

Corrosion Behaviour of Commercial NdFeB Magnets- The Effect of Magnetization

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Abstract: The low corrosion resistance of NdFeB magnets is a reason for concern since it also results in deterioration of their magnetic properties. Many of the corrosion studies on these materials have used specimens in the demagnetized state for experimental convenience. Preliminary tests carried out at our laboratory indicated magnetization to have a significant effect on corrosion resistance. Subsequently, investigation was undertaken to study the effect of magnetization. Bare commercial magnets of NdFeB were tested while magnetized and non magnetized. The corrosion behaviour was investigated in sodium chloride solution (3.5 wt %) by means of weight loss measurements, analysis of the corrosive medium for dissolved and precipitated corrosion products and scanning electron microscopy. Magnetization affected the corrosion behaviour of the magnets. The magnetic properties were diminished by corrosion degradation.

Introduction

Rare Earth based magnets were developed in the 60's. The first generation magnets corresponded to permanent magnets of SmCo_5 . These were followed by $\text{Sm}_2\text{Co}_{17}$, a decade later. The maximum energy product of these magnets was 33 MGOe. At the beginning of the 80's, a new magnetic material, based on the NdFeB alloy, was produced by powder metallurgy, with a maximum energy product between 36 and 50 MGOe. The NdFeB magnets are progressively replacing the Sm-Co ones.

Despite their excellent magnetic properties, NdFeB magnets are unstable at moderate to high temperatures and show low corrosion resistance in aqueous environments. The literature has associated the low corrosion resistance of these magnets to their complex microstructure[1-9]. The complex microstructure of NdFeB magnets consists of at least three phases, the main magnetic phase (ϕ), a Nd rich phase and a B rich phase. The multiple phases of different electrochemical potentials leads to galvanic corrosion in the presence of an electrolyte[6,9-12].

In the magnets produced by powder metallurgy (PM) the ϕ grains are surrounded by intergranular regions where there is a mixture of phases. The Nd rich phase located at the grain boundaries of the ϕ phase is one of the most active phases present in the PM NdFeB magnets. The preferential attack of this phase leads to intergranular corrosion[9], and can result in the detachment of ϕ grains leading to disintegration of the material[8,9]. This causes the deterioration of the magnetic properties and affects the performance of other components in the neighbourhood, due to loose corrosion products[10-12].

Coatings application is one of the main methods used for protection of NdFeB magnets against corrosion. Besides, coatings on NdFeB magnets hold magnetic particles which otherwise would be loose. This is very important in applications where the surface must be clean and free of magnetic particles, such as applications in computer components[12].

Another corrosion protection method much used consists in the use of corrosion inhibitors, such as phosphates, chromates, nitrates, molybdates, among others. Phosphating as a corrosion inhibiting treatment for NdFeB magnets has been investigated[13,14]. It can be applied as a pre-treatment on NdFeB magnets before coatings application and has the advantage of providing protection at defective regions of the coating. Phosphates act by forming a protective film on the anodic surface of the metal/alloy and the inhibiting characteristics of the films formed depend on the material and the conditions used.

In general, the literature available on the corrosion behaviour of NdFeB magnets does not mention the magnetization state of the specimens tested. One of the few studies which considered the effect of the magnetization on the corrosion behaviour of NdFeB magnets is that of Bala and Szymura[15]. It was observed that magnetization affected the dissolution of Nd₁₅Fe₇₇B₈ in acid solution at high cathodic overpotentials. This was called abnormal dissolution and was attributed to the hydrogenation of the magnet surface and consequently mechanical degradation. Also according to their work, the abnormal dissolution consisted of the separation of small particles (~0,01 mm), which were subsequently dissolved in the solution. It was found that the magnetized Nd₁₅Fe₇₇B₈ specimens dissolved to a lesser extent than those demagnetized and this was attributed to the magnetic field which held some magnetic particles on the surface. However, according to the same authors[15], the surface degradation of both specimens, magnetized or demagnetized, were of the same order.

