High-Resolution Electron Microscope Study of the Grain Boundary Phase in Rapidly Quenched Nd-Fe-B Permanent Magnet Alloys

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The grain boundary phase in rapidly quenched Nd-Fe-B magnets has been characterized by high-resolution transmission electron microscopy. The grain boundary phase structure is the same in both isotropic and oriented magnets; it is ordered face-centered cubic with a lattice parameter of 5.58 Å. The composition of this phase has not been determined directly, but is most likely a Nd/Fe ratio of 3, with possibly some interstitial B. In both isotropic and oriented magnets, some grain boundaries are completely free of any second phase, and when the grain boundary phase is present, its thickness is highly variable.

1 Introduction

FOR most applications, the best available permanent magnet materials are based on the tetragonal intermetallic compound $Nd_2Fe_{14}B$. These magnets may be prepared in one of two ways: the first is a more or less conventional powder metallurgy process first introduced by Sumitomo Special Metals.[1] Bulk material is reduced to powder in the size range well below 10 μm, and the (single crystal) powder particles are aligned by a strong magnetic field, compressed, sintered, and (usually) heat treated for optimum properties. The second method, introduced by General Motors, starts with rapid solidification of the alloy into a sheet or ribbon that is at least partly amorphous.[2] The ribbon is crushed into polycrystalline flakes that are hot pressed at about 700 °C into a fully dense, fully crystalline isotropic magnet; this material is known as MQ-2 (MQ stands for the trademark name MagneQuench). If MQ-2 is further compressed about 50% in a closed die at about 750 °C, it develops a strong crystallographic texture, with the *c*-axis parallel to the compression axis. This is MQ-3, which is magnetically anisotropic, with properties similar to those of aligned sintered magnets.

The ductility of the NdFeB magnets at the hot deformation temperature is surprising, because $Nd_2Fe_{14}B$ is an intermetallic compound, brittle at room temperature, with a melting temperature above 1100 °C. Single crystals of the compound are brittle to at least 900 °C,[3] and no dislocations are observed in either the oriented or nonoriented magnets.[4] Previous work has suggested that this ductility depends on the presence of a low-melting Nd-rich grain boundary phase, combined with the very small grain size of the rapidly quenched alloy.[4,5] Sintered magnets, with much larger grain size, have little ductility at 700 °C. Practical magnets all contain Nd in excess of the stoichiometric amount required for $Nd_2Fe_{14}B$, partly to compensate for preferential oxidation of Nd but partly to ensure the presence of the Nd-rich grain boundary phase.

The authors believe that, at the hot pressing temperature, $Nd_2Fe_{14}B$ dissolves into the liquid grain boundary phase and is transported from unfavorably oriented grains to favorably oriented grains, thus producing the preferred orientation and the change in external shape without plastic deformation of the individual grains. The energy difference between the favorably and unfavorably oriented grains is created by the difference in elastic moduli interacting with the applied stress.

The grain boundary phase in rapidly quenched NdFeB magnets contains less oxygen than the same phase in sintered magnets, because oxygen is picked up during the ball milling operation that precedes sintering. Therefore, oxygen is not a significant component of the grain boundary phase; this is the phase the authors have tried to characterize.

The grain boundary phase is generally much thinner (a few nanometers) in rapidly quenched NdFeB magnets than in sintered magnets. It is therefore difficult to get local information on the grain boundary phase in rapidly quenched NdFeB by conventional transmission electron microscopy (CTEM) using selected area diffraction (SAD), because the diffraction aperture is usually bigger than the thickness of the grain boundary phase. High-resolution electron microscopy (HREM), however, can in principle obtain this local information easily, because the point-to-point resolution can be less than 0.2 nm.

The grain boundary phase structure has been variously reported as bcc, fcc, hexagonal, and amorphous,[6-9] mainly based on bright field TEM images or selected area diffraction from triple-point grain junctions of $Nd_2Fe_{14}B$ grains. The authors have recently concluded from HREM observations that this phase in MQ-3 is ordered fcc.[10]

This paper focuses on the characterization of grain boundaries and the grain boundary phase in rapidly quenched NdFeB magnets, both MQ-2 and MQ-3, using high-resolution electron microscopy.

