

THE CORROSION RESISTANCE AND CYTOTOXICITY OF A COMMERCIAL Nd-Fe-B MAGNET IN SIMULATED PHYSIOLOGICAL SOLUTION

Mara Cristina Lopes de Oliveira

Instituto de Pesquisas Energéticas e Nucleares (CCTM)
Av. Prof. Lineu Prestes, 2242, CEP 05508-900, São Paulo-SP, Brasil
Email: mcolivei@net.ipen.br

Sizue Ota Rogero,

Instituto de Pesquisas Energéticas e Nucleares (CQMA)
Av. Prof. Lineu Prestes, 2242, CEP 05508-900, São Paulo-SP, Brasil
Email: sorogero@net.ipen.br

Mitiko Saiki

Instituto de Pesquisas Energéticas e Nucleares (CRN)
Av. Prof. Lineu Prestes, 2242, CEP 05508-900, São Paulo-SP, Brasil
Email: mitiko@curiango.ipen.br

Isolda Costa

Instituto de Pesquisas Energéticas e Nucleares (CCTM)
Av. Prof. Lineu Prestes, 2242, CEP 05508-900, São Paulo-SP, Brasil
Email: icosta@net.ipen.br

Abstract. *In this investigation, in vitro corrosion tests have been carried out in naturally aerated Hank's solution at 25 °C, to evaluate the corrosion resistance of a commercial sintered NdFeB magnet by immersion test and electrochemical techniques. Generalized corrosion occurred and Instrumental Neutron Activation Analysis (INAA) was applied to analyze elements leached into Hank's solution. The results showed that Co, Fe and Nd have been released into the physiological medium. In the cytotoxicity test by neutral red uptake and agar diffusion methods, the commercial Nd-Fe-B magnet tested did not present toxicity.*

Keywords. Corrosion, Biomaterials, Cytotoxicity, Sintered Magnets, Nd-Fe-B.

1. Introduction

Magnets have been used in dentistry since the 1950's to improve retention and stability of dental prostheses (Freedman, 1953). In the past, however, the large size required to produce adequate forces limited their extensive use (Moghadam and Scandrett, 1979; Behrman, 1964; Javid, 1971; Wilson et al, 1999). Since the introduction of Rare Earth magnets it has become possible to produce magnets with small enough dimensions to be used in dental applications as retentive devices for overdentures, mainly due to their strong force and compactness (Becker, 1970; Sagawa et al, 1984; Tsutsui et al, 1979). These magnets show great improvements in the maximum energy product comparatively to the old types, leading to a huge reduction in the size required to generate a particular magnetic flux (Harris, 1990).

Dental materials should present high corrosion resistance and be innocuous to human tissues, however, Nd-Fe-B magnets are highly susceptible to corrosion. One of the main problems associated with the use of Rare Earth-Fe-B magnets in clinical use is corrosion once these types of magnets have low corrosion resistance in aqueous media. For dental applications they are usually encapsulated in a stainless steel or titanium can. However, due to wear of the can or failure of the laser weld, saliva is able to leak into the can and cause corrosion of the magnet.

Therefore, there is a continuing concern on investigating the potentially harmful biological effects caused by toxic elements released from the magnet due to corrosion.

In this study, the corrosion resistance of a commercial sintered Nd-Fe-B magnet in Hank's solution has been investigated by electrochemical impedance spectroscopy and potentiodynamic polarization curves. The toxicity of magnetized and demagnetized Nd-Fe-B magnet was also investigated in the neutral red uptake and agar diffusion cytotoxicity assays. The corrosion products leached into Hank's solution were analyzed by instrumental neutron activation analysis (INAA).

2. Experimental

The magnet used in this study was a sintered commercial grade Nd-Fe-B supplied by CRUCIBLE Co., known as Crumax, whose chemical composition is given elsewhere (Rogerio et al, 2003). Magnets were tested in two conditions, magnetized to saturation in a pulsed magnetic field of 6 T and demagnetized.

The surfaces of the magnets specimens were prepared by sequential grinding with silicon carbide paper from grit #120 to #1000. Subsequently, they were immersed in Hank's solution, composition given elsewhere (Lavos-Valereto et al, 2002), at 25 °C, to evaluate their corrosion performance in this medium. After a period of 10 days, the magnets surfaces were examined by scanning electron microscopy (SEM) and the corroded area was analyzed by EDS. The test solution where the specimens remained during 10 days (extract) was chemically analysed using INAA.

