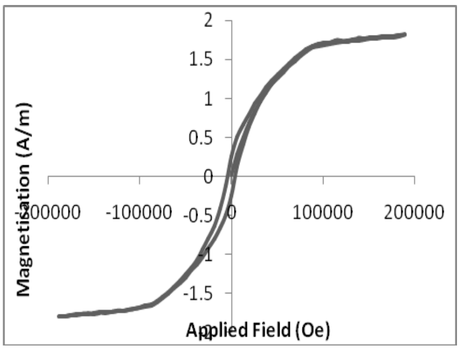


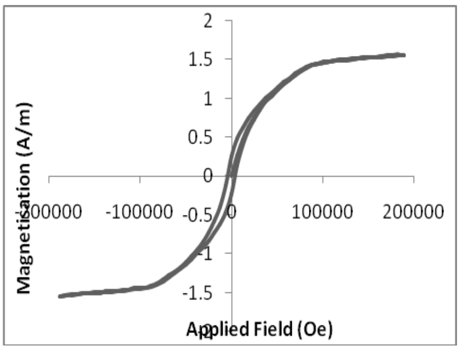
Fig. 3. Plot against bath temperature and Hardness Number(a)Without Thiourea (b) with thiourea of 2gm/L.

2.4. Magnetic studies

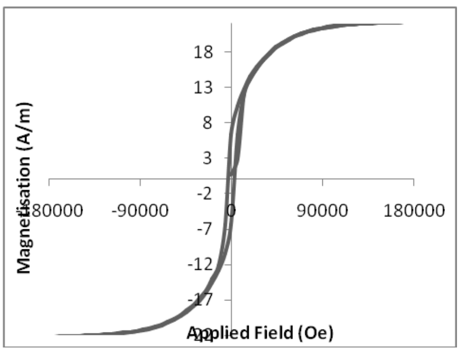
Fig 3 exhibits the hysteresis loop for NiMnWP magnetic thinfilms without and with thiourea of 2gm/l calculated using Lakeshore VSM 7410S-vibrating sample magnetometer. The above table 3 represents the magnetic properties of film with 45minutes of deposition time and bath temperature of 35,45,and 55^{0}C.In the case of without thiourea as the bath temperature increases there is an increase in magnetization, retentivity and coercivity of the but within a small range , whereas in NIMnWP magnetic thin films with thiourea of 2gm/l there is a steep increase in magnetization and retentivity .This is because of decrease in manganese and increase in the Nickel concentration. The squareness value calculated as a ratio between retentivity and magetaisation lies between 0.139 to 0.304.



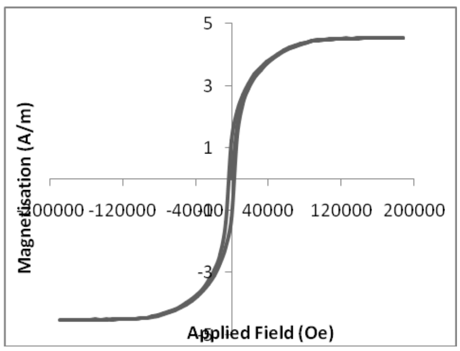
(a)



(b)

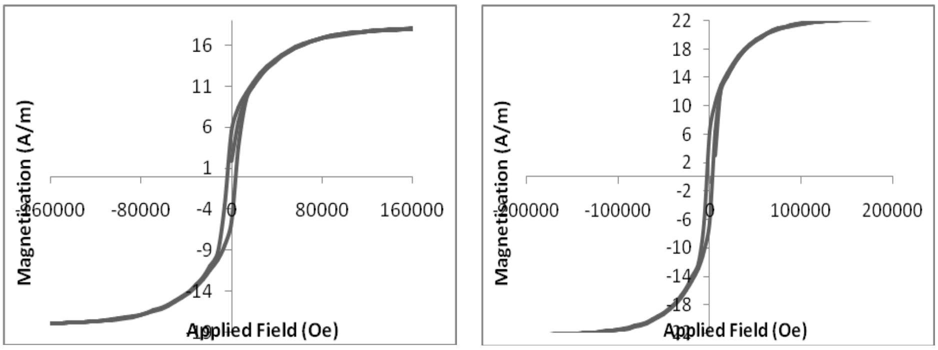


(c)



(d)

Fig. 3. VSM images for NiMnWP films electrodeposited at 45 min at 35,45 and 55^{0}C without thiourea (a,b,c) and with thiourea (d,e,f)



(e) *(f)*

Fig. 3. VSM images for NiMnWP films electrodeposited at 45 min at 35,45 and 55^{0}C without thiourea (a,b,c) and with thiourea (d,e,f)

Table 3. VSM studies for NiMnWP magnetic thin films at different temperature at 45mins deposition time.

Additive	Bath temperature(^{0}C)	Magnetisation (x10^{-3}emu)	Retentivity (x10^{-3}emu)	Coercivity (Oe)	Squareness
Without Thiourea	35	1.3539	0.19583	315.68	0.144
	45	1.5576	0.23997	318.21	0.154
	55	1.8122	0.25190	324.78	0.139
With Thiourea 2gm/l	35	4.53	1.2500	236.80	0.275
	45	18.077	5.498	301.7	0.304
	55	22.304	6.3485	249.71	0.284

3. Conclusion

From the above studies of NiMnWP magnetic thin films deposited with varying deposition time and bath temperature without and with thiourea of 2gm/L the following conclusion were made.

The XRD studies confirms the end centered monoclinic structure and exhibited NiWP (820), (622) plane and cubic Mn (422) plane. The appearance of the film is found to be shiny silver for NiMnWP thin film without thiourea whereas addition of thiourea leads the film to show slightly darker in appearance. From the SEM studies even though the crystallite size decreases with temperature in both the cases the NiMnWP magnetic thin film with thiourea of 2gm/l leads to the very low crystallite size of 12.33nm, and higher strain and dislocation density. The addition of thiourea leads to a very clear grain with nano flower structure without any pin holes. The Elemental analysis observed from the EDAX and clearly shows that in the film without thiourea a considerable amount of Mn, W and P were observed but in the case of with thiourea it reveals that nickel composition is found to be dominating compared to the other elements which leads to a increase in magnetization up to 22 x 10^{-3}emu, as observed from the magnetic studies.

As the deposition time and bath temperature increases the thickness of the film increases, likely the hardness of the film also increases, where the films with thiourea shows the maximum hardness making them a good hard magnetic materials. Addition of thiourea leads to a increase in the retentivity to 6.3 x 10 $^{-3}$emu, an the squareness lies between 0.139 to 0.304 which confirms it as a perfect square loop. Thus NiMnWP magnetic thin film with thiourea is has an enhanced the morphological, mechanical and magnetic studies hence making them suitable in magnetic storage devices and in industries.

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