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Investigation of the reactivity of powder surfaces by abrasive voltammetry

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Abstract The ability of abrasive voltammetry to reflect the reactivity of iron powder immobilized on paraffin-impregnated graphite electrodes was investigated. Normal pulse voltammetry was used as the preferred method. The peak shape and position on the potential/time axis reflected both the reactivity of iron powder particles as well as their size fraction. “Relative peak height” defined as peak height to area ratio, i.e., current to charge ratio, correlated well with the rate of the electrochemical dissolution process. It showed not only a decreasing dissolution rate with an increase in particle size, but also the differences in the dissolution rate of iron powder of various reactive surfaces as a consequence of various pretreatment methods. It was found that chemical pretreatment of the powder always resulted in a faster dissolution process in comparison with other non-chemical pretreatment methods.

Key words Abrasive voltammetry · Powder particles · Electrochemical dissolution · Surface reactivity

Introduction

Conductive powder material, mainly iron powder, is frequently used as a basic material in powder metallurgy. In order to achieve the required properties of the final product, such as hardness, corrosion resistance, etc., it is necessary to add alloying components to this basic material. Uniform distribution of the alloying component, which is of utmost importance for its ho-

mogeneity and consequently for its quality, may very advantageously be reached by electrochemical plating of the powder material by the alloying metal [1–3]. As in every electrochemical plating process, the reactivity of the plated surfaces prior to electrolysis should be ensured. In the case of solid surfaces, this is usually performed by degreasing, chemical etching, and other conventional procedures. In the case of plating powder particles, additional pretreatment methods may be used such as grinding, annealing, and their combinations with chemical reduction and etching procedures [2].

It is highly desirable to obtain some information on the reactivity of powder surfaces prior to the electrolytical plating process and consequently, on the basis of this knowledge, choose the best pretreatment method for the respective powder material. One of the classical methods of determining the surface reactivity of the powder is the measurement of its dissolution rate by measuring the content of a dissolved substance in a suitable medium. However, this is a rather slow and work-consuming method. Earlier work was carried out in our laboratory in order to develop some faster electrochemical methods reflecting the state of the surface of the powder [4]. Measurements of the potential and anodic dissolution current of carbon paste electrode modified by the investigated Fe powder used in the above mentioned work proved this electrode not to be an ideal electrochemical sensor owing to both the presence of insulating paraffin oil as binder and the uncertainty in estimating the metallic part of the electrode surface. Better results with this electrode were reached using acidic binders such as hydrochloric acid, but the substances used in these studies [5, 6] were less soluble iron oxides. The same binder, 1 M HCl solution, was also used [7, 8] to study iron and copper oxides. In the case of a metallic Fe modifier, it may be supposed that the acidic binder would react with it and complicate the interpretation of the results.

In the present work, the possibility was investigated of applying paraffin impregnated graphite electrodes

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(further referred to as PIGEs) developed by Scholz et al. [9] as a sensor for the electrochemical determination of the reactivity of powders expressed as the reaction rate of their electrochemical dissolution.

The described PIGE electrode had already been successfully applied to the study of electrochemical dissolution processes of various powder materials: iron(III) oxides and hydroxy-oxides [10, 11], powder mixtures such as HgS + HgO, HgO + PbO, MnO₂ + FeOOH [12], iron(III) and chromium(III) oxides and ferrites [13]. Various electrochemical techniques were used in these investigations, mainly cyclic voltammetry.

The preferred method used here was the normal pulse voltammetric (NPV) technique because it provides an easily measured signal. Both peak current and potential are well defined and relatively well reproducible. Cyclic voltammetry (CV) was used as a complementary informative method.

