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LA 96153

2nd NACE
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september 1996

THE CORROSION BEHAVIOUR OF RE-IRON-BORON MAGNETS IN AN INHIBITING SOLUTION

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SUMMARY

The corrosion behaviour of RE-Iron-Boron magnets (RE = Nd and Pr) in a solution consisting of 0.15 M NaH_2PO_4 has been studied by means of electrochemical techniques, including potentiodynamic polarization and electrochemical noise measurements. The results indicated a strong inhibiting effect of the test solution used for all the magnets tested. The inhibiting effect was slightly dependent on the magnet investigated.

Keywords: corrosion, rare earth magnets, permanent magnets, inhibitors.

1. INTRODUCTION

Sintered magnets based on neodymium-iron-boron (1) have already reached an advanced degree of development. Recently, more attention has been directed to Pr-Fe-B magnets, as they possess a magnetocrystalline anisotropic field higher than that of Nd-Fe-B magnets and can reach high coercivity (2-5)Despite the excellent magnetic properties of Nd-Fe-B magnets (6,7), they are highly susceptible to corrosion in aqueous environments. The poor corrosion properties are apparently linked to the presence of multiple phases in these type of magnets, leading to galvanic corrosion in the presence of an aggressive environment. The Nd-Fe-B magnets complex microstructure consists of the main magnetic phase (ϕ), a Nd rich phase, and a boron rich phase. According to the literature (8), in the magnets produced by the powder metallurgy route, the grains of the main magnetic phase (ϕ) are surrounded by intergranular regions containing a mixture of phases, including the Nd rich phase. The Nd rich phase is electrochemically more active than the main magnetic phase(9). Consequently, sintered Nd-Fe-B magnets are sensitive to intergranular corrosion, where the Nd rich intergranular regions are attacked preferentially. This could eventually lead to detachment of the ϕ grains (10-12).Most efforts to improve the corrosion resistance of RE magnets have been directed at the development of corrosion resistant coatings to these magnets (9-12). The corrosion resistance of uncoated magnets, as substrates for coatings, has also been investigated (13-15). Attempts have also been made towards improving corrosion resistance of RE magnets by the addition of alloying

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elements (16-21). However, improving corrosion resistance by alloying usually deteriorates the magnetic properties.

One method of corrosion protection which has been overlooked consists in the use of corrosion inhibitors. Corrosion inhibitors have the advantage of being easier to apply than coatings.

Also the use of passivating inhibitors could be considered as a pre-treatment before coating application, increasing the corrosion resistance of defect regions in the coating. Phosphate-based inhibitors have been used for many years with ferrous materials and their mechanistic behaviour is well known. Environmental and health considerations also led towards the phosphates as a suitable inhibitor candidate for the magnets tested.In the present study, the electrochemical behaviour of two commercial Nd-Fe-B magnets, and a laboratory made
Pr-Fe-B magnet exposed to a phosphate solution has been investigated.

2. EXPERIMENTAL METHOD

The electrochemical behaviour of the magnets was studied by means of potentiodynamic polarization measurements and eletrochemical noise methods.

2.1 Specimen preparation

Two commercial Nd-Fe-B magnets and a Pr-Fe-B magnet have been investigated. The Prl6 Fe76 B8 magnet was laboratory made by powder metallurgy and the hydrogen decrepitation (HD) process(5). The magnets studied and
processing conditions are shown in Table I.

Table I - Magnets investigated and their processing condition.

Magnet	Processing condition
Crumax	powder metallurgy
Neomax	powder metallurgy
$Pr_{16}Fe_{76}B_8$	HD

After have been cold mounted in an epoxy resin, the surface of the various specimens was prepared by griding with silicon carbide paper up to grade 1000. The specimens were then degreased with acetone in an ultrasonic bath, rinsed in deionized water, and dried in a dessicator over silica gel under vacuum.

