

The corrosion protection of RE-Iron-Boron magnets by a phosphate treatment

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Abstract— The effect of a phosphate treatment as a corrosion inhibitor for a RE-Iron-Boron magnet has been investigated. The corrosion characteristics of the magnet in a phosphate solution, which consisted of 0.15 M NaH_2PO_4 , were analyzed by electrochemical impedance and electrochemical noise measurements. The immersion of the magnet in the phosphate solution resulted in the formation of a passive layer on its surface causing a prolonged corrosion protection after removal from the solution. The protective layer was found to consist of phosphate/pyrophosphate and oxide by XPS analysis.

I. INTRODUCTION

Rare Earth(RE)-Iron-Boron magnets present poor corrosion properties in aqueous environments [1]-[3]. Efforts have been made towards improving their corrosion resistance by the addition of alloying elements [4]-[6]. Despite the improvements made, corrosion protection methods still have to be adopted for practical applications. Coatings application has been the most usual corrosion protection method [7]-[9]. Little is however known concerning the effect of corrosion inhibitors on the corrosion performance of these materials. In this study, the use of film forming corrosion inhibitors has been investigated. This treatment can be used as a pre-treatment before coatings application, increasing the corrosion resistance of defect regions in the coating. The possibility of using this treatment as a corrosion prevention measure in itself was also object of investigation.

II. EXPERIMENTAL

For this study, a commercial magnet of Neomax type composition has been used. The specimens for investigation were cold mounted and their surface were prepared by polishing with silicon carbide paper up to grade 1000. After surface polishing the specimens were immersed in the test solution, which consisted of 0.15 M NaH_2PO_4 , and their electrochemical behaviour was studied as a function of immersion time by means of electrochemical impedance and electrochemical noise measurements.

For the electrochemical noise measurements, a pair of "identical" magnet electrodes was immersed in the 0.15 M NaH_2PO_4 test solution. A saturated calomel electrode was brought into close proximity with one electrode. The SCE served to measure E_{CORR} and its fluctuations. An automated Zero Resistance Ammeter was used to take current and voltage

measurements, simultaneously, at a sampling interval of 1 s. Electrochemical noise measurements were taken during the first 18 hours immersion in the test solution. After 3 days immersion, one specimen was removed from solution and stored for 10 days. Subsequently, this specimen was re-immersed in the phosphate solution and electrochemical impedance measurements were taken for 9 days. At the end of this period, this specimen was again removed from the phosphate solution and immersed in distilled water. Electrochemical impedance data were then produced for three consecutive days.

The electrochemical impedance measurements were carried out under potentiostatic control at the open circuit potential in the frequency range between 10^4 and 10^3 Hz.

One specimen was prepared for surface analysis by being immersed in the 0.15 M NaH_2PO_4 solution for three days and then stored in desiccator over silica gel. The film formed was analyzed by X-ray photoelectron spectroscopy (XPS).

In order to investigate the corrosion resistance of the film formed, two specimens, one with and another without phosphate treatment, were exposed outdoors for 10 days and their surface was observed during the exposure period.

III. RESULTS AND DISCUSSION

The electrochemical noise amplitude spectrum, after 18 hours immersion, using fast Fourier transforms (FFT), is shown in Fig. 1. The noise amplitude spectrum 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 at the range from 1 to 100 mHz, approached -60 dB/decade. According to the literature [10], roll-off slopes of more than -30 dB/decade represent a passive state, whereas slopes of -20 dB/decade or less indicate pitting corrosion.

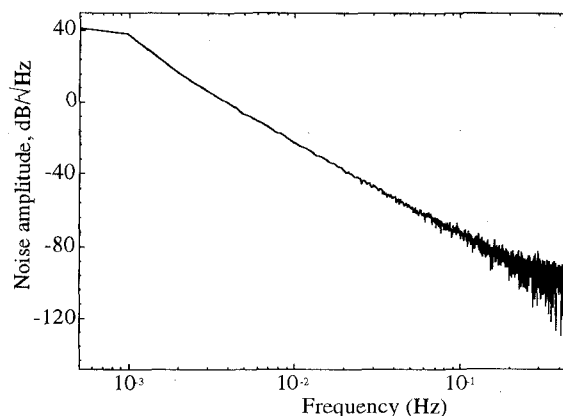


Fig. 1 - Electrochemical noise amplitude spectrum obtained for the magnet after 18 hours immersion in 0.15 M NaH_2PO_4 solution.

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Relatively high noise amplitude levels were obtained at low frequencies. Passive corrosion currents 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 electrochemical impedance diagrams (Bode plots) for the specimen at increasing immersion days in the 0.15 M NaH_2PO_4 solution are shown in Fig. 2.

