CORROSION BEHAVIOR OF SINTERED SURFACE-TREATED Nd-Fe-B MAGNETS

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Permanent sintered neodymium–iron–boron magnets find many applications due to their excellent magnetic properties. However, these materials are highly susceptible to corrosion due primarily to their complex microstructure and inherent porosity. For applications in corrosive environments they are usually surface treated and coated or encapsulated. One of the surface treatments used is chromating, which, although effective, generates toxic Cr(VI) and carcinogenic residues. Thus it is important to find environmentally friendly treatments to replace those based on Cr(VI). The aim of the present work was to evaluate and compare the effectiveness of the corrosion protection afforded by two different surface treatments: a NaH_2PO_4-based conversion treatment and chromating with Cr(III) compounds, and to compare the corrosion response with that resulting from Cr(VI) chromating. The corrosion resistance of untreated and surface-treated magnets was evaluated by electrochemical tests performed in a phosphate-buffered solution (PBS) at a neutral pH to simulate body fluids. Surface treatments with Cr(III) improved the corrosion resistance but phosphating provided superior corrosion resistance to chromating. Microstructural characterization showed that immersion in the phosphating solution resulted in a selective attack of the magnetic phase in the neighborhood of the neodymium-rich phase. There is also evidence that increased corrosion resistance is provided by the formation of a thin layer of phosphate on the magnetic phase.

INTRODUCTION

The outstanding magnetic properties of neodymium–iron–boron magnets are derived from the magnetic $Nd_2Fe_{14}B$ intermetallic phase. Magnets based on this phase are of commercial interest since their energy product significantly exceeds that of samarium–cobalt magnets.[1] They also exhibit high coercivity and are suitable for permanent magnet applications.[2] Due to their excellent magnetic properties, they have been the subject of numerous studies and find many applications.[3] However, these magnets exhibit low corrosion resistance[4–8] due primarily to the fact that the rare-earth elements are electrochemically active, as well as to their complex microstructures. The microstructure of neodymium–iron–boron magnets is composed of two primary phases, the magnetic φ phase ($Nd_2Fe_{14}B$),[9] and a neodymium-rich phase.[10] The electrochemical potential differences among the various phases is significant, generating galvanic cells and attendant preferential dissolution of the most active phases. The most active is the neodymium-rich phase which surrounds the φ phase, leading to intergranular corrosion.[11]

These powder metallurgy (PM) sintered magnets exhibit intrinsic porosity, which further decreases their corrosion resistance. This class of magnets is useful in many applications, including small parts in the electro–electronics industry and larger parts in industrial machinery and dentistry.

Magnets have been used in dentistry since the 1950s to improve the retention and stability of dental prostheses.[12] In the past, however, the large size required to produce adequate forces limited their use.[13–16] Since the introduction of rare-earth magnets, it is now possible to produce magnets with small dimensions for use in dental applications

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as retentive devices for overdentures, mainly due to their strength and compactness.[2,17,18] These magnets exhibit improvements in their maximum energy product compared with older types, leading to a significant reduction in the size required to generate the necessary magnetic flux.[19]

Dental materials mandate a high resistance to corrosion and must be inert to human tissues; however, neodymium–iron–boron magnets are highly susceptible to corrosion. One of the main problems associated with the clinical use of rare-earth–iron–boron magnets is corrosion due to their low corrosion resistance in aqueous media. For dental applications these magnets are usually encapsulated in a stainless steel or titanium can. However, due to wear of the can or failure of the laser weld, saliva can leak into the can and lead to corrosion of the magnet.

Due to their low corrosion resistance, neodymium–iron–boron permanent magnets need corrosion control methods to improve their viability as an engineering material and attempts have been made to improve their corrosion resistance by metallic coatings,[20] by organic coatings,[21] or by alloying.[7] The corrosion control treatments must not decrease magnetic performance. Phosphating treatments have been used to prepare the surface of ferrous alloys for subsequent organic coating. However, only limited research has been reported on the effect of phosphating on the corrosion resistance of neodymium–iron–boron sintered magnets. Results suggest a significant improvement in their corrosion resistance compared with the untreated condition.[22–25] Phosphating in a NaH_2PO_4 solution at room temperature has been shown to result in a substantial improvement in corrosion resistance.[24] The aim of the present work was to evaluate the effect of phosphating and chromating with Cr(III) baths on the corrosion resistance of sintered neodymium–iron–boron magnets as environmental friendly alternatives to surface treatment with solutions containing Cr(VI).

