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Intergranular Phases and Coercivity in Nd-Fe-B Magnets

Frank P. Missell*
Instituto de Física, Universidade de São Paulo
Caixa Postal 20516, 01498-970 *São Paulo, SP, Brasil*

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The Nd-rich material which occurs in the intergranular regions of sintered Nd-Fe-B magnets is important in the liquid phase sintering process and also serves to magnetically isolate the $Nd_2Fe_{14}B$ grains. In ternary magnets, this material consists of several phases, one of which may be the metastable, ferromagnetic phase referred to as A_1. This phase also occurs in binary Nd-Fe and other alloys. This paper discusses the magnetic and structural properties of A1 and discusses its role in the coercivity of NdFeB magnets. Annealing A_1 in binary alloys transforms it into a new intermetallic compound Nd_5Fe_{17}, whose properties are also discussed. Additions of Al, Cu, Ga, V, Nb, and other elements to ternary magnets result in the formation of new intergranular phases whose influence on the coercivity can be quite remarkable.

I. Introduction

Sagawa et al.[1] at the Sumitomo Special Metals Co. initially reported the fabrication of permanent magnets based on the $Nd_2Fe_{14}B$ phase via a powder metallurgy process. Croat et al.[2] at General Motors also reported high performance Nd-Fe-B permanent magnets produced by melt-spinning. Compounds such as $R_2Fe_{14}B$ possess a tetragonal structure and, at room temperature, the easy magnetization direction is the tetragonal axis. Thus, the outstanding properties of these magnets are due to the high saturation magnetization and magnetocrystalline anisotropy of the $Nd_2Fe_{14}B$ phase.

The world-wide Nd-Fe-B magnet industry which has grown up since 1984 is based almost entirely on the powder metallurgy process patented by Sumitomo. After grinding the alloy and alligning the powder in a magnetic field, the green compacts are typically sintered for one hour around 1080°C and then rapidly quenched. To develop high coercivity values, the as-sintered magnets are heated for one hour at 600°C. The increase in H_c after this 600°C heat treatment can be seen in Figure 1 for a magnet of composition Nd-73.5at%Fe-6.5at%B. One of the important questions concerning these magnets is the nature of the changes which take place during this heat treatment, thereby giving rise to the observed coercivity increase.

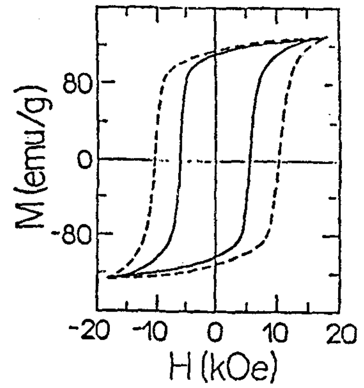

Figure 1.: M vs. H for sintered Nd-73.5at.%Fe-6.5at.%B magnets. Solid curve corresponds to magnet sintered 1h/1040°C; dashed curve was sintered 1h/1040°C and annealed 1h/600°C. [From Ref. 10].

In this respect, attention has been focused on both the surfaces of the $Nd_2Fe_{14}B$ grains and on the Nd-rich intergranular regions. Depending upon the composition of the magnet, the Nd-rich intergranular region may constitute up to 10% of the magnet volume. It possesses a composition close to that of the binary eutectic[3]. During sintering, this material is in the liquid phase and aids in reconstituting the surfaces of $Nd_2Fe_{14}B$ grains. Since this region is highly susceptible to corrosion, it is desirable to limit its volume. The phases which occur in this part of the magnet may affect magnetization reversal, as will be discussed below.

