

Electrode Process of Copper and Nickel Deposition on Pressed Iron Powder Electrodes

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Both cyclic voltammetry and galvanostatic electrolyses were used for investigating the electrode process of Cu and Ni deposition and dissolution on the surface of electrode formed by pressed Fe powder. Mechanical pretreatment of the powder material by grinding leads in most cases to promotion of the activity of the electrode made of it. Cyclic voltammetry records show negative shift of the anodic dissolution peak of the Fe electrode material pretreated by grinding prior to electrolysis. The peak currents of Cu deposition and dissolution are at ground electrodes higher than at unground ones. Cathodic current efficiency observed in galvanostatic electrolysis of Cu deposition may be considered as uninfluenced by the pretreatment of the electrode Fe powder material. The current efficiency of Ni deposition is in general higher than in the case of Cu deposition and lower at electrodes prepared from material pretreated by grinding when compared with those prepared from untreated Fe powder material.

Electrochemical deposition of metals on dispersed metallic powder carried out in order to alloy the powder material brings about, in comparison with deposition on a solid electrode, additional theoretical as well as practical problems. So far, most of the works in that field coped more or less satisfactorily with the latter ones [1, 2] with the aim to apply the results in preparation and utilization of the required powder materials. The theoretical problems arise from statistically changing electrode surface area as a consequence of powder particles touching and abandoning the solid cathode during the electrolysis. The contact time, the so-called lifetime of the particle during which it undergoes the electrolytical coating in contact with the cathode, depends on many variables such as rate of movement of the suspension formed by powder and electrolyte, its density and viscosity which is apparently influenced by the shape and concentration of the powder particles. In addition to this, the powder coated must be activated prior to electrolysis as any other solid electrode, only other activation procedures are used.

The aim of the present work was to gain some information on the nature of the electrochemical process applicable for alloying of powder material. In order to do so, pressed Fe powder electrodes, untreated as well as treated by grinding and annealing were studied. The powder was pressed into the form of cylinder and was used as a working electrode with constant surface in cyclic voltammetry and galvanostatic electrolysis experiments. The former method (cyclic voltammetry, hereafter as CV) was expected to give some information on parameters like depo-

sition and dissolution potentials, peak currents, etc., whereas the latter one (galvanostatic electrolysis, GE) on the cathodic current efficiency and composition of binary Ni—Cu deposit.

EXPERIMENTAL

The original powder was prepared by water pressure atomization and then pretreated prior to the electrode preparation by grinding, in some cases followed by annealing. Mechanical pretreatment by grinding was carried out in a vibration mill for 30 min. Annealing took place in a reduction atmosphere of H₂ at 800 °C for 1 h. Thus, three kinds of powder were used for electrodes preparation: untreated, mechanically treated, mechanically and thermally treated. Working electrodes were prepared by pressing the powder into a cylinder shape and put in a polyethylene tube. The geometric surface area of thus prepared electrode was 0.785 cm². Saturated calomel electrode served as a reference, stainless steel plate of about 10 times the surface area of the working electrode served as a counter electrode.

For cyclic voltammetry measurements the potentiostat OH 405 (Radelkis, Budapest) in connection with LP 4103 recorder was applied.

The electrolyte used in both CV and GE measurements was the same but for the electroactive component concentration. Its composition was: $c(\text{NH}_4\text{OH}) = 6.6 \text{ mol dm}^{-3}$, $c(\text{NH}_4\text{Cl}) = 0.6 \text{ mol dm}^{-3}$, and $c(\text{NiSO}_4 \text{ and/or } \text{CuSO}_4) = 5 \times 10^{-2} \text{ mol dm}^{-3}$ for CV and 0.06—0.6 mol dm⁻³ for GE measurements.

The electrolytically obtained coatings were dissolved in HNO_3 , diluted and analyzed by atomic absorption spectrometry.

