

An Investigation on the Corrosion Behaviour of Nd-Fe-B Magnets in a Chloride Solution

I. Costa¹, M.C.L. Oliveira¹, H.G. de Melo², R. N. Faria¹ *Junior*

¹Instituto de Pesquisas Energéticas e Nucleares, IPEN/CNEN-SP, Centro de Ciência e Tecnologia de Materiais - Laboratório de Corrosão, Caixa Postal 11049, Pinheiros, CEP 05422-970, São Paulo, Brasil

²EPUSP - Departamento de Engenharia Química, SP, Brasil.
icosta@net.ipen.br

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Abstract: In this study, the corrosion behaviour of a sintered commercial Nd-Fe-B magnet has been investigated in naturally aerated and deaerated 3.5 (m/v)% sodium chloride solutions. Magnetized specimens were used in this investigation. The corrosion behaviour of the specimens was monitored at increasing test times by means of electrochemical impedance spectroscopy (EIS). Potentiodynamic polarization curves and surface observation by scanning electron microscopy (SEM), were also carried out after 30 days of immersion in the test solutions. Experimental results indicated that the corrosion resistance was affected by aeration of the solution. The corrosive attack penetrates deeply into the specimens and, consequently, the magnetic properties decreased with immersion time. The magnetic properties most influenced by corrosion were the remanence (B_r) and the maximum energy product (BH_{max}), both presenting a reduction corresponding to 6%, after 30 days of immersion.

Introduction

Nd-Fe-B magnets have excellent magnetic properties. These are derived from the magnetic $Nd_2Fe_{14}B$ intermetallic phase. Magnets based on this phase are of great commercial interest since their energy product significantly exceeds that of samarium-cobalt materials [1]. They also exhibit high coercivity and are very suitable for permanent magnet applications [2]. Due to their outstanding magnetic properties, they have been the subject of numerous studies [3,4]. However, they have very weak corrosion resistance [5-9] that is mainly due to the fact that rare-earth elements are among the most electrochemically active metals.

Nd-Fe-B sintered magnets are useful for many applications, since computer disk drives, many important parts of fine electro-electronic industry to large industrial machines. The cost of Nd based permanent magnets is also much lower than that of the samarium containing alloys, mainly due to the relative abundance of Nd and Fe. Nevertheless, this very reactive alloying element (Nd) makes them highly susceptible to corrosion and the corrosive attack results in deterioration of its magnetic properties.

Due to their low corrosion resistance, Nd-Fe-B permanent magnets need corrosion control methods to improve their viability as an engineering material and attempts have been made to improve corrosion resistance of these magnets either by metallic coatings [10], organic coatings [11], or alloying [12]. However, it is unacceptable to adopt corrosion control methods that are likely to compromise magnetic performance. Phosphating seems to result in significant improvement of their corrosion resistance as compared with the untreated ones [13,14], and it should not affect their magnetic properties.

Much of the research work reported in the literature has been carried out with demagnetized specimens. However, previous results obtained in our laboratory indicated that the magnetization state of the specimens affected the corrosion behaviour of Nd-Fe-B commercial magnets [15]. The present work aims at the electrochemical evaluation of the corrosion resistance of magnetized Nd-Fe-B permanent magnet in chloride containing solutions, either naturally aerated or deaerated.

Material and Methods

Due to the large number of samples and in order to maintain sample uniformity commercial sintered Nd-Fe-B magnets produced by Crucible were used in this investigation. The composition, given in Table 1, was determined by X-ray fluorescence analysis and atomic absorption measurements. The corrosion resistance of the magnets was investigated in naturally aerated and deaerated 3.5 (m/v)% NaCl solutions by electrochemical measurements, specifically, potentiodynamic polarization curve and electrochemical impedance spectroscopy. Chloride electrolytes are considered most relevant to service applications and was, therefore, chosen as test solution. Nd-Fe-B magnets were tested in magnetized state. Magnetization of samples was carried out up to saturation in a pulsed field of 60 kOe. Scanning Electron Microscopy (SEM) was used for magnets surface observation after a 30 day immersion period.

Specimen preparation: For the electrochemical measurements, electrodes with an area of approximately 130 mm² were prepared by cold resin mounting. The electrode surface was prepared by grinding with silicon carbide paper up to grade #1000, degreasing with acetone, rinsing with deionized water and drying under a hot air stream. Magnetization was carried out after surface preparation.

