Effect of Molybdate on Phosphating of Nd-Fe-B Magnets for Corrosion Protection

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Nd-Fe-B magnets are highly susceptible to corrosion and need protection against environment attack. The use of organic coatings is one of the main methods of corrosion protection of these materials. Data related to the effect of conversion coatings, such as phosphating, on corrosion performance of these magnets is still scarce. Studies about the effect of phosphating on the corrosion resistance of a commercial Nd-Fe-B sintered magnet indicated that it increases the corrosion resistance of these magnets, compared to non-phosphated magnets. In this study, the solution chemistry of a phosphating bath was altered with the addition of molybdate and its effect on the corrosion resistance of magnets investigated. Sintered magnet specimens were phosphated in solutions of 10 g/L NaH_2PO_4 (pH 3.8), either with or without molybdate [10^{-3} M MoO_4^{2-}], to improve their corrosion resistance. The effect of phosphating time was also evaluated, and specimens were phosphated for 4 and 18 hours. To evaluate the corrosion performance of phosphated and unphosphated specimens, a corrosion test based on monitoring hydrogen evolution on the surface of the magnets was used. This technique revealed that the addition of molybdate to the phosphating solution improved the corrosion resistance of the magnets phosphated by immersion for short periods but had no beneficial effect if phosphated by immersion for longer periods.

Keywords: *corrosion, Nd-Fe-B magnets, phosphating, molybdate*

1. Introduction

Nd-Fe-B magnets produced by powder metallurgy have a wide range of applications, from computer disk drives, many important parts of fine electro-electronic industry to large industrial machines. However, these magnets have low corrosion resistance and their surfaces need protection. The low corrosion resistance is due partially to its complex microstructure, with two electrochemically different primary phases (φ-phase and Nd-rich), that leads to galvanic corrosion. Moreover, magnets produced by powder metallurgy (PM) techniques are porous, which decreases further its corrosion resistance.

Corrosion control methods are necessary to make it viable to use Nd-Fe-B magnets as an engineering material. One of the most widely used corrosion control method, for this kind of magnet, is coating the magnet, mainly with organic coatings. Unfortunately, organic coatings are not defect free. Therefore, pre-treated surfaces are used, either to improve coating adhesion or to improve the corrosion resistance at the defects in the coating.

Phosphating as a pre-coating surface treatment is the object of this study. Previous studies carried out in our laboratory[1-6] indicated that phosphating in a solution of NaH_2PO_4 increased the corrosion resistance of these magnets as compared to unphosphated ones. The complex microstructure of sintered Nd-Fe-B magnets, with phases exhibiting different electrochemical behavior, and pores, affect phosphating, impeding thus the formation of a continuous conversion layer.

Bala et al.[7] carried out experiments with individual phases of Nd-Fe-B magnets that were synthetically prepared, and showed that the corrosion potential of the individual phases was significantly different and dependent on the solution pH. The Nd-rich phase rapidly dissolved into Nd^{3+} in solutions with pH less than 3.5.

Saliba-Silva et al.[2-5] reported increased corrosion resistance of Nd-Fe-B magnets phosphated in a solution with pH of approximately 3.8. According to literature[8], in solutions with pH between 3.5 and 5, a Nd hydroxide tends to form on the surface, and this probably impairs the formation of a stable phosphate layer on the surface of the magnet. Previous results 2 have shown that in very low pH (pH ≤ 2) solutions, no protective layer formed on Nd-Fe-B magnet.

The use of oxidants in phosphating solutions is normal practice, as they accelerate the first stage of phosphating (acid attack), hindering the H_2 evolution reaction and permitting access of large molecules, such as PO_4^{3-}, to the metallic surface, to form a primer layer of phosphate.

There are several ways of accelerating commercial phosphating of ferrous materials, for instance, by using nitrates and chlorates. These substances are however very active and promote severe corrosion of Nd-Fe-B magnets, mainly of the Nd-rich phase[9]. Lorin[10] suggested a variety of accelerators, even molybdates, which are not as corrosive as nitrates and chlorates. According to Gentil[11], the molybdate anion (MoO_4^{2-}) should be an adequate inhibitor for post-phosphating treatment, to seal the phosphate layer. Studies with molybdates have shown that they are good inhibitors for ferrous alloys[12,13]. Normally in commercial practice, molybdates are not used as phosphating accelerators, but are being considered as a replacement for chromatizing.

