Journal of Alloys and Compounds, 186 (1992) 201–208
JALCOM 282

Corrosion behaviour of hot-worked Nd–Fe–B and Nd–Fe–Cu–B permanent magnets

J. P. Nozières, D. W. Taylor
Laboratoire Louis Néel, C.N.R.S., BP166X, 38042 Grenoble Cedex (France)

H. Bala, M. Malik
Department of Chemistry, Technical University of Czestochowa, Al. Armii Krajowej 19, 42-200 Czestochowa (Poland)

S. Szymura
Institute of Physics, Technical University of Czestochowa, Al. Armii Krajowej 19, 42-200 Czestochowa (Poland)

H. Stokłosa
Department of Metallography, Technical University of Czestochowa, Al. Armii Krajowej 19, 42-200 Czestochowa (Poland)

(Received January 8, 1992)

Abstract

The corrosion resistance of hot-worked Nd–Fe–B and Nd–Fe–B–Cu magnets is studied. In atmospheric conditions, the corrosion rate is the same for sintered or hot-worked magnets. In acidic solutions, however, the hot-worked magnet exhibit a lower corrosion resistance. In addition, the corrosion mechanism involved appears to differ due to the lower reactivity of the intergranular Nd-rich and B-rich phases. The addition of copper is found to strongly improve the corrosion resistance of hot-worked magnets. With an addition of only 2% Cu, the corrosion resistance of hot-worked magnets turns out to be higher than that of sintered Nd–Fe–B magnets in both environments, neutral and acidic.

1. Introduction

Among the various permanent magnets, the high performance Nd–Fe–B have the poorest corrosion resistance. The corrosion mechanism involved in such magnets has been already discussed by several authors [1–4]. It assumes a preferential dissolution of the intergranular Nd- and B-rich non-magnetic phases followed by the separation of the $Nd_2Fe_{14}B$ magnetic grains from the surface before their further dissolution in the bulk solution. The rapid surface degradation and pulverization can thus be attributed to the lack of corrosion resistance of the intergranular phases [5, 6]. In order to improve the corrosion resistance of these magnets, attention has been focused on small additions (1–5%) of alloying elements such as Cr, Ti [1], Zr [1, 7], Ni [8] and Co [4]. However, there is a lack of systematic attempts to determine the role of the preparation method and the subsequent microstructure on the corrosion behaviour.

Apart from the classical powder metallurgy preparation route, the hot-working of cast ingots has proved to be among the most promising alternative techniques [9–11]. A recent study had shown that the magnetic properties of hot-worked magnets were less affected than that of sintered magnets when tested in a neutral aqueous aerated media [12]. Such a difference was ascribed to a higher density and to a lower residual oxygen content after processing. However, the most dangerous depolarizer in the corrosion of Nd–Fe–B magnets is the hydrogen ion, and corrosion with hydrogen depolarization turns out to be responsible for most of the damage in these magnets. To obtain a better description of the corrosion characteristics of hot-worked magnets, their behaviour in more aggressive acid solutions and in industrial environment conditions (air containing SO_2) has therefore to be investigated. In this paper we present the results of accelerated tests performed on hot-worked Nd–Fe–B and we discuss the effect of small copper additions, known to increase the magnetic properties of such magnets [11], on their corrosion behaviour.

2. Experimental details

The samples were prepared by hot-pressing ingots with a diameter of 25 mm at 830 °C under normal atmosphere. In order to prevent oxidation the ingots were cast in a steel container which was subsequently capped and sealed. After hot-working, the residual metallic sheath is removed by mechanical means. Three kinds of compositions were tested: $Nd_{16}Fe_{77}B_6Al_{0.5}$ (standard hot-worked Nd–Fe–B magnet, referred to as sample 1); $Nd_{17}Fe_{77}Cu_1B_5$ (referred to as sample 2); $Nd_{17}Fe_{76}Cu_2B_5$ (referred to as sample 3). For comparison purposes, a $Nd_{16}Fe_{76}B_8$ sintered magnet prepared by the classical powder metallurgy route (referred to as sintered magnet) and specpure iron were also tested.