Experimental

All experiments were carried out with help of an electrochemical analyzer (ECM 700, Berlin, Germany) in a three-electrode arrangement. The working PIGE electrodes were prepared by vacuum impregnation of spectral pure graphite rods of 5 mm diameter by melted paraffin for about 2 h [9]. The investigated Fe powder, the estimated amount of which ranged from 1 to 10 µg, was immobilized by light abrasion onto the surface of the electrode. The electrode was then immersed carefully into the electrolyte solution so that only the face of the electrode contacted the solution [9, 12]. The experiments were performed using an Ag/AgCl reference electrode with 3 mol dm⁻³ KCl (potential +0.222 V vs. NHE), and platinum sheet of about 0.5 cm² surface as the counter electrode. KCl solution (1 mol dm⁻³) was used as the electrolyte. All solutions were deaerated by purified nitrogen before inserting the prepared working electrode and recording the *i*-*E* curves.

Iron powder of WV-200 type was prepared at ZVL, Metalsint Dolný Kubín, Slovakia, by a pressure water atomization process. It contained less than 1% of impurities: C, S, O₂, P, Mn, and Si. Following the pretreatment, Fe powder was separated by sieving into five granulometric classes: 0–45, 45–63, 63–100, 100–125, and 125–160 µm.

The pretreatment ways were as follows. No activation (N) was applied to the as-received powder sample. Mechanical activation (M): grinding in a Pallmann-type mill with two pressing disks with a rotation rate 11000 rpm, in an air atmosphere for 1 h.

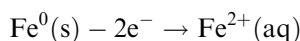
Thermal activation (T): annealing at 850 °C in a reducing atmosphere consisting of H₂ and N₂ in a stoichiometric ratio of 3 : 1 for 1 h.

Chemical activation (CH): treating in an aqueous reducing solution of 10% hydrazinium hydrochloride at room temperature for 3 min, filtering, rinsing by distilled water, methanol, and drying. A combination of two or even three of the above methods were also used.

The potential ranges for the CV and NPV studies are given in the respective figures or tables.

Results and discussion

The overall reaction taking place at the electrode may be considered as electrochemical dissolution of Fe powder:



Since the experiments were done in the absence of oxygen and other oxidizing agents, it may be assumed that neither oxide formation nor other passivating reactions took place at the electrode. The detailed mechanism of this reaction was not investigated.

Cyclic voltammetric measurements were applied in the present experiments in order to obtain basic information as to the range of potentials at which the dissolution of Fe powder to Fe(II) ions as well as the reverse process, the reduction of Fe(II) ions, occur at the PIGE electrode in 1 M KCl as the supporting electrolyte.

It may be seen in Fig. 1 that on increasing the concentration of Fe(II) ions in solution the cathodic reduction peak of Fe(II) at -1.08 V versus the reference electrode increases. At the same time, the anodic dissolution peak of the Fe deposited in the preceding cathodic cycle appears. Figure 2 confirms the identity of the CV records in the case of Fe powder immobilized on a PIGE

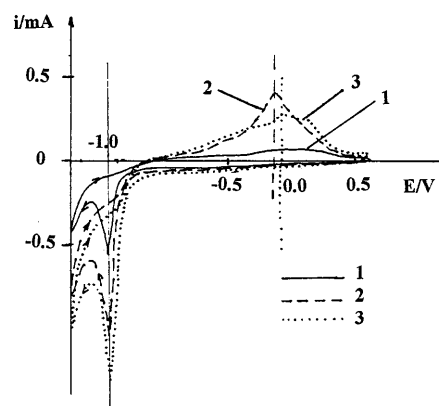


Fig. 1 Cyclic voltammogram (CV) of the electrode process in the presence of Fe²⁺ ions in the basic electrolyte (1 mol dm⁻³ KCl solution) on the paraffin-impregnated graphite electrode (PIGE). Concentration of Fe²⁺ ions: curve 1 0.005, curve 2 0.01, curve 3 0.015 mol dm⁻³. Reference electrode Ag/AgCl, scan rate 100 mV s⁻¹

