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Preparation and magnetic properties of Fe-Ni and Cu-Ni composite coatings

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This paper reports some results on the preparation and magnetic properties of Fe-Ni and Cu-Ni composite coatings. Fe-Ni and Cu-Ni composite coatings have been synthesised by chemical electrodeposition in a three electrode cell. The morphology of electrodeposited composite coatings was studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Structural investigations of the samples were performed by X-ray diffraction (XRD). The reduced hysterezis 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.

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Keywords: Fe-Ni and Cu-Ni, Composite coatings, Electrodeposition process, Magnetic properties

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 [1]. Magnetic particles embedded in a nonmagnetic matrix exhibit giant magnetoresistance phenomena and are currently under investigation for applications (e. g. magnetic heads, recording media, etc.).

Three main mechanisms were previously suggested to explain the difference in the ability to deposit various types of solid particles:

(1) mechanical entrapment: the particles are driven to the cathode by vigorous bath agitation and are incorporated in the growing metal layer only if the contact period is long enough and the metal deposition rate is high enough;

(2) electrophoresis: charged particles are moving under the influence of an applied electric field. The electrophoretic velocity is directly proportional to the zeta potential (ξ-potential), which is defined as the potential at the shear surface;

(3) adsorption: near the cathode, particles will be subjected to various attractive forces. Once adsorbed onto the cathode, the particles are embedded in the growing metal layer.

One of the earlier models, often cited in literature on codeposition, was developed by Guglielmi. It considers two different adsorption steps, but hydrodynamic effects are not taken into account [2].

In this work, we report some results on the preparation and magnetic properties of Fe-Ni and Cu-Ni composite coatings obtained by codeposition process.

2. Experimental details

Composite Fe-Ni and Cu-Ni coatings were electrochemically synthesised 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.

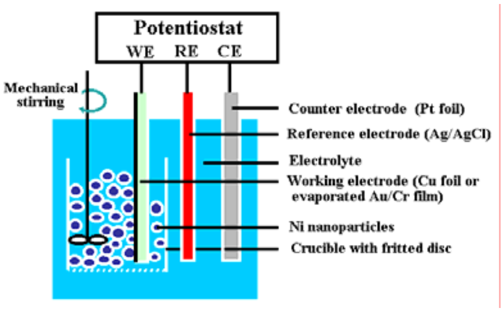


Fig. 1. Schematic diagram of the electrodeposition process.

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 µm and with a surface area of 4 cm^2, or glass substrates with a surface area of 1.32 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 were determined by Dynamic Light Scattering (DLS), with a Nanotrac device. The size of Ni nanoparticles ranges between 250 – 500 nm.

The plating bath composition for the electrodeposition of Fe-Ni composite coatings was: $FeSO_4 \cdot 7H_2O$ (420 g/l), K_2SO_4 (1 g/l), $H_2C_2O_4 \cdot 2H_2O$ (1 g/l) and $Al_2(SO_4)_3 \cdot 18\ H_2O$ (85 g/l). The plating bath composition for the electrodeposition of Cu-Ni composite coatings was: $CuSO_4 \cdot 5H_2O$ (250 g/l) and H_2SO_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 for obtaining composite coatings.

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	60	40	40	40
pH	1.32	1.32	1.05	1.05
Current density (mA/cm^2)	112.6	22.7-37.8	32.5-42.5	7.5-15.2
Content of Ni nanoparticles in solution (g/l)	20-40	20	60	60
Electroplating time (minutes)	35	15	60-120	15

