

# Current Efficiency of the Electrochemical Metal Deposition Process on Fe Powder Particles

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The coating of powder particles with a metallic layer can be realized in an arrangement known as "fluidized bed" where the electrolyte is formed by a suspension of the bath solution and the powder particles. In the present case, the Fe powder particles have been coated with a nickel layer. The thickness of the metallic layer on the powder particles is controlled, beside other parameters, by the reactivity of the powder surface, density of suspension, current intensity, and the size of the coated powder particles. Theoretical calculation of the composition of the coated product based on an earlier developed model of charge distribution between the solid cathode and the powder particles was compared with the experimentally obtained results. Good agreement between theory and experiment was found. The differences are explained as an influence of hydroxy complexes of Fe and Ni formed in the course of the process.

Improvement of properties of basic material for powder metallurgy can efficiently be done by using the electrochemical coating of basic Fe powder. Electrochemical deposition of metal plating on the powder gives the best results as to the homogeneity of the product. Experimentally, this process was to a great deal solved for case of electrolytical coating of nickel on the surface of Fe powder particles [1, 2]. A model dealing with the change of the solid electrode surface as a consequence of its contacts with the powder particles for various suspension densities and mean particle size was suggested in [2]. Instead of a homogeneous electrolyte, the suspension of powder in the electrolyte solution was used and kept in fluidized state by intensive circular stirring. Similar arrangement with vertical upside down electrolyte flow is known in electrochemistry as fluidized bed electrode. The arrangement with circular stirring was used also in the present work.

The mechanism of the charge transfer in fluidized bed electrodes has been studied by many authors. Charge transfer due to the elastic collisions of charged powder particles in the bulk of suspension is discussed by *Fleischmann* and *Oldfield* [3, 4]. Such a mechanism is called "collision mechanism". Another possibility, the so-called conductive mechanism was described by *Sabacky* and *Evans* [5] and *Plimley* and *Wright* [6]. In this case particles form aggregates and chains with short lifetime contacting either the electrode or other chains. Charges pass through the chains by electronic

conduction. *Yen* and *Yao* [7, 8] describing the application of fluidized bed electrode for metal recovery from diluted electrolyte solutions made an analysis of the bipolar behaviour of the powder particle as a single solid sphere in the fluidized bed and suggested a corresponding mathematical model. *Gabrielli* and coworkers [9, 10] based their model of the fluidized bed electrode in a dynamic regime upon an earlier work by *Newman* and *Tobias* [11] concerning porous electrode model.

In the present case the quantity being of the utmost interest from the practical point of view is the amount of Ni deposited on the powder particles or, in other words, the thickness of the Ni layer on the Fe powder. This is influenced by many hydrodynamic, granulometric, and electrochemical parameters. Three of them, the intensity of the current passing through the cell, the density of the electrolyte—powder suspension, and the size of the powder particles were investigated in the present work. These parameters play an important role in the distribution of charge between the solid cathode and the powder particles on one side, and between the required Ni coating process and side reactions on the other. The amount of Ni coating on the powder particles in dependence on the three above-mentioned parameters was calculated according to the model suggested in [2] and extended in [12]. Their comparison with the experimentally obtained values was the subject of investigations.

## EXPERIMENTAL

Electrolytical coating of Fe powder particles with nickel in an electrolyte of pH 2 containing 1.2 M- $\text{NiSO}_4$ , 0.6 M- $\text{NaCl}$ , and 0.6 M- $\text{H}_3\text{BO}_3$  was studied. Fe powder separated by sieving into the five granulometric groups characterized by mean particle size of  $\phi/\mu\text{m}$  = 20, 50, 80, 112.5, and 142.5 was used. The electrolytic cell consisted of two separate compartments: the cathodic one of 150  $\text{cm}^3$  and anodic one of 600  $\text{cm}^3$  volumes. Both compartments were separated by a diaphragm (textile net with mesh size of about 0.04 mm) and separately stirred. As a negative electrode – current feeder in the fluidized bed electrolysis terminology – a stainless steel solid plate of geometric surface 15.74  $\text{cm}^2$  was applied. The counter electrode placed opposite the current feeder in the anodic compartment was made of pure nickel. The movement of the stirrer in the cathodic compartment was electronically controlled and kept constant within  $\pm 10 \text{ min}^{-1}$ . The rotation speed was chosen with the intention to prevent sedimentation of the particles.

