

## Investigation on the corrosion resistance of Nd-Fe-B magnets used in dentistry coated with phosphate conversion and silane coatings

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### Abstract:

*The aim of this work is to evaluate the effectiveness of corrosion protection due to two different surface treatments: a phosphate conversion and a non-functional silane (BTSE) layer on commercial sintered Nd-Fe-B magnets used in dentistry by electrochemical methods. The electrochemical tests were performed in a phosphate buffered solution (PBS) at neutral pH. The corrosion behavior was monitored by means of electrochemical impedance spectroscopy (EIS) and anodic potentiodynamic polarization curves. Scanning electron microscopy and Energy-dispersive spectroscopy (SEM-EDS) analyses were used to monitor coating deposition. The results indicated a good performance of the phosphate layer, whereas the BTSE layer did not improve the corrosion resistance of the magnets. Impedance results evidenced the occurrence of diffusion-controlled phenomenon, likely linked to the presence of pores in the magnet microstructure.*

**Keywords:** Corrosion, Nd-Fe-B magnets, EIS, Dentistry

## INTRODUCTION

Since Nd<sub>2</sub>-Fe<sub>14</sub>-B-based rare earth magnets were first reported in the 1980s<sup>1</sup>, they have been applied in various different fields owing to their excellent magnetic properties such as high magnetization and high coercivity. These magnets have found use in automobiles, personal computers, consumer electronics, acoustics, and biomedical applications.<sup>2</sup>

Magnets have also been used in dentistry for many years, most commonly to aid retention of oral and maxillo-facial prosthesis. In orthodontics, they are used both for research purposes and in clinical practice, particularly in the treatment of unerupted teeth, in the tooth movement, expansion, fixed retention, and more recently in the correction of an anterior open bite. These magnets have shown spectacular improvements in the maximum energy products, and this has led to important reductions in the size required to produce a particular magnetic flux.<sup>3</sup>

However, at the same time, Nd-Fe-B magnets are notorious for their poor corrosion resistance due to intrinsic porosity and complex microstructure. Corrosion causes degradation and, thereby, might significantly deteriorate the magnetic properties. The main reason for the low corrosion resistance of these magnets is the high propensity to oxidation of the Nd-rich (Nd<sub>4</sub>Fe, η- phase) phase located around the grains of the Φ-phase (tetragonal compound Nd<sub>2</sub>Fe<sub>14</sub>B)<sup>4</sup>. Numerous attempts have been conducted to improve the corrosion behavior of Nd-Fe-B magnets, such as alloying elements additions<sup>5</sup>, and surface coatings by metals<sup>6</sup> (commonly Ni or Zn) or polymer resin<sup>7</sup>.

Treatments based on the use of organo-silane coupling agents are attractive for environmental compliance and good corrosion and adhesion properties. Thin protective silane films are normally obtained by the interaction between hydrolyzed silane solutions and metal substrates by forming strong covalent bonds Si-O-Me (Me stands for metals). In the last years, silanization has been investigated as protective method for iron<sup>7</sup>, aluminum alloys<sup>8</sup>, zinc or electro-galvanized steels<sup>9</sup>, magnesium<sup>10</sup>, and copper<sup>11</sup>. Hu et al.<sup>12</sup> reported only a poor increase in the corrosion resistance of silane coated Nd-Fe-B magnets in NaCl solution, and this was ascribed to preferential adsorption of the silane film on the Fe-rich phase and also to the porous nature of the material.

Phosphating is an environmentally friendly surface treatment, often used as pretreatment prior to coatings application. Only recently, phosphating of Nd-Fe-B magnets and its effect on their corrosion resistance has been studied<sup>13-14</sup>.

The purpose of the present work is to investigate the anticorrosion properties of two different surface treatments applied on Nd-Fe-B magnets, namely: phosphate conversion coating and a non-functional silane (BTSE). The electrochemical investigation was carried out through electrochemical impedance spectroscopy (EIS) and anodic polarization curves. Scanning Electron Microscopy (SEM) and energy dispersive X-ray analysis (EDS) were employed to assess the microstructure and the composition of the coatings, respectively.

## EXPERIMENTAL

The material used in this study was a Nd-Fe-B commercial magnet supplied by CRUCIBLE Co. (known as Crumax). This magnet is prepared by powder metallurgy, and its chemical composition is given in Table 1. The chemical elements Dy, Al, Nb, Co, Si and Cu are added to increase and improve the magnetic and corrosion properties and Na, Ca and S are probably impurities.

