Metastable Phase Formation from Nd-Dy-Fe-B Undercooled Melt

Shumpei OZAWA1, Akira ITOU2, Kazuhiko KURIBAYASHI3, Noriyuki NOZAWA4, and Satoshi HIROSAWA5

1 Department of Aerospace Engineering, Tokyo Metropolitan University, Tokyo, Japan, shumpei.ozawa@tmu.ac.jp
2 Graduate school of Tokyo Metropolitan University, Tokyo, Japan, akira.itou@isas.jaxa.jp
3 Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency, Sagamihara, Japan, kuribayashi@isas.jaxa.jp
4 Magnetic Materials Research Laboratory, NEOMAX Company, Hitachi Metals, Ltd., Mishima, Japan, noriyuki_nozawa@hitachi-metals.co.jp
5 Magnetic Materials Research Laboratory, NEOMAX Company, Hitachi Metals, Ltd., Mishima, Japan, sahoshi_hirosawa@hitachi-metals.co.jp

Abstract

Nd10-xDyxFe85B5 (x = 0-3) alloy samples were melted and then solidified in the containerless state of a drop tube at oxygen partial pressure of 10^-1 Pa. The calculated cooling rate of the spherical sample was over 10^3 K/s. The Nd10Fe85B5 sample consists of the Nd2Fe17Bx metastable phase together with the α-Fe dendrite. The metastable phase was partially decomposed into small grains of Nd2Fe14B and α-Fe phases by a solid state decomposition reaction. The substitution of Dy for Nd in the range from 10 to 20 atomic percent was effective to suppress the primary formation of the α-Fe dendrite and to promote the formation of the RE2Fe17Bx metastable phase. When the substitution rate of Dy increased to 30 atomic percent, a large amount of the α-Fe dendrite was formed because an oxide layer of rare earth elements was generated at the sample surface due to the easy oxidization tendency of Dy.

1. Introduction

Nanocomposite magnets are theoretically expected to have high maximum energy products due to an exchange interaction if nano-scale hard and soft magnetic phases are arranged in the most appropriate manner 1). This magnet is currently prepared by the annealing of amorphous melt-spun ribbon 2). In this case the volume fraction of Nd2Fe14B hard magnetic phase is inevitably limited because the alloy composition of Fe3B/Nd2Fe14B which has high amorphous formability is used, resulting in a much lower coercivity of the magnet 2). Furthermore, the resultant nanocomposite magnets have limited shape such as powder and ribbon.

When the Nd3Fe5B5 alloys (x = 10-14) solidify from the undercooled melt using containerless processing such as an electromagnetic levitation and drop tube method, the Nd3Fe5B5 metastable phase is crystallized 3-5). The metastable phase is decomposed into a nanosized microstructure which consists of the magneto soft α-Fe and hard Nd2Fe14B phases by a solid state decomposition reaction 4, 5). If this decomposed microstructure can be applied to the production of nanocomposite magnets, they could be mass produced. The volume fraction of the Nd3Fe5B5 phase increases more than that of the practical Nd3Fe5B5/Fe3B nanocomposite magnet. Moreover, the α-Fe phase whose saturation magnetization is larger than that of the Fe3B phase acts as a soft magnetic phase 2, 6). Thus, the maximum energy product of the magnets is improved. These are major advantages compared with the Nd3Fe5B5/Fe3B type nanocomposite magnet prepared by rapid solidification techniques.

In order to apply the decomposition of the metastable phase to the development of the nanocomposite magnets, coarse α-Fe dendrites which grow at a small undercooling level should be eliminated because it decreases the coercivity of the magnet 7, 8). Furthermore, the alloy size should be enlarged from the view point of productivity. Preparing the alloy to respond to the cooling rate and undercooling level simultaneously is contradictory; high cooling rate and large undercooling level of the melt are important to suppress the α-Fe dendrite though these values are decreased when the alloy size becomes large 4, 5).

Grieb et al. reported that the substitution of Tb or Dy for Nd in the rapidly solidified RE2Fe14B (RE = Nd + Dy or Tb) alloy expands the formation temperature range of the Nd2Fe17 type metastable phase as shown in Fig. 1 9). Furthermore, the formation region of the α-Fe phase becomes narrow with an increased substitution ratio of Dy or Tb. This suggests that there is a possibility of forming the metastable phase without the α-Fe formation even at a small undercooling of the melt. Consequently, a large alloy would be produced.

In the present study, the Nd3Fe5B5 alloys (x = 0-3) alloys were solidified from the undercooled melt using drop tube processing. The relationships among the constituent phase, substitution ratio, and sample diameter were examined. The purpose of this investigation is to explore the possibility of the formation of the metastable the phase free from the α-Fe formation in a bulk alloy. Furthermore, the
thermal stability of the metastable phase was investigated.