2 Experimental

The samples for this study were provided by General Motors and were made by the rapid quenching method. The nominal composition is $Nd_{13.5}Fe_{81.7}B_{4.8}$. Specimens for HREM observation were first mechanically thinned to 20 to 40 μm by means of a hand lapper and then further thinned by a Gatan ion mill on a cold stage cooled by liquid nitrogen. The ion accelerating voltage was 5 to 6 kV and the angle between the sample

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surface and the ion beam was 10 to 20°: High-resolution electron microscopy was done on a JEOL-4000EX operating at 400 kV. The specimen was loaded onto the top-entry double tilt holder using a vacuum tweezer to avoid breakage.

3 Results and Discussion

It has been reported or suggested that the $Nd_2Fe_{14}B$ grains in rapidly quenched NdFeB magnets are each surrounded by a Nd-rich grain boundary phase 1 to 2 nm in thickness.[8,9] High-resolution electron microscopy clearly shows, however, that there are some "clean" boundaries that have no second phase present. Figures 1 and 2 show such boundaries. Figure 1 (MQ-2) and Fig. 2 (MQ-3) each show a boundary between two $Nd_2Fe_{14}B$ grains. By matching the observed interplanar spacings with X-ray diffraction data and matching all measured interplanar angles with calculated angles based on the angle formulas for tetragonal structures, one can index all the planes in the figures and determine the zone axis and the projection of the major phase unit cell. The projection of the major phase unit cell in the Z direction is shown by the square in Fig. 1, and in

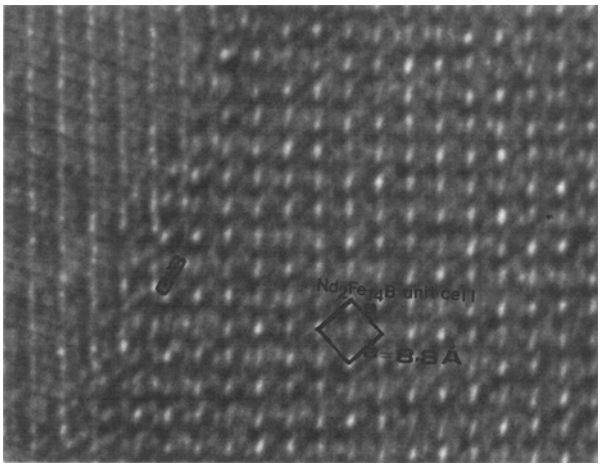

Fig. 1 High-resolution electron microscopy image of MQ-2 sample. The square is the projection of the $Nd_2Fe_{14}B$ tetragonal unit cell of the c direction. No second phase fringes are present in the grain boundary.

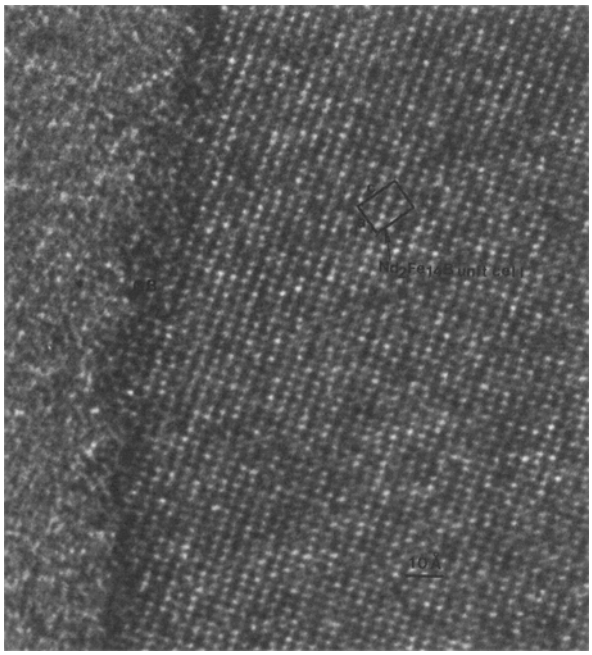

Fig. 2 High-resolution electron microscopy image of MQ-3 sample. The rectangle is the projection of the major phase unit cell in the a direction. There is no evidence for the presence of a grain boundary phase. Note that no dislocations are visible in this deformed sample.

