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Morphology and composition of the Fe–Ni powders electrodeposited from citrate containing electrolytes

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ABSTRACT

The electrodeposition of the Fe–Ni powders from citrate containing electrolytes for different Ni/Fe ions concentration ratios, using Fe(III) and Fe(II) salts at pH 4.5 and pH 4.0 respectively was investigated by the polarization measurements and cyclic voltammetry. The morphology and composition of the electrodeposited powders were investigated by SEM and EDS analysis. The EDS analysis of the alloy powders confirmed anomalous co-deposition of Fe and Ni from both solutions, with the one obtained using Fe(III) salt being more pronounced. The morphology of electrodeposited powders was found to depend on the Ni/Fe ions concentration ratio, as well as on the valence of Fe ions used. A common characteristic for all powder samples was the presence of cone shaped cavities and nodules, while for the ratio Ni/Fe =9/1 in both electrolytes pagoda like crystals, corresponding to the FeNi₃ single crystal, have been detected. In the case of Fe(III) containing electrolytes current efficiency for powder electrodeposition varied between about 15% and 8% depending on the Ni/Fe ratio.

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1. Introduction

The Fe–Ni alloys are of worldwide economic interest because of their usage in a great variety of products [1]. Due to their magnetic properties these alloys have many applications in the area of memory devices for computers, and they are also resistant to corrosion, receptive to chrome, ductile etc. [1]. Their mechanical and magnetic properties are widely investigated [2–6], while the best known example is Permalloy (Fe–Ni alloy used for soft magnetic read/write heads [7–9]).

Most of the investigations concerning their electrodeposition are in connection with the deposition of compact coatings and some of them are discussed below.

The parameters influencing the electrodeposition of Fe–Ni alloys, such as the presence of sulfate or chloride solutions, addition of boric acid, citric acid and L-ascorbic acid at different pH values (2 and 3) were investigated in the paper of Kieling [10] and Yin and Lin [11]. Among the anomalous character of Fe and Ni co-deposition these investigations showed that the deposition of Fe–Ni alloys with larger Fe content occurred with lower current efficiency [10]. The addition of saccharin up to 3 g dm⁻³ in the electrolyte produced smooth and bright deposit of uniform thickness in comparison with

burnt and torn deposit obtained from a pure chloride electrolyte [12]. Nucleation and growth of Fe–Ni alloys from chloride solution at pH 2 and pH 4 was investigated by current transient measurements, showing that the nucleation mechanism is instantaneous with typical 3D nucleation and growth for all investigated solutions [13].

The electrodeposition of Fe–Ni alloy powders was the subject of only few papers. Zhelibo et al. [14,15] suggested a method for producing very fine Fe-Ni alloy powder by the electrolysis in a two-layer electrolytic bath using a hydrocarbon solvent from an oil refining fraction as an upper organic layer with evaporation at 180°C and subsequent reduction annealing in a hydrogen atmosphere. Powders were electrodeposited from the simple Fe(II) and Ni(II) salts of different concentrations. The composition of Fe-Ni powders varied between 31 at.% and 50 at.% of Ni, depending on concentration of metal ions and the temperature of the electrolysis. The influence of the reduction annealing temperature [14] and the electrolysis temperature [15] on the formation, chemical and phase composition, structure and magnetic properties of highly dispersed Fe-Ni alloy powders were investigated and the optimal thermal conditions for the production of powders with micron-sized particles were determined [14,15]. By the SEM investigation the Fe powder particles were found to be dendritic, while the Fe-Ni alloy powder particles were fern-like in the case of electrolysis at 40 °C. With the increase of electrolysis temperature to 60°C particles became significantly larger, while at the temperature of 80 °C they became again smaller and their shape changed to rounded ones.

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Because of low magnification the internal structure of obtained particles could not be identified. The effect of complexing agents (citric and oxalic acid of the concentration of 0.05 M) on the process of Fe-Ni alloy powders was also investigated in the range of pH values between 3.4 and 6.0 [16]. It was shown that complexing agents influence the kinetics of powders electrodeposition, as well as the morphology of the Fe-Ni powders. According to the conclusion of the author finer powders were produced in the presence of citric acid in comparison with those obtained in the presence of oxalic acid [16]. It should be mentioned here that at the magnification used agglomerates could not be seen in the powders and that the surfaces of certain agglomerates were investigated by the SEM analysis. Nodule like particles were present in both cases (Figs. 8-11 of Ref. [16]), except that the dimension of nodules was smaller in the powders electrodeposited from citrate containing electrolyte. Hence, it could be stated only that the dimension of nodules on the surface of powder particles was smaller in the presence of citrate complexing agent. In the absence of complexing agents all powder particles were dendritic and fern-like. Unfortunately no data about the alloy composition were presented [16].

In this study an attempt was made to investigate the process of the Fe–Ni powders electrodeposition from citrate-sulfate and citrate-ammonium chloride containing electrolytes in the presence of either Fe(III) or Fe(II) salts, as well as their morphology and composition. The Fe(III) salts were used to prevent inevitable oxidation of Fe(II) into Fe(III) on the anode during the powders electrodeposition. Our intention was to find out how much the anomalous character of Fe–Ni alloy powders deposition is pronounced in order to obtain powders with desired composition (for example NiFe₂ powder which can be used for further oxidation into NiFe₂O₄ magnetic material [17]).