The coercive field H_c of rare earth permanent magnets has frequently been treated in terms of a phenomenological equation[4,5] :

$$H_c = \alpha H_A - N_{eff} M_s \tag{1}$$

In this equation H_A is the anisotropy field and M_s the saturation magnetization. N_{eff} is an effective demagnetizing coefficient which takes into account the self-demagnetizing field of each grain as well as the demag-

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*Present address: Laboratoire Louis Néel, CNRS, B.P. 166, 38042, Grenoble Cedex, France.

netizing fields of the neighboring grains. The coefficient α describes the reduction in the anisotropy field due to microstructural effects[5]. This equation was used, for example, by Sagawa and Hirosawa[6] to study the effect of the 600°C heat treatment on the coercive field. These authors observed an increase in α and a reduction in N_{eff} upon annealing and attributed these changes to a smoothing of the $Nd_2Fe_{14}B$ grain surfaces. The elimination of sharp corners along grain boundaries would thus give rise to a microstructure similar to that of the ideal microstructure shown in Figure 2. Transmission electron microscopy (TEM) appears to show a smoothing of the grain surfaces and apparently is consistent with these conclusions.

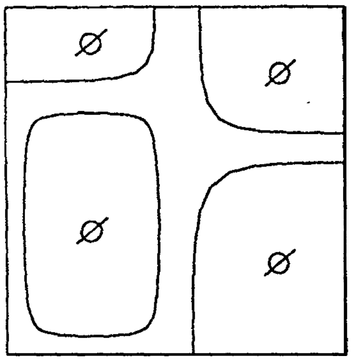

Figure 2.: Ideal microstructure for a Nd-Fe-B magnet where each grain of $Nd_2Fe_{14}B$ (ϕ) is surrounded by Nd-rich material. [From Ref. 43].

It is worth remembering, however, that TEM investigations are very dependent upon sample preparation and the Nd-rich intergranular regions may give rise to artefacts due to sample oxidation[6]. In fact, Hiraga et al.[7] reported the observation of a nonequilibrium bcc phase along the grain boundaries in sintered Nd-77at.%Fe-8at.%B magnets. This phase, assumed to be magnetically soft, would reduce the nucleation field at the grain boundaries. Later, however, it was claimed[8,9] that the bcc phase was an artefact produced during the ion thinning of the sample.

Another approach to understanding the grain boundary region has involved the study of eutectic alloys[10] whose composition is very close to that of the Nd-rich intergranular material encountered in Nd-Fe-B magnets. Thus Schneider et al.[10] reported a coercive field $H_c = 3.9$ kOe in an as-cast alloy of composition Nd-15at%Fe-5at%B and attributed this to a metastable ferromagnetic phase (A_1) with $T_c = 245°C$. This composition is very close to that of the material found in the intergranular regions. Although the A_1 phase is magnetically hard, it is softer than the $Nd_2Fe_{14}B$ phase. After annealing for 2 h at 600°C, they found $H_c = 14.1$ kOe. Subsequent investigation[11] showed that the metastable A_1 phase had been transformed into $Nd_2Fe_{14}B$ by the annealing. Schneider et al.[10,12] thus attributed the beneficial effect of the 600°C anneal in commercial magnets to the elimination of the metastable ferromagnetic A_1 phase from the intergranular regions. The process by which a relatively soft ferromagnetic phase can aid magnetization reversal in a harder phase is illustrated in Figure 3.

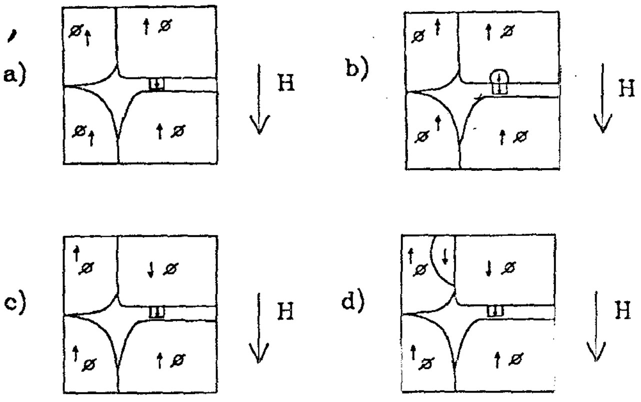

Figure 3.: a) Magnetization reversal in a soft ferromagnetic phase in the intergranular region due to the magnetic field H; b) nucleation of a domain in the direction of H in a grain of Φ ($Nd_2Fe_{14}B$); c) propagation of this domain throughout the grain; d) magnetization reversal in a neighboring Φ grain. [From Ref. 43].

