

A New Process for Nd-Fe-B Powder and Magnets

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Keywords

corrosion, magnetic properties, Nd-Fe-B magnet, Nd-Fe-B powder, passivation, processing

1. Introduction

THE sensitivity of Nd-Fe-B powder, with or without Dy additives, to corrosion is well known. Current practices for producing Nd-Fe-B magnets use jet milling or ball milling of powder in organic liquids. The powder is compacted as soon as possible after milling to prevent corrosion during exposure to air. Magnets produced by these techniques have poor corrosion resistance due to the high chemical activity of neodymium.

Recently, a new technique for the production of corrosion-resistant Nd-Fe-B-C/N powder and magnets with outstanding magnetic properties was introduced.^[1] The AQUANIDETM method* involves milling the alloy in water, followed by passivation with nitrogen or carbon dioxide gas. A passivated layer develops on the surface of each powder particle, which protects the powder, as well as magnets made from this powder, from corrosion. This article presents results of an investigation of the influence of passivation on the crystal structure, magnetic properties, and corrosion resistance of AQUANIDE-processed powder and magnets.

2. Procedures

2.1 Sample Preparation

Ingots of Nd-Fe-B alloy were crushed in a disc pulverizer under nitrogen to produce a 50-mesh powder. The 50-mesh powder was attritor milled, using stainless steel balls and water as the milling medium. After milling, the powders were dried and then passivated in carbon dioxide or nitrogen atmospheres at various temperatures and times. The passivated powders were then compacted in a magnetic field, sintered, and heat treated. Additionally, some powders were produced using hexane as the milling medium (conventional technique).

2.2 Corrosion Testing

Corrosion resistance of the powder was evaluated by the change in weight after exposure in (1) laboratory air at room temperature and at 175 °C for 346 h, and (2) in a humidity chamber with a relative humidity of 95% at room temperature and at 75 °C for 12 h.

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*AQUANIDETM is a trademark of SPS Technologies Inc.

2.3 Analysis of Crystal Structure and Magnetic Properties

The phases present in the powder and magnets were determined using X-ray diffraction methods. All X-ray diffraction analysis was conducted using filtered and monochromatic $\text{CuK}\alpha$ radiation with Bragg-Brentano focusing in a RIGAKU diffractometer. The X-ray tube was operated at 45 kV and 35 mA.

The degree of alignment of the powder in a magnetic field was determined by mixing it with an epoxy resin. This mixture was allowed to set in the presence of a magnetic field. The degree of alignment was then determined by comparing the intensities of diffraction peaks from the aligned particles with peaks obtained from an unaligned sample. A sufficient number of peaks was ensured by using radiation from a copper tube.

The alignment factor for each crystal direction (P_{hkl}) is

$$P_{hkl} = \frac{I_{hkl}}{I_{Ohkl}} \times \frac{1}{I_{hkl}/I_{Ohkl}}$$

where I_{hkl} is the intensity of a reflection from a crystalline plane for an aligned specimen and I_{Ohkl} is the intensity of a reflection from a crystalline plane for an unaligned powder.



600X

Fig. 1 Photomicrograph of AQUANIDE Nd-Fe-B powder with passivated surface layer.

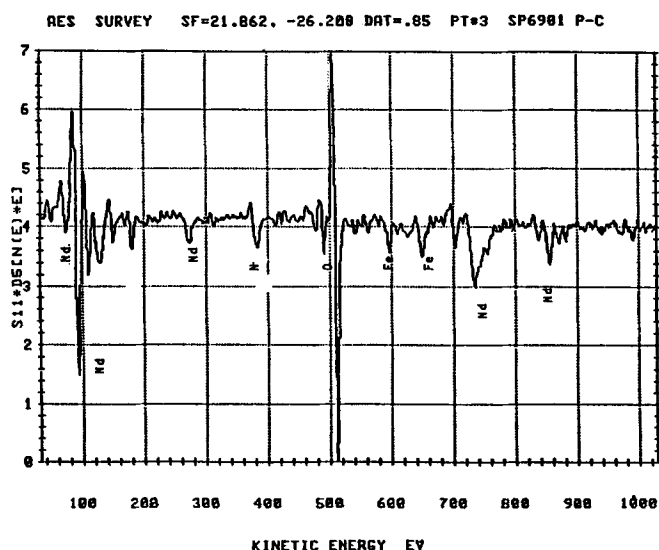


Fig. 2(a) Auger spectrum showing element distribution after sputtering for 5 min in Nd-Fe-B powder particles passivated with nitrogen. Nitrogen peak is evident.

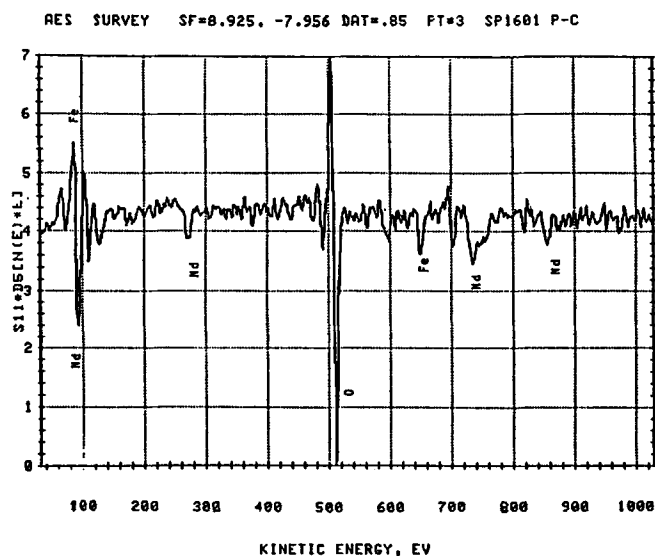


Fig. 2(b) Auger spectrum showing element distribution after sputtering for 15 min in Nd-Fe-B powder particles passivated with nitrogen. Nitrogen peak is absent.

