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Effects of Cu addition on Nd-Fe-B sintered magnets with High-Br

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Higher remanence for Nd-Fe-B sintered magnets is essentially required for various kinds of applications. Higher alignment and lower Nd content, which will result in increased Br, cause lower coercivity. It has not been possible to achieve high remanence and high coercivity simultaneously in the conventional ternary composition materials. It was found that a small amount of Cu addition improves coercivity drastically in Nd-Fe-B sintered magnets with high grain orientation and low Nd content, without remanence decreasing. Furthermore, Cu addition also improved squareness (Hk/HcJ) in a demagnetization curve. The optimum Cu content for coercivity and remanence is found to be 0.04 mass%. More Cu addition was not useful for improving coercivity any more and caused degradation of remanence. As a result, high performance magnetic properties of Br = 1.543 mT, HcJ = 682 kA/m, (BH)max = 466 kJ/m^3 were obtained for the composition of 28.0mass%Nd-1.00B-0.04Cu-0.06Co-0.01Al-bal.Fe. A microstructural analysis by a TEM observation made it confirmed that Cu exists neither in $Nd_2Fe_{14}B$ grains nor in triple junctions, but in grain boundaries.
Key words: Nd-Fe-B, Cu-addition, Coercivity, Microstructure

1. INTRODUCTION

Nd-Fe-B sintered magnets have been utilized in many electronic devices, such as voice coil motors (VCM) and pick-ups for optical recording (CD and DVD applications). For these applications, higher remanence is highly required.

In order to obtain high remanence for Nd-Fe-B sintered magnets, it is very important to control the composition of the magnets as close as to that of $Nd_2Fe_{14}B$ intermetallic compound and improve the orientation of $Nd_2Fe_{14}B$ grains. However, these means, which are applied to improve Br, may cause lower coercivity. It has not been able to achieve, in our previous researches, high remanence and coercivity simultaneously for the conventional ternary materials with compositions close to $Nd_2Fe_{14}B$.

It has been well known that coercivity can be improved by substituting Dy for Nd and adding Al, Mo, V, and Ga [1-8]. Further, coercivity can be improved by a small addition of Cu without causing a degradation of remanence [9,10]. However, an effect of the Cu addition on microstructure hasn't been well examined.

In this study, effects on the Cu addition on the magnetic properties, as well as the microstructure, were examined for a low Nd content composition close to $Nd_2Fe_{14}B$, expecting high remanence.

2. EXPERIMENTS

Several alloys with different compositions were prepared. Each alloy was milled by hydrogen decrepitation treatment and by using a jet-mill. Then, each alloy was finely ground so as to have average particle size in a range of 5 to 6 μm. The particle size distribution of the powder was measured by using a laser diffraction type analyzer. After chemical composition analyses, alloy-powder was mixed together so as to have an accurate composition of 28.0-29.0 mass%Nd and 0.00-0.10Cu and 1.0B-bal. Fe. In order to adjust the compositions close to $Nd_2Fe_{14}B$, unintentional impurities of any transition elements, other than Fe and Cu, were restrained. However, the chemical analyses showed that the compositions contained 0.05-0.1mass%Co and 0.01%Al approximately.

In order to obtain highly orienting $Nd_2Fe_{14}B$ grains, a compacting process was carried out in a condition described below. The powder were filled into a rubber mold with filling density of 2.8Mg/m^3. Before pressing, a magnetic pulse with a field of 3.98MA/m (50kOe) or 11.15MA/m (140kOe) was applied to the filled powder. For each magnitude of the field, the pulse was applied repeatedly 5 times, in one direction and the opposite direction alternately. The pressing process was carried out by using CIP (Cold Isostatic Press). The pressing condition was set to have a pressure of 4.9MPa/m^2 for 60 seconds.

Green compacts were then sintered at temperatures in a range of 1030 to 1070℃ for 4 to 36 hours. These sintering conditions were selected, aiming at the density of sintered body more than 7.50 Mg/m^3 without an occurrence of coarse grains caused by abnormal (discontinuous) grain growth. Sintered body was annealed in a 2 step pattern, 900℃ for a hour followed by 550℃ for a hour. All processes, from milling to sintering, were carried out in a nitrogen or argon atmosphere to prevent the oxygen content from increasing.

Magnetic properties were measured by using a B-H loop tracer with a maximum applied field of 2.39MA/m (30kOe). The shapes of specimens were cylindrical with a diameter of 10 mm. Microstructural analysis was carried out by using a field-emission transition electron microscopy (FE-TEM).

