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Corrosion Protection of a Commercial NdFeB Magnet by Phosphating

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Abstract: NdFeB magnets are susceptible to corrosion in normal working environments and are therefore protected against corrosion with coatings of epoxies, electrodeposited nickel, etc. Eventual failure of these coatings expose the surface of the magnet to corrosion. Hence, protection of magnets prior to the application of coatings is one way of overcoming the corrosion problems associated with coating failures. Phosphating is a well known process to protect carbon steels and other ferrous alloys in general, and is often used as a pretreatment before the application of coatings. This study reports the experimental work carried out to obtain a corrosion inhibiting layer directly on NdFeB magnet surfaces, that is also structurally coherent with the substrate. The electrochemical characteristics of the surface layer on the bare magnet surface, obtained by immersion in a solution of 0.15M NaH_2PO_4 and acidified with H_2SO_4, was determined. The corrosion resistance of the layer was tested in a solution of 1%(wt) NaCl plus 5mM H_2SO_4 with pH of 2.9, by electrochemical impedance spectroscopy (EIS) and cyclic polarization tests. The results indicated that NdFeB magnets can be protected in fairly aggressive media by a phosphate layer. Anodic polarization measurements indicated breakdown of the phosphate layer and corrosion of the magnet, only at an overpotential of approximately 400 mV.

Introduction

NdFeB magnets are susceptible to corrosion in fairly aggressive environments [1-3]. To improve their corrosion performance, they are usually protected by coatings of nickel [4], aluminum, [5] and epoxies. In practice, it is very difficult to produce defect free coatings and often, defects in the coatings occur under normal working conditions. The metal exposed at coating defects, to the corrosive environment, corrode freely. The large ratio between the cathodic area (coated surface) and the anodic area (metal exposed at the defect) also cause an increase in the corrosion rate of the exposed metal.

To improve the corrosion resistance of the substrate material, pretreatments can be given before coatings are applied. Phosphating is a well known technique to increase the corrosion resistance of surfaces. In this technique, a stable tetragonal array of (PO_3)-Fe, X is formed, where X is any other element that is similar to Fe and is present in the base material[6]. This phosphate film also helps increase the adherence of coatings applied subsequently to the substrate.

In this investigation a commercial NdFeB magnet was phosphated with the aim of protecting the magnet. The corrosion resistance of the magnet with a surface layer formed by phosphating was determined by electrochemical impedance spectroscopy (EIS) and by cyclic polarization.

Material and Methods

Material

The magnet investigated in this study was commercial grade NdFeB named CRUMAX and supplied by CRUCIBLE Co.. It had the following composition (wt.%):

Table 1 – Chemical composition of the NdFeB magnet. (wt.%)

Fe	Nd	B	Dy	Al	Co	Si
60.59	28.31	1.00	2.09	3.73	1.28	1.39

Specimen preparation

The magnet specimens were prepared as electrodes for the electrochemical tests. They were cold resin mounted after installing an electrical contact with copper wire on one of its surfaces. The surface of the electrode to be exposed to the electrolyte was prepared by sequential grinding with silicon carbide paper from grit #120 to #2000. The ground specimen surfaces presented a specular appearance. The specimens were subsequently immersed for 24 hours in a 0.15 M NaH_2PO_4 solution acidified with H_2SO_4, and dried for 3 hours at 50°C, in a muffle furnace to form a film on the surface Three specimens were used to replicate the tests. The surface area of each electrode exposed to the electrolyte was. 1.25 cm^2.

Test solutions

Two test solutions were used to investigate the corrosion resistance of the surface film. The electrochemical impedance spectroscopy (EIS) tests were carried out in a solution of 0.1N Na_2SO_4. Fresh solution was always used to avoid contamination. Potentiodynamic polarization of the phosphated magnets was carried out in 0.5 mM H_2SO_4 + 1wt % NaCl solution with pH controlled in the range of 2.95-2.85.

Experimental set-up

A three electrode cell arrangement was used for the electrochemical tests, with a graphite rod as the counter-electrode and a saturated calomel electrode (SCE) as the reference electrode. All experiments were carried out at room temperature (25°C).