MATERIAL AND METHODS

Neodymium–iron–boron magnets produced by the Crucible Materials Corporation were used in this investigation. The composition (Table I), was determined by X-ray fluorescence analysis and atomic absorption. The corrosion resistance of the magnets was investigated by electrochemical measurements, specifically, potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) in a PBS of composition NaCl 8.77 g/L, Na_2HPO_4 1.42 g/L and KH_2PO_4 2.72 g/L at a pH 7, to simulate body fluids. Immersion tests were also carried out in sodium chloride electrolytes, specifically Hank's solution and 3.5 w/o NaCl solution, since these simulate aggressive service applications. The neodymium–iron–boron magnets were tested in the demagnetized state. Scanning electron microscopy (SEM) was used for surface characterization following the corrosion tests.

Specimen Preparation:

For the electrochemical measurements, electrodes with an area approximately 130 mm^2 were prepared by cold resin mounting. The electrode surface for exposure to the electrolyte was prepared by grinding on silicon carbide paper up to grade #600, degreasing with acetone, rinsing in deionized water, and drying under a hot-air stream. Some specimens were phosphated in a 10 g/L NaH_2PO_4 solution (pH 3.8) for times up to 4 h; others were chromated in two commercial solutions (SurTec 652 and SurTec 650) for Cr(VI) and Cr(III), respectively, at a concentration of 20 g/L (pH 3.7) for 3 min at 40°C.

Experimental Set-Up:

A three-electrode cell arrangement was used for the electrochemical measurements, with a platinum wire and a saturated calomel electrode (SCE) as the counter and reference electrodes, respectively. EIS measurements were made with a 1255 Solartron frequency response analyzer coupled to an EG&G 273A potentiostat. All the EIS measurements were performed in the potentiostatic mode at an open circuit potential, E_{ocp}. The amplitude of the perturbation signal was 10 mV, and the frequency range studied was from 10^5 to 10^{-2} Hz, with 6 points per decade. The test medium was a PBS, naturally aerated at 23 ± 2°C. The potentiodynamic polarization measurements were

TABLE I. CHEMICAL COMPOSITION OF NEODYMIUM–IRON–BORON MAGNET (w/o)

Fe	Nd	B	Dy	Al	Co	Si	Cu	Nb	Na	Ca	S
60.59	28.31	1.00	2.09	3.73	1.28	1.39	0.18	0.66	0.41	0.15	0.16

carried out with the potentiostat coupled to a computer with a scan rate of 1 mV/s. All the corrosion studies were carried out in a PBS at 25°C.

RESULTS AND DISCUSSION

Figure 1 shows the surface of the magnets after different periods of immersion in the various solutions. As expected, all the samples exhibited corrosion, independent of the electrolyte used, but the form of corrosion was dependent on the aggressiveness of the test solution.

