Effect of molybdate on phosphating of Nd-Fe-B magnets for corrosion protection

A.M.Saliba-Silva, M.C. L. Oliveira, I. Costa*

Instituto de Pesquisas Energéticas e Nucleares, IPEN/CNEN-SP
Centro de Ciência e Tecnologia de Materiais
Caixa Postal 11049, Pinheiros, CEP 05422-970, São Paulo, Brasil

Abstract

The effect of phosphating on the corrosion resistance of a commercial Nd-Fe-B sintered magnet has been 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-}], for improving their corrosion resistance. The effect of phosphating time was also evaluated, with specimens phosphated during 4 hours and 18 hours. To evaluate the corrosion performance of phosphated and unphosphated specimens, a corrosion test based on monitoring hydrogen evolution on the magnets surface was used. This technique revealed that molybdate addition into the phosphating solution improves the corrosion resistance of the phosphated magnets for shorter periods of immersion but has no beneficial effect for longer phosphating times.

Introduction

Nd-Fe-B magnets produced by powder metallurgy have a wide range of applications since computer disk drives, many important parts of fine electro-electronic industry and in large industrial machines. Nd-Fe-B magnets, however, have low corrosion resistance and need surface protection. The low corrosion properties are partially due to their complex microstructure with two electrochemically different main phases (φ-phase and Nd-rich), leading to galvanic

corrosion. Moreover, the magnets produced by powder metallurgy (PM) techniques present porosities that decrease further their corrosion resistance.

Corrosion control methods are necessary to improve Nd-Fe-B magnets viability as an engineering material. One of the most used corrosion control methods for this kind of magnets is coating, mainly organic coatings. Unfortunately, organic coatings are not defect free and consequently a surface pre-treatment is generally used, either to improve coating adhesion or to improve the corrosion resistance at the defective areas of the coating.

Phosphating as a pre-coating surface treatment is 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 of different electrochemical behaviour and porosities, affects phosphating, impeding the formation of a continuous conversion layer.

Bala el al.[7] carried out experiments with individual phases of Nd-Fe-B magnets, 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 lower than 3.5.

Saliba-Silva et al.[2-5] reported increased corrosion resistance related to Nd-Fe-B magnets phosphated in a solution with pH of approximately 3.8. According to literature [8] in solutions of pH between 3.5 and 5, a Nd hydroxide tends to develop on the surface, and this might impair the formation of a stable phosphate layer on the magnets surface. Previous results [2] have shown that in solutions of very low pH ($pH \leq 2$) a protective layer was not formed on Nd-Fe-B magnet.

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

There are several possibilities of accelerating commercial phosphating of ferrous materials, for instance, by using nitrate and chlorates compounds. However, these substances are very active and promote severe corrosion of Nd-Fe-B magnets, mainly of the Nd-rich phase [9]. Lorin [10] suggested all kind of accelerators, even molybdates, which are not as corrosive as nitrates and chlorates. According to Gentil [11] molybdate anion (MoO_4^{2-}) should be an adequate inhibitor for post-phosphating treatment, to seal the phosphate layer. Studies on molybdates [12,13] have shown that they are good inhibitors for ferrous alloys. Molybdates are not normally used for phosphating acceleration in commercial practices, but they are being investigated to replace chromatizing.

In this work, the corrosion resistance of Nd-Fe-B magnet specimens, either unphosphated or phosphated in solutions of NaH_2PO_4 (pH 3.8), 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 magnets surface. This method is based on monitoring the stages of hydrogen evolution reaction on the magnets surface, that is, nucleation, growth and H_2 bubbles release from unphosphated or phosphated magnets immersed in acid solution, at increasing times, and fitting the results to Avrami's equation [14].

2. Experimental Procedure

2.1 Material

A commercial sintered Nd-Fe-B magnet produced by Crucible – U.S.A., whose composition is 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, using an ultrasonic bath, and drying under a hot air stream. The remaining areas were coated with varnish.

