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## Parameters influencing the electrodeposition of a Ni-Cu coating on Fe powders. II. Effect of particle size fraction, suspension density and rotation speed

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**Abstract** The composition of a two-component Ni-Cu coating and the efficiency of its electrochemical deposition on Fe powder was studied by constant current electrolysis. A fluidized bed arrangement was applied. The variable parameters were: the particle size fraction, the density of the suspension of the Fe powder in the plating bath, and the intensity of the stirring of the fluidized bed. Both the Cu and Ni contents in the deposit decrease with increase in the particle size, and with decrease in the suspension density. Thus, the surface area available for the electrochemical process proved to be of high importance. Another important factor is the quality of the contacts of the powder particles with the current carrying compact electrode during which the deposition of Ni is preferred. This influence is manifested in a decrease of the Ni-Cu ratio in the deposit with an increase in the particle size and rotation speed and, consequently, with a decrease in the suspension density. The current efficiency values on the powder for optimum conditions reached 80%.

**Keywords** Binary Ni-Cu deposit · Electrochemical plating · Fe powder

### Introduction

As mentioned in Part I [1], two- and multicomponent layers on basic metallic components may improve the functional properties of such materials in a required manner. This is important not only for the metallurgy and decorative electroplating industries but also recently

for microelectronics [2, 3, 4, 5]. The direction towards ever smaller and smaller surfaces to be coated brings about the necessity of working with dispersed powder particles as electrodes. Such processes can be realized in a fluidized bed arrangement [6].

Basic parameters affecting every electrochemical process, i.e. the composition of the electrolyte and the current density, were analysed in detail in Part I [1] from the point of view of their capability of bringing closer the deposition potentials of Ni and Cu. It was observed that a large excess of Ni is required in order to suppress the preferential deposition of the more electropositive Cu. The addition of sodium citrate as complexing agent reduces significantly the currentless deposition of Cu on Fe powder, which is a consequence of the fast redox reaction between metallic Fe and Cu ions in solution. An increase in current density leads, as expected, to the preference of the less noble metal, i.e. Ni, in the deposit on the powder.

In addition to these usually applied parameters, in the process of plating two-component coatings onto the powder particle surfaces, the quantities of control are extended to hydrodynamic parameters such as particle size, density and rotation speed of the suspension of powder particles in the electrolyte in the case of fluidized bed electrolysis.

The present paper deals with the effect of the above-mentioned parameters, i.e. the Fe powder particle size fraction, the density of the suspension of the Fe powder in the plating bath, and the rotation speed of the fluidized bed, upon the composition and amount of the Ni-Cu coating on the Fe powder particles as well as upon the current efficiency of the plating process.

### Experimental

The two-component coating was deposited from a bath containing 0.7 M NiSO<sub>4</sub> and 0.01, 0.04 or 0.004 M CuSO<sub>4</sub>; 0.25 M sodium citrate was used as complexing agent.

Fe powder was sieved into five granulometric classes: 0–45, 45–63, 63–100, 100–125 and 125–160 μm; values of the suspension

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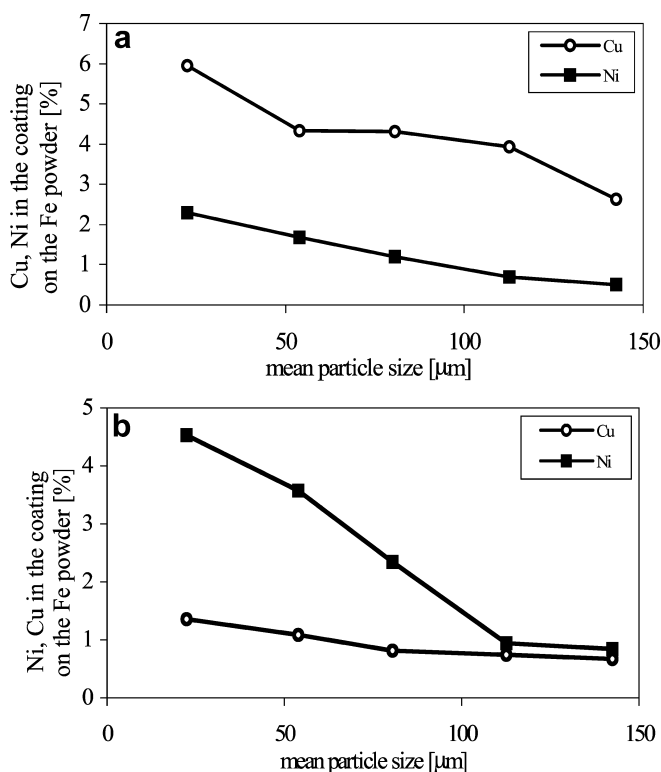
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densities,  $(1-\epsilon)\times 10^3$ , were: 4.3, 8.3, 12.7, 16.7 and 20.6, respectively (for details, see Part I [1]). The fluidized bed system was realized by circular stirring of the electrolyte suspension. The rate of stirring was 350 rpm, if not stated otherwise. The galvanostatic electrolysis time was 30 min; a diaphragm separated the cathodic and anodic compartments of the cell. A stainless steel cathode and a Ni sheet anode were used. The current density changed from 3.5 to 9.8 A dm<sup>-2</sup>, corresponding to the particle size; see the calculation of the electrode surface described in detail in Part I [1]. The two-component Ni-Cu coating was analysed using the fast scan differential pulse polarography (FSDPP) method with a PA-4 analyser. The working parameters were: a static mercury dropping electrode, a scan rate of 10 mV s<sup>-1</sup> and a pulse amplitude of +12.5 mV.

