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Parameters influencing the electrodeposition of a Ni-Cu coating on Fe powders. I. Effect of the electrolyte composition and current density

Abstract Electrochemical deposition of a two-component Ni-Cu coating onto Fe powder particles was studied by constant current electrolysis. The influence of the Ni(II) to Cu(II) salts ratio in the electrolyte, of the addition of sodium citrate as complexing agent to the electrolyte, and of the current density with respect to the total surface of compact and dispersed electrodes was studied. It was shown that the less noble Ni deposition is facilitated mainly by its large excess in the electrolyte and by an increase in current density. The addition of a complexing agent exhibits only a very slight influence on the coating composition but does suppress the spontaneous deposition of Cu. The current efficiencies of Ni, Cu and Ni-Cu deposition on the powder particles decrease with increasing sodium citrate concentration and current density.

Keywords Fe powder · Electrochemical plating · Ni-Cu deposition

Introduction

The electrodeposition of two-component coatings is a rather complicated process, but, if successfully carried out, the product has superior properties regarding the quality in general and the homogeneity in particular. Such a way of preparing two-component and multi-component coatings suits the high requirements of metallurgy, microelectronics and the aircraft building industry. In microelectronics, ferromagnetic thin films of Ni-Fe alloys [1, 2], as well as the magnetic properties of Co-Ni [3, 4], Co-W [5] and Co-Cr [6] coatings, are highly appreciated.

In metallurgical production, especially in powder metallurgy, such one-, two- or multilayer coatings are required on powder surfaces, most frequently on Fe powders, which, in the course of further heating and/or pressing treatment, produce a basic material properly alloyed and with the required properties such as hardness, corrosion resistance, etc. Ni coating deposition on Fe powders was first basically investigated by the authors of the present work [7, 8].

Electrochemical processes on powders may be realized in a cell with a fluidized bed electrode [9], where the powder particles get into the fluidized state either by vertical flow of the electrolyte through the bed of solid powder particles [10] or by circular stirring of the electrolyte together with the powder particles [11]. Moving powder particles repeatedly come into contact with the solid electrode, overtaking its charge and becoming instantly a part of the electrode [12, 13]. In an electrolytic cell with a cathodic compartment in the fluidized state, the result of such a process may be the formation of a metallic coating on the powder particles.

The electrolytic process proceeds only in the defined volume near to the solid electrode, the so-called "working volume" [14]. The surface of the Fe powder in this volume was calculated by a model published earlier [15].

Deposition of a two-component binary metallic coating on compact as well as on dispersed electrodes is a much more complicated process than that of a one-component coating. It may be controlled in several ways, depending on the actual case. Presently, the electrodeposition of a two-component Ni-Cu coating onto the surface of Fe powder particles was studied in our laboratory.

The standard reduction potentials for copper $(+0.34 \text{ V})$ and nickel (-0.25 V) are rather far apart. The deposition potentials need to be brought together by shifting the deposition potential of the nobler component (Cu) negatively. It may be attained, in

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addition to other ways, by changing the activity of the discharging ions, by adding a suitable complex-forming substance or by inhibiting the rate of reduction of the more noble metal. In our work, Ni-Cu alloy was deposited from a sulfate electrolyte with addition of sodium citrate. This can function also as a brightening, levelling and buffering agent, thus eliminating the need for other additives [16].

Changing the current density of the process may be another way of bringing the deposition potentials closer. An increase of current density causes the cathode potential to become more negative and this condition should increase the proportion of the less-noble metal in the deposit [17, 18]. A temperature increase exhibits a similar effect.

In the present paper, the influence of the change of the following parameters was investigated: the Cu(II) to Ni(II) salts ratio in the electrolyte, the concentration of sodium citrate as the complexing agent, and the current density. The observed quantities were: the composition of the Ni-Cu coating and the current efficiency on the powder particles. The effect of current density was evaluated by including the powder particle surfaces in the "working volume" as a part of the electrode [15].

The results of the influence of the particle size fraction, of the suspension density and of the rotation speed of the fluidized bed will be published in a following paper (Part II).

Experimental

The two-component coating was deposited from a solution containing 0.7 M NiSO$_4$ with addition of 0.01, 0.04 or 0.004 M CuSO$_4$; sodium citrate in the concentration range from 0.1 to 0.7 mol dm^{-3} was used as the complexing agent. The pH of the electrolyte varied accordingly from 3.7 in solutions without sodium citrate up to 4.5–4.9 in solutions containing sodium citrate. During measurements, the temperature in the electrolytic cell was kept constant at 38 ± 2 °C.

