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## Electrochemical processes during plating Fe powder particles by Ni and Ni/Cu coating in the fluidized bed

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**Abstract** Ni electrodeposition on Fe powder was studied with respect to an inhibiting adsorbed hydroxycomplex layer. Its elimination was done in three possible ways: by increasing the rotation speed of the circular stirring of the suspension, by chemical dissolution of the adsorbed layer during interrupted electrolysis, and by addition of a complexing agent – sodium citrate into the electrolyte. The simultaneous deposition of a Cu/Ni coating was enabled by proper electrolyte composition as to the ratio of both metallic compounds and by the addition of a suitable complexing agent. The Cu/Ni ratio was influenced, beside electrochemical parameters, also by the particle size of the Fe powder and by the suspension density. Increasing the suspension density supports the deposition of Ni, and increasing the particle size supports the deposition of Cu.

**Keywords** Fluidized bed · Powder particles · Electrolysis

### Introduction

Fluidized bed electrolysis can be used advantageously for preparing some new materials. In the fluidized bed electrolysis, first described in Ref. [1], powder particles get into the fluidized state either by vertical flow of the

electrolyte upside down or by horizontal circular stirring of the electrolyte [2]. Moving powder particles come into contact with the solid electrode and, thus, instantly become a part of the electrode. A model treating this idea for circular movement and defining the so-called “working volume” of the electrolytic cell was developed in Ref. [3] and was further extended in Ref. [4]. It was assumed in this model that the electrolytic process proceeds only in the defined volume immediately attached to the solid electrode. The distribution of charge between the solid feeder electrode and the particles was calculated and the partial current efficiency on the particles was determined [5]. Under optimum conditions of the particle size and the suspension density the partial current efficiency ranged between 33 and 35%.

Fluidized bed electrolysis has recently been frequently used in many fields of modern technology and techniques, for instance, in powder metallurgy [5, 6], in waste electrolyte, in water treatment [7], etc. The theoretical basis for possible ways of transfer of the charge in such systems was developed only recently [8, 9, 10].

In the classical Ni sulphate electrolyte used for Ni coating, the formation of hydroxycomplexes was observed [11]. These compounds adsorb onto the solid surface and inhibit the electrolysis process. The dependence of the efficiency of electrolysis on the particle size and the suspension density was investigated. With increasing particle size the efficiency decreased. The suspension density – the powder-to-electrolyte volume ratio – increase causes a decrease in the efficiency of electrolysis [4]. The efficiency of metal deposition on the powder particles is based on the suggested model, i.e., the quantity of metal deposited on the powder particles is only considered as an efficient process. The intensity of stirring proved to have an important role in suppressing the competitive adsorption process [12]. The reactivity of the powder surface [13] can influence the electrolytic process efficiency; therefore, in all cases the powders to be coated were chemically activated prior to electrolysis.

In the present work, firstly, the elimination of hydroxycomplex formation during Ni deposition was

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studied. Secondly, some aspects of the deposition of the two-component Ni/Cu system on Fe powder was investigated.

## Experimental

1.2 M NiSO<sub>4</sub> with addition of 0.6 M NaCl and 0.6 M H<sub>3</sub>BO<sub>3</sub> was used for one-component Ni deposition. For Ni/Cu deposition 0.7 M NiSO<sub>4</sub> with addition of 0.04 or 0.004 M CuSO<sub>4</sub> was used. 0.25 M sodium citrate was used as the complex-forming agent. 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 realised here by circular stirring of the electrolyte suspension. The rate of stirring was 200–600 rpm. In galvanostatic electrolysis, the cathodic and anodic compartments of the electrolyser were separated by a diaphragm. A stainless steel cathode and a Ni sheet anode were used. In the current–potential curve measurements, paraffin impregnated graphite was used as a working electrode, Ag/AgCl as a reference electrode, and Pt wire as a counter electrode. The working electrode was polarized from zero to –1550 mV and back to +1225 mV, finishing again at zero potential. Spectrophotometric analyses were done to determine the one-component coating and adsorbed layer composition; two-component Cu/Ni coating was analysed using the differential pulse polarography method with a PA-4 analyser. The working parameters were a static mercury dropping electrode, a drop time of 2 s, a scan rate of 5 mVs<sup>-1</sup>, and a pulse amplitude of 12.5 mV.

