Structure of Nd$_2$Fe$_{14}$B / Fe
Resulting from Reaction of Nd$_2$Fe$_{17}$ and B

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A novel method to prepare anisotropic composite magnetic material was described. A block of Nd$_2$Fe$_{17}$\,compound was heated with the surrounding B (or B$_2$O$_3$) powder and the reaction accelerator Ca. In the reaction region, rod-shaped Fe precipitates were formed inside Nd$_2$Fe$_{14}$B matrix grains. The longitudinal directions of those are parallel to the B diffusion path, while perpendicular to the c-axis of Nd$_2$Fe$_{14}$B crystals. The Fe diameter depends on the heating temperature, below 100\,nm at 1123\,K. This structure is regarded as eutectic, and differ from that formed by peritectic solidification. The similar reaction product was formed in the powder form by using Nd$_2$Fe$_{17}$ powder instead of the bulk material. That product has larger magnetization than Nd$_2$Fe$_{14}$B, but has no coercivity and the small anisotropy field about 1.6\,MA/m.

**Key words:** anisotropic nanocomposite magnetic material, Nd$_2$Fe$_{14}$B, Fe, Nd$_2$Fe$_{17}$, B, eutectic structure

1. **Introduction**

Anisotropic nanocomposite magnets are of concern in the view of their expected high performance. These magnets are composed of a soft-magnetic phase with high saturation magnetization and an oriented hard-magnetic phase. Simulations have shown that the energy product of anisotropic nanocomposite magnets is possibly made higher than that of single phase Nd$_2$Fe$_{14}$B.

On the other hand, nanocomposite samples so far afforded have been isotropic ones, either obtained by crystallization of amorphous ribbon or mechanically alloyed powder, having random orientation of hard phase.

In this paper, a novel method was applied to prepare the anisotropic nanocomposite magnetic material in Nd$_2$Fe$_{14}$B / Fe system.

Nd$_2$Fe$_{17}$ intermetallic compound was used for the raw material. There are two characteristics common to Nd$_2$Fe$_{17}$ and the preceding amorphous materials. One is Fe concentration which is higher than that of Nd$_2$Fe$_{14}$B stoichiometric composition. The other is uniform distribution of Fe and Nd atoms throughout materials.

Nd$_2$Fe$_{17}$ was heated with surrounding B. The formation of Nd$_2$Fe$_{14}$B phase by the reaction of Nd-Fe alloy and B has been reported. However, in that report, Fe phase was not formed due to the existence of Nd-rich phase.

In the absence of Nd-rich phase, the following reaction is expected.

\[ \text{Nd}_2\text{Fe}_{17} + B \rightarrow \text{Nd}_2\text{Fe}_{14}B + 3 \text{Fe} \]  \hspace{1cm} (1)

The volume ratio of products is estimated as Nd$_2$Fe$_{14}$B : Fe = 87 : 13.

In the decomposition of Nd$_2$Fe$_{14}$B by hydrogenation, it has been reported that the size of Fe phase formed along with Nd hydride was sub-micron order. Similar scale may be expected for Fe formed by reaction of Eq. (1), in which B atoms play the same role as H atoms in hydrogenation; the decomposition of raw phase, formation of a new phase and precipitation of Fe phase.

2. **Experiments**

Samples were prepared in two different forms, i.e., bulk and powder.

Sample A : Fe-10.8at\% Nd alloys were prepared by arc-melting. Nd concentration was designed to be slightly higher than Nd$_2$Fe$_{17}$ stoichiometric composition in order to depress the primary Fe phase. Ingots were solution treated, and were cut in the blocks. The blocks were placed on the pellets consisting of Ca granules and B powder. B$_2$O$_3$ powder is also used instead of B. The whole was heated at 1123-1373K for 10-24 hours under an Ar atmosphere.

Sample B : Fe-11at\% Nd alloys were ground into powder below 500 \,µm grain size. The mixture consisting of alloy powder, B (or B$_2$O$_3$) powder and Ca granules was pelletized and heated under the same conditions.

In the both sample A and B, Ca acts as the reaction accelerator at temperature above its melting point 1112K because of fine contact with Nd$_2$Fe$_{17}$ interface and increasing diffusion rate of B atoms. In addition, Ca has the strong ability to reduce oxides, so that the process using B$_2$O$_3$ powder leads to the same result as using B powder.

After heated, samples were leached with a sugar solution in order to remove Ca. Structure and magnetic domains were observed by Kerr effect microscope and electron probe micro analyzer (EPMA). Magnetic properties were measured by non-magnetic vibrating sample magnetometer (VSM).

3. **Result and Discussion**

Sample A was used for the observation of the structure. Two new regions were found in the interface of Nd$_2$Fe$_{17}$ and mixture of B and Ca. Fig. 1 is the schematic view of the section in sample A.

