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ELECTRODEPOSITION AND CHARACTERISATION OF THIN MAGNETIC Ni-Fe FILMS ON COPPER SUBSTRATES

ELEKTROOSADZANIE I CHARAKTERYSTYKA CIENKICH WARSTW MAGNETYCZNYCH Ni-Fe NA PODŁOŻU Z MIEDZI

In the present work, conditions for the Ni-Fe alloy electrodeposition on polycrystalline copper substrates from weakly acid sulphate-citrate electrolytes have been developed. Total and partial polarization curves for the deposition of nickel and iron separately as well as for their codeposition under controlled hydrodynamic conditions were determined. It has been established that Ni-Fe deposition process is mainly controlled by the mass transfer of the Fe(II) species towards the electrode. The chemical composition of such electrochemically produced films varies with their thickness, which significantly affects their physical properties. The change in coercive force of films as a function of thickness has been investigated and discussed, taking into account the influence of the chemical composition gradient of Ni-Fe alloy.

Keywords: electrodeposition, Ni-Fe films, citrate baths

Praca przedstawia wyniki badań poświęconych procesowi elektroosadzania, na podłożu z polikrystalicznej miedzi, warstw stopów dwuskładnikowych Ni-Fe ze słabo kwaśnych kąpieli siarczanowo-cytrynianowych. Określono, dla stałych i kontrolowanych warunków hydrodynamicznych, całkowite oraz parcjalne krzywe polaryzacji katodowej dla procesu indywidualnego osadzania niklu i żelaza oraz dla ich współwydzielania. Ustalono, że proces elektroosadzania stopu Ni-Fe kontrolowany jest głównie ograniczeniem dyfuzyjnym reakcji elektroredukcji jonów Fe(II). Skład chemiczny uzyskanych warstw zmienia się z ich grubością, co znacznie wpływa na ich właściwości fizyczne. Określono i przedyskutowano zmiany siły koercji warstw Ni-Fe w funkcji grubości, uwzględniając występujący w nich gradient składu.

1. Introduction

The Ni-Fe alloys have unique magnetic properties and they could have a wide range of application. Thin magnetic films of Ni-Fe alloy are used in storage and memory devices and are applicable as magnetic sensors [1-4]. Ni80Fe20 alloy, known as permalloy, is particularly interesting because of its non-magnetostrictive characteristics. The Ni-Fe alloy coatings can also be used as decorative and protective materials. Among the several methods for preparation of Ni-Fe layers, electrolysis has proven to be an efficient, low cost and suitable for automation technique [5-7]. In addition, the electrodeposition process of these binary alloys is also worthy of interest for theoretical reasons. It is characterized by a so called anomalous behaviour i.e. the less noble metal (iron) deposits preferentially [8]. Hence, the percentage of iron in the electrochemically produced Ni-Fe alloy is higher than in the bath from which it is deposited. Moreover, a trend to a composition gradient as a function of the film thickness occurs owing to the lower deposition rate of nickel compared to that of iron. This phenomenon is not yet sufficiently understood and electrodeposition process requires a more rigid control of the plating conditions. Although several hypothesis [9] have proposed various explanations of the anomalous codeposition this mechanism is still not clear.

In the present work, the effect of the Ni-Fe citrate electrolyte composition on the partial polarisation behaviours was investigated under potentiostatic conditions using a rotating disk electrode (RDE) system. The relationship between electrodeposition parameters, structural and magnetic properties have also been determined.

2. Experimental procedure

The Ni-Fe films were deposited electrochemically from a sulphate-citrate baths containing 0.5-0.75 M

