Magnetic Properties of Ni-Mn Thin Films Electrodeposited From Chloride-Citrate Bath

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Abstract: **NiMn thin films were electroplated from chloride-citrate bath at various current densities and at various concentrations of citrate. The magnetic properties of NiMn thin films were analyzed with a Vibrating Sample Magnetometer. The Vibrating Sample Magnetometer (VSM) results shows that the coercivity is a function of grain size and low coercivity has been obtained for the film prepared with 20gl^{-1} concentrations of tri sodium citrate bath. The variation of crystallite size with magnetic properties has been explored.**

Key words: **NiMn thin film; magnetic property; electrodeposition, current density**

1. INTRODUCTION

Electrodeposition of NiMn alloy is of particular attention due to its structure which may be due to the ferromagnetic nickel and paramagnetic manganese combined together to form NiMn alloy[1]. Magnetic properties of a material were influenced by the changes in the grain size of the thin film[2]. Electrodeposition of Ni and NiMn alloy thin films were discussed for a variety of LIGA and MEMS applications due to their enhanced strength and temperature performance. Spin valve reading heads that demand soft ferromagnetic thin films with suitable corrosion resistance as in NiMn thin films[3-5]

Magnetic properties of NiFe, NiCo, NiP, NiW and NiCoP[6-10] have been investigated in the past. To our knowledge, magnetic properties of NiMn thin have not been reported much. Hence with the intention to get the fullest potential of NiMn thin film it is essential to examine the magnetic properties of this alloy with various baths and at various current densities. This builds the intention to prepare NiMn thin film from chloride-citrate bath and the effect of current densities are also discussed.

2. MATERIAL AND METHODS

2.1 Electrodeposition of NiMn thin films from tri sodium citrate bath

The bath composition of NiMn alloy thin film is shown in Table 1. The deposition was carried out by varying the tri sodium citrate bath concentration (10, 20 and 30gl^{-1}) at various current densities (2, 4 and 6 mAcm^{-2}) with different time durations (10, 20 and 30 min). A copper substrate of size 9 x 2 cm as the cathode and nickel of the same size as anode were used for this present investigation. The electrolytic bath has been prepared by using AR grade chemicals in tri sodium citrate bath. The copper substrates were polished to mirror grade by the process of buffing and then degreased by using a detergent solution further it was cleaned with distilled water and dipped in sulphuric acid for a few seconds followed by final rinsing with double distilled water. Cleaned and dried substrate has been masked off with an adhesive tape except the area on which the deposition was desired. Bath pH has been varied from 3 to 7 but a good quality of the deposit was obtained for the bath pH 4.0. Hence, the tri sodium citrate bath pH was adjusted to 4.0. The magnetic properties of the NiMn thin films from tri sodium citrate bath were studied with the help of VSM and elemental compositions of the film were analysed using EDAX.

Table.1 Chemical composition and deposition parameters for the electrodeposition of NiMn thin films from tri sodium citrate bath

S.No	Name of chemicals and deposition parameters	Conditions for the deposition
1.	Nickel chloride	25 gl^{-1}
2.	Manganese chloride	25 gl^{-1}
3.	Tri sodium citrate	10, 20 and 30 gl^{-1}
4.	Ammonium chloride	10 gl^{-1}

5.	pH value	4.0
6.	Current density	2, 4, 6 $mAcm^{-2}$
7.	Time duration	20, 40 and 60 min

3. RESULTS AND DISCUSSION

3.1. Elemental composition of the deposits

The elemental composition of the NiMn film deposited from tri sodium citrate bath has been obtained from the EDAX study and the weight percentages of the films are tabulated as in Table 2. EDAX results showed that the weight percentage of manganese found to be increased due to the increment of the bath concentration. The film prepared at 20 gl^{-1} citrate bath concentration having 4.90 wt% of manganese content.

Table 2 Results of EDAX analysis of NiMn thin films deposited from tri sodium citrate bath

S.No	Tri sodium citrate concentration (gl^{-1})	Ni wt%	Mn wt%
1	10	98.14	1.86
2	20	95.10	4.90
3	30	94.62	5.38

Due to the increment of the bath concentration, tensile stress of the film may also increase, which leads to the reduction in coercivity. This is because tensile reduces the coercivity of electroplated nickel based alloy thin films. Hence the NiMn films can be used to manufacture devices like magnetic recording heads.

3.2 Magnetic properties of the deposits

The magnetic properties of the electrodeposited NiMn thin films from various concentrations of tri sodium citrate have been obtained from VSM are tabulated as shown in Table 3, 4 and 5. The magnetic hysteresis loops for NiMn alloy thin films are shown in Figure 1. The film coated with citrate bath concentration of 20 gl^{-1} exhibits lower coercivity and film prepared at 10 gl^{-1} exhibits higher magnetization with higher coercivity at 2 $mAcm^{-2}$ current density. But coercivity plays a major role to decide the magnetic nature of the material. It was observed that the magnetization and coercivity of that film was 1.197 emu and 76.948 Oe which is the lowest value of coercivity of all deposits prepared from tri sodium citrate bath. From the analysis, we conclude that the citrate bath concentration of 20 gl^{-1} at 6$mAcm^{-2}$ for the time duration of 60 min was optimized as a suitable bath condition to prepare the soft magnetic NiMn thin films.