In the studies of the eutectic alloys, it is important to demonstrate that the phenomena observed in the alloy are representative of those occuring in real magnets. This essentially involves the extrapolation of the experimental results to the limit in which the Nd-rich alloy is a small fraction of the magnet under study. It is difficult to observe the A_1 phase in real magnets. The most significant result was obtained by Nozières[13] for a magnet of composition Nd-73.5at.%Fe-5.5at%B. For the as-sintered Nd-rich (21at.%) magnet, measurements perpendicular to the alignment direction of the magnet showed a $T_c = 245°C$ (A_1 phase) as well as $T_c = 310°C$ ($Nd_2Fe_{14}B$). After annealing the magnet at 600°C for one hour, the coercivity of the magnet had increased from 2.7 kOe to 8.5 kOe and the magnet showed a small Curie event at 237°C. This result indicates that the nature of the intergranular material had changed during the annealing process. Microstructural evidence of a similar kind was obtained by Landgraf[14]. He presented micrographs showing intergranular phases in a Nd-rich magnet. After annealing at 600°C for one hour, the micrographs showed that these intergranular phases had disappeared.

Other researchers have shown that it is possible to modify magnet properties by modifying the intergranular regions. Tenaud et al.[15,16] showed that it is possible to obtain substantial improvements in coercivity and corrosion resistance by adding specific combinations of V, Co, and Al to ternary magnets. The V inhibits grain growth and leads to the formation of V-rich borides $V_{3-x}Fe_xB$, which result in the elimination of soft magnetic impurity phases. The corrosion resistance of the magnets is greatly improved by the V addition, which stabilizes the Nd-rich intergranular region. Theoretical treatments of exchange-coupling of hard magnetic grains by a softer magnetic phase have recently been given[17]. Similar results are obtained by Mo addition[17]. Another important case where the modification of intergranular phases results in improved coercivity is in PrFeBCu magnets, which can be produced by casting and hot working. Kajitani et al.[18] showed that a 2 hour anneal at 480°C results in a drastic improvement in coercivity when the antiferromagnetic $Pr_6Fe_{13}Cu$ phase is formed in the grain boundary. An extensive series of tetragonal compounds $R_6Fe_{13}M$ (M = Cu, Al, Ag, Sn, Pb, SE, Bi,....) may be formed with largely compensated magnetic structures. These are thought to have beneficial effects on coercivity when they occur in permanent magnets.

The remainder of this paper will be concerned with the properties of the metastable A_1 phase as well as those phases which may be formed from it upon annealing (Nd_5Fe_{17}, $Nd_6Fe_{13}Al$).

II. Properties of the Metastable A_1 Phase

Magnetic measurements on as-cast Nd-rich binary Nd-Fe alloys reveal the presence of a hard magnetic phase with $T_c = 245°C$ and $H_c \approx 5$ kOe. Micrographs[19] show the presence of primary Nd and a very fine ($\approx 1\mu m$) A_1 + Nd eutectic. The high coercivity of approximately 4.5 kOe in neodymium-rich Nd-Fe alloys, reported for the first time in 1935 [20], can be explained as being due to the magnetically hard A_1 phase, with a small grain size, embedded in a non-ferromagnetic neodymium matrix. Samples which have been annealed around 600°C for short periods of time show different eutectic microstructures, which, however, present the same T_c value. Results to be presented below show that these different morphologies all possess the same Mossbauer spectrum, suggesting, therefore, that they all correspond to the same phase. As-cast Nd-rich ternary Nd-Fe-B alloys also show the presence of a eutectic microstructure[10,19] similar to that found in as-cast binary alloys and magnetic measurements show that the magnetic phase has $T_c = 245°C$. This led to the suggestion that the ternary eutectic microstructure is also A_1. Later re-examination of the ternary phase diagram[3,14] showed that the solidification of ternary alloys may terminate in or near the binary eutectic, thus explaining how the A_1 phase could appear in both binary and ternary alloys.

