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Effect of additives on the structural and magnetic properties of electrodeposited NiMn thin film

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Abstract*: Nanocrystalline Ni-Mn thin films were deposited by electrodeposition method on copper substrate with different additives such as saccharin and urea at 50°C and 70°C temperatures. The structural and surface properties of Ni-Mn thin films were studied by using X-ray Diffractometer (XRD) and Scanning Electron Microscopy (SEM). Elemental compositions of the films were measured by means of Energy Dispersive X-ray Spectroscopy (EDAX). Magnetic properties of the thin films were studied with the aid of Vibrating Sample Magnetometer (VSM). Hardness of the films was measured by using Vickers Hardness Number (VHN). Micro hardness testing was carried out to determine the relation between these mechanical properties with crystallite size. The deposits of Ni-Mn thin films were found to be shiny, smooth, nanocrystalline and good adherence to the substrate. The deposits were found to have face centered cubic (FCC) structure. NiMn thin films electrodeposited with saccharin as an additive found to have higher magnetization with lower coercivity and are suitable for MEMS devices.*

Key words*: NiMn thin film; magnetic property; mechanical property; MEMS application;*

I. Introduction

Soft magnetic films with a high magnetic moment are used in variety of applications, such as magnetic recording systems, high frequency plasma inductors and modern non-volatile magnetic memory [1]. Permalloy (NiFe) is the best known thin film alloy in MEMS applications [2], because of their higher saturation flux density, lower coercivity, higher saturation magnetization and lower magnetostriction. The stress free thin film alloys with enhanced magnetic properties were very much used in magnetic recording heads and MEMS [3]. The well known stress reducing agents [4], [5] for nickel based electro deposition are sulfur containing organic additives (saccharin, thiourea, etc). The electrodeposited film exhibit grain sizes less than 100 nm. In most of the investigations, Ni-Mn alloys were electrodeposited from sulphate and sulfamate baths and very few from chloride bath. Fathi et al reported that the percentage of Mn content presents in the film increases with increasing current density. Moreover the effectiveness of cathode has enhanced by chloride ions and films were deposited even at low voltages due to the high conductivity of chloride bath [6], [7]. The Ni-Mn alloy is an intellectual combination to investigate further in their abundant inimitable properties viz, the contradictory type of magnetic alignment in their fundamental state is one among them. The ferromagnetic nickel and paramagnetic manganese come together to produce Ni-Mn alloys with attractive magnetic properties [8]. Babanov et al reported that $Ni_{75}Mn_{25}$ shows paramagnetic behavior at room temperature and $Ni_{80}Mn_{20}$ shows ferromagnetic behavior [9]. By keeping this context in mind, in the current investigation Ni-Mn alloy thin films were electrodeposited from chloride bath by means of glycine used as an additive. As literature reveals that the effects of bath temperature for the eletrodeposition of NiMn thin film have not been reported so far. This makes the interest to study the effect of bath temperature. This paper reports the preparation of NiMn thin films by electro deposition method. In order to enhance magnetic properties of the film, additives like saccharin and urea were added and the effects of additives and the effect of temperature on the structural, magnetic and mechanical properties of the NiMn films in chloride glycine bath were studied and are reported here.

II. Experimental Part

A. Electrodeposition of NiMn thin films

NiMn thin film was electrodeposited on copper substrate in chloride-glycine bath at 50˚C and 70˚C temperature with the additives such as saccharin ($2gl^{-1}$) and urea ($2gl^{-1}$). The chemical compositions of the electroplating bath are $25gl^{-1}$ of Nickel chloride and Manganous chloride, 20 gl^{-1} of glycine and 10 gl^{-1} of ammonium chloride. A copper substrate of size (2 x 6 cm) as cathode and pure nickel of same size as anode were used for electrodeposition of NiMn 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 double distilled water. Copper 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 4.5 by adding few drops of HCl solution. The films were galvanostically deposited on copper substrate by applying a constant current of

6mA/cm^2 for a period of 60 minutes at 50˚C and 70˚C bath temperature. Electro deposited NiMn thin films were decomposed when the bath temperature increased to 80˚C. Hence the temperature was optimized to 70˚ C for these NiMn thin films.

B. Characterization of NiMn 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 analysis of the films was 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. Magnetic properties (Coercivity, Magnetization, and retentivity) were studied using Vibrating Sample Magnetometer (VSM).Hardness of the as deposited and annealed film was measured by Vickers Hardness Test (VHN) and thickness of the film was measured by digital micrometer.

III. Results and Discussion

A. Composition of the electro deposited NiMn thin films

The electrodeposited NiMn alloy films were smooth, uniform, adherent. The composition of the NiMn film from chloride-glycine bath and annealed film was obtained from the EDAX analysis and the weight percentages of the electro deposited films are tabulated as shown in Table 1. EDAX result showed that when the temperature was increased then the Mn percent was reduced accordingly.