An EG&G 273A potentiostat was used for the cyclic potentiodynamic polarization tests and a Solartron 1255 frequency response analyser coupled to EG&G 273A potentiostat were used for EIS measurements. The perturbation amplitude of voltage for the EIS test was 10 mV and the frequency range was from 100 kHz to 10 mHz. The Boukamp program EQVCRT was used to analyze the EIS results

Results and Discussion

The EIS results produced by the magnet with the film formed on the surface and the proposed equivalent circuit after data fitting using the Boukamp EQVCRT program, are shown in fig.1.
At least two phase constants can be identified in the EIS diagrams of the phosphated magnet. One time constant was attributed to the magnet matrix and the other, to the film on the magnet surface. A high resistance associated with the film (greater than 10 kΩ) can be seen in fig.1. This suggests that the film on the surface is coherent, compact and insulating.

The data produced was modeled to fit a convenient equivalent circuit using the Boukamp program EQVCRT, and the values of the proposed equivalent circuit components are shown in table 2.

After the EIS test, the magnet with the film on the surface was polarized from –1000 mV (SCE) up to 1200 mV (SCE), and later the polarization direction was reversed, with the polarization cycle ending at –1000 mV (SCE). The polarization curve in both directions is shown in fig.2.

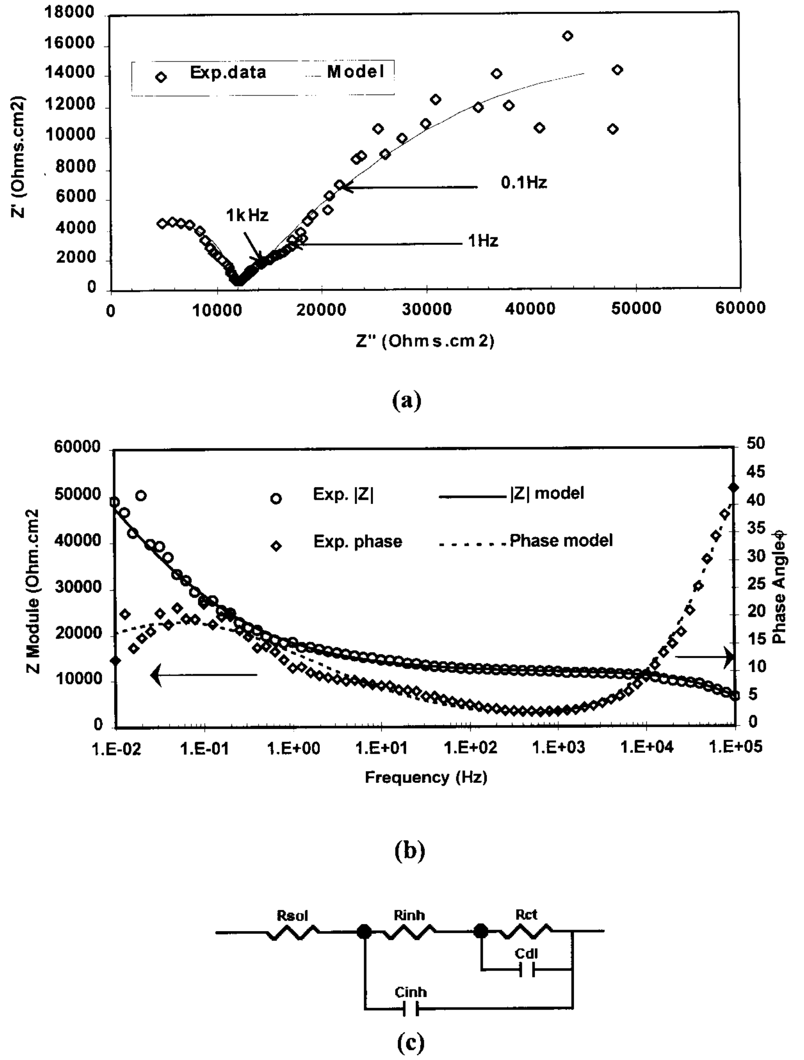


Fig. 1- (a) Nyquist and (b) Bode diagrams of NdFeB magnet after the phosphating treatment, in 0.1 N Na_2SO_4 solution. (c) Proposed equivalent circuit.