## Results

### Deposition of Ni – elimination of the inhibition effect

Current–potential curves of Ni-coating deposition and dissolution are presented in Fig. 1. The process occurring in the negative potential region results in Ni deposition on the solid cathode as well as on the powder particles. In the positive potential region the dissolution of the deposited Ni layer takes place. The courses of the polarization curves are not smooth: in the potential region between –750 and –1000 mV a sudden current drop in the curves occurs (curve 1). It was proved [11] that this effect can be assigned to the formation of insoluble hydroxocomplexes of Ni and Fe arising in the vicinity of the surfaces to be coated as a consequence of the increasing pH in the course of the electrolysis. They adsorb on the surface and the adsorbed layer can inhibit the deposition of further metal.

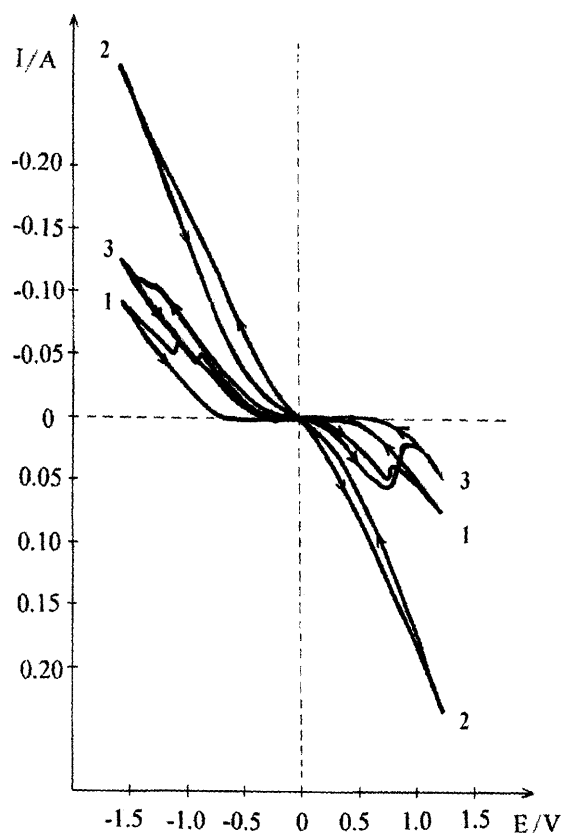
The composition of the adsorbed layer was investigated and is presented in Table 1. The dependence on the suspension density shows that the content of Fe compounds in the adsorbed layer increases as a conse-

quence of partial dissolution of the powder and, thus, the number of Fe ions increases in the solution. On the other hand, the content of Ni compounds in the adsorbed layer decreases in the same way as the Ni content on the powder.

The following ways of elimination of this unwanted inhibition effect were tried successfully:

- Increase in the rotation speed.
- Addition of complexing agent.
- Chemical removal of the adsorbed layer from the powder surface.

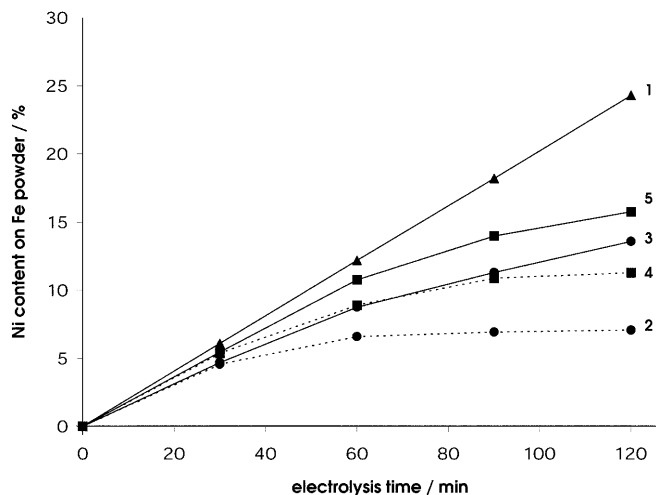
The first and second ways are presented in Fig. 1. Curve 2 shows the influence of increasing the rotation speed of stirring – no inhibition of the Ni deposition process is observed. Curve 3 proves that the addition of



