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Electrochemical corrosion resistance of Fe–Nd–B permanent magnets

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The corrosion behaviour of three permanent magnets based on the Fe–R–B system, namely $Fe_{76.9}Nd_{15.1}B_8$ (Vacodym 335), $Fe_{76.7}Nd_{14.3}DyB_8$ (Vacodym 370) and $Fe_{77}Nd_{15}B_8$ (Neomax 35) was investigated in 0.5 M H_2SO_4 using mass loss and electrochemical techniques. Differences in the chemical composition of the tested magnets did not affect the runs of polarization curves in the active dissolution range or in the cathodic one, but they influenced the runs of these curves in the passive state. The magnets show distinct lack of resistance to acid corrosion both in the magnetized and demagnetized state. Weak corrosion resistance appears also at strongly cathodic polarizations, and the rate of this abnormal dissolution increases with the rise of the hydrogen evolution rate on the surface of the magnets

1. Introduction

Ternary intermetallic compounds with the $R_2Fe_{14}B$-(especially $Nd_2Fe_{14}B$)-type structure can exhibit high coercivity and are therefore very suitable for permanent magnet applications [1].

Because of their very useful magnetic properties, $R_2Fe_{14}B$ intermetallic compounds are not only the subject of the numerous technological and physical studies, but also tend to be applied more and more widely [2, 3], despite recent reports about their exceptionally weak corrosion resistance [4–6]. This is understandable when one considers the fact that rare-earth elements belong to the most active metals; their standard potentials are $\varphi^0_{Me/Me^{n+}} = -2.3$ to -3.4 V. According to the results in [7] the addition of only 0.5 wt % of rare-earth metals accelerates the corrosion rate of the steel 5 to 10 times. Co_5Sm magnets, as our research has shown [8], corrode in acid medium (pH $\approx$ 0) approximately 30 times faster than spec-pure cobalt, whereas in the neutral medium (pH = 7) the corrosion rates of Co_5Sm and cobalt are comparable. It should be added that the state of magnetization hardly affects the corrosion of Co_5Sm magnets.

The present work aims at the electrochemical evaluation of the corrosion resistance of Nd–Fe–B permanent magnets in acid medium.

2. Experimental procedure

Three commercial permanent magnets Nd–Fe–B were used for the study: $Fe_{76.9}Nd_{15.1}B_8$ (Vacodym 335), $Fe_{76.7}Nd_{14.3}DyB_8$ (Vacodym 370) and $Fe_{77}Nd_{15}B_8$ (Neomax 35). For both polarization and gravimetric studies, disc specimens of 0.071 cm^2 surface area were used. Potentiokinetic tests were carried out at a disc rotation rate of 13.8 r.p.s. and a potential sweep rate of 100 mV min^{-1}, starting with a cathodic potential of -0.75 V and going up to potentials close to $+2.5$ V (against SCE (Saturated Calomel Electrode)). The rate of spontaneous dissolution of magnets was determined with a weight-loss method and also by applying periodic analysis of Fe^{2+} ions in the solution, by means of a colorimetric method using 1.10 phenanthroline [9]. In the same way the rate of dissolution of magnets at cathodic polarization (below φ_{corr}) was determined. As a test solution, an argon-saturated 0.5 M H_2SO_4 solution prepared from concentrated acid and doubly-distilled water was used. All the experiments were performed at 25 ± 0.1° C. Detailed data concerning the apparatus and the test method are given in [10 and 11].

3. Results and discussion

Figure 1 shows the anodic and cathodic behaviour of the three magnets and, for comparison, of spec-pure iron measured in 0.5 M H_2SO_4 (pH $\approx$ 0) solution. Comparing polarization curves in Fig. 1 it can be seen that for the tested magnets their runs in the active range are similar; differences are seen at potentials > 0.7 V. At this potential there appears a tendency of Nd–Fe–B magnets to passivate, which is strongest for Vacodym 335 and weakest for Neomax 35. However, anodic currents measured in this passive range are relatively high (> 10 mA cm^{-2}), at least three orders of magnitude greater than the appropriate currents for iron.

The dependence of anodic currents in the passive range on the chemical composition of Nd–Fe–B magnets in 10% H_3PO_4 was observed by Chin *et al.* [6], but they did not record the passivation of Nd–Fe–B magnets in 0.5 M H_2SO_4 solution.