RESULTS AND DISCUSSION

Cyclic Voltammetry of the Electrode Processes at the Pressed Iron Powder Electrodes

Fig. 1 presents the CV record of the supporting electrolyte on the untreated and mechanically treated electrodes. On the anodic sweep of both voltammograms a peak representing the dissolution of Fe from the electrode is observed, the potential of which is shifted of about 165 mV positively at the untreated electrode as compared with the pretreated

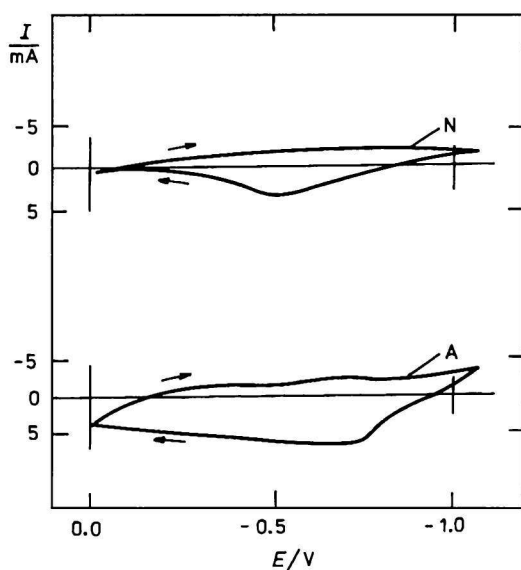


Fig. 1. Cyclic voltammetry record of the supporting electrolyte: $c(\text{NH}_3) = 6.6 \text{ mol dm}^{-3}$, $c(\text{NH}_4\text{Cl}) = 0.6 \text{ mol dm}^{-3}$ at untreated (N) and treated (A) pressed Fe powder electrodes. Sweep rate: 0.15 V min^{-1} .

one; *i.e.* the anodic dissolution proceeds much easier at the pretreated electrode. The remarkable potential difference proves great positive influence of the mechanical activation of powder upon its electrochemical reactivity. The above said was observed and proved by earlier measurements showing higher dissolution rate in sulfuric acid of the activated in comparison with the nonactivated Fe powder [2].

Fig. 2 shows the CV record of the same solution with depolarizer concentration $c(\text{CuSO}_4) = 5 \times 10^{-3} \text{ mol dm}^{-3}$. On the cathodic sweep, two waves appear belonging obviously to two-step copper deposition. The first wave is rather poorly defined. Therefore, for potential evaluation the second wave while for current evaluation the sum of both waves were taken. On the anodic sweep, three peaks appear belonging to the two steps of copper dissolution and

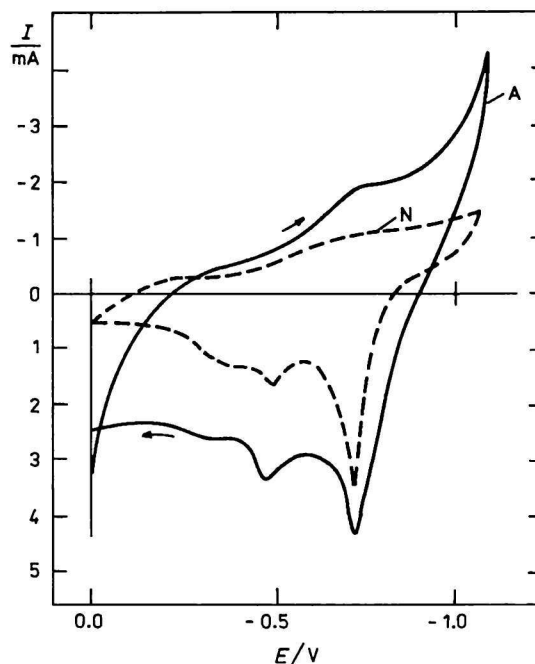


Fig. 2. Cyclic voltammetry record of copper reduction and oxidation at untreated (N) and treated (A) pressed Fe powder electrodes. Electrolyte composition: $c(\text{NH}_3) = 6.6 \text{ mol dm}^{-3}$, $c(\text{NH}_4\text{Cl}) = 0.6 \text{ mol dm}^{-3}$, $c(\text{CuSO}_4) = 5 \times 10^{-3} \text{ mol dm}^{-3}$. Sweep rate: 0.15 V min^{-1} .

to the one of iron dissolution from the electrode. The most important result, however, is the fact that both cathodic and anodic peak currents are higher at the electrode made of pretreated Fe powder material than at that made of untreated one.