2.2 Experimental set-up

After surface preparation, the specimens were immersed in distilled water and their potential was measured relatively to a calomel reference electrode, as a function of immersion time. The open circuit potential (Eoc) of the magnets was fairly stable after approximately 4 hours immersion. Subsequently, polarization measurements were carried out. The experimental set-up adopted for polarization measurements consisted of a three electrode cell, the magnet working electrode, a graphite counter electrode and a saturated calomel (reference) electrode (SCE).

Polarization data was then produced by changing the electrode potential by two hundred millivolts from the open circuit potential (Eoc) at a rate of 0.3 mV/s. After performing the measurements in distilled water, NaH2PO4 was added until making up a 0.15 M NaH2PO4 solution. Polarization data for the same conditions above was also produced after 3 hours exposure in the 0.15 M NaH2PO4 solution. Potentiodynamic polarization measurements were also carried out in the 0.15 M NaH2PO4 solution for larger applied voltage. This was accomplished by sweeping the electrode potential in the range from the open circuit potential (Eoc) to 1.2 V (SCE) and then returning to Eoc at a rate of 5 mV/s. Three consecutive cycles were completed.For the electrochemical noise (EN) measurements, a pair of "identical" magnet electrodes was immersed in a 1 electrochemical cell, containing the 0.15 M NaH2PO4 test solution. A saturated calomel electrode (SCE) was brought into close proximity with one electrode. The mounted electrodes were separated by 3 mm and kept in a stable position with holders. The SCE served to measure ECOIT and its fluctuations. An automated Zero Resistance Ammeter was used to take current and voltage measurements, simultaneously, at a sampling interval of 1 s. The EN measurements were taken after 18 h immersion in the test solution.All experiments were conducted at room temperature and the volume of solution used was approximately 700 ml for each cell. The pH of the bulk solution corresponding to 0.15 M NaH2PO4 was 4.3.

3. RESULTS AND DISCUSSION

The open circuit potential corresponding to the magnets studied, in distilled water (4 hours stabilization) and in the 0.15 M NaH2PO4 solution (3 hours stabilization), is indicated in Table II.

Table II - Open circuit potential, Eoc (mV vs SCE) of the magnets in the test environments used.

Magnet	E_{OC} (Distilled water)	E_{OC} (0.15 M NaH_2PO_4)
Crumax	-660	-300
Neomax	-630	-170
$Pr_{16}Fe_{76}B_8$	-660	-280

After the addition of NaH2PO4 to distilled water, the potential of the specimens dislocated to more positive values, as figure I shows. A large drift in the nobler direction was verified. This indicates an anodic inhibiting effect of the 0.15 M NaH2PO4 solution on the corrosion of the magnets investigated. The change in potential and stabilization occurred much more rapidly for the Neomax magnet. The rate of change in potential and potential values of the other two magnets, were very similar.The polarization curves produced in distilled water and in the NaH2PO4 solution, are shown in Figure II.

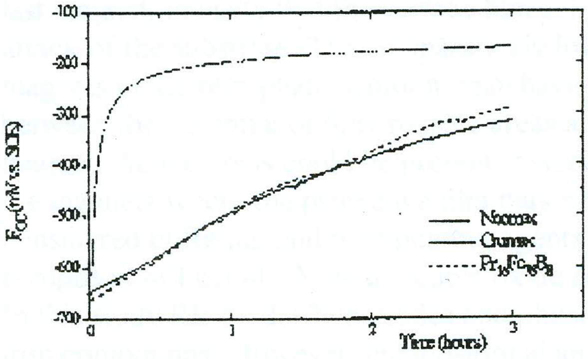


Figure I - Open circuit potential of magnets investigated after addition of NaH2PO4 to distilled water.