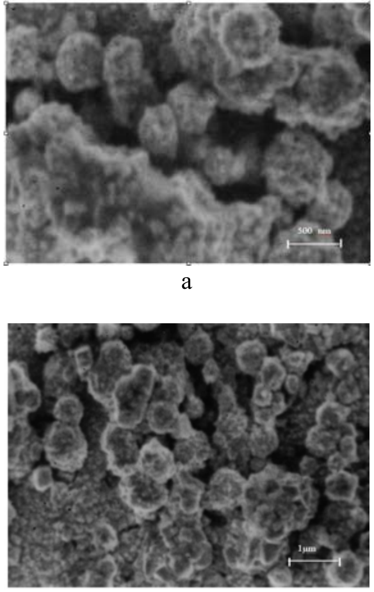
The crystallographic structure of electroplated Fe-Ni and Cu-Ni composite coatings was examined by X-ray diffraction analysis (XRD). An X-ray diffractometer with monochromatized Co Kα radiation (λ = 0.1789 nm) was used.

The reduced hysterezis 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

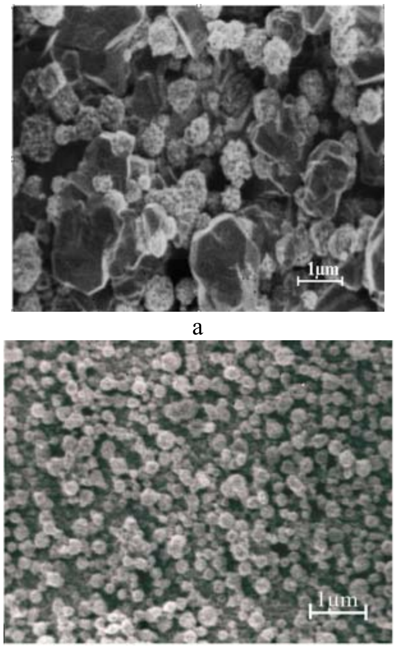
The surface morphology of the electroplated composite coatings was studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM). In fig. 2 are shown the surface morphology of Fe-Ni composite coating onto Cu foil (a) and Fe-Ni onto Au/Cr thin film (b). Fig. 3 shows the surface morphology of Cu-Ni composite coating onto Au/Cr thin film (a and b) and a cross-section of Cu-Ni composite coating onto Cu foil (c).



a

b

Fig. 2. SEM micrographs of Fe-Ni composite coatings.



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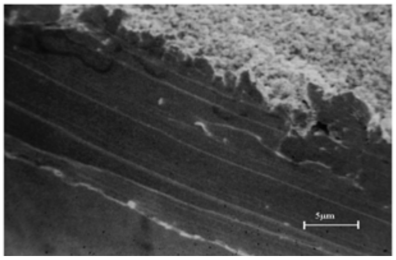


c

Fig. 3. SEM micrographs of Cu-Ni composite coatings.

In Fig. 4 is shown an AFM 3-d image of as-prepared Cu-Ni composite coatings onto Au/Cr thin film.

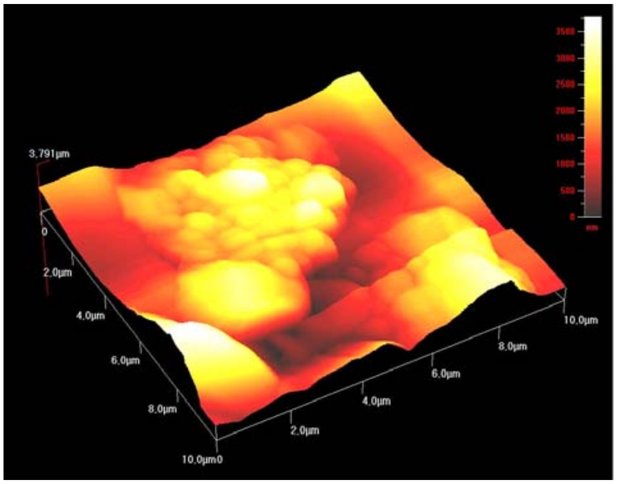


Fig. 4. AFM 3-d image of Cu-Ni composite coating.