The chemical composition at the surface and at different depths in the powder particles was determined using Auger spectroscopy techniques. Resolution was approximately 200 μm , and the spectrometer was operated at a primary beam voltage of 10 kV and a current of 0.1 mA. Depth profiles were conducted using argon sputtering techniques. The concentrations were determined from a multipoint analysis, with a narrow energy window selected for each element scanned.

Analysis of the magnetic properties of the powder was conducted on a vibrating sample magnetometer. Fifty-milligram samples of the Nd-Fe-B powder were mixed with an epoxy and mounted in 3-mm copper capsules. These capsules were then placed in a magnetic field to align the powder particles as the epoxy cured.

Magnetic properties of sintered magnets were measured on an AMH 1050 hysteresisgraph, with the sample impulse magnetized prior to measuring.

3. Discussion of Results

3.1 Passivation of Powder

The degree of passivation is influenced by passivation temperature and time and depends on such factors as powder particle size, surface area, and defect density within the crystal structure of the particle. After passivation with carbon dioxide or nitrogen, a passivated layer is formed on the surface of the powder particles, as shown in Fig. 1.

Passivation is accomplished by the absorption of a passivating gas, such as nitrogen and carbon dioxide, onto the surface of the particles, the subsequent diffusion of carbon or nitrogen atoms within the crystal lattice forming a corrosion-resistant

layer. The results of Auger spectroscopy analysis given for nitrogen-treated samples and X-ray diffraction analysis for carbon dioxide-treated samples are shown in Fig. 2(a) and (b) and 3(a) and (b), respectively. These results indicate that the layers are composed of nitrogen-containing and neodymium carbide phases.

The test results also indicate that removal of the particle surface layer by chemical polishing practically eliminates these nitrogen or carbide phases. It is assumed that these phases occur in the surface region of the particles and create a high defect density within the crystal lattice.

The magnetic properties of the powder are influenced by the passivating gas, temperature, and time, as illustrated in Fig. 4 to 7. For the powder tested in this work, the optimum magnetic properties are achieved when the powder is passivated with carbon dioxide at 175 $^{\circ}\text{C}$ for 20 s, or with nitrogen at 225 $^{\circ}\text{C}$ for 20 s. Other passivation conditions may be required for different alloy composition, particle size distribution, or powder type.

Increasing passivation temperature or time results in higher concentrations of carbon and nitrogen, as shown in Fig. 8 and 9. Coercive force of the powder increased rapidly over the initial 20 s of passivation, and residual induction decreased monotonically with increasing time. These variations in magnetic properties are related not only to carbon and nitrogen concentrations, but also may be due to the formation of additional defects by diffusion of the passivating species within the surface layer. It is believed that these defects result in the increased half widths of X-ray diffraction peaks, shown in Fig. 10 and 11, for (820) and (410) crystalline planes of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase. The decrease of remanent magnetization and subsequent decrease in coercive force on samples passivated for an extended time is the result of the increasing levels of microstrain and distortion of the crystal lattice and subsequent decreased align-

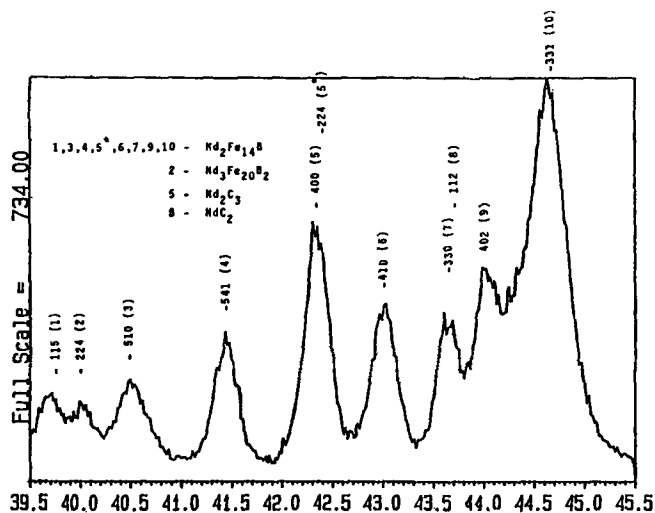


Fig. 3(a) X-ray diffraction pattern of Nd-Fe-B powder passivated with CO₂ and chemically polished for 5 min. Neodymium carbide peaks are evident.