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$NiSO_4$, 0.22 M $Na_3C_6H_5O_7$, 0.03-0.05 M $FeSO_4$, 1.1 g/l NaCl, 0.6 g/l saccharin of the pH 4.2. The electrolysis was carried out in 750 ml cell in a system with a rotating disc electrode (RDE), supplied by the potentiostat PARA 273A. The deposition was conducted at a bath temperature of 25°C. The cathode were the polycrystalline copper or silver disks of 0.028 dm^2 rotating at 11 - 68 rad s^{-1}, whereas a platinum sheet (0.05 dm^2) was used as anode. The cathode potentials were referred to the saturated calomel electrode (SCE) and were corrected for ohmic drop by the current interrupt method. The charge used for hydrogen evolution was calculated from the difference between the charge which was passing and the charge used to deposit nickel and iron. The cell was surrounded by a coil which generated a uniform magnetic field (10-100 Oe). Chemical analysis of the deposits has been carried out by atomic absorption spectroscopy method using UNICAM 09 spectrophotometer. Additionally, the Ni-Fe chemical composition was determined by electron dispersive spectroscopy (EDS) using a LINK-ISIS apparatus. Thickness of films was estimated from amounts of deposited metals and current efficiency. It was controlled by microscopy (SEM) observations and by multi-beam interference method. The morphology of films was evaluated by scanning electron microscopy on a SEM Philips XL-30. Texture and the phase composition of the deposits were studied by an XRD method (Philips PW 1710, X'Pert-ATC3, CoK_α cathode). The coercive force (H_c) and the anisotropy field (H_k) of the films were measured using a hysteresiscope. A domain walls were revealed by the Bitter's powder figure method (using colloidal suspension of Fe_3O_4 particles).

3. Results and discussion

3.1. Electrochemical study

The standard single electrode potentials for Ni and Fe are ca. 0.2 V apart (Ni^{2+}/Ni: $E^0 = -0.25$ V/SHE; $Fe^{2+}/Fe = -0.44$ V/SHE). Complex sulfate-citrate electrolytes were used to bring the deposition potentials of these metals closer. From the results of investigations of the citrate complexes of Ni(II) it follows that the nature and concentration of the complex compounds depend mainly on pH and on the bath composition [10]. In the investigated conditions (pH = 4.2) nickel ions occur mainly as aqua-complexes and neutral citrate or sulfate complexes: $[NiH_2Cit]^0$ and $NiSO_4^0$ (Cit = $[C_6H_4O_7]^{4-}$). Citrate Ni(II) complexes form preferentially to Fe(II)-citrate compounds: $[FeH_2Cit]^0$ and $[FeHCit]^-$, which dominate in pH range 3-8 [11, 12]. Moreover, the Fe(II) ions easily undergo an oxidation by air oxygen and probably the mixed valence complexes as $[Fe^{II}Fe^{III}(HCit)_2]^-$ are created. It is obvious that pH changes at cathode surface during electrodeposition can involve a modification of the complex species and their equilibrium. On the other hand, citrate ion easily dissociates to give H^+ ions. The kinetics of the dissociation, which appear to be the crucial factor for surface buffering, are much faster for citrate ion than for boric acid. Hence, citrate ions provide efficient, and better than boric acid, control of the surface pH [6, 13].

The global and partial polarization curves for Ni-Fe electrodeposition were investigated for various electrode rotation speeds. These curves were compared to the polarization curves obtained for the separate discharge of nickel and iron species. Figure 1 shows an example of the polarization curves recorded for a stagnant solution (not agitated forcefully), whereas Figure 2 presents such curves recorded at 68 rad s^{-1}.

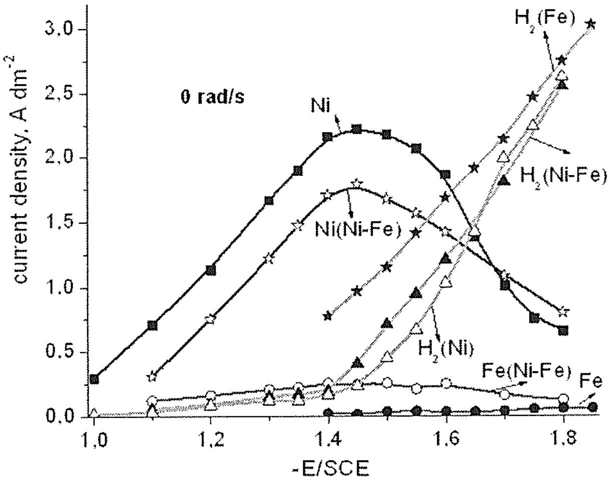

Fig. 1. Steady-state polarization curves recorded at still disk electrode for the binary Ni-Fe deposition