The activation of the Fe powder prior to the electrolysis is similarly necessary as in any other solid surface plating process. It removes the passivating layers and improves the coating efficiency of the process. The main activation procedures tested here were mechanical, thermal, and chemical activation. Mechanical activation (samples marked M) consisted of grinding in a Pallmann-type mill with two pressing discs with a rotation rate  $11000 \text{ min}^{-1}$  in air atmosphere for 1 h. Thermal activation (samples marked T) was realized by annealing in a reduction atmosphere of split ammonia at  $850^\circ\text{C}$  for 1 h. Chemical activation (samples marked C) was carried out by immersing the powder into a reducing solution of 10 % hydrazinium chloride for 3 min, filtering, rinsing with distilled water

and methanol, and drying. Combination of these procedures (samples marked MT, MC) as well as non-activated powder (samples marked N) were also used [2].

## RESULTS AND DISCUSSION

## Pretreatment of the Powder

The results concerning the powder preactivation for different mean particle size by various ways are shown in Fig. 1. The parameter evaluated is the so-called “partial current efficiency” expressing the ratio of experimentally found amount of nickel deposited on the powder particles to the theoretical amount calculated according to the Faraday’s law.

The first set of bars in Fig. 1 representing the results of grinding the powder in air atmosphere shows very low values of the partial current efficiency most likely due to the air-supported passivating oxide layer formation during the grinding process. The mechanical treatment followed by both thermal and chemical treatment – shown in the second and third set of bars in Fig. 1 – brings about a remarkable increase in the partial current efficiency values due to the reducing effects of  $\text{N}_2 + \text{H}_2$  atmosphere in thermal and of hydrazinium chloride in chemical parts of treatment. Still better results obtained by chemical treatment only are shown in the last set of bars in Fig. 1. This effect may be explained by the fact that while during the mechanical treatment process the surface irregularities are ground down, during the chemical treatment they are preserved and new surface destruction occurs as a consequence of etching. In the course of further experiments, the chemical treatment was adopted which, in addition to the high values of the partial current efficiency reached, possesses further advantages: a simple

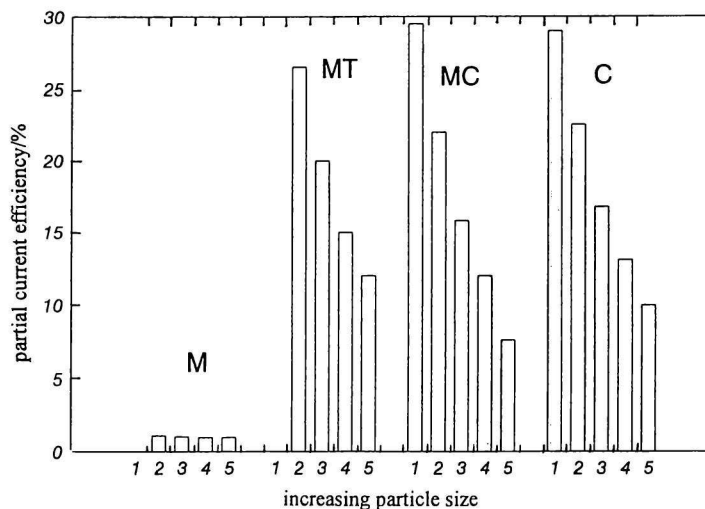


Fig. 1. The values of partial current efficiency of Ni coating process on Fe powder particles for different pretreatment ways of the powder. Mean particle size of the powder  $\phi/\mu\text{m}$ : 1. 20, 2. 50, 3. 80, 4. 112.5, 5. 142.5.

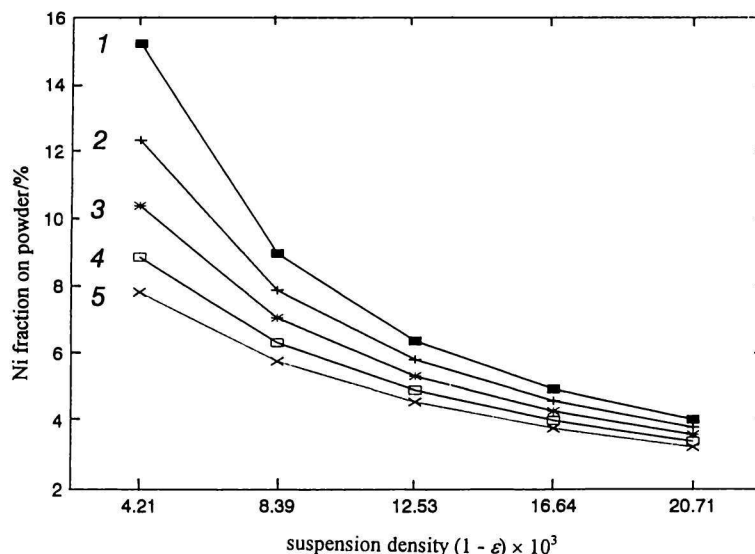


Fig. 2. Calculated changes of Ni fraction in electrolytically coated Fe powder particles with increasing suspension density expressed in terms of voidage factor  $(1 - \epsilon) \times 10^3$ . Mean particle size  $\phi/\mu\text{m}$ : 1. 20, 2. 50, 3. 80, 4. 112.5, 5. 142.5, electrolysis time: 60 min, current 1 A.