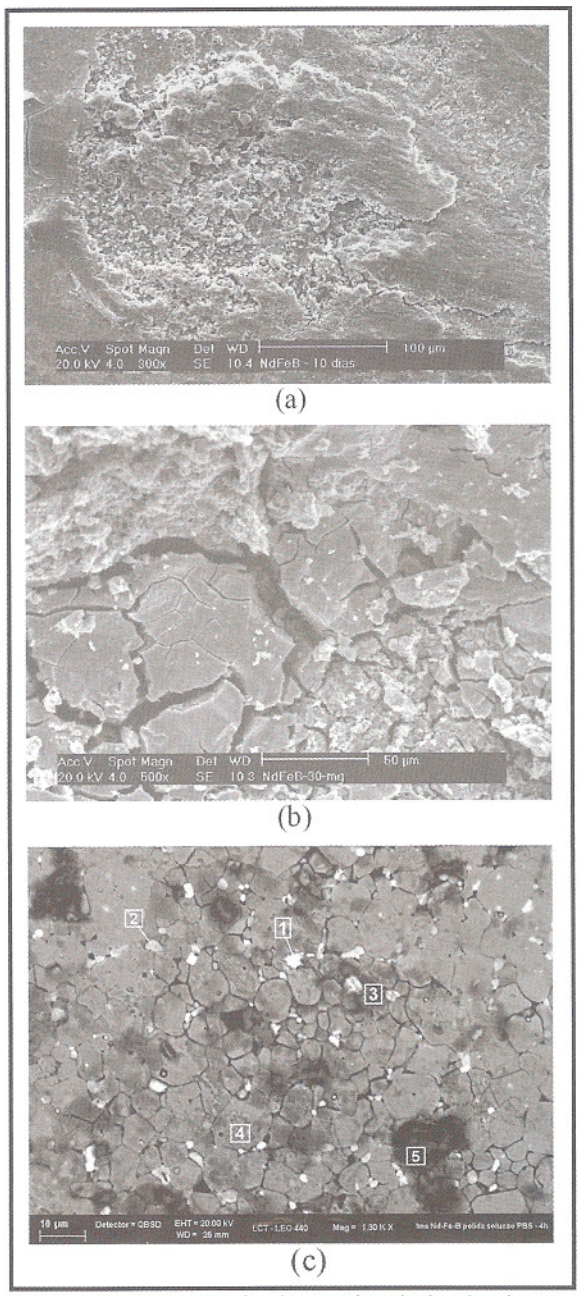

Figure 1. Representative surface images of neodymium–iron–boron magnets after: (a) 10-day immersion in Hank's solution; (b) 30-day immersion in 3.5 w/o NaCl; (c) 4 h immersion in PBS. Markers 1 and 2 correspond to the neodymium-rich phase, 3 and 5 to pores, and 4 to the magnetic phase. SEM/secondary electron images

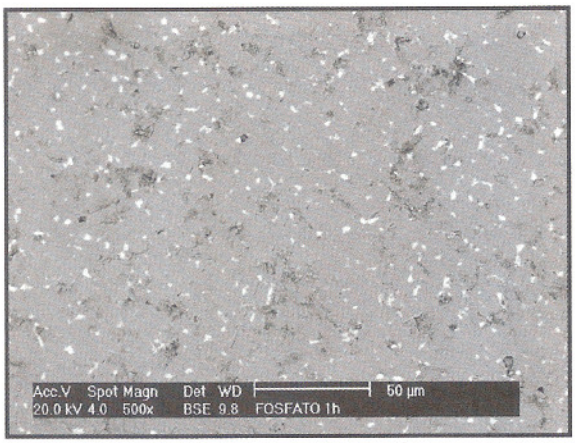

Figure 2. Representative micrograph of neodymium–iron–boron magnet phosphated for 1 h and subsequently immersed for 4 h in PBS. SEM/backscattered electron image

Intergranular corrosion was observed on the samples that were immersed in the PBS for short times (4 h). After this period of immersion, many areas of the neodymium-rich phase remained on the specimen surface but the areas surrounding this phase were generally attacked.

In previous studies[26] the same magnet demonstrated pitting corrosion after immersion in a cell culture medium for 10 days. Chloride was detected on the corroded area, showing that it must have initiated the corrosion process. The pitting corrosion found in the samples immersed in the culture medium also demonstrated passivation of some regions on the surface. In Hank's solution a passive state was absent and corrosion was of a generalized type. These results are related to the increased aggressiveness of Hank's solution compared with the cell culture medium. The combination of a porous sintered structure, a complex microstructure (mixture of phases of different electrical potential), and the presence of chlorides in the test medium are the primary causes of corrosion in these magnets.

Figure 2 shows a representative SEM image of the surface of a phosphated magnet after 4 h of immersion in the PBS. After this period, only limited signs of corrosion are visible, confirming the beneficial effect of the phosphating treatment on corrosion resistance.