3. RESULTS AND DISCUSSION

3.1. Magnetic properties

Table I shows the Nd and oxygen content with sintering conditions, classified into 3 specimen groups. It is well known that the lower oxygen content in materials could easily induce occurrences of coarse grains caused by abnormal grain growth in Nd-Fe-B sintered magnets. For avoiding abnormal grain growth, other additives are also effective, such as high melting point metal elements. However, in such case, decrease of Br is inevitable. So that, lower temperature and longer time sintering for materials with less than 0.15 mass% oxygen content (specimen group-C) were carried out, in order to prevent the abnormal grain growth and decrease of Br. In all specimens, coarse grains caused by the abnormal grain growth were not observed.

Table I . Nd, oxygen content and typical sintering condition of studied specimens

Specimen Group	Nd content [mass%]	oxygen content [mass%]	Sintering condition
A	29.0	0.18 - 0.20	1070℃-4hrs
B	28.6	0.13 - 0.15	1070℃-4hrs
C	28.0	0.07 - 0.10	1030℃-36hrs

Figure 1 shows HcJ dependence on the Cu content. In this study, a magnetic pulse with a field of 3.98MA/m was applied to the specimens in the compacting process. For the specimen group -A and B, HcJ increased with the Cu content increasing up to 0.04mass%. However, the increase of HcJ was not elucidate in a range of more than 0.04mass% . Figure 2 shows Br dependence on the Cu content. Br was almost unchanged by the Cu addition from 0.0 to 0.06 mass%, however the more addition of Cu degraded Br. For the specimen group -C,

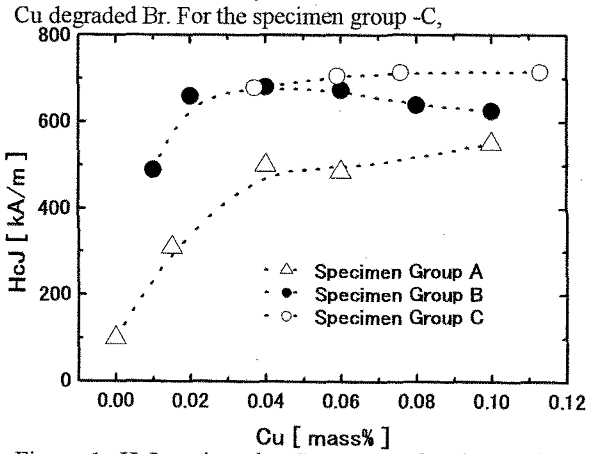

Figure 1. HcJ against the Cu content for the studied specimens

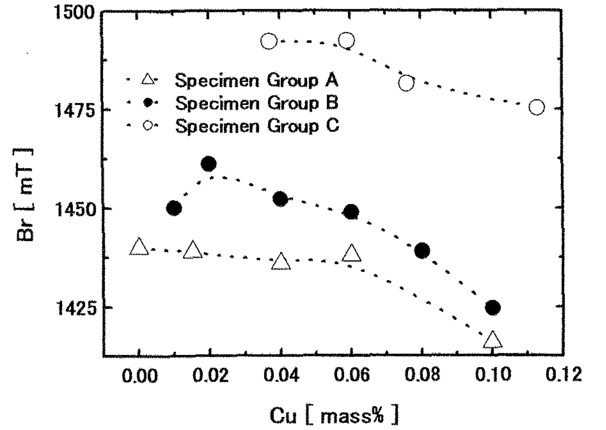

Figure 2. Br against the Cu content

the tendencies of HcJ and Br dependence on the Cu content was similar to those for the specimen groups –A and B.

Furthermore, the Cu addition also improved the squareness (Hk/HcJ). With the Cu content increasing from 0.01 to 0.04mass%, the squareness was improved from 86.3% to 96.8%.

From the above results, it can be concluded that a small addition of Cu improves the magnetic properties significantly. It was also found that the optimum Cu content is 0.04 mass%.

In order to improve the orientation of $Nd_2Fe_{14}B$ grains, a magnetic pulse with a field of 11.15MA/m was applied instead of 3.98MA/m. Magnetic measurements were carried out for the magnets with a 0.04mass% Cu content in the specimen group -C.

HcJ slightly decreased by 20-30 kA/m with an increase of the pulse magnetic field applied for the grain orientation from 3.98MA/m to 11.15MA/m, while Br increased by 40-50mT. It is concluded that the higher pulse magnetic field resulted in the higher orientation of $Nd_2Fe_{14}B$ grains on green compact, therefore higher Br was obtained in the sintered body. As a result, high performance magnetic properties of Br = 1543mT, HcJ = 682kA/m (8.57kOe), (BH)max = 466kJ/m^3 were obtained for the composition of 28.0mass%Nd-1.00B-0.04Cu-0.05Co-0.01Al-0.04C-0.08O-bal.Fe. Figure 3 shows a demagnetization curve of the magnet.