2.1. Electrochemical methods

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 a EG&G 273A Potentiostat. A microcomputer was used for the data acquisition. All measurements were performed in potentiostatic mode at the corrosion potential, E_{corr} . The amplitude of the perturbation signal was 10 mV, and the frequency range studied from 10^5 to 10^{-2} Hz. The solution was quiescent, naturally aerated and at a temperature of $(20 \pm 2)^\circ\text{C}$. Potentiodynamic polarization curves were also obtained in Hank's solution. The EISI and potentiodynamic polarization measurements were carried out after 3 days of immersion in the Hank's solution. The scanned potential range varied from -500 mV below the corrosion potential up to 500 mV (SCE) and the scanning rate was 1 mV/s.

2.2. Instrumental Neutron Activation Analysis – INAA

The solution test with corrosion products was analyzed according to the procedure already described in a previous paper (Saiki et al, 2001). 500 μL of the solution were pipetted and dried in polyethylene capsules from Faculty of Biology, (Vie Universities, Amsterdam) for irradiation at the IEA-R nuclear reactor with elemental synthetic standards. These synthetic standards were prepared drying 50 μL of multielemental standard solutions in polyethylene capsules. Samples and standards were irradiated for 5 min and 16 h with thermal neutron flux of $5 \cdot 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$. After adequate decay times, gamma ray measurements were carried out using hyperpure Ge detector. Blank of the Hank's solution was also evaluated using the same experimental conditions used to the solutions with corrosion products.

2.3. Cytotoxicity assay

The cytotoxicity test was carried out by two different methodologies, using the cell line NCTC clone 929 from American Type Culture Collection (ATCC). The methodology was described in a previous paper (Rogerio et al, 2003). The two methodologies were neutral red uptake assay and agar diffusion assay. In the neutral red uptake assay, the extract of Nd-Fe-B, obtained by immersion of the magnet in Hank's solution during 10 days at 37 °C, was serially diluted and then added to the cell culture for 24h. The cytotoxic effect was evaluated by cell viability due to the ability of living and no damaged cells to uptake neutral red. The negative control used was Ti and the positive control consisted of phenol solution (0.02%), following the International Standard Organization (ISO document 10993-5, 1992). In the agar diffusion assay, a piece of Nd-Fe-B was left on top of the agar overlaid on cell culture for 24 hours at 37 °C. The cytotoxic effect was evaluated by the damage caused to the cells, resulting in an halo around the sample, observed by unaided eyes and by optical microscopy.

2.4. SEM/EDX analysis

Scanning electron microscopy and chemical analysis (EDX) of the corrosion products formed during immersion in Hank's solution for 10 days was carried out using a Philips XL-30 onto which an EDX detector had been mounted.

3. Results and Discussion

The typical potentiodynamic polarization curves for the demagnetized and magnetized specimens after three days in Hank's aerated solution, are shown in Fig. (1). The corrosion potentials for the magnetized specimens and demagnetized specimens obtained from these curves were -786 mV (SCE) and -734 mV (SCE), respectively. A comparison of the corrosion rates (i_{corr}), estimated by extrapolating the cathodic part of polarization curves to the corrosion potential (E_{corr}), indicates that i_{corr} for the magnetized specimen ($13.6 \mu\text{A}\cdot\text{cm}^2$) was about an order of magnitude larger comparatively to the demagnetized ($1.1 \mu\text{A}\cdot\text{cm}^2$). Results of gravimetric tests with specimens magnetized and demagnetized, both immersed in 3.5% (wt) NaCl solution, results presented elsewhere (Costa et al, 2001), also indicated larger corrosion rates related to magnetized specimens comparatively to demagnetized types. These results suggest that the magnetic field affects the corrosion resistance of the tested material, and that the magnetized samples have lower corrosion resistance than the demagnetized ones.