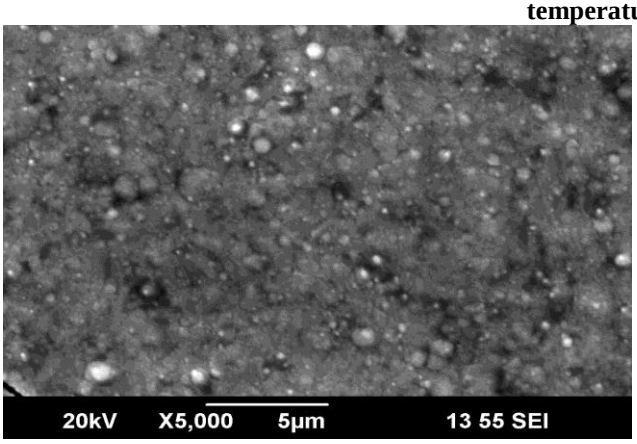
Table 1. Results of EDAX analysis

S.No	Name of the Additive	Temperature ˚C	Ni Wt%	Mn Wt%
1	Saccharin 2 g/l	50	99.7	0.3
		70	99.83	0.17
2	Urea 2 g/l	50	99.55	0.45
		70	99.59	0.41

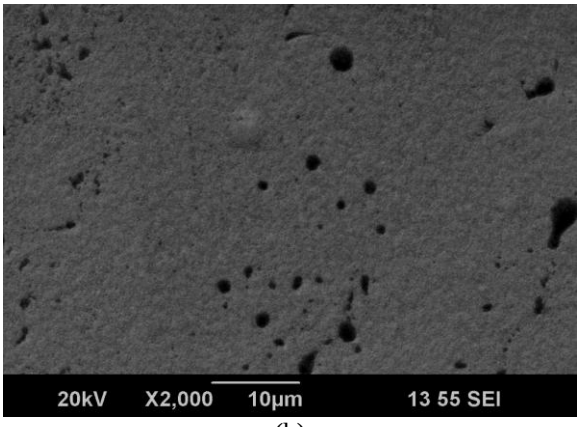
B. Morphology of the deposits

The surface morphology of the NiMn thin films with the saccharin and urea at different temperature are investigated by scanning electron microscopy (SEM). The SEM images of electrodeposited NiMn thin films from chloride-glycine bath are shown in Figure 1.

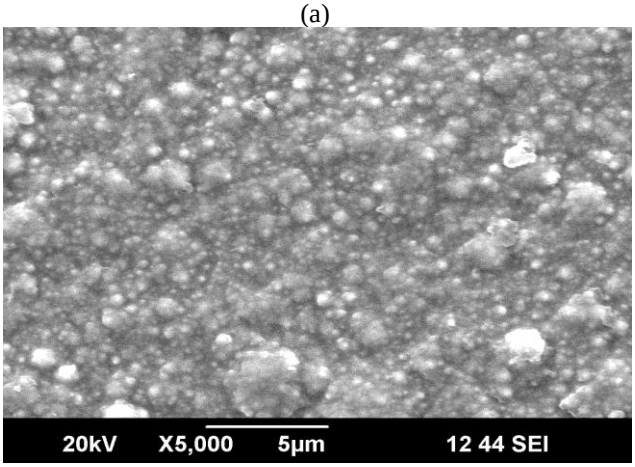
Figure 1. SEM images of Electro deposited NiMn thin film with saccharin as an additive (a) deposited at 50˚C, at 70˚C bath temperature and urea as an additive (c) deposited at 50˚C, (d) at 70˚C bath temperature.



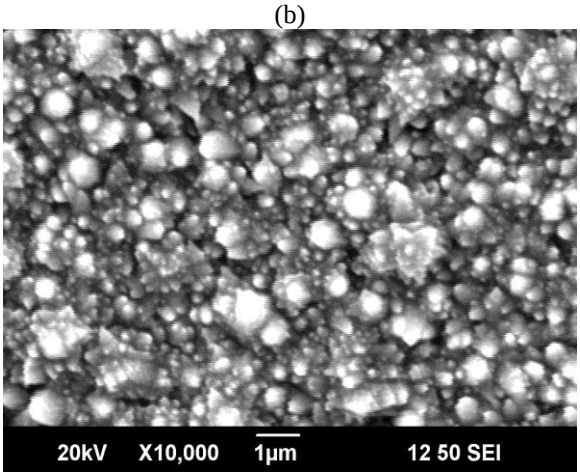
(a)



(b)



(c)