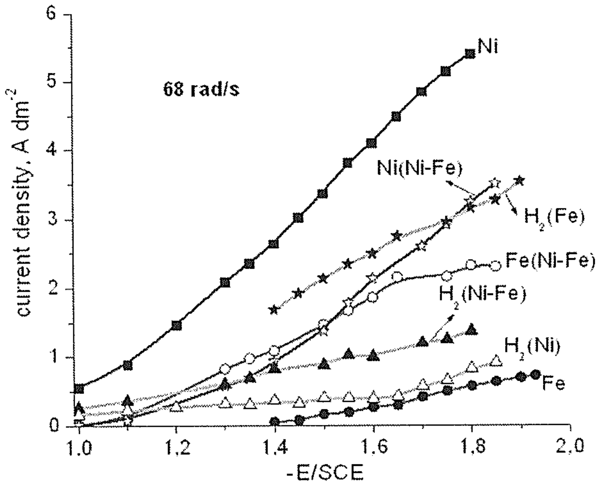

Fig. 2. Steady-state polarization curves recorded at 68 rad s^{-1} for the binary Ni-Fe deposition

As can be seen over the whole polarization range and hydrodynamic conditions (0-68 rad s^{-1}), nickel deposition is strongly inhibited compared to its separate discharge, whereas iron deposition is stimulated. Under the examined conditions, Ni-Fe electrodeposition shows an anomalous behaviour with less noble iron being the preferentially deposited metal. The effect, related to the kinetics of Fe(II) discharge, becomes more distinct when the electrode rotation speed is increased. As it is clearly seen from Fig. 2, the Fe(II) diffusion-controlled discharge is obtained at higher cathode polarization, where a linear dependence of the partial current as a function of the square root of the electrode rotation speed is observed. Consequently, nickel content and current efficiency are reduced with decreasing thickness of the diffusive layer. In the case of a stagnant bath (Fig. 1), a decrease of the Ni(II) electroreduction rate occurs, at the cathode potentials lower than -1.4 V/SCE, and hydrogen evolution becomes the main reaction. The effect is related to the pH rise at the cathode layer, resulting in formation of iron hydroxides, which progressively block the cathode surface. The obtained results of the Ni-Fe electrodeposition kinetics in citrate solution, in comparison to the bath of the same composition but with the boric acid addition (instead of sodium citrate) [6], indicate that the alkalization of the cathodic layer plays a significant role in an anomalous co-deposition and that the mechanism of the electrode reactions is consistent with the model suggested by Dahms [9]. Simultaneously, due to the nickel preferred complexing by citrate ions, a higher rate of iron deposition and a stronger inhibition of Ni(II) discharge in citrate solution are observed.

3.2. Characterization of the Ni-Fe deposits

The XRD patterns of all electrodeposited films exhibit the fcc (face centred cubic) structure of Ni-Fe solid solutions. The scanning electron micrograph of the surface of the typical Ni-Fe film is shown in Figure 3. The films deposited from complex citrate bath show a shiny-gray appearance and compact morphology with small crystallites.

Besides the preferential deposition of less noble metal, the electrodeposition of Ni-Fe alloys has been found to have another characteristic feature of the significant composition gradient in the first several hundreds nanometers of electrodeposits [14]. Figure 4 shows as an example the percentage of iron in the Ni-Fe film in function of its thickness for various cathode current densities. It can be seen that as the current density increases, the differences in film composition are increased, the composition being fixed only when the thickness exceeds 0.3-0.4 µm.

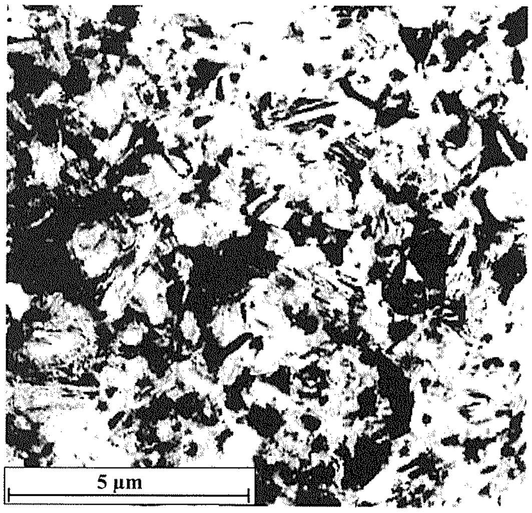

Fig. 3. SEM image of the Ni-Fe film surface (0.2 µm) electrodeposited from citrate solution with 0.6 g/l saccharin