Table 2 – Values of the components of the proposed equivalent circuit after data fitting.

	Solution resistance R_{sol} / Ω.cm^2	Inhibiting film resistance R_{film} / Ω.cm^2	Capacitance of inhibiting film C_{film} / nF/cm^2	Charge transfer resistance R_{ct} /Ω.cm^2	Double layer capacitance [C_{dl}]/ μF/cm^2	CPE(*) (mhos.cm^2)
Magnet after phosphating	19.6	13597	3.4	92632	217	-
Magnet after polarization	24.5	-	-	168.8	5931	Y_o = 0.05269 n=0.507

(*) to simulate the Warburg diffusion zone present in the EIS-low frequency region in fig.3

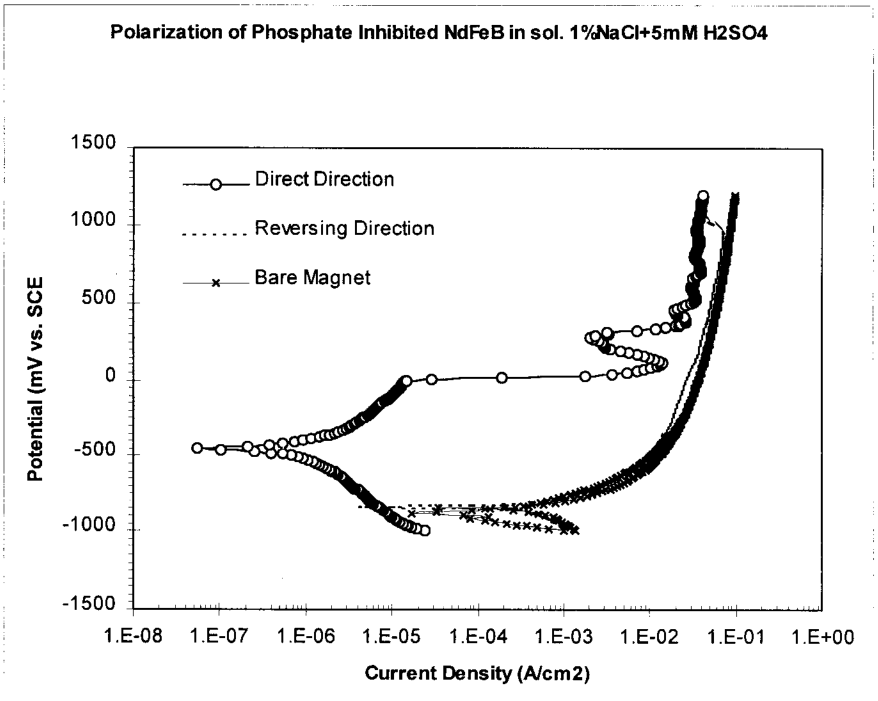
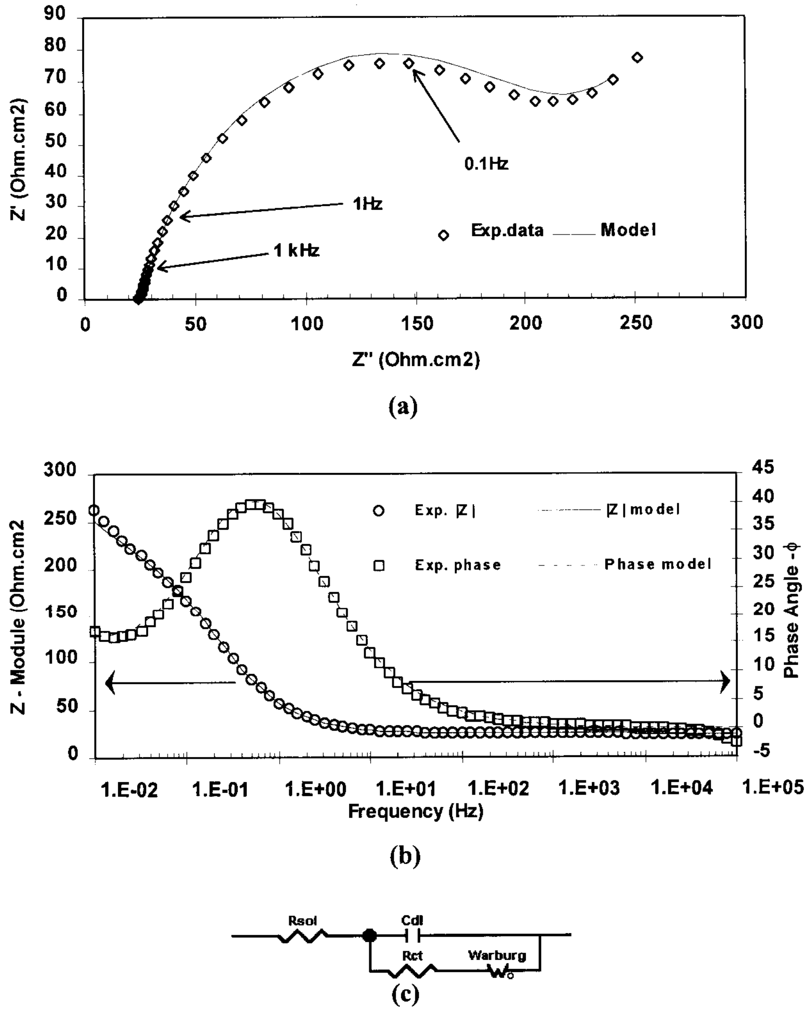


