

# Synthesis and magnetic properties of Fe-Ni and Cu-Ni composite coatings

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This paper reports some results concerning the preparation and magnetic properties of Fe-Ni and Cu-Ni composite coatings obtained by codeposition process. Fe-Ni and Cu-Ni composite coatings were electrochemically synthesized from iron and copper sulphate baths, respectively, containing Ni nanoparticles with sizes ranging between 250 and 500 nm. The surface morphology of the obtained coatings was studied by scanning electron microscopy and atomic force microscopy. Structural investigations of the samples were performed by X-ray diffraction technique. The reduced hysteresis loops as well as the temperature dependence of the reduced magnetization was carried out using a vibrating sample magnetometer, in an external magnetic field of 600 kA/m.

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**Keywords:** Codeposition process, Composite coatings, Reduced hysteresis loops, Fe-Ni and Cu-Ni coatings

## 1. Introduction

The codeposition of metallic nanoparticles within an electroplating process is a promising technique that offers the opportunity of obtaining new materials with unique physical, chemical and mechanical properties for different engineering applications. During electrodeposition, insoluble particles, which are added to the plating bath, can be incorporated in the deposit. The coatings obtained by this process are usually called composite coatings. The embedded particles can be selected to fulfil specific mechanical, electrical, piezoelectrical or magnetic properties in thin coatings. Magnetic particles embedded in a nonmagnetic matrix exhibit giant magnetoresistance phenomena and are currently under investigation for applications in magnetic recording heads [1].

A very rigorous model focused on codeposition of spherical particles on a rotating disk electrode has been developed by Fransaer et al. (1992), clearly demonstrating the complexity of the codeposition process. This model takes into account all forces acting on a particle, divided into hydrodynamic forces and other forces, including gravity, buoyancy and particle-electrode interaction forces [2].

In this paper we reports some results concerning the preparation and magnetic properties of Fe-Ni and Cu-Ni composite coatings obtained by codeposition process. Fe-Ni and Cu-Ni composite coatings were electrochemically synthesized from iron and copper sulphate baths, respectively, containing Ni nanoparticles with sizes ranging between 250 and 500 nm.

## 2. Experimental details

Composite Fe-Ni and Cu-Ni coatings were electrochemically synthesized from iron and copper sulphate baths, respectively, containing commercial Ni nanoparticles (Carbonyl-Nickel pulver from Fluka).

Electrochemically deposition of the samples was performed using an electrochemical cell with three electrodes. The synthesis of all electrodeposits containing Ni nanoparticles was controlled by a potentiostat PGZ 100.

Fig. 1 shows schematically the electrodeposition procedure for the preparation of the Fe-Ni and Cu-Ni composite coatings.

For the electrodeposition of composite coatings a platinum piece was used as counter electrode and an Ag/AgCl electrode as reference electrode. The composite coatings were electrodeposited onto non-magnetic substrates: Cu foil with average thickness of 100  $\mu\text{m}$  having a surface area of 4  $\text{cm}^2$ , or glass substrates with a surface area of 1.32  $\text{cm}^2$ , over which an electroconductive thin film of about 100 nm (Au/Cr) was deposited by thermal evaporation.

The process was carried with intensive mechanical stirring (1700 rpm) to maintain the Ni nanoparticles in suspension.

The size distribution of the Ni nanoparticles was determined by Dynamic Light Scattering (DLS), with a Nanotracc device. The size of Ni nanoparticles ranges between 250 – 500 nm.

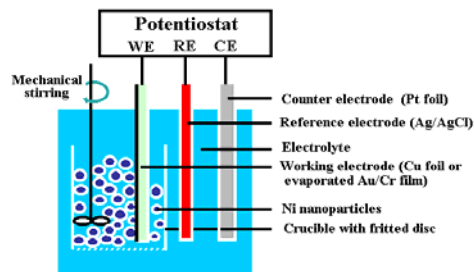


Fig. 1. Schematic diagram of the electrodeposition process.

The plating bath composition for the electrodeposition of Fe-Ni composite coatings was:  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (420 g/l),  $\text{K}_2\text{SO}_4$  (1 g/l),  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  (1 g/l) and  $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$  (85 g/l). The plating bath composition for the

electrodeposition of Cu-Ni composite coatings was:  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (250 g/l) and  $\text{H}_2\text{SO}_4$  (9.2 g/l). The plating conditions for obtaining Fe-Ni and Cu-Ni composite coatings are shown in Table 1.

