Determination of the Surface Activity of Powders by Electrochemical Methods

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Two electrochemical methods are suggested in order to control the surface reactivity of metallic powder particles with regard to the following electrolytic plating. It is the determination of both the open circuit potential and anodic dissolution current of a specially constructed carbon paste electrode containing the investigated powder particles. Iron powder of different granulometric classes activated by grinding, annealing, and chemical reduction was used to prove the suitability of the chosen methods. It was found that both experimental parameters reflect the state of the surface.

The electrochemical coating of powders was studied for the purpose of improving the properties of the base powder material in powder metallurgy. The results of this study were described elsewhere [1, 2].

Reactivity of the metallic powder material is an important property in the process of its electrolytical coating, similarly as is the reactivity of any solid surface being coated electrochemically or otherwise. Chemical and electrochemical etching are the methods usually applied for activation of solids. In the process of activating powders prior to electrolytical coating, grinding and annealing can also be used.

In order to carry out the electrolysis efficiently it is important not only to detect the extent of the powder activation in advance but also to learn something more about the effects caused by the respective activation processes in the powder particles.

There are several direct as well as indirect methods for determining the resulting activity of the powder surface. To the direct methods belong, *e.g.* measuring the kinetics of powder dissolution, the electrochemical potential of the surface, the anodic dissolution current, *etc.* Indirect methods are presented, for instance, by the determination of the amount of metal deposited on the surface of powder particles as compared with the total theoretical amount of the deposited metal. This parameter corresponds to the so-called partial current efficiency defined in [1]. The results of the latter method are analyzed in detail also in [1].

The choice of electrochemical methods such as potential or anodic current measurements brings about the problem of proper preparation of the working electrode. Several possibilities exist. One of them described in [3] consists in pressing the powder into the form of cylindrical electrode with defined surface. This method, however, cannot prevent that some changes occur in the surface structure during pressing the powder. More reliable way to prepare the electrochemical sensor used in the present work consists in constructing a carbon paste electrode (CPE) mixed with the respective activated iron powder in a suitable ratio. Such electrode will hereafter be referred to as "composite" and marked Fe-CPE. Recently, the so-called abrasive electrode was referred to in the literature [4, 5] being actually a graphite electrode impregnated by paraffin in vacuum (with an abbreviation PIGE given by the authors). The measured powder is transferred to and kept at the electrode surface by light abrasion. After each measurement the powder sample in the surface is renewed and thus rather reproducible results are obtained.

In addition to the electrochemical methods, the chemical dissolution rate of the pretreated Fe powder in a proper solution could be measured. The results of such investigations will be presented later.

In the present work, both the composite and PIGE electrodes were prepared. Most of the measurements were, however, carried out on the composite electrode. The PIGE electrode measurements were used only occasionally in order to prove the values of the measured parameters. Two electrochemical quantities were measured in order to reflect the surface activity of the powder: first, the open circuit potential and second, the anodic dissolution current of the powder containing electrodes in the respective electrolyte. Both quantities represent the state of surface of the powder.

EXPERIMENTAL

Iron powder W-V-200 prepared in ZVL Dolný Kubín, Slovak Republic, by pressure water atomization process containing less than 1 % of impurities (Mn, S, P, and C) was used for preparation of the composite electrode. The following ways of activating the powders were applied:

Mechanical activation by grinding in a Pallmann type mill with two pressing disks, with a rotation rate 11 000 min^{-1}, in air atmosphere for 1 h.

Thermal activation by annealing in reduction atmosphere of H_2 and N_2 in a volume ratio 3:1 for 1 h.

Chemical activation by treating with reducing agent of 10 % hydrazinium chloride solution for 3 min, filtering, rinsing by distilled water and methanol, and drying.

Combinations of two or even three of the above methods were used, too.

Following the activation, the powder was screened into five granulometric size fractions (ø/mm) 0.00—0.040, 0.040—0.063, 0.063—0.100, 0.100—0.125, and 0.125—0.160.

Fe-CPE electrode was prepared by mixing properly graphite and iron powders in a mass ratio 9:1 with addition of paraffin oil and acetone. Approximately 0.7 to 0.8 cm^3 of oil was added to 1 g of the powder mixture. After evaporation of acetone, the obtained paste was filled into a plastic injection syringe. After each measurement, the surface of the electrode was renewed by pushing out and cutting the used paste and polishing the surface with glossy paper. PIGE electrode was prepared according to [5]: graphite rod was put into molten paraffin under vacuum and kept there for 2 to 3 h at elevated temperature of about 85 °C. The transfer of powder sample to the rod surface is realized by gentle rubbing the end of the rod on the sample. The electrode is then dipped into the electrolyte and raised just above the level of the solution.