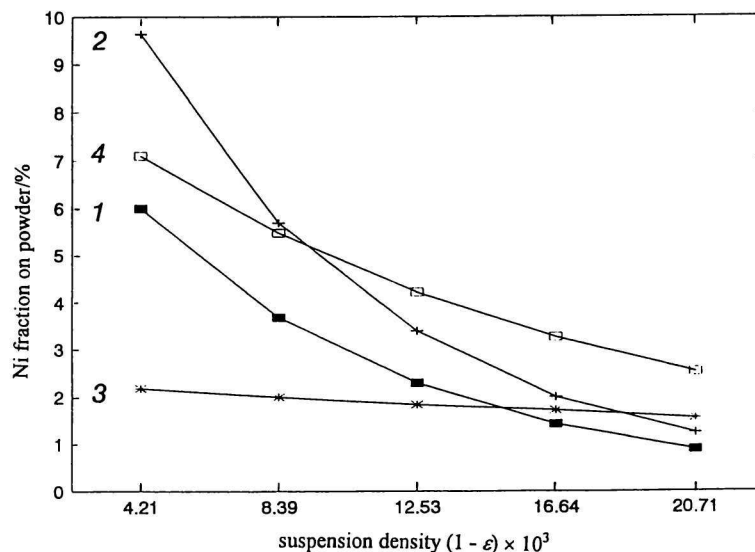


Fig. 3. Experimental values of Ni fraction on Fe powder vs. suspension density expressed in terms of voidage factor  $(1 - \epsilon) \times 10^3$  for different mean particle size and electrolysis current. 1. 50  $\mu\text{m}$ , 1 A; 2. 50  $\mu\text{m}$ , 3 A; 3. 112.5  $\mu\text{m}$ , 1 A; 4. 142.5  $\mu\text{m}$ , 3 A.

way of performance, room working temperature, and a better reproducibility of results owing to identity of time passing between the activation and electrolysis processes at every sample.

### Influence of the Suspension Density

The suspension density is expressed in terms of "voidage factor" defined by [13] as the ratio of volume occupied by the electrolyte to the total volume of suspension formed by solid phase (powder particles) plus electrolyte. In order to plot the increasing suspension density on the  $x$ -axis, the quantity  $(1 - \epsilon)$  was used. The parameter evaluated was the fraction of Ni on the

powder particles determined by independent analytical methods.

Theoretical considerations regarding the distribution of charge between the solid cathode and the powder particles are discussed in detail in [12]. They are based on the idea of the calculation of the so-called "working volume of the electrolytic cell" depending upon the cell geometry. This working volume represents that part of the suspension attached to the electrode in which the contacts between the powder particles and the solid cathode occur. In the electrolytic cell applied, the working volume represents 3.72 % of the whole cathodic compartment volume. The calculation of the surface area of the particles present in the

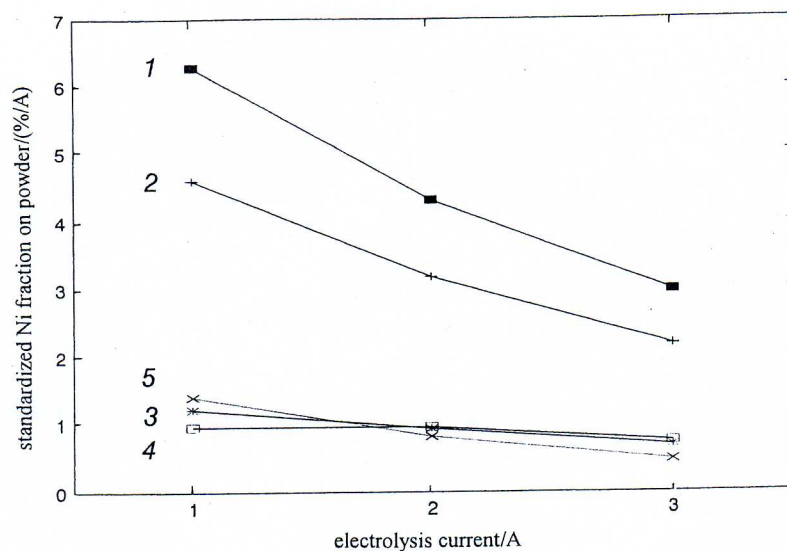


Fig. 4. Experimental plot of Ni fraction on Fe powder *vs.* electrolysis current for different suspension densities. Suspension density expressed in terms of voidage factor  $(1 - \epsilon) \times 10^3$ . 1. 4.21, 2. 8.39, 3. 12.63, 4. 16.64, 5. 20.71.

