

# Electrochemical aspects of corrosion in sintered and hot-deformed Nd–Fe–B magnets

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## Abstract

General corrosion behaviour of Nd–Fe–B alloys and magnets was studied by electrochemical tests in acid environment. Sintered and hot-deformed magnets of different compositions were tested. Stoichiometric alloys such as NdCu and Nd<sub>6</sub>Fe<sub>13</sub>Cu, corresponding to intergranular phases present in hot-pressed material, were also examined. The results indicate reduction in critical corrosion currents in doped materials. The significant influence of porosity and the fraction of the intergranular Nd-rich phase in the sintered sample is reported.

*Keywords:* Corrosion; Magnets; Rare-earths; Hot deformation; Sintering

## 1. Introduction

The alloys and magnets based on the Nd–Fe–B ternary system, in spite of their known elevated magnetic properties, exhibit also high susceptibility to corrosion attack leading to faster oxidation. The main reason for this is the complex nature of the microstructure where around 10% of the volumetric fraction of the standard composition Nd<sub>15</sub>Fe<sub>77</sub>B<sub>8</sub> is constituted by Nd-rich phases. The reactivity of these phases is greater even in non-severe environmental conditions. The corrosion process initiates by the formation of oxide films changing the surface chemical composition. This brings about a decrease in the local anisotropy, deteriorating the magnetic properties [1]. If the oxide formation does not result in passivation, i.e. the process is not interrupted, the corrosion will proceed irreversibly causing the degradation of both the material and its magnetic properties.

The Nd–Fe–B magnetic alloys exhibit some electrochemical peculiarities which differentiate them from other conventional materials. High corrosion rates are observed even in cathodic potentials (reduction conditions). It was also reported that they degrade faster when exposed to corrosion in the magnetized state [2]. These phenomena, not clearly understood yet, indicate a complex net of physical factors acting simultaneously in the system.

Some attention has been given to the influence of additives on corrosion characteristics [3,4]. However, the influence of those elements on the passivation of the  $\phi$  (Nd<sub>2</sub>Fe<sub>14</sub>B) phase is not completely clear [4,5]. The practical solution for corrosion protection is still the use of organic [1] or metallic [6] coatings as an alternative technique aiming to avoid the direct magnet–environment contact.

In this work, emphasis is given to a general electrochemical characterization of alloys and magnets based on the Nd–Fe–B system, comparing two types of processing routes: sintering and hot deformation. The influence of porosity and the presence of intergranular phases in the doped materials is presented.

## 2. Experimental details

The tests were carried out using the potentiokinetic polarization technique in a non-stirred argon-saturated H<sub>2</sub>SO<sub>4</sub> solution at room temperature applying a potential sweep rate of 100 mV/min<sup>-1</sup>. The starting potential was in the cathodic region close to the rest potential of the sample.

The operation surface areas were 50 mm<sup>2</sup>. The sample served as the anode and a platinum electrode was used as the cathode, having a saturated calomel electrode (SCE) as reference. The instrumental apparatus was a potentiostat PAR 375.

The following samples were tested:

(i) sintered  $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$  alloy (1080 °C for 1 h in vacuum);

(ii)  $\text{Nd}_{15}\text{Fe}_{75.5}\text{B}_8\text{Al}_{1.5}$  alloy, as cast and sintered;

(iii)  $\text{Nd}_{15}\text{Fe}_{72}\text{B}_{6.7}\text{Cu}_{1.2}\text{NbAl}$  alloy, as cast, sintered and hot pressed (deformation, 80%);

(iv) alloys  $\text{NdCu}$  and  $\text{Nd}_6\text{Fe}_{13}\text{Cu}$ , homogenized (1000 °C for 3 h), corresponding to intergranular phases observed in deformed material [7].

All samples were demagnetized. The volumetric distribution of the phases was measured according to the ASTM E562 standard (point count method).

### 3. Results and discussion

#### 3.1. The influence of processing

The sample identification is summarized in Table 1, which also presents the volume fractions of  $\phi$  phase and the relative porosity.