## Results and discussion

### Effect of the particle size fraction

Figure 1a and Fig. 1b show the effect of increasing the particle size upon the content and composition of the binary Cu-Ni deposit on the Fe powder particles for different Cu(II) ion concentrations in the electrolyte. For a 0.04 mol dm<sup>-3</sup> concentration of Cu(II) in the electrolyte, Cu prevails in the deposit (Fig. 1a); for a 0.01 mol dm<sup>-3</sup> concentration of Cu, Ni prevails in the deposit (Fig. 1b). In both cases the total metal content on the powder decreases. The decrease can probably be



**Fig. 1** The effect of increasing particle size upon the content and composition of a binary Cu-Ni deposit on Fe powder particles for different Cu(II) ion concentrations in the electrolyte; suspension density,  $(1-\epsilon)\times 10^3=8.3$ ; NiSO<sub>4</sub> concentration, 0.7 mol dm<sup>-3</sup>; Na<sub>3</sub>Cit concentration, 0.25 mol dm<sup>-3</sup>; 7.874 A dm<sup>-2</sup>; 350 rpm. **a** For 0.04 mol dm<sup>-3</sup> Cu<sup>2+</sup> concentration in the electrolyte; **b** for 0.01 mol dm<sup>-3</sup> Cu<sup>2+</sup> concentration

attributed to the fact that the total surface area available for the electrodeposition, i.e. the sum of the surface of the compact electrode and of the powder in the “working volume” near the electrode, is reduced with increasing particle size. The decrease of the amount of Ni on the powder has already been observed in connection with one-component Ni deposition on Fe powder [7] and emphasized also by other authors [8, 9].

The change of the Ni to Cu mass ratio in the deposit with increasing particle size is summarized in Table 1. The data clearly show that with increasing particle size the portion of Ni in the deposit is reduced. This is an interesting result that can be explained in terms of the different quality of contacts of smaller and larger powder particles with the compact electrode. The contact of the former ones with the solid electrode is realized on a larger surface area and is of higher quality since they are also able to fit the unevenness in the surface. The contact of the latter ones is, consequently, worse. The portion of Ni on the smaller particles is higher due to the preferential deposition of Ni on the compact cathode reported upon in Part I [1].

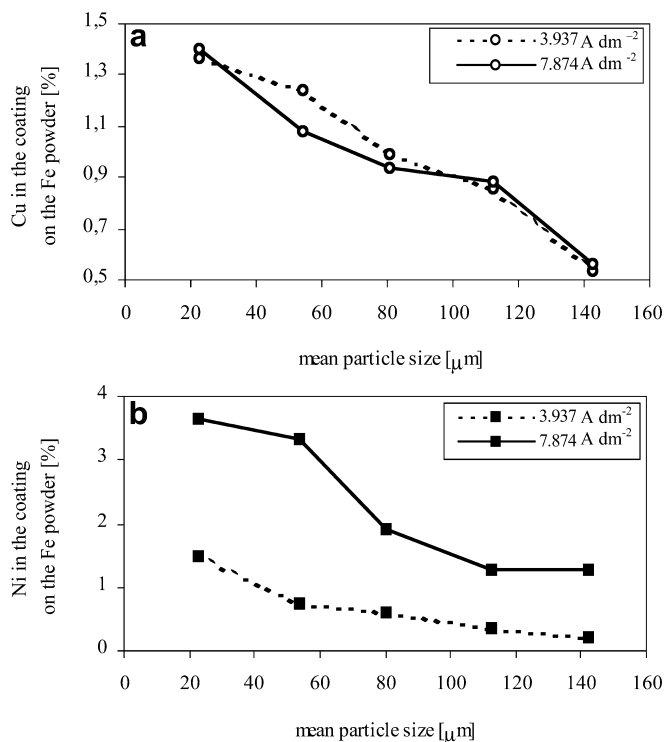
The powder particles after contacting the compact cathode take over some charge and thus become part of the electrode for a short period of time and in limited positions in the cell. For more details on these ideas, see [10] and [11]. With increasing particle size their total surface area is lower and therefore the current density on the powder particle surface is higher, as compared with smaller particles at an identical current passing through the cell. With regard to the literature data [12, 13] and respecting classical electroplating experience and knowledge, as well as the results of experiments increasing the external current density [1], at higher current density the deposition of the more negative metal should be preferred; in this case, it is the deposition of Ni. The results observed here, however, show the opposite effect, documenting a higher significance of the effect of the total electrode surface available for the electrodeposition over the effect of a higher current density on the powder surface.