Experimental set-up: A three-electrode cell arrangement was used for the electrochemical measurements, with a graphite rod and a saturated calomel electrode (SCE) as counter and reference electrodes, respectively. Electrochemical impedance spectroscopy (EIS) measurements were accomplished with a 1255 Solartron frequency response analyzer coupled to an EG&G 273A Potentiostat. All EIS measurements were performed in potentiostatic mode at the open circuit potential, E_{ocp} . The amplitude of the perturbation signal was 10 mV, and the frequency range studied from 10⁵ to 10⁻² Hz, with 6 points per decade. The test medium was 3.5 (m/v)% NaCl solution, naturally aerated and deaerated, and at (23 ± 2)°C. The potentiodynamic polarization measurements were carried out after 30 days of immersion by means of an EG&G 273A potentiostat coupled to a computer, in the potential range from -1300 mV (SCE) to 0 mV (SCE) with the scan rate of 1 mV/s. The EIS measurements were obtained at increasing test times, from 1 until 30 days of immersion.

Demagnetization curves: The magnetic properties of specimens, before and after increasing times of test in naturally aerated solution, were determined in a permeameter. Measurements were performed after saturation in a pulsed field of 60 kOe.

Results and Discussion

The electrochemical impedance diagrams for the Nd-Fe-B magnets at increasing immersion times in aerated and deaerated chloride solutions are shown in Fig. 1.

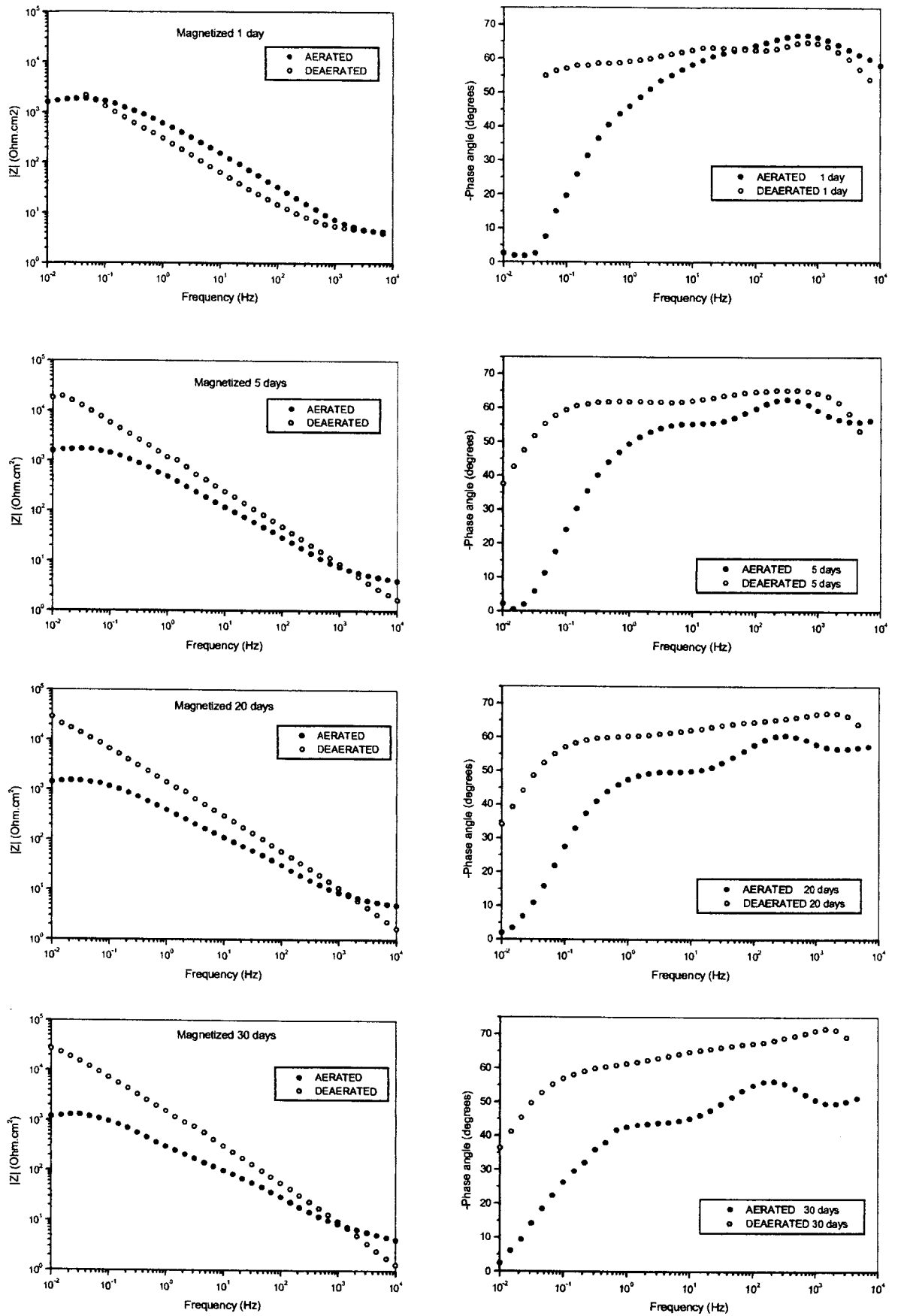


Fig.1 . Bode plots for magnetized Nd-Fe-B specimens at increasing immersion times in 3.5 (m/v)% NaCl naturally aerated and deaerated solutions.