Preliminary experimental results in our laboratory indicated that the magnetization state of the specimens had a significant effect on the corrosion behaviour of NdFeB commercial magnets. This was observed by means of weight loss measurements and chemical analysis of the solution after immersion test. The reason for this behaviour however is not yet understood. In the present work, an investigation was carried out in an attempt to reveal the reason for this behaviour.

Material and Methods

Material: The material used was a NdFeB commercial magnet provided by Crucible, known as Crumax. The surface condition was obtained by sequential grinding with silicon carbide paper from grit #600 to #1200 followed by drying in a hot air stream. Two specimens were used to obtain replicate data. The corrosion behaviour of the NdFeB magnet was studied in both states, magnetized and non magnetized.

Methods: After surface preparation, the specimens were weighed. Some of the specimens were then magnetized up to saturation using a pulsed field of 60 kOe. Subsequently, both types of specimens, magnetized and non magnetized, were tested by immersion in a solution of 3.5 (wt%) NaCl. After 21 days of immersion the specimens were removed from the test solution, the loose corrosion products were removed using a soft brush, washed, dried with a hot air stream and finally weighed. The magnetized specimens had to be demagnetized (400 °C, 10⁻⁵ mbar) before weighing. After demagnetization, some particles of the magnets were released from their surface, and they were also collected for weighing after drying. The test solutions after the immersion period had precipitates.

In order to evaluate the corrosion products, the precipitate and the solution were analysed by instrumental neutron activation analysis (INAA). Firstly, the precipitate was separated from the solution by centrifugation. For its analysis, this precipitate was dissolved using drops of HNO_3 and then diluting to 10 mL with distilled water. For irradiation 500 μL of the sample solutions were pipetted and dried in a clean polyethylene capsule.

The experimental condition used in these analyses consisted of irradiation, at the IEA-R1 nuclear reactor, of samples and synthetic standards of Fe and Nd in capsules for 16 hours under a thermal neutron flux of $10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$. After adequate decay times, samples and standards were measured using a hyperpure Ge detector coupled to EG&G Ortec ADCAM 918A Multichannel Buffer and this to a microcomputer. The gamma ray spectra were processed using appropriate software and the concentrations of the elements were calculated by comparative method. Also the blank of the 3.5 % NaCl was analyzed in order to evaluate the contributions of the elements from this medium.

The magnetic properties of the NdFeB magnets were determined before and after immersion using a permeameter. The surface of the magnet after the immersion period was analysed by Scanning Electron Microscopy (SEM).

Results and discussion

The mean values from the weight loss percentage measurements of the magnets after 21 days immersion in the solution of 3.5 (wt%) NaCl are showed in Figure 1.

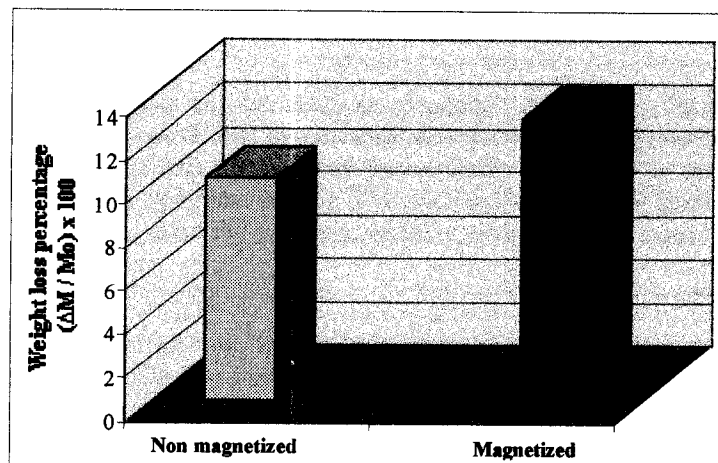


Figure 1 – Weight loss percentage of NdFeB magnets (non magnetized and magnetized) exposed to a solution of 3.5 (wt%) NaCl for 21 days.