Another remarkable effect of the change in particle size is demonstrated in Fig. 2a and Fig. 2b, showing the

**Table 1** The change of Ni to Cu mass ratio in the deposit with increasing particle size<sup>a</sup>

Mean particle size (μm)	Ni:Cu ratio			
	0.04 M Cu <sup>2+</sup>	0.004 M Cu <sup>2+</sup>	0.01 M Cu <sup>2+</sup>	
			7.874 A dm <sup>-2</sup>	3.937 A dm <sup>-2</sup>
22.5	0.39	18.75	3.33	1.09
54.0	0.38	11.39	3.30	0.61
81.5	0.28	7.5	2.90	0.69
112.5	0.17	4.44	1.26	0.34
142.5	0.19	5.66	1.25	0.37

<sup>a</sup>Suspension density,  $(1-\epsilon)\times 10^3=8.3$ ; NiSO<sub>4</sub> concentration, 0.7 mol dm<sup>-3</sup>; Na<sub>3</sub>Cit concentration, 0.25 mol dm<sup>-3</sup>



**Fig. 2** The content of the respective metals on the powder with the change in particle size for current densities of  $7.874 \text{ A dm}^{-2}$  and  $3.937 \text{ A dm}^{-2}$ ; suspension density,  $(1-\epsilon) \times 10^3 = 8.3$ ;  $\text{NiSO}_4$  concentration,  $0.7 \text{ mol dm}^{-3}$ ;  $\text{CuSO}_4$  concentration,  $0.01 \text{ mol dm}^{-3}$ ;  $\text{Na}_3\text{Cit}$  concentration,  $0.25 \text{ mol dm}^{-3}$ ; 350 rpm

content of the respective metal with the change in particle size for various current densities. According to these results, the deposition of Ni is electrochemical in nature, based on Faraday's law, whereas the deposition of Cu shows independence on the amount of current passing and, thus, is predominantly based on an electroless redox process connected with Fe dissolution.

In Table 2, the current efficiencies are shown of individual metal deposition processes on the powder particles as well as on the compact electrode. With increasing particle size, the contribution of particle surfaces to the total electrode surface decreases, thus resulting in an increase in current density at constant current. It may also be assumed that the quality of the

contacts of smaller particles with the compact cathode is much better due to better fitting of the roughness extent on the cathode surface with their size. Owing to both of these effects, the current efficiencies of Cu as well as Ni deposition on the powder decrease. The efficiency decrease on the compact electrode is rather negligible, thus confirming the above statements.

#### Effect of the suspension density

Increase in the suspension density, i.e. in the concentration of powder particles in the electrolyte, is manifested by enlargement of the surface area coated and, therefore, the total amount of metal deposited on the powder by a given charge increases. This course is clearly shown in Fig. 3, with the exception of the highest measured suspension density in the case of Cu.

The values of the Ni to Cu ratios in the deposit (see Table 3) show an increase with increasing suspension density. Probably, the prevailing electrode process of metal deposition proceeds during the contacts with the compact electrode and not during mutual contacts of powder particles in the so-called working volume of the electrolytic cell. Thus, with increasing suspension density, more powder particles participate in the electrode process on the compact electrode, i.e. the preferential deposition of Ni occurs.

The total current efficiency for the sum of both metals increases with increasing suspension density, as is presented in Table 4. Ni makes the main contribution to this increase. The current efficiency of Cu deposition on the powder is nearly uninfluenced by the increase in suspension density.