The CV peak potentials are summarized in Table 1. Comparison of the Cu cathodic reduction potentials in column 1 and 3 shows a negative shift at untreated electrode ranging from 40 to 20 mV in dependence of the depolarizer concentration. The potentials of anodic oxidation in columns 2 and 4 are in most cases shifted negatively on the treated electrode, in average

Table 1. Cyclic Voltammetry Peak Potentials of Copper Reduction and Oxidation on the Pressed Fe Powder Electrodes

$c(\text{CuSO}_4)$ mol dm^{-3}	Potential vs. SCE/mV			
	Treated electrode		Untreated electrode	
	Cathodic sweep	Anodic sweep	Cathodic sweep	Anodic sweep
0				
Supporting electrolyte	–	– 715	–	– 550
5×10^{-3}	– 710	– 690	– 750	– 685
		– 440		– 480
		– 230		– 240
1×10^{-2}	– 710	– 710	– 740	– 680
		– 470		– 440
		– 230		– 220
4.76×10^{-2}	– 710	– 700	– 730	– 670
		– 360		– 385
		– 200		– 100

Supporting electrolyte: $c(\text{NH}_3) = 6.6 \text{ mol dm}^{-3}$, $c(\text{NH}_4\text{Cl}) = 0.6 \text{ mol dm}^{-3}$. Sweep rate: 0.6 V min^{-1} .

also of 20–40 mV. Again, the potential shifts prove the decrease in the activation energy of the electrochemical process on the activated electrode.

CV measurements were carried out at two various scan rates: 150 and 600 mV min⁻¹. Fig. 3 shows the effect of increasing scan rate at the activated electrode.

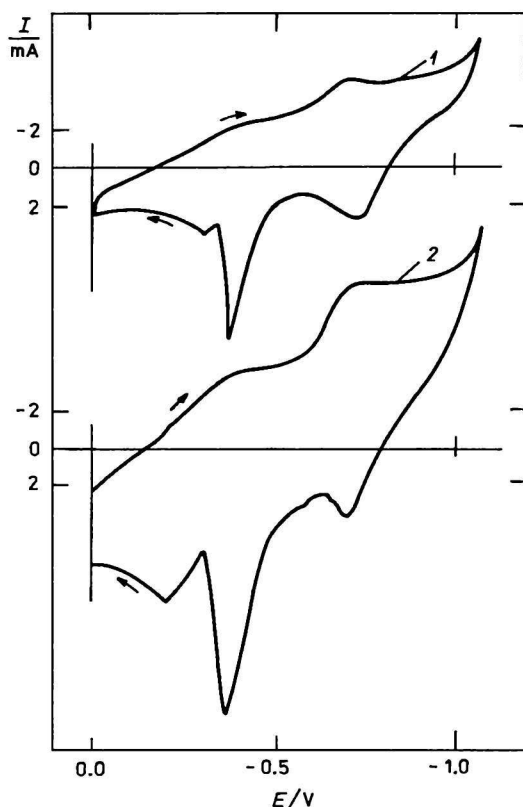


Fig. 3. Cyclic voltammetry record of the reduction and oxidation of copper on the mechanically treated pressed Fe powder electrode at different sweep rates: 1. 0.15 V min⁻¹; 2. 0.60 V min⁻¹. Electrolyte composition: $c(\text{NH}_3) = 6.6 \text{ mol dm}^{-3}$, $c(\text{NH}_4\text{Cl}) = 0.6 \text{ mol dm}^{-3}$, $c(\text{CuSO}_4) = 4.8 \times 10^{-2} \text{ mol dm}^{-3}$.