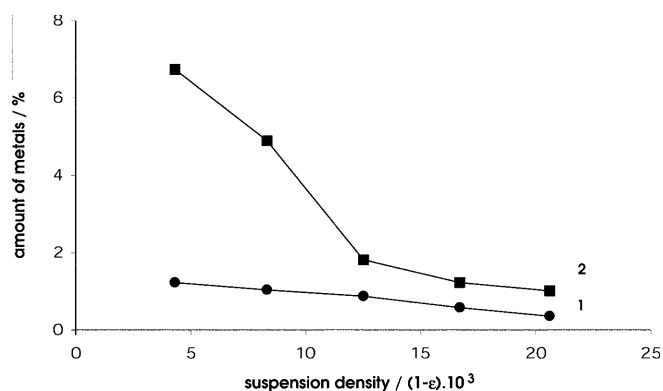
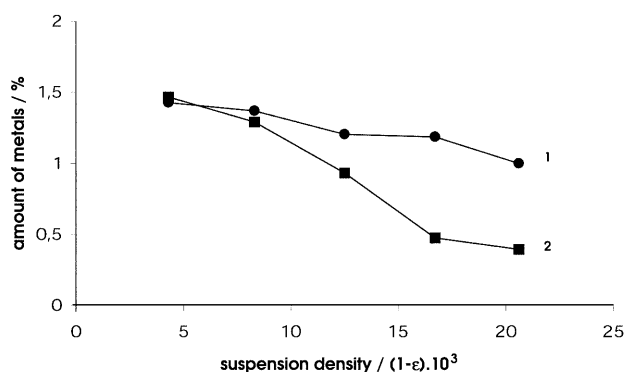
**Fig. 1** Polarization curves of Ni deposition on Fe powder. Polarization curve of Ni deposition from a Ni sulphate electrolyte. 1: rotation speed 250 rpm; 2: rotation speed 600 rpm; 3: sodium citrate added, rotation speed 250 rpm

**Table 1** The dependence of the experimentally determined amounts of hydroxocomplexes of Fe and Ni at the powder surface on the suspension density. The mean particle size of the powder was 81.5 μm

Suspension density [(1-ε)×10 <sup>3</sup> ]	Content of Fe in the adsorbed compound (mg/cm <sup>2</sup> )	Content of Ni in the adsorbed compound (mg/cm <sup>2</sup> )
4.3	0.085	0.0140
8.3	0.177	0.0120
12.5	0.282	0.0095
16.7	0.394	0.0072
20.6	0.604	0.0042



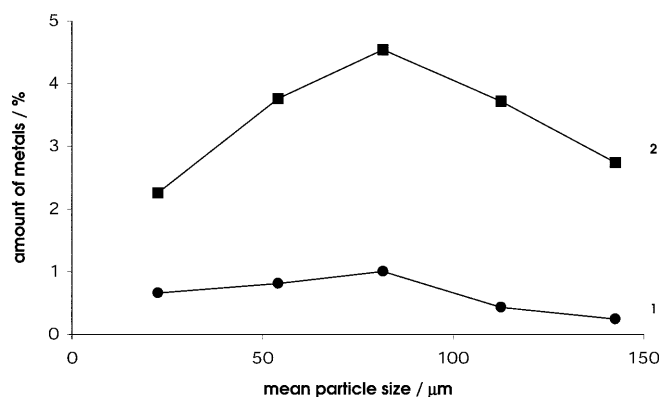
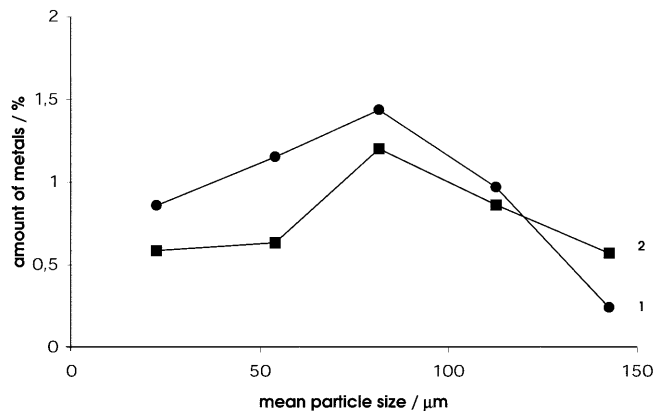
**Fig. 2** Dependence of the amount of Ni coating on Fe powder. 1: theoretical amount; 2: sulphate electrolyte; 3: sulphate electrolyte, adsorbed layer removed; 4: addition of citrate; 5: addition of citrate, adsorbed layer removed