#### Effect of the rotation speed of the fluidized bed

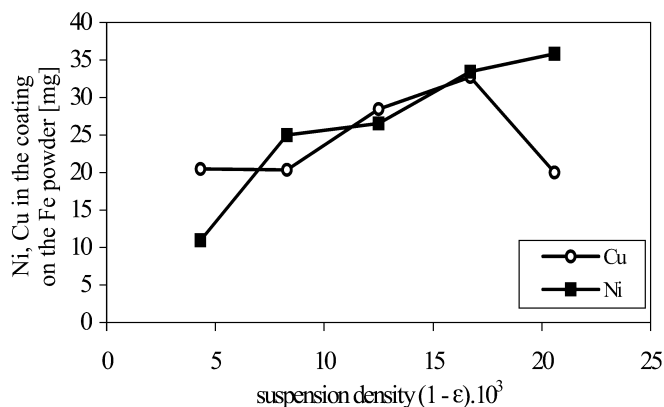
Owing to experimental circumstances of the necessity to keep the powder in the fluidized state on the one hand and hydrodynamic destabilization of the whole bed on the other, it is rather difficult to change the rotation speed of the bed over a sufficiently wide range in order to make serious conclusions. Even so, the experimental results presented in Fig. 4 show some influence of the

**Table 2** The current efficiencies of the individual metal deposition processes on the powder particles in the bed as well as on powder from the compact electrode<sup>a,b</sup>

Mean particle size ( $\mu\text{m}$ )	$7.874 \text{ A dm}^{-2}$					$3.937 \text{ A dm}^{-2}$				
	$\eta_{\text{Cu}}$ (%)	$\eta_{\text{Ni}}$ (%)	$\eta_{\text{Cu}^*}$ (%)	$\eta_{\text{Ni}^*}$ (%)	$\eta_{\text{total}}$ (%)	$\eta_{\text{Cu}}$ (%)	$\eta_{\text{Ni}}$ (%)	$\eta_{\text{Cu}^*}$ (%)	$\eta_{\text{Ni}^*}$ (%)	$\eta_{\text{total}}$ (%)
22.5	7.85	22.28	3.32	34.51	67.96	15.39	18.11	6.41	42.69	82.61
54.0	6.06	20.63	3.09	39.08	68.89	13.94	9.24	6.75	32.69	62.61
81.5	5.26	11.56	3.29	37.98	58.1	10.0	7.41	6.75	37.87	62.02
112.5	5.35	7.71	3.21	32.32	48.58	11.81	4.38	6.99	31.7	54.88
142.5	3.14	7.87	2.06	32.14	45.21	6.07	2.45	4.35	40.57	53.45

<sup>a</sup>The values marked by an asterisk belong to the powder removed from the compact electrode

<sup>b</sup>Other parameters as Table 1



**Fig. 3** The dependence of the total amount of metals deposited on Fe powder on the increase in the suspension density; particle size fraction, 63–100  $\mu\text{m}$ ;  $\text{NiSO}_4$  concentration, 0.7  $\text{mol dm}^{-3}$ ;  $\text{CuSO}_4$  concentration, 0.01  $\text{mol dm}^{-3}$ ;  $\text{Na}_3\text{Cit}$  concentration, 0.25  $\text{mol dm}^{-3}$ ; 3.937  $\text{A dm}^{-2}$ ; 350 rpm

**Table 3** The variation of the Ni to Cu mass ratio in the deposit with increasing suspension density for three types of electrolyte<sup>a</sup>

Suspension density, $(1-\epsilon) \times 10^3$	Ni:Cu ratio		
	0.004 M $\text{Cu}^{2+}$	0.01 M $\text{Cu}^{2+}$	0.04 M $\text{Cu}^{2+}$
4.3	4.88	0.54	0.081
8.3	4.72	1.23	0.089
12.7	4.96	0.93	0.09
16.7	5.24	1.02	0.1
20.6	5.37	1.79	0.2

<sup>a</sup>Particle size fraction 63–100  $\mu\text{m}$ ;  $\text{NiSO}_4$  concentration, 0.7  $\text{mol dm}^{-3}$ ;  $\text{Na}_3\text{Cit}$  concentration, 0.25  $\text{mol dm}^{-3}$