The polarographic analyzer PA 3 (Laboratorní přístroje, Prague) was used for cyclic-voltammetric measurements of the anodic dissolution current. For potential measurements, a QTK compensation bridge (Metra Blansko) was applied. The electrolyte consisted at both potential and current measurements of 0.095 mol dm^{-3} NaCl and 0.0075 mol dm^{-3} HCl. An inert atmosphere of nitrogen saturated with the electrolyte was applied. Silver chloride electrode with a saturated KCl salt bridge was used as reference. Each potential measurement was repeated 4—7 times, the measurement of the anodic dissolution current values was repeated 8—12 times. Both parameters were evaluated statistically.

Estimation of the Metallic Portion in the Electrode Surface Area

Experimental estimation was realized by metallographic microscope measurements of the metallic part in the CPE surface. Direct measurement of the Fe-CPE surface was not possible due to the poor ability of the microscope to distinguish between the carbon and iron surfaces in the paste material containing paraffin oil. The same is valid for other accessible methods as EDAX, electron microscope, etc. The following procedure had therefore to be adopted: 1.8 g of carbon and 0.2 g of the respective Fe powder of various size fraction processed by various pretreatment ways was homogenized with acrylic polymer and allowed to harden for 24 h in a glass vessel. After this period, the glass was broken and the obtained surface was cut and polished. Under the microscope it was divided into 12—26 sections each of which was scanned microscopically for determination of the metallic portion.

Table 1. Mean Values and Corresponding Standard Deviations of the Open Circuit Potential ($-E$/mV) Measured *vs.* Ag/AgCl Reference Electrode on the Fe-CPE Containing Variously Pretreated Fe Powders

	Pretreatment way	Size fraction/μm				
		0—40	40—63	63—100	100—125	125—160
		$-E$/mV				
1	M-CH	602 ± 2	604 ± 3	602 ± 2	611 ± 6	585 ± 2
2	CH	552 ± 2	573 ± 11	586 ± 7	563 ± 5	590 ± 4
3	CH-T	516 ± 2	557 ± 3	540 ± 7	545 ± 2	544 ± 3
4	M	538 ± 9	531 ± 19	540 ± 17	530 ± 14	562 ± 6
		562 ± 3*	560 ± 3*		565 ± 3*	561 ± 3*
5	M-CH-T	528 ± 4	534 ± 3	522 ± 6	537 ± 9	545 ± 5
6	M-T		513 ± 3	517 ± 7	520 ± 2	521 ± 1
7	T		510 ± 2	507 ± 5	517 ± 5	510 ± 2
8	Without pretreatment	531 ± 6	547 ± 3	575 ± 4	573 ± 13	585 ± 9
			568 ± 3*		565 ± 3*	

* Values measured by the PIGE electrode.

RESULTS AND DISCUSSION

Measurements of the Potential of Powder

The concept of correlation between the decrease in potential and increase in reactivity of the metal – see, *e.g.* the electrochemical series of standard electrode potentials of metals – is applied here in order to compare the efficiency of various pretreatment ways: the more negative the potential of the powder sample, the higher the reactivity of its surface with respect to the following electrolysis.

The results of measurement of open circuit potentials of the Fe-CPEs containing variously pretreated Fe powders of different granulometric size fractions are summarized in Table 1 in terms of mean potential and the respective standard deviation values.

Independence of the measured potential values on the particle size would be expected and is indeed observed in Table 1 with the exception of the "as received" sample. The surface of this sample is, however, badly defined due to its unknown history and therefore will not be analyzed. As to the efficiency of various pretreatment ways, the sequence from most to least efficient ways is as follows:

M-CH / CH / CH-T / M / M-CH-T / M-T / T

M, T, and CH mean mechanically, thermally, and chemically treated Fe powder samples, respectively.

The sequence is identical for middle granulometric classes, the lowest and highest particle size classes differ slightly.

Two conclusions may be drawn from these results: chemical activation treatment is efficient when applied alone or in combination with other ways whereas thermal treatment leads to deactivation rather than to activation of the surface. The same sequence was observed when determining the amount of metal deposited on the respectively pretreated powders [1]. Thus, the efficiency of powder electroplating decreased in the cases where the electrode potential values measured here showed an increase. This effect was explained on the basis of X-ray measurements and micrographic records as being caused by surface and subsurface structural changes occurring in the course of the pretreatment process. It was discussed in detail in [1].

