

THE EFFECT OF GALLIUM ADDITION ON THE CORROSION RESISTANCE OF A Pr-Fe-Co-B-Nb PERMANENT MAGNET ALLOY

M.C.L.Oliveira^{a,*}, R.N.Faria^a, I. Costa^a

^aInstituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN
Av Lineu Prestes, 2242, São Paulo 05422-970, Brazil
e-mail: mcolivei@ipen.br

ABSTRACT

The effect of gallium addition (0.5 wt. %) on the corrosion resistance of a Pr-Fe-Co-B-Nb permanent magnet alloy has been investigated. The electrochemical behavior was assessed using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The electrochemical tests were carried out during 30 days using a naturally aerated 0.02M Na₂HPO₄ solution at room temperature as electrolyte. The specimens were annealed for 20h at 1100°C prior to immersion in the electrolyte. The results pointed towards a beneficial effect of Ga addition on the resistance of the surface film to breakdown. The surface film was formed upon immersion in the phosphate solution used as test medium. In this solution, the corrosion resistance of both alloys tested, either with or without Ga, increased with time of immersion due to the continuous growth of the phosphate film on their surfaces.

Keywords: permanent magnets; Pr-Fe-Co-B-Nb-Ga; corrosion

INTRODUCTION

The magnetic properties of rare earth based permanent magnets have been investigated by several authors¹⁻⁴. If one envisages the successful application of these materials in personal computer hard disks or electric motors it is of prime interest to maximize their remanence, Curie temperature and intrinsic coercivity. This

objective may be reached by incorporating specific alloying elements in the magnets composition. Elements such as Co, Zr, Ga, Al and Nb have been used with this purpose². Faria et al³ studied the effect of Co, Zr, Nb, Ga and Dy additions on the magnetic properties of HDDR Pr-Fe-B powder magnets after annealing and in the as cast condition. They found that Ga decreased intrinsic coercivity of the material. On the other hand, according to Kirchner et al.⁴ Ga addition may increase both remanence and coercivity of rare earth based magnetic alloys.

The low corrosion resistance of rare earth based permanent magnets is a major drawback. This limitation arises from their complex microstructure formed by at least two phases. The first is the hard magnetic ϕ phase, whose mean composition is given by $\text{Pr}_2\text{Fe}_{14}\text{B}$. The second is a Pr rich phase. These two phases present significantly different electrochemical potentials. Consequently, the formation of galvanic couples is favored with the subsequent dissolution of the most active phase⁵. Co and Ga may lead to the formation of nobler intergranular phases, depending on their contents, reducing the corrosive attack at the grain boundaries⁶. The aim of this work was to investigate the effect of Ga addition on the corrosion resistance of the magnetic alloy $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$ using electrochemical impedance spectroscopy and potentiodynamic polarization.

EXPERIMENTAL

The $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$ and $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Ga}_{0.5}$ ingots were cut into small rectangular samples. These samples were then annealed under vacuum atmosphere (10^{-4} e 10^{-5} mbar) at 1100 °C for 20h. The annealed samples were then welded to a copper wire, embedded in epoxy resin, leaving an exposing area of 1.0 cm^2 to the electrolyte and ground with SiC up to #1200. The corrosion performance was evaluated using EIS and potentiodynamic polarization. The test solution was a 0.02M Na_2HPO_4 naturally aerated solution. The evolution of the electrochemical behavior was assessed from the first hours of immersion up to 30 days in the electrolyte using EIS. The experimental set-up comprised a three-electrode cell arrangement with a platinum wire as counter-electrode and saturated calomel electrode as reference electrode. EIS plots were obtained using a Solartron 1255 equipment coupled to a potentiostat/ galvanostat (EG & G 273A) with an amplitude of 10mV in the frequency range of 10kHz to 10mHz. At 30 days of immersion, the

samples were anodically polarized at $1 \text{ mV}\cdot\text{s}^{-1}$ from $-500 \text{ mV}_{\text{ECS}}$ up to $0 \text{ mV}_{\text{ECS}}$. All the electrochemical tests were carried out at room temperature. SEM images have been taken of as cast and annealed specimens of both alloys. EDS analysis was undertaken to assess the mean composition of the phases present on each specimen.