2. Experiment

Small segments of Nd-Fe-B alloy with the nominal composition of Nd\(_{10-x}\)Dy\(_x\)Fe\(_{85}B_5\) (x = 0-3) were charged into a quartz crucible with an orifice from 0.1 to 0.5 mm in diameter at the bottom. The quartz crucible filled with the alloy was fixed in a chamber rigged at the top of the drop tube as shown in Fig. 2. The free fall length of the drop tube is 26 m. The drop tube was initially evacuated to the order of 10\(^{-3}\) Pa and then backfilled with 99.999% pure He. The oxygen partial pressure of the refilled gas was less than 10\(^{-1}\) Pa. The alloy was inductively melted and superheated to temperatures approximately 100 K higher than the liquidus temperature. The temperature of the melt was monitored at the center of the crucible by a thermocouple encased in a quartz glass sheath. The molten alloy was ejected from the orifice into the drop tube by helium gas pressurized to 0.15 MPa higher than the surrounding environment. The ejected melt shaped into small droplets of various sizes which rapidly solidified during free fall. The calculated cooling rate of the sample is shown in Fig. 3. The detail of the calculation can be found elsewhere \(^{10}\).

The constituent phases of the as-solidified samples were identified by powder X-ray diffraction (XRD) analysis using Cu-K\(_{α}\) radiation at room temperature. The microstructure of the sample was examined by scanning electron microscopy (SEM) using an energy dispersive X-ray (EDX) analyzer. The accelerating voltage of EDX analysis was controlled at 10 kV. It was carried out on the surface of the cross section, which was polished only mechanically so as not to lose the details of the microstructure. The differential thermal analysis (DTA) of the sample was carried out in an argon atmosphere at a heating rate of 0.5 K s\(^{-1}\).

3. Results and Discussions

Fig. 4 shows the XRD profiles of the as-dropped samples. The XRD profile of the Nd\(_{10}\)Fe\(_{85}\)B\(_5\) with a diameter range of 850 µm and 1200 µm indexed to the diffraction peaks of the Nd\(_2\)Fe\(_{14}\)B phase, \(α\)-Fe phase and metastable Nd\(_2\)Fe\(_{17}\)B\(_x\) phase.

Even when the sample diameter is comparatively large in the range of 1200 µm to 1500 µm, the diffraction peaks of the RE\(_2\)Fe\(_{14}\)B phase disappear in the XRD profile of the Nd\(_{10}\)Dy\(_2\)Fe\(_{85}\)B\(_5\) sample as shown in fig. 4 (b). Furthermore the relative intensity of the diffraction peaks of the \(α\)-Fe phase becomes half when compared with the 850 µm and 1200 µm diameter range sample of Nd\(_{10}\)Fe\(_{85}\)B\(_5\), implying that the volume fraction of the \(α\)-Fe phase decreases by 50% due to the substitution of Dy for Nd. These results reveal that the substitution of Dy for Nd is effective for enhancement of the formability of the RE\(_2\)Fe\(_{14}\)B phase and for suppressing the \(α\)-Fe formation. Almost the same XRD profile is obtained in the Nd\(_{10}\)Dy\(_2\)Fe\(_{85}\)B\(_5\) sample.

The Fe\(_3\)RE, Fe\(_3\)B, RE, and RE\(_2\)O\(_3\) phases are formed...
when the substitution ratio of Dy for Nd is increased to 30%. As a result, the volume fraction of the metastable phase is decreased in the sample.

Fig. 5 exhibits the typical microstructures of the as-dropped samples. In the ternary Nd\textsubscript{10}Fe\textsubscript{85}B\textsubscript{5} samples, \( \alpha \)-Fe dendrite is embedded in the Nd\textsubscript{2}Fe\textsubscript{17}B\textsubscript{x} phase as shown in fig. 5 (a). This indicates that the \( \gamma \)-Fe phase, which transforms into the \( \alpha \)-Fe phase at room temperature, was formed directly from the melt as the properitectic phase and followed by the Nd\textsubscript{2}Fe\textsubscript{17}B\textsubscript{x} phase. The Nd\textsubscript{2}Fe\textsubscript{14}B phase, which fills the area between the Nd\textsubscript{2}Fe\textsubscript{17}B\textsubscript{x} phases, would be finally solidified from the remaining melt \cite{5}. The Nd\textsubscript{2}Fe\textsubscript{17}B\textsubscript{x} metastable phase is partially transformed into the \( \alpha \)-Fe and Nd\textsubscript{2}Fe\textsubscript{14}B phases by solid state decomposition reaction.