Table 3 Soft magnetic properties of NiMn deposits from 10 gl^{-1} tri sodium citrate bath concentration

Current density ($mAcm^{-2}$)	Time (min)	Thickness (µm)	Coercivity H_c (Oe)	Magnetization M_s (emu)	Retentivity M_r (m emu)	Squareness (M_r / M_s)
2	20	5.0	418.926	1.625	44.921	0.028
	40	5.5	415.731	1.602	44.530	0.028
	60	6.0	403.695	1.578	42.986	0.027
4	20	5.0	412.845	1.593	43.562	0.027
	40	6.0	404.359	1.741	42.230	0.024
	60	6.5	394.752	1.562	41.485	0.027
6	20	6.0	399.915	1.574	41.862	0.027
	40	6.5	397.681	1.569	41.158	0.026
	60	7.0	390.956	1.561	46.679	0.030

Table 4 Soft magnetic properties of NiMn deposits from 20 gl^{-1} tri sodium citrate bath concentration

Current density ($mAcm^{-2}$)	Time (min)	Thickness (µm)	Coercivity H_c (Oe)	Magnetization M_s (emu)	Retentivity M_r (m emu)	Squareness (M_r / M_s)
2	20	5.5	88.629	1.405	55.646	0.040
	40	5.5	84.812	1.302	52.483	0.040
	60	6.0	82.465	1.248	48.699	0.039

4	20	5.5	83.815	1.265	49.681	0.039
	40	6.5	82.614	1.238	47.631	0.362
	60	7.0	79.784	1.224	44.843	0.037
6	20	6.5	80.765	1.214	45.541	0.038
	40	7.0	78.516	1.208	43.676	0.036
	60	7.5	76.948	1.197	41.966	0.035

Table 5 Soft magnetic properties of NiMn deposits from 30 gl^{-1} tri sodium citrate bath concentration

Current density ($mAcm^{-2}$)	Time (min)	Thickness (µm)	Coercivity H_c (Oe)	Magnetization M_s (emu)	Retentivity M_r (m emu)	Squareness (M_r / M_s)
2	20	6.0	333.925	0.958	97.673	0.102
	40	6.5	327.628	0.874	88.672	0.101
	60	7.0	309.547	0.865	82.499	0.095
4	20	6.5	315.584	0.829	85.670	0.103
	40	6.5	308.659	0.784	80.154	0.102
	60	7.0	299.649	0.752	78.867	0.105
6	20	7.0	298.529	0.721	77.950	0.108
	40	7.5	295.174	0.653	77.712	0.119
	60	8.0	279.569	0.611	76.619	0.125

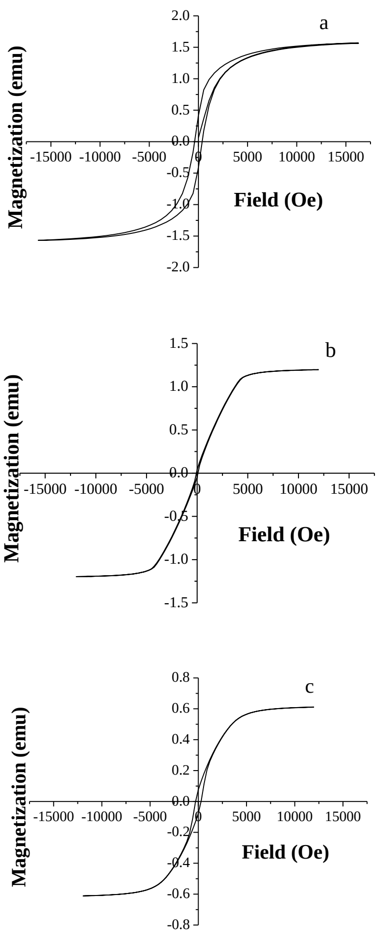

Figure 1 Magnetic hysteresis loop of NiMn thin films deposited from different citrate concentrations (a) 10 gl^{-1} (b) 20 gl^{-1} and (c) 30 gl^{-1}

The increment of the bath concentration caused to vary the coercivity of the film. The variation of coercivity as a function of the current density is shown Figure 2 and as a function of citrate bath concentration is shown in Figure 3.