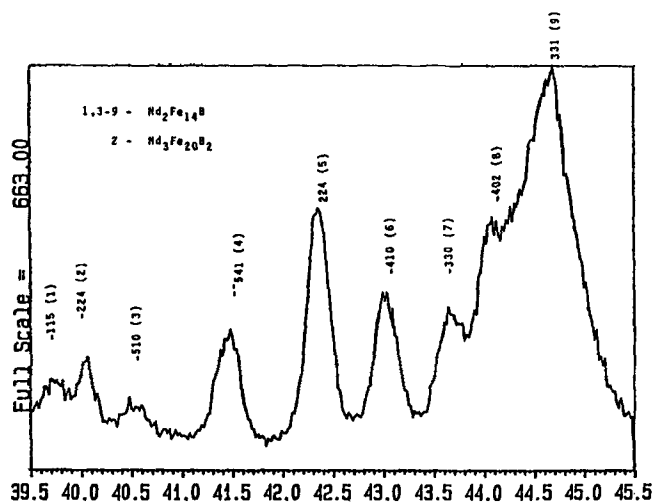


Fig. 3(b) X-ray diffraction pattern of Nd-Fe-B powder passivated with CO₂ and chemically polished for 15 min. Neodymium carbide peaks are absent.

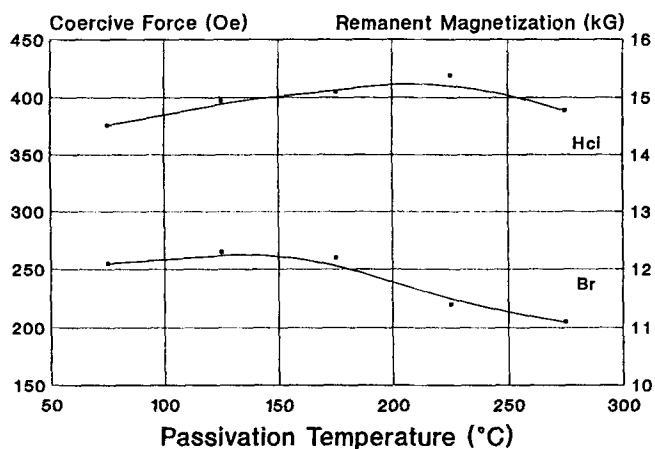


Fig. 4 Influence of passivating temperature on coercive force (*Hci*) and remanent magnetization (*Br*) of Nd-Fe-B powder passivated with CO₂ for 1 min.

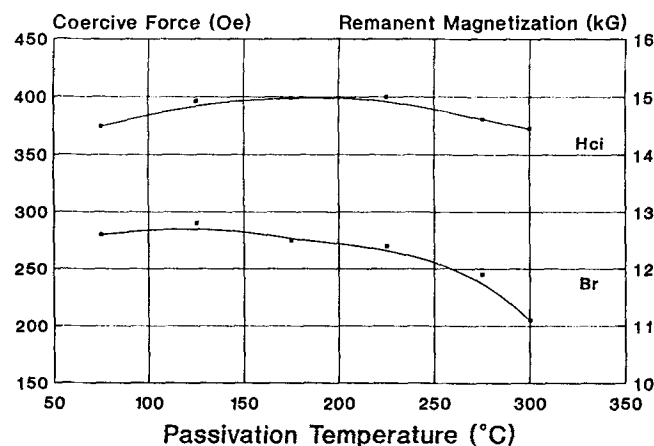


Fig. 5 Influence of passivating temperature on coercive force (*Hci*) and remanent magnetization (*Br*) of Nd-Fe-B powder passivated with N₂ for 1 min.

ment of the powder in a magnetic field, as illustrated in Fig. 12 and 13.

For powders passivated with carbon dioxide, the alignment of the (006) crystalline plane (P_{006}) increased with temperature and exhibited a maximum level when passivated at 175 °C (Fig. 12). Increasing the temperature resulted in a decrease in alignment of the (006) crystalline plane and a corresponding increase in the alignment of various other planes.

When passivated with nitrogen, the maximum alignment of the (006) crystalline plane was obtained when the powder was passivated at a temperature of 125 °C. Passivating at temperatures in excess of 125 °C resulted in a decrease in alignment of the (006) crystalline plane and a rapid increase of various other planes. See Fig. 13, in which alignment factors are plotted on a logarithmic scale.

3.2 Corrosion Testing

The weight gain of powders exposed to laboratory air and a humid environment increased rapidly during the first 2 h of exposure and then increased at a reduced rate (Fig. 14 and 15).

However, the weight gain of AQUANIDE-processed powder (Fig. 15) was considerably less than that experienced by the conventionally produced powder (Fig. 14). Note that the maximum value of the ordinate in Fig. 15 is more than ten times lower than that in Fig. 14.

A comparison of the weight gain results for powders exposed to laboratory air and a high-humidity atmosphere shows that conventionally processed powder exhibits a greater susceptibility to corrosion than the AQUANIDE-processed powder. The influence of exposure temperature and time on coercive force (*Hci*) and remanent magnetization (*Br*) of both

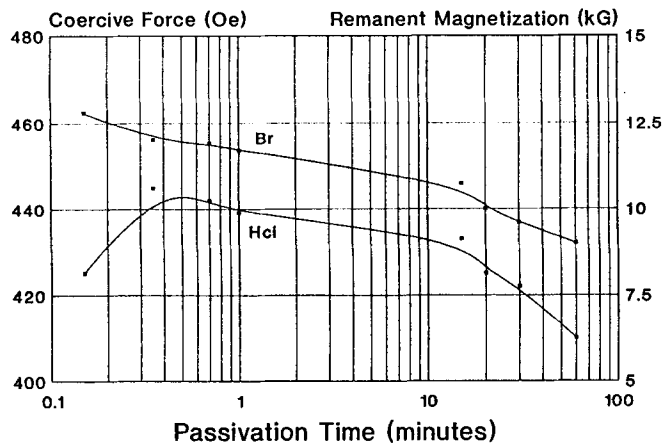


Fig. 6 Influence of passivating time on coercive force (H_{ci}) and remanent magnetization (Br) of Nd-Fe-B powder passivated with CO_2 at $175^\circ C$.