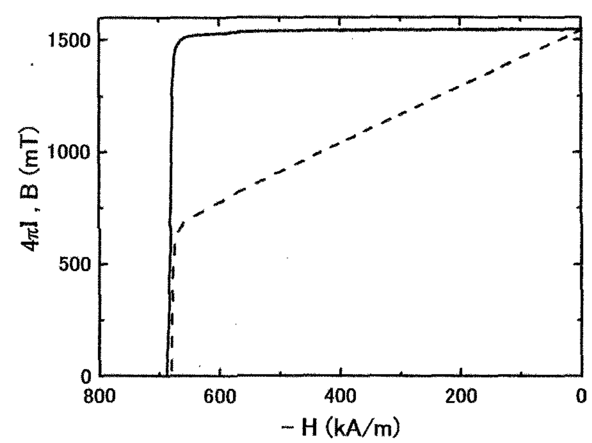

Figure 3. Demagnetization curve with (BH)max of 466 kJ/m^3

3.2. Microstructure

A microstructural analysis was also carried out. The magnet composition was that of the specimen group -C with 0.04mass% Cu content. Figure 4 shows an image, which shows a grain boundary with a width of 2 nm between $Nd_2Fe_{14}B$ grains. An EDS analysis shows that Nd content at point -(2) is higher compared with that at point (1) and point -(3). It is clearly observed that Cu is enriched at point (2) which lies in a grain boundary as shown in fig.4-(c). On the other hand, Cu could not be detected at the points -(1) and -(3), which are positioned apart from the grain boundary by 5nm approximately. These results indicate that thin grain boundary phase shown in fig.4 -(a) have Nd and Cu rich content, while $Nd_2Fe_{14}B$ grains do not contain Cu even at the point near grain boundary phase.

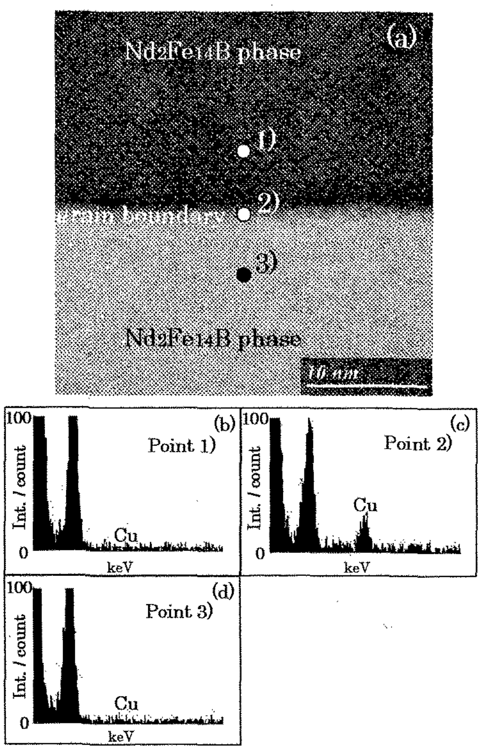

Figure 4. (a) HRTEM image around the grain boundary, (b)-(d) EDS spectrums at respective point.

Figure 5 shows an image around a triple junction in the specimen. EDS analyses were carried out at several points around the triple junction. Cu is slightly enriched at the point -(8) and point -(12), which are located on surfaces of a $Nd_2Fe_{14}B$ grain. Cu was not detected at point -(11) (in $Nd_2Fe_{14}B$ grains) and at point -(9) (at a center part of Nd rich phase).

Compared with intensity of Cu peak at point -(12) in fig.5 and at point -(2) in fig.4, it is clear that the intensity at point -(12) has a tendency to be weaker than that at point -(2), that is attributed to the grain boundary. It is considered that the Cu content at the grain boundary phase is higher than that at $Nd_2Fe_{14}B$ grain surface in the Nd rich phase.

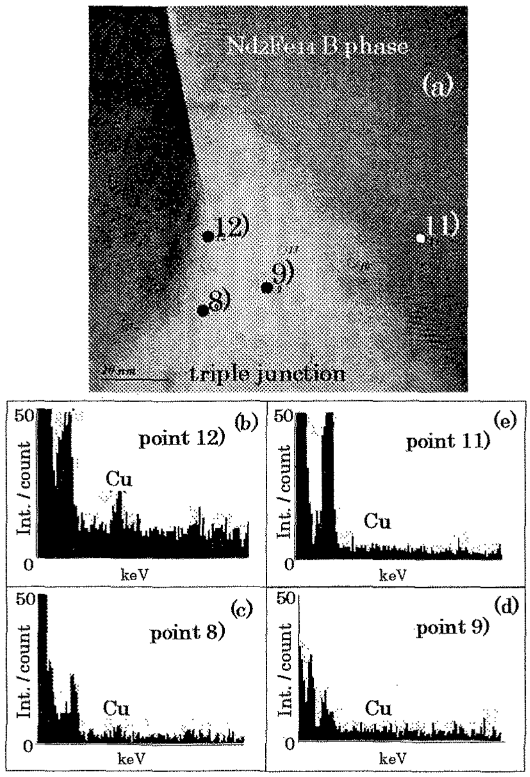

Figure 5. (a) HRTEM image around the grain triple junction, (b)-(e) EDS spectrums at respective points