RESULTS AND DISCUSSION

Backscattering SEM images of $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$ alloy in the as-cast and annealed conditions are shown in Figures 1a and 1b, respectively. The image of $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Ga}_{0.5}$ in the annealed condition is shown in Figure 1c.

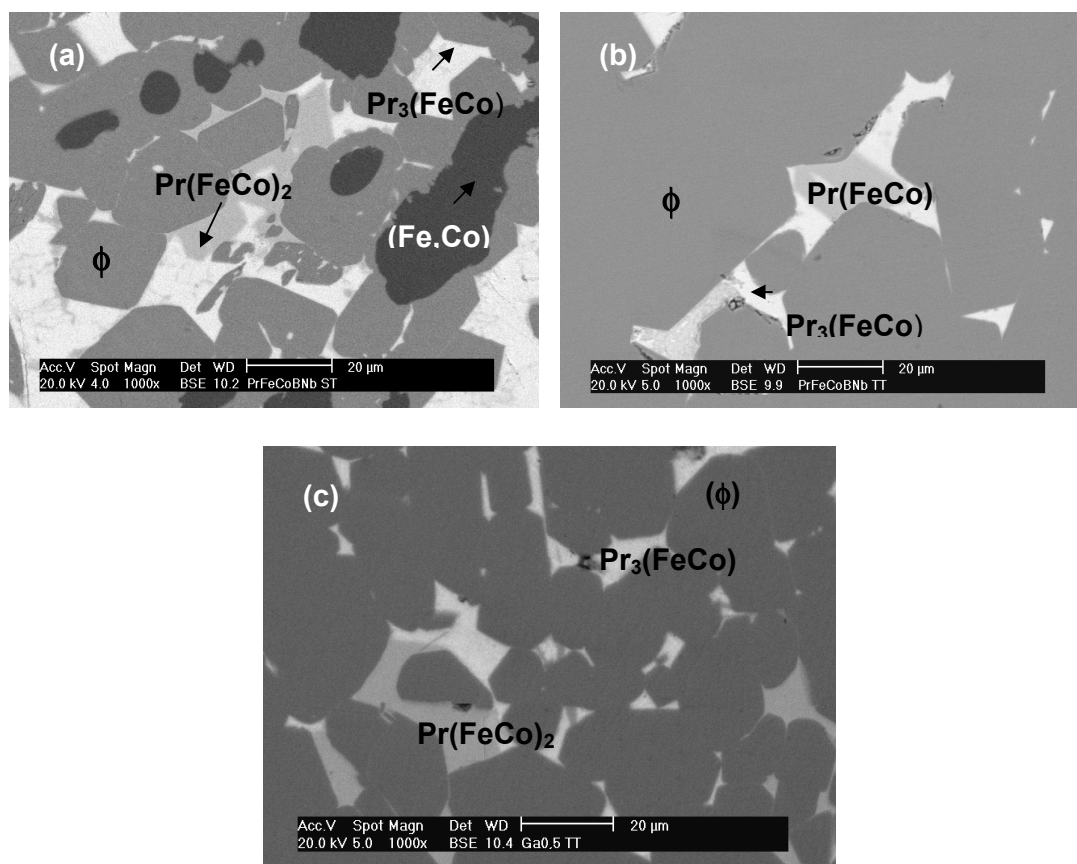


Figure 1 – SEM micrographs of $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$ alloy (a) in the as-cast condition and (b) annealed at $1100 \text{ }^\circ\text{C}$ for 20 h; (c) $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Ga}_{0.5}$ alloy annealed at $1100 \text{ }^\circ\text{C}$ for 20 h.