Corrosion behaviour was tested with the following accelerated tests:

(i) An acid corrosion test consisting of room temperature weight loss measurement during spontaneous dissolution of the samples in non-stirred, deaerated 0.5 M H_2SO_4 acid solution.

(ii) Measurement of the potentiokinetic polarization curve in deaerated solution of 0.5 M H_2SO_4. The potential *vs.* saturated calomel electrode (SCE) ranged from $\phi = -0.75$ V to $\phi = +2.5$ V with a scan rate of 100 mV $\min^{-1}$. Each run was averaged over three independent measurements.

(iii) An accelerated test of atmospheric corrosion (imitating an industrial environment) in which the samples are exposed to 40 °C steam-saturated air containing 3 mg of SO_2.

(iv) An abnormal dissolution test consisting of room temperature weight loss measurement at a strong cathodic polarization ($\phi = -1.00$ V *vs.* SCE) in a deaerated 0.5 M H_2SO_4 solution.

3. Results and discussion

3.1. *Acid corrosion test*

The etching kinetic curves in the 0.5 M H_2SO_4 solution are presented in Fig. 1. In this plot, the solid line refers to the reference sintered Nd–Fe–B magnet. It must be stressed that the absolute corrosion rates of rare earth containing magnets are extraordinarily high when compared with pure iron or carbon steel (in the same solution, pure iron corrodes at a rate of 0.1 mg cm^{-2} h^{-1} [13]). As can be seen, the etching curves for the hot-worked magnets do not show minima in the initial stage, as observed for the sintered magnet. This indicates a different mechanism of acid corrosion for hot-worked and sintered magnets. It has previously been shown that for sintered magnets, in the initial stage of acid corrosion, Nd- and B-rich intergranular phases are preferentially etched and the corrosion rate at first decreases. Then, in a second stage of etching, called steady-state corrosion, the $Nd_2Fe_{14}B$ particles are detached and dissolved in the bulk solution [1, 3]. In hot-worked magnets, the content of oxygen as well as of other contaminant elements (N, C, ...) is found to be lower than in sintered magnets by more than an order of magnitude [14]; this can be ascribed to the bulk-state of the alloy throughout the hot-working process. This leads to a lowered reactivity of the intergranular Nd- and B-rich phases.

The addition of copper to the Nd–Fe–B alloy is found to improve the acid corrosion resistance of hot-worked magnets. Samples 2 and 3 corrode respectively 20 and 45% slower than sample 1 (see Fig. 1). Since copper is not dissolved in the $Nd_2Fe_{14}B$ phase (less than 1%) it is found in the intergranular phase where it forms precipitates such as $NdCu_2$ or Nd(Fe,Cu) [15]. These intergranular precipitates could be responsible for the lowered corrosion rate by reducing the intergranular ionic diffusion. Such a positive effect has already been reported in the case of vanadium addition in sintered magnets [16]. However, the Cu-containing samples still exhibit a disadvantage: during the acid corrosion process of samples 2 and 3, large $Nd_2Fe_{14}B$ particles

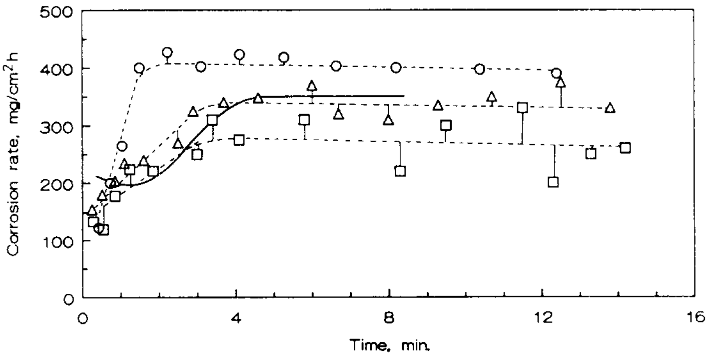

Fig. 1. Etching kinetic curves in deaerated 0.5 M H_2SO_4 solution (25 °C, no stirring). Solid line, sintered magnet; ○, Nd–Fe–B; △, Nd–Fe–B + 1% Cu; □, Nd–Fe–B + 2% Cu.