Excluding large \( \alpha \)-Fe dendrites the microstructure of the Nd\textsubscript{9}Dy\textsubscript{1}Fe\textsubscript{85}B\textsubscript{5} and Nd\textsubscript{8}Dy\textsubscript{2}Fe\textsubscript{85}B\textsubscript{5} samples with a diameter of 1200 – 1500 \( \mu \)m are almost the same as that of the Nd\textsubscript{10}Fe\textsubscript{85}B\textsubscript{5} samples with a diameter of 850 – 1200 \( \mu \)m. A part of the Nd\textsubscript{2}O\textsubscript{3} phase is decomposed into the \( \alpha \)-Fe and Nd\textsubscript{2}Fe\textsubscript{14}B phases as is the case of the ternary Nd\textsubscript{10}Fe\textsubscript{85}B\textsubscript{5} sample, indicating that the substitution of Dy for Nd up to 20at\% does not influence the decomposition of the Nd\textsubscript{2}Fe\textsubscript{17}B\textsubscript{x} phase. However, the RE elements were oxidized at the melt surface preferentially when

In the XRD profile of Nd\textsubscript{9}Dy\textsubscript{1}Fe\textsubscript{85}B\textsubscript{5} and Nd\textsubscript{8}Dy\textsubscript{2}Fe\textsubscript{85}B\textsubscript{5} samples with a diameter range of 1200 \( \mu \)m to 1500 \( \mu \)m, no appreciable diffraction peaks for the Nd\textsubscript{2}Fe\textsubscript{14}B phase would be detected. As mentioned above, the substitution of Dy for Nd up to 20% is very effective to enhance the formability of the RE\textsubscript{2}Fe\textsubscript{17}B\textsubscript{x} phase and to suppress the \( \alpha \)-Fe formation. However, the RE elements were oxidized at the melt surface preferentially when

\[ \text{XRD profiles of (a) as-dropped Nd}_{10}\text{Fe}_{85}B_{5} \text{ samples with a diameter of } \phi 850 - 1200 \mu m, \text{ (b) Nd}_{9}Dy_{1}\text{Fe}_{85}B_{5} \text{ samples with a diameter of } \phi 1200 - 1500 \mu m, \text{ and (c) Nd}_{8}Dy_{2}\text{Fe}_{85}B_{5} \text{ samples with a diameter of } \phi 1200 - 1500 \mu m. \]

Fig. 5 Backscattered SEM micrographs of (a) as dropped Nd\textsubscript{10}Fe\textsubscript{85}B\textsubscript{5} samples with a diameter of \( \phi \)850 - 1200 \( \mu \)m, and (b) Nd\textsubscript{9}Dy\textsubscript{1}Fe\textsubscript{85}B\textsubscript{5} samples with a diameter of \( \phi \)1200 - 1500 \( \mu \)m.
4. Conclusions

Nd-Fe-B alloys with nominal compositions of Nd$_{10-x}$Dy$_x$Fe$_{85}$B$_5$ (x = 0-3) were solidified in the containerless state during their free fall at oxygen partial pressure of 10$^{-2}$ Pa. The influences of the substitution of Dy for Nd in the Nd$_{10}$Fe$_{85}$B$_5$ alloys solidified from the undercooled melt were investigated. The calculated cooling rate of the spherical sample was over 10$^8$ K/s.

The Nd$_{10}$Fe$_{85}$B$_5$ sample with a diameter in the range of 850 $\mu$m to 1200 $\mu$m consisted of Nd$_2$Fe$_{17}$B$_x$ metastable phase and Nd$_2$Fe$_{14}$B phase together with a large dendrite of the $\alpha$-Fe phase. The metastable phase was partially transformed into the Nd$_2$Fe$_{14}$B and $\alpha$-Fe phases by solid state decomposition reaction.

Although almost the same microstructures were observed in the Nd$_{10}$Dy$_1$Fe$_{85}$B$_5$ and Nd$_{10}$Dy$_2$Fe$_{85}$B$_5$ samples, the $\alpha$-Fe dendrite was not observed even when the sample diameter was 1200 $\mu$m to 1500 $\mu$m. The RE$_2$Fe$_{17}$B$_x$ metastable phase, where Nd was partially substituted by Dy, decomposed into the RE$_2$Fe$_{14}$B and $\alpha$-Fe phases through the solid state decomposition reaction as was the case of the ternary Nd$_2$Fe$_{17}$B$_x$ metastable phase.

When the substitution rate of Dy for Nd was increased to 30%, a thick oxide layer of the rare earth element formed at the sample surface. A huge amount of a large $\alpha$-Fe dendrite was formed due to the consumption of the rare earth elements.

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