Distinct separation in the Bode diagrams is indicated by the appearance of a reduction in slope in the mid frequency region, Fig. 2 (a) and by the two phase angle maxima, Fig. 2 (b), effectively splitting the Bode diagrams into two sections, one at high frequencies (10 kHz - 10 Hz) and one at lower frequencies (10 Hz - 10 mHz). The capacitance associated to the high frequency time constant was around $1 \mu\text{F}/\text{cm}^2$, characteristic of very good oxide films, indicating that the high frequency data is related to the protective film formed.

The estimated value of the capacitance related to the low frequency data was around $15 \mu\text{F}/\text{cm}^2$, and varied very little during the whole test period. This capacitance value is slightly lower than those corresponding to metals and a little higher than those characteristic of oxides. This suggests that the low frequency data refers to the substrate, which could be slightly oxidized.

It can also be noticed in the impedance Bode diagrams, Fig. 2, that no significant change occurred in the characteristics of the passivating film during the 9 days immersion. This indicates that after the film has been formed on the surface it is fairly stable.

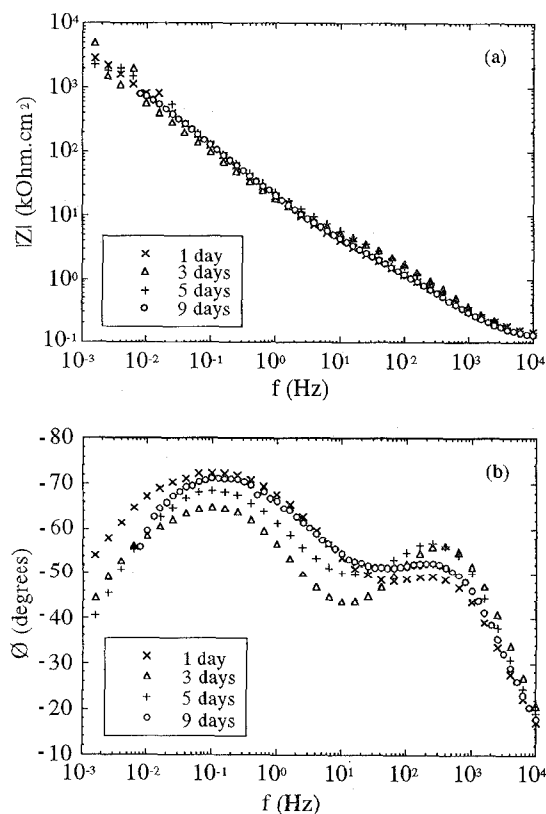


Fig.2. Impedance Bode diagrams (a) $\log |Z|$ vs. $\log f$, and (b) Phase angle (\emptyset) vs. $\log f$, after 1, 3 and 5 and 9 days immersion in 0.15 M NaH_2PO_4

The resistance associated to the passivating film, high frequency region, was estimated as around $1 \text{ k}\Omega \cdot \text{cm}^2$, which can be considered large enough to offer protection to the substrate.

The Bode diagrams (Fig. 2 (a) and (b)) also indicated diffusion effects at the low frequency region, suggesting that the corrosion reaction is strongly influenced by the diffusion of the reacting species. When there is no diffusion impedance, the low frequency portion of the $\log |Z|$ vs. $\log f$ curve is a line horizontal to the frequency axis indicating a purely resistive value of the modulus of impedance $|Z|$ and the phase angle approaches zero. As diffusion impedance effects become more important, the low frequency of the $\log |Z|$ vs. $\log f$ curve is no longer horizontal but curves upwards, becoming steeper and approaching a slope of -0.5. The corresponding low frequency region of the phase angle diagram show values of phase angle approaching -45° . At the low frequency portion of the $\log |Z|$ vs. $\log f$ curves, the estimated values of the slope were approximately -0.65 for the whole test period. The Bode phase diagrams also show the low frequency portions approaching -45° .

Diffusion effects often occur when a reactant must diffuse through a surface film. Also diffusion of reactants or corrosion products within pores of the film and the substrate might have a significant contribution to the corrosion rate. The specimens tested in this study present both, a protective film on its surface and porosity (sintered magnet).

In order to check the effect of diffusion on the corrosion process, two impedance runs were carried out after 9 days test, one with and another without stirring the solution. The corresponding Bode diagrams are shown in Fig. 3.

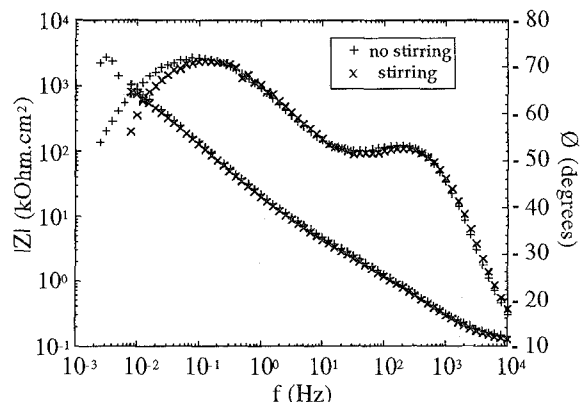


Fig. 3 - Bode diagrams corresponding to the magnet immersed in 0.15 M NaH_2PO_4 solution with and without stirring.

