Magnetization behaviour of electrodeposited Ni–Mn alloys

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Abstract

Ni–Mn alloys were electrodeposited from acidic sulphate baths and their magnetization behaviour was studied so as to understand the effects of the bath composition and deposition current density. The magnetic properties of alloys are very sensitive to Ni/Mn ratio in the bath as well as the current density. Increase in particle size causes a significant drop in the magnetization. © 1998 Published by Elsevier Science S.A. All rights reserved.

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1. Introduction

Ni–Mn electrodeposits are recently gaining importance as sacrificial coatings for mild steel [1]. Since manganese has a well defined localised magnetic moment, the Ni–Mn system is ideal for magnetic studies. There is only limited information available on magnetic studies of cast Ni–Mn alloys [2]. However, little is known regarding the magnetic properties of electrodeposited Ni–Mn alloys though magnetization studies have appeared in some electrodeposited alloy systems [3–6]. This is despite the fact that interesting changes in magnetic behaviour can be expected to occur on alloying the ferromagnetic nickel with antiferromagnetic manganese by electrodeposition over a non-magnetic substrate like stainless steel [7]. In fact, the magnetic characterisation of these alloys are necessary not only to understand the magnetic structure but also to assess useful properties like electrochemical activity [8]. Any attempt to study the correlation between magnetic properties and deposition parameters could be of immense use.

Ni–Mn alloys could be readily deposited from different types of baths with additives [9]. The plating variables, like bath composition, current density, pH, temperature, etc. are known to change the properties of the deposits vastly [10]. In this work, the magnetization behaviour of the electrodeposited Ni–Mn system, prepared from sulphate baths, has been studied in terms of Ni/Mn metal ratio in the bath and deposition current densities.

2. Experiments

Ni–Mn alloys were electrodeposited on pretreated stainless steel substrates from simple acidic sulphate baths with ammonium sulphate as the additive. Bagged graphite blocks were used as anodes. The various bath compositions and deposition current densities for different deposits were labeled and are given in Table 1. In all the cases, bath pH value and temperature were maintained at 3.0 and 27°C, respectively.

The deposits were mechanically removed from the substrate and folded in aluminum foils for magnetization experiments. The magnetic hysteresis measurements were carried at 27°C in EG&G PAR vibrating sample magnetometer with the maximum field of 6 KOe. X-ray diffraction measurements, for determination of particle size, were performed with a Siefert's high-resolution, Guinier-type X-ray powder diffractometer fitted with a quartz monochromator to select $CuK_{\alpha 1}$ ($\lambda = 1.540598$ A) radiation.

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Table 1
Preparation parameters of electrodeposited Ni–Mn alloys

Deposit no.	Bath composition		Deposition CD (mA cm^{-2})
	NiSO$_4$ 6H$_2$O (g l^{-1})	MnSO$_4$ H$_2$O (g l^{-1})	
1	20	150	30
2	40	150	30
3	80	150	30
4	120	150	30
5	150	150	30
6	150	100	30
7	150	75	30
8	150	50	30
9	150	25	30
10	40	150	60
11	80	150	60
12	120	150	60
13	150	120	60
14	150	75	60
15	150	25	60

All deposits are with 50 g l^{-1} (NH$_4$)$_2$SO$_4$ as additives, pH value is 3.

3. Results and discussions

The concentration of nickel sulphate in the bath was varied from 10 to 150 g l^{-1} by keeping the manganese sulphate content at 150 g l^{-1}. Thereafter, NiSO$_4$ was kept constant at 150 g l^{-1} and the other constituent, MnSO$_4$, was varied from 150 to 10 g l^{-1} gradually. The deposits were made with a current density of 30 mA cm^{-2} for the above set of concentrations. But only information on nine selected deposits, as shown in Table 1, were labeled accordingly and used for investigations. The applied magnetic fields versus magnetic moments for these different deposits are plotted and shown in Fig. 1.
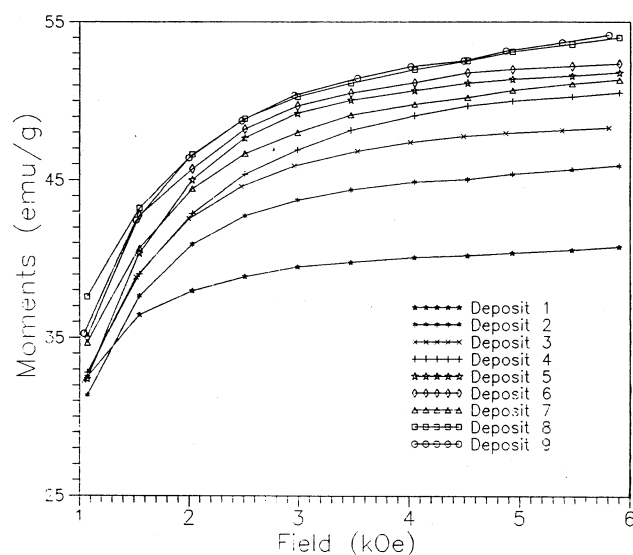

Fig. 1. Influence of bath concentration on the saturation magnetization (σ_s) of Ni–Mn alloys electrodeposited at 30 mA cm^{-2}.