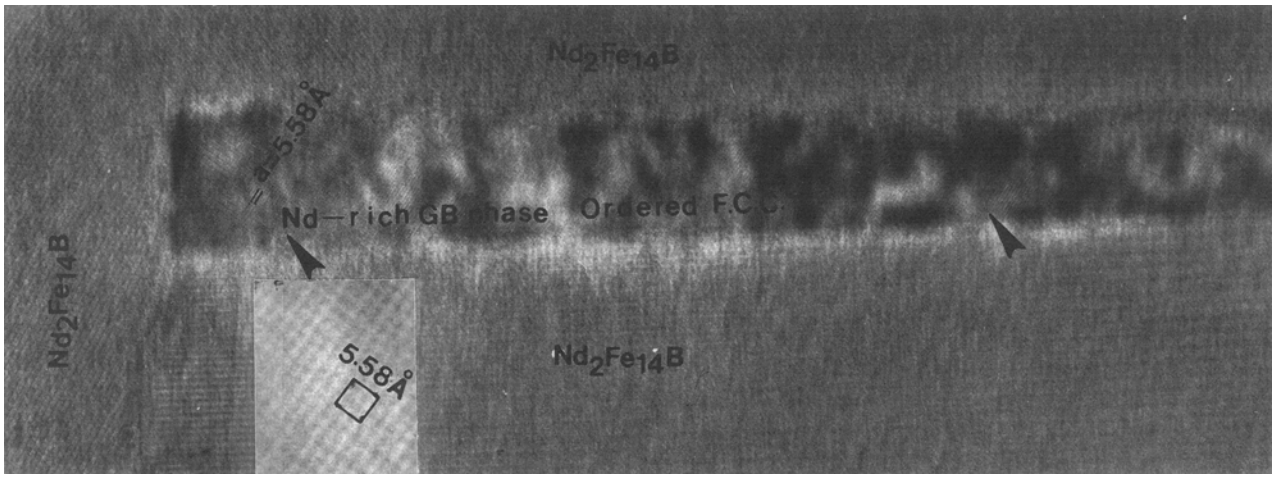

Fig. 3 Grain boundary phase between $Nd_2Fe_{14}B$ grains in MQ-3 sample. The strong-weak-strong modulation indicates an ordered structure. The zone axis of the grain boundary phase is [001]. The boundary phase is ordered fcc (see text).