The polarization curve for the demagnetized specimen (Fig. (1)) has the typical behavior of activation polarization from approximately -650 mV (SCE) to nearly -500 mV (SCE) with an approximately linear variation of current density with overpotential, which indicates a possible agreement with Tafel's law. The anodic Tafel slope (b_a) of this straight line is approximately 69 mV/decade. From -500 mV (SCE) to about 500 mV (SCE) the curve shows large current densities (order of $\text{mA}\cdot\text{cm}^{-2}$), showing an essentially active behavior in the whole range of anodic polarization. The polarization curve of the magnetized specimen also displays a behavior typical of activation polarization from the corrosion potential to approximately -500 mV (SCE) and an anodic Tafel slope (b_a) of approximately 118 mV/decade in this range of potentials. However, a slight reduction in current density (i) occurred around -300 mV (SCE). Despite the decrease in current density, it remained large enough in the whole range of polarization (order of $\text{mA}\cdot\text{cm}^{-2}$), showing that it was not related to an active-passive transition. The decrease in current was most likely due to precipitation of insoluble corrosion products on the magnetized specimens or to the accumulation of Fe^{2+} ions on the magnet/solution interface. It is noteworthy that the corrosion current densities of the magnetized specimens were larger comparatively to that of demagnetized specimens, and this could facilitate the accumulation/precipitation of corrosion products on the magnetized specimens surface producing a barrier effect and consequently a decrease in current density. From potentials around 0 mV (SCE) up to 500 mV (SCE) the current density displays many oscillations which probably is related to a competition between the release and formation of corrosion products inside the pores at the high overpotentials applied.

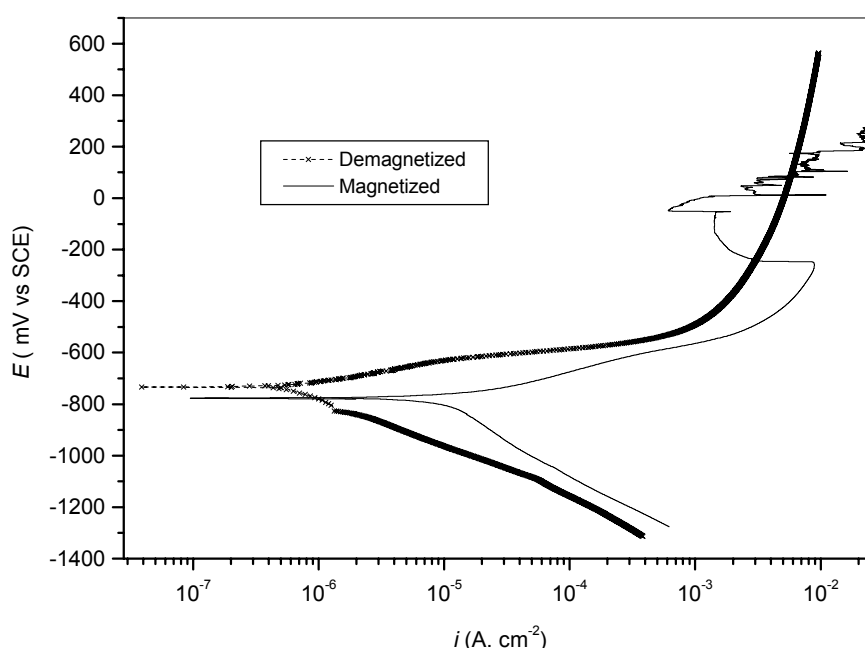
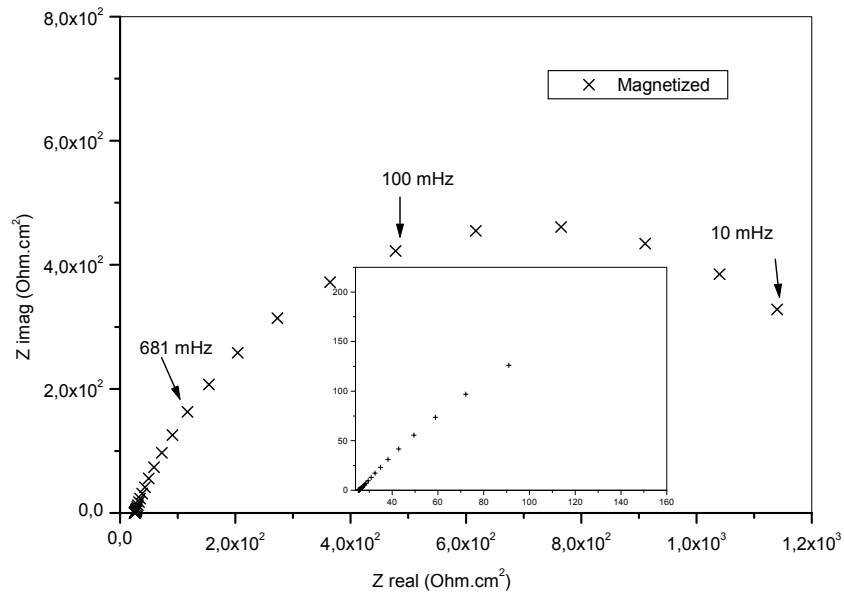