Fig. 1 shows the potentiokinetic anodic curves of samples D, E and F. The curves of commercially pure Fe and Nd are also plotted for comparison. Although the tested samples did not exhibit typical passivation characterized by a significant current reduction as observed in Fe, they exhibited stable regions of current. Samples D and F had lower critical currents and a tendency to passivation with a supposed transpassive region up to approximately 1.0 V (SCE).

The same composition in the sintered state (sample E) exhibited high current densities similar to the polarization curve of Nd, indicating the influence of porosity inherent to the processing route. This aspect might be confirmed by means of the curves on Fig. 2, for sintered samples B and C, where the corrosion currents appear directly dependent on the porosity of the samples. Those samples undergo selective etching on Nd-rich phases because of their more exposed surface, hiding any possible passivation effect on  $\phi$  phase. This implies that low residual porosity guarantees not only good magnetic properties but also better

corrosion resistance, i.e. high density should be considered fundamental in magnet processing.

#### 3.2. $\phi$ Passivation and the influence of added elements

An attempt to verify the passivation of  $\phi$  was also made in samples A, B and C (Fig. 2), where there is a variation in the fraction of the  $\phi$  phase. The composition  $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$  (sample A) exhibited the higher volume fraction of  $\phi$  and samples B and C were Al doped. It is noted that a higher volume fraction of  $\phi$  does not result in stabilization of the current, i.e. the curve has a continuous increase profile longer than any passivation aspect. No significant effect was detected on Al addition on the tests, agreeing with Jacobson and Kim's thermoweight results [8]. Regarding the critical current, the reduction in intergranular phase fraction causes reduction in current density. This correlation is plotted in Fig. 3. The current stabilization observed in the case of samples E, D and F cannot therefore be related to the volume fraction of  $\phi$  but to the influence of the added alloying elements. These dopants, being present mostly in the intergranular phases, act through the better corrosion resistance of these phases.

The main reason for dopant addition is to enhance the magnetic properties. In magnets produced by hot deformation, dopants such as Cu increase also the workability of the alloy, lowering the eutectic temperature. The aluminium-doped magnets contain in the intergranular region ternary phases  $\mu$  and  $\delta$ ; the copper forms binary  $\text{NdCu}$  and the ternary  $\delta$  phases, all considered as having higher resistance to corrosion than the regular Nd-rich phase [7]. The beneficial effect of Nb additions on the corrosion resistance is supposed to be different but is still not clear [9]. Fig. 4 shows the microstructure of the hot-pressed Nd–Fe–B–Cu–Nb–Al magnet sample D of Table 1. The phases  $\text{NdCu}$  and  $\delta$  occupy in this alloy a significant volume of the intergranular region, decreasing the relative amount of the extremely corrosive regular Nd-rich phase.

Table 1  
Identification and metallurgical conditions of the tested samples

| Samples | Composition  | Condition   | $\phi$<br>(vol.%) | Porosity<br>(%) |
|---------|--|-------------|-------------------|-----------------|
| A       | $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$                                 | Sintered    | $91.54 \pm 0.40$  | $4.5 \pm 0.3$   |
| B       | $\text{Nd}_{15}\text{Fe}_{75.5}\text{B}_8\text{Al}_{1.5}$                | As cast     | $86 \pm 0.87$     | <1              |
| C       | $\text{Nd}_{15}\text{Fe}_{75.5}\text{B}_8\text{Al}_{1.5}$                | Sintered    | $81.2 \pm 0.52$   | $8.9 \pm 0.4$   |
| D       | $\text{Nd}_{18.1}\text{Fe}_{72}\text{B}_{6.7}\text{Cu}_{1.2}\text{NbAl}$ | As cast     | $78.5 \pm 0.89$   | <1              |
| E       | $\text{Nd}_{18.1}\text{Fe}_{72}\text{B}_{6.7}\text{Cu}_{1.2}\text{NbAl}$ | Sintered    | $69 \pm 0.94$     | $7.3 \pm 0.2$   |
| F       | $\text{Nd}_{18.1}\text{Fe}_{72}\text{B}_{6.7}\text{Cu}_{1.2}\text{NbAl}$ | Deformed    | $76 \pm 1.28$     | <1              |
| G       | $\text{NdCu}$  | Homogenized | –                 | <1              |
| H       | $\text{Nd}_6\text{Fe}_{13}\text{Cu}$                                     | Homogenized | –                 | <1              |