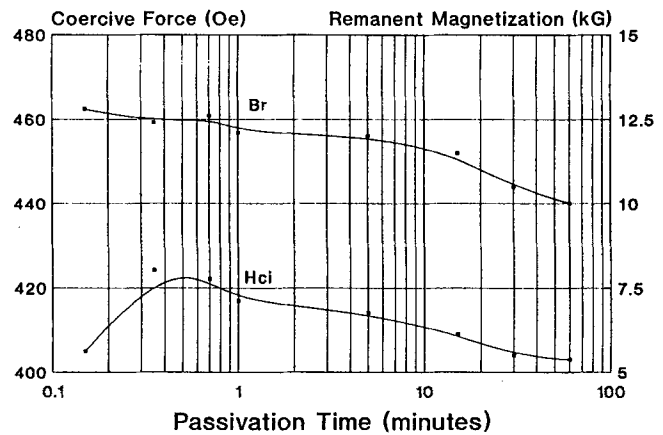


Fig. 7 Influence of passivating time on coercive force (H_{ci}) and remanent magnetization (Br) of Nd-Fe-B powder passivated with N_2 at $225^\circ C$.

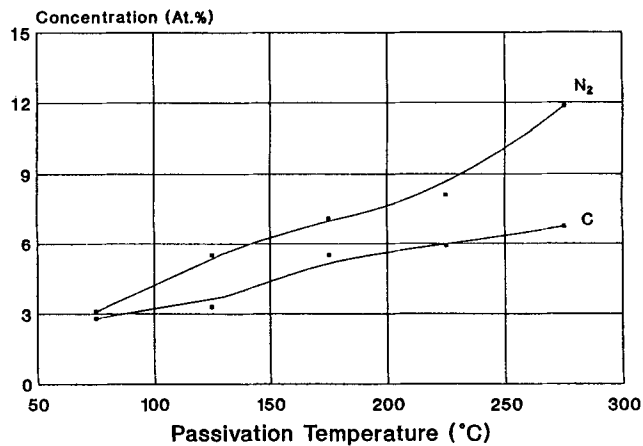


Fig. 8 Influence of passivating temperature on nitrogen and carbon concentration in the surface layer of the Nd-Fe-B powder particles.

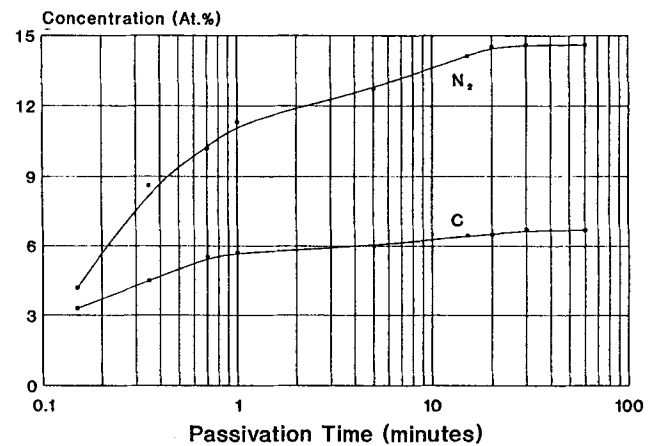


Fig. 9 Influence of passivating time on nitrogen and carbon concentration in the surface layer of the Nd-Fe-B powder particles passivated at 225 and $175^\circ C$, respectively.

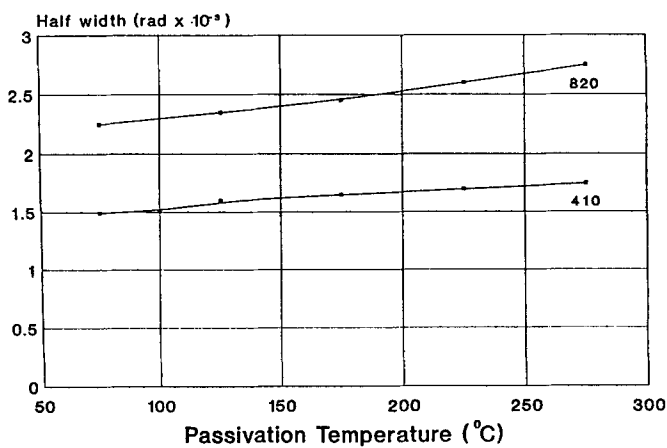


Fig. 10 Variation in half widths of (410) and (820) diffraction peaks versus passivation temperature for powder passivated with CO_2 .

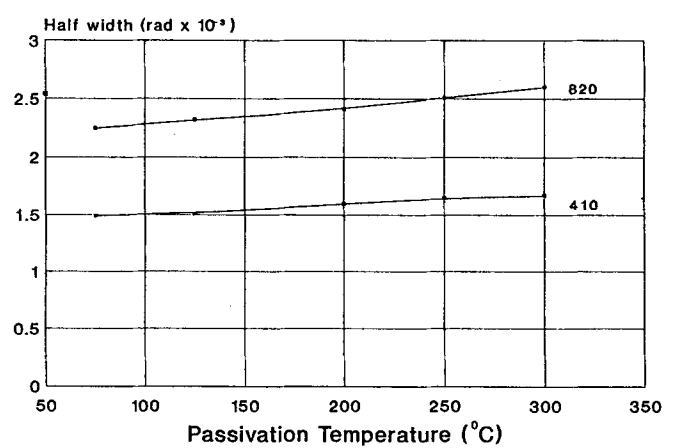


Fig. 11 Variation in half widths of (410) and (820) diffraction peaks versus passivation temperature for powder passivated with N_2 .

