Direct Crystallization of the Nd$_2$Fe$_{14}$B Peritectic Phase by Containerless Solidification in a Drop Tube

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Nd$_2$Fe$_{14}$B molten alloy droplets were containerlessly solidified using a 25 m drop tube. The relationship between the sample diameter and the microstructure was investigated. The diameter of the resultant spherical samples was in range of 150 to 2000 μm. When sample diameter was larger than 500 μm, the microstructure of the spherical sample consisted of the α-Fe phase embedded in matrix of the Nd$_2$Fe$_{14}$B phase within entire sections. In the spherical sample with diameter of 400 μm, the microstructures consisted of two regions, one was columnar grains of the Nd$_2$Fe$_{14}$B phase and the other was α-Fe phase embedded in matrix of the Nd$_2$Fe$_{14}$B phase. The columnar Nd$_2$Fe$_{14}$B region expanded as the sample diameter decreased from 400 to 350 μm. When sample diameter reduced to 250 μm, the microstructure of a spherical sample consisted of the pure dendritic Nd$_2$Fe$_{14}$B phase without any α-Fe phase.

(Received November 21, 2002; Accepted February 17, 2003)

Keywords: containerless solidification, undercooling, direct crystallization, neodymium–iron–boron

1. Introduction

Neodymium–iron–boron (Nd–Fe–B) permanent magnets are one of the highest performance magnets. It has been reported$^1$ that the Nd–Fe–B magnets can yield the maximum energy products of more than 444 kJ m$^{-3}$. This value is over 10 times larger than that of ferrite magnets that are widely applied at present. Therefore, the production volume of the Nd–Fe–B magnets will increase due to the expanding needs in various applications such as computer and electric devices.

The superiority of the magnets originates from the Nd$_2$Fe$_{14}$B intermetallic compound that exhibits a large saturation magnetization and a high anisotropy field.

According to the Nd–Fe–B ternary alloy phase diagram, the Nd$_2$Fe$_{14}$B phase is formed via the peritectic reaction from liquid phase and primary iron phase. Therefore, the primary iron phase always remains between the Nd$_2$Fe$_{14}$B phase in alloy ingots due to the nature of peritectic reaction. The primary iron phase transforms to the soft magnetic α-Fe phase at room temperature, which deteriorates the hard magnetic property of the Nd–Fe–B magnets. Thus, it is crucial to reduce the amount of the primary iron phase in Nd–Fe–B alloy ingots.

A large undercooling is one of the most promising alternatives for yielding peritectic compounds directly from a melt. The most common technique to obtain a large undercooling is the rapid solidification processing such as melt-spinning or splat-quenching. Furthermore, it has been reported that an undercooling can be achieved by containerless solidification. In the containerless technique, a bulk liquid material may experience a large undercooling prior to solidification because of the absence of container wall that may act as heterogeneous nucleation sites.

In this study, an Nd–Fe–B spherical alloy with the stoichiometric Nd$_2$Fe$_{14}$B composition was produced by containerless solidification processing in a drop tube of 25 m in height. It is expected that the molten alloy droplets experience a large undercooling prior to solidification by drop tube processing. Such a large undercooling may favor the direct crystallization of the Nd$_2$Fe$_{14}$B hard magnetic phase from the undercooled melt. The purpose of this study is to investigate the relationship between the sample size and the microstructure. The particular interest in the investigation was to confirm the critical diameter of a spherical sample, in which direct crystallization of the Nd$_2$Fe$_{14}$B phase can be achieved without the primary iron phase.

2. Experimental Procedure

Figure 1 shows a schematic diagram of the drop tube experiment. Small segments of Nd–Fe–B alloy ingots with stoichiometric composition of Nd$_2$Fe$_{14}$B were charged in a

![Schematic diagram of the drop tube experiment.](image-url)
quartz glass crucible with an orifice from 0.3 to 1.0 mm in diameter at the bottom. The quartz crucible with ingots was fixed in a chamber at the top of the drop tube. The drop tube was evacuated to $1 \times 10^{-3}$ Pa and backfilled with 99.999% helium. The ingots were induction heated up to 1650 K that is about 100 K above the equilibrium liquidus temperature. The temperature of the melt was monitored by a thermocouple encased in a quartz glass sheath placed at the center of the sample. The molten alloy was ejected into the drop tube through the orifice by controlling the helium pressure, and shaped into comparatively uniform droplets continuously. The rapid solidification of the droplets was accomplished during their free fall in a containerless state. The sample accumulated at the bottom of the drop tube was spherical grain. The resultant samples were sifted into various groups according to sample diameter, ranging from 100 to 2000 µm with regard to the nozzle diameter and ejection pressure.

After spherical samples were polished and etched in 1% Nital, the microstructures and accurate diameter of the spherical samples were examined under scanning electron microscope (SEM) equipped with an electron probe microanalyzer (EPMA) for analyzing chemical composition. The phases of the samples were identified by powdered X-ray diffraction (XRD) using Cu-K$_\alpha$ radiation at room temperature.