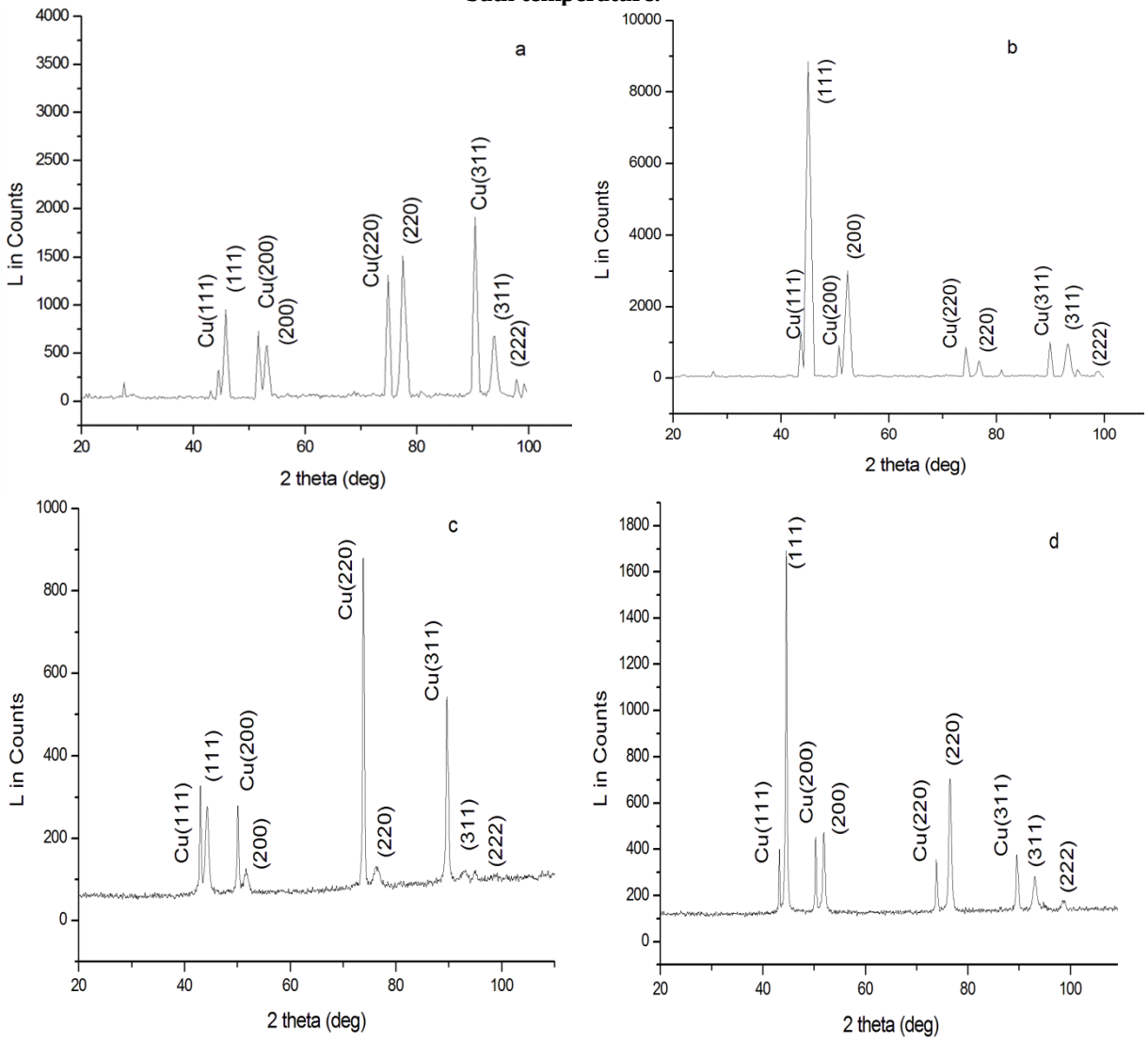
(d)

The films obtained at different temperature do not have micro cracks. The film was uniform and bright. The grain sizes were visible and very clear. At 50˚C having smaller crystallites and granular. This is due to uniform crystal orientation during electrodeposition. Hence the film has low stress. Film coated at 50˚C is having ball like structure and 70˚C is found to have pinholes in the surface for the bath contains saccharin. Film coated at 50˚C is having cauliflower structure and for 70˚C film found to have flower like structure for the bath contains urea as an additive.

C. Structural and mechanic properties of NiMn thin films.

Electrodeposited NiMn film from chloride-glycine bath at 50˚ C and 70˚ C was subjected to XRD studies and it is shown in Figure 2. Mechanical properties of the film were measured by Vickers hardness tester. The crystalline size of NiMn alloy films and other structural and mechanical are tabulated as shown in Table 2.