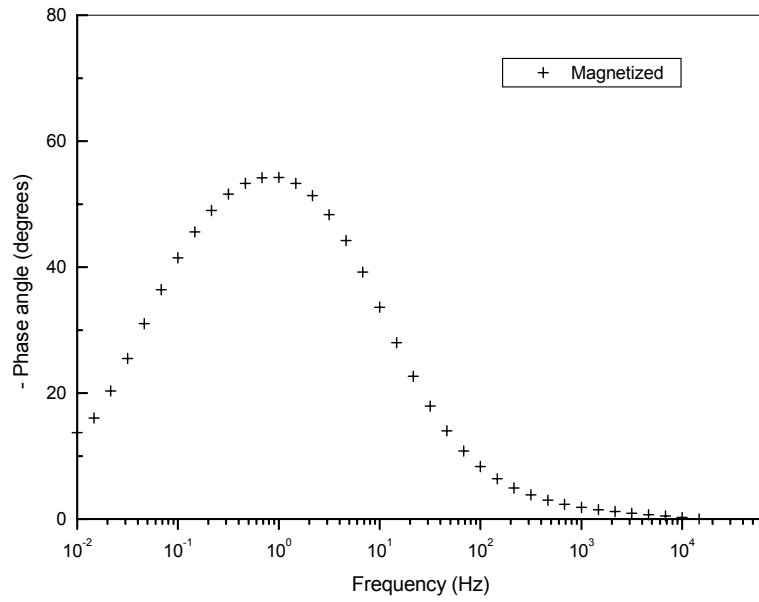
Figure 1. Polarization curves of NdFeB magnets in naturally aerated Hank's solution at 25°C .

The EIS results, as Nyquist and Bode diagrams, for the magnetized and demagnetized specimens after 3 days of immersion in Hank's naturally aerated solution are presented in Figs. 2 and 3, respectively. For the magnetized specimen, the Nyquist diagram displays at high frequencies (insert in Fig. 4) a behavior typical of porous material followed by a very flattened capacitive arc that it is not complete at low frequencies. The Nyquist diagram for the demagnetized specimen at high frequencies also indicates a behavior typical of porous materials that was followed by a flattened capacitive arc from medium to low frequencies, and an inductive arc at low frequencies. This inductive behavior is likely related to iron dissolution due to corrosion (Saliba-Silva, 2001).

The main differences found in the results from EIS for both types of specimens occurred at low frequencies and suggest that different corrosion mechanisms are active on the magnetized and demagnetized specimens. The Bode phase diagrams of both specimens show only a peak at frequencies around 1 Hz, that is likely related to a charge transfer response. The more flattened arc of the magnetized specimen comparatively to the demagnetized, indicates that a more complex mechanism acts on magnetized specimens. Results obtained in 3.5% NaCl also indicated that the corrosion mechanism of this magnets must be dependent on the magnetization state of the material (Oliveira et al, 2002).