3. Results and Discussion

The spherical samples had a metallic surface in spite of a high oxidation tendency of the neodymium in the alloy. In the drop tube experiment, the melt solidifies without the container wall that may act as the heterogeneous nucleation site. Moreover, the reduction of the number of the potential heterogeneous nuclei in a fine droplet is favorable to enhance the undercooling level. Therefore, it is important to examine the influence of sample diameter on the phase selection and microstructure formation. It has been reported that a number of metals and alloys can experience an undercooling $\Delta T$ of 0.2 x $T_0$ prior to solidification.$^{11,12}$ When it is assumed that the Nd$_2$Fe$_{14}$B melts experience an undercooling of 0.2 x $T_0$ prior to solidification, the free fall distance as a function of the sample diameter is shown in Fig. 2. This value is estimated by the following equations;

$$dT/dt = -6/\rho C_p d_h(T - T_0) + \sigma_S B \varepsilon (T^4 - T_0^4)$$  \hspace{1cm} (1)

$$dV/dt = g(\rho - \rho_g)/\rho_g - 3/4D_r \rho (V^2/\rho d)$$ \hspace{1cm} (2)

$$h = K_g/d(2.0 + 0.3Pr^{0.3}Re^{0.6})$$ \hspace{1cm} (3)

$$D_r = 24/Re \quad (Re < 1)$$ \hspace{1cm} (4)

$$D_l = (0.55 + 4.8/Re^{1/2})^2 \quad (1 < Re < 10^4)$$ \hspace{1cm} (5)

where $d$ is the diameter of droplets, $\rho$ and $\rho_g$ are the density of the droplet and gas, $C_p$ is the specific heat of the droplet, $h$ is heat transfer coefficient, $T$ and $T_0$ are the melt temperature and ambient temperature, $\sigma_S B$ is Stefan-Boltzmann constant, $\varepsilon$ is the droplet surface hemispherical total emissivity, $g$ is the gravitational acceleration, $D_r$ is the drag coefficient, $V$ is the relative velocity between the droplet and the gas and, $K_g$ is thermal conductivity of the gas.$^{33}$ The physical properties used in the estimation are listed in Table 1. Maximum diameter of the melt which can experience the undercooling of 0.2 × $T_0$ during free fall in the drop tube is about 2150 µm. In this study, the spherical sample with 150 to 2000 µm in diameter is obtained. Hence, the molten Nd$_2$Fe$_{14}$B droplet may experience such a large undercooling.

Figure 3 shows the XRD patterns of the spherical Nd$_2$Fe$_{14}$B alloys with various diameters solidified during free fall in the drop tube. For comparison, the XRD pattern of the alloy ingot is also depicted. The XRD pattern of the alloy ingot is well indexed to tetragonal Nd$_2$Fe$_{14}$B phase and the $\alpha$-Fe phase. This indicates that the alloy ingot contains some $\alpha$-Fe phase together with the Nd$_2$Fe$_{14}$B phase. In the stoichiometric Nd$_2$Fe$_{14}$B alloy, the $\alpha$-Fe phase should coexist with other phase such as Nd phase and Fe$_2$B phase.$^{41}$ However, no detectable diffraction peaks of other phase can be found in the XRD pattern. When the diameter of the spherical sample is 2000 µm, the XRD pattern of the samples shows the diffraction peaks of the Nd$_2$Fe$_{14}$B phase and the $\alpha$-Fe phase as is the case of the ingot. Virtually the same XRD patterns are obtained from the spherical samples with 500 µm and 400 µm in diameter. This indicates that the spherical samples with diameter in range of 2000 to 400 µm contain some $\alpha$-Fe phase together with the Nd$_2$Fe$_{14}$B phase as in that alloy ingot. It is expected that the primary $\gamma$-Fe phase was transformed to the stable $\alpha$-Fe phase. The primary iron phase was not completely transformed into the Nd$_2$Fe$_{14}$B phase by the
peritectic reaction and thus remained as the α-Fe phase in the spherical samples with diameter in range of 2000 to 400 μm. Although the diffraction peaks of the α-Fe phase can still be found in the XRD pattern of the spherical sample with 350 μm in diameter, the intensity of the diffraction peaks of the Nd$_2$Fe$_{14}$B phase become slightly strong. This implies that the amount of the Nd$_2$Fe$_{14}$B phase in the spherical sample with 350 μm in diameter increases, in short, the volume fraction of the α-Fe phase decreases. The XRD pattern of the sample with 250 μm in diameter shows only the diffraction peaks of the Nd$_2$Fe$_{14}$B phase. No appreciable diffraction peaks of other phase are observed. This indicates that the spherical sample with 250 μm in diameter only consists of the Nd$_2$Fe$_{14}$B phase.