It can be noticed that the stirring of the solution only had a slight effect on the low frequency data, confirming the effect of the diffusion on the corrosion process. Since stirring only affects diffusion of reactants or products in the solution, the small effect observed could suggest that diffusion through the surface film or the pores of the substrate might have been the main contributing factor in the diffusion effect found.

The effect of exposing the magnet with the surface film to distilled water has also been investigated by electrochemical impedance measurements. Impedance runs were taken for three days after immersion of the surface treated specimen in distilled water. The impedance Bode diagrams after 3 hours, 1 day and 3 days of exposure are shown in Fig. 4.

The large resistance associated to the high frequency data (order of tenths of $k\Omega\cdot\text{cm}^2$) and its fast decrease with time indicates the effect of water resistance. Although the phase angle peak (high frequency region) was dislocated to higher frequencies, it can still be identified in the Bode phase diagrams (Fig. 4), indicating the presence of the film on the surface. Little effect was noticed on the low frequency data, suggesting that the corrosion resistance was not much affected. In fact, the specimen did not show any sign of corrosion products on its surface after the third day of exposure. The Bode phase diagrams also indicated that diffusion effects have an important role on the corrosion process, ϕ approaching -45° in the low frequency region.

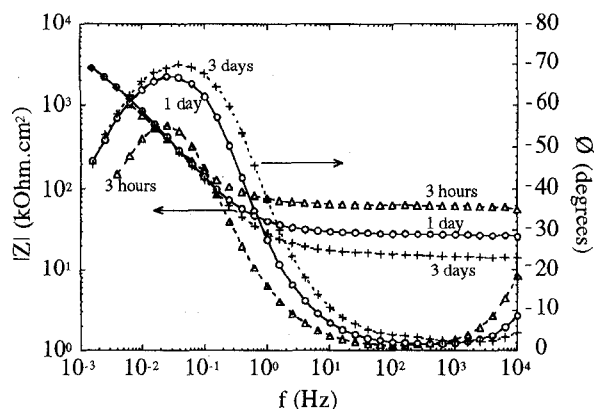


Fig. 4 - Bode diagrams corresponding to the phosphate treated magnet after immersion in distilled water.

Warren, Gao and Li [3] used the same solution adopted in this study to investigate the electrochemical corrosion behaviour of sintered NdFeB magnets provided by different manufacturers. The electrochemical method employed in their investigation consisted of anodic polarization test. A deaerated solution was used as their test medium. They observed a limited degree of passivation of the magnet. Current densities of the order of 10^{-4} A/cm², considered fairly high for a passive state, were obtained. They hypothesized that a complex Fe-Nd oxide and/or hydroxide, as indicated by Jacobson and Kim [11], formed the passive film.

The results of this study also showed the formation of a passive film in the presence of an aerated solution. The analysis of the composition of the passive film formed (XPS analysis) demonstrated the presence of a mixture of phosphate (NdPO_4) / pyrophosphate ($\text{Nd}_4(\text{P}_2\text{O}_7)_3$), oxide (Nd_2O_3) and hydroxide ($\text{Nd}(\text{OH})_3$). Although a phosphate/pyrophosphate was not mentioned by Warren et al. [3], their supposition was partially confirmed by the results of the present investigation. The use of an ac technique (electrochemical impedance) in the current study (a dc technique was adopted by Warren et al.) allowed to obtain information on the characteristics of the passive film formed (capacitance and resistance).

The film formed on the magnet surface under immersion in the phosphate solution was adherent and had a bluish colour. This film remained on the surface after removal from solution providing protection to the surface during storage periods.

The two specimens which were exposed outdoors, one with the phosphate protective film and the other with a bare surface, showed very distinct corrosion resistance during the exposure period. After five days exposure outdoors, the

phosphate treated specimen showed very little corrosion on its surface whereas the bare specimen was getting heavily corroded. At the end of the exposure period (10 days), slight superficial corrosion was noticed on the specimen which had been immersed in the 0.15 M NaH_2PO_4 solution while the specimen without treatment was heavily corroded.

CONCLUSIONS

The immersion of a magnet of RE-Fe-B type in a solution consisting of 0.15 M NaH_2PO_4 produced a protective film on the magnet surface. This surface film was found to consist of phosphate/pyrophosphate and oxide by XPS analysis. The protective film caused prolonged corrosion protection of the magnet during storage periods. Protection was also afforded when the specimen was immersed in the solution. Diffusion through the surface film seemed to be one of the main factors controlling the corrosion rate. The protective film was found to persist on the surface after immersion in distilled water impairing corrosion. These results pointed to the possibility of using this treatment as a corrosion protection measurement in itself or as a pre-treatment before coatings application, affording protection at the defective regions of the coating.

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