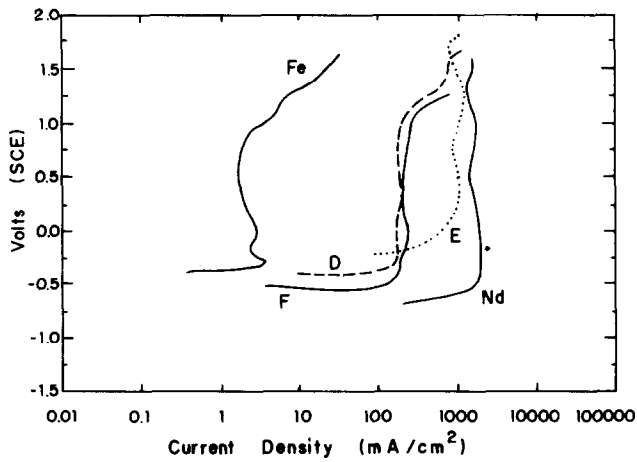


Fig. 1. Potentiokinetic polarization curves of samples D, E and F. Results for commercially pure Fe and Nd are also plotted for comparison (0.5 M H<sub>2</sub>SO<sub>4</sub>, 100 mV min<sup>-1</sup>).



Fig. 4. Microstructure of sample D, with 80% deformation, showing intergranular and intragranular phases: 1, Nd<sub>2</sub>Fe<sub>14</sub>B; 2, Nd<sub>6</sub>Fe<sub>13</sub>Cu ( $\delta$ ); 3, NdFeB; 4, Nd-rich phase; 5, NdCu(Al).

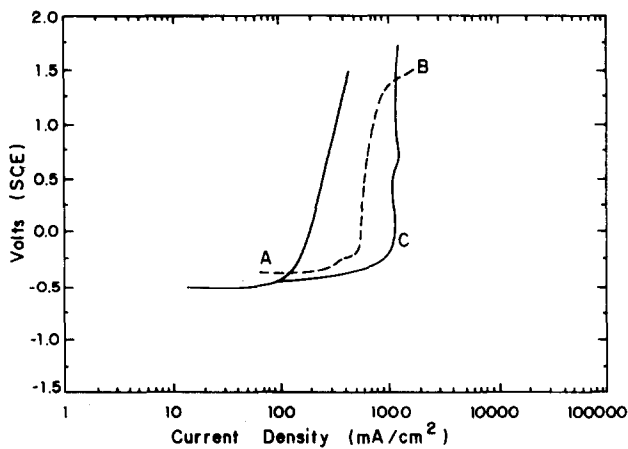


Fig. 2. Potentiokinetic polarization curves of samples A, B and C (0.5 M H<sub>2</sub>SO<sub>4</sub>, 100 mV min<sup>-1</sup>).

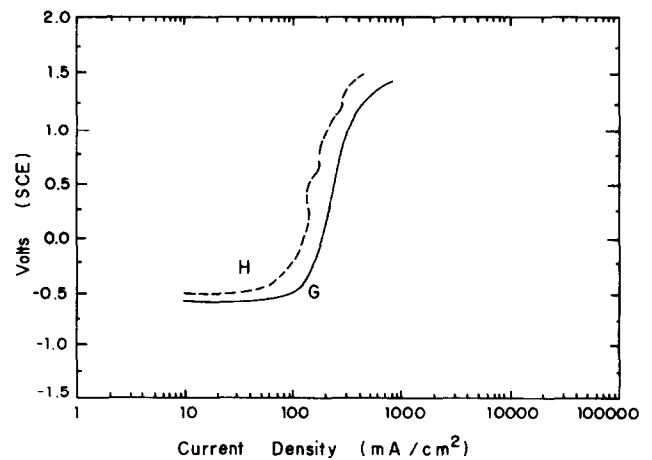


Fig. 5. Potentiokinetic polarization curves of samples G and H (0.5 M H<sub>2</sub>SO<sub>4</sub>, 100 mV min<sup>-1</sup>).