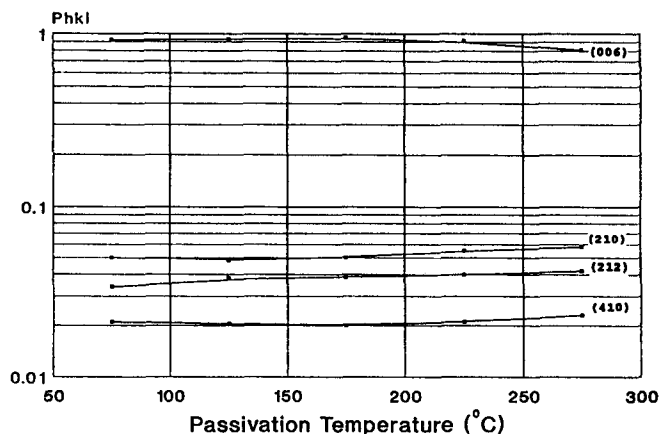


Fig. 12 Alignment factors of crystalline planes versus passivating temperature for Nd-Fe-B powder passivated with CO₂.

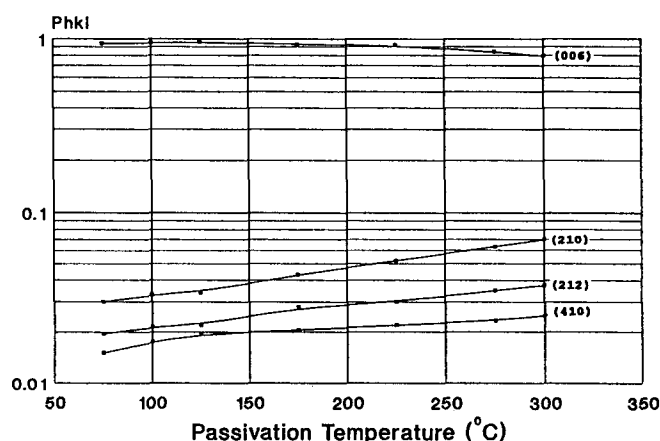


Fig. 13 Alignment factors of crystalline planes versus passivating temperature for Nd-Fe-B powder passivated with N₂.

conventionally processed and AQUANIDE-processed powders is shown in Fig. 16 and 17, respectively.

When the conventionally processed powder was exposed to laboratory air, both coercive force and remanent magnetization decreased rapidly during the initial hours of exposure. Over the full exposure time, the conventionally produced powder lost 60 to 83% of its initial coercive force and 75 to 95% of the initial remanent magnetization (Fig. 16a and 17a). A more rapid loss of properties was observed when the conventionally processed powder was exposed to conditions of high humidity (Fig. 16b and 17b). The AQUANIDE-processed powder showed a similar trend. However, the decrease in properties for AQUANIDE-processed powder was not as severe as for the conventionally processed powder (Fig. 16 and 17).

The improved corrosion resistance of the AQUANIDE-processed powder reduces the rate of property degradation. This reduced rate, combined with the superior initial properties, results in magnetic properties at the end of the exposure tests that are comparable to the properties of the conventionally processed powder before exposure.

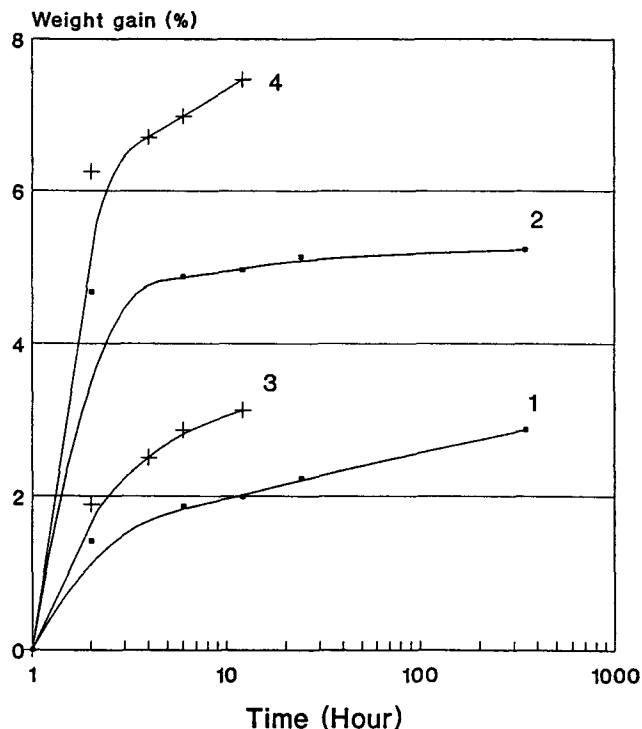


Fig. 14 Weight gain versus time for conventional powder exposed to: laboratory air at (1) room temperature and (2) 175 °C; and to high relative humidity at (3) room temperature and (4) 75 °C.