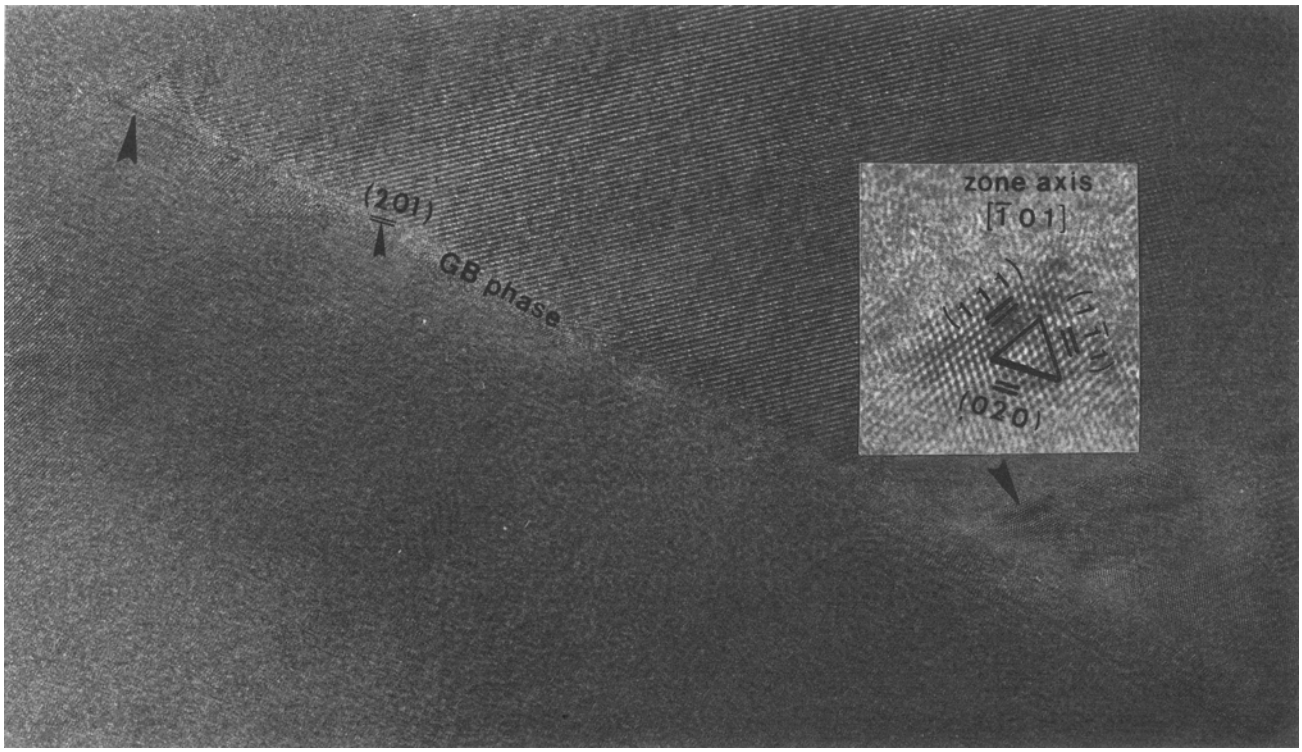

Fig. 4 Grain boundary phase in MQ-2 sample. The cross-fringes in the phase at the triple point show the pattern of the [$\bar{1}$01] zone axis, which indicates the structure is same as that in MQ-3.

Fig. 2, the rectangle is the projection of the unit cell in the *X* direction. The major phase has a nearly perfect crystal lattice, with no observable dislocations (or at least no dislocations with an edge component) visible either before or after hot deformation.

The important observation here is that there are no fringes in the grain boundaries to indicate the presence of a second phase. Careful observation of the figures shows that the major phase fringes extend up to the grain boundary, so that one can confidently say that not all boundaries contain a Nd-rich film in either MQ-2 or MQ-3. The resolution of this HREM is easily sufficient to reveal a grain boundary phase 1 to 2 nm in thickness.

However, there is often a grain boundary phase at boundaries between $Nd_2Fe_{14}B$ crystals, but the thickness of the grain boundary phase is highly variable. For instance, Fig. 3 (MQ-3) shows a grain boundary phase with a width of 15 nm, which is similar to the grain boundary layer thickness in sintered samples. Figure 4 (MQ-2) shows an example of a grain boundary phase with a thickness of about 2 nm. The thickness of the boundary layer seems to be related to the relative orientation of the neighboring $Fe_{14}Nd_2B$ grains and to the grain shapes. Generally speaking, flat (001) surfaces of the major phase have thicker grain boundary phase layers.

The grain boundary phase is definitely crystalline in both MQ-2 and MQ-3 samples. In Fig. 3, the grain boundary phase fringes (especially at the left of the figure) show a strong-weak-strong modulation, which clearly indicates that this is an ordered structure. The appearance of two sets of equally spaced orthogonal planes shows that the structure is cubic or tetragonal, with an interplanar spacing of 0.558 nm. Observations of this kind led to the conclusion that the grain boundary phase is ordered fcc.[10]

In Fig. 4, a boundary exists between two $Nd_2Fe_{14}B$ grains in MQ-2 connecting two "pockets" where there are two sets of planes with 0.322 nm spacing intersecting at 70.4° and another set of planes with 0.28 nm spacing that intersect the previous planes at 54.2°. A cubic structure with lattice parameter a = 0.558 nm has {111} planes spaced by 0.322 nm and {200} planes spaced at 0.28 nm. The calculated angle between (020) and (111) is 54.2° and the angle between two {111} planes is 70.4°. Thus, one can be sure that the structure is cubic. The zone axis in Fig. 3 is [001], and in the insert in Fig. 4, the zone axis is [$\bar{1}$01]. The fringe spacing in the boundary between the two grains is 0.25 nm, which is the {210} spacing.

A simple calculation[10] shows that a hard sphere fcc stacking of Nd atoms gives a lattice parameter closer to the experimental value of 0.558 nm than does a bcc stacking. The appearance of {111} and {210} diffraction spots in Fig. 4 also rules out the bcc structure and, combined with the evidence for ordering in Fig. 3, demonstrates that the grain boundary phase in MQ-2 is the same as in MQ-3, namely ordered fcc.