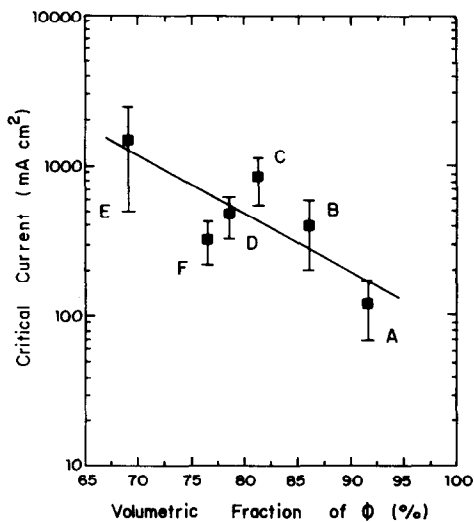


Fig. 3. Critical current and phase volumetric relation.

The occurrence of these phases led us to prepare the pure NdCu and  $\delta$ , samples G and H. Their polarization curves (Fig. 5) do not display passivation transitions but the current densities are considerably lower than those observed in magnets, indicating low reactivity. These data show that the doping elements, when present in intergranular phases, result in an increase in general corrosion resistance as observed in samples D and E and presented in Table 2.

The material degradation in the Nd–Fe–B system is used by the corrosion resistance of the intergranular region, which results in a lower corroding rate in alloys with high volume fraction of  $\phi$ . The corrosion sequence in doped alloys may be summarized following Szymura and co-workers' model [10]. The phases on the surface exposed to corrosive environment oxidize with different intensities. An oxide layer mixed of iron and neodymium oxides forms on the surface of the  $\phi$  phase without a passivation effect. The degradation of the intergranular Nd-rich region proceeds more easily because of the

Table 2  
Electrochemical features

| Material | $E_{\text{corr}}$<br>(mV) <sup>a</sup> | Observed<br>passivation <sup>b</sup> |
|----------|--|--------------------------------------|
| A        | –580                                   | No                                   |
| B        | –482                                   | No                                   |
| B        | –502                                   | No                                   |
| C        | –485                                   | Yes                                  |
| D        | –223                                   | No                                   |
| E        | –485                                   | Yes                                  |
| F        | –680                                   | No                                   |
| G        | –580                                   | No                                   |

<sup>a</sup> Corrosion potential.

<sup>b</sup> With current reduction.

high reactivity of neodymium, which counts for about 95% of the Nd-rich phase. This results in the detachment of the  $\phi$  grains, exposing a new surface to the action of the corrosive environment. The phases formed in the doped materials (i.e.  $\delta$ ,  $\mu$  and NdCu) substitute part of the highly reactive Nd-rich phase, which results in an increase in the overall corrosion resistance. Since the corrosion of the Nd-rich phase is still preferential, the detachment of the  $\phi$  grains cannot be avoided, i.e. the material will degrade in the same manner but more slowly. A total substitution of the Nd-rich phase by the above-mentioned phases would result in a significant increase in the corrosion resistance but could not yield passivation.

#### 4. Conclusions

(1) The reduction in the amount of the Nd-rich intergranular phase implies the corrosion current decrease; however, it does not result in passivation.

(2) The additional phases observed in the doped materials (Cu, Nb, Al employed here) do not cause passive transitions, although they contribute to reducing the general corrosion characteristics of the magnetic alloys.

(3) The alloys processed by sintering, independently of the composition, present high current densities related to the porosity inherent to the process.

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