The effect of chromatizing the neodymium–iron–

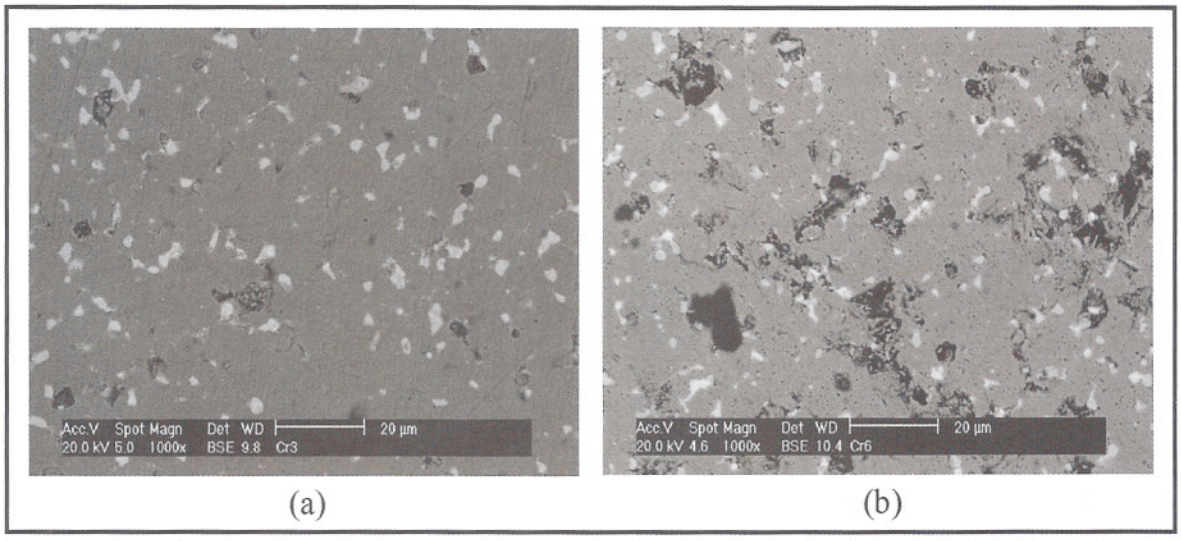

Figure 3. *Representative micrographs of the surface of neodymium–iron–boron magnets after: (a) immersion in Cr(III) and (b) immersion in Cr(VI)-containing baths. SEM/backscattered electron images*

boron magnet in a Cr(III)-containing bath on its corrosion resistance was also investigated as another alternative to the toxic Cr(VI)-containing baths. Figure 3 shows SEM images of the surface of specimens treated with Cr(III) or Cr(VI)-containing baths.

The surface treatments localized the attack primarily at the pores and the boundaries between the neodymium-rich phase and the magnetic phase. However, the Cr(VI) bath was more aggressive and increased localized corrosion was identified in the SEM image. The formation of chromate layers from the Cr (III) or Cr (VI) baths is due to oxidation of either the $HCrO_4^-$ (chromate) or the $Cr_2O_7^{2-}$ (dichromate), both of which are known to exist at high CrO_3 concentrations.[27] These species are involved in a redox process leading to precipitation of the chromate layer (Cr(III)). It is possible that the heterogeneous nature of the magnet surface leads to precipitation of the conversion layer in preferred sites. Accordingly, oxidation of the substrate takes place only at the more active sites