2.3 Phosphating

Phosphating was carried out by immersion of magnets specimens for periods of 4 hours or 18 hours, in either of the 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

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

$$X= 1-\exp(-K.t^n) \qquad (1)$$

where: X is the surface ratio covered with H_2 bubbles, due to the corrosive attack 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 interface[15]. Saliba-Silva[3] in a previous work, found that n=0.86 produces good fitting results for Nd-Fe-B sintered magnets under similar conditions.

Results and Discussion

The magnets surface, unphosphated or phosphated, at increasing times of immersion in the testing solution, are shown in Fig. 1. The evolution of H_2 bubbles on the magnets surface at increasing times of immersion in diluted HCl solution (pH 2.0) is clearly indicated in this Figure.

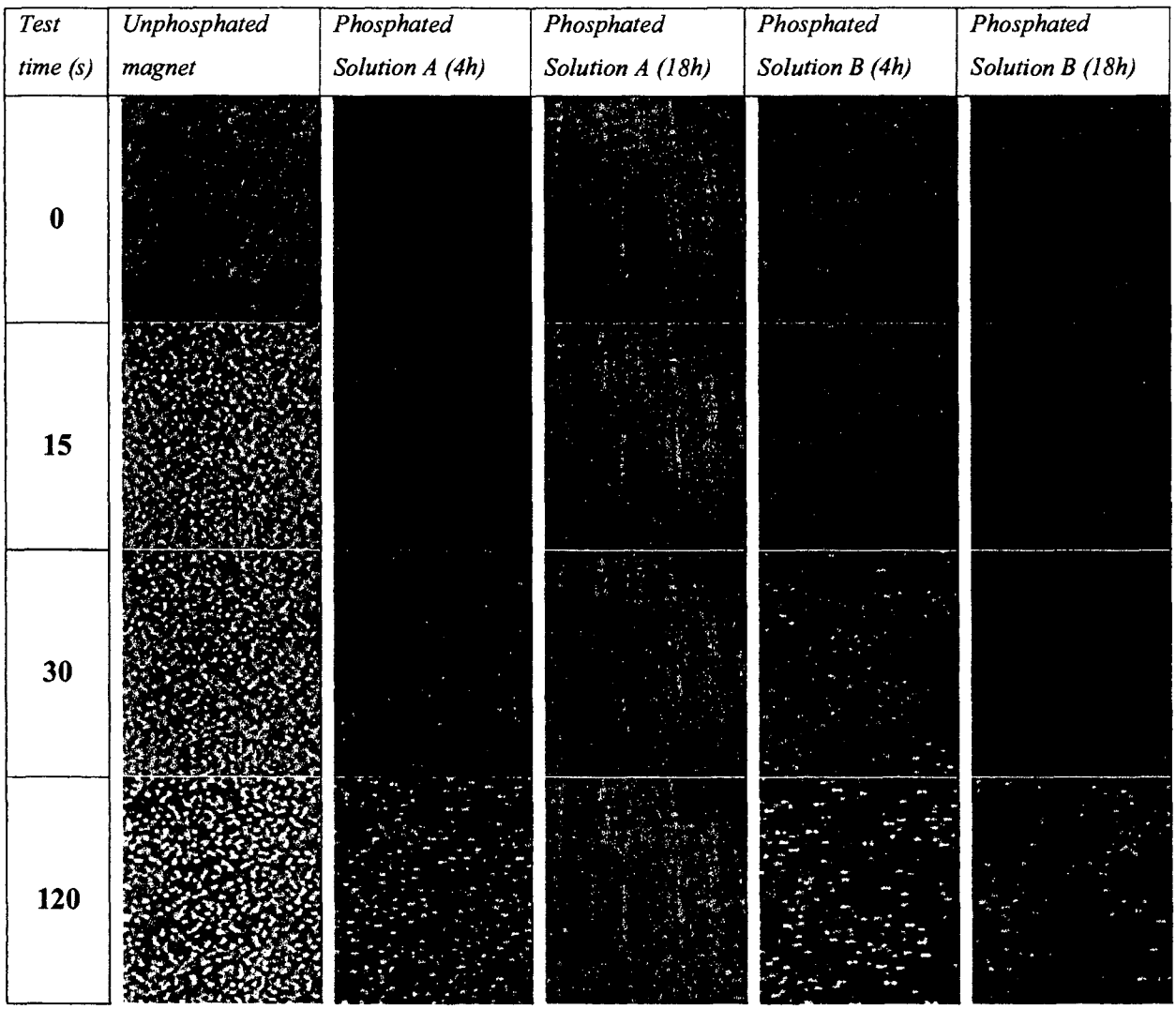

Fig. 1. Surface of sintered Nd-Fe-B magnets, unphosphated or phosphated in solutions A or B, for periods of 4h or 18h, at increasing times of immersion in acid solution (diluted HCl solution with pH adjusted to 2). The nucleation, growth and H_2 bubbles release from the magnets surface, is easily seen.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

Few bubbles are seen on the unphosphated magnet surface immediately after immersion. After 15 seconds, the unphosphated surface is completely covered with H_2 bubbles, suggesting a fast kinetics of nucleation and growth on its whole surface. The phosphated magnets showed different behaviour 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 a fast growth kinetics from that time onwards. The best corrosion performance among all the specimens tested was obtained for the magnets phosphated in solution A during 18 hours. For this last type of specimen, only a few bubbles were nucleating on its surface after 120 seconds of immersion in the acid solution. Phosphating in molybdate containing solution (solution B), resulted in corrosion resistance improvement of the magnets surface comparatively to the unphosphated specimens, but the increase in phosphating time in this solution was not as effective as that associated to the solution without molybdate. A comparison of the magnets surface 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 of treatment.

The ratio of the magnets 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 Fig. 2. The curves in Fig. 2 could be divided in three regions. There is an initial period, when none or very few H_2 bubbles are seen on the magnets 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 comes out where there is a competition between H_2 bubbles growth and their release from the surface, resulting in slower variation of the surface ratio with H_2 bubbles with time (gas evolution period).