The value of the open circuit potential of CPE only – without Fe powder – was determined as (-320 ± 20) mV All values measured for Fe containing CPEs are by 200 to 300 mV more negative, which points out to the fact that the Fe powder particles carry negative charge.

The values of potentials measured by the abrasive electrode are also presented in Table 1 (marked by asterisk). With regard to both the standard deviation and negligible change of the potential values with the particle size they could be regarded as more reliable in comparison with those obtained with Fe-CPE. This is due not only to the electrode nature but also to the measurement procedure – they were obtained by voltammetric measuring of polarization curves in the linear μA current region. Basically, however, good agreement is observed between both sets of values. The small differences between potential values measured on PIGE and Fe-CPE electrodes may be caused by the fact that the powder particles at the former electrode are directly exposed to the electrolyte while at the latter one they are at least partially covered by the layer of organic phase.

Values of the Anodic Dissolution Current

Fig. 1 presents the cyclic voltammetry (CV) record of CPE without (curve *1*) and with (curve *2*) Fe powder. It may be clearly seen that the anodic current in the presence of powders is of more than two orders of magnitude higher and thus the powder-free CPE anodic current line may be taken as a base line.

The mean values and the corresponding standard deviations of the anodic dissolution current measured at a potential of -200 mV *vs.* Ag/AgCl electrode
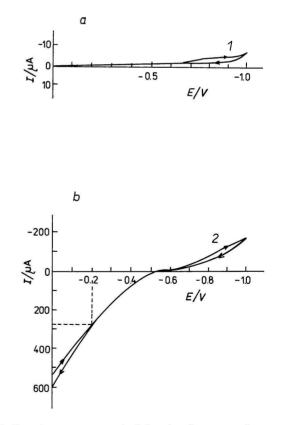

Fig. 1. Cyclic voltammetry record of the *a*) carbon paste electrode, *b*) carbon paste electrode containing mechanically activated Fe powder of the size fraction 0.00—0.04 mm. Sweep rate: 50 mV s^{-1}, electrolyte: 0.095 mol dm^{-3} NaCl + 0.0075 mol dm^{-3} HCl, reference electrode: Ag/AgCl.

Table 2. Mean Values and Corresponding Standard Deviations of the Anodic Dissolution Current ($I/\mu A$) Recorded at -200 mV vs. Ag/AgCl Electrode on the Fe-CPE Containing Variously Pretreated Fe Powder

	Pretreatment way	Size fraction/μm				
		0—40	40—63	63—100	100—125	125—160
		$I/\mu A$				
1	CH	370 ± 20	650 ± 80	660 ± 90	600 ± 20	620 ± 80
2	M-CH	840 ± 5	900 ± 10	540 ± 80	500 ± 15	570 ± 10
3	CH-T	290 ± 60	620 ± 50	500 ± 10	420 ± 55	390 ± 30
4	M-CH-T	200 ± 20	380 ± 20	270 ± 30	300 ± 10	320 ± 30
5	M	290 ± 5	270 ± 30	250 ± 20	300 ± 15	260 ± 30
6	M-T		115 ± 5	120 ± 10	190 ± 10	220 ± 15
7	T		100 ± 40	85 ± 15	30 ± 10	60 ± 15
8	Without pretreatment	110 ± 30	250 ± 40	270 ± 10	250 ± 10	210 ± 5

Table 3. Values of Calculated and Measured Specific Surface Areas and Metallic Portion in the Surface Area for Various Size Fraction Classes of the Fe Powders

Size fraction/μm	$10^3 \cdot$ specific surface area values/(m^2 g^{-1})		Measured metallic portion of the electrode surface/%
	Calculated	Measured	
		*	**
0—40	38.07		$< 10—31 >$
40—63	15.23	66.7	$< 14—40 >$
63—100	9.52	42.3	$< 12—32 >$
100—125	6.77	21.8	$< 8—32 >$
125—160	5.34	7.5	$< 22—52 >$

*Measured by the BET method.
**Values estimated by metallurgical microscope in acrylic polymer media, data interval in percentage of the whole electrode surface.

are summarized in Table 2. Comparison of the data given in Table 2 with those in Table 1 presents nearly the same sequence for both anodic dissolution current and potential values for various pretreatment ways. This may be considered as a proof for the fact that both chosen electrochemical experimental parameters reflect the reactivity of the powder surface.