(0.05 to 0.2 mm in diameter) are detached by chance from the surface. These large particles may be responsible for the unusual scatter observed in the Cu-containing alloys in Fig. 1.

The surfacial microstructures of the hot-worked magnets after etching is presented in Fig. 2. In sample 1 the grains are generally fine and their sizes hardly differ from each other (Fig. 2(a)). On the contrary for samples 2 and 3 containing copper, larger particles are observed at the magnet surface. This disagrees with previous observations showing that the addition of copper in Nd–Fe–B alloys inhibits the $Nd_2Fe_{14}B$ grain growth, thus leading to a reduced grain size in hot-worked magnets [14, 15]. However, it should be pointed out that none of the etched samples showed any grains greater than 10–15 μm whereas as-processed hot-worked magnets exhibit grains ranging from a few microns up to a hundred microns [14]. Thus, further cracking, crumbling and degradation of the grains due to the hydrogen uptake occurs during the acid treatment, which is to be expected from the high

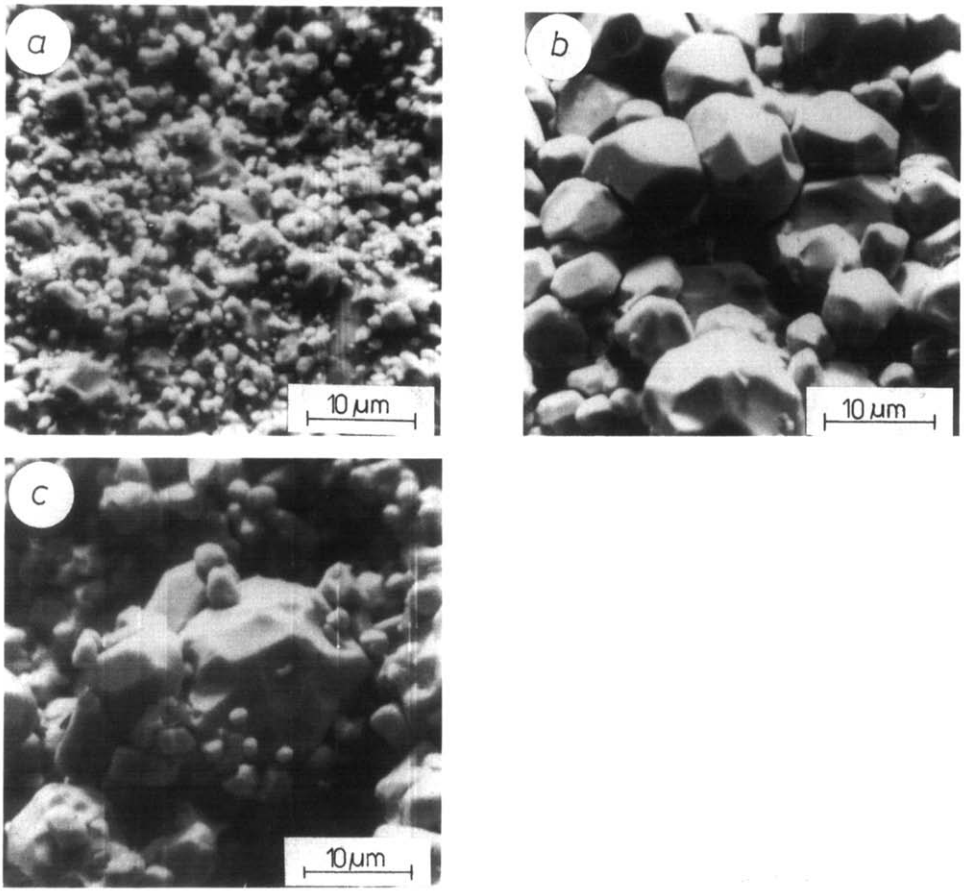

Fig. 2. SEM micrographs of hot-worked magnets after exposure for 15 min in a 0.5 M H_2SO_4 solution: (a) Nd–Fe–B; (b) Nd–Fe–B + 1% Cu; (c) Nd–Fe–B + 2% Cu.