In this work, the corrosion resistance of Nd-Fe-B magnet specimens, either unphosphated or phosphated in NaH_2PO_4 (pH 3.8) solutions, with or without molybdate [10^{-3} M MoO_4^{2-}], for 4 hours and 18 hours, has been evaluated by a corrosion test based on monitoring the hydrogen evolution reaction on the magnet's surface. This method consists of monitoring the stages of the hydrogen evolution reaction on the magnet's surface, that is, nucleation, growth and H_2 bubble release from unphosphated or phosphated magnets immersed in acid solution, at increasing times, and fitting the results to Avrami's equation[14].

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2. Experimental Procedure

2.1. Material

A commercial sintered Nd-Fe-B magnet produced by Crucible – U.S.A., (composition given elsewhere[3]) was used in this investigation.

2.2. Specimen preparation

Nd-Fe-B magnets had one of their surfaces, with an area of approximately 130 mm^2 for exposure to the test solution, prepared by grinding with silicon carbide paper up to #1000, followed by degreasing with acetone in an ultrasonic bath, and drying in a hot air stream. The remaining areas were coated with varnish.

2.3. Phosphating

Phosphating was carried out by immersion of the magnet specimens for periods of 4 hours or 18 hours, in either one of two solutions: i) solution A: a solution made with 10 g/L NaH_2PO_4 and acidified with H_3PO_4 to pH 3.8; and ii) solution B: 10 g/L NaH_2PO_4 solution with addition of 1 mM of ammonium molybdate.

2.4. Corrosion testing

Corrosion testing of Nd-Fe-B magnets, either phosphated or unphosphated, was carried out by immersing the magnet specimens in an acid solution (diluted HCl with pH adjusted to 2.0) and monitoring the H_2 evolution reaction on the surface of the magnet. The nucleation, growth and release of H_2 bubbles from the magnet's surface, either phosphated or unphosphated, were followed with time and captured on film. The method adopted consists of fitting the surface ratio covered with H_2 bubbles at increasing times of immersion, to Avrami's equation:

$$X = 1 - \exp(- K.t^n) \tag{1}$$

where: X is the surface ratio covered with H_2 bubbles, due to the corrosion in the acid test solution; K is a constant related to the system activation energy; t is the reaction time; and n is a parameter, characteristic of the system, that is lower than 1 for liquid/gas interfaces[15]. Saliba-Silva[3] in a previous work, found that n = 0.86 gave results that fitted well for Nd-Fe-B sintered magnets under similar conditions.

3. Results and Discussion

The magnet surfaces, unphosphated or phosphated, at increasing times of immersion in the test solution, are shown in Figure 1. The figure clearly shows the evolution of H_2 bubbles on the magnet surfaces at increasing times of immersion in dilute HCl solution (pH 2.0).

There are few bubbles on the unphosphated magnet surface immediately after immersion. After 15 seconds, H_2 bubbles completely covered the surface of the unphosphated magnet, suggesting fast kinetics of nucleation and growth on the surface. The phosphated magnets showed different behavior depending on phosphating conditions. The specimen phosphated in solution A for 4 hours showed bubbles on its surfaces after only 15 seconds of immersion and fast growth kinetics from that time onwards. The magnets phosphated in solution A for 18 hours demonstrated the best corrosion performance among all the specimens that were tested. On these specimens, only a few bubbles nucleated on its surface after 120 seconds of immersion in the acid solution. Phosphating in molybdate containing solution (solution B), resulted in improved corrosion resistance of the magnet surfaces compared to unphosphated specimens, but the increase in phosphating time in this solution was not as effective as that in the solution without molybdate. A comparison of the magnet

surfaces phosphated for 18 hours in solutions A and B, indicates that molybdate has no beneficial effect on phosphating of Nd-Fe-B magnets for long periods.

The ratio of the magnet's surface with H_2 bubbles, unphosphated or phosphated, as a function of immersion time was fitted to Avrami's equation, and the results are shown in Figure 2. The curves in Figure 2 consist of three distinct regions. There is an initial period, when no bubbles or very few H_2 bubbles are seen on the magnet's surface (nucleation period), an intermediate region where the surface ratio covered with H_2 bubbles increases rapidly with immersion time (growth period). A final region appears where there is a competition between H_2 bubble growth and its release from the surface, resulting in reduced variation of the surface ratio with H_2 bubbles, with time (gas evolution period).