The anodic dissolution current values shown in Table 2 reflect, however, not only the reactivity but also the area of the metallic part in the surface of Fe-CPE which is different for various granulometric size fractions of the powder. In order to eliminate this effect, the current density instead of current values should be taken into account, which requires knowledge of the metallic part area in the Fe-CPE surface. In order to solve this problem, trials were made to determine this value experimentally by optical microscope observations of the Fe-CPE surface. Owing to the low distinguishing ability of the equipment between carbon and iron surfaces in the paste electrode these measurements did not provide any results. Substitution of paraffin oil in the carbon paste by acrylic polymer enabled to obtain some results as to the metallic part in the surface of electrode. They are obtained as percentage from the whole electrode surface area. The fluctuation of the values is rather high, therefore it is more relevant to give the interval of percentage for various

granulometric size classes. These values presented in Table 3 show that there is no essential difference between the metallic portions in various size fractions but for the largest granulometric class 0.125 to 0.160 mm where the metallic portion is higher. This effect is most likely due to the gravitation segregation of the heavy iron particles in the acrylic polymer media. The same undesirable but in acrylic polymer unavoidable effect may occur also in lower particle size fractions. Consequently, application of thus obtained results for calculation of the current density values is unsuitable. It is, however, reasonable to assume that in the case of Fe-CPE electrode the gravitation segregation is negligible due to the high viscosity of the paste medium.

Since the aim of the presented work is to find some correlations between the reactivity of the Fe powder surface and the way of activation it is assumed that the measured values of current may be transformed to current density by using the specific surface area values taken from the model calculation as published in [6]. The basic ideas of the model are presented in detail in the original work. Simplifying assumptions of the model relevant to the present problem are the following:

Powder particles are assumed to be spherical; for calculation of the sphere surface the mean value of the radius in the given granulometric class was taken.
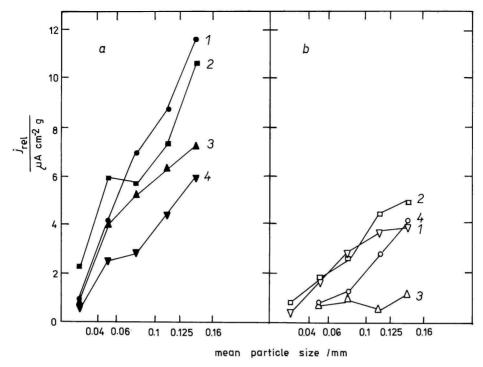
Fig. 2. Values of the relative anodic dissolution current densities on the carbon paste electrode containing variously pretreated Fe powder for different granulometric size fractions. Way of pretreatment: *a)* *1.* chemical, *2.* mechanical and chemical, *3.* chemical and thermal, *4.* mechanical, chemical, and thermal activation; *b)* *1.* nonactivated sample, *2.* mechanical, *3.* thermal, *4.* mechanical and thermal activation.

Fe powder is homogeneously distributed in the whole volume of the CPE.

The Fe powder distribution in the working part of the electrode surface is identical with that in the electrode volume.

The same portion of the powder is in contact with the electrolyte solution in all particle size fractions. This assumption follows from the previous one.

Based on the above simplifications, the specific surface area of the powder particles was calculated for each size fraction taking into account the mean linear dimension in the given granulometric class. The results obtained are published in [6] but for the sake of clarity and comparison they are shortly summarized again in Table 3.

For verification of the calculated specific surface area values measurements using the BET method were done. The obtained values given for comparison in Table 3 show agreement in order of magnitude and in trend. The differences may arise from two facts – the measured values fluctuate around the detection limit of the BET method and the real particles are more structured than spheres assumed in the model.

The measured values of the anodic dissolution current were then transferred by means of the calculated specific surface areas to the "relative current densities" which represent the correction of the measured currents to the different extent of the metallic portion in the CPE surface for various granulometric size

fractions. The values of thus obtained "relative anodic current densities" are presented in Fig. 2.

The sequence of the relative anodic current density from most to least values for various pretreatment ways shown in both parts of Fig. 2 is as follows:

CH / M-CH / CH-T / M-CH-T / M / M-T / T

Justification of applying the model for calculation of current density is based on the validity of assumptions and simplifications introduced. To verify them, other suitable independent methods should be used. Next, the more complete measurements with the above-mentioned abrasive electrode are planned. In the present state, the obtained values of anodic dissolution current densities are not the absolute values and therefore may be used only in order to compare the efficiency of various ways of activation of the powder.

As a conclusion it may be stated that both methods reflect the efficiency of the way of the powder pretreatment.

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