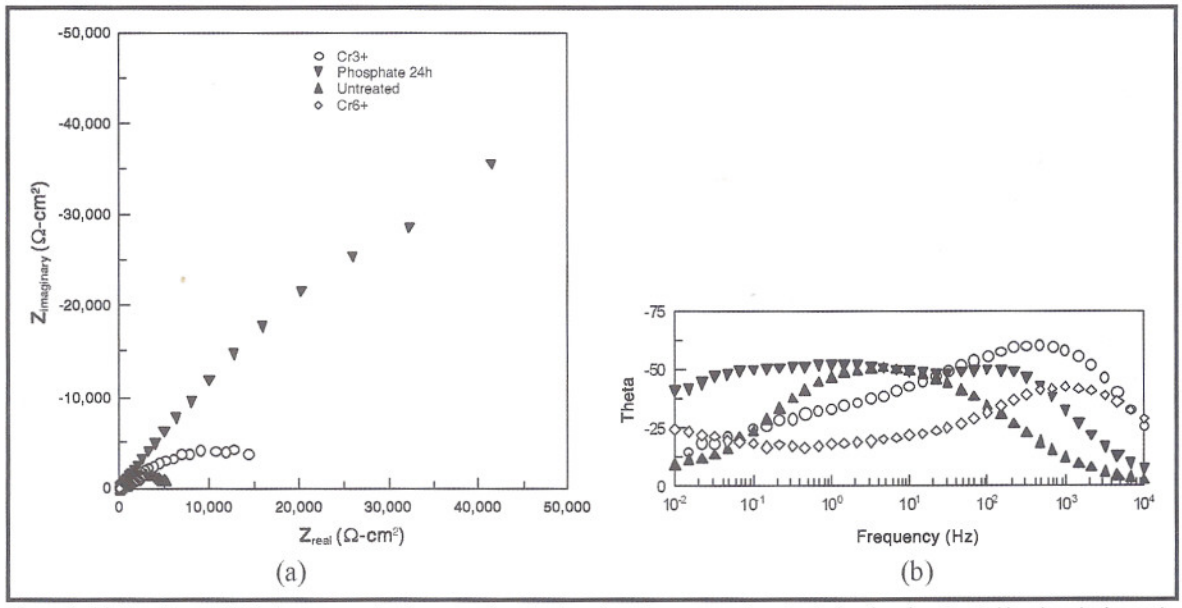

Figure 4. *(a) Nyquist and (b) Bode phase-angle diagrams of neodymium–iron–boron magnets untreated and surface treated by phosphating and chromating in (Cr(III) and Cr(VI)) baths*

leading to the localized corrosion depicted in Figure 3(b).

The EIS diagrams for the neodymium–iron–boron untreated magnet, and for the phosphated and chromated (Cr(III) and Cr(VI))-treated samples are shown in Figure 4 as Nyquist and Bode (phase-angle) diagrams. The Nyquist diagrams exhibit a depressed capacitance loop at medium to low frequencies. The flattened appearance of this time constant is related to the complex electrochemical processes taking place on the heterogeneous magnet surface and is indicative of the superposition of several time constants. For samples tested under the same conditions, a larger diameter corresponds to a higher corrosion resistance.

The Bode phase-angle diagrams for all surface treated specimens show a peak at high frequencies associated with the conversion coating, indicating the presence of a surface layer independent of the corrosion protection afforded; this feature is absent in the untreated sample. For the two chromate layers, the increased high-frequency phase angle of the sample protected with the layer formed in the Cr(III) bath is indicative of its superior performance, as verified in the Nyquist diagrams. Conversely, the corrosion resistance of the sample treated in the Cr(VI) bath is inferior to that exhibited by the uncoated sample, Figure 5.

The phosphate-treated samples exhibit a broader phase angle (indicative of the superposition of several phenomena) and the 45° angle between the Nyquist diagram and the real axis is indicative of a porous electrode response, consistent with de Levie theory.[28] The results presented in Figure 4 allow for a ranking of the corrosion protection afforded by the surface treatments as follows: phosphate > Cr(III) > Cr(VI). While the two former treatments improve corrosion resistance, the latter treatment results in decreased corrosion resistance.

With phosphating, the solution is acidic (pH 3.8) and will have a small corrosive effect on the magnet surfaces during treatment. Commercial phosphating baths with a lower pH (2.7) have also been evaluated but were too aggressive. Consequently, phosphating solutions must be specifically developed for use with these magnets. The solution adopted in the present study had a higher pH than commercial baths and allowed the formation of a thin and adherent phosphate layer on essentially all the magnet surfaces.