Fe powder was sieved into five granulometric classes: 0–45, 45–63, 63–100, 100–125 and 125–160 μm. The fluidized bed system was realized by circular stirring of the electrolyte suspension at a rate of stirring of 350 rpm. The suspension density $(1-\epsilon)$ was calculated from the equation for expansion of a fluidized bed: $\epsilon = V_e/(V_e + V_s)$, where V_e is volume of the electrolyte and V_s is volume of the solid phase. The values of the suspension densities, $(1-\epsilon) \times 10^3$, were: 4.3, 8.3, 12.7, 16.7 and 20.6. The galvanostatic electrolysis time was 30 min. A stainless steel cathode and a Ni sheet anode were used as electrodes. A diaphragm separated the cathodic and anodic compartments of the electrolytic cell. The current density changed from 3.5 to 9.8 A dm^{-2}. The two-component Ni-Cu coating was analysed by the fast scan differential pulse polarography (FSDPP) method using a PA-4 analyser. The working parameters were: a static mercury dropping electrode, a scan rate of 10 mV s^{-1} and a pulse amplitude of +12.5 mV.

Results and discussion

Effect of the electrolyte composition

Since Cu is a much more positive element than Ni, their simultaneous deposition should be facilitated by an excess of Ni(II) salt in solution. An electrolyte containing significant excess of NiSO$_4$ over CuSO$_4$ (see Experimental) was suggested for Cu-Ni simultaneous deposition [16] and applied in this work.

In Fig. 1 the composition of a Ni-Cu coating on Fe powder is shown versus the Cu(II) salt concentration in the electrolyte. Only at very low concentrations of Cu(II) does the metallic Ni prevail in the deposit. Above a concentration ca. 0.02 mol dm^{-3}, the more positive Cu is dominant in the deposit, in spite of the significant excess od Ni content in the solution. Figure 2 presents the effect of increasing the concentration of complexing agent (sodium citrate) upon the binary coating composition. The concentration of sodium citrate usually applied in the plating electrolyte used is 0.25 mol dm^{-3}. Thus, with respect to the Ni salt concentration, the free or hydrated Ni(II) ions prevail in solution and, consequently, also in the coating. At 0.7 mol dm^{-3} of citrate the representation of both metals in the coating is nearly equal, which is in accordance with similar values of the stability constants of the complexes prevailing in solution [16, 19, 20] corrected to the ionic strength value of 3.0 mol dm^{-3}:

$$L^{1-} \quad (CuH_2Cit)^+ \log\beta(I=3) = 2.42 \quad L^{2-} \quad (CuHCit)^0 \log\beta(I=3) = 8.26$$
$$(NiH_2Cit)^{1-} \log\beta(I=3) = 1.91 \quad (NiHCit)^0 \log\beta(I=3) = 7.50$$

$L^-(CuH_2Cit)^+$; $\log\beta(I=3)=2.42 L^{2-}(CuHCit)^0$; $\log\beta(I=3)=8.26(NiH_2Cit)^+$; $\log\beta(I=3)=1.91(NiHCit)^0$; $\log\beta(I=3)=7.50$

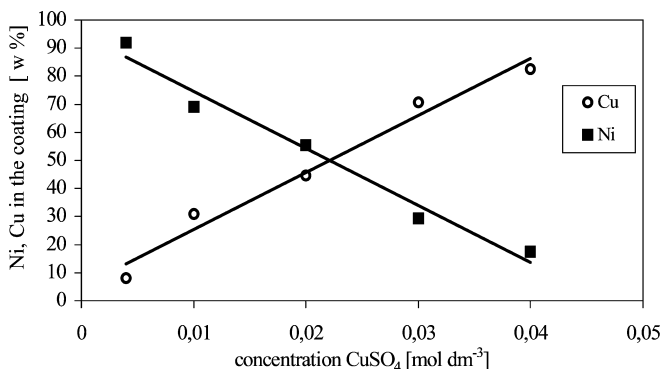It is interesting to note the effect of decreasing the citrate concentration below the value 0.25 mol dm^{-3}.