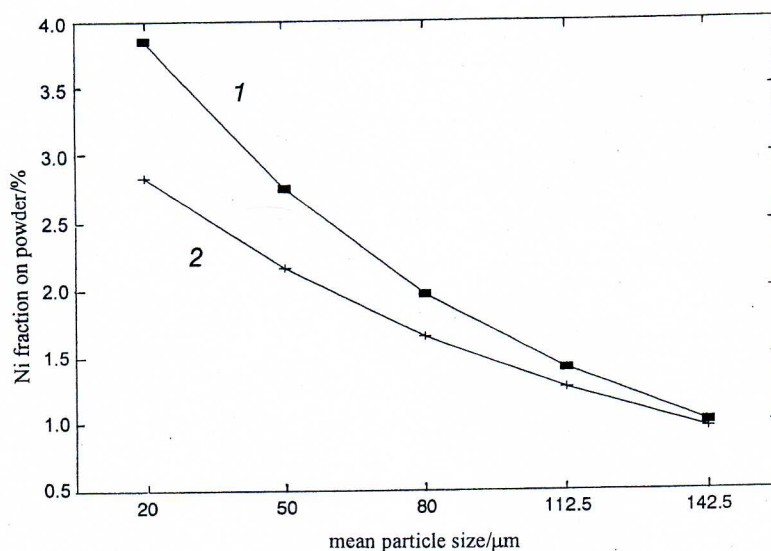


Fig. 5. Experimental plot of Ni fraction on Fe powder *vs.* mean particle size for two different suspension densities  $(1 - \epsilon) \times 10^3$ . 1. 12.53, 2. 20.71.

working volume is based on the assumption of uniform spheres with diameter equal to the mean linear dimension of the given granulometric fraction. The distribution of charge between the solid cathode and the powder particles and thus the theoretical distribution of the amount of nickel deposited on the appropriate surfaces is considered as being uniform and proportional to the surface areas.

The results of theoretical calculation of the fraction of Ni deposited on the powder are shown in Fig. 2. The increase in suspension density obviously results in the decrease in the fraction of Ni deposited on powder particles under conditions of identical amount of charge passed through the electrolyte. Corresponding

experimental results confirming the theoretical considerations are shown in Fig. 3. The theoretical trend is more obvious for smaller particles (see curves 1 and 2) and for lower current intensities (*cf.* curves 3 and 4).

#### Influence of Current Intensity

In Fig. 4 the standardized fractions of Ni coating on the powder particles related to current intensity unit for various suspension densities are shown. A decrease of current efficiency with increasing current intensity would normally be expected due to the hydrogen evolution reaction from acidic bath of pH 2. The expected



effect actually occurs and is manifested in a decrease in the fraction of Ni coating on the Fe powder. It proves that the above side reaction takes place also on the powder particles. Comparing curves 1 and 2 with the other three curves 3, 4, and 5 it may be stated that the above effect is more significant in case of lower suspension densities. In a more dense suspension, the current density at all surfaces is very low due to a large surface area and thus, the probability of occurring side reactions is also lower.

### Influence of the Particle Size

With the increase in the linear dimension of the powder particles both fraction of Ni on the powder and partial current efficiency decrease, which is confirmed by the experimental results shown in Figs. 1 and 5. In Fig. 5 the unfitted points present the change in fraction of Ni on the powder with increasing particle size for two different suspension densities. This effect is obviously connected with the decrease in the surface area per mass unit of larger powder particles. As a consequence, a lower surface area is available in the working volume of the electrolytic cell for participating in the charge distribution.

### CONCLUSION

The results presented show that the electrolytical plating of powder particles by metallic coating can be realized in the fluidized bed electrolysis. The thickness of the coating as well as the current efficiency of the process on powder particles is influenced, beside other, by the following parameters:

- the current intensity: with its increase the current efficiency decreases;
- the size of the coated powder particles: both the

amount of nickel on the powder and the current efficiency decrease with increasing particle size;

– the powder to electrolyte ratio indicated here as suspension density: the influence of this parameter is rather complicated but it is analyzed in detail in the present study.

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