SHORT COMMUNICATION

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Application of abrasive stripping voltammetry in corrosion science. I. determination of the corrosion potentials of metals

Abstract The application of abrasive stripping voltammetry for the determination of the corrosion potential of metal powders is described. Micro amounts of a metal are fixed on a paraffin-impregnated graphite electrode immersed in suitable electrolyte solutions and polarization curves are recorded. The value of the corrosion potential is determined by Tafel analysis. The precision of the method is $\pm 0.5\%$ (mean rel. dev.) of the final potential value.

Key words Abrasive stripping · Corrosion potential

Introduction

Here it is shown that abrasive stripping voltammetry, more generally called voltammetry of immobilized microparticles, originally introduced by Scholz and coworkers [1–5], proved to be suitable for the determination of the corrosion potential of metals, especially advantageous in the case of powdered metals.

Experimental

A small amount of metallic powder was spread on the surface of a glazed porcelain tile and, by rubbing its surface, a micro amount of the powder was fixed on the lower base of a small paraffin-impregnated graphite rod forming the electrode (PIGE) fixed in a metallic holder enabling the electrical contact. This working iron powder PIGE, which together with a suitable reference electrode (1 M Ag/AgCl electrode) and an auxiliary Pt electrode formed a three-electrode system, was fixed in the plastic head of the Metrohm electroanalytical vessel filled with 50 ml of a solution mixture containing 0.0925 M NaCl and 0.0075 M HCl. This solution was previously deaerated by bubbling through with pure nitrogen. The iron PIGE was fixed in such a way that its base with

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metallic powder touched tangentially only the upper level of the solution.

The iron powder being investigated was of "two nine" purity containing less than 1% overall impurities (Mn, C, S, P); all other chemicals used were of analytical grade purity.

Cyclic voltammetric measurements were performed under following conditions: the potential of the working iron PIGE potential ranged between -0.45 V and -0.7 V, starting at -0.6 V for both the cathodic as well as the anodic sides. The chosen starting potential corresponds roughly to the value of the zero-current electrode potential of metallic iron immersed in the electrolytic solution used. For the voltammetric measurements a multipurpose polarograph (Mehrzweck-Polarograph GWP 673) was used.

Results and discussion

The recorded polarization curves (Fig. 1) had the expected shape, with cathodic and anodic parts featuring clear a dependence of the sequence of voltammetric cycles, not enabling a precise determination of the zero-current potential. The anodic part the polarization curve ($i < 0$) corresponds to the electrolytic dissolution of iron according to the equation $Fe \rightarrow Fe^{2+} + 2e^-$ (the hydrolysis of the originating Fe^{2+} ions is prevented by the presence of the sufficiently acid supporting electrolyte solution corresponding to pH = 2). The cathodic part then corresponds to the hydrogen evolution reaction $2H^+ + 2e^- \rightarrow H_2$. The zero-current potential is attained when the rates of both cathodic and anodic processes are equal. The current values in Fig. 1 were corrected for the background current values obtained by polarization of the pure deaerated supporting electrolyte.

Figure 1 reveals that the voltammetric dependence of each investigated sample changes after repeated cycles: the first voltammetric cycle proceeds on the fresh virgin surface of the particles without any previous electrolytical treatment; during the second and all following cycles the surface of the particles decreases owing to their anodic dissolution. A further effect contributing to the decreasing slope of the recorded polarization curves can mainly be due to a progressive decay of the originally
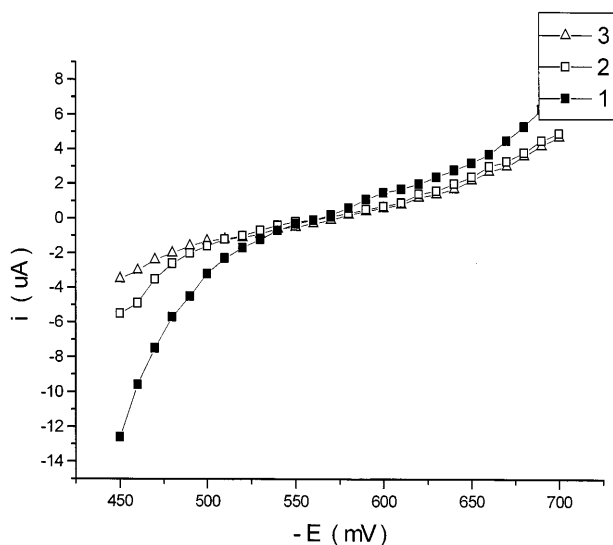
Fig. 1 The simplified polarization curves from experimentally obtained cyclic voltammograms of pure iron in a mixed solution of 0.0925 M NaCl + 0.0075 M HCl: *1* first cycle, *2* second cycle, *3* third cycle

Fig. 2 The semilogarithmic form of the same polarization curves as Fig. 1

present passivation or corrosion layer. (This effect is, however, more important for the limited change of the value of the corrosion potential in the case of repeated polarization, as will be shown further.)