Fig. 1 Composition of the Ni-Cu coating on Fe powder versus the Cu(II) salt concentration in the electrolyte; particle size fraction, 63–100 μm; suspension density, $(1-\epsilon) \times 10^3 = 8.3$; NiSO$_4$ concentration, 0.7 mol dm^{-3}; Na$_3$Cit concentration, 0.25 mol dm^{-3}; 7.874 A dm^{-2}; 350 rpm
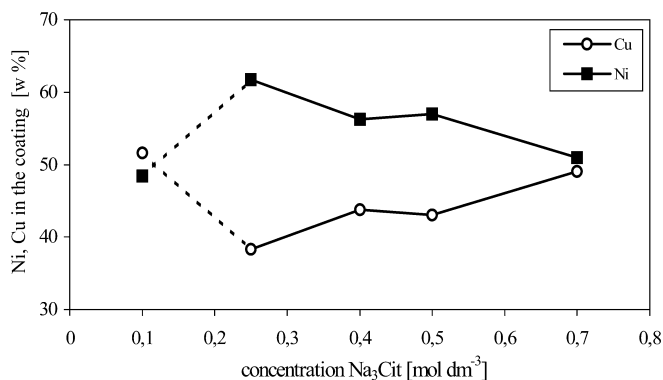
Fig. 2 Effect of increasing the concentration of complexing agent (sodium citrate) upon the binary coating composition; particle size fraction, 63–100 μm; suspension density, $(1-\epsilon)\times10^3 = 8.3$; NiSO$_4$ concentration, 0.7 mol dm^{-3}; CuSO$_4$ concentration, 0.01 mol dm^{-3}; 7.874 A dm^{-2}; 350 rpm

The Cu content on the powder particle increases, the process proceeds very fast, almost instantly after adding the powder to the electrolyte, and is accompanied by a temperature increase of nearly 20 °C. This seems to be evidence that a fast, spontaneous current-free deposition of Cu on the Fe powder occurs if the concentration of complexing agent is not sufficient (Eq. 1):

$$Fe(0) + Cu(II) \quad \rightarrow \quad Fe(II) + Cu(0) \tag{1}$$
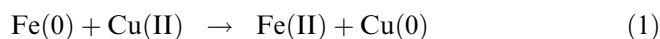
At the same time, the electrodeposition of Ni is suppressed.

Calculation of the surface area of the powder

In order to calculate the actual current density, the surface area of the powder particles present instantaneously in the working volume has to be calculated since it is regarded as part of the electrode.

The values for the surface area of the Fe powder particles were calculated according to the model described in detail previously [14, 15]. The model assumes the existence of uniform spheres with mean dimensions for the given fraction; further, it assumes participation in the electrode reaction of only those particles that are immediately present in the vicinity of the compact cathode, i.e. in the "working volume" of the electrolytic cell. The total surface area, S_{pow}, of the powder participating as the

electrode surface area is then calculated according to the equation:

$$S_{pow} = m_{pow} \times 3/(r\rho)K \tag{2}$$

where m_{pow} is the total mass of Fe powder given to the cathodic compartment of the cell, r is the radius of the powder particles, ρ is the specific mass of Fe, 7.88 g cm^{-3}, and K is a dimensionless parameter expressing the ratio of the working to the total electrolytic cell volumes.

Table 1 shows the calculated values of the powder surface area in the working volume (in the first column), the total surface area, i.e. of the compact electrode and the powder particles (in the second column) and, finally, the calculated current density for 1 A of total current passing through the cell (in the third column) for various particle sizes and suspension densities.

Effect of current density

The composition of the binary coating on the powder versus current density is presented in Fig. 3. As expected, with increasing current density the deposition of the less-noble metal, i.e. Ni, is preferred. However, the value of the current density over which this preference takes place is relatively high, 5.0 A dm^{-2}.

A characteristic accompanying effect for fluidized bed electrolysis of the type used here is that after contacting the electrode a part of the powder remains attached to its surface. Such powder was removed from the electrode and analysed. The data are presented in Fig. 4 and show a different composition of the coating on such powders: a significant excess of Ni can be seen in all experiments on powders removed from the compact electrode surface. The explanation of this effect may be due to the composition of the compact cathode itself, which is stainless steel containing about 10% Ni. On such surfaces, spontaneous Cu deposition is prevented on one side since very little Fe is dissolved in the solution. On the other side the electrolytic deposition of Ni is supported on a surface with a relatively high Ni content.

