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ALUMINUM SUBSTITUTIONS IN ND-FE-B SINTERED MAGNETS

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ABSTRACT

A microstructural and microanalytical study of aluminum substituted Nd-Fe-B sintered permanent magnets were carried out to determine the effect, if any, of aluminum on structure, composition, and magnetic properties, particularly on the observed increase in coercivity. It was found that Al enrichment occurred in the Nd-rich phase at the grain boundaries. The possible role(s) of this enrichment on the observed coercivity increase are discussed.

INTRODUCTION

Ever since its introduction about three years ago, the Nd-Fe-B ternary system has made a big impact on the permanent magnet industry. [1] Since then, many alloying substitutions have been carried out in hopes of increasing this system's magnetic properties. One of the most prominent substitutional elements for increasing the coercivity is aluminum. [2,3] In an effort to

explain this effect, two Nd-Fe-B permanent magnet alloys were prepared in identical fashion, except that 2 at.% Al was substituted for B in the second alloy (see Table 1). Both alloys were also given the same, optimizing post-sintering heat treatments, after which the magnetic properties were measured. As clearly shown, the Al-substituted alloy has a 25% increase in coercivity, with only a 3% decrease in saturation magnetization, relative to the standard Nd-Fe-B alloy.

This dramatic coercivity increase can be partially attributed to the increase in anisotropy field (H_A) in Al-substituted Nd-Fe-B magnets, where Al substitutes for Fe in the $\text{Nd}_2\text{Fe}_{14}\text{B}$ hard magnetic phase. [2] If the expected coercivity increase is scaled by the increase in anisotropy field

Table I

Processing Conditions and Magnetic Properties of Alloys Studied

Alloy Composition	Post-Sintering Heat Treatment	B Sat [Tesla]	Coercivity [kA/cm]
$\text{Nd}_{14}\text{Fe}_{78}\text{B}_8$	950°C/1 hr, slow cooling to 630°C/1hr, rapid cooling to RT	1.28	6.9
$\text{Nd}_{14}\text{Fe}_{78}\text{B}_6\text{Al}_2$	"	1.24	8.6

alone, using values of H_A from Young et. al., it is possible to determine to a first approximation the contribution of the anisotropy field to the coercivity increase. As shown in Fig. 1, these expected coercivities are far below the measured coercivity, leading to the conclusion that Al-induced structural or compositional changes are the primary reason for the coercivity increase. In order to investigate such possible changes, the structure of the two alloys in Table 1 were carefully compared. The microstructure of the standard Nd-Fe-B alloy has been determined previously. [4,5] This microstructure consists primarily of two phases, viz, large nearly perfect grains about 10

μm in diameter of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ hard magnetic phase, surrounded by a highly defective fcc Nd-rich phase, which extends from the grain boundaries to the grain junctions. This Nd-rich phase also contains about 20 at.% oxygen, 10 at.% iron, and no boron. Trace amounts of the tetragonal boride phase NdFe_4B_4 was also found intragranularly. The Al-substituted alloy was then compared to this "standard" alloy, from both microstructural and microanalytical viewpoints.

EXPERIMENTAL

The magnets were prepared from powdered alloys which were magnetically aligned, pressed, then sintered at 1070°C for one hour. After sintering, they were cooled rapidly and annealed as shown in Table 1. The magnetic properties were measured at room temperature with a Foner sample magnetometer. X-ray diffraction with $\text{Cu K}\alpha$ radiation was carried out on bulk magnets, which were mechanically polished with sub-micron diamond paper.

Transmission electron microscope (TEM) specimens were prepared by mechanically thinning a $250\ \mu\text{m}$ disk to thicknesses of around $100\ \mu\text{m}$, followed by dimpling to around $20\ \mu\text{m}$. They were then argon ion-milled to electron transparency. Precautions were taken to reduce and identify specimen preparation artefacts as discussed in an earlier paper. [5] The specimens were examined in a Philips 400 TEM/STEM fitted with a Be window energy dispersive (EDS) detector operating at 100 kV, and a JEOL 200CX TEM/STEM fitted with an ultra-thin window EDS detector operating at 200 kV.

In order to detect the low aluminum concentrations, each EDS spectra contained a minimum of 100,000 counts, and over 50 spectra were taken to confirm the observed trends. Quantification was carried out using the system k-factors, which were checked against the standard $\text{Nd}_2\text{Fe}_{14}\text{B}$ matrix phase.

RESULTS/DISCUSSION

As shown in Fig. 2, there is essentially no difference between the x-ray diffractograms of the standard Nd-Fe-B and the Al-substituted Nd-Fe-B alloys. The similarity of these diffractograms has three important implications:

- a) No precipitation of a new phase has been induced by the Al-substitution.
- b) The hard magnetic phase 2:14:1 is essentially the same in both alloys, with no detectable changes in lattice parameter.
- c) The similarity of the minor peaks which may be indexed as arising from the Nd-rich and NdFe_4B_4 phases indicate that both phases are still present, and are not altered by the Al-substitution.