A further evaluation of the voltammetric curves obtained was performed by means of a Tafel plot (Fig. 2). The value of the corrosion potential, i.e. the zero-current potential, can be determined by extrapolating the linear parts of the Tafel plot up to their intersection. This value can be determined graphically or, more precisely, by means of a regression analysis of each section. The general equation has the form $\log |i| = -aE + b$. The corrosion potential value can now be calculated as follows: $E_{\text{corr}} = (b_c - b_a)/(a_a - a_c)$, where a_c and a_a are the slopes of the c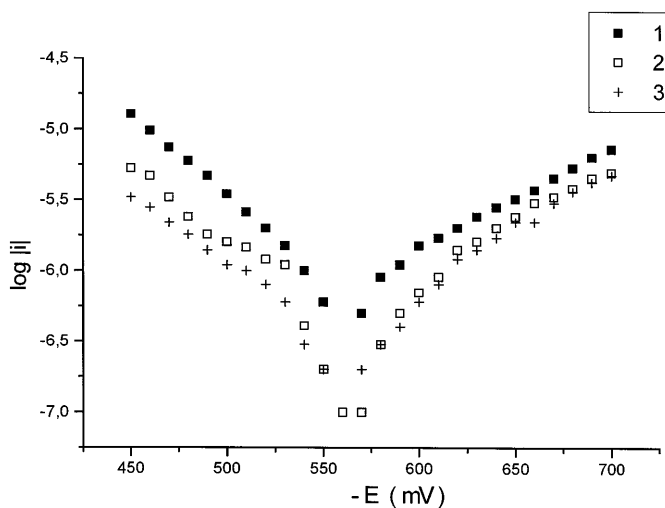orresponding plots of the cathodic and anodic sections of the Tafel plot, and b_c and b_a are their corresponding intercepts on the $\log |i|$ axis. The precision of this determination is very good, i.e. about ± 0.003 V, which corresponds to approx. $\pm 0.5\%$ as the mean relative deviation.

In the course of this study it was observed that the corrosion potential, determined in the way described, slightly shifts from one cyclic polarization to the other until the values finally remain constant after five to ten cycles (cf. Fig. 3). This effect can be explained as the result of a progressive decrease of the originally present passivation places or layers on the surface of the metal grains. This can cause a shift of the standard electrode potential of the anodic process and consequently a shift of the entire anodic part of the corrosion process to more positive values.

The described method has been developed for and applied in a research program dealing with the me-

Fig. 3 The dependence of the corrosion potential on the polarization cycles
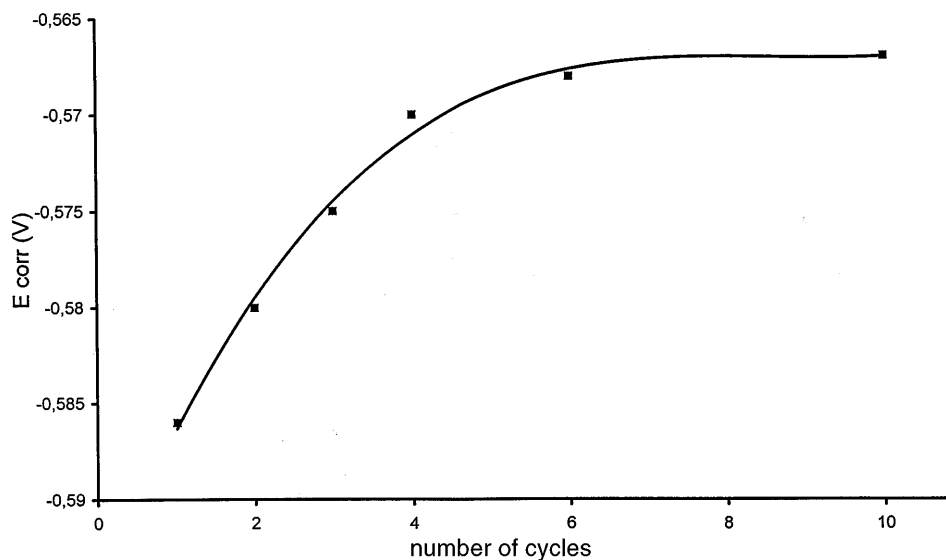
chanochemical activation and electroplating of powdered iron [6]. For this purpose we tested several iron powder fractions of different granulometric size ranging from 40 to 160 µm and one sample without a previous fractionation. The final corrosion potentials (after several voltammetric cycles) ranged between −0.560 V and −0.568 V with a mean deviation of ±0.003 V for one individual measurement (corresponding to approx. ±0.5% of rel. error), independent of the granulometric fraction size of the sample. The mean values of the corrosion potentials of all samples studied have been calculated as −0.562 ± 0.003 V. The precision of the method proved to be satisfactory.

The relation of these results to the above-mentioned mechanochemical research are discussed elsewhere [6].

Conclusion

This study shows that a mechanical immobilization of the particle of a metal powder on the surface of a suitable graphite electrode allows determination of the corrosion potential by simple cyclic polarization measurements and a Tafel plot evaluation of the data.

There are two alternatives: the use of paste electrodes, usually made from graphite, metal powder and an oil as the binder, or the fabrication of sintered electrodes from the metal powder. While paste electrodes prepared from the same metal powder as reported in this work yielded very scattered corrosion potentials between −0.530 V and −0.585 V with a standard deviation almost 10 times higher than with the mechanical immobilized particles, sintered electrodes [7] cannot be regarded as a good choice either. They suffer from corrosion and it cannot be taken for granted that the sintering will not alter the surface and corrosion properties of the powder.

The described method for the determination of corrosion potentials of powdered metals prevents all the mentioned problems. It is a micro method and it offers sufficient precision and reproducibility.

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