The corrosion rate of the magnets tested increases with time. Directly after immersing the magnets in the solution, i_{corr} is 30 to 50 mA cm^{-2} (compare Fig. 2; 1 mA cm^{-2} corresponds to 0.9125 mg cm^{-2} h^{-1}). Values

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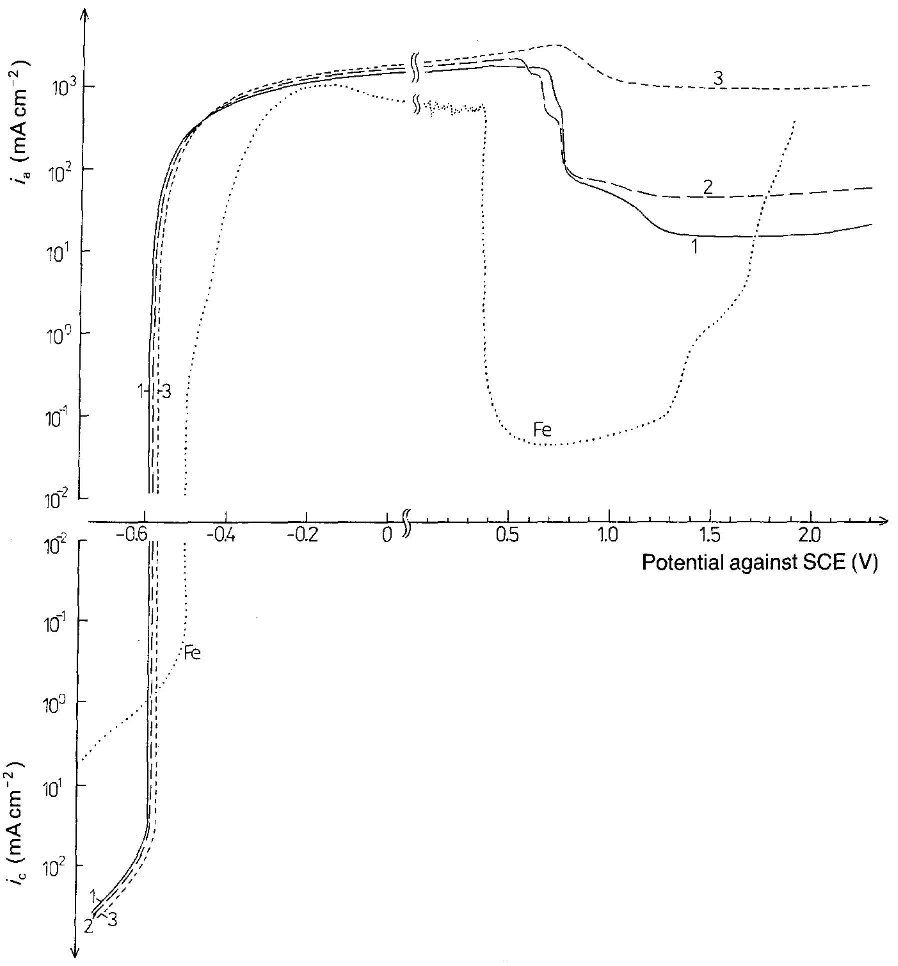

Figure 1 Potentiokinetic polarization curves of three commercial magnets and, for comparison, of spec-pure iron in 0.5 M H_2SO_4 argon; 100 mV min^{-1}; 13.8 r.p.s.; 25° C. 1, Vacodym 335, 2, Vacodym 370; 3, Neomax 35.

for i_{corr} of similar order can be obtained also from the extrapolation of linear segments of cathodic curves to φ_{corr}. The corrosion rate of the magnets reaches practically constant level (170 to 210 mA cm^{-2}) not before 3 to 5 min of exposition in the solution; for pure iron, the corrosion rate in the same solution is $i_{corr,Fe}$ = 0.1 mA cm^{-1} [12].