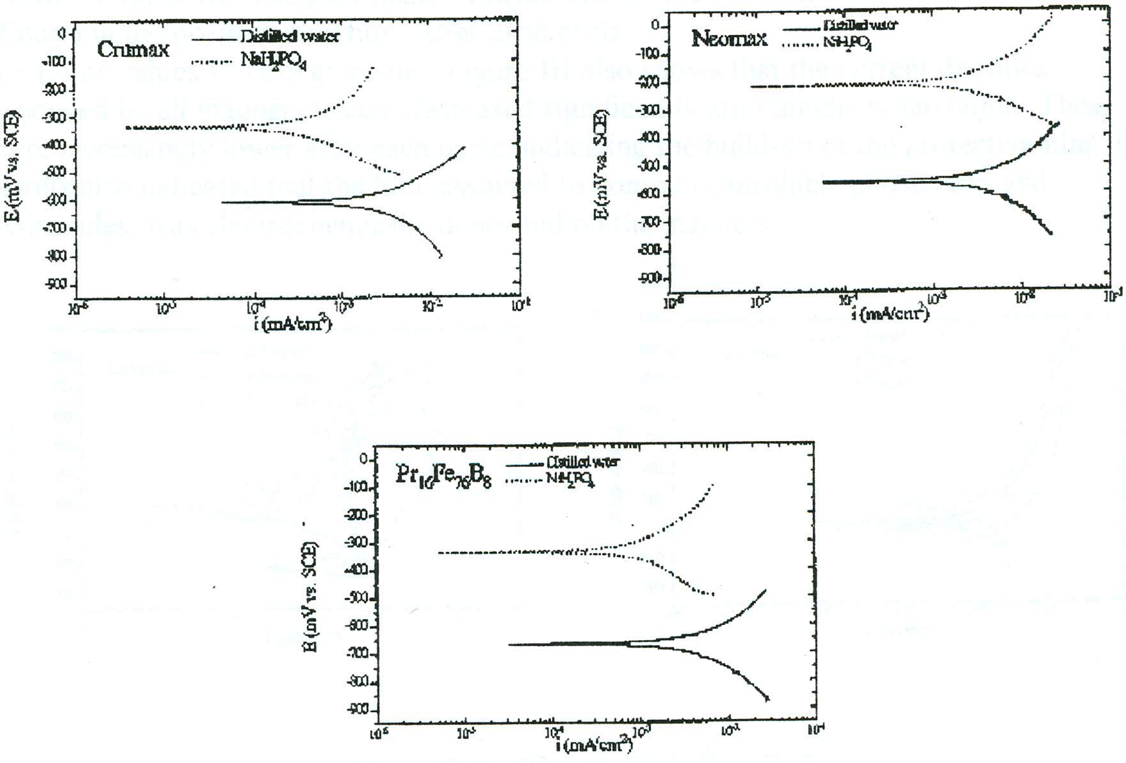


Figure II - Polarization curves corresponding to the magnets studied.

The inhibiting effect of the NaH2PO4 solution on the corrosion characteristics of the magnets investigated, is also demonstrated in figure II. The results showed a reduction in current density followed by the dislocation of the electrode potential to nobler values. This indicates the anodic inhibiting effect of the solution used.The role of the inhibitor has been associated to protection against oxide film breakdown, or to the restoration of defects in the air formed oxide film (22). Oxide breakdown is believed to occur mainly at grain boundaries or inclusion sites (23). The faster the process of film repair, the better the inhibitor is. Therefore, the results presented in figure I, suggest that the inhibiting effect of the solution used was more effective on the Neomax magnet. Also, the nobler and very stable values of open circuit potential for this

last magnet, indicate that the surface film is highly protective, hindering the corrosion attack of the substrate. The comparatively lower potential of the Crumax and Prl6Fe76B8 magnets in the phosphate solution, may have been due to a mixed potential, intermediate between the potential of fully passive areas and some slightly active anodic areas on the magnet. Active areas could be present, associated to microstructure inhomogeneities in the magnets where the protective film may have not been uniform.Phosphate inhibitors are considered buffering and precipitating agents which act by forming a passive film on iron composed of Fe3O4 - Y Fe2O3 cubic oxide and y- FeOOH plus some FePO4. 2H2O (22). In this study RE oxides/hydroxides and phosphates might have been formed together, with iron compounds. However, compositional analysis of the surface after prolonged immersion is yet to be carried out.In order to investigate further the effect of the 0.15 M NaH2PO4 solution as a passivating solution, three cycles potentiodynamic polarization measurements were carried out after potential stabilization. The results produced are shown in figure III. The polarization caused the dislocation of the corrosion potential (Ecorr) in the positive direction. After each cycle,
the Ecorr values were even nobler. Figure III also shows that the current densities produced by all magnets tested, decreased significantly after anodic polarization. These were increasingly lower after each cycle, indicating the build-up of the protective film. The results also indicated that the film, assumed to consist of insoluble phosphates and hydroxides, was electrochemically deposited on the magnets.