The diagrams presented in Fig. 1 show that when immersed in deaerated solution the magnets exhibit higher impedance. It is also verified that the impedance associated to this solution increases from the first to the fifth day of immersion, and then maintains a fairly constant behavior throughout the rest of the experiment period, when it exhibits impedances one order of magnitude higher than in aerated solution. The reason for the former behavior is not yet fully understood and must be further investigated. On the other hand, the sample immersed in the aerated solution presented a constant and slow diminution of the impedance all along the immersion time. Bode phase angle diagrams obtained in the deaerated solution present a single broad time constant, which must be likely related to the charge transfer phenomena at the electrode/electrolyte interface. The flattened appearance of this time constant must be related with the presence of macropores/crevices formed on the electrode surface due to the corrosion process as could be seen in the SEM images presented later.

The comparison of Bode phase angle diagrams for both samples presented in Fig. 1 shows that the corrosion mechanism must be different according to the presence or absence of oxygen in the electrolyte, even though no sign of diffusion controlled phenomena is discernible in the cathodic branch of the polarization curves presented in Fig. 2. It is likely that in aerated solution, dissolved oxygen plays a role in the corrosion process, which impedance response is characterized by a steep decrease of the phase angle in the low frequency region indicating faster interfacial kinetics. These diagrams, when obtained in aerated solution, revealed the existence of a high frequency feature present as a small shoulder, which was displaced to lower frequencies for longer immersion times. We are prone to believe that this time constant must be due to the influence of the magnetic field on bulk oxygen diffusion, due to the paramagnetic properties of this molecule [16] accelerating the interfacial corrosion process. A deeper discussion on this subject has been presented elsewhere [17]. Conversely, for aerated solution, Bode phase angle diagrams are flatter than those obtained in deaerated one, and the angle steadily decreases for longer immersion time approaching the 45° behavior associated with porous electrodes [18]. This kind of behavior can be associated with the increasing of the porosity of the magnet surface due to the presence of adhered corrosion products as will be discussed later in the analysis of SEM images. These products would difficult the access of the electrolyte to the electrode surface giving rise to the onset of diffusion controlled phenomena. The adhered products would also reduce the magnetic properties of the sample influencing the bulk transport of dissolved oxygen whose response is displaced to lower frequencies as verified experimentally.

Corrosion rate (i_{corr}) values for the magnets in the magnetized state were obtained in aerated and deaerated solutions, from the polarization curves shown in Fig. 2, by extrapolation of linear segment of cathodic curves to E_{corr} . Larger i_{corr} values and more noble potentials were obtained for the magnets in aerated solution, as it was expected. The i_{corr} in the aerated solution was approximately $8 \mu\text{A}\cdot\text{cm}^{-2}$ whereas in the deaerated solution it is about 4-fold lower. The large current increase that occurs at potentials above -700 mV (SCE) is likely related to the dissolution of the iron rich magnetic phase. According to literature [9], the corrosion potential of this last phase in a solution of pH similar to that used in this study, is approximately -700 mV (SCE) .

The surfaces of magnetized specimens after 30 days of test in deaerated and naturally aerated solution are shown in Fig. 3 (a) and (b), respectively. Larger amounts of corrosion products were seen on the specimens tested in naturally aerated solution than in deaerated one, supporting the results from polarization measurements. Intense corrosive attack occurred and substantial amount of corrosion products remained attached to the surface leading to deeper cracks as shown in Fig. 3.