The comparison of mass losses of the etched sample, determined on the basis of gravimetric and analytical tests (in the latter case only the changes of Fe^{2+} ions in the solution were studied), showed that iron, neodymium and boron solubilize in the same proportion as they appear in the magnets. Anodic dissolution of neodymium according to the reaction

$$\mathrm{Nd} - 3\mathrm{e} \rightarrow \mathrm{Nd}^{3+} \quad (\varphi^0 = -2.431\,\mathrm{V}) \quad (1)$$

can occur at much more negative potentials than the corrosion potential of the alloy, while amorphous boron is exceptionally reactive and oxidizes immediately to boric acid

$$\mathrm{B} + 3\mathrm{H_2O} - 3\mathrm{e} \rightarrow \mathrm{H_3BO_3} + 3\mathrm{H}^+ \quad (\varphi^0 = -0.869\,\mathrm{V}) \quad (2)$$

or reduces to boron hydride

$$2\mathrm{B} + 6\mathrm{H}^+ + 6\mathrm{e} \rightarrow \mathrm{B_2H_6} \quad (\varphi^0 = 0.142\,\mathrm{V}) \quad (3)$$

For the corrosion potentials (that is, −0.6 V against SCE = −0.35 V against NHE (Normal Hydrogen Electrode)) oxidation to H_3BO_3 predominates, because for the reaction:

$$\mathrm{B_2H_6} + 6\mathrm{H_2O} - 12\mathrm{e} \rightarrow 2\mathrm{H_3BO_3} + 12\mathrm{H}^+ \quad (4)$$

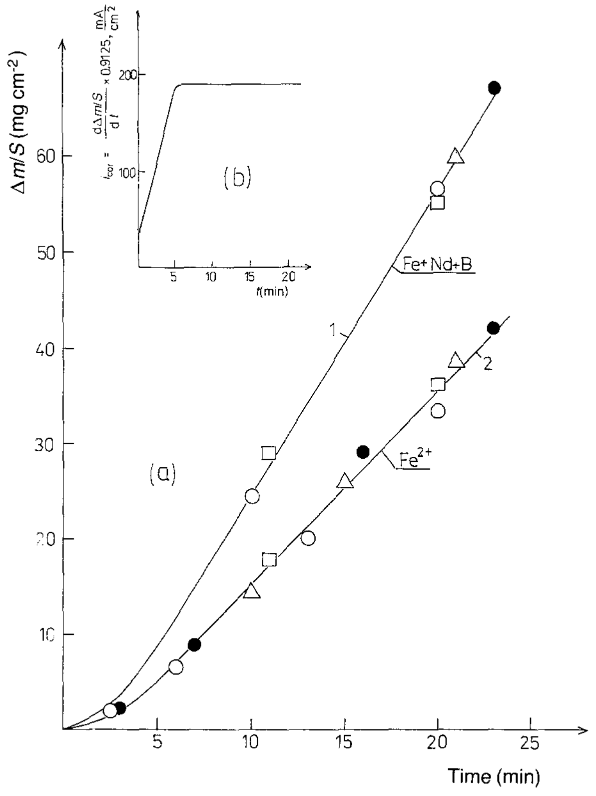

Figure 2 Weight loss of Nd-Fe-B magnets in 0.5 M H_2SO_4 as a function of exposition time. (a) 1, Gravimetric tests; 2, analytical tests (Fe^{2+} ion concentration). (b) Dependence of corrosion current on exposition time calculated on the basis of curve 1. Argon; 13.8 r.p.s.; 25° C; open symbols, demagnetized state; filled symbols, magnetized state. ○, Neomax 35; △, Vacodym 335; □, Vacodym 370.

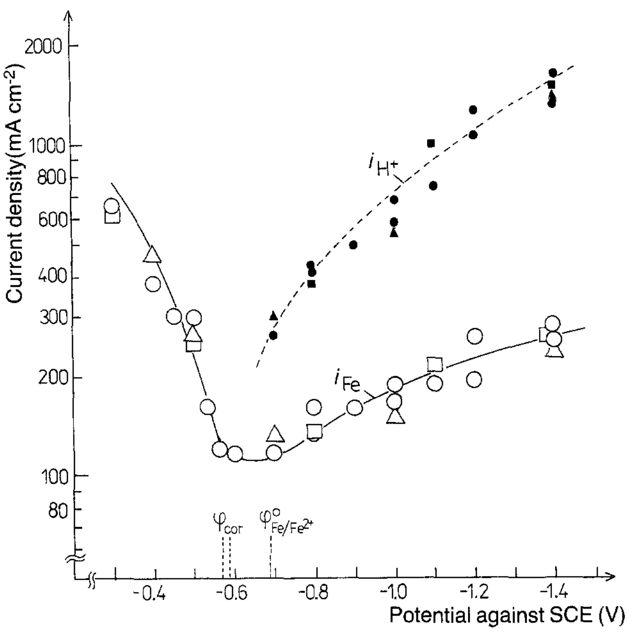

Figure 3 Partial current densities of iron dissolution from Nd–Fe–B magnets and of hydrogen ion reduction (i_{H+}) as a function of electrode potential. Argon, 0.5 M H_2SO_4; 13.8 r.p.s.; 25° C. ○, ●, Neomax 35; △, ▲, Vacodym 335; □, ■, Vacodym 370.