2. Experimental

The polarization diagrams were recorded in a threecompartment standard electrochemical cell at the temperature of 25 ± 1 °C. The platinum foil counter electrode and the reference – saturated silver/silver chloride, Ag/AgCl – electrode (E_{ref} = 0.20 V vs. NHE) were placed in separate compartments. The latter was connected to the working electrode by a Luggin capillary positioned at the distance of 0.2 cm from the working electrode surface. The working electrode was glassy carbon rod (d = 0.3 cm) sealed in epoxy resin so that only the surface area of the disc of 0.071 cm² was exposed to the solution and was placed parallel to the counter electrode in a vertical position. Before each experiment working electrode surface was polished down to 0.05 µm alumina impregnated polishing cloths, cleaned in an ultrasonic bath for 10 min, thoroughly washed with distilled water and transferred to the electrochemical cell.

The polarization measurements were performed by a computercontrolled potentiostat (PAR M273A) using the corrosion software (PAR M352/252, version 2.01) with the sweep rate of 1 mV s^{-1} . For obtaining polarization curves corrected for *IR* drop, the current interrupt technique, with the time of current interruption being 0.5 s, was used.

All powders were electrodeposited at the room temperature in the cylindrical glass cell (total volume of 1 dm^3) with cone shaped bottom of the cell in order to collect powder particles. Fe–Ni alloy powders were deposited under galvanostatic conditions on glassy carbon cylinder (d=0.5 cm, h=3 cm) at the appropriate limiting current density (see Section 3.1). Ni powder was washed with distilled water and alcohol after deposition. In the case of solutions with Fe(III) salts Fe in the alloy powders was protected from oxidation during the subsequent drying in the air at 100 °C [18]. The powders of Fe–Ni alloys were washed with the solution containing 0.1% of sodium soap Sap G-30 (which contains 78% of total fatty acids) in distilled water [18]. In the case of solutions with Fe(II) salts, after washing powders with distilled water and alcohol, alloy powders were protected from oxidation by subsequent drying in the N₂ atmosphere at 95 °C. All solutions were made from analytical grade purity chemicals (NiSO₄, Na₃C₆H₅O₇, Na₂SO₄, Fe₂(SO₄)₃, NiCl₂, NH₄Cl, FeCl₃ and FeCl₂) and distilled water by the following procedure: Na₃C₆H₅O₇ was first dissolved, then the pH was adjusted to slightly higher value than desired by corresponding acid; in the next step metal (Fe(III), or Fe(II) or Ni) salts were dissolved and finally supporting electrolyte was added and pH adjusted to the exact value. Concerning stability of solutions it is well known that during the investigation some Fe(II) become oxidized into Fe(III). This should be particularly pronounced during the deposition of powders for 1 h or 2 h. Taking into account that in all cases Fe(II) or Fe(III) made very stable complexes with citrate anions, we did not experience problems in the case of polarization measurements (polarization curves were practically the same after 3-4 measurements), but for any case before each experiment fresh solution has been made and used for investigation, as well as for powder electrodeposition.

For better understanding of the electrochemical process some experiments were performed on a rotating disc electrode made of Au $(0.312 \, \text{cm}^2)$ using Tacussel Controvit rotating system and Gamry potentiostat Reference 600 with the software PHE 200. Before each experiment working electrode surface was polished down to 0.05 μ m alumina impregnated polishing cloths, cleaned in an ultrasonic bath for 10 min, thoroughly washed with distilled water and transferred to the electrochemical cell.

The morphology of the electrodeposited powders was examined using scanning electron microscope (SEM), Tescan VEGA TS 5130MM equipped with an energy-dispersive X-ray spectroscopy (EDS), INCAP enta FET-x3, Oxford Instruments. Accordingly, composition of powders was determined by the EDS analysis.

The chemical analysis of the composition of some powder samples was performed by AAS using SPECTRO ICP-OES 17.5 MHz spectrometer. Samples for the analysis of about 30 μ g were dissolved in 5 cm³ HCl (1:1) at slightly elevated temperature.

Each experiment was repeated three times and the average values are presented in the paper. The variation of the results was $\pm 5\%$.

3. Results and discussion

Experiments were performed in two supporting electrolytes: 1 M Na₂SO₄ and 1 M NH₄Cl. In sulfate supporting electrolytes NiSO₄, Fe₂(SO₄)₃ and FeSO₄ salts were used, while in ammonium chloride supporting electrolyte NiCl₂, FeCl₃ and FeCl₂ salts were used in order to keep the same anions in the solution. It appeared that the supporting electrolyte did not influence the shape of the polarization curves and powder morphology in the presence of either Fe(III) or Fe(II) salts. The only difference was higher current density for powders electrodeposition from the electrolyte containing 1 M NH₄Cl (see Fig. 1) and very small change in the position of polarization curves depending on the supporting electrolyte used.

Four different electrolytes, with total metal ions concentration of 0.1 M, were used for the alloy powders electrodeposition in the presence of either Fe(III) or Fe(II) salts: $x \text{ M Ni}(\text{II}) + 1 \text{ M } (\text{Na}_2\text{SO}_4$ or NH₄Cl)+0.2 M Na₃C₆H₅O₇ + y M Fe(III) or Fe(II) with x = 0.09 M, 0.075 M, 0.05 M and 0.025 M and y = 0.075 M, 0.05 M, 0.025 M and 0.01 M. In such a way the Ni/Fe ions concentration ratios were 9/1, 3/1, 1/1 and 1/3, while the pH of the solution was kept constant (pH 4.5 in the case of sulfate supporting electrolyte and pH 4.0 in the case of ammonium chloride supporting electrolyte) by adding H₂SO₄ or HCl respectively. Polarization diagrams were also Download English Version:

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