Because of the very fine eutectic microstructure, it has been extremely difficult to study the structure or determine the composition of the A_1 phase. One recent neutron diffraction study[21] of A_1 has reported the existence of structural correlation at a distance of 25 Å, suggesting an amorphous or nanocrystalline phase. However, recent Mössbauer results[22] are consistent with a description of A_1 in terms of a crystalline phase. Attempts to measure the composition of this phase have also been hindered by the fact that the regions corresponding to A_1 in the A_1 + Nd eutectic are about the same size as the resolution of the EDS measurement. Be that as it may, EDS measurements of A_1 platelets[3] showed ≈ 34 at% Nd and no Al contamination. This value for Nd is similar to that found by Grieb et al.[23] for the μ phase in the Nd-Fe-Al system and similar to the value (33at%) found by Schneider et al.[24] in the feathery eutectic of DTA samples. Givord et al.[25] presented an analysis from magnetic measurements suggesting that the composition of A_1 corresponds to 31at% Nd. Thus there is rough agreement about the composition even though the structure is still uncertain.

As was mentioned previously, the maximum coercive field observed for the A_1 phase is about 5 kOe. The room temperature saturation magnetization of this phase has been estimated[25] to be 150 emu/g. The temperature dependence of the anisotropy field H_A was measured for Nd-xat%Fe ($2.5 < x < 40$) alloys by the singular point detection (SPD) technique[26] and the room temperature value of $H_A = 19$ kOe was found for a Nd-20 at%Fe alloy. The room temperature Mossbauer spectra[22] of an as-cast and an annealed A_1 sample is shown in Figure 4. These spectra were fit with four magnetically split subspectra and the fitting parameters are given in Ref. 22. The great similarity between these spectra suggests that the Fe atoms have the same local environments in both the as-cast and annealed alloys. This suggests that the different morphologies of A_1 actually correspond to the same phase. It is worth commenting also on one of the subspectra with an exceptionally large hyperfine field ($B_{hf} = 339$ kG.) which gives rise to the well-resolved line at ≈ 6 mm/s. This subspectrum - characterized by a B_{hf} largely exceeding the average, a positive isomer shift, and a large quadrupole shift, but having a small linewidth - obviously corresponds to a well-defined crystallographic site. The same features are also encountered in R_2Fe_{17} compounds, in which they characterize the "dumbbell" Fe sites. This coincidence leads us to believe that the present phase might have some structural elements in common with Nd_2Fe_{17}.

We have included in Figure 4 the Mössbauer spectrum of a Nd-58at%Fe-5at%Al alloy, annealed at 600°C for 20 days to produce the ternary μ phase. These spectra were recalculated to display only the characteristics of the main ferromagnetic phase. The similarity with the other two spectra cannot be overlooked. In particular, the dumbbell-like subspectrum (here with $B_{hf} = 320$kG) is clearly present. It is tempting to assume that the A_1 phases described here are identical