It is evident that the alloy in the as-cast condition presents high amounts of $\alpha(\text{Fe,Co})$ phase (dark grey phase). This constituent is an adverse magnetically soft phase and does not contribute to the high magnetic properties that should be inherent

to a permanent magnet. Additionally, there are three other phases: $\text{Pr}_2(\text{Fe,Co})_{14}\text{B}$, $\text{Pr}(\text{Fe,Co})_2$ and $\text{Pr}_3(\text{Fe,Co})$. The first one is called ϕ or matrix phase which is magnetically hard. The last two are intergranular phases, namely the grey or Laves phase ($\text{Pr}(\text{Fe,Co})_2$) and the white praseodymium-rich phase ($\text{Pr}_3(\text{Fe,Co})$). Annealing proved to be effective as the $\alpha(\text{Fe,Co})$ regions were completely removed from the structure of both alloys, leaving only $\text{Pr}_2(\text{Fe,Co})_{14}\text{B}$, $\text{Pr}(\text{Fe,Co})_2$ and $\text{Pr}_3(\text{Fe,Co})$ for both alloys. In spite of the Ga addition, this element was not detected in any of the phases present. Probably the addition of only 0.5 at.% was not sufficient to form a distinguishable Ga-rich micro constituent. These results agree well with other findings in the literature³.

Bode phase angle plots of $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$ and $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Ga}_{0.5}$ obtained at 1, 10, 20 and 30 days of immersion in 0.02M Na_2HPO_4 solution are shown in Figure 2.

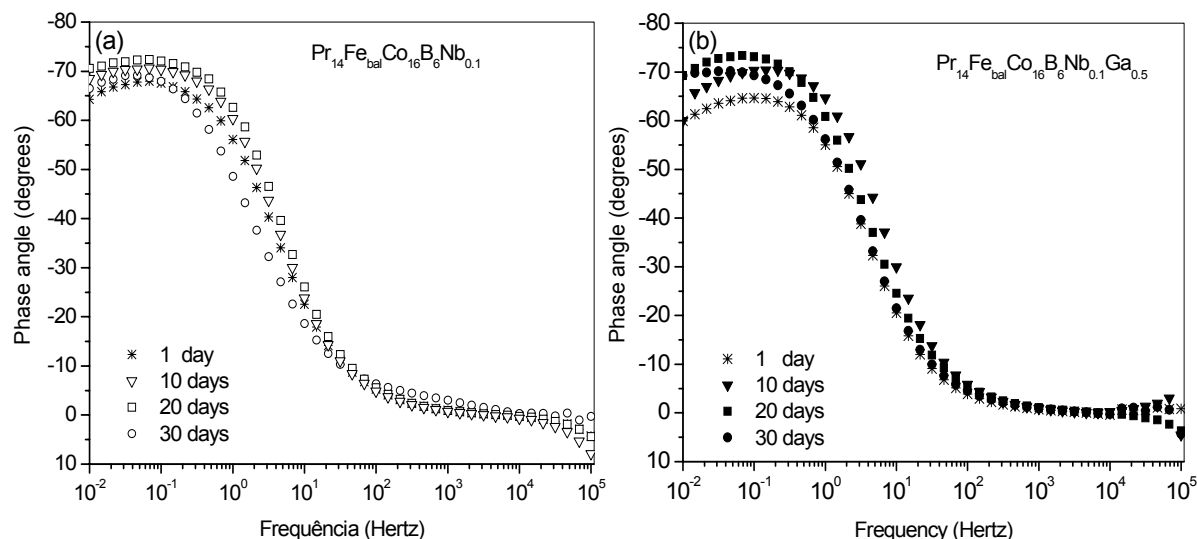


Figure 2- Bode phase angle plots of: (a) $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$ and (b) $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Ga}_{0.5}$ after 1, 10, 20 and 30 days of immersion in 0.02M Na_2HPO_4 solution.

Bode plots of both alloys present one single capacitive time constant during the whole immersion period. This time constant is marked by a shoulder at 0.1Hz which is likely due to charge transfer reactions. The electrolyte used in the test contains phosphate ions. It is known that rare earth phosphates are hardly soluble and form precipitates with corrosion inhibition properties. This phenomenon may explain the

relative high phase angle values at low frequencies of $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$ alloy for all the immersion periods. Additionally, it is possible that the phosphate layer thickness increase with the immersion time as the phase angle values increased for longer periods.