Figure 1 shows that the magnetized specimens had higher weight losses comparatively to those non magnetized. The difference in weight loss was in the range of 15 to 20%. It is important to mention that particles of the magnet were released from the surface after demagnetization, showing that the intense magnetic field held particles on the magnet surface (magnetized specimens), which otherwise would be freed from the surface either by gravity or by brushing. The particles released

after demagnetization were collected and weighed, and they corresponded to 13 to 19 % of the total mass loss measured, demonstrating that they were in a significant amount.

The results of Fe and Nd analyses, either in solution or in the precipitated, obtained by INAA, are presented in Table 1.

Table 1 – Results of Fe and Nd analyses obtained by INAA of test solution.

State of magnetization	Solution*		Precipitate**	
	Fe($\mu\text{g/mL}$)	Nd ($\mu\text{g/mL}$)	Fe (mg)	Nd (mg)
Non magnetized	0.92 \pm 0.09 (0.46)***	3.45 \pm 0.01 (1.725)***	21.58 \pm 0.08	5.34 \pm 0.03
Non magnetized	0.86 \pm 0.09 (0.43)***	3.24 \pm 0.01 (1.62)***	23.34 \pm 0.08	5.43 \pm 0.03
Magnetized	0.7 \pm 0.1 (0.35)***	2.701 \pm 0.009 (1.351)***	13.24 \pm 0.05	2.91 \pm 0.02
Magnetized	0.17 \pm 0.04 (0.085)***	0.0109 \pm 0.0002 (0.005)***	12.34 \pm 0.05	2.43 \pm 0.01

(*) – indicates the element concentration dissolved in the test solution

(**) – indicates the total mass of the element in the precipitate

(***) Mass of element (mg) in 500mL of test solution

The total content of Fe and Nd detected in the test solution plus precipitate due to corrosion was much greater for the solutions where non magnetized specimens were immersed. Magnetic particles were retained on the surface of the magnetized specimens whereas in the non magnetized specimens they were released to the test medium. This was partially responsible for the differences in the contents of Nd and Fe elements in the test solutions where the magnetized and non magnetized specimens were immersed. However, whereas the percentage of mass held on the surface by the magnetic field varied from 13% to 19% of the total mass loss, the total content of Fe removed due to corrosion and associated to the non magnetized specimens varied from 1.6 to 1.9 times that associated to the magnetized specimens. This result suggests that the holding of magnetic particles on the surface of the magnetized specimens must have affected the corrosion behaviour, as it was shown by the observation of the corroded surfaces of both specimen types, magnetized and non magnetized. Nevertheless, the ratio of Fe/Nd removed by corrosion for the magnetized and non magnetized specimens were of the same order, varying from 3.1 to 5.1.

Table 1 also shows that most of the Fe (> 90 %) and Nd (> 60%) released to the test medium due to corrosion was in the precipitate. The magnetic properties of the specimens (magnetized to saturation) before and after 21 days of immersion were measured and they are showed in figure 2 and table 2.

Table 2 – Magnetic properties of the magnets before and after immersion (error: \pm 2%).

3.5% NaCl	Br [kG]	iHc [kOe]	bHc [kOe]	(BH) _{max} [MGOe]	SF
Before test	17.9	12.3	11.7	36.3	0.96
After test	18.4	11.2	10.0	28.0	0.55
Δ %	8.9	3.1	14.5	22.9	42.7

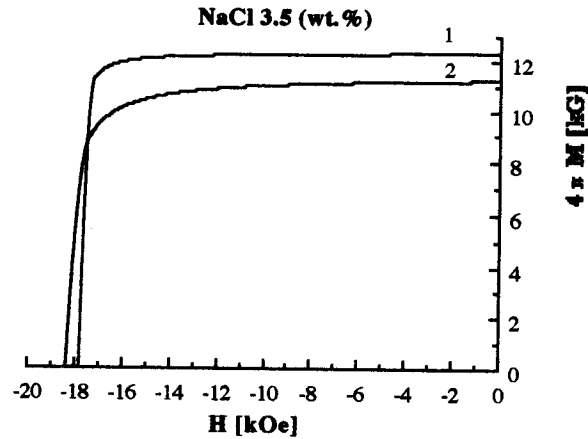


Figure 2 - Magnetization curves of NdFeB magnets before and after 21 days immersion in a solution of NaCl 3.5 (wt %). (1 = Before and 2 = After immersion).