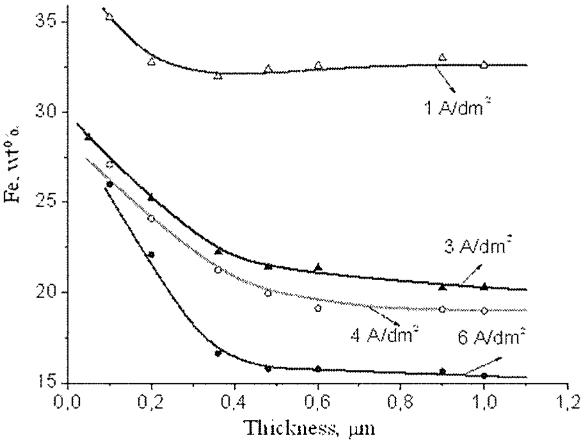

Fig. 4. Average iron content (wt%) in Ni-Fe films in function of thickness

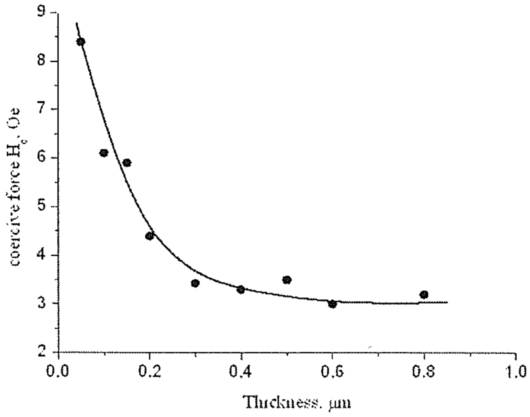

Fig. 5. Coercive force (H_c) in function of thickness of electrodeposited permalloy films, at -1.6 V/SCE

On the other hand, an increase in current density is accompanied by a decrease in the iron level. This effect is related to the diffusion control of Fe(II) discharge reaction. Since the actual cathode area is not known with sufficient accuracy because of substrate roughness, areas change during plating etc., it is difficult to determine the current density and therefore the cathode potential was used instead as a control. In order to see how the film thickness affects their magnetic properties, the films with various thicknesses were deposited, from citrate solution of Ni(II)/Fe(II) concentration ratio equals to 10, by keeping the cathode potential at -1.6 V/SCE (Fig. 5). Due to the chemical composition gradient (i.e. the decrease of the iron content in films with increasing their thickness) a decrease in the coercivity values of thicker layer is observed.

The Ni-Fe films were electrodeposited in the outer magnetic field of the intensity range of 10-100 Oe and of the same direction as the magnetic field generated, during electrodeposition process, by the electrolysis current. Two different kinds of substrates were used: the copper rolled sheet with the {110} <112>, {112} <111> texture and the silver rolled (98%) ribbon with the only one distinct {110} <112> texture. It was found (from magnetic measurements) that the easy axis is in-plane direction of the parallel film, according to direction of applied magnetic field. In the absence of the outer magnetic field, the easy direction is parallel to the <111> preferred crystallographic orientation of Ni-Fe film. It was determined that the intensity of the applied magnetic field does not essentially impact on the coercive force (H_c) values. On the contrary, a decrease of the anisotropy field parameter (H_k) value is observed, due to an increase of the film magnetic anisotropy with increasing intensity of magnetic field.

It was found that the magnetic parameters of Ni-Fe films are closely connected with nature and quality of a substrate. The best films were obtained on the copper disc, previously electrochemically covered by the smooth glossy copper sub-layer, in magnetic field of 100 Oe. Electrodeposited, under these conditions, permalloy films (0.4 μm) with bulk chemical composition of 81 wt%. Ni and 19 wt%. Fe show rectangular magnetic hysteresis loop (Fig. 6) with relatively low coercivity (H_c = 3.2±0.4 Oe), while the minimum of anisotropy field (H_k) value amount to 9.3±1.4 Oe. On the basis of the observation of the Bitter's powder figures, it was concluded, that very thin films (<0.1 μm) are characterized by the presence of the cross-tie magnetic domain walls (Fig. 7a), which have been changed to the Bloch walls with increasing thickness (Fig. 7b).