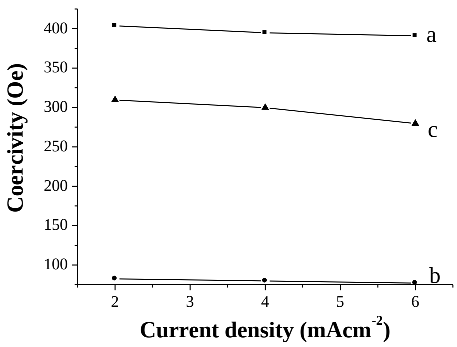

Figure 2 Variation of coercivity as a function of current density of the film prepared at different citrate bath concentrations a) 10 gl^{-1}, b) 20 gl^{-1} and c) 30 gl^{-1}

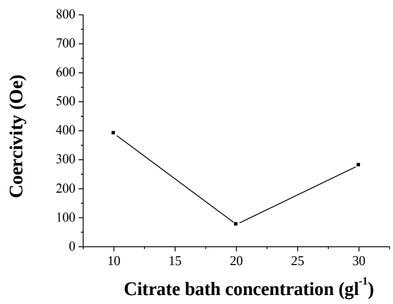

Figure 3 Variation of coercivity as a function of citrate bath concentration

Coercivity of the films was gradually decreased with decreasing Ni content of NiMn based films and the lower coercivity was obtained from the film containing 95.10 wt% of nickel content. Since the nickel content decreases, manganese content increases, in connection with this the grain size of the films were reduced as expected. The reduction in grain size reduces the coercivity. Due to the increase in current density and the time of deposition, the coercivity of the film found to be reduced gradually.

The influence of the time period of deposition on the coercivity is shown in Figure 4. By analyzing the results, it is clearly understood that the electroplated NiMn films from tri sodium citrate bath concentration of 20 gl^{-1}possess the best soft magnetic property at room temperature. It is concluded that the tri sodium citrate bath concentration of about 20 gl^{-1} is optimized to obtain better soft magnetic NiMn films.

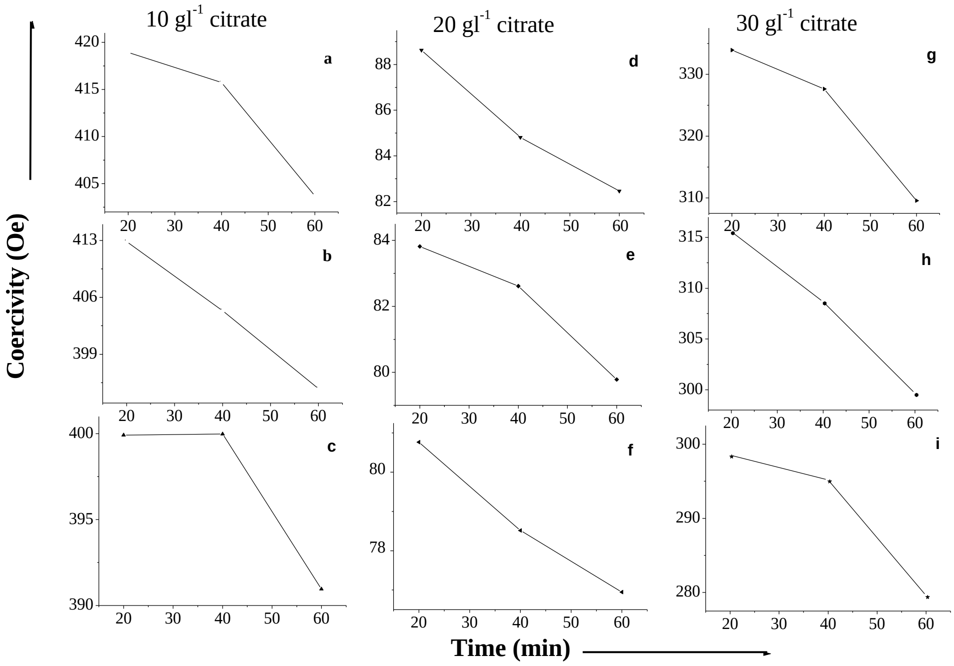

Figure 4 Variation of coercivity as a function of time duration at different current densities with 10 gl^{-1} of citrate a) 2 $mAcm^{-2}$, b) 4 $mAcm^{-2}$, c) 6 $mAcm^{-2}$, with 20 gl^{-1} of citrate d) 2 $mAcm^{-2}$, e) 4 $mAcm^{-2}$, f) 6 $mAcm^{-2}$ and 30 gl^{-1} of citrate g) 2 $mAcm^{-2}$, h) 4 $mAcm^{-2}$ and i) 6 $mAcm^{-2}$

4. CONCLUSION

In this investigation, NiMn alloy thin films were prepared from various citrate concentrations. The increase in the citrate bath concentration affected the soft magnetic properties of NiMn thin films. The electroplated NiMn films from chloride-citrate bath concentration of 20 gl^{-1} have low coercivity. This is due to the reduction in grain size of the thin film. Film prepared at this concentration is having a uniform surface morphology and smooth surface.

5. REFERENCES

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