Table 1 – Chemical composition (wt %) of the Nd-Fe-B used in the present study

Fe	Nd	B	Dy	Al	Co	Si	Cu	Nb	Na	Ca	S
50.59	28.31	1.0	2.09	3.73	1.28	1.39	0.18	0.66	0.41	0.15	0.16

For electrochemical evaluation, disc specimens of 12 mm diameter and 4 mm thickness were embedded with cold resin setter, after all the electrical contacts had been adequately established, leaving only one face exposed. The specimens were then ground up to 1200 emery paper and cleaned with distilled water and alcohol prior to the corrosion tests. All the corrosion studies were carried out at room temperature ( $25 \pm 2^\circ\text{C}$ ) in a PBS solution, whose composition is shown in Table 2.

Table 2 – Composition of the PBS solution.

NaCl g.L <sup>-1</sup>	Na <sub>2</sub> HPO <sub>4</sub> g.L <sup>-1</sup>	KH <sub>2</sub> PO <sub>4</sub> g.L <sup>-1</sup>
8.77	1.42	2.72

The BTSE (bis-1,2-triethoxysilylethane) solution was prepared by adding 4% (w/w) of BTSE molecules to a 50%/50%(w/w) ethanol/water solution, which, afterwards, had its pH adjusted to a value between 3,5-4,0 by the addition of acetic acid. The solution was then left to hydrolyze for 30 minutes. For coating deposition the magnets were immersed in the hydrolyzed solution during 2 minutes. Curing was performed in an oven during 24 hours at a temperature of  $(25 \pm 2^{\circ}\text{C})$ .

The phosphate conversion coating was obtained in a solution of  $10 \text{ g L}^{-1} \text{ NaH}_2\text{PO}_4$ , acidified with  $\text{H}_3\text{PO}_4$  to pH 3.8, at room temperature, by immersion of the magnets for up to 24h.

All the electrochemical tests were performed using a classical three electrodes cell with Ag/AgCl and a platinum grid as reference and counter electrode, respectively. For the EIS experiments, a Solartron<sup>®</sup> 1260 frequency response analyser coupled to a Solartron<sup>®</sup> 1287 electrochemical interface was used. The measurements were performed at the open circuit potential (OCP) in the 10 kHz to 10 mHz frequency range. The acquisition rate was 10 points per decade and the ac signal amplitude 15 mV. OCP was recorded prior and after the completion of each experiment in order to evaluate whether the stationary requirements were obeyed.

Anodic potentiodynamic polarization curves were obtained at  $1.0 \text{ mV}\cdot\text{sec}^{-1}$  scan rate using the same electrochemical interface employed in the EIS experiments. The curves were initiated after OCP stabilization and were obtained in separate measurements.

The equipment used to perform the SEM/EDS analyses was a Philips XL-30 scanning microscope equipped with an EDS spectrometer. The acceleration voltage used to perform the EDS analyses was 20 keV, giving a penetration depth of approximately  $1 \mu\text{m}$ . Semi-quantitative elemental analyses were performed using internal standards of the equipment.

## RESULTS AND DISCUSSION

Figure 1 presents the anodic polarization curves for the polished Nd-Fe-B magnet and for samples protected with the two different coatings. The curve for the sample protected with the BTSE layer presents a net depolarization when compared with the polished magnet, indicating that this coating is inefficient. On the other hand, a more polarized curve was obtained for the phosphated sample.

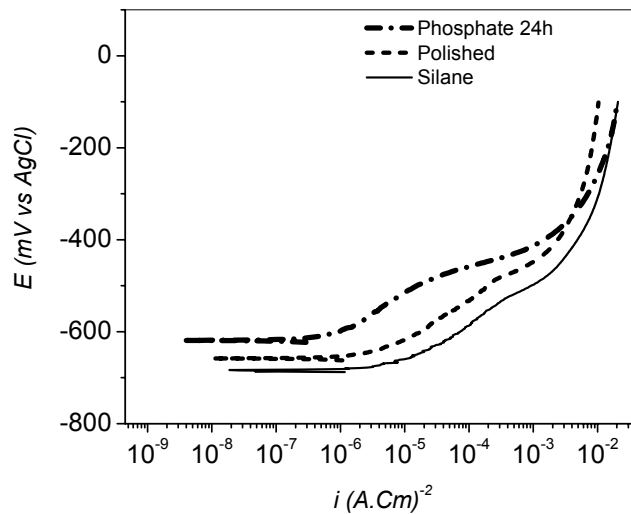


Figure 1 - Anodic polarization curves for samples with phosphate conversion coating, silane coating and uncoated (polished) in the PBS solution.