These results show that the corrosiveness of the phosphate solution must be precisely controlled to avoid attack of the magnets surfaces. Previous work carried out with the same magnet and a phosphated solution of similar composition (but with the pH adjusted to 2) exhibited severe attack of the substrate accompanied by formation of a white corrosion products after 1 day of immersion.

During acid attack in the first step of phosphating (formation of cations for primary phosphate formation), NdH_2 tends to form, which may result in the following reactions, depending on the pH:[29]

$$NdH_2 + 3H^+ \rightarrow Nd^{3+} + 5/2H_2 \quad (pH \leq 3.5) \qquad (1)$$

$$NdH_2 + 3H_2O \rightarrow Nd(OH)_3 + 5/2H_2 \quad (pH \text{ range from } 3.5 \text{ to } 5) \qquad (2)$$

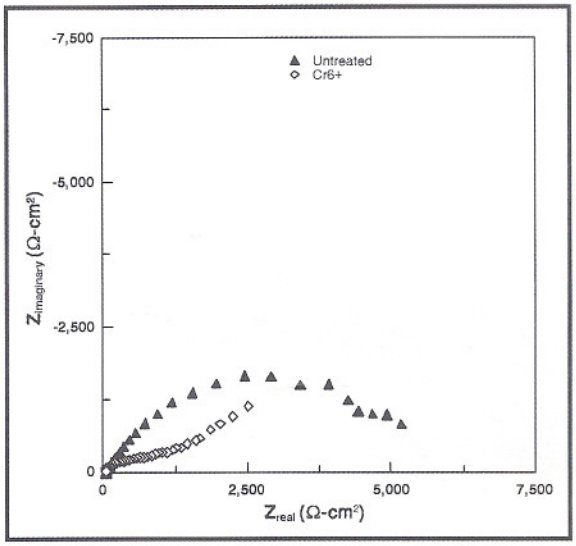

Figure 5. Nyquist diagrams of untreated and chromated Cr(VI) neodymium–iron–boron magnets in PBS

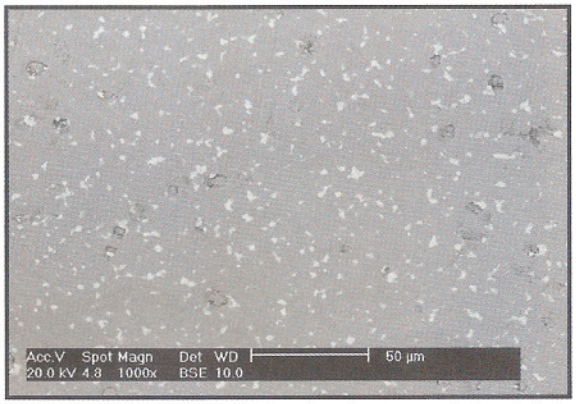

Figure 6. Micrograph of neodymium–iron–boron magnet phosphated 1 h in 10 g/L NaH_2PO_4. SEM/backscattered electron image

Local changes in pH can favor the first reaction leading to localized corrosion processes. However, under normal conditions at a higher pH, the formation of a protective hydroxide or phosphate occurs, depending on the solution chemistry.

Upon immersion in the NaH_2PO_4 solution, phosphating of the neodymium–iron–boron magnets occurred resulting in a thin surface film with interference colors. Some surface attack occurred during this treatment, as shown by the SEM observations, Figure 6. As documented in the images, areas attacked corresponded to the magnetic (φ) phase surrounded by the neodymium-rich phase. Unpredictably, this phase was not attacked, whereas the nobler φ phase around it was corroded. Thus a polarity inversion must have resulted from the phosphating treatment. This is attributed to the rapid formation of a protective phosphate film on the neodymium-rich phase, leading to its ennoblement, and to the attack of surrounding areas of the magnetic phase. The *extremely low solubility of neodymium phosphate* explains this behavior. Phosphating of the magnetic phase also occurs, but the kinetics are slower than that of the neodymium-rich phase.