The magnetic moments for all the deposits increased with increasing the applied magnetic field, which exposed the ferromagnetic nature of the deposits. The magnitude of the saturation magnetization (σ_s) for the deposits 1–4 increases with increase in nickel concentration. The same trend is also observed in equal concentration baths (NiSO$_4$ 150 g l^{-1}; MnSO$_4$ 150 g l^{-1}) i.e. deposit no. 5, which is also as per expectations.

In further electrodeposition experiments, NiSO$_4$ was kept at 150 g l^{-1} and the MnSO$_4$ was decreased from 150 to 10 g l^{-1} gradually. Results indicate that the magnitude of the σ_s continues to rise for these deposits (nos 6, 8, 9). But, in the case of deposit 7 (NiSO$_4$ 150 g l^{-1}; MnSO$_4$ 75 g l^{-1}), a significant fall is seen in the magnitude of σ_s. The fall in magnetization is due to sizeable increase in particle size as sensed from XRD measurements. The particle size D, as calculated by the Scherrer [11] technique, falls in the range 35–40 nm for all the deposits except deposit 7. A particle size as high as 52 nm was seen in deposit 7. Hence, increase in particle size coupled with surface magnetism effects have led to contradictory and significant drops in σ_s. Interesting variations of magnetic moments with applied fields are observed for the deposits 6–9. There is initial linear rise in the moments with respect to fields which subsequently reach saturation at higher fields (> 4 KOe). On the other hand, saturation behaviour starts even at low fields for the deposits 1–4. Saturation at higher fields for deposits 6–9 reveals that the magnetic energy required to align the nickel magnetic moments is substantially increased due to the increase in the number of Ni–Ni interactions. Hence, the results show that the magnetic structure of the deposit with low manganese content in nickel rich phases (deposits 6–9) differ from low nickel in manganese rich phases (deposits 1–4).
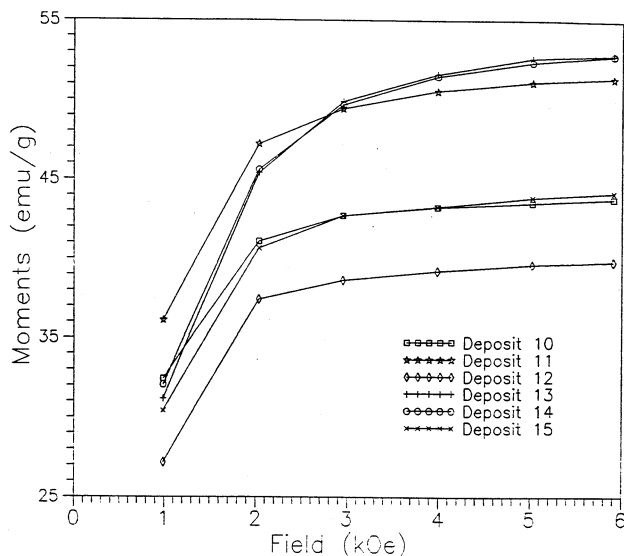
Fig. 2. Influence of bath concentration on the saturation magnetization (σ_s) of Ni–Mn alloys electrodeposited at 60 mA cm^{-2}.

In the above manner, deposits were plated with a higher current density of 60 mA cm^{-2} and their magnetization behaviour are shown in Fig. 2. For the deposits 10–12, MnSO$_4$ concentration was fixed at 150 g l^{-1} but NiSO$_4$ was varied from 40 to 120 g l^{-1}. The magnitude of the σ_s is found to depend on the nickel concentration in the bath. However, deposit 12 shows lower σ_s values. In the case of deposits 13–15, MnSO$_4$ was decreased from 120 to 25 g l^{-1}, whereas NiSO$_4$ was kept at 150 g l^{-1}. The magnitude of σ_s increases with decrease of manganese concentration in the bath. However, the deposit with diluted MnSO$_4$ concentration (deposit 15) shows a fall in σ_s values. The fall in σ_s seen for deposits 12 and 15, despite enrichment in nickel, is due to increase in particle sizes as was the case seen earlier for the samples prepared at 30 mA cm^{-2}. For all the samples prepared at 60 mA cm^{-2}, the particle size, as calculated from XRD investigations, falls in the range from 15 to 17 nm, except samples 12 and 15. A much larger particle size of 25 nm was found in deposits 12–15. The general reduction witnessed in particle size for samples prepared at higher current densities is as per expectations [12]. Also in these deposits we have observed that moments increase linearly up to the field of 3 KOe and reach saturation. The magnetic phases prevailing in the samples prepared at 60 mA cm^{-2} appear to be different from those obtained at 30 mA cm^{-2} as judged from the greater slope of the curves in the initial fields 1–2 KOe. But the influence of particle size, amongst this class, is also the same as seen in the alloys plated at lower current densities.

4. Conclusions

The magnetization behaviour of the electrodeposited Ni–Mn system can be altered to some extent by variation in Ni/Mn metal ratio in the bath. Low manganese concentrations in the baths enable production of Ni–Mn alloys of magnetization even higher than nickel. The samples, in general, exhibit increased magnetization with nickel enrichment. But, in case of abnormal increase in particle size, there is significant reduction in magnetization despite increase in nickel content.

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