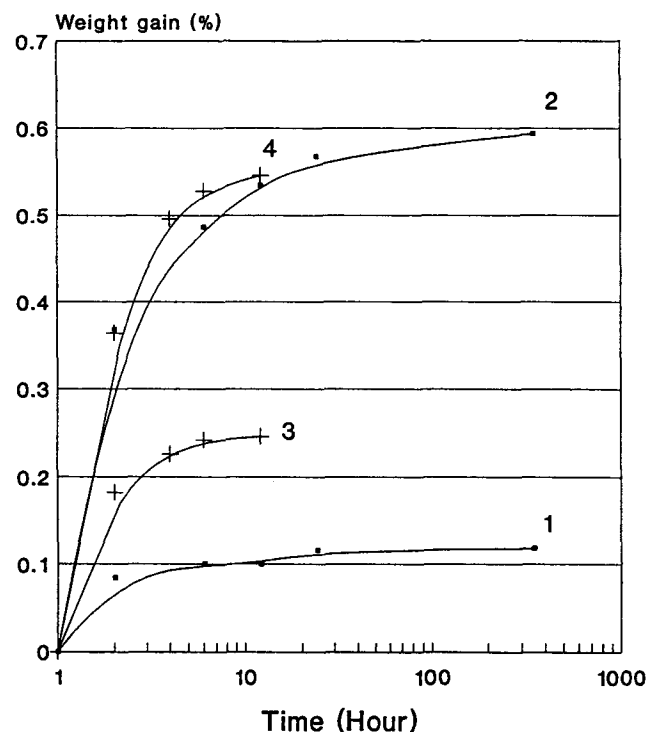


Fig. 15 Weight gain versus time for AQUANIDE-processed powder exposed to laboratory air at (1) room temperature and (2) 175 °C; and to high relative humidity at (3) room temperature and (4) 75 °C.

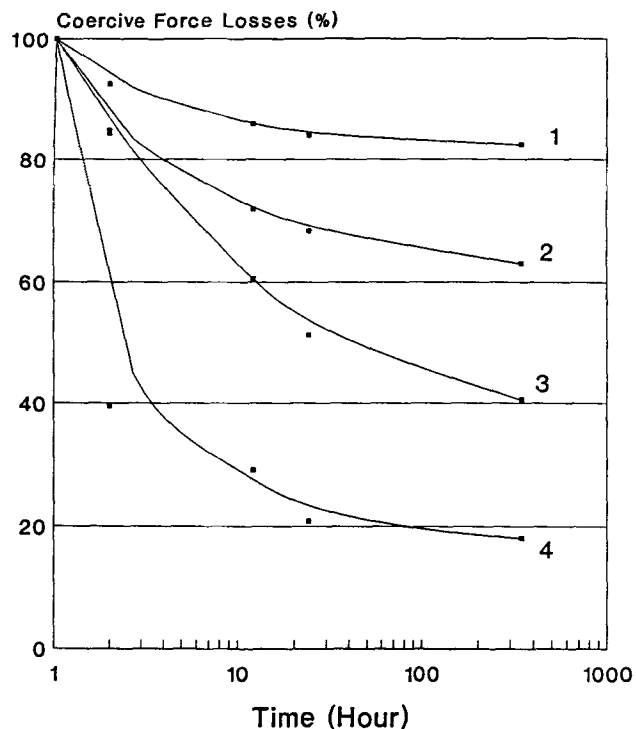


Fig. 16(a) Coercive force losses of powders exposed to laboratory air. AQUANIDE-processed powder at (1) room temperature and (2) 175 °C. Conventional powder at (3) room temperature and (4) 175 °C.

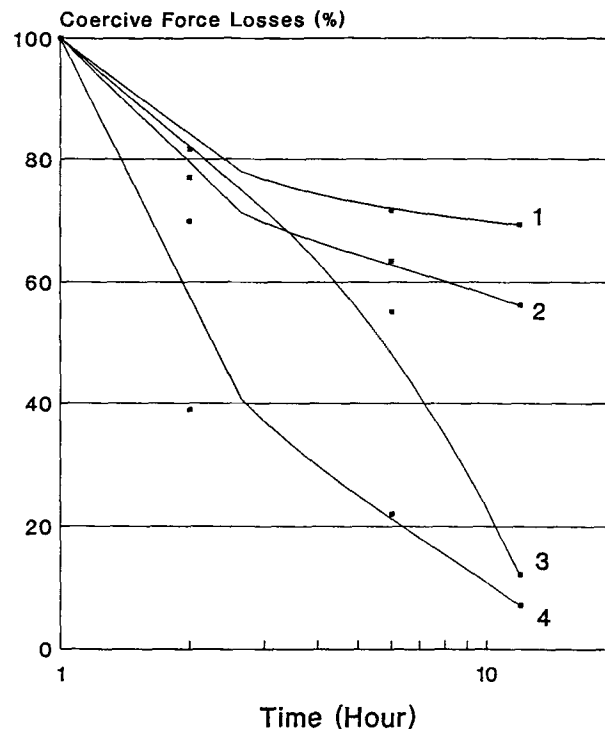


Fig. 16(b) Coercive force losses of powders exposed to high relative humidity. AQUANIDE-processed powder at (1) room temperature and (2) 75 °C. Conventional powder at (3) room temperature and (4) 75 °C.