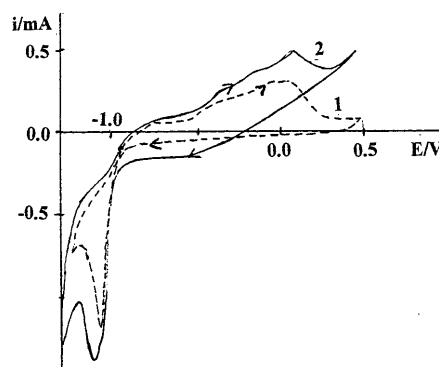


Fig. 2 CV of the electrolyte containing 0.015 mol dm⁻³ Fe²⁺ ions on the PIGE electrode in the absence (curve 1) and in the presence (curve 2) of Fe powder on the electrode. Reference electrode Ag/AgCl, scan rate 100 mV s⁻¹

electrode and Fe(II) ions reacting from solution. Figures 1 and 2 show that the oxidation/reduction process is highly irreversible in the electrochemical sense: the oxidation of solid Fe powder takes place in the range around zero potential value, whereas the peak of the reduction of Fe(II) ions occurs roughly at -1.0 V versus the Ag/AgCl reference electrode. As will be shown later, the potential at which this process occurs changes with the particle size and with the reactivity of their surface. This result corresponds with other studies on various microcrystalline metal oxides [11, 13, 14] where the potential of the dissolution peaks changed with the particle size. With regard to the subject of this work, only the dissolution process of the solid powder was further investigated.

The CV technique proved to be useful for identification of the electrode processes connected with the dissolution of solid Fe powder. In further experiments, however, the NPV technique turned out to be more favourable owing to better defined peaks, more reproducible results, and shorter times of each experiment. In Fig. 3a and b the comparison of CV and NPV peak shapes is presented.

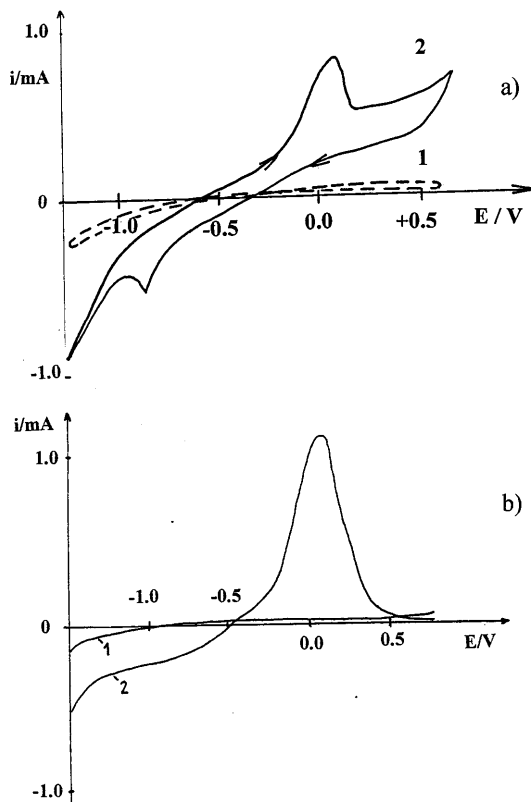


Fig. 3 CV (a) and normal pulse voltammetry (NPV) (b) records on the PIGE electrode. Curves 1 records of basic electrolyte, curves 2 records with immobilized Fe powder. Basic electrolyte solution: 1 mol dm^{-3} KCl, reference electrode Ag/AgCl. Scan rate: CV, 100 mV s^{-1} ; NPV, 10 mV s^{-1}

It is further demonstrated that the shape of the NPV peak could give more accurate information as to the rate of the electrochemical reaction. In Fig. 4, the NPV records are presented for electrochemical dissolution of small (curve 1) and large (curve 2) Fe powder particles. The difference in the peak shapes is obvious. The peak belonging to the dissolution of small particles is steep and well defined whereas the shape of the peak of the dissolution of large particles is broad and ill defined. The position of the maximum of the dissolution peak shifting anodically with increasing particle size is one of the indications for the rate of the respective electrochemical reactions.

The measurement of each dissolution peak position on the potential axis was carried out 7–10 times. The mean values and corresponding standard deviations of the anodic NPV peak potentials for all studied granulometric classes of the powder, as well as for all the pretreatment ways used, are summarized in Table 1. From these results it is evident that the NPV peak potential of Fe powder oxidation shifts with increasing particle size towards more positive values, i.e. a more positive potential is required for anodic dissolution of larger particles.