Figure 4 shows the typical cross section microstructures of the spherical Nd$_2$Fe$_{14}$B alloys with various diameters and further magnified microstructures at center position. The microstructure of the spherical sample with 500 μm in diameter consists of “isolated fragmented dendrite” embedding in matrix. EPMA study reveals that the fragmented dendrite and matrix are the α-Fe phase and the Nd$_2$Fe$_{14}$B phase, respectively. Schwarz et al. have reported that such a fragmentation is resulted in a comparatively low cooling rate. Even though the XRD studies does not confirm the existence of any other phase, the EPMA studies reveals that the grain boundary is Nd-rich phase. The volume fraction of this Nd-rich phase is so small that it is beyond the detectable limit of XRD.

In the spherical sample with diameter of 400 μm, the microstructure consists of two regions though almost the same microstructure is still observed at about 10 percent of the spherical samples. One is columnar grains together with grain boundary and the other is fragmented dendrites embedding in the matrix as that evidenced in the spherical samples with 500 μm in diameter. On the other hand, the columnar grains and grain boundaries were the Nd$_2$Fe$_{14}$B phase and Nd-rich phase, respectively. When the Nd$_2$Fe$_{14}$B phase is formed by peritectic reaction, it surrounds the primary iron phase and prevents further peritectic reaction. As a result, the primary iron phase always remains in the resultant Nd$_2$Fe$_{14}$B phase. However, no primary iron phase was observed in the current columnar Nd$_2$Fe$_{14}$B grains. Similar columnar grains of Nd$_2$Fe$_{14}$B phase can be observed in the microstructures of the Nd–Fe–B alloys solidified from the undercooled melt. Hence, the Nd$_2$Fe$_{14}$B columnar grains may be formed directly from the undercooled melt. As a diameter of the droplet is decreased, the probability for a droplet to contain potential catalytic site for heterogeneous nucleation is reduced and the cooling rate increases. Thus, the undercooling level may be enhanced by reduction of the sample diameter. Even if a number of droplets experience a large undercooling, it is expected that
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Spherical Nd–Fe–B alloy ingots with the stoichiometric composition of Nd$_2$Fe$_{14}$B were produced by a containerless solidification processing in a 25-m drop tube. The relationship between the sample size and microstructure was investigated and then, the critical diameter for forming the Nd$_2$Fe$_{14}$B phase without the α-Fe phase was determined. The microstructure of the sample with 500μm in diameter consisted of the “fragmented dendrites” of the α-Fe phase and matrix of the Nd$_2$Fe$_{14}$B phase. The growth of primary iron phase is due to a low cooling rate and low undercooling level. In the sample diameter was 400μm and 350μm, almost all the microstructure consisted two regions, one is primary Nd$_2$Fe$_{14}$B columnar grains and the other is “fragmented dendrites” of the α-Fe phase in matrix of the Nd$_2$Fe$_{14}$B phase. The region that consists of Nd$_2$Fe$_{14}$B columnar grains expands as the sample diameter decreases from 400 to 350μm. Such a direct growth of the Nd$_2$Fe$_{14}$B columnar depends on the enhancement of the undercooling level. When sample diameter reduced to 250μm, the microstructure consisted of only primary Nd$_2$Fe$_{14}$B dendrites without the α-Fe phase. High cooling rate of the sample must be responsible for the primary Nd$_2$Fe$_{14}$B dendrites without the α-Fe phase. The critical diameter for forming the Nd$_2$Fe$_{14}$B phase without the α-Fe phase was in range of 250μm and 350μm.

4. Conclusion

Spherical Nd–Fe–B alloy ingots produced by a containerless solidification processing in a 25-m drop tube. The relationship between the sample size and microstructure was investigated and then, the critical diameter for forming the Nd$_2$Fe$_{14}$B phase without the α-Fe phase was determined. The microstructure of the sample with 500μm in diameter consisted of the “fragmented dendrites” of the α-Fe phase and matrix of the Nd$_2$Fe$_{14}$B phase. The growth of primary iron phase is due to a low cooling rate and low undercooling level. In the sample diameter was 400μm and 350μm, almost all the microstructure consisted two regions, one is primary Nd$_2$Fe$_{14}$B columnar grains and the other is “fragmented dendrites” of the α-Fe phase in matrix of the Nd$_2$Fe$_{14}$B phase. The region that consists of Nd$_2$Fe$_{14}$B columnar grains expands as the sample diameter decreases from 400 to 350μm. Such a direct growth of the Nd$_2$Fe$_{14}$B columnar depends on the enhancement of the undercooling level. When sample diameter reduced to 250μm, the microstructure consisted of only primary Nd$_2$Fe$_{14}$B dendrites without the α-Fe phase. High cooling rate of the sample must be responsible for the primary Nd$_2$Fe$_{14}$B dendrites without the α-Fe phase. The critical diameter for forming the Nd$_2$Fe$_{14}$B phase without the α-Fe phase was in range of 250μm and 350μm.

Acknowledgments

This work was financially supported by a grant-in-aid for Scientific Research from The Ministry of Education, Culture, Sports, Science and Technology. We also thank Dr. S. Hirosawa (Research and Development Center, Sumitomo Special Metals Co., Ltd JAPAN) for supplying the Nd–Fe–B alloy ingot. One of authors (M. Li) is grateful to Japan Society for the Promotion of Science (JSPS) for offering a JSPS fellowship.

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