Galvanostatic Electrolyses at the Pressed Iron Powder Electrodes

The basic difference between CV and GE lasting 10 or 20 min is given by the fact that the CV process — at least in the first cycle — proceeds on free, uncovered surface and thus the influence of the electrode material nature can be better observed. In GE, only the results of the whole integral electrode process can be evaluated such as cathodic current efficiency and, in the case of binary Cu—Ni coating, the composition of the deposit. The cathodic current efficiency of Cu deposition for various concentrations of CuSO₄ is plotted in Fig. 4 evidencing the above said: the cathodic current efficiency shows no significant difference for untreated and mechanically treated electrodes.

The results of the cathodic current efficiency determination of Ni deposition presented in Fig. 5 show a surprising effect: the current efficiency at the untreated (curve 1) powder electrodes is higher than at the treated (curve 2) ones, the difference in the case of the highest NiSO₄ concentrations being 11.5 %. This effect, however, corresponds to the results obtained in different experimental series of electrolytical coating of dispersed Fe powder material by Ni [3]. In that work it was explained by accumulation of passivating oxide layers and adsorbed oxygen at the surface of the material treated by grinding.

Comparison of the results in Figs. 4 and 5 shows a lower cathodic current efficiency for electrodeposition of Cu than that of Ni under otherwise identical conditions.

In Table 2 the results of simultaneous Cu and Ni electrodeposition are summarized. The total current efficiency for the sum of both metals ranges from 80 to 100 % at the activated electrodes. Interesting is the effect of current efficiency seemingly overreaching 100 % which appears at highest CuSO₄

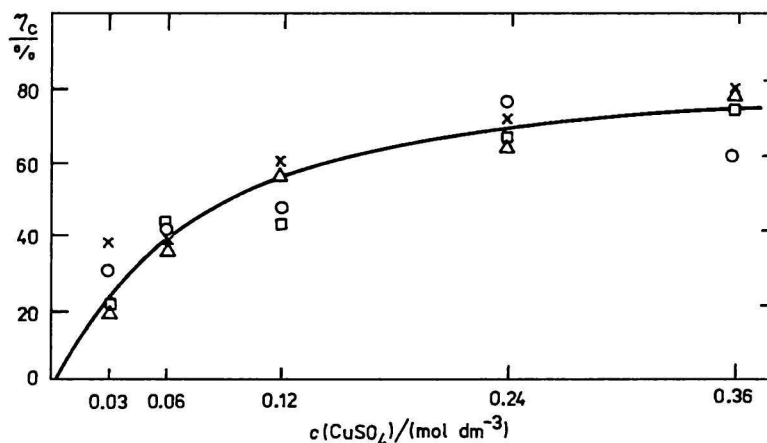


Fig. 4. Plot of the cathodic current efficiency at Cu deposition vs. CuSO₄ concentration for untreated and mechanically treated pressed Fe powder electrodes at different current densities. Total charge passed: 24 C. x Current density 2.5 A dm⁻², mechanically treated electrode; O current density 2.5 A dm⁻², untreated electrode; Δ current density 5 A dm⁻², mechanically treated electrode; □ current density 5 A dm⁻², untreated electrode.

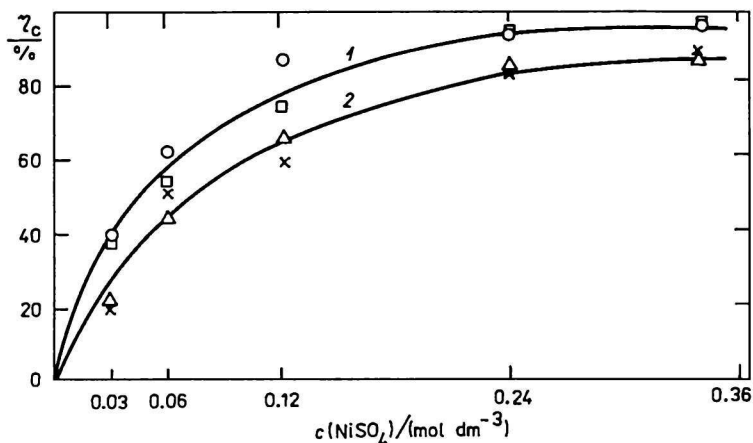


Fig. 5. Plot of the cathodic current efficiency at Ni deposition vs. NiSO_4 concentration for untreated (1) and mechanically treated (2) pressed Fe powder electrodes. Total charge passed: 24 C. Current density: \circ , \square 2.5 A dm^{-2} ; \triangle , \times 5 A dm^{-2} .

concentrations used, at untreated electrodes. It obviously may be ascribed to spontaneous chemical deposition of Cu at the electrode. This assumption is supported by the fact that traces of Fe ions have been observed in the vicinity of the electrode. It is hardly to explain that the effect is observable neither at mechanically treated electrodes nor in the case of Cu deposition only.

