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Correlation between crystallographic texture, microstructure and magnetic properties of pulse electrodeposited nanocrystalline Nickel–Cobalt alloys

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ABSTRACT

This paper reports the evolution of microstructure and texture in Nickel–Cobalt electrodeposits fabricated by pulse electrodeposition (PED) technique and the correlation of these attributes with the magnetic properties. The structural and microstructural investigation using X-ray diffraction and transmission electron microscopic studies indicate the presence of nanocrystalline grains and nanotwins in the electrodeposits. Convoluted Multiple Whole profile fitting reveals an increase in dislocation density and twin density with increasing cobalt content in the as-deposited samples. Strengthening of <111> fibre texture and weakening of <200> fibre texture with increasing cobalt concentration has been observed with X-ray texture analysis. A corresponding significant increase in the saturation magnetization and coercivity observed with increasing cobalt content. A significant improvement in the soft magnetic character in the electrodeposits in terms of increase in saturation magnetization and decrease in coercivity has been observed with thermal annealing.

1. Introduction

Nickel–cobalt binary alloys are the promising engineering materials for industrial application owing to their superior properties like high strength [1], good wear resistance [2], heat-conductivity and electro-catalytic activity [3]. These alloys are particularly more important in electronic industry for their use in memory drums and tapes [4] because of their superior magnetic properties as compared to pure metals [5]. Some of the potential application of Ni–Co alloys are sensors, actuators and micro-relays [6,2]. In addition, for the technological application, it is necessary to develop materials with superior combination of functional and mechanical properties. Nanocrystalline materials with thermally stable microstructure are desirable for improved properties in service [7,8]. However, the presence of excess defects in the form of grain boundaries leads to instability in the microstructure [9]. Therefore, for the potential use of these materials, it is essential to have high thermal stability of the microstructure.

Amongst the several available methods [10–12], electrodeposition is the most simple and economical route to fabricate nanocrystalline Ni–Co samples. In addition, it is also easy to tune the microstructure, morphology and composition of the deposits by controlling the process parameters and bath conditions during electrodeposition [13,14]. So far, electrodeposition has been employed for the synthesis of metallic coatings such as Ni–Fe [15], Zn–Mn [16], Zn–Ni [17] etc. In-spite of the fact that Ni–Co exhibits excellent magnetic properties, no rigorous work has been carried out on the evolution of texture and microstructure in nanocrystalline electrodeposits materials and its correlation with magnetic properties. It is envisaged that there is plenty of scope to improve the properties (saturation magnetization and coercivity) by suitable optimization of electrodeposition process parameters. Dolati et al. [18] have studied the effect of Co^{2+} ion concentration on the cathodic electrodeposition of Ni–Co. Chung et al. [19] studied the role of pulse electrodeposition on the fabrication of smooth and densely packed films. Recently, Madhavan et al. have studied the effect of deformation texture on the magnetic properties of Ni–20Co electrodeposits [20].

Investigations on Ni–Co electrodepoits fabricated by co-electrodeposition have indicated that the magnetic properties strongly depend on the cobalt content in the binary alloy. The effect of several deposition parameters such as pH, bath current, electrolyte composition and temperature on the hardness, strength and magnetic properties of binary Ni–Co alloys have been extensively studied and reported [21–23]. It is reported that the presence of crystallographic preferred orientation of crystals strongly influence the magnetocrystalline anisotropy of the film. For FCC

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Ni–Co crystal, easy axis of magnetization lies along ⟨1 1 1⟩ direction of unit cell [24]. Nasirpouria et al. [25] have reported that for the nanocrystalline nickel films having preferred ⟨1 1 1⟩ crystallographic texture, the magnetocrystalline anisotropy factor facilitates the saturation when the field is applied perpendicular to the electrodeposit. However, the same is not true for films having preferred (100) orientation. There are ample literature available that report the correlation between electrodeposition conditions and the thermal stability [26], microstructure and magnetic properties of the films [14]. However, a systematic study on the effect of different process parameters on the texture, microstructure and magnetic properties of Ni–Co electrodeposit have not been documented. In the present study, a detailed analysis has been performed to understand the correlation between structure-texture-magnetic properties of electrodeposited Ni–Co electrodeposits.