Table 1.

Plating conditions	Composite coatings			
	Fe-Ni onto Cu foil	Fe-Ni onto Au/Cr thin film	Cu-Ni onto Cu foil	Cu-Ni onto Au/Cr thin film
Temperature ( $^{\circ}\text{C}$ )	60	40	40	40
pH	1.32	1.32	1.05	1.05
Current density ( $\text{mA}/\text{cm}^2$ )	112.6	22.7-37.8	32.5-42.5	7.5-15.2
Ni nanoparticles in solution (g/l)	20-40	20	60	60
Electroplating time (minutes)	35	15	60-120	15

The crystallographic structure of electroplated Fe-Ni and Cu-Ni composite coatings was examined by X-ray diffraction analysis (XRD). A X-ray diffractometer with monochromatized  $\text{Co K}\alpha$  radiation ( $\lambda = 0.1789 \text{ nm}$ ) was used.

The reduced hysteresis loops as well as the temperature dependence of the reduced magnetization of the samples were carried out using a vibrating sample magnetometer (VSM), in an external magnetic field of 600 kA/m.

### 3. Results and discussion

#### 3.1. Morphology of the electroplated composite coatings

The surface morphology of the electroplated composite coatings was studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM). In Fig. 2 the surface morphology of Cu-Ni composite coatings onto Cu foil (a) and onto Au/Cr thin film (b), are shown.

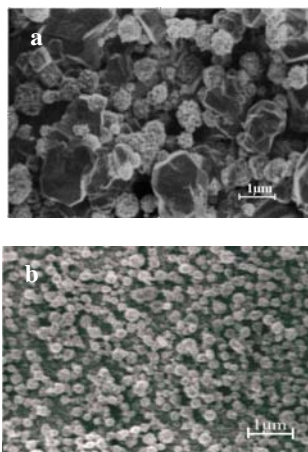


Fig. 2. SEM micrographs of Cu-Ni composite coating.

During vigorous agitation of plating solution, the Ni nanoparticles are driven to the cathode and are embedded in the growing Fe or Cu layers, respectively.

Fe-Ni and Cu-Ni composite coatings present a mat and rough surface, the roughness of obtained composites being affected by amount of embedded Ni nanoparticles.

The thickness of the obtained Fe-Ni composite coatings onto Cu foil ranged between 10-12  $\mu\text{m}$  and 10-20  $\mu\text{m}$  for Cu-Ni composite coatings, respectively. The thickness of the obtained Fe-Ni and Cu-Ni composite coatings onto Au/Cr thin film ranged between 2.5-16  $\mu\text{m}$  and 3.25-6.45  $\mu\text{m}$ , respectively.

The Fe-Ni and Cu-Ni composite coatings prepared by electrodeposition show good adhesion to the copper and Au/Cr thin film. The Ni nanoparticles are uniformly embedded into the iron and copper matrix with tendency to agglomerate.

#### 3.2. Structural features of the composite coatings

The X-ray diffraction patterns (figure 4) of Fe-Ni composite coatings onto Cu foil (a) and onto Au/Cr thin film (b), show the presence of sharp reflexes, characteristic for Fe and for embedded Ni nanoparticles, and also the sharp reflexes, characteristic for Cu foil and Au/Cr thin film substrates, respectively.

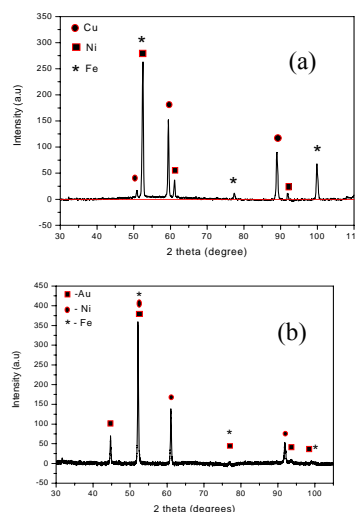


Fig. 4. X-ray diffraction pattern of the Fe-Ni composite coatings.

### 3.3. Magnetic properties of Fe-Ni and Cu-Ni composite coatings

In Fig. 5 the temperature dependence of the reduced magnetization (a) and the hysteresis loops (b) as a function of the Ni content in plating bath for the Fe-Ni composite coatings onto Cu foil, are presented.