EIS tests carried out in the PBS, for sample surfaces treated in a 10 gL^{-1} NaH_2PO_4 solution (pH 3.8) for varying times, showed an increase in the impedance with time. The EIS results showed the presence of a high frequency (HF) time constant that can be ascribed to a thin phosphate layer on the surface (confirmed by EDS analysis and visual observations through interference colors). The EIS results also showed that the neodymium–iron–boron behaves as a porous electrode, and the phosphate layer is also formed on the pore walls, hindering the corrosion reaction.

The results of the present study also determined that the phosphate treatment time is an important parameter. Even though the EIS results indicated an increase in the impedance of the magnets with phosphating time from 1 h to 4 h, SEM observations of the surfaces revealed that the degree of attack also increased (Figure 7). The preferential attack of the matrix occurred at the vicinity of the neodymium-rich phase, due probably to a combination of surface defects and passivating phosphate film on this phase. This result indicates that the phosphating treatment should not be carried out for long periods of time.

CONCLUSIONS

Surface treatment of neodymium–iron–boron *sintered magnets in Cr(III) solutions improved* corrosion resistance, but phosphating provided better corrosion resistance than chromating, as demonstrated by EIS. The solution pH and time of treatment are important variables that must be controlled in order to optimize anticorrosion performance. SEM characterization of the magnets after surface treatment showed that immersion in the phosphating solution resulted in selective attack of the magnetic phase at the boundaries with the neodymium-rich phase, whereas this

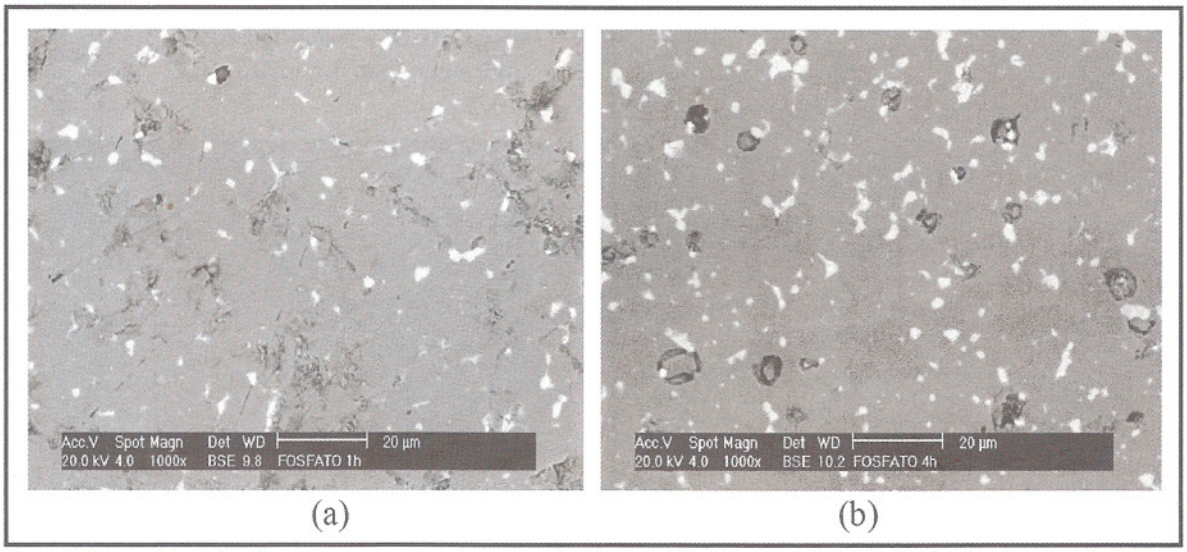

Figure 7. Micrographs of phosphated neodymium–iron–boron magnets (a) 1 h, and (b) 4 h in 10 g/L NaH_2PO_4. SEM/backscattered electron images

phase was not unattacked. This is attributed to the formation of a protective phosphate film on the neodymium-rich phase, due to the low solubility of neodymium phosphates. After the formation of this film, a polarity inversion occurred causing attack of the magnetic phase surrounding the neodymium-rich one. There was also evidence that a thin phosphate layer formed on the magnetic phase, confirmed by EDS analysis and visual observations through interference colors. This contributed to the increase in the corrosion resistance of the phosphated magnets.

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