2. Experimental

2.1. Synthesis of nanocrystalline nickel–cobalt alloys

Nano-crystalline Ni–Co electrodeposits with varying cobalt concentrations were deposited using pulse electro-deposition technique. Pure nickel and cobalt plates were used as anodes, and titanium was used as a cathode substrate. The electrolyte used for the deposition consists of cobalt sulphate, nickel sulphate, nickel chloride, boric acid, and saccharin. The electrolyte was contained in a double jacketed glass jar and is stirred continuously by a magnetic stir bar. Two pulse power supplies (one for each of the anodes) were used with a pulse on-time of 5 ms and off-time of 40 ms (duty cycle = 11.11%). A schematic of electrodeposition set up used in the present study is shown in Fig. 1. The pH of the electrolyte was maintained at 2 and was measured using a digital μ-pH meter (SYSTRONICS, Model – μ pH system 361). The temperature of the bath was maintained at 65 °C, to enhance the diffusivities of Ni and Co ions in the electrolytic medium, by circulating hot water through the jar. The bath concentration in terms of the ratio of nickel sulphate and cobalt sulphate was adjusted to obtain Ni–Co deposits with specific alloy composition. The composition of the electrolyte bath used in the present study is listed in Table 1. The composition of the electrodeposits across the thickness was determined by wavelength dispersive spectroscopy (WDS) using an Electron Probe Micro-Analyzer (EPMA) (JEOL JXA-8530F).

Table 1
Bath conditions and deposition parameters for electrodeposition of Ni–Co alloys.

Bath composition	Concentration
Nickel Sulfate ($NiSO_4{\cdot}7H_2O$)	150 to 300 g/L
Cobalt Sulfate ($CoSO_4{\cdot}7H_2O$)	5–60 g/L
Boric Acid (H_3BO_3)	45 g/L
Saccharine ($C_7H_4NNaO_3S{\cdot}H_2O$)	0 to 2 g/L
Electrodeposition parameter	**Value**
Current density	0.2 A/cm^2
t_{on} and t_{off}	5 and 40 ms
pH	2
Temperature	340 K

2.2. Characterization of as-deposited samples

The structural characterization of the as-deposited samples was performed by X-ray diffraction (Bruker D8 Discover) with Cu Kα radiation, and by transmission electron microscopy using FEI Tecnai T20 transmission electron microscope (TEM) operating at 200 kV. Crystallographic textures of the deposited samples were measured using X-ray texture goniometer which is based on Schulz reflection technique. Three incomplete pole figures, namely (1 1 1), (2 0 0) and (2 2 0) were measured along Psi (ψ) from 0 to 75° with a step of 3° and around Phi (φ) from 0 to 360° with a step of 3°. Measured data were plotted and analysed using Labotex texture analysis software. The magnetic properties of the samples was measured using a LakeShore Vibrating Sample Magnetometer (VSM). The thermal stability of the as-deposited samples were evaluated by performing heating and cooling cycle in a differential scanning calorimetry (DSC) (METTLER) at a scanning rate of 10 K/min. The samples were retained for further grain size measurement studies through X-ray diffraction and transmission electron microscopy (TEM).

3. Results and discussion

3.1. Deposition process

The composition of the electrodeposits is varied by adjusting the ratio of cobalt sulphate to nickel sulphate concentrations in the bath electrolyte. Fig. 2 shows that the cobalt concentration in

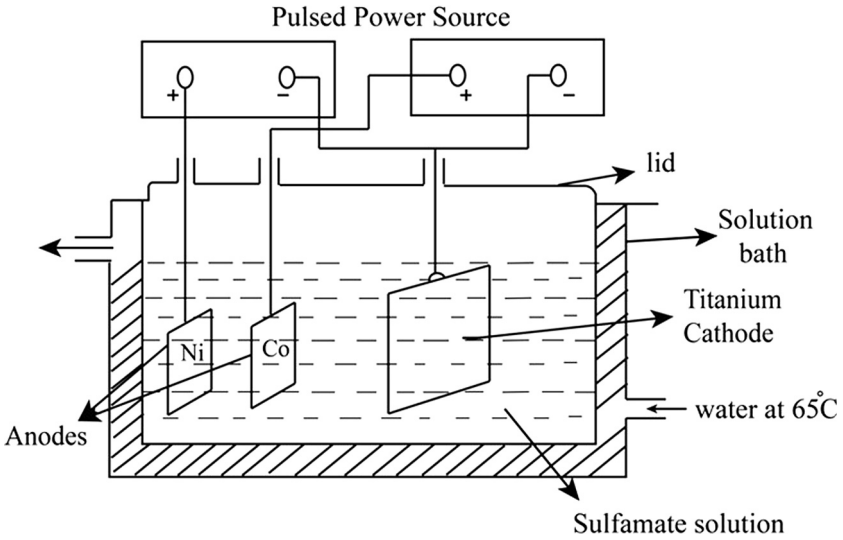

Fig. 1. Schematic of electrodeposition setup used in the present study.