Figure 2. XRD pattern of Electro deposited NiMn thin film with saccharin as an additive (a) deposited at 50˚C, at 70˚C bath temperature and urea as an additive (c) deposited at 50˚C, (d) at 70˚C bath temperature.



The data obtained from the XRD pattern compared with the standard JCPDS data and were found to have FCC structure. The presence of sharp peaks in XRD patterns of film reveals that the films are crystalline in nature. The peaks corresponding to (111), (200), (220), (311) and (222) reflections were observed in deposited films. It almost matches with JCPDS for nickel with the slight shift in the peak position due to the low percent of Mn in the film. Remaining peaks are corresponding to Cu substrate. Crystallite size increases due to the increment of temperature in the bath which contains saccharin and urea as an additive. Stress present in the film decreases with the reduction of Mn% [10]. Film stress has been reduced much in the film coated at 70°C with saccharin as an additive.

Adhesion of the film (deposited at temperature 50˚ C and 70˚ C) with the substrate is tested by bend and scratch test. It showed that as deposited film having good adhesion with the substrate. Hardness of the film was examined using a Vickers hardness tester by the diamond intender method. The results are tabulated and shown in Table 2.

Table 2. Effect of saccharin ($2gl^{-1}$) on the structural and mechanical properties on NiMn thin film electrodeposited from chloride glycine bath at 6 mA cm-2 current density for 60 min

Additive	Temperature °C	Crystalline size (nm)	Internal strain $X10^{-3}$	Stress (MPa)	Dislocation denstity	Lattice parameter	Vickers Hardness (VHN)
Saccharin	50	24.85	1.457	276.83	2.05	3.581	380
	70	77.46	0.467	088.80	2.84	3.587	542
Urea	50	22.09	1.639	311.30	6.24	3.627	377
	70	32.3	1.121	212.96	9.58	3.522	252

The results show that the hardness increases with increment of bath temperature for saccharin bath and decreases for the urea bath. Highest hardness value of 542 is obtained at 70˚ C for the bath contains saccharin.

D. Magnetic Properties of electrodeposited NiMn thin films.

The hysteresis loop parameters, saturation magnetization (M_s), Coercivity (H_c), retentivity (M_r), magnetic flux density (B_s) of the films were evaluated by using VSM. The magnetic properties of the NiMn thin films deposited at 50℃ and at 70℃ have been observed from VSM are tabulated as shown in Table 3.

Table 3. Effect of saccharin ($2gl^{-1}$) and Urea ($2gl^{-1}$) with temperature on the thickness and magnetic properties of Ni-Mn thin film from chloride-glycine bath.

Additive	Current density ($mAcm^{-2}$)	Temperature °C	Thickness (µm)	Coercivity (Oe)	Magnetic saturation (emu g^{-1})	Remanence (emu g^{-1})	Squarness	Flux density Tesla
Saccharin	6	50	1.8	493.28	58.09	12.94	0.223	8.163
		70	2.1	417.05	57.83	20.73	0.358	8.128
Urea	6	50	1.9	430.82	44.38	17.55	0.395	6.235
		70	2.3	485.2	34.13	12.17	0.357	4.797

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 [11], [12]. The soft magnetic properties are strongly dependent on the microstructure of the thin films. The microstructure contribution to magnetization arises from morphology properties such as magnetic anisotropy, magnetostriction and coercivity [13]. When the bath temperature increases grain size of the film also increases [14] and due to that saturation magnetization decreases [15]. Very low magnetization of 34.13emu g^{-1} is obtained for the film coated at 70℃ with the urea as an additive and high magnetization with the reduced coercivity has been obtained for the film deposited at 70℃ with the saccharin as an additive and it exhibits good magnetic properties than the other film. Thickness of the film found to be increased with the increment of temperature. 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 bath temperatures, the electro deposited film has low stress. This is due to uniform crystal orientation during electro deposition.

IV. Conclusion

Nano crystalline NiMn electrodeposited coating was deposited on Cu substrate. The effects of temperature and additives on structural and magnetic properties of the films were systematically studied. The results show that,

1. Due to the increment of temperature, the crystalline size increases.
2. The coercivity of the film was decreased from $493.28O_e$ to $417.05O_e$. Saturation magnetization of the film was fond to be decreases, retentivity, suareness and flux density were found to be decreased as temperature of the bath (contains saccharin) increases. Hardness of the annealed film increased from 380 VHN to 542 VHN.

3. Stress of the film has been reduced much in the film deposited at 70°C with saccharin as an additive.
4. This shows that the soft magnetic properties of NiMn thin films are greatly enhanced by increasing bath temperature to 70˚ C with saccharin which can be used for MEMS applications.

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