standard potential is $\varphi^0 = -0.506$ V [13]. In fact, chemical analysis of the solution after etching Nd–Fe–B magnets at $\varphi < \varphi_{corr}$ showed the presence of boric acid in the solution. However, this does not exclude the possibility of the appearance of boron hydride, especially at strong cathodic polarizations. As shown in [13], B_2H_6 brought into contact with water hydrolizes at once, producing H_3BO_3 according to the reaction:

$$B_2H_6 + 6H_2O \rightarrow 2H_3BO_3 + 6H_2 \qquad (5)$$

In view of the high chemical reactivity of neodymium and boron it could have been expected that in the range of potentials lower than the reversible potential of the reaction

$$\mathrm{Fe} - 2e \rightarrow \mathrm{Fe}^{2+} \quad (\varphi^0 = -0.440\,\mathrm{V}) \qquad (6)$$

only boron and neodymium would undergo selective dissolution. It turned out, however, that at $\varphi \ll \varphi_{corr}$ Fe^{2+} ions also appear in the solution in considerable amounts. In Fig. 3, stationary partial polarization curves of the magnets tested in the range of potentials −0.3 to −1.4 V (against SCE) are presented. The rate of iron dissolution (i_{Fe}) was determined by the analysis of Fe^{2+} ions in the solution. Total current of the magnet dissolution defined as

$$i_a = i_{Fe} + i_{Nd} + i_B \qquad (7)$$

was determined with a gravimetric method by measuring mass losses of the sample at given potentials. It is easy to check that each of the partial currents i_x at φ = const., lacking selective dissolution, must comply with the dependence

$$i_x = i_a \frac{P_x z_x}{\sum P_x z_x} \qquad (8)$$

where P_x is the atomic percentage of element x in the magnet, and z_x the number of electrons transferred per one atom x. Substituting in Equation 8 the corresponding values of P_x and z_x we obtained $i_{Fe} = 0.69 i_a$, $i_{Nd} = 0.20 i_a$ and $i_B = 0.11 i_a$.

In the case of lack of selective dissolution of the magnetic components, Faraday's law states that

$$i_a = \frac{\Delta m}{t} F \frac{\sum P_x z_x}{\sum M_x P_x} \qquad (9)$$

where Δm is the mass loss of the magnet during etching at given potential, t = time of etching, and F = Faraday's constant, equal to 96500 As. Substituting in Equation 9 adequate numerical values of P_x, z_x and $M_{Fe} = 55.85$, $M_{Nd} = 144.24$, $M_B = 10.81$ we get

$$i_a[\mathrm{mA}] = 0.9125 \frac{\Delta m}{t} [\mathrm{mg\,h^{-1}}]. \qquad (10)$$

The above formula was applied to the determination of the current density of magnet dissolution on the basis of gravimetric tests. From Equations 8 and 10 we obtain $i_{Fe} = 0.63 \Delta m / t$, which within the error limits ±5% was confirmed in all the tests we performed (Fig. 2).

From Fig. 3, which shows partial currents of iron dissolution and currents of H^+ ion reduction as a function of the potential of Nd–Fe–B magnets, one result is difficult to interpret: Fe^{2+} ions are generated in the solution even below the standard potential of iron ($\varphi^0_{Fe/Fe^{2+}} = -0.44$ V against NHE = −0.68 V against SCE). Also as φ increases towards negative values, i_{Fe}, instead of decreasing, rises quite distinctly. At the same time iron dissolution currents in the cathodic range take on values of the same order or even greater than the spontaneous dissolution rate ($> 190\ \mathrm{mA\,cm^{-2}}$). The occurrence of such dependence was stated for all of the three tested Nd–Fe–B magnets. A similar phenomenon was observed by other authors, mainly for pure metals (chromium, nickel, iron, manganese) [14–16], but the currents of abnormal dissolution measured by them in the cathodic range were as a rule lower than $1\ \mathrm{mA\,cm^{-2}}$.