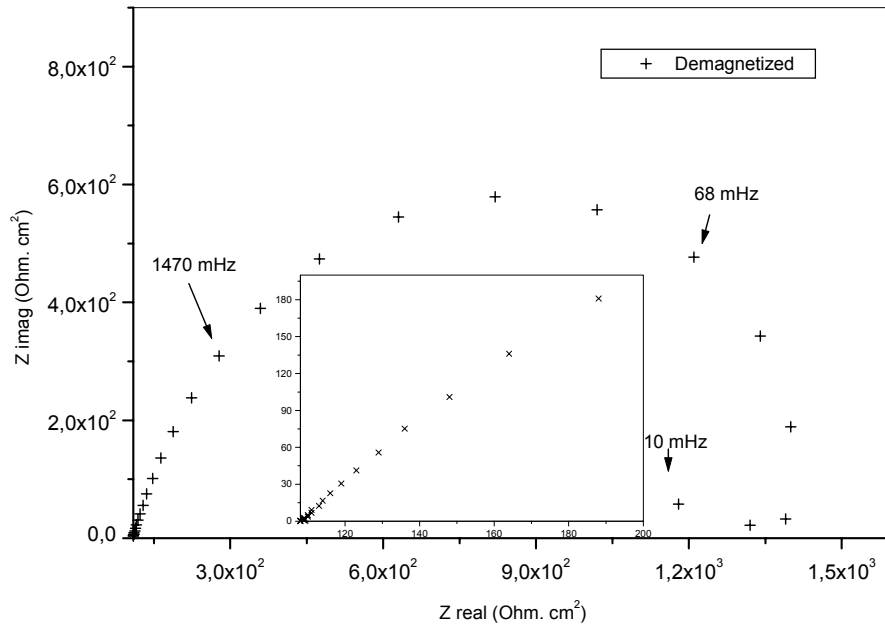


(a)

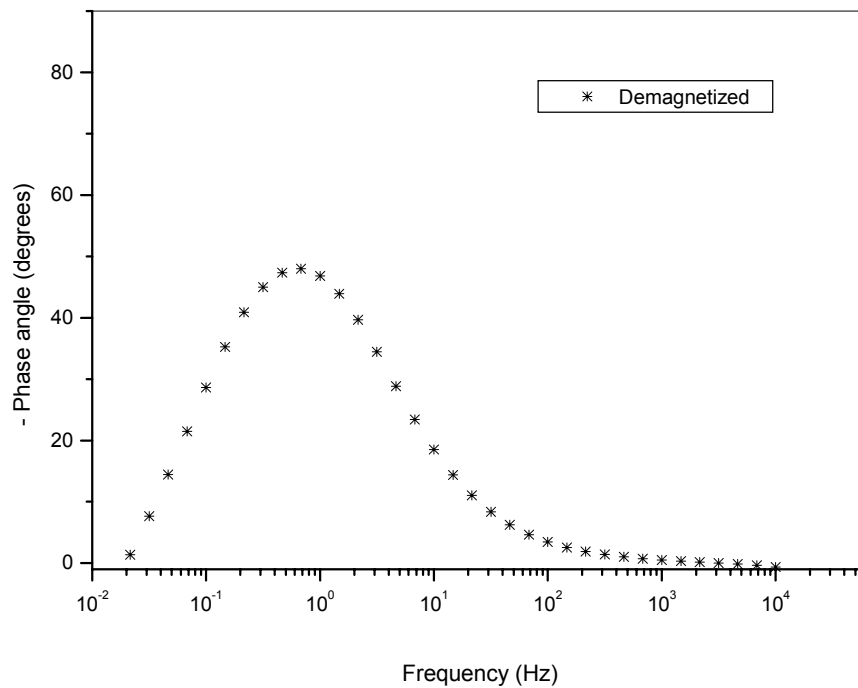


(b)

Figure 2. EIS results for Nd-Fe-B magnetized samples after 3 days of immersion in Hank's naturally aerated solution at 25 °C. (a) Nyquist and (b) Bode diagrams.