reactivity of bulk Nd–Fe–B alloys to hydrogenation [17, 18]. From the observations of Fig. 2, we can then assume that copper addition tends to lower the magnet sensitivity to the surfacial degradation caused by hydrogenation.

3.2. *Polarization curves*

The potentiokinetic polarization curves are presented in Fig. 3. They show a very similar behaviour from $\phi = -0.75$ V to $+0.60$ V (*vs.* SCE). Considerable differences in the polarization curves are observed at potentials more noble than $+0.60$ V. For hot-worked samples, the tendency for passivation is more distinct than for sintered material. However, the anodic currents in this passive state are comparatively large, so we cannot talk about effective protection of the samples. For this range of potential, the addition of copper has a rather disadvantageous effect on the corrosion behaviour of hot-worked magnets.

In the case of specpure iron, at potentials greater than 1.5 V the anodic current rises again, due to oxygen evolution. For the magnets tested in this study, this latter process does not occur according to the principles of electrochemical kinetics.

3.3. *Atmospheric corrosion test*

The results of the atmospheric corrosion test in a so-called industrial environment are reported in Fig. 4. As seen, the behaviour of the standard hot-worked magnet (open circles) is comparable to that of the sintered magnet (full line). However, copper addition considerably inhibits the atmospheric corrosion process, especially after long time exposures (more than 10 h).

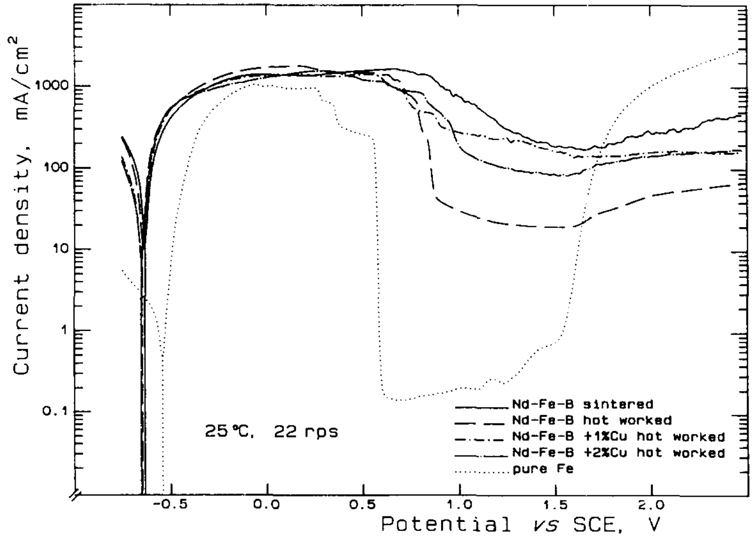

Fig. 3. Potentiokinetic polarization curves in deaerated 0.5 M H_2SO_4 solution. Solid line, sintered magnet; dotted line, pure iron.