The corrosion of the NdFeB magnets resulted in the deterioration of remanence, energy product and squareness factor. The intrinsic coercivity, rather surprisingly, was the property that was less affected by the immersion test.

The surfaces of the magnets observed by SEM before and after the immersion test are shown in figure 3. As it can be seen, the attack on the non magnetized specimens was more uniform and superficial, whereas on the magnetized specimens it was deeper and more concentrated at some areas. Intergranular corrosion seems also to have occurred, as indicated in figure 3, due to the attack of the more active phases (Nd rich phase) located at the grain boundaries of the magnetic phase.

One possible reason for the deeper penetration of corrosion on the magnetized specimens would be the attachment of the magnetic phase on the surface, which could impair corrosion on the covered areas and lead to the continuation of corrosion at the areas which were initially and preferentially attacked.

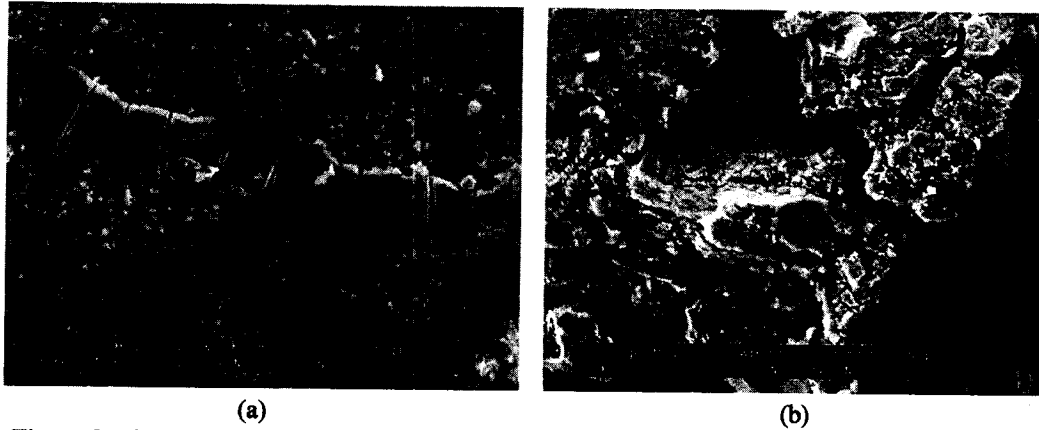


Figure 3 – SEM of NdFeB specimens (a) non magnetized and (b) magnetized, after 21 days of immersion in 3.5 (wt%) NaCl.

Conclusions

The corrosion behaviour of the NdFeB magnet investigated was affected by the magnetization state of the specimens tested. The intense magnetic field associated to NdFeB magnets in the magnetized state held magnetic particles on their surface, which otherwise would have been released into the corrosive environment. This affected the corrosion mechanism. Whereas corrosion was more superficial and uniform on the non magnetized specimens, the corrosive attack on the magnetized specimens showed deeper penetration at some regions of the material. The magnetic particles attached to the surface, after their surroundings have been attacked by the aggressive medium, could favour localized corrosion, and lead to the higher weight loss associated to the magnetized specimens. Corrosion resulted in a significant deterioration in the squareness factor of the specimens, whereas the intrinsic coercivity remained somewhat unchanged after corrosion. Further investigation using electrochemical impedance spectroscopy analysis are underway to explain the different corrosion behaviour of the magnetized and non magnetized materials.

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