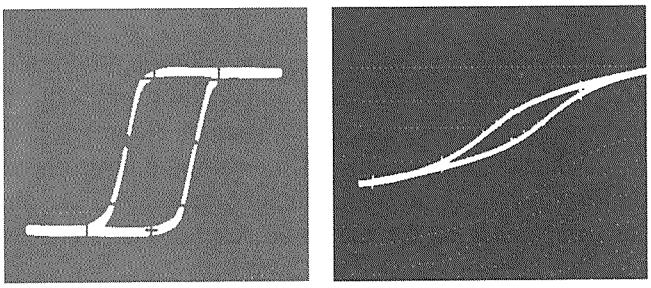

Fig. 6. Magnetic hysteresis loops for (0.4 μm) permalloy film (81 wt%Ni and 19 wt%Fe)

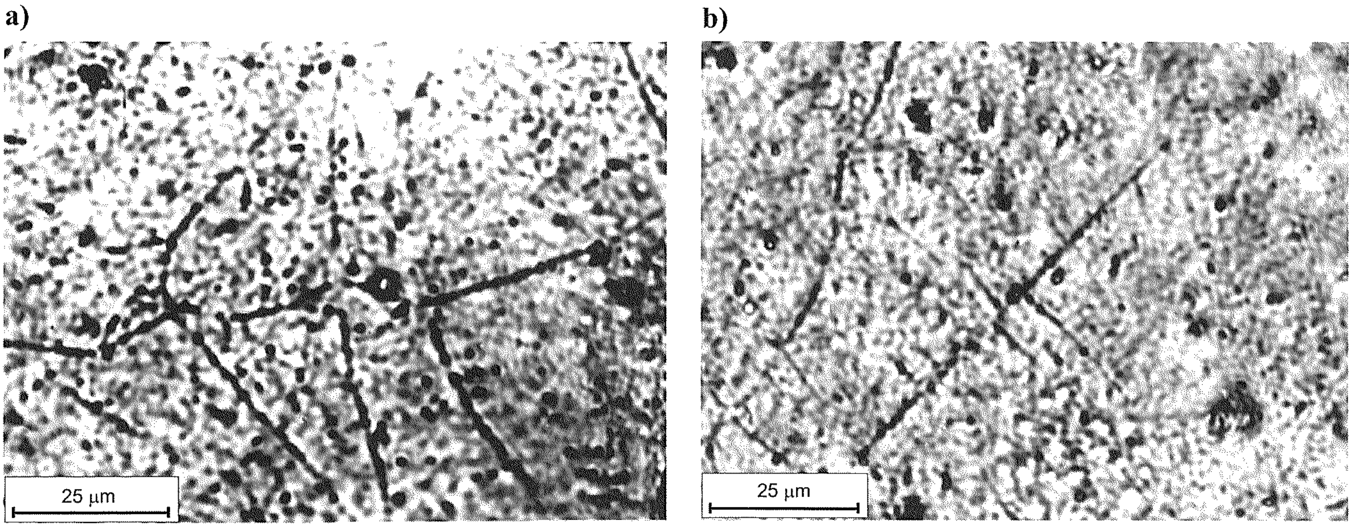

Fig. 7. The Bitter's powder figures on the surface of permalloy films: a) 0.06 μm, b) 0.4 μm

4. Conclusion

Electrodeposition is a suitable way to obtain thin films of the magnetically soft Ni-Fe alloys on the polycrystalline copper substrate from a weakly acid sulfate-citrate bath. The Ni-Fe electrodeposition shows the anomalous behaviour i.e. the less noble iron deposited preferentially with strong inhibition of the Ni(II) discharge. The effect becomes more pronounced in the presence of complexing agent, due to the nickel preferred complexing by the citrate ions. The Ni-Fe electrodeposition process is mainly controlled by the mass transfer of the Fe(II) species towards the electrode. The X-ray diffraction patterns of all electrodeposited films exhibit the fcc (face centred cubic) structure of Ni-Fe solid solutions. The magnetic measurements show that the magnetic properties are very sensitive to the film thicknesses, the nature and quality of substrate as well as to the intensity of magnetic field applied during electrodeposition process. Due to the chemical composition gradient, a compatibility between the dependence of film composition and coercive force on film thickness has been observed.

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