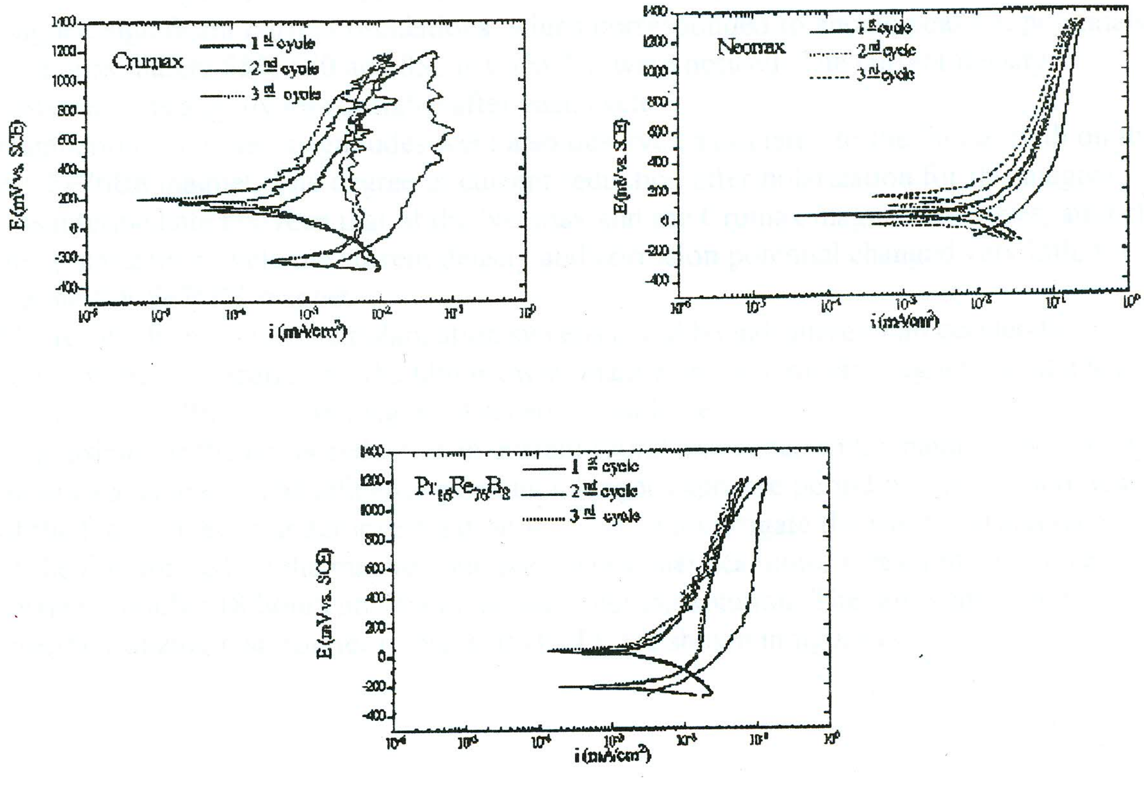


Figure III - Cyclic potentiodynamic polarization curves of the magnets in the 0.15 M NaH2PO4 solution.

A comparison of the electrochemical characteristics of the film formed, based on the results obtained, is presented next. The results indicated that the process of film formation/deposition is faster on the Neomax magnet. Also, the protective film on this magnet was associated to fairly steady currents comparatively to that on the other magnets.