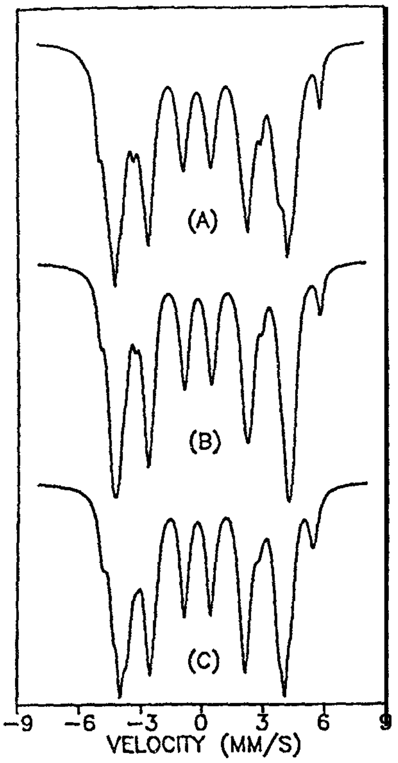

Figure 4.: Room temperature Mössbauer spectra, recalculated with fitted hyperfine parameters of main ferromagnetic phase only (A) as-cast Nd-27at.%Fe; (B) annealed Nd-20at.%Fe (600°C/2h); (C) μ phase Nd-58at.%Fe-5at.%Al. [From Ref. 22].

or very similar to the μ phase for vanishing Al content. If this is true, the smaller B_{hf} values for the Nd-Fe-Al alloy($< B_{hf} >$=258 kG) are explained by the presence of nonmagnetic Al. This conclusion is consistent with data on composition and microstructure. Delamare et al.[27] recently reported a TEM study of the μ phase of the Nd-Fe-Al system. They found the structure of μ to consist of a long period stacking of planes typical of polytypism. The basal planes showed a diffraction pattern with a sixfold symmetry, characteristic of a two-dimensional hexagonal structure with a = 1. G5 nm. A 12R stacking sequence with c = 15 nm was observed. Further investigations would be desirable to show the structural elements revealed here.

It is important to mention, finally, that A_1 is unstable upon annealing. However, the phase which is stable after annealing is different for binary Nd-Fe and ternary Nd-Fe-B alloys. After annealing binary Nd-Fe alloys containing A_1 at GOO°C for short times (24h) one obtains the new intermetallic compound Nd_5Fe_{17}, which will be discussed in the next section. In ternary Nd-rich alloys containing A_1, short anneals at 600°C transform A_1 into $Nd_2Fe_{14}B$ [11,12]. Schneider et al.[10,12] thus attributed the beneficial effect of the 600°C anneal in commercial magnets to the elimination of metastable A_1 from the intragranular regions.

III. Intermetallic Compounds R_5Fe_{17} (R = Pr, Nd, Sm)

As was mentioned above, short annealings of Nd-rich alloys containing A_1 will result in the formation of a new intermetallic compound Nd_5Fe_{17} [12,28]. This compound has T_c = 230°C, almost no coercivity, and hexagonal P6$_3$/mcm symmetry[29]. It was previously refered to as A_2 by Schneider and coworkers. The Nd and Fe atoms are well separated in this material, forming long columns in a highly anisotropic structure. The new binary phase diagram for Nd-Fe [19] shows that Nd_5Fe_{17} forms peritectically between 770 and 790°C. See Figure 5. It can be obtained from Fe-rich, nearly stoichiometric alloys, after annealing for times up to 2 months[12,28]. The extremely slow formation of this compound explains why it has eluded researchers until recently.

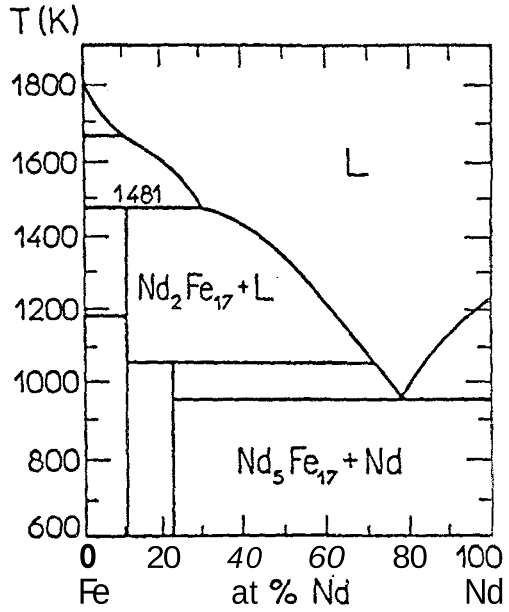

Figure 5.: Revised binary Nd-Fe phase diagram. From [Ref. 19].