Figure 2 depicts the EIS diagrams for an uncoated (polished) magnet and for samples protected with the two different coatings. In accordance with the results presented in Figure 1, the phosphated sample presented a higher impedances than the polished magnet, while the BTSE-coated sample showed the lowest impedances. The analysis of the HF region of the Nyquist diagrams (insert in Figure 2(a)) indicates a diffusion-controlled process, which is likely due to the porous nature of the Nd-Fe-B magnet.

The Bode plots, Figure 2(b), for the phosphated and BTSE-coated samples, are clearly composed of two time constants. The one in the high frequency (HF) region is ascribed to the presence of the coating itself, while the lower frequency one can be attributed to corrosion processes occurring at the magnet surface. The HF capacitive response of the phosphated sample indicates that its better anticorrosion behavior can be ascribed to the presence of the protective layer. The analysis of the low frequency (LF) response presented in these plots indicates that the presence of the phosphate layer delays the corrosion process, as it displaces this time constant to lower frequency. On the other hand, the LF time constant of the silane-coated sample appears on the same frequency range as the polished sample, confirming the low effectiveness of this treatment for corrosion protection of Nd-Fe-B sintered magnets.

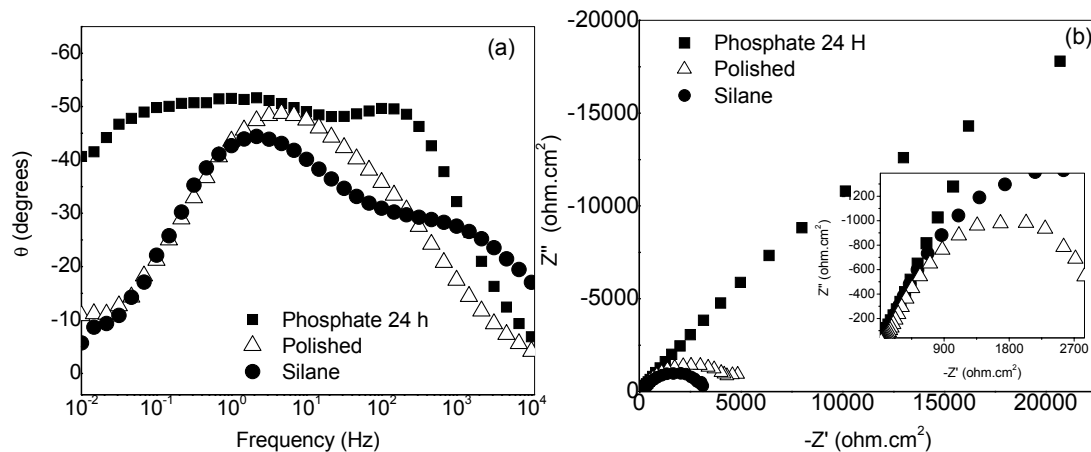


Figure 2 - Bode phase angle (a) and Nyquist (b) plots of polished, phosphate and silane-coated Nd-Fe-B magnets. Diagrams obtained at the OCP after 24 h immersion in PBS solution.

Figure 3 shows a SEM micrograph from the surface of a silane-coated magnet. The image shows that the BTSE film does not deposit homogeneously onto the magnet surface. Regions of heavy silane deposition, identified by EDS analysis, co-exist with poorly coated ones. Particularly striking is the low affinity of the BTSE molecules for the Nd-rich regions, which present poor silane coverage even in regions of heavy silane deposition. This uneven distribution of the silane on the magnet surface can explain the poor corrosion resistance exhibited by these particular samples as galvanic cells can be formed between coated and uncoated regions. Moreover, few holes are also visible in the magnet surface, indicating that the acidic hydrolysis solution can attack the magnet surface.

Figure 4 shows the SEM image of the surface of a magnet treated with the phosphate conversion layer. The surface reveals the preferential attack and detachment of the Nd-rich phase (white phase) in the acidic phosphate solution, remaining the grains of the magnetic phase (Fe-rich phase) surrounded by the cavities (porosities) created by Nd-rich phase removal. It also indicates that the phosphate layer must be formed on the remaining and nobler phases of the magnet. The protective action of the phosphating treatment is twofold: it removes the most active phases located at the grain boundaries of the matrix (magnetic phase), avoiding the formation of galvanic cells upon exposure to the solution, and protects the remaining phase by the precipitation of a thin phosphate layer on it.