$\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Ga}_{0.5}$ alloy presented a similar behavior, suggesting that Ga did not cause significant changes in the electrochemical behavior of the original alloy. However, the phase angle values at low frequencies are lower than those of the alloy without Ga addition after 1 day of immersion. For this alloy, there is a possible incorporation of Ga at the grain boundaries, leading to the formation of nobler intergranular phases in comparison with $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$ alloy. Consequently, the corrosive attack at the more active sites and the formation of protective rare-earth based phosphates would be reduced. The phase angle values increased with the immersion time and the time constant shoulder shifted to lower frequencies. Thus, it is likely that the formation of protective phosphate precipitates occurs continuously during the test.

Nyquist plots of $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$ and $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Ga}_{0.5}$ alloys for 1, 10, 20 and 30 days of immersion in 0.02M Na_2HPO_4 solution at room temperature are shown in Figures 3 and 4, respectively.

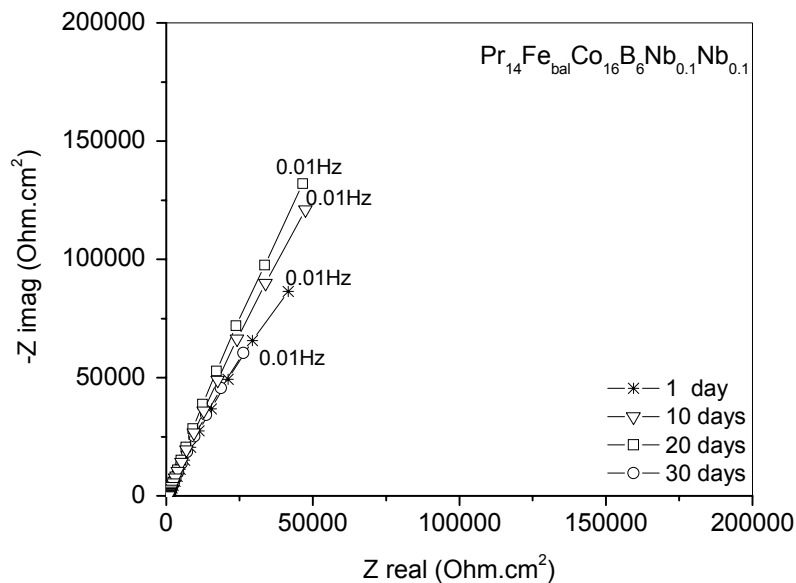


Figure 3 – Nyquist plots of $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$ alloy for 1, 10, 20 and 30 days of immersion in 0.02M Na_2HPO_4 solution at room temperature.

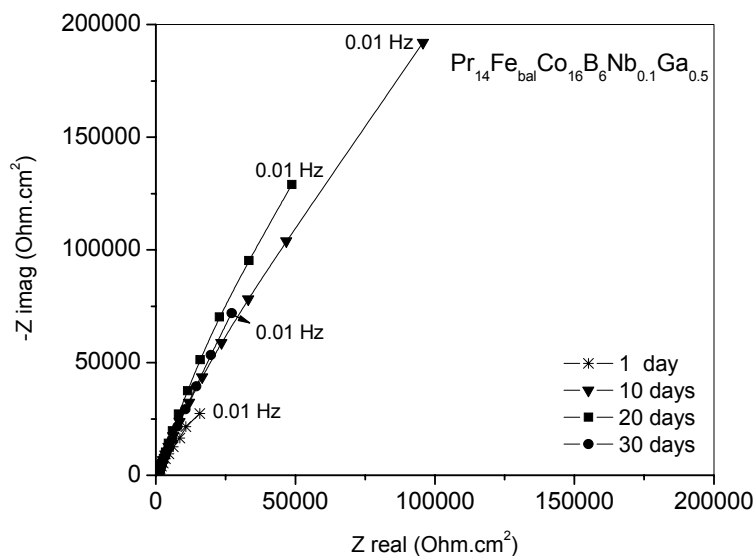


Figure 4 - Nyquist plots of $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Ga}_{0.5}$ alloy for 1, 10, 20 and 30 days of immersion in 0.02M Na_2HPO_4 solution at room temperature.