On the other hand, the smallest reduction in current after exposure to the inhibiting solution was connected to this magnet. It is easily noticed in figure III, that the corrosion potential dislocation to nobler potentials was not followed by a drastic reduction in current density. The polarization curves in figure II, also indicated a low reduction in current after the exposure to the 0.15 M NaH2PO4 solution.These last results seem to contradict the previous results from the open circuit potential measurements, which indicated a more effective film on the Neomax magnet.

The process of film formation on the Crumax and Pr16Fe76B8 magnets showed similar characteristics. Although it seemed to be initially slower on these two magnets, the rate of change in potential suggested that after few hours exposure to the inhibiting solution its growth rate was still high. The decrease in current for these two magnets was the largest in the first scan. The largest reduction in current was in fact associated to the protective film on the Crumax magnet. The polarization measurements also indicated a larger reduction in current after exposure to the inhibiting solution, related to this last magnet (figure II). Despite the largest current reductions associated to the protective film on the Crumax magnet, significant current oscillations, which corresponded to anodic peaks at potentials of approximately 550, 650 and 850 mV (SCE), were noticed. The current density however, was slightly less unstable after each cycle.

Fluctuations of lower magnitudes were also observed associated to the film growth on the Prl6Fe76B8 magnet. The degree of current reduction after polarization for this magnet was intermediate between that of the Neomax and the Crumax magnet. However, after the first polarization cycle the current density and corrosion potential changed very little for the the Prl6Fe76B8 magnet.

The results from the cyclic polarization sweeps could be indicative of an accelerating effect of the polarization on the film growth, mainly on the Crumax magnet and at a less degree on the Prl6Fe76B8 magnet. This effect could be responsible for the larger reduction in current found associated to the passivating film on these two magnets. The influence of a much longer exposure period on the characteristics of the film formed is under investigation.In order to investigate the passive characteristics of the film formed on the magnets surface, electrochemical noise measurements were carried out after 18 hours immersion in the inhibiting solution. The noise amplitude spectra, utilizing fast Fourier transforms (FFT), are shown in figure IV.

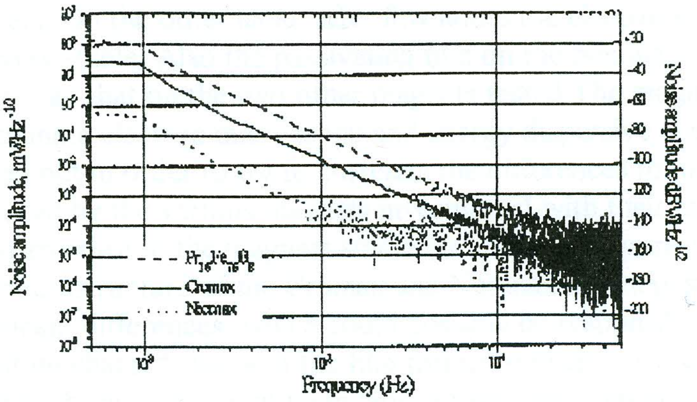


Figure IV - Electrochemical noise amplitude spectra obtained after 18 h exposure to 0.1 5M NaH2PO4 solution .

The noise amplitude plots obtained showed similar features for the passive film on all the magnets investigated. Their noise amplitude spectra showed a low frequency plateau with a "roll-off" at a frequency of 1 mHz. At frequencies superior to 1 mHz, the noise amplitude decreased as the frequency increased, indicating a 1/f type of noise. The roll-off slope for all magnets, at the frequency range from 1 to 10 mHz, approached -60 dB/decade.