**Fig. 3** Dependence of the content of Cu and Ni in the coating on the suspension density; 1: Ni; 2: Cu. Electrolyte composition: *upper* 0.7 M  $\text{NiSO}_4 + 0.004 \text{ M CuSO}_4 + 0.25 \text{ M sodium citrate}$ ; *lower* 0.7 M  $\text{NiSO}_4 + 0.04 \text{ M CuSO}_4 + 0.25 \text{ M sodium citrate}$

sodium citrate as a complexing agent reduces remarkably the inhibition effect.

The results of the chemical removal of the adsorbed layer can be seen in Fig. 2. In a separate experiment galvanostatic electrolysis were realised in such a way that the current was interrupted after 30 min, the cathode



**Fig. 4** Dependence of the content of Cu and Ni in the coating on the mean particle size. 1: Ni; 2: Cu. Electrolyte composition: *upper* 0.7 M  $\text{NiSO}_4 + 0.004 \text{ M CuSO}_4 + 0.25 \text{ M sodium citrate}$ ; *lower* 0.7 M  $\text{NiSO}_4 + 0.04 \text{ M CuSO}_4 + 0.25 \text{ M sodium citrate}$

compartment was disengaged, the powder was washed with  $\text{NH}_4\text{OH}$  to remove adsorbed Ni compounds, then with citric acid to remove the adsorbed Fe oxide/hydroxide compounds, dried, put back into the electrolyser, and further electrolysed (interrupted electrolysis). This procedure was repeated several times. In all cases with interrupted electrolysis the coating efficiency was higher than in electrolysis without interruption.

In Fig. 2, curve 1 represents the theoretical amount of Ni on the powder calculated according to the model [3], whereas curve 2 represents the experimentally observed amount of Ni deposited from the sulphate electrolyte which after a period of electrolysis time reaches a limiting value owing to the adsorption of insoluble hydroxocompounds. By removing this adsorption layer after each interruption, the amount of Ni obviously increases (curve 3). The previously mentioned effect of addition of complex forming agent – sodium citrate – into the electrolyte was confirmed; this is proven by the data in curve 4 – citrate addition – and curve 5 – citrate addition and interrupted electrolysis with chemical removal of the adsorbed layer. In the optimum case of both complexing agent presence and interrupted electrolysis the course of curve 5 is up to 60 min of electrolysis very close to the theoretical curve 1.

## Deposition of the two-component Ni/Cu system

The theory of electrolytic deposition of two-component layers on solid surfaces was developed about 30 years ago [14, 15, 16]. The aim of this work was to verify some of these principles in the case of deposition on powders where the granulometric and hydrodynamic parameters play an important role.

The composition and structure of a deposited alloy depend upon the conditions of electrolysis. The approaching of the distant deposition potentials of two metals may be realised either in thermodynamic or kinetic ways. To the thermodynamic ways belong change of the concentration ratio of both metal compounds in the electrolyte, addition of complexing agents, and solvate formation of different strength. To the kinetic ways belong, among others, the change of overvoltage of the deposition process by changing the current density, the temperature, the rate of stirring, etc. The kinetics of the process is also influenced by the structure of the deposited layer; it may be a eutectic mixture, a homogeneous solid solution, an intermetallic compound, or an alloy system consisting of several of the phases mentioned. In the present work, the influence of the concentration ratio of both metals in the electrolyte as well as the

addition of complexing agent on the composition of the coating was investigated for various particle size fractions and densities of the powder – electrolyte suspension.