Nyquist plots of both alloys present high impedance values at low frequencies which increased with the elapsing of time up to 20 days. From 20 days to 30 days, however, there is a significant decrease in the impedance values. This behavior confirms the beneficial effect of increasing immersion times on the corrosion resistance of these alloys but only up to a 20 days which was followed by its protective properties degradation from 20 days to 30 days. The high impedance values support the hypothesis of the presence of a protective layer on the specimens surface formed during immersion in the phosphate medium used as electrolyte. Thus, there is a subsequent decrease of the interfacial electrochemical processes kinetics from 1 to 20 days. The formation of the phosphate layer depends on the surface activity. From 20 days to 30 days, the surface activity must have decreased due to prior phosphate precipitation and the deterioration of the precipitated layer leads to the increase of the kinetics of the charge transfer reactions. Despite of this slight degradation of properties, higher impedance values were obtained at 30 days relatively to 1 days of immersion.

Nd and Pr magnetic alloys are highly active and prone to corrosion in a wide variety of media ⁷. So, it is expected that phosphate formation occurs on the most

active sites of the alloys, especially for $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$. Anodic polarization curves of $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$ and $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Ga}_{0.5}$ magnetic alloys after 1 and 30 days of immersion in 0.02M Na_2HPO_4 solution at room temperature are shown in Figure 5.

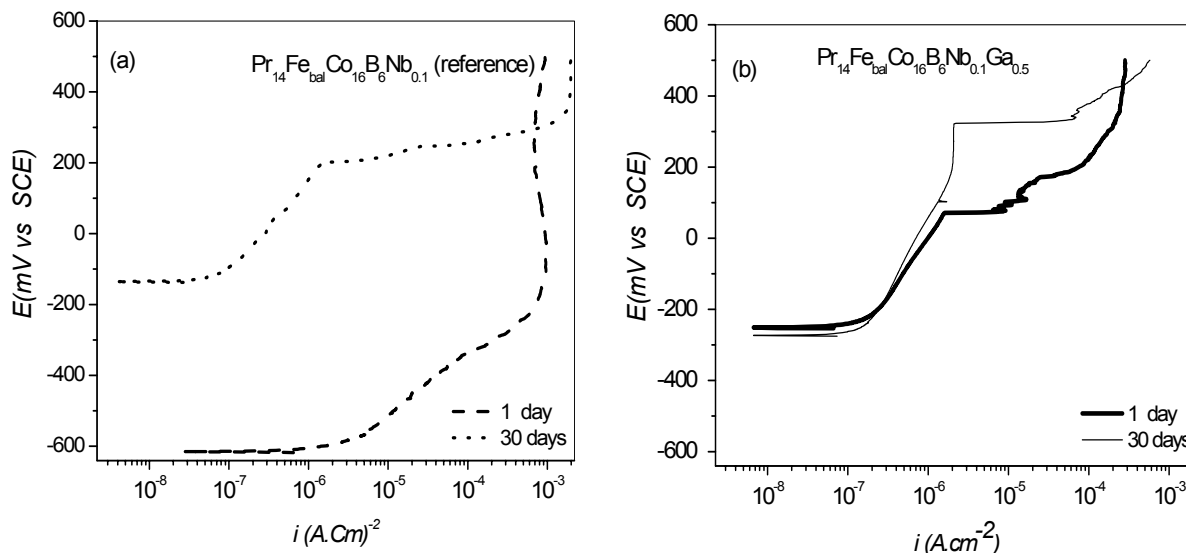


Figure 5 – Anodic polarization curves of (a) $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$ and (b) $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Ga}_{0.5}$ after 1 and 30 days of immersion in 0.02M Na_2HPO_4 solution at room temperature.

The results for $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$ alloy show a significant ennoblement of corrosion potential from 1 to 30 days of immersion (from -610 mV_{ECS} to -140 mV_{ECS}) and a large decrease in the current densities showing the polarization of the anodic reaction, likely due to phosphate precipitation. The corrosion current density, estimated as the extrapolation of the anodic Tafel region up to the corrosion potential value greatly decreased after 30 days of immersion. These features are most probably related to the formation of a protective phosphate layer for longer test periods as discussed from EIS plots. The very low current density values indicate that this alloy is in a passive state in the phosphate medium. Furthermore, the protective properties of this layer seem to be improved as time elapses. The sharp increase of current density at around 200 mV_{ECS} after 30 days of immersion points towards a break of the passive phosphate layer.