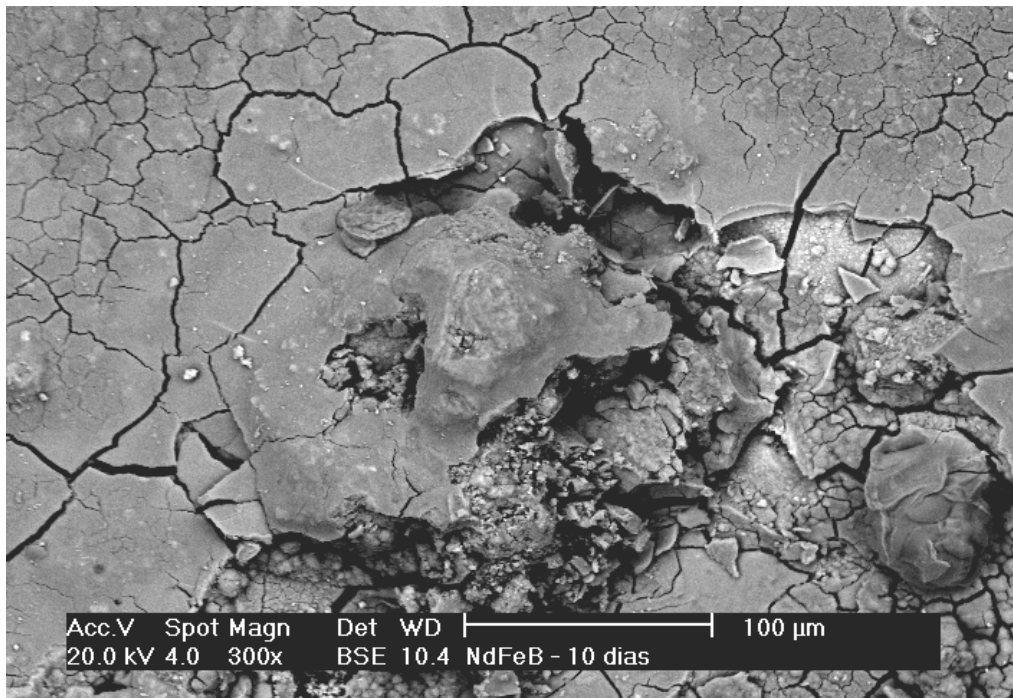
(a)



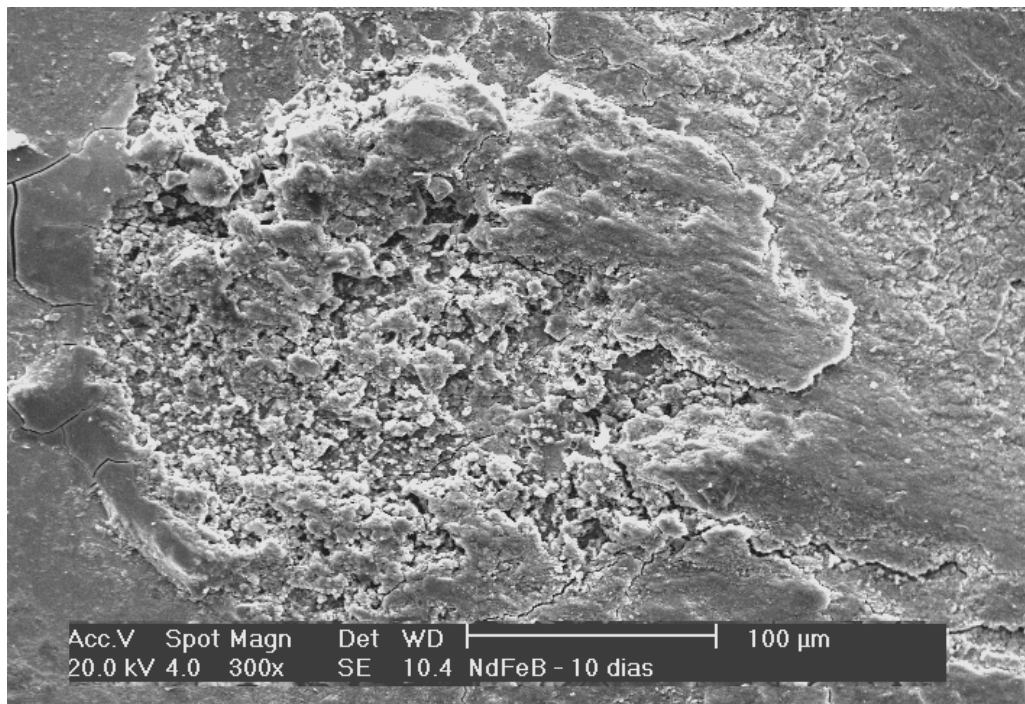
(b)

Figure 3. EIS results for Nd-Fe-B demagnetized samples after 3 days of immersion in Hank's naturally aerated solution at 25 °C. (a) Nyquist and (b) Bode diagrams.

After 10 days of immersion in Hank's solution the surfaces of the magnets, magnetized and demagnetized, were observed by Scanning Electron Microscopy. Figure 4 shows the surface of the corroded magnets. Corrosion occurred over the whole surface of the magnetized specimens leading to voluminous corrosion products that cracked after drying. Larger amounts of corrosion products were related to the magnetized specimens, Fig. (4a), comparatively to the demagnetized (Fig. 4 (b)). For this last type of specimens, corrosion was more superficial and only few cracks were seen on the surface. For both types of specimens, pitting corrosion was not found. The corrosion type related to both magnets tested in Hank's solution was generalized corrosion.