Simultaneous deposition of Ni and Cu was supported by the addition of sodium citrate as a complexing agent into the electrolyte. The respective stability constant values of the corresponding complexes formed are favourable for simultaneous deposition of a Ni/Cu coating on the powder surfaces [17]. The coating composition is plotted against suspension density for two different CuSO<sub>4</sub> contents in the electrolyte in Fig. 3. For a lower concentration of CuSO<sub>4</sub> (0.004 M) in the region of low suspension density the difference in the coating composition is negligible, but with an increase in the suspension density, the deposition of Ni is preferred. For 10 times higher CuSO<sub>4</sub> concentration (0.04 M) the deposition of Cu is obviously preferred in the whole suspension density region; however, at low suspension densities this preference is more remarkable. So far it may be stated that low suspension densities support the deposition of the positive metal, Cu. The curves in Fig. 3 resemble in their course those obtained in the case of the one-component Ni-coating deposition [5], i.e., the amount of both metals in the coating decreases with increasing suspension density.

**Table 2** The dependence of Cu/Ni ratio in the coating on the suspension density for various electrolyte compositions

Suspension density [(1-ε)×10 <sup>3</sup> ]	Composition of electrolyte	
	0.004 M CuSO <sub>4</sub> , 0.7 M NiSO <sub>4</sub>	0.04 M CuSO <sub>4</sub> , 0.7 M NiSO <sub>4</sub>
	Cu/Ni ratio in the coating	
4.3	1.028	5.48
8.3	0.944	4.71
12.5	0.774	2.07
16.7	0.400	2.11
20.6	0.394	2.79

**Table 3** The dependence of Cu/Ni ratio in the coating on the particle size for various electrolyte compositions

Mean particle size (μm)	Composition of the electrolyte	
	0.004 M CuSO <sub>4</sub> , 0.7 M NiSO <sub>4</sub>	0.04 M CuSO <sub>4</sub> , 0.7 M NiSO <sub>4</sub>
	Cu/Ni ratio in the coating	
22.5	0.68	3.41
54.0	0.55	4.62
81.5	0.83	4.51
112.5	0.89	8.61
142.5	2.375	11.13

**Table 4** Effect of the electrolyte composition on the Ni/Cu coating deposition

Concentration in the electrolyte (mol dm <sup>-3</sup> )			Starting potential of electrodeposition (mV)	Appearance of the coating on the powder surface
NiSO <sub>4</sub>	CuSO <sub>4</sub>	Sodium citrate		
1.2	0	0	-200	Silverlike
0	0.04	0	-50	Red
0.7	0	0.25	-250	Silverlike
0	0.004	0.25	-600	Red
0	0.04	0.25	-300	Red
0.7	0.004	0.25	-550	Pink
0.7	0.04	0.25	-350	Pink

On the other hand, the dependence of the coating composition on the particle size (Fig. 4) shows a maximum in both the Ni and the Cu content in the coating at particle size fractions from 63 to 100  $\mu\text{m}$ . Again, at low  $\text{CuSO}_4$  concentrations and in the presence of sodium citrate it is possible to obtain coatings containing an excess of Ni in spite of the large difference in the values of their standard potentials (0.772 V) in favour of Cu deposition.

The Cu/Ni ratios presented in Tables 2 and 3 show that with increasing suspension density this ratio decreases, while with increasing particle size it increases for both  $\text{CuSO}_4$  concentrations used in the electrolyte. Thus, an important conclusion follows: both the size of the particles and the suspension density may remarkably influence the composition of the coating, in addition to the so far well-known parameters previously mentioned.

The results are completed by the values of the starting deposition potentials and the appearance of the coating under various electrolyte compositions in Table 4. The addition of sodium citrate shifts the deposition potential naturally to negative values.

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## Conclusions

Fe powder can be coated electrochemically by a metallic layer using the fluidized bed arrangement. Ni and Ni/Cu alloy deposition was investigated. An inhibition effect caused by adsorption of insoluble hydroxocompounds of Fe and Ni occurred during electrolysis. Its existence and composition was proved not only by the course of the current–potential curves and by a limited amount of metal on the powder surface with proceeding galvanostatic electrolysis but also by independent analyses of the adsorbed layer. It can be suppressed by the addition of a complexing agent, by using intensive stirring, and by interrupted electrolysis.

The simultaneous deposition of a Cu/Ni coating was enabled by proper electrolyte composition as to the ratio of both metallic compounds and by addition of a suitable complexing agent. Various Cu-to-Ni ratio coatings can be deposited by varying the particle size fraction and the suspension density, in addition to the electrolyte composition. Increasing suspension density supports the deposition of Ni, and increasing the particle size supports the deposition of Cu in the two-component coating.

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