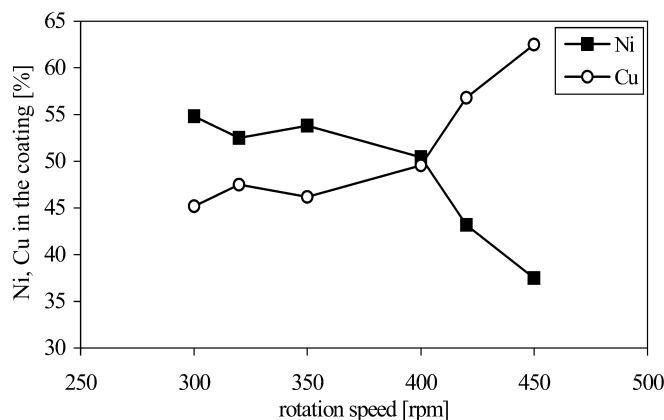
**Table 4** The change of the total current efficiency for both metals with increasing suspension density<sup>a,b</sup>

Suspension density, $(1-\epsilon) \times 10^3$	$\eta_{\text{Cu}}$ (%)	$\eta_{\text{Ni}}$ (%)	$\eta_{\text{Cu}^*}$ (%)	$\eta_{\text{Ni}^*}$ (%)	$\eta_{\text{total}}$ (%)
4.3	6.92	4.02	4.62	29.99	42.55
8.3	9.02	90.4	7.59	33.42	55.79
12.7	9.6	9.68	10.8	42.91	73.01
16.7	11.03	12.2	11.34	42.58	77.15
20.6	6.75	13.07	19.85	35.23	74.90

<sup>a</sup>Particle size fraction, 63–100  $\mu\text{m}$ ; current density 3.937  $\text{A dm}^{-2}$ ; other parameters as Table 1

<sup>b</sup>The values marked by an asterisk belong to the powder removed from the compact electrode

rotation speed exceeding 400 rpm on the composition of the binary Ni-Cu coating on the Fe powder. The Cu content increases while the Ni content decreases abruptly. The same effect is encountered in the case of particle size increase: with increasing rotation speed the contact of particles with the compact cathode becomes worse and, thus, the conditions for depositing Ni are less favourable. This is proved also by the data in Table 5. The efficiencies for individual metals as well as the total



**Fig. 4** Influence of the rotation speed of the fluidized bed on the composition of the binary Ni-Cu coating on the Fe powder; particle size fraction, 63–100  $\mu\text{m}$ ; suspension density,  $(1-\epsilon) \times 10^3 = 8.3$ ;  $\text{NiSO}_4$  concentration, 0.7  $\text{mol dm}^{-3}$ ;  $\text{CuSO}_4$  concentration, 0.01  $\text{mol dm}^{-3}$ ;  $\text{Na}_3\text{Cit}$  concentration, 0.25  $\text{mol dm}^{-3}$ ; 7.874  $\text{A dm}^{-2}$

**Table 5** The variation of the Ni to Cu mass ratio in the deposit with increase in rotation speed<sup>a,b</sup>

Rotation speed (rpm)	Ni:Cu	Ni*:Cu*
300	1.21	11.95
320	1.09	15.75
350	1.17	15.09
400	0.97	14.75
420	0.74	15.51
450	0.40	11.27

<sup>a</sup>Particle size fraction, 63–100  $\mu\text{m}$ ; suspension density,  $(1-\epsilon) \times 10^3 = 8.3$ ;  $\text{NiSO}_4$  concentration, 0.7  $\text{mol dm}^{-3}$ ;  $\text{CuSO}_4$  concentration, 0.01  $\text{mol dm}^{-3}$ ;  $\text{Na}_3\text{Cit}$  concentration, 0.25  $\text{mol dm}^{-3}$ ; 7.874  $\text{A dm}^{-2}$

<sup>b</sup>The values marked by an asterisk belong to the powder removed from the compact electrode

current efficiency are very slightly affected by the rotation speed.

## Conclusions

The influence of the hydrodynamic parameters of the fluidized bed, such as particle size, particle concentration in the plating bath, and the rotation speed of the bed, is manifested through the changes in the surface area available for the electrochemical deposition of Ni-Cu alloy on Fe powder particles, as well as through the quality of the contacts between the solid cathode and the powder particles. The former effect is observable in the total amount of deposit on the powder, while the latter one is shown in the Ni to Cu ratio in the deposit. Thus, with increasing particle size and decreasing suspension density the surface area decreases and, consequently, also the total amount of deposit is reduced. The quality of the contacts worsens with increase in particle size and rotation speed, which results

in a lower portion of Ni in the deposit due to the preferential Ni deposition on the compact cathode.

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