In order to elucidate when Cu enrichment at the grain boundary was occurred, the same analysis was carried out for the magnets before annealing (as sintered). Figure 6 is an HR-TEM image showing a grain boundary, accompanied with EDS spectrums. Cu is enriched at point (22) which lies on a grain boundary. Cu was not detected at the point (21) and (23), which is positioned apart from grain boundary by 25nm. This result coincides with the result obtained for fig. 4. It can be concluded that the Cu enrichment was occurred during the sintering process before annealing.

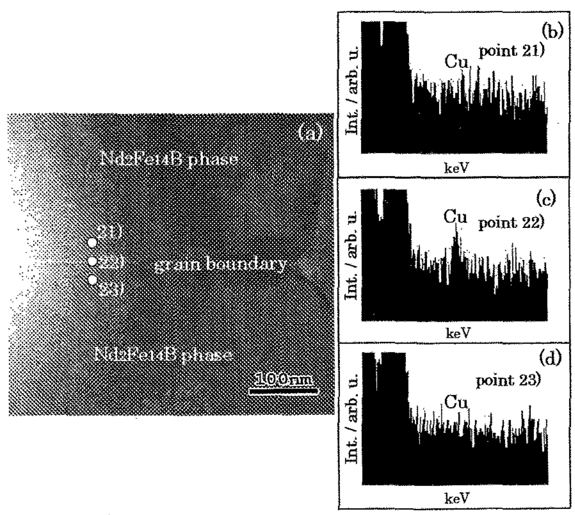

Figure 6. (a) TEM image around the grain boundary, (b)-(d) EDS spectrums at respective point

Here, effects of Cu addition on Nd-Fe-B sintered magnet will be discussed. From the microstructural analysis, it is confirmed that Cu is enriched at grain boundaries and surfaces of $Nd_2Fe_{14}B$ grains and it is likely that the concentration of Cu in a triple junction is lower than that in the grain boundaries. It is recognized that the enrichment of Cu at grain boundaries has occurred in the sintering process, but not in the annealing process.

From these results, the Cu enrichment at grain boundaries is supposed to occur in a following way; Cu rich liquid phase was formed at a lower temperature compared with Cu-free Nd-Fe-B system, and $Nd_2Fe_{14}B$ grains were covered with Cu rich liquid phase at a early stage in sintering. During grain growth, Cu was not included in $Nd_2Fe_{14}B$ grains, as a result, Cu remains at grain boundaries and surfaces of $Nd_2Fe_{14}B$ grains after the sintering process.

From the magnetic measurements, it was found that a small addition of Cu improves coercivity and squareness significantly. Cu is enriched at grain boundaries, which could be most influential to coercivity. So, it can be presumed that coercivity is improved by the Cu addition. The reason of enriched Cu of grain boundaries increases coercivity has not been elucidated so far.

On the other hand, Cu doesn't exist in the $Nd_2Fe_{14}B$ phase. The reason why remanence of the specimens with 0.04 mass% Cu additions are same as that of the specimens without Cu could be explained by presuming that Cu additives do not degrade magnetization of $Nd_2Fe_{14}B$ phase.

4. CONCLUSION

We studied the effects of Cu addition on Nd-Fe-B sintered magnets with 28.0-29.0mass% Nd content, by examining magnetic properties and analyzing microstructure. Cu addition improves the coercivity drastically, without decrease of remanence. We found that the optimized Cu content is 0.04 mass%. More Cu addition leads decrease of Br and do not improve coercivity any more. As a result, high performance magnetic properties of Br = 1543mT, HcJ = 682kA/m (8.57kOe), (BH)max = 466kJ/m^3 was obtained at the composition of 28.0mass%Nd-1.00B-0.04Cu-0.06Co-0.01Al-0.04C-0.08O-bal. Fe.

From microstructual analyses, it is confirmed that Cu is enriched at grain boundaries and surfaces of $Nd_2Fe_{14}B$ grains. And for non-annealed (as sintered) magnets, Cu is also enriched at grain boundaries. Therefore, it can be conclude that this phenomenon has occurred in the sintering process but not in the annealing process. On the other hand, Cu doesn't exist in the $Nd_2Fe_{14}B$ phase. 0.04mass% Cu additives dose not deteriorate magnetization of $Nd_2Fe_{14}B$ phase.

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