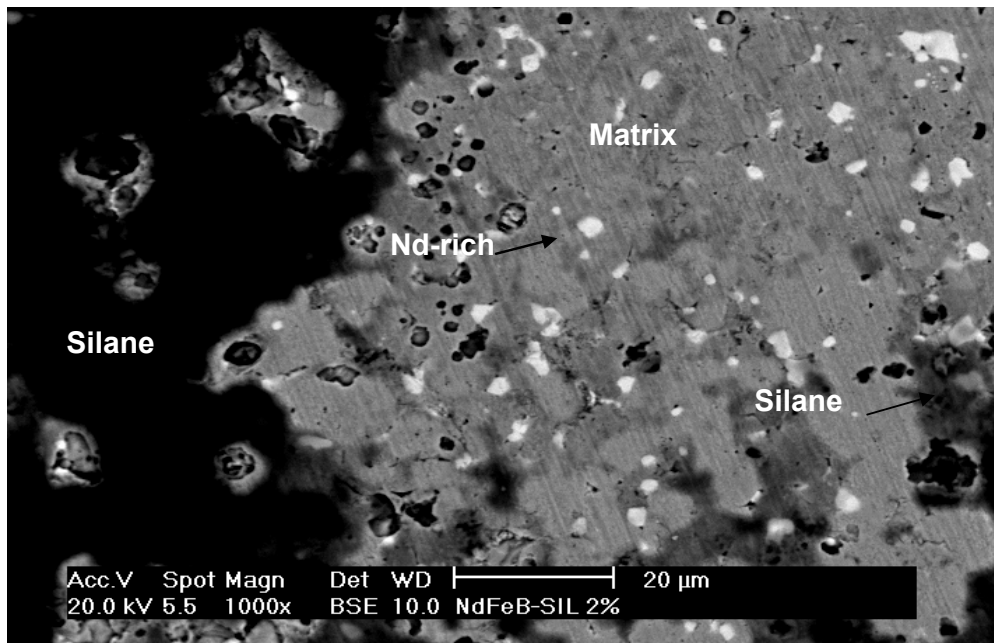


Figure 3 – SEM micrograph of a silane-coated Nd-Fe-B magnet.

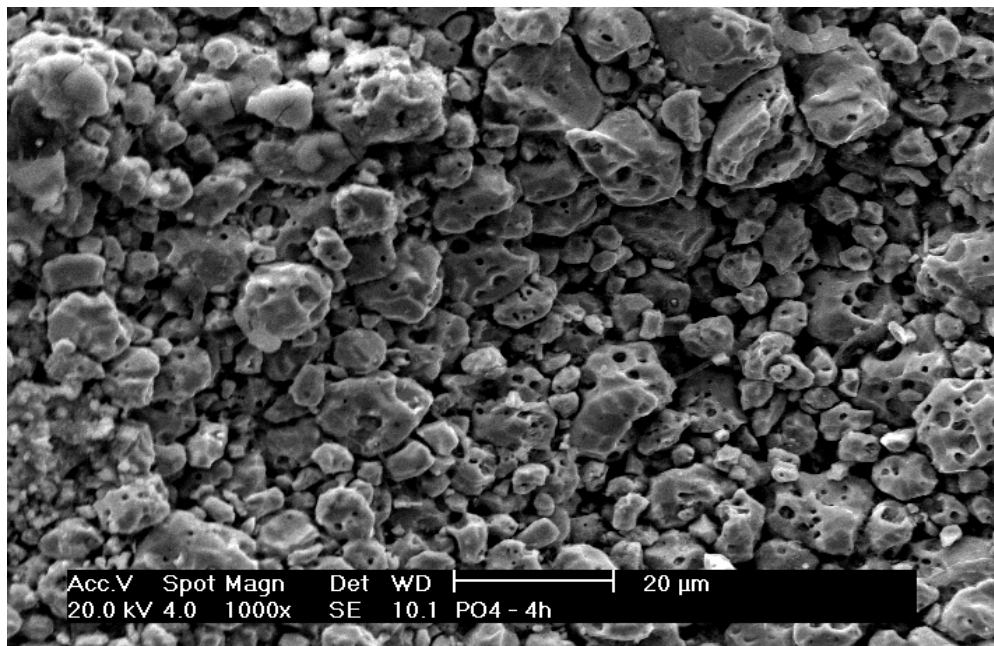


Figure 4 SEM image of the surface of a magnet coated with the phosphate conversion layer.

## CONCLUSIONS

The surface treatment of Nd-Fe-B sintered magnet with silane (BTSE) showed a low affinity of the BTSE molecules for the Nd-rich regions, leading to poor silane coverage even on the regions of heavy silane deposition. The uneven distribution of silane on the magnet surface explains the poor corrosion resistance exhibited by this coating, as galvanic cells can be formed between coated and uncoated regions.

The phosphating treatment resulted in selective attack of the most active Nd-rich phase of the Nd-Fe-B magnet and the protection of the remaining magnetic phase by a thin layer of deposited phosphate.

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