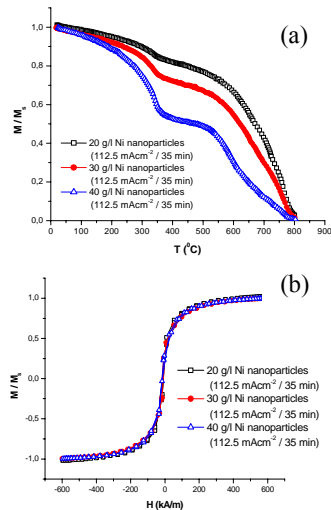


Fig. 5. Temperature dependence of reduced magnetization and hysteresis loops of Fe-Ni composite coatings as a function of Ni content in plating bath.

The temperature dependence of reduced magnetization of Fe-Ni composite coatings indicates clearly the presence of Ni nanoparticles embedded in Fe coating through Curie temperatures of Ni ( $\sim 380^\circ\text{C}$ ) and Fe ( $\sim 770^\circ\text{C}$ ). The composition of Fe-Ni composite coatings depends strongly on Ni nanoparticles content in the plating bath. A higher content of Ni nanoparticles in the Fe matrix is obtained for a concentration of Ni nanoparticles in the plating bath of 40 g/l. Fe-Ni composite coatings onto Cu foil, have coercivities  $H_c$  between 2 and 2.5 kA/m.

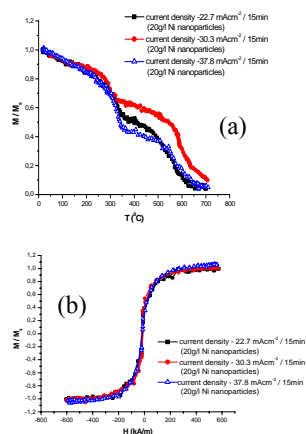


Fig. 6. Temperature dependence of the reduced magnetization and hysteresis loops of Fe-Ni composite coatings as a function of applied current density in plating bath.

In Fig. 6 the temperature dependence of reduced magnetization (a) and the hysteresis loops (b) of Fe-Ni composite coatings electrodeposited onto Au/Cr thin film at various current densities, are shown. A higher content of the embedded Ni nanoparticles was obtained with increase of applied current density.

Fe-Ni composite coatings electrodeposited onto Au/Cr thin film, have coercivities  $H_c$  between 2 and 6 kA/m.

In Fig. 7 is shown the temperature dependence of reduced magnetization (a) and hysteresis loops (b) of Cu-Ni composite coatings electrodeposited onto Au/Cr thin film at various current densities.

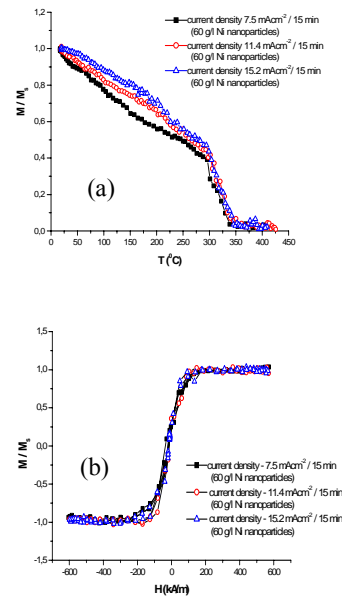


Fig. 7. Temperature dependence of the reduced magnetization and hysteresis loops of Cu-Ni composite coatings as a function of applied current density in plating bath.

The composition of Cu-Ni composite coatings depends also on the current densities, a higher content of the embedded Ni nanoparticles was obtained with increase of applied current density. Cu-Ni composite coatings onto Au/Cr thin film have coercivities  $H_c$  between 3 and 12 kA/m.

## 4. Conclusions

Fe-Ni and Cu-Ni composite coatings can be electrodeposited from aqueous iron and copper sulphate baths, respectively, containing Ni nanoparticles between 250 and 500 nm diameter. The obtained Fe-Ni and Cu-Ni composite coatings electrodeposited onto Cu foils and Au/Cr thin films present good magnetic properties.

The principals parameters for uniformly embedding of Ni nanoparticles in iron and copper matrix during the codeposition process are: concentration of Ni

nanoparticles in plating bath, current density, deposition time and mechanical stirring speed.

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