Figure 5 (MQ-2) shows the grain boundary phase surrounding an incomplete platelet $Nd_2Fe_{14}B$ grain. The shape of the platelet maximizes the area of the low-energy (001) surface. In this sample, the platelet grain growth is driven by differences in

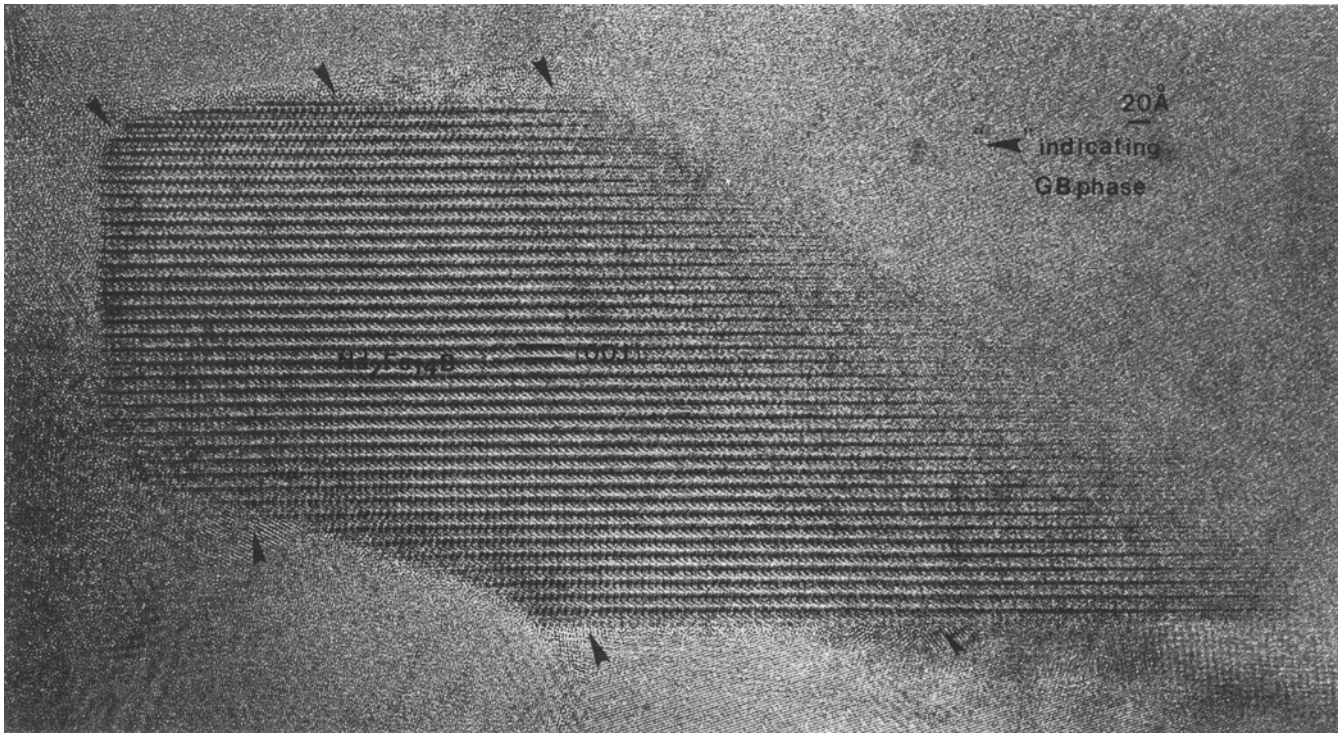

Fig. 5 Grain boundary phase surrounds an incomplete platelet $Nd_2Fe_{14}B$ grain in MQ-2. The boundary phase shows variable thickness, and the grain boundary phase is definitely crystalline.

surface energy, whereas under uniaxial compression the platelet growth is driven by differences in elastic strain energy between differently oriented grains. The strain energy driving force should be much larger.[5] However, both types of grain growth occur by mass transport through the liquid grain boundary phase. High-resolution electron microscopy shows the necessary grain boundary phase is generally present around the major phase grains, although the thickness is variable. At triple points where three grains meet, the Nd-rich boundary phase tends to be thicker.

Some parts of the boundary phase in Fig. 5 do not show good fringes. This is not because the phase is amorphous, as has been suggested,[8,9] but because a zone axis is not properly oriented to show clear fringes of the grain boundary phase. Most parts of the boundary do show clear fringes, indicating that the boundary phase is definitely crystalline but with some lattice distortion.

The authors' previous study[4] showed that the melting point of this grain boundary phase is below 550 °C, and according to the literature,[8] the composition of this phase is near Nd_3Fe, containing neither B nor O. No melting point in the most recent published Nd-Fe-B ternary phase diagram[11] is lower than 550 °C, and the diagram also shows a binary eutectic existing at Nd_3Fe. Thus, it has been believed that the grain boundary phase in NdFeB is this eutectic. However, none of the authors' HREM pictures show any eutectic. Only a single phase is observed at the boundary, which is incompatible with the published phase diagram.

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