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

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

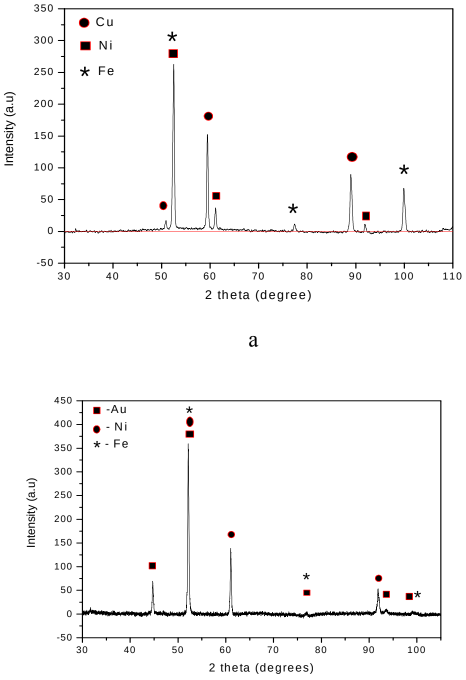
The thickness of the obtained Fe-Ni composite coatings onto Cu foil ranged between 10-12 µm and 10-20 µm, respectively, for Cu-Ni composite coatings. The thickness of the obtained Fe-Ni and Cu-Ni composite coatings onto Au/Cr thin film ranged between 2.5-16 µm and 3.25-6.45 µm, respectively.

The Fe-Ni and Cu-Ni composite coatings prepared by electrodeposition show good adhesion to the copper foil 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 (Fig. 5) 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 matrix and for embedded Ni nanoparticles and also the sharp reflexes, characteristic for Cu foil and Au/Cr thin film substrates, respectively.

The X-ray diffraction patterns (Fig. 6) of Cu-Ni composite coatings onto Cu foil (a) and onto Au/Cr thin film (b), show the presence of sharp reflexes, characteristic for Cu matrix and for embedded Ni nanoparticles and also the sharp reflexes, characteristic for Au/Cr thin film substrate.

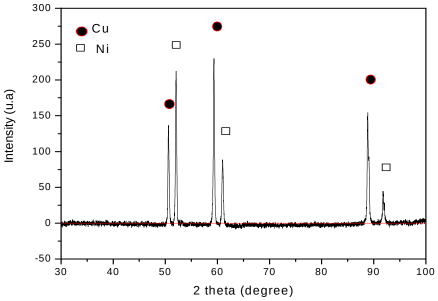


a

b

Fig. 5. X-ray diffraction patterns of Fe-Ni composite coatings.

In Fig. 6 are presented the X-ray diffractions patterns of Cu-Ni composite coatings onto Cu foil (a) and onto Au/Cr thin film (b).



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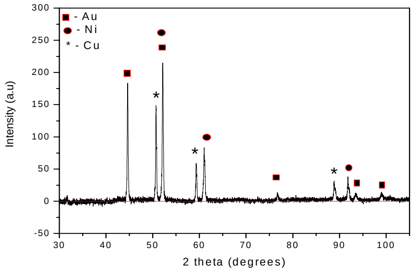


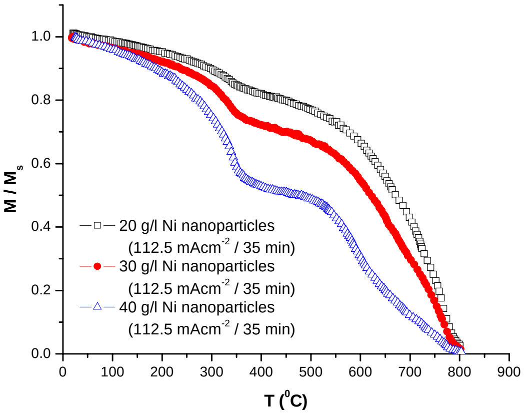
b

Fig. 6. X-ray diffraction patterns of Cu-Ni composite coatings.

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

In Fig. 7 are presented 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.

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 (~380ºC) and Fe (~770ºC). 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.