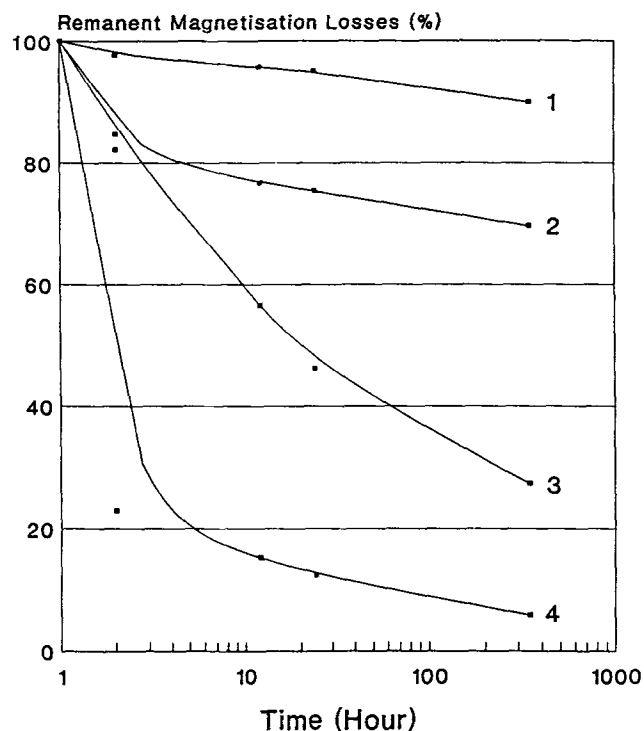


Fig. 17(a) Remanent magnetization losses of powders exposed to laboratory air. AQUANIDE-processed powder at (1) room temperature and (2) 175 °C. Conventional powder at (3) room temperature and (4) 175 °C.

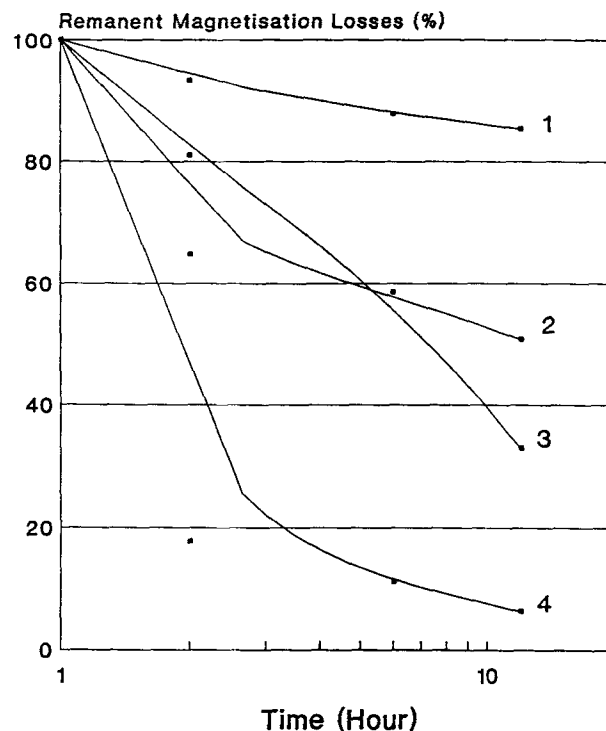


Fig. 17(b) Remanent magnetization losses of powders exposed to high relative humidity. AQUANIDE-processed powder at (1) room temperature and (2) 75 °C. Conventional powder at (3) room temperature and (4) 75 °C.

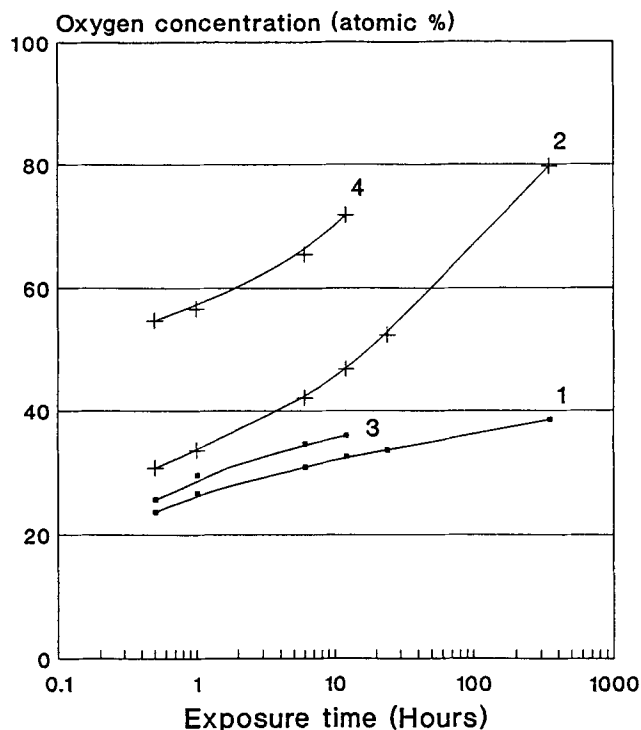


Fig. 18 Oxygen concentration on surface of powders exposed at 25 °C to laboratory air: (1) AQUANIDE and (2) conventional. Exposed at 25 °C to high relative humidity: (3) AQUANIDE and (4) conventional.