Figure 2 shows a distinct behavior for the various types of surfaces that were tested. A very short nucleation period is followed by a short growth period of very fast kinetics, and then a prompt gas evolution period for the unphosphated magnet. Longer nucleation periods for all phosphated magnets, signaling the formation of a protective conversion layer on their surfaces. The kinetics of the growth period was dependent on the phosphating conditions. For the magnets phosphated in the molybdate containing solution (solution B), similar kinetics was obtained for the two times of phosphating (4 hours and 18 hours). The increase in phosphating time in this solution had a significant effect only on the nucleation period, causing its increase, but no substantial effect on either the growth or gas evolution period.

Based on previous results obtained by Saliba-Silva[3], who found that n = 0.86 produced good fitting between experimental results for Nd-Fe-B sintered magnets and Avrami's equation, under conditions similar to those used in this study, n = 0.86 was adopted in Avrami's equation, to obtain the following equation:

$$\ln(1 - X) = - K.t^{0.86} \tag{2}$$

The results presented in Figure 2 were adjusted to Equation 2, and good fitting ($R^2 > 0.99$) was attained, obtaining linear plots from which the K values, shown in Table 1, were estimated. The K values are related to the kinetics of the growth period. Table 1 also indicates the nucleation period, estimated as the time during which the surface ratio with H_2 bubbles was approximately zero.

As shown in Table 1, phosphating in the NaH_2PO_4 solution without molybdate causes an increase in the corrosion resistance of the magnet with increase in phosphating time. This reflects a strong effect of phosphating time on the development of the conversion layer. Phosphating for 18 hours in this solution resulted in an extremely well protected surface, which significantly extended the nucleation period, to approximately 20 times, compared to the unphosphated surface. It also caused a substantial decrease in the kinetics of the growth period.

A comparison of the results of magnets phosphated in solutions A and B, show that the effect of molybdate for short phosphating times was mainly on the kinetics of the growth period. For longer phosphating times (18 hours), molybdate had no beneficial effect on the corrosion resistance of the magnet's surface compared to that phosphated in solution A. In fact, comparison of magnets phosphated for 18 hours in both solutions indicates that the molybdate had a detrimental effect on the corrosion resistance. One of the possible reasons for this behavior is that a surface oxide is essential for corrosion inhibition of ferrous materials by the molybdate ions[16]. According to literature[17], an oxide layer can exist on the surface up to the bulk pH of (as low as) 4. As the pH of the solution used for phosphating was 3.8, it is possible that the MoO_4^{2-} ions could not act as a corrosion inhibitor. Moreover, phosphate and molybdate ions must compete for the surface, and