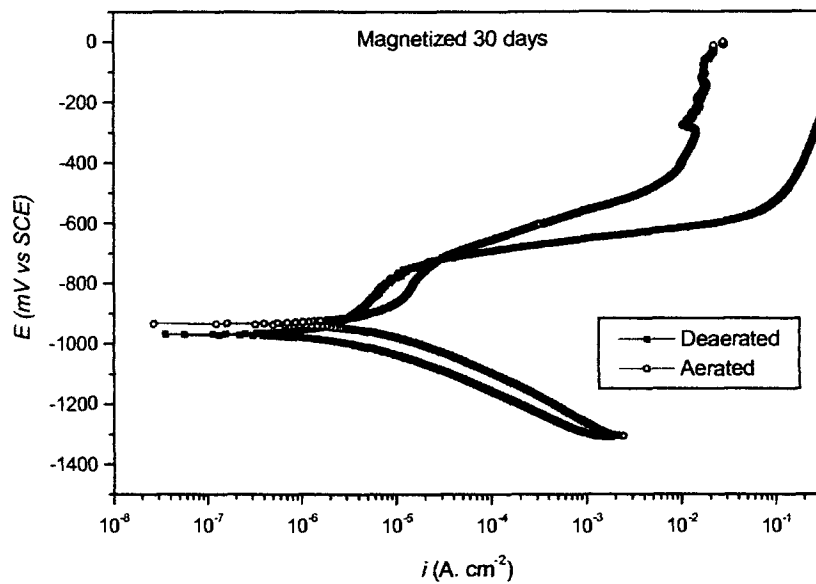


Fig. 2. Polarization curves for magnetized Nd-Fe-B specimens in 3.5 (m/v)% NaCl solutions.

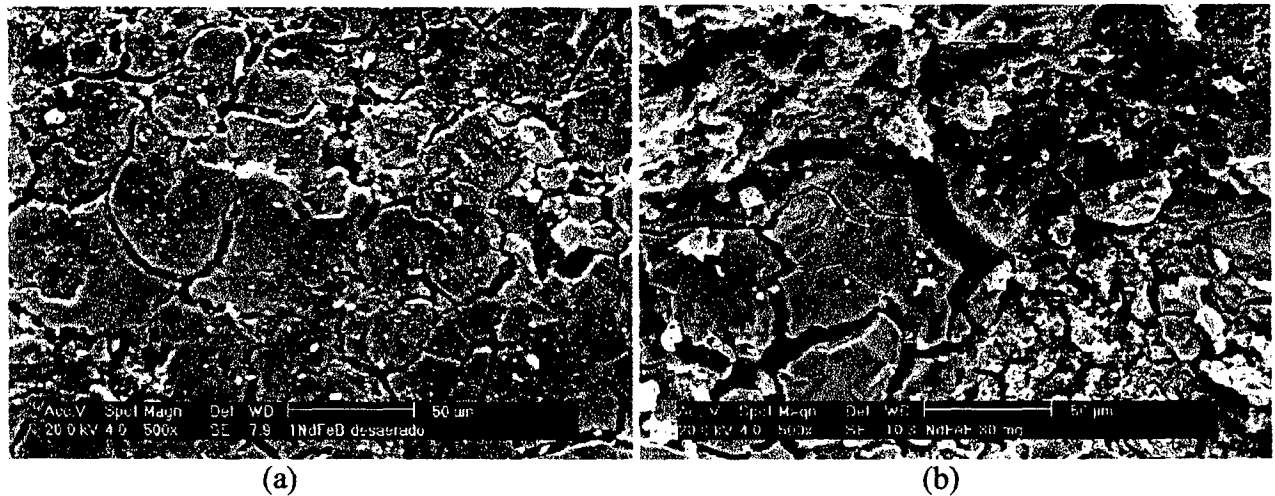


Fig. 3. SEM of magnetized Nd-Fe-B magnets after 30 days of immersion in (a) deaerated and (b) naturally aerated 3.5 (m/v)% NaCl solutions.

The magnetic properties of the magnets decreased as the immersion time increased as indicated in Table 1. The results show that the magnetic properties most influenced by corrosion were the remanence (B_r) and the maximum energy product (BH_{max}), both presenting a reduction of around 6%.

Table 1. Magnetic properties obtained from demagnetization curves (error: $\pm 2\%$), before and after increasing times of immersion in NaCl 3.5 (m/v) % naturally aerated solution.

Period	Magnetic properties		
	B_r (T)	$\mu_0 iH_c$ (T)	BH_{max} (kJ.m^{-3})
Before test	1.22	1.60	293
After 10 days	1.18	1.59	286
After 30 days	1.15	1.58	275

Conclusions

Intense corrosive attack of the Nd-Fe-B magnet occurred in the test solution used and the magnetic properties decreased with immersion time. Larger i_{corr} values and more noble potentials were obtained for the magnet in aerated solution comparatively to the deaerated one. The magnetic properties most influenced by corrosion were the remanence (B_r) and the maximum energy product (BH_{max}), and both presented a reduction corresponding to 6%, after 30 days of immersion in naturally aerated solution.

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