The increase of corrosion resistance with immersion time is much less pronounced for $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Ga}_{0.5}$ alloy. Corrosion potential and corrosion

current density (i_{corr}) values are little altered from 1 to 30 days. The low i_{corr} values suggest that the alloy was in a passive state during immersion as observed for $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$ alloy. However, the breakdown potential for the Ga-containing alloy is significantly higher comparatively to the alloy without this alloying element, showing that the alloy with Ga has a greater resistance to passivity breakdown in the test electrolyte adopted.

According to literature findings^{6,8} Ga additions positively influences the corrosion resistance of rare-earth based magnetic alloys. This element replaces iron in the crystal structure and may form nobler intergranular phases. As a result, the tendency of galvanic attack between phases with different electrochemical potentials in the microstructure of the alloy is reduced. However, the results obtained from SEM observations did not allow to distinguish between phases present on $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Ga}_{0.5}$ and $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$ alloys (Figure 1). The low Ga content was probably insufficient to produce a different Ga-rich phase. Even though no different phase was observed in the Ga-containing alloy the results of the electrochemical tests show that the addition of this element to the original alloy may improve the protective character of the film formed in phosphate solution.

CONCLUSIONS

$\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}\text{Ga}_{0.5}$ and $\text{Pr}_{14}\text{Fe}_{\text{bal}}\text{Co}_{16}\text{B}_6\text{Nb}_{0.1}$ alloys presented high corrosion resistance in the phosphate electrolyte used in the electrochemical tests. This behavior is likely due to the formation of a phosphate layer which becomes more protective for longer immersion times. The addition of 0.5 at.% of Ga did not produce significant changes in the electrochemical behavior of the original alloy but caused an increase of the breakdown potential value in the electrolyte

ACKNOWLEDGEMENT

M.C.L.Oliveira thanks CNPq (Brazil) for a research fellowship. The authors also gratefully acknowledge FAPESP (Brazil) for funding this work.

REFERENCES

- [1] SAGAWA, M., FUJIMURA,; YAMAMOTO, H.; MATSUURA,Y. New material for permanent magnets on a base of Nd and Fe. **J. appl. Physics.**, v.55(6), p. 2083-87,1984.
- [2] JIANG, S.Y.; CHEN, H.Y.;CHENG, S.F.; BOLTICH,E.B.; SANKAR,S.G.; LAUGHLIN,D.E.;WALLACE,W.E. Magnetic properties of R-Fe-Co-Al-B magnets (R= Pr and Nd). **J. appl. Physics.**, v. 64(10), p. 5510-12, 1988.
- [3] FARIA, R.N.; BROWN, D.N.; HARRIS, I.R. The influence of alloying additions and process parameters on the magnetic properties of PrFeB based bonded magnets. **J. Alloys and Compounds**, v.296, p. 219-222, (2000).
- [4] A. KIRCHNER, D. HINZ, V. PANCHANATHAN, O. GUTFLEISCH, K. H. MULLER, SCHULTZ. Improved hot workability and magnet properties in NdFeBCoGaB hot deformed magnets.; **IEEE Trans. Magn**, v. 39, n.5, p. 2947-2949, 2003.
- [5] W. BLOCH, K. GREDEL, H. STAUBACH, in Proceedings 11th International Workshop on Rare Earth Magnets and Their Applications, Pittsburgh, 108, October, p. 21-24, 1990.
- [6] A. A. EL-MONEIM, O. GUTFLEISCH, A. PLOTNIKOV, A. GEBERT, Corrosion behaviour of hot-pressed and die-upset nanocrystalline NdFeB-based magnets, **J. Magn. Magnetic Materials**, v. 248, p. 121-133, 2002.
- [7] I.COSTA, M.C.L. OLIVEIRA, H.G.DE MELO, R.N. FARIA, The effect of the magnetic field on the corrosion behavior of Nd-Fe-B permanent magnets, **Journal of Magnetism and Magnetic Materials**, v. 278, p. 348-358, 2004.
- [8] T. V. JAYARAMAN, N. SRISUKHUMBOWORNCHAI, S. GURUSWAMY, M. L. FREE, Corrosion studies of single crystals of iron–gallium alloys in aqueous environments, **Corrosion Science**, v. 49, p. 4015-4027, 2007.