The same parameter can be used to reflect various pretreatments. From the data in Table 1, the comparison of chemical with other ways of pretreatment can also be done. It is clearly seen that chemical activation is very efficient as to the activation of powder and therefore to the rate of dissolution: all types of chemically activated powders, i.e., chemically only and in combination with other pretreatment ways, dissolve at more negative potentials, i.e., better than those not chemically activated. Compare, for instance, the values in the column marked M with that marked CH, the column marked M with that marked M-CH, etc. Thus, chemical pretreatment of Fe powder is one of most efficient.

In the discussion the following simplifying assumptions have to be adopted. First, Fe powder material

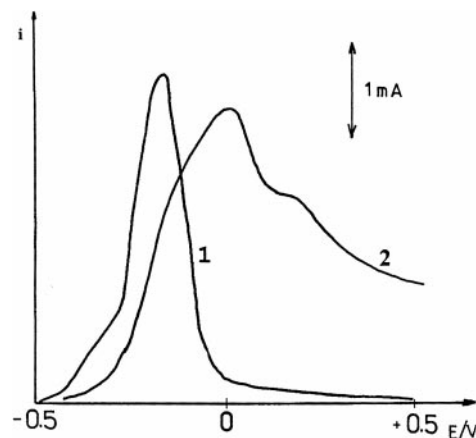


Fig. 4 NPV of Fe powder on the PIGE electrode. Scan rate 10 mV s^{-1} , reference electrode Ag/AgCl, pulse amplitude 10 mV . Mean particle size of the mechanically and chemically pretreated powder: curve 1 22.5 μm , curve 2 142.5 μm

Table 1 Change of the normal pulse voltammetry (NPV) peak position with the mean particle size and various activation pretreatment processes of the powder. Basic electrolyte 1 M KCl, reference electrode 3 M Ag/AgCl, potential range from -0.5 to +0.5 V

Mean particle size (μm)	Position of the NPV peak values in V with standard deviation													
	CH		M		T		M-T		M-CH		T-CH		M-T-CH	
	σ	σ	σ	σ	σ	σ	σ	σ	σ	σ	σ	σ	σ	σ
22.5	-0.136	± 0.014	-0.151	± 0.007	-0.163	± 0.019	-0.203	± 0.013	-0.141	± 0.011	-0.097	± 0.014	-0.151	± 0.013
54	-0.119	± 0.016	-0.107	± 0.028	-0.135	± 0.019	-0.114	± 0.019	-0.113	± 0.016	-0.084	± 0.015	-0.091	± 0.008
81.5	-0.068	± 0.024	-0.027	± 0.020	-0.075	± 0.022	-0.070	± 0.017	-0.032	± 0.012	-0.033	± 0.018	-0.064	± 0.019
112.5	-0.027	± 0.027	-0.004	± 0.032	-0.027	± 0.013	-0.011	± 0.025	-0.019	± 0.023	-0.012	± 0.013	-0.012	± 0.023
142.5	0.019	± 0.026	0.003	± 0.034	0.000	± 0.021	0.016	± 0.012	0.010	± 0.018	0.033	± 0.039	0.000	± 0.021

consists inside the given granulometric fraction of monodisperse spheres with a diameter corresponding to the mean diameter value of the sieved fraction. Second, their electrochemical dissolution proceeds uniformly from the whole surface, thus keeping the spherical shape of the particles during the electrode reaction.

The reactivity of the powder particles in general is given by the number of active sites on their surface. This depends – apart from other influences neglected in this discussion – on two parameters: the surface area, which is an extensive parameter, and the specific number of active surface sites, which is an intensive parameter. The former parameter is given by the particle size: the larger the particles, the lower the total surface and vice versa. The latter parameter is influenced by the activation process: the more efficient the activation pretreatment, the more active centers are formed and the higher is the reactivity of the powder and, consequently, the rate of any reaction on its surface.