The causes of abnormal dissolution of metals have not been explained so far. Some authors [15, 16] relate this effect to the mechanical degradation of the surface, caused by its hydrogenation during cathodic polarization in a strongly acid medium. Hydrogenation of metals is conducive to the appearance of crevices, pits and microcracks, which results in separation of the alloy particles from the surface of metal, and their further dissolution inside the solution. It should be a natural consequence of such a mechanism that the rate of abnormal dissolution of metal increases according to the growth of cathodic polarization. However, such an effect has not been observed so far. Since the currents of abnormal dissolution measured in [15, 16] were too small and the scatter of results too large the authors usually assumed i_{Me} = const. for $\varphi \ll \varphi_{corr}$.

The results obtained here (see Fig. 3) support clearly the argument for mechanical degradation of the surface as a result of its hydrogenation. Detailed analysis of the data show that the current of abnormal dissolution of iron is directly proportional to the square root of the hydrogen-ion reduction current (Fig. 4). It is known from the literature [17, 18] that the rate

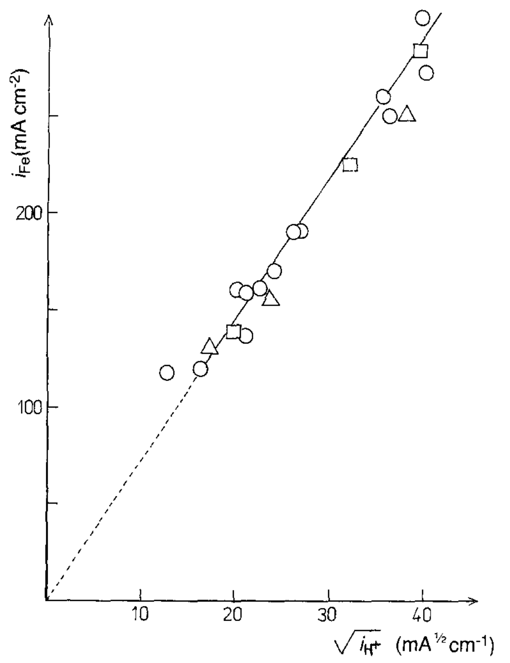

Figure 4 Rate of abnormal iron dissolution from Nd–Fe–B magnets in 0.5 M H_2SO_4 as a function of the square root of cathodic current density. Argon, 13.8 r.p.s.; 25° C. ○, Neomax 35; △, Vacodym 335; □, Vacodym 370.

of hydrogen permeation to the crystal lattice of metal is as a rule proportional to $i_{H^+}^{1/2}$. Thus the relationship of the abnormal dissolution of Nd–Fe–B magnets with their hydrogenation seems to be justified. High abnormal dissolution excludes the possibility of using cathodic protection in order to inhibit the corrosion of Nd–Fe–B magnets.

The results of the accelerated corrosion tests given here showed exceptionally low resistance to acid corrosion of Nd–Fe–B magnets. The cause of such low resistance (about 2000 times lower than iron is primarily the presence of rare-earth elements in magnets. In the case of Co_5Sm magnets [8] containing a quantity ($\sim$ 30 wt %) of rare-earth elements similar to that of Nd–Fe–B magnets, the decrease in corrosion resistance was not that drastic (Co_5Sm corroded $\sim$ 30 times faster in comparison to spec-pure cobalt). Thus it can be assumed that slight additions of cobalt to Nd–Fe–B magnets should advantageously affect their corrosion resistance, preserving high magnetic properties. This was stated by Ohashi *et al.* [5]: the addition of $\sim$ 10 wt % cobalt clearly improves the corrosion resistance of Nd–Fe–B magnets in 95% humidity at 60° C, which is related to cobalt segregation in the neodymium-rich phase.

The tests performed in this work also pointed out a dangerous effect connected with the drastic degradation of the surface of Nd–Fe–B magnets at highly cathodic polarizations. This problem is only mentioned here, as its explanation requires complex potentiostatic studies with altered stirring rates, pH values of the solutions, and different states of magnetization. These investigations will be the subject of subsequent papers.

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