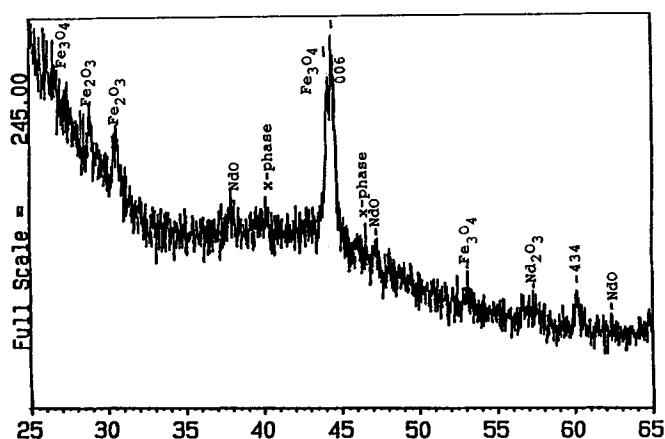


Fig. 19 X-ray diffraction pattern of conventional $\text{Nd}_2\text{Fe}_{14}\text{B}$ powder aligned in magnetic field after 12-h exposure to high relative humidity at room temperature.

The low weight gain and reduced losses of magnetic properties during exposure of the AQUANIDE-processed powder are due to the existence of a protective, passive layer on the surface of the powder particles. The conventionally processed powder does not have this protective layer.

The oxygen content on the surface of both the conventionally processed powder and the AQUANIDE-processed powder increased during exposure to both dry and humid environments

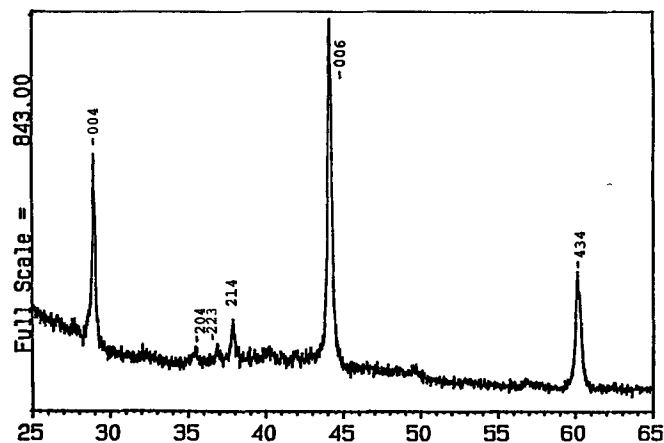


Fig. 20 X-ray diffraction pattern of AQUANIDE $\text{Nd}_2\text{Fe}_{14}\text{B}$ powder aligned in magnetic field after 12-h exposure to high relative humidity at room temperature.

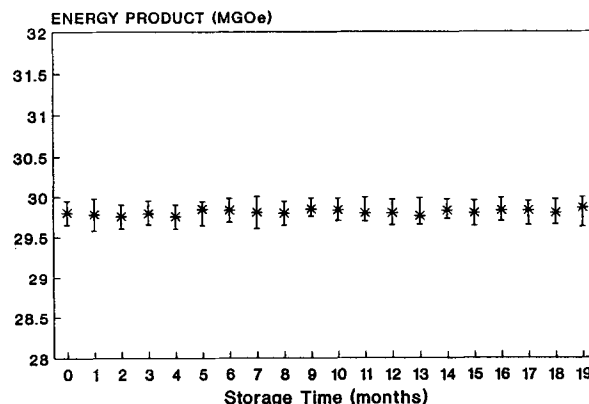


Fig. 21 Energy product of magnets made from powder milled up to 19 months prior to compacting and sintering.

(see Fig. 18). The humid atmosphere produced a greater increase in oxygen concentration in both powders. However, the increase in oxygen in the AQUANIDE-processed powder was not as great as that observed in the conventionally processed powder.

Exposure of the conventionally processed powder to a laboratory air atmosphere at room temperature resulted in the development of additional phases. X-ray diffraction results identify those phases as Nd_2O_3 , Fe_2O_3 , and NdO (Fig. 19). Diffraction patterns obtained from AQUANIDE-processed powder aligned in a magnetic field exhibit fewer peaks, corresponding to the Nd-Fe-B phase, that were well defined and of much greater intensity (Fig. 20).

AQUANIDE-processed powder may be stored in a laboratory environment for extended periods with little loss of magnetic properties. Magnets compacted and sintered up to 19 months after milling exhibited no appreciable loss in magnetic properties when compared to magnets compacted immediately after milling of the powder (Fig. 21).

4. Conclusions

4.1 *Conventionally Processed Powder*

During exposure to the dry and humid environments, conventionally processed powder developed oxide phases that increased the weight of the powder. The oxide phases developed as a result of the chemical reaction between neodymium and iron and oxygen absorbed from the surrounding atmosphere.

4.2 *AQUANIDE-Processed Powder*

The AQUANIDE-processed powder developed a small amount of oxide phase on the surface of the powder particles, slightly reducing the alignment in a magnetic field. The powder has a very low susceptibility to corrosion, and the magnetic properties remain stable over an extended period of time. Magnets made from AQUANIDE powder that had been stored in a

normal laboratory air atmosphere for extended periods of time showed no appreciable degradation in magnetic properties.

The results of this study clearly demonstrate the superior corrosion resistance of AQUANIDE-processed Nd-Fe-B powder compared to conventionally processed material.

Acknowledgments

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Reference

1. Y. Bogatin, D. Li, M. Robinson, and P. Behan, Magnetic Properties of and Crystal Structure of Nd-Fe-B-C/N Powder and Magnets, *Advances in Powder Metallurgy*, Vol 5, MPIF, Princeton, NJ, 1991, p 195-207