On the other hand, the equivalent Pr compound has not been observed[30-32]. However, a recent study of Nd-Pr-Fe alloys[33] has shown that the solubility limit of Pr in the Nd_5Fe_{17} phase corresponds to about $(Nd_{75}Pr_{25})_5Fe_{17}$. Determination of the exact limit is hampered by the fact that samples with higher Pr/Nd ratios have slower formation rates for the 5/17 compound. One can also try to make the 5/17 compound with Sm. A phase with the same structure is observed in sputtered Sm-Fe-Ti samples with coercivities of up to 50 kOe at room temperature[34,35].

The fact that Nd_5Fe_{17} is magnetically soft, while the corresponding Sm compound shows high coercivity, suggests that the magnetic anisotropy in the Nd compound is planar, while that of the Sm alloy is uniaxial. X-ray diffraction measurements on Nd_5Fe_{17} powder which had been aligned in a magnetic field indeed indicate[36] planar anisotropy in Nd_5Fe_{17}. Thus, the appearance of the Nd compound in the intergranular region of a permanent magnet would be prejudicial to coercivity, in general. Recently, however, Wallace and coworkers[37] have reported the *synthesis* and properties of a magnetically hard 5/17 phase in Sm-Fe-Co-Ti sintered magnets.

IV. Other Intergranular Phases

As was mentioned in the introduction, many groups have examined the influence of various dopants on the coercivity of Nd-Fe-B magnets. The effect of the dopants can be divided into two categories, each with similar microstructural features. Both types of dopants increase the coercivity or improve corrosion resistance[38]. The main feature of type-1 dopants (Al, Ga, Cu,...) is the formation of a ternary phase with R and Fe while that of the type-2 dopants is their low solubility in the 2/14/1 phase. The type-2 dopants form ternary Fe-borides which may precipitate within the 2/14/1 grains or may appear as new intergranular phases.

The addition of Al and Ga to permanent magnets has been considered by many groups. Although the addition of Ga is more beneficial than that of Al because the solubility of Ga in the 2/14/1 phase is limited to small values, Al addition will be discussed here because of its widespread use in commercial magnets. Grieb and coworkers[23,39,40] have made extensive studies of the ternary phase diagram Nd-Fe-Al, as well as the properties of the ternary intermetallic compounds referred to as μ and S. The δ phase ($Nd_6Fe_{13}Al$) possesses tetragonal symmetry and a compensated spin structure. Since the solubility of Al in the 2/14/1 phase is relatively low[41], it can reach relatively high concentrations in the intergranular regions of Nd-Fe-B permanent magnets. Knoch et al.[41] estimate the Al concentration in the intergranular region to be 7.5-9 at.% for a magnet whose overall Al concentration is 3 at.%. Politano and coworkers[42,43] have recently studied the addition of Al on the magnetic properties of the A_1 phase in Nd-(20-x)at.%Fe-xat.%Al ($x = 1 - 10$) alloys. When x exceeds 5at.% Al, annealing of the A_1 phase at 600°C results in the formation of the δ phase, which is paramagnetic at room temperature. Thus, it was suggested that the beneficial effect of aluminum in commercial Nd-Fe-B magnets may be due in part to its role in eliminating ferromagnetic intergranular phases.

V. Conclusion

This paper has discussed the magnetic and structural properties of the metastable, ferromagnetic phase referred to as A_1, which occurs in Nd-Fe, Nd-Fe-B, and other Nd-Fe-M alloys. We have insisted that the elimination of this phase from the intergranular region is a possible explanation of the beneficial effect of the 600°C anneal in commercial magnets. Similarly, the improved coercivity observed in magnets which have been doped with various elements seems to have its explanation in the modification of the intergranular phases. There remain, however, many unanswered questions about the detailed nature of the processes under discussion.

Acknowledgments

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