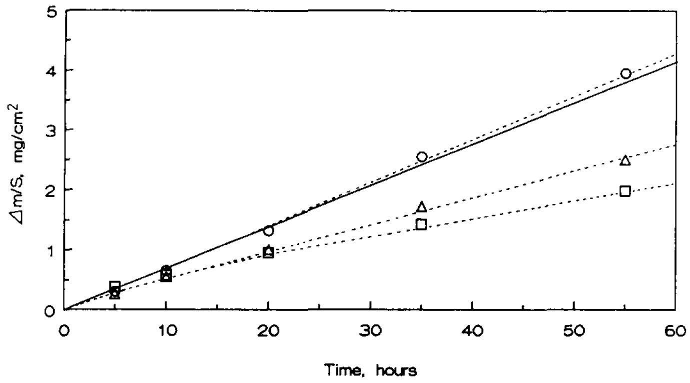

Fig. 4. Atmospheric corrosion kinetics in steam-saturated air + 3 mg SO_2 l^{-1} (40 °C). Solid line, sintered magnet; ○, Nd–Fe–B; △, Nd–Fe–B + 1% Cu; □, Nd–Fe–B + 2% Cu.

TABLE 1

Corrosion rates at a cathodic potential $\phi = -1.00$ V *vs.* SCE. Exposure time 15 min, deaerated 0.5 M H_2OSO_4, 22 rev s^{-1}, $T = 25$ °C

Sample	External cathodic current density (A cm^{-2})	Corrosion rate (mg cm^{-2} h^{-1})
Sintered	0.9 ± 0.1	370 ± 40
Hot-worked	1.0 ± 0.1	850 ± 60
Hot-worked + 1% Cu	1.3 ± 0.2	330 ± 50
Hot-worked + 2% Cu	1.1 ± 0.2	220 ± 10

Moreover, qualitative observation showed a much greater adherence of the corrosion products to the surface of hot-worked magnets than to the surface of sintered magnets, which means that the binding between the intergranular phases and the $Nd_2Fe_{14}B$ matrix is increased in the former. This is again a consequence of the reduced corrosion of the intergranular phases in hot-worked magnets, due to their lower oxygen content [12].

3.4. *Abnormal dissolution*

Rare earth containing magnets exhibit large corrosion rates at strongly cathodic polarizations as a result of the selective dissolution of rare earth and boron-rich phases, followed by hydrogen uptake and separation of the magnetic particles from the surface [19, 20]. The rates of this so-called abnormal dissolution are reported in Table 1 for the present samples. Within experimental error, all the cathodic current densities can be considered to be the same, which means that the surface hydrogenation is similar for all magnets. However, the corrosion rates differ strongly from one sample to another. Sample 1 exhibits an extraordinarily high corrosion rate (850 mg cm^{-2} h^{-1}), over two times greater than that of the sintered magnet. This rate is definitely the highest among a number of rare earth magnets [1, 3]. It could be a consequence of the reduction of the mean grain size of the corroded surface as a result of acid interaction with the surfacial grains of the $Nd_2Fe_{14}B$ phase, their hydrogenation and cracking, since it has previously been found that this kind of corrosion could be stimulated by decreasing the grain size [21].

A 2% addition of copper is found to inhibit the corrosion rate of hot-worked magnets by nearly a factor of 4. Such behaviour is not well understood since we would have expected the corrosion rate to increase in the Cu-containing samples where the as-processed grain size is reduced. However, the grain sizes are strongly modified during etching in H_2SO_4 (see Fig. 2) and thus it is difficult to draw any conclusion from this argument. It is possible that a greater concentration of copper in the intergranular phase could be responsible for the inhibition of the hydrogen adsorption process and consequently of the magnet hydrogenation: it is known that the activation energy of hydrogen chemisorption on metal surfaces is decreased only in the presence of empty d-orbitals and unpaired d-electrons [22]. In copper, in contrast to iron or neodymium, the d-orbitals are filled and consequently the hydrogen uptake process is reduced.

Nevertheless, taking into account the fact that the most effective additions to Nd–Fe–B sintered magnets (*e.g.* 5 at.% Co or 1 at.% Sn [1, 3]) decrease the abnormal dissolution rates around a level of 100 mg cm^{-2} h^{-1}, the addition of copper is very promising as a protection of hot-worked Nd–Fe–B permanent magnets against acid corrosion.

4. Conclusions

(1) The hot-working process changes the corrosion mechanism of hot-worked magnets. Hot-worked magnets exhibit a shorter initial stage of preferential dissolution due to the lower reactivity of the intergranular phases.