Cathodic current efficiencies on powder particles

The values of the cathodic current efficiencies on powder are calculated as a ratio of the charge realized on the

Table 1 Calculated values of the powder surface area in the working volume, A_{pow}, the total surface area, i.e. the sum of the compact electrode and the powder particle surfaces, A_{total}, and the calculated current density, j, for 1 A of total current passing through the cell for various particle sizes and suspension densities

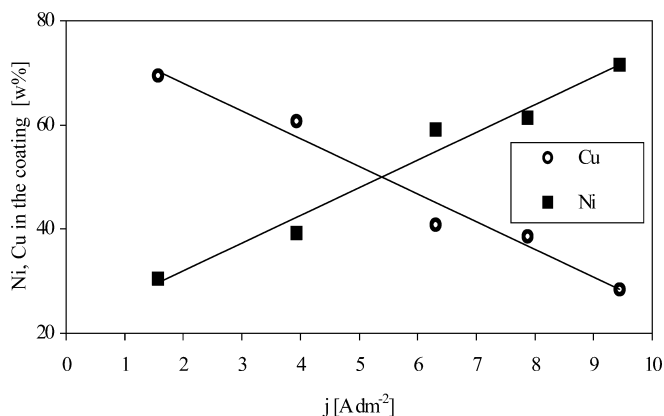| Mean particle size (μm)	A_{pow} (cm^2)	A_{total} (cm^2)	j (A dm^{-2})	Suspension density, $(1-\epsilon)\times10^3$	A_{pow} (cm^2)	A_{total} (cm^2)	j (A dm^{-2})
22.5	19.44	27.28	3.666	4.3	2.43	10.27	9.737
54.0	7.77	15.62	6.402	8.3	4.86	12.7	7.874
81.5	4.86	12.7	7.874	12.5	7.3	15.14	6.605
112.5	3.46	11.3	8.850	16.7	9.73	17.57	5.692
142.5	2.73	10.57	9.461	20.6	12.6	20.01	4.998

Fig. 3 Composition of the Ni-Cu coating on Fe powder versus current density; particle size fraction, 63–100 μm; suspension density, $(1-\epsilon)\times10^3 = 8.3$; NiSO$_4$ concentration, 0.7 mol dm^{-3}; CuSO$_4$ concentration, 0.01 mol dm^{-3}; Na$_3$Cit concentration, 0.25 mol dm^{-3}; 350 rpm
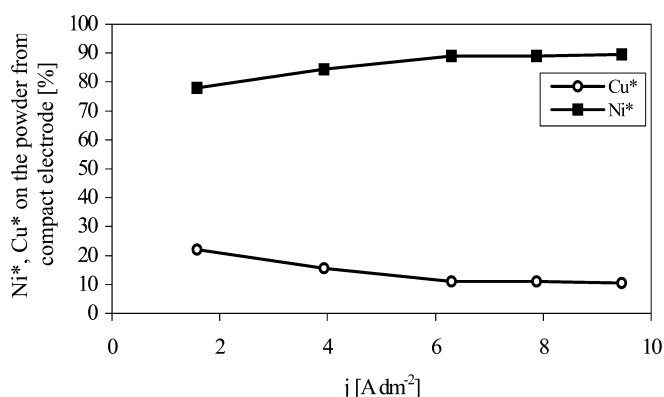

Fig. 4 Composition of the coating on powder removed from the compact electrode versus current density; particle size fraction, 63–100 μm; suspension density, $(1-\epsilon)\times10^3 = 8.3$; NiSO$_4$ concentration, 0.7 mol dm^{-3}; CuSO$_4$ concentration, 0.01 mol dm^{-3}; Na$_3$Cit concentration, 0.25 mol dm^{-3}; 350 rpm

powder particles to the total charge passing through the cell. The charge realized on the powder is calculated according to Faraday's law by means of analysing the amount of deposit on it. The total charge value includes, in addition to the above value, the charge realized in hydrogen evolution on the particles, as well as that realized on the solid cathode for both metal coating and

hydrogen evolution [15]. The experimentally obtained values as a function of the concentration of complexing agent are summarized in Table 2.

The values of the current efficiency on the powder particles are generally low and decrease with an increase in the complexing agent concentration, with the exception of the lowest value where the deposition of Ni is suppressed owing to the spontaneous deposition of Cu, as discussed above. The efficiency on powder particles removed from the compact electrode is much higher, but only in the case of Ni deposition. The total efficiency data given in the last column of Table 2 not exceeding 52% do not include the powder deposited on the compact electrode itself, only on the powder immobilized on it. The codeposition of hydrogen also occurs, causing consumption of charge and, consequently, decrease in current efficiency.

The stated distribution of charge among the metal coating on powder in solution and on the compact cathode on one side and hydrogen evolution on powder and on the compact cathode on the other is evident from the data in Table 3. In the second column of the table, the decreasing efficiency of Cu with increase in current density caused by preference of deposition of the more negative elements, Ni and H$_2$, is documented. At the lowest current density values, the effect of spontaneous Cu deposition is remarkable. The values in column 3 confirm the increased efficiency for the deposition of the more negative metal (Ni) on powder particles with an increase in current density. These two opposite tendencies affect the values in column 4, which, consequently, shows no monotonous course. Columns 5, 6 and 7 represent the efficiencies on powder particles removed from the compact electrode. From the values in column 8, which are the sums of the values in columns 4 and 7, it can be concluded how much charge is consumed for hydrogen evolution both on the powder and on the compact cathode, as well as for the metal coating process on the compact cathode itself. The total efficiency at low current densities reaches 91.6%; at higher values, it ranges from 60% to 65%.