Region I adjoins the unreacted Nd$_2$Fe$_{17}$ phase and consists of new columnar crystals. Magnetic domains are observed clearly in region I by Kerr effect, while it is difficult to find domains in Nd$_2$Fe$_{17}$ due to a weak contrast, as shown in Fig. 2. As described later, the new phase in
region I is identified to Nd$_3$Fe$_4$B by X-ray diffraction. Furthermore, there are rod-shaped precipitates inside the matrix grains. Back scattered electron image is shown in Fig. 3. Fig.4 shows concentration maps by EPMA. Each of Nd, B, and Fe elements is distributed uniformly throughout the matrix crystals. In precipitates, Fe concentration is higher than that of matrix, and both of Nd and B scarcely exist. This phase are possibly assigned as Fe.

The longitudinal directions of Fe precipitates are vertical to the reaction interface, that is, are parallel to the B diffusion path. On the other hand, the pattern of magnetic domains in Nd$_3$Fe$_4$B matrix is a maze or a horizontal stripe state. These patterns indicates that c-axis of Nd$_3$Fe$_4$B crystals is perpendicular to the B diffusion path.

The diameter of Fe precipitates decreases as heating temperature decreases. An average diameter is about 400nm in sample heated at 1373K and 70-80nm in sample heated at 1123K, which are estimated by EPMA.

These characteristic of the structure differ clearly from peritectic solidification, and is similar to eutectic. It suggests the presence of metastable structure in Nd$_3$Fe$_4$B/Fe system.
Reaction region II, which is also product, is shown partly in Photo.3. Region II consists of only Fe phase accompanied with many vacancies. Similar sample using a block of Nd$_2$Fe$_{17}$B instead of Nd$_5$Fe$_{18}$B was prepared to examine this structure. In this sample, same phase as region II was formed, whereas region I was not observed. The following reaction is supposed to be responsible for this coarse Fe phase.

\[
\text{Nd}_5\text{Fe}_4\text{B} + (2X-1) \text{B} \rightarrow 14\text{Fe} + 2\text{Nd}_2\text{B}
\]  

(2)

Nd boride is presumed to be exhausted with Ca in the process of leaching. Excess B is considered to result in the decomposition of Nd$_5$Fe$_4$B.

Sample B, which were powder forms, also consisted of coarse Fe phase and polycrystalline Nd$_5$Fe$_4$B phase containing Fe precipitates.

X-ray diffraction patterns of sample B show peaks of Nd$_5$Fe$_4$B and Fe, as shown in Fig.5. Fe peaks correspond to coarse Fe phase because which is formed in the surface of particles. This peak was decreased with increasing Ca ratio in the mixture. It is considered that decrease in B concentration results in depression of the reaction of Eq.(2). Sharpness of Nd$_5$Fe$_4$B peaks also increases as Ca ratio increases, but the reason is not clear.

The relationship between c-axis of Nd$_5$Fe$_4$B and direction of Fe precipitates is kept constant. However, plural of Nd$_5$Fe$_4$B crystals differing in orientation were included in a grain of sample B. It is due to unsettled diffusion path of B atoms which is vertical to surface of the raw material grains.

The powder of product were ball-milled for 2 hours in order to obtain single-crystalline material. After that, powder were oriented under magnetic field 1.2MA/m and fixed with paraffin. Magnetic properties were measured for the samples. Magnetization curves are shown in Fig.6. The sample was compared with Nd$_5$Fe$_{18}$B reference sample which is prepared by using powder milled for Fe-12.3at%Nd-5.9at%B alloy. Because of the following reasons, magnetization of reference sample is smaller than 1.6T. One is Nd concentration which is slightly higher than that of stoichiometric component. The other is amorphous phase formed in surface of particles by ball-milling. The present sample has larger magnetization than Nd$_5$Fe$_4$B reference, but has scarcely coercivity and small anisotropy field nearly 1.6MA/m.

![Fig. 6 Magnetization curves of sample B after milling.](image)

Some factors as following are expected.

1) Coarse Fe phase still remains in sample.
2) Powder after milling are not single-crystalline.
3) Fe precipitates inside Nd$_5$Fe$_4$B decrease anisotropy of system.

4. Conclusion

The new method was attempted in order to prepare anisotropic nanocomposite magnet.

Nd$_5$Fe$_4$B and Fe are formed by reaction of Nd$_5$Fe$_{18}$ compound and B. Each of orientation of Nd$_5$Fe$_4$B crystals and longitudinal direction of Fe precipitates depend on B diffusion path. The Fe diameter in sample heated at 1123K is below 100nm. The structure is regarded as eutectic, and differ from that formed by peritectic solidification.

The powder of product has larger magnetization than Nd$_5$Fe$_4$B, but has scarcely coercivity and small anisotropy field nearly 1.6MA/m.

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References