Fig. 2 – Cyclic polarization curves(direct and reverse directions) of phosphated and bare magnet in 5 mM H_2SO_4 + 1 (wt%) NaCl solution.

Fig.2 shows a low corrosion rate of the magnet at E_{corr} (order of few μA/cm^2) indicating that the magnet, after phosphating was passive in the solution of 5 mM H_2SO_4 + 1% NaCl.

The polarization curve of a bare magnet is also shown in fig.2, and it indicates a corrosion rate of a few mA/cm^2, approximately 1000 times higher than that of the phosphated magnet. This reveals the passivating effect of the phosphate film on the surface of the magnet. A marked increase in current density occurs at potentials around 0 mV (SCE), corresponding to breakdown of the phosphate film. The polarization curve in the reverse direction coincided with that of the bare magnet, providing further evidence of the breakdown of the passive film.

After the cyclic polarization test, the magnet was once again tested by EIS. The Nyquist and Bode diagrams and the proposed equivalent circuit are shown in fig.3. The values estimated for the components of the proposed equivalent circuit are given in table 2.



(a)

(b)

(c)

Fig.3 – (a) Nyquist and (b) Bode diagrams after polarization of the phosphated magnet in 0.1 N Na_2SO_4 solution. (c) Proposed equivalent circuit.

The EIS diagrams in fig.3 showed only a time constant, characteristic of the magnet/electrolyte interface. The resistance of approximately 169 Ωcm^2 was of the same order of that associated with the bare magnet, in contrast with a resistance of nearly 93 $k\Omega cm^2$, of the phosphated magnet. Moreover, the phosphate layer on the NdFeB magnet showed resistance to corrosion in indoor environments. No major changes were observed on the surface of the magnets after 1500 hours of exposure to a laboratory atmosphere.

Conclusions

The EIS technique has been shown to be adequate for evaluating the characteristics of surface films formed by the phosphate treatment on NdFeB magnets. This treatment consisted of immersion of NdFeB magnets in a solution of 0.15 M NaH_2PO_4. The NdFeB magnet was protected against corrosion by the phosphate film formed. The corrosion rate of the magnet after phosphating was approximately 1000 times lower than that of the bare magnet in a fairly aggressive solution of 5 mM H_2SO_4 + 1% NaCl. The film showed resistance to polarization, since its breakdown occurred only at an overpotential of nearly 400 mV. The resistance of the formed film was more than 90 $k\Omega.cm^2$ in Na_2SO_4 0.1N solution..

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