In the course of an electrochemical oxidation/dissolution process, the microcrystalline solid immobilized on the PIGE electrode surface is completely or to a great extent consumed during the heterogeneous reaction, which reduces the rate of the electrode reaction. On the other hand, the increase of the potential applied accelerates the electrode process. Both these effects have been extensively discussed [14]: the rate of such an electrochemical reaction is a function of both the potential applied and the degree of conversion of the powder. Therefore, the position of the peak maxima is given not only by the potential but also by the actual extent of the dissolution of the electroactive substance.

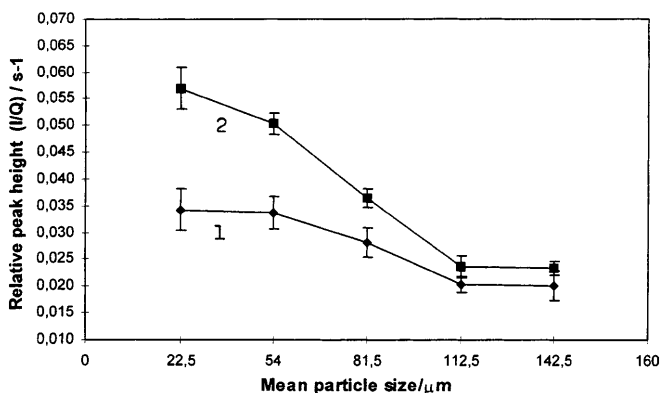
However, the original goal of the present work was to find an adequate electrochemical parameter to distinguish among variously pretreated and thus variously reactive powders.

In order to achieve results better reflecting the rate of the electrode reaction, a parameter suggested in [14] was used. It was obtained as peak current I to the total charge passing Q_T ratio in the given potential/time region (from -0.5 to +0.5 V). This relative peak height with a dimension s^{-1} is directly proportional to the rate of the electrochemical dissolution reaction at the peak potential:

$$s = i_p/Q_T$$

It is demonstrated both in Fig. 5 and in Table 2 that so-defined parameter reflects different sizes of the reacting particles as well as various ways of pretreating the powders. It can clearly be seen from Fig. 5 that with increasing particle size the relative peak height, and thus the reaction rate, decreases.

The results shown in Fig. 5 prove further that solely mechanically treated particles react more slowly than those mechanically and chemically treated. Table 2 summarizes the values of the relative peak heights for all investigated particle sizes and ways of pretreatment. The trends are as follows: in all cases the chemical treatment

**Fig. 5** Dependence of the NPV relative peak height on the powder particle size. Basic electrolyte: 1 mol dm^{-3} KCl solution, reference electrode Ag/AgCl. Activation procedure of the Fe powder investigated: curve 1 M, curve 2 M-CH**Table 2** Change of the NPV relative peak height I/Q_T with various activation procedures and different mean particle sizes

Mean particle size (μm)	Values of the relative peak height $I/Q_T \times 10^2$ (s^{-1})							
	N	CH	M	M-CH	T	T-CH	M-T	M-T-CH
22.5	3.89	5.51	3.43	5.70	3.28	6.04	2.87	4.90
54.0	3.58	5.30	3.37	5.03	3.26	5.26	2.84	4.30
81.5	3.44	4.47	2.82	3.65	3.10	4.45	2.79	3.66
112.5	2.77	3.38	2.04	2.37	2.58	3.48	2.27	2.69
142.5	2.53	3.28	2.01	2.33	2.33	2.64	2.15	2.35

increases the dissolution rate in comparison with the respective non-chemical treatment. Therefore, the chemically treated particles dissolve faster than untreated ones, the thermally and chemically treated particles dissolve faster than those treated only thermally, and so on. Mechanical activation by grinding in air can cause two effects responsible for reducing the rate of the dissolution reaction of powder: removing the larger surface roughnesses and thickening of the original oxide layers. Thermal treatment on the one hand removes the passivating oxide layers from the powder surface but, on the other hand, brings about recovery of the crystal lattice, resulting in its higher arrangement and thus in lowering the surface activity of the powders. The M-T treatment combines the above effects.

In conclusion it may be stated that the experimental results confirm the justification of using the relative peak height as a parameter most generally reflecting the active state and thus the dissolution rate of the powder particles.

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