(a)



(b)

Figure 4. SEM of magnets after 10 days of immersion in Hank's naturally aerated solution at 25 °C. (a) Magnetized and (b) demagnetized samples.

In previous studies (Rogero et al, 2001) the same magnet presented pitting corrosion after being immersed in a cell culture medium for 10 days. Chloride was detected on the corroded area, showing it must have participated in the corrosion process. The pitting corrosion found in the samples immersed in the culture medium also indicated the passivation of parts of the surface. In the Hank's solution a passive state was not favoured and corrosion was of a generalized type. These results are related to the increased aggressivity of the Hank's solution comparatively to the cell culture medium. Generalized corrosion was also found for these magnets in a sodium chloride solution (Costa et al, 2001; Oliveria et al, 2002). The combination of a porous structure (sintered magnet), a complex microstructure (mixture of phases of different potentials) and the presence of aggressive species in the test medium are the main causes of corrosion in these magnets.

The analyses of the test solution with corrosion products indicated the release of Co, Fe and Nd from Nd-Fe-B magnet (Tab. (1)). The elements Ca, Cl, Cr and Na were also found in the test solutions, however in the same magnitude of the blank of Hank's solution plus polyethylene capsule used for the sample irradiation. Fe, Nd and Co are the main alloying elements of the magnets studied and their presence in the solution were caused by the corrosion process.

Table 1. Element concentrations due to corrosion determined in the solution where magnetized and demagnetized specimens were immersed and in the blank. (Extract = Hank's solution; Time of immersion = 10 days)

Elements	Solution after immersion of demagnetized Nd-Fe-B samples *	Solution after immersion of magnetized Nd-Fe-B samples d *	Blank
Ca, $\mu\text{g mL}^{-1}$	5.8 ± 0.2	3.5 ± 0.3	6.5 ± 0.2
Cl, $\mu\text{g mL}^{-1}$	5834 ± 113	6126 ± 123	5703 ± 106
Co, ng mL^{-1}	360 ± 5	11191 ± 232	4.3 ± 0.3
Cr, ng mL^{-1}	826 ± 6	895 ± 6	903 ± 9
Fe, ng mL^{-1}	340 ± 102	8370 ± 648	n.d
Na, $\mu\text{g mL}^{-1}$	3459 ± 64	3644 ± 67	3137 ± 59
Nd, ng mL^{-1}	63 ± 4	311 ± 11	55 ± 4

(*) Contribution of the blank was not discounted

The results of the cytotoxicity assay by neutral red uptake method of magnetized and demagnetized samples showed that none of the samples presented toxicity, as indicated in Fig 5. The literature reports that Nd-Fe-B magnets showed toxic effect in an *in vitro* cytotoxicity test, specifically modified agar overlay technique (Donohue et al, 1995) In order to investigate this effect, a similar technique was used, agar diffusion cytotoxicity assay (results shown in Tab. (2)). Both types of magnets tested did not present cytotoxic effect in the agar diffusion method, contradicting the literature. The reason for this contraction is not yet known, but it could have been caused by samples of different compositions.

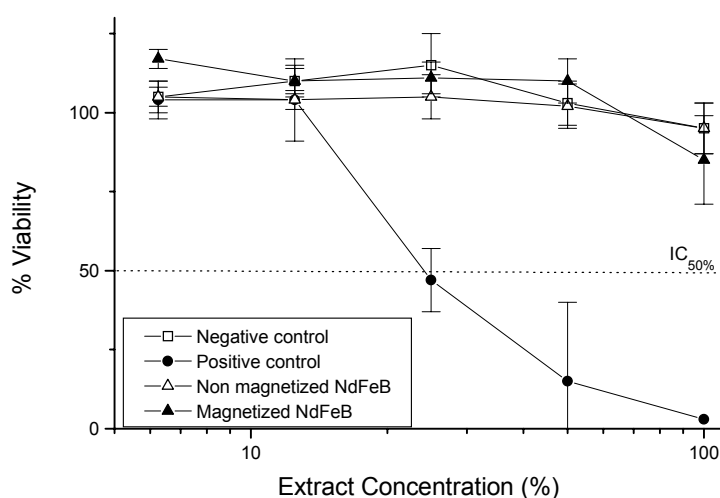


Figure 5. Results of cytotoxicity test - Viability curves of magnetized and demagnetized Nd-Fe-B samples by neutral red uptake assay. Extract immersion time: 10 days.