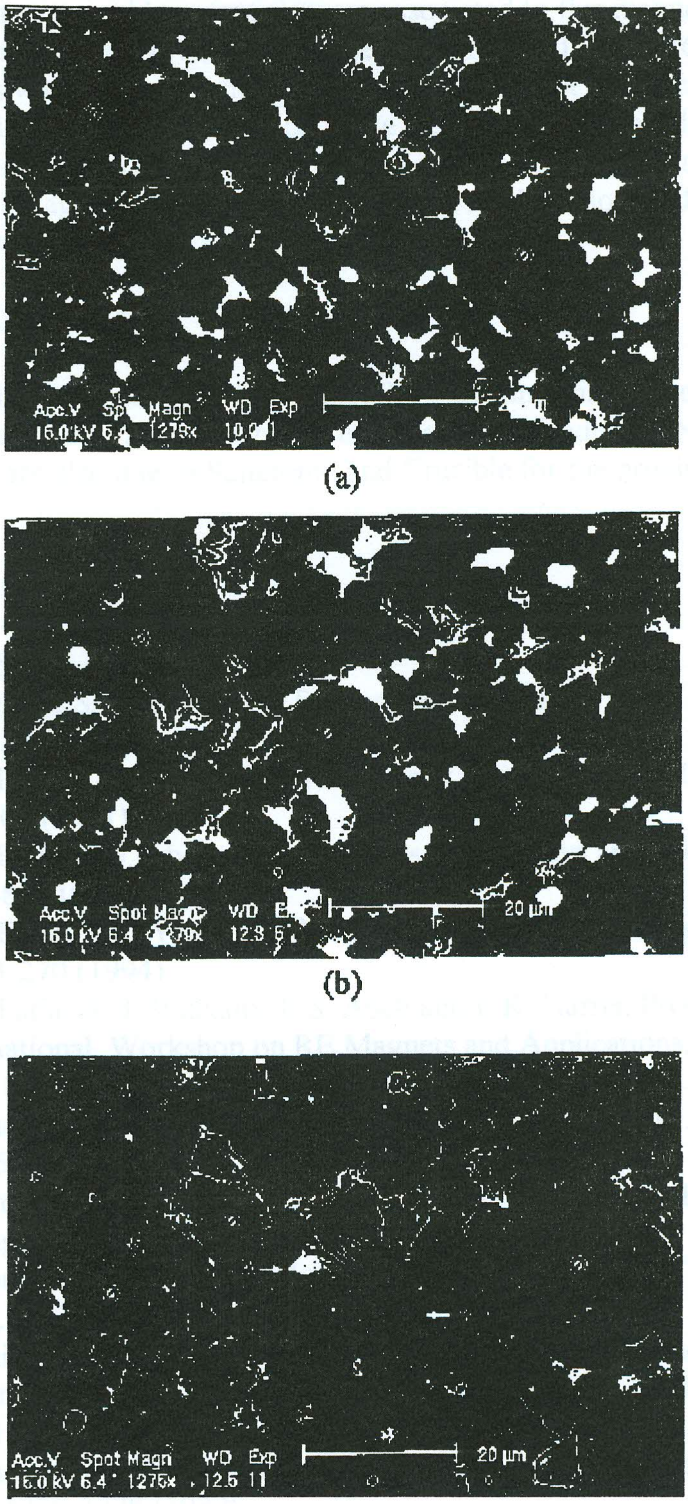
According to the literature (24,25), roll-off slopes of more than -30 dB/decade represents a passive state or general corrosion, whereas slopes of -20 dB/decade or less are indicative of pitting corrosion. Passive corrosion currents are believed to result in very low-frequency fluctuations, generating noise of high amplitude in the low-frequency region and steep slopes, such as those observed in this study.
The literature (24) indicates that the typical l/f noise, observed in figure IV for frequencies superior to 1 mHz, should result in a slope of up to -10 dB/decade on the amplitude spectrum plot. The high slopes obtained for the magnets studied in the passivating solution, could have been caused by secondary effects such as the contributions of two resistance-capacitance (R-C) combinations (24). The effect of each R-C combination would result in an increase of the slope by -20 dB/decade. Also a diffusion contribution would be responsible for an increase of -10 dB/decade. This may have been associated with the growth of the passive film. The slow diffusion of reaction species through the passivating film and the randomness ot the passivating film deposition reaction, may have also contributed to the potential fluctuations and consequently the relatively high amplitude noises produced.The overall noise amplitude levels corresponding to the Neomax magnet were normally some 35 dB lower compared to those produced by the Crumax magnet, and those associated to this last magnet were always approximately 15 dB higher than the noise levels related to the Prl6Fe76B8 magnet. These results could have been due to the differences found in the rate of the growth of passivating film. The passivating film formation was found to be faster for the Neomax magnet compared to the other two magnets. In fact, after 18 hours immersion the potential was still moving in the direction of nobler potentials, for Crumax and Pr16Fe76B8 magnets, suggesting that the film was still growing