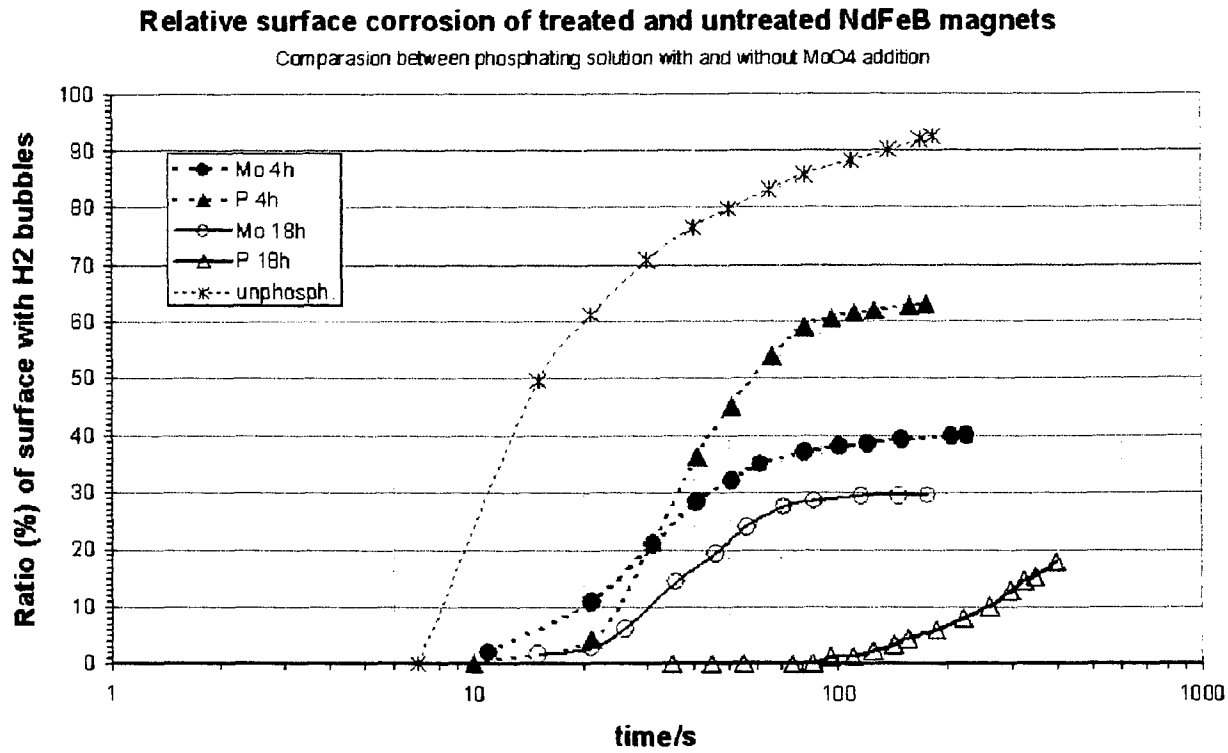

Fig. 2 – Nd-Fe-B magnets surface ratio with H_2 bubbles with time of immersion in diluted HCl solution (pH adjusted to 2). Magnets were tested either unphosphated or phosphated in solution A (10g/L NaH_2PO_4) or solution B (10g/L NaH_2PO_4+ 1mM MoO_4^{2-}) for 4 h or 18 h.

Fig. 2 shows very distinct behavior for the various types of surfaces tested. A very short nucleation period followed by a short growth period of very fast kinetics and a prompt gas evolution period was observed for the unphosphated magnet. Longer nucleation periods were obtained 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 used. For the magnets phosphated in molybdate containing solution (solution B), similar kinetics was obtained for the two times of phosphating (4 h and 18 h). The increase in phosphating time in this solution had a significant effect only on the nucleation period, causing its increase, but no substantial effect was observed 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, in similar conditions to those used in this study, n=0.86 was adopted in Avrami's equation, obtaining the following equation:

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

The results presented in Fig. 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 can be related to the kinetics of the growth period. Table 1 also indicates the nucleation period, which was estimated as the time during which the surface ratio with H_2 bubbles was approximately zero.

Table 1 – K values and nucleation period obtained from experimental results fitted to Avrami's equation for the various types of magnets surface 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

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 a surface of outstanding protection, extending significantly

the nucleation period, approximately 20 times comparatively 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 shorter phosphating times was mainly on the kinetics of the growth period. For longer phosphating times (18 h), molybdate had no beneficial effect on the corrosion resistance of the magnets surface comparatively to that phosphated in solution A. In fact, a detrimental effect of the molybdate on the corrosion resistance is noticed when magnets phosphated for 18 hours in both solutions are compared. One of the possible reasons for this behavior is that a surface oxide is essential for corrosion inhibition of ferrous materials by 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 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.

It must be pointed out, however, that for the specimens phosphated during 4 hours, molybdate apparently had 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 improvement could be foreseen with the addition of molybdate into the phosphating solution since not long periods of phosphating were used. The effect of a two stage process, where phosphating is carried out in solutions without molybdate followed by immersion in a molybdate based solution, is under investigation.

Conclusions

Molybdate addition (10^{-3} M) to a phosphating solution 10 g/L NaH_2PO_4 (pH 3.8) had a marginal positive effect on the corrosion resistance of Nd-Fe-B magnets phosphated for 4 hours in comparison to a similar phosphating solution, and had a detrimental effect when 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 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, corrosion tested by immersion in an acid solution (pH = 2).