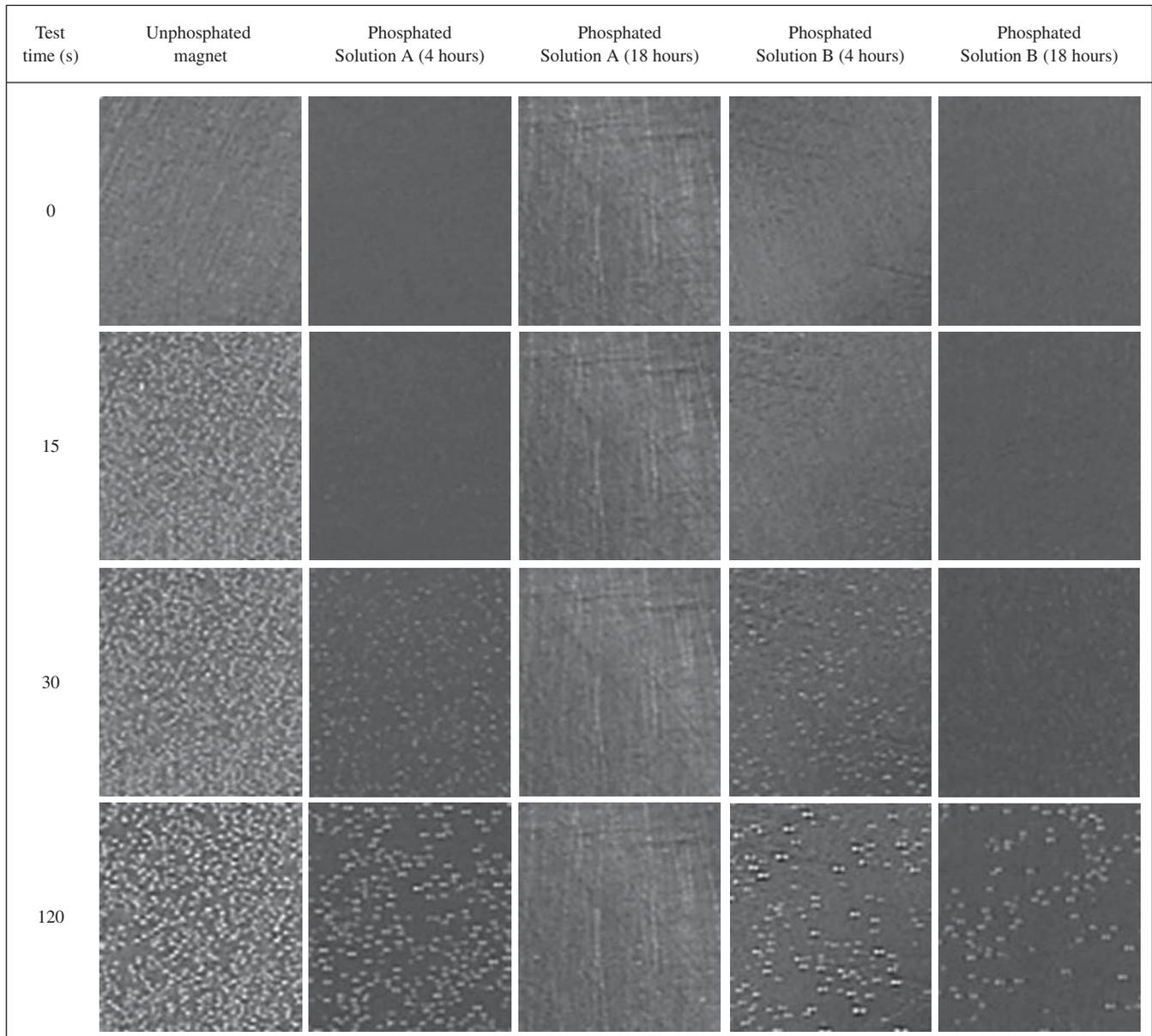| Test time (s)	Unphosphated magnet	Phosphated Solution A (4 hours)	Phosphated Solution A (18 hours)	Phosphated Solution B (4 hours)	Phosphated Solution B (18 hours)
0					
15					
30					
120					

Figure 1. Surface of sintered Nd-Fe-B magnets, unphosphated or phosphated in solutions A or B, for periods of 4 hours or 18 hours, at increasing times of immersion in acid solution (dilute HCl solution with pH adjusted to 2). The nucleation, growth and H_2 bubble release from the magnet surfaces, is easily seen. Photographs [magnitude: 10 x] were obtained from time-controlled film recording.

Table 1. K values and nucleation period obtained from experimental results fitted to Avrami's equation for the various types of magnet surfaces that were tested.

Magnets	- K	Nucleation period (s)
Unphosphated	1.01	7
Phosphated Sol. A (4 h)	0.75	20
Phosphated Sol. A (18 h)	0.23	148
Phosphated Sol. B (4 h)	0.35	14
Phosphated Sol. B (18 h)	0.29	19

the eventual adsorption of molybdate on some metallic sites makes the surface negatively charged, repelling the charged PO_4^{2-} ions, and consequently impairing phosphating of the surface.

Nevertheless, for specimens phosphated for 4 hours, the molybdate seems to have some beneficial effect on the corrosion resistance of the magnet, as indicated by a reduction in the kinetics of the growth period. Taking into account this observation, some technological improvements are necessary to add molybdate to the phosphating solution, as long periods of phosphating are used. The effect of a two-stage process, with phosphating first in solutions without molybdate followed by immersion in a molybdate-based solution, is under investigation.

4. Conclusions

Molybdate addition (10^{-3} M) to a phosphating solution 10 g/L NaH_2PO_4 (pH 3.8) had a marginally positive effect on the corrosion resistance of Nd-Fe-B magnets phosphated for 4 hours compared to a similar phosphating solution, and had a detrimental effect when a longer phosphating period (18 hours) was used.