The results of simultaneous Cu—Ni deposition on variously pretreated electrode powder material are compared in Table 3. The coating composition, basically influenced by the metal content ratio in the bath, is almost identical for the untreated and both mechanically and thermally pretreated electrode material and only slightly lower for mechanically activated powder. In earlier study [3], the positive influence of thermal treatment of the powder after mechanical grinding has been observed. The total amount of metal deposited is the lowest at untreated electrode. The cathodic current efficiency at both only ground and ground and annealed powder electrodes is close to 100 %, at the untreated one it is 92 %. The above results hold for the first decisive stage —

Table 2. Dependence of the Cathodic Current Efficiency of Cu—Ni Coating Deposition on the Pressed Fe Powder Electrodes upon the Electrolyte Composition for Variously Pretreated Electrode Material

$c(\text{CuSO}_4)$ mol dm^{-3}	Cathodic current efficiency/%			
	Current density/ (A dm^{-2})			
	2.5		5.0	
	Electrode		Electrode	
	Untreated	Mechanically treated	Untreated	Mechanically treated
0.06	—	—	92	100
0.12	77	88	72	71
0.24	53	89	83	93
0.36	123	87	110	91

Electrolyte composition: $c(\text{NH}_3) = 6.6 \text{ mol dm}^{-3}$, $c(\text{NH}_4\text{Cl}) = 0.6 \text{ mol dm}^{-3}$, $c(\text{NiSO}_4) = 0.6 \text{ mol dm}^{-3}$. Total amount of charge passed: 24 C.

Table 3. Electrolytic Deposition of Cu—Ni Coating on the Variously Pretreated Pressed Fe Powder Electrodes

Electrode	Total charge passed C	Amount of metal deposited/mg Cathodic current efficiency/%					
		Cu		Ni		Cu + Ni	
		mg	%	mg	%		
Untreated	24	1.3	19	5.5	81	6.8	92
	48	1.5	15	8.5	85	10	68
Treated by grinding	24	1.7	23	5.7	77	7.4	101
	48	2.2	20	9.2	80	11.4	78
Treated by grinding and annealing	24	1.4	18	6.0	82	7.4	100
	48	1.8	16	9.0	84	10.8	73

Electrolyte composition: $c(\text{NH}_3) = 6.6 \text{ mol dm}^{-3}$, $c(\text{NH}_4\text{Cl}) = 0.6 \text{ mol dm}^{-3}$, $c(\text{NiSO}_4) = 0.6 \text{ mol dm}^{-3}$, $c(\text{CuSO}_4) = 0.6 \text{ mol dm}^{-3}$. Current density: 5 A dm^{-2} .

first 10 min — of electrolysis when the electrode material nature could play still a role. In the later stages of electrolysis, the amount of Cu deposited sinks while the amount of Ni increases. These observations imply again the idea of spontaneous chemical Cu deposition at the uncovered or slightly covered electrode surface in the first stages of electrolysis.

The conclusion may be drawn that the deposition of Ni at powder electrode may be better controlled than the deposition of Cu. The pretreatment of the powder electrode material influences more Ni than Cu deposition.

REFERENCES

1. Kurvyakova, L. M., Zhanov, A. M., and Zakharova, E. P., *Poroshkovaya metallurgiya*, No. 12, 214 (1979).
2. Molnár, F., Dudrová, E., Gálová, M., and Lux, L., *Proceedings of the 1st International Conference on Mechanochemistry*, p. D22. Košice, 1993.
3. Gálová, M., Lux, L., Dudrová, E., and Šepelák, V., *J. Mat. Sci.*, in press.

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