on them. On the other hand, after few hours the electrode potential of the Neomax magnet was very stable. Also the passivating film on the Neomax magnet was apparently more stable than that on the two other magnets tested.The magnets microstructure was analysed by scanning electron microscopy and energy dispersive spectroscopy. This analysis was carried out in order to try to correlate the differences found in the electrochemical data produced by the various magnets investigated with their microstructure. The microstructure of the magnets studied is shown in Figure V(a) to (c).
The microstructure of the Crumax and Neomax magnets studied apparently do not show significant differences, which could possibly be responsible for the differences found in the inhibiting characteristics of the film formed on them. They both show a large amount of Nd rich phase in the grain boundaries of the main magnetic phase. The boron rich phase was not easily identified in the two Nd-Fe-B magnets. The Prl6Fe76B8 magnet studied, however showed small differences in its microstructure. The Pr rich phase was found in fewer amounts and the boron rich phase was easier to be identified. Further studies of the magnets, such as analysis of the oxygen content in the magnet, the volumetric fraction of RE and boron rich phases, are necessary.

Specimens of all magnets tested were stored in a desiccator over silica gel after removal from distilled water and from the inhibiting 0.15 M NaH2PO4 solution. The specimens which were exposed only to distilled water were heavily corroded after only few days. On the other hand, the surface of the specimens which had been immersed in the inhibiting solution, presented a bluish colour and no visible corrosion on it, even after months from being removed from the solution. This layer, which is believed to consist mainly of iron phosphate, but might also contain iron oxide/hydroxide, was found to be adherent and thin. It was also found to remain on the surface after removal from the inhibiting solution. Its corrosion protection characteristics were demonstrated by the lack of corrosion products on
the magnets surface, even months after the specimens have been removed from it. This was an important observation, since the low corrosion resistance of the magnets studied was attested by the formation of corrosion products on their surface, even after a few days of storage before being used.The results produced in this study suggest that a recommended corrosion protection practice for the magnets type investigated would consist on their immersion in the 0.15 M NaH2PO4 solution for some hours. At this stage, it is believed that this procedure would be beneficial for the corrosion protection of the magnets studied, either as a
corrosion treatment by itself or as a pre-treatment, before coating application. The characteristics of the protective layer formed are to be further investigated.

4. CONCLUSIONS

The test solution used in this study (0.15 M NaH2PO4) had a strong inhibiting effect on the corrosion performance of all the magnets investigated. It acted by forming an adherent protective layer on the magnets surface, which
remained on the surface after removal from the solution. This resulted in prolonged protection of the magnets thereafter. The current densities produced during consecutive cycles of polarization increasingly decreased, suggesting the build-up of the protective



(a)

(b)

(c)

Figure V - Microstructure of the magnets investigated. (a) Crumax, (b) Neomax and (c) Prl6Fe76B8. (A) Nd/Pr rich phase, (B) Boron rich phase, ϕ - main magnetic phase.

layer on the magnets surface. The process of inhibition was faster for the Neomax magnet and also nobler and more stable potentials were associated to this magnet. Similar results were produced by the other two magnets studied (Crumax and Pr16Fe76B8) The higher stability of the passivating layer formed on the Neomax magnet comparatively to the other magnets, was confirmed by electrochemical noise measurements. The electrochemical noise amplitude associated to the passivating layer on the Neomax magnet was the smallest. At this stage, the differences found could not be associated to characteristics of the magnets microstructure.

5. ACKNOWLEDGEMENTS

The authors would like to acknowledge FAPESP for the financial support provided in this work. One of the authours (I.J.S.) wishes to express his gratitude to CNPq for provision of a grant. Thanks are also due to Sumitomo and Crucible for the provision of magnets for this study.

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