As shown in Fig. 3, the general microstructure of the Al-substituted magnet is also essentially the same: namely, large nearly perfect grains about 10 μm in diameter of the tetragonal 2:14:1 hard magnetic phase, surrounded by an fcc grain boundary phase that extends into the grain junctions. To compare the composition of the grain boundary and matrix phase in the Al-substituted alloys, typical EDS spectra from the two regions are superimposed as shown in Fig. 4. The usual Nd-enrichment of the grain boundary phase is also observed in these alloys, along with an Al enrichment, as shown in Fig. 4(b). If a line analysis is done across a grain junction region by taking point analyses along a line with a 200 $\text{\AA}$ probe, as schematically illustrated in Fig. 5, a composition profile across the Nd-rich phase is obtained as shown in Fig. 6. This profile clearly illustrates the Al-enrichment at the grain boundary phase.

Some comments on the EDS data need to be made here. First, when trying to detect an element that is less than 1 wt.% of the nominal composition, great care must be exercised in carrying out the experiment. A large number of counts must be collected so that the signal peak can be clearly distinguished from the background. This requires high count rates, long counting times, and an extremely low system background. Secondly, for highly absorbed x-rays such as Al, quantification must be carefully done. Factors such as the relative absorption of the different phases due to differences in composition and thickness must be accounted for. Finally, the detected Al concentration was fairly inhomogeneous throughout each specimen in both the Nd-rich and matrix phases. Consequently, many specimens and many regions within each specimen were analyzed before the observed Al enrichment in the Nd-rich phase was acknowledged.

Given that the primary microstructural change induced by the Al-substitution is the enrichment of Al in the Nd-rich phase, the next logical consideration is how the Al enrichment increases the coercivity. Burzo et. al. have considered the possibility that Al increases the fluidity of the Nd-rich phase during sintering, leading to greater magnetic isolation, and consequently higher coercivities through more effective coating of the matrix grains. The resulting thinner Nd-rich phase would also be more effective at pinning the domain walls. [3] Alternatively, Ramesh et. al. have proposed that oxygen de-adsorption at the matrix/grain boundary interface during post-sintering heat treatments is important for high coercivity. This de-adsorption process may be greatly facilitated by Al enrichment in the Nd-rich phase. [6] Although both suggestions are plausible, much more work needs to be done before the role of Al can be completely understood.

CONCLUSION

In conclusion, the Al-induced compositional changes at the grain boundaries are believed to be the primary reason for the coercivity increase. No major changes were observed in either the crystal structure/lattice parameter of the hard magnetic 2:14:1 phase, nor the general microstructure of the magnet.

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Figure Captions

- Fig. 1. Comparison of measured coercivity increase with predicted increase from variations in anisotropy field with x in $\text{Nd}_2(\text{Fe}_{1-x}\text{Al}_x)_{14}\text{B}$. H_A values are based on measurements by Young et. al. [2]
- Fig. 2. X-ray diffractograms from both the standard Nd-Fe-B and Al-substituted Nd-Fe-B sintered magnets.
- Fig. 3. General microstructure of the Al-substituted Nd-Fe-B sintered magnet.
- Fig. 4. (a) Superimposed EDS spectra from both the Nd-rich and matrix phases in the Al-substituted Nd-Fe-B sintered magnet.
(b) Same as (a), except for a vertical magnification.
- Fig. 5. Schematic illustration of an EDS concentration profile across a Nd-rich phase.
- Fig. 6. (a) Concentration profile across the Nd-rich phase of the Al-substituted Nd-Fe-B sintered magnet. Arrows mark the the interface.
(b) Same as (a), except for a vertical magnification.

Microstructural vs. Anisotropy Field
Contribution to Coercivity Increase

Variation of coercivity with x in $\text{Nd}_2(\text{Fe}_{1-x}\text{Al}_x)_{14}\text{B}$.

Note: Predicted values are based on anisotropy field contributions only, using measurements by Y. C. Yang, W. J. James, et. al.

XBL 874-1780

XBL 874-1714

XBB 874-3148

13-Apr-1987 16:28:45

NATIONAL CENTER for ELECTRON MICROSCOPY

H-AL01 #8 vs H-AL03 #8

Preset= 100 secs

Vert= 1913 counts Disp= 1 Comp= 3

Elapsed= 100 secs

XBL 874-1712

13-Apr-1987 16:42:46

NATIONAL CENTER for ELECTRON MICROSCOPY

H-AL01 #8 vs H-AL03 #8

Vert= 200 counts Disp= 1

Comp= 3

Preset= 100 secs

Elapsed= 100 secs

*

XBL 874-1711

SCHEMATIC ILLUSTRATION OF EDS
CONCENTRATION
PROFILE ACROSS ND-RICH PHASE

XBL 874-1756

Concentration Profile Across Nd-Rich Phase

(a)

(b)

XBL 874-1713

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