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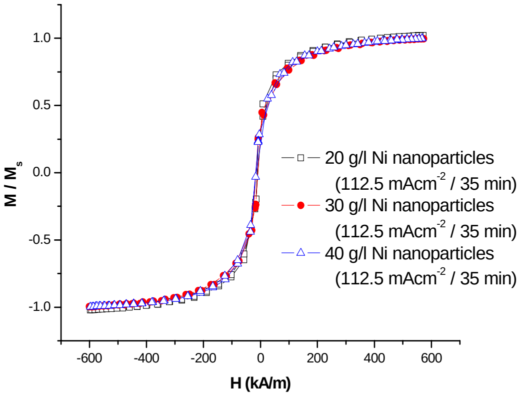
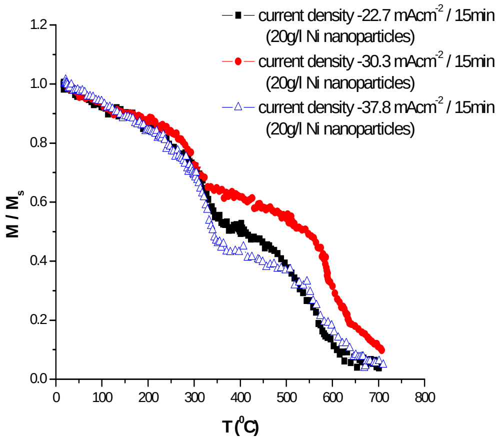


b

Fig. 7. Temperature dependence of reduced magnetization and hysteresis loops of Fe-Ni composite coatings as a function of Ni content in plating bath.

In Fig. 8 are shown 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. A higher content of the embedded Ni nanoparticles was obtained with of 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.



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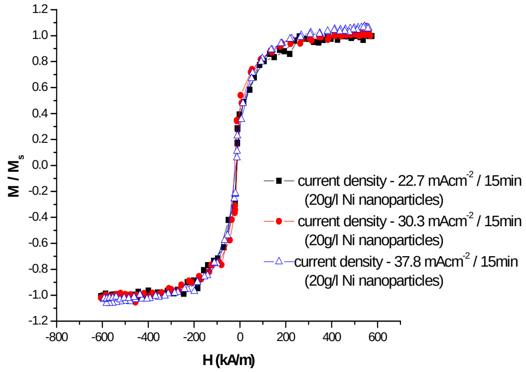
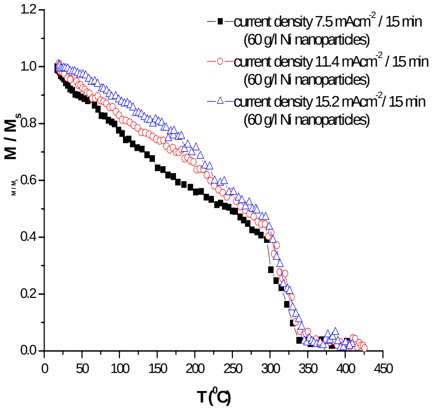


b

Fig. 8. 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. 9 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.

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



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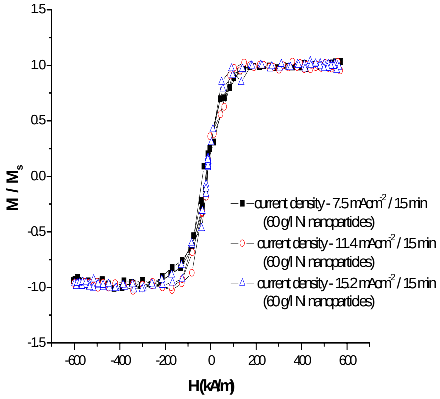

b

Fig. 9. Temperature dependence of the reduced magnetization (a) and hysteresis loops (b) of Cu-Ni composite coatings as a function of applied current density in plating bath.

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 exhibit good magnetic properties.

The main 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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