Table 2. Results of cytotoxicity test by agar diffusion method of Nd-Fe-B magnets (magnetized and demagnetized).

Sample	Transparent halo (cm)	Result
Negative control	0.0	No toxic
Positive control	21.0	Toxic
Magnetized Nd-Fe-B	0.0	No toxic
Demagnetized Nd-Fe-B	0.0	No toxic

4. Conclusions

Nd-Fe-B sintered magnets showed generalized corrosion when immersed in Hank's solution leading to the formation of large amounts of corrosion products. The corrosion products of magnetized and demagnetized magnets presented no cytotoxicity by the neutral red uptake and the agar diffusion assays. However, the corrosion behaviour of the magnets showed dependence on the state of magnetization. Magnetized samples presented lower corrosion resistance and consequently were related to the formation of larger amount of corrosion products than demagnetized samples.

Acknowledgements

To FAPESP and CNPq for financial support.

5. References

- Becker, J., Scientific American 223 (1970), p. 92.
- Behrman, S.J., J. Am. Dent. Associ. 68 (1964), p. 206.
- Costa, I., Oliveira, M.C.L., Takiishi, H., Saiki, M., Faria, R.N., Corrosion behaviour of commercial NdFeB magnets – the effect of magnetization, Key Engineering Materials, v.189-191, (2001), p.340.
- Donohue, V.E., MacDonald, F., Evans, R., J.Appl.Biomat. 6(1) (1995), p. 69.
- Freedman, H., J.Am. Dent. Assoc. 47 (1953), p. 288.
- Harris, I.R., Mater Sci. Technol. 6 (1990), p.962.
- ISO document 10993-5, 1992 Biological evaluation of medical devices, Part 5, Tests for cytotoxicity: in vitro methods.
- Javid, N., J. Prosthet. Dent. 25 (1971), p. 334.
- Lavos-Valereto, I. C., Costa, I., Wolyneec, S., J Biomed Mater Res., 63 (5), (2002) p. 664.
- Moghadam, B.K., and Scandrett, F.R., J.Prosthet.Dent. 41 (1979), p. 26.
- Oliveira, M.C.L., Faria, R.N., Melo, H.G., Costa, I. Corrosion behaviour of a NdFeB magnet in chloride medium, Proceedings of 22nd Brazilian Congress on Corrosion, Salvador–BA, Brazil (*In Portuguese*).
- Rogero, S.O.,Lugão, A.B., Ikeda, T.I., Cruz, A.S., *In vitro* cytotoxicity test: a comparative study of two methodologies. Materials Research, 6(2), 2003 (*In Portuguese*)
- Rogero, S.O., Dantas, E.S.K., Oliveira, M.C.L., Cruz, A.S., Ikeda, T.I., Costa, I., Materials Science Forum, v.416-418 (2003), p. 76
- Rogero, S.O., Oliveira, M.C.L., Saiki, M., Costa, I., SEM of corroded NdFeB magnets in a culture medium, Acta Microscopica, (2001), p.47.
- Sagawa, M., Fugimura, S., Togawa, N., Yamamoto, H., and Matsuura, Y., J. Appl. Phys. 55(6) (1984), p. 2088
- Saiki, M., Rogero, S.O., Costa, I., Correa, O.V., Higa, O.Z., J. Radioanal. Nucl. Chem. 248 (1) (2001), p. 133.
- Saliba-Silva, A.M., PhD Thesis, IPEN - University of Sao Paulo, 2001 (*In Portuguese*) 139 p.
- Tsutsui, H., Kinouchi, Y., Yoshida, Y., Sasaki, H., Shiota, M., and Ushita, T., J. Dent. Res. 58 (6) (1979) p. 1597.
- Wilson, M., Kpendem, H., Noar, J.H., Hunt, N., and Mordan, N., J. Biomaterials 16 (1999), p. 721.