References

1. Costa, I., Sayeg, I.J, Faria, R.N., *IEEE Transactions on Magnetics*, v.33, n.5, p. 3907, 1996
2. Saliba-Silva, A. M., Ph.D. Thesis, CNEN-IPEN - USP, São Paulo, SP, Brazil, 2001.
3. Saliba-Silva, A.M., Costa, I., *Key Engineering Materials*, v.189-191, p. 363-368, 2001
4. Saliba-Silva, A. M., de Melo, H. G., Baker, M.A., Brown, A.M., Costa, I., *Materials Science Forum*, v.416-418, p. 54-59, 2003
5. Saliba-Silva, A.M., de Melo, H.G., Costa, I., *5th Int. Symp. on Electrochemical Impedance*, Marilleva, Trento, Italy, 17-22 June/2001
6. Saliba-Silva, A.M., Baker, M.A., de Melo, H.G., Costa, I., *Surface Treatment V, Series: Computational and Experimental Methods,* Ed. Brebbia, C.A., p. 65, 2001.
7. Bala, H., Pawlowska, G., Szymura, S., Rabinovich, Y.M., *British Corrosion Journal*, v.33, n.1, p.37, 1998
8. Rupp, B., Resnik, A., Shaltiel, D., Rogl, P., *J. Mat. Science*; v.23, n.6, p.2133, 1998
9. Tokuhara, K., Hirosawa, S., *Journal of Applied Physics*, v.69, n.8, p. 5521, 1991

10. Lorin, G., *Phosphating of Metals-Constituition*, Finishing Publications Ltd. Middlesex, England, 1974

11. Gentil, V. *Corrosão* , 3rd Edition, LTC Editora, Rio de Janeiro, Brazil , p. 213, 1996

12. Magalhães, A.A.O., Margarit, I.C.P., Mattos, O.R., *7th Int. Symp. on Electrochemical Methods in Corrosion Research,* paper 100, 28 May – 1 Jun/ 2000

13. Martini, E. M. A., Azambuja, D.S., Piatnicki, C.S., Muller, I.L., *20th Brazilian Corrosion Congress and 2nd Seminar on Materials Degradation*-paper R071 [CD], Fortaleza, Brazil, 12 – 15 Sept. 2000.

14. Avrami, J., *Journal of Chem. Phys.*, v.7, p. 1103, 1939

15. Smith, G. W., *Thermochimica Acta*, v. 291, p. 59, 1997.

16. Farr, J. P. G., Seeney, A.M Bentley, A.J., Earwaker, L.G., *Surface Tech.*, v.23, p 99, 1984.

17. Uhlig, H. H., *Corrosion and Corrosion Control*, John Wiley and Sons, London, Eng., p.85, 1967

IPEN/CNEN-SP
BIBLIOTECA
"TEREZINE ARANTES FERRAZ"

Formulário de envio de trabalhos produzidos pelos pesquisadores do IPEN para inclusão na Produção Técnico Científica

AUTOR(ES) DO TRABALHO:
A .M. SALIBA; M.C.L. OLIVEIRA; I. Costa

LOTAÇÃO: CCTM RAMAL:9359

TIPO DE REGISTRO:

art. / periód.:		Publ. IPEN		. resumo	
cap. de livro		Art. conf	X	outros (folheto, relatório, etc...)	X

TITULO DO TRABALHO:
EFFECT OF MOLYBDATE ON PHOSPHATING OF Nd-Fe-B MAGNETS FOR CORROSION PROTECTION

APRESENTADO EM: (informar os dados completos - no caso de artigos de conf., informar o título da conferência, local, data, organizador, etc..)
PTECH 2003
19 A 31 de Novembro de 2003 - Guarujá- Brasil

PALAVRAS CHAVES PARA IDENTIFICAR O TRABALHO:
Nd-Fe-B MAGNETS; CORROSION; MOLYBDATE

ASSINATURA: _____

DATA: 10/12/2003