(2) The standard hot-worked magnet shows a lower corrosion resistance than the sintered magnet both in acidic solutions and under conditions of cathodic exposure. This greater sensitivity has direct relevance to the greater tendency to surface hydrogenation. In atmospheric conditions, the two types of magnets corrode with the same rate.

(3) Small additions of copper (1–2 at.%) considerably decrease the corrosion rate of hot-worked Nd–Fe–B magnets in an industrial environment, in acidic solutions and under conditions of cathodic exposure. Since copper has been reported to increase both coercivity and remanence of hot-pressed Nd–Fe–B magnets [15], it is a very promising additive which could be a breakthrough of the hot-working process.

References

1 H. Bala, G. Pawłowska, S. Szymura, V. V. Sergeev and Yu. M. Rabinovich, *J. Magn. Magn. Mater.*, *87* (1990) L255.

2 H. Bala and S. Szymura, *Proc. 11th Int. Corrosion Congress, Florence, April 2–6, 1990,* Vol. 5 p. 143.

3 H. Bala, S. Szymura, Yu. M. Rabinovich, V. V. Sergeev, G. Pawłowska and D. V. Pokrovskij, *Rev. Phys. Appl., 25* (1990) 1205.

4 K. Ohashi, Y. Tawara, T. Yokoyama and N. K. Kobayashi, *Proc. 9th Int. Workshop on Rare Earth Magnets and their Applications, Bad Soden, August 31–September 2, 1987,* p. 355.

5 C. J. Williams and K. S. V. L. Narashiman, *J. Appl. Phys., 61* (1987) 3766.

6 T. Minowa, M. Yoshikawa and M. Honshima, *IEEE Trans. Magn., MAG-25* (1989) 3776.

7 K. Yajima, H. Nakamura, O. Kohmoto and T. Yoneyama, *J. Appl. Phys., 64* (10) (1988) 5528.

8 H. Bala, S. Szymura and J. J. Wyslocki, *IEEE Trans. Magn., MAG-26* (1990) 2646.

9 J. P. Nozières, R. Perrier de la Bathie and J. Gavinet, *J. Phys. (Paris), 49* (1988) C8-667.

10 J. P. Nozières, R. Perrier de la Bathie and D. W. Taylor, *J. Magn. Magn. Mater., 80* (1989) 88.

11 T. Shimoda, K. Akioka, O. Kobayashi and T. Yamagami, *IEEE Trans. Magn., MAG-25* (1989) 4099.

12 J. P. Nozières and D. W. Taylor, *J. Less-Common Met., 162* (1990) L1.

13 H. Bala, *Electrochim. Acta, 30* (1985) 1043.

14 J. P. Nozières, *Thesis Universite J. Fourier, unpublished.*

15 T. Shimoda, K. Akioka, O. Kobayashi and T. Yamagami, *J. Phys. (Paris), 49* (1988) C8-631.

16 P. Tenaud, F. Vial and M. Sagawa, *Proc. Intermag 1990, Brighton, April 1990.*

17 D. Fruchart, P. Wolfers, P. Vuillier, A. Yaounac, R. Fruchart and P. L'Héritier, *Proc. Work on Rare Earth Magnets, Brussels, 1984,* p. 173.

18 I. R. Harris, C. Noble and T. Bailey, *J. Less-Common Met., 106* (1985) L1.

19 H. Bala, S. Szymura and J. J. Wyslocki, *J. Mater. Sci., 25* (1990) 571.

20 S. Szymura, H. Bala and J. Gega, *Mikrochim. Acta, 3* (1989) 43.

21 S. Szymura, H. Bala, Yu. M. Rabinovich, V. V. Sergeev, G. Pawłowska and D. V. Pokrovskii, *J. Phys. Cond. Mater., 3* (1991) 5893.

22 G. C. Bond, *Heterogeneous Catalysis: Principles and Applications,* Clarendon Press, Oxford, 1974.