Figure 5 presents an optical micrograph of the Ni-Cu coating on Fe powder particles. It shows sufficient uniformity of the coating thickness, thus ensuring the homogeneity of the product after subsequent thermal and/or mechanical treatment.

Table 2 The values of the cathodic current efficiency on powder particles from the fluid electrode and from the compact electrode as a function of the concentration of complexing agent; particle size fraction, 63–100 μm; suspension density, $(1-\epsilon)\times10^3 = 8.3$; current density, 7.874 A dm^{-2}

$c_{\text{sodium citrate}}$ (mol dm^{-3})	η_{Cu}(%)	η_{Ni}(%)	$\eta_{(Ni+Cu)}$(%)	η_{Cu*}(%)[a]	η_{Ni*}(%)[a]	η_{total}(%)
0.1	4.39	4.57	8.96	3.51	38.44	50.9
0.25	5.24	10.12	15.36	3.56	37.92	56.84
0.4	4.22	6.03	10.25	2.89	30.99	44.12
0.5	3.88	5.48	9.36	2.48	30.46	43.3

[a]The values marked by an asterisk belong to the powder removed from the compact electrode

Table 3 The values of the cathodic current efficiency on powder particles from the fluid electrode and removed from the compact electrode as a function of the current density; particle size fraction, 63–100 μm; suspension density, $(1-\epsilon)\times10^3 = 8.3$

j (A dm^{-2})	η_{Cu} (%)	η_{Ni} (%)	$\eta_{(Cu+Ni)}$ (%)	η_{Cu*}(%)[a]	η_{Ni*} (%)[a]	$\eta_{(Cu*+Ni*)}$ (%)[a]	η_{total} (%)
1.575	20.25	4.92	25.15	13.5	52.96	66.45	91.60
3.937	8.44	5.84	14.28	7.42	43.46	50.88	65.16
6.299	6.33	8.9	15.23	4.43	39.03	43.46	58.69
7.874	5.24	10.12	15.36	3.56	41.09	37.92	56.84
9.449	4.36	15.22	20.84	4.36	39.72	44.08	64.92

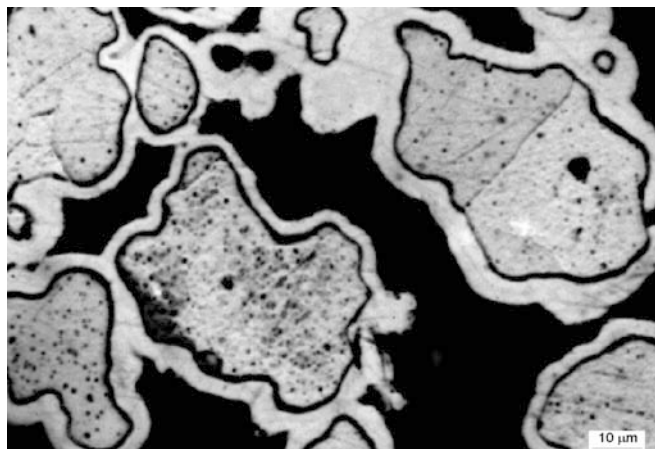[a]The values marked by an asterisk belong to the powder removed from the compact electrode

Fig. 5 Optical micrograph of the Ni-Cu coating on Fe powder particles

Conclusions

The electrolytic deposition of a two-component Ni-Cu coating on Fe powder particles may be realized in a fluidized bed arrangement. The process on the powder is influenced by spontaneous current-free deposition of Cu, which is suppressed by addition of a complexing agent, sodium citrate, to the electrolyte. On the stainless steel compact cathode, as well as on powder adhered to it, the electrolytic deposition of Ni is highly preferred. The cathodic current efficiencies of Ni, Cu and Ni-Cu deposition on the Fe powder surfaces respectively range from 52% to a maximum of 91%, reached at relatively low current densities. A large portion of charge is consumed by the process on the compact electrode and by hydrogen evolution. However, the quality as well as the homogeneity of the coating on powder under optimum conditions is sufficiently high to substitute these losses and to substantiate the application of such a process. The conditions were given for depositing a two-component Ni-Cu coating of required composition, appearance, quality and adherence on Fe powder particles.

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