A new method of evaluating the corrosion resistance of conversion coating layers, based on fitting the experimental results of H_2
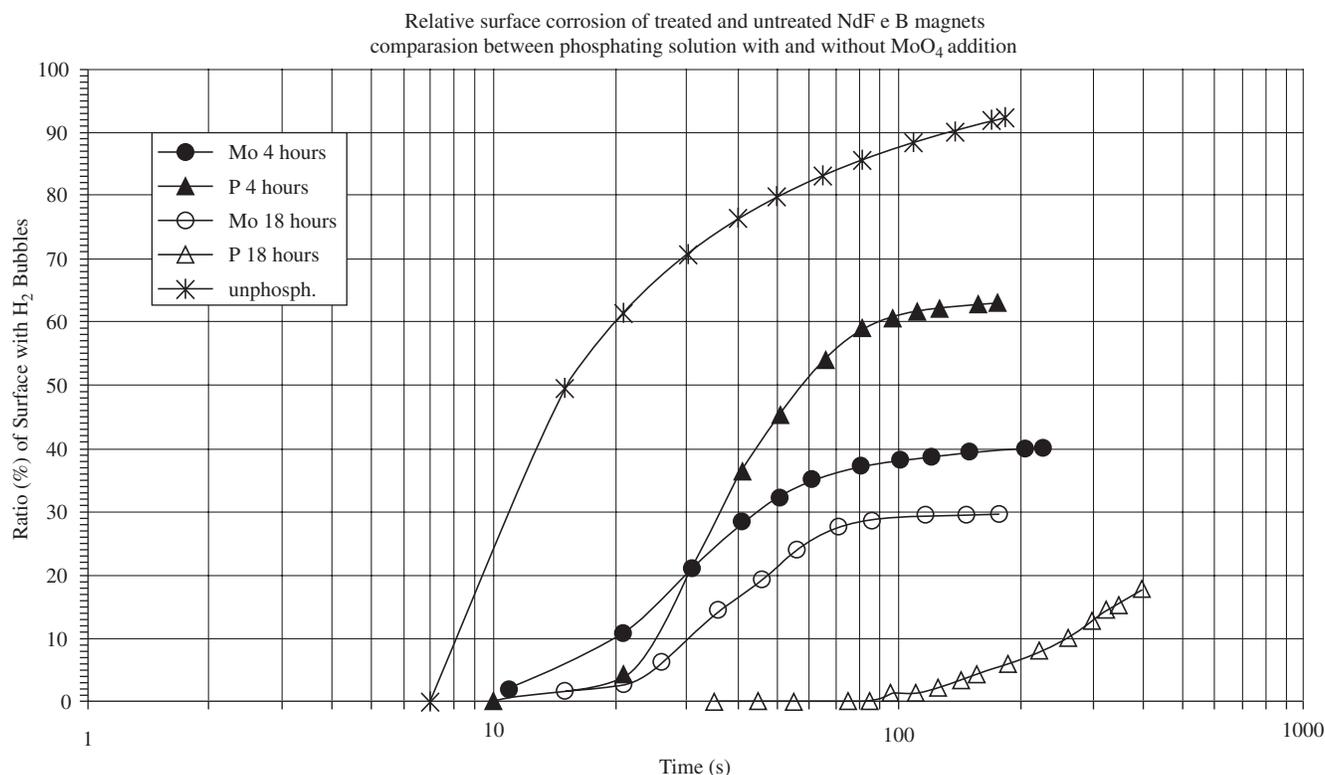
Relative surface corrosion of treated and untreated NdF e B magnets
comparasion between phosphating solution with and without MoO₄ addition

Figure 2. Nd-Fe-B magnet's surface ratio with H$_2$ bubbles with time of immersion in dilute HCl solution (pH adjusted to 2). Magnets were tested either unphosphated or phosphated in solution A (10g/L NaH$_2$PO$_4$) or solution B (10g/L NaH$_2$PO$_4$+ 1mM MoO$_4^{2-}$) for 4 hours or 18 hours.

evolution on the treated surface to Avrami's equation is proposed. This method showed good results for the sintered Nd-Fe-B magnet, either phosphated or unphosphated, that were corrosion tested by immersion in an acid solution (pH = 2).

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