Microstructure of Nd-Fe-B Alloys Solidified under Microgravity Conditions^{*1}

Shunpei Ozawa^{*2}, Jun Yoshizawa^{*2}, Tetsuji Saito and Tetsuichi Motegi

Department of Metallurgical Engineering, Chiba Institute of Technology, Narashino 275-0016, Japan

Nd-Fe-B alloy ingots with the stoichiometric composition of Nd₂Fe₁₄B were melted and then quenched in microgravity conditions of $9.8 \times 10^{-5} \text{ m s}^{-2}$ achieved by drop shaft experiments. The resultant alloy ingots showed virtually the same size of the equiaxed Nd₂Fe₁₄B grains throughout the entire sections. However, x-ray diffraction and electron microprobe analysis studies revealed that the alloy ingots contained of small amounts of α -Fe and Nd-rich phases as was the case for the alloys solidified under 9.8 m s^{-2} conditions.

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1. Introduction

Nd-Fe-B permanent magnets have been widely used for various applications, due to their superior energy products.¹⁾ The superiority of these magnets originates from the Nd₂Fe₁₄B intermetallic compound, which has a large saturation magnetization and a high anisotropy field.²⁾ These magnets are currently prepared either by sintering techniques or by rapid solidification processing techniques.^{1,3)} The Nd-Fe-B magnets with the maximum energy products of more than 400 KJ m^{-3} have been reported.⁴⁾ These magnets are produced by sintering techniques in conjunction with prior green compaction of the crushed ingot powders in an applied magnetic field. In order to achieve the high maximum energy products in the sintered magnets, the homogeneity in the microstructure of the alloy ingots are crucial. There are several processing techniques such as rapid solidification processing or containerless solidification processing techniques to produce the alloys with homogeneous microstructures.^{5,6)} Although the rapid solidification processing techniques give the alloys with the desired microstructures, the shapes of the alloys are limited. In the containerless solidification processing techniques, the melts experience a large undercooling as is the case for rapid solidification processing techniques. However, the following slow cooling may result in the formation of the primary phase.

It has been reported that the melts solidified under microgravity conditions may give the alloys with homogeneous microstructures.⁷⁾ Motegi *et al.* have been reported that the Sn-Pb alloy ingots solidified under microgravity conditions have very homogeneous microstructures.⁸⁾ The purpose of this study was to investigate the possibility of producing Nd-Fe-B alloys with homogeneous microstructures by the solidification under microgravity conditions. The microstructures of the resultant alloy ingots were compared with that of the alloy ingots solidified under 9.8 m s^{-2} conditions.

2. Experimental Procedure

A master alloy ingot with the stoichiometric composition of Nd₂Fe₁₄B was produced by induction melting under an argon atmosphere. Small amounts of the ingots were melted and superheated to about 1650 K (about 100 K above the equilibrium liquidus temperature) by an electric furnace in a BN crucible under an argon atmosphere. The temperature of the sample was monitored by a thermocouple encased in a quartz glass sheath. The BN crucible with the superheated melt was quenching into the cooling bath of the molten In-53.6%Bi alloy. (The temperature of the cooling bath was 353 K.) The quenching of the superheated melt was performed in microgravity conditions. The microgravity conditions of less than $9.8 \times 10^{-5} \text{ m s}^{-2}$ for 10 seconds were achieved by dropping a capsule with the electric furnace into a 500 m long shaft at the Japan Microgravity Center (JAMIC). For comparison, the BN crucible with the superheated melt was quenching into the cooling bath in 9.8 m s^{-2} conditions.

The samples were removed from the crucible and then cut along their horizontal equatorial plane for the measurements. The microstructure of the samples were observed under an optical microscope and a scanning electron microscope (SEM) equipped with an electron probe microanalyzer (EPMA) after polishing and etching in 10% Nital. The phases in the samples were analyzed by x-ray diffraction (XRD) using CuK α radiation.

3. Results and Discussion

Figure 1 shows the cooling curve of Nd-Fe-B alloy ingots solidified under microgravity conditions. For comparison, the cooling curve of Nd-Fe-B alloy ingot solidified under 9.8 m s^{-2} conditions is also shown as a dotted line. The liquidus temperature and peritectic temperature for the alloy are 1542 K and 1452 K, respectively.⁹⁾ The samples were melted and superheated to about 1650 K. The superheated melts were then quenched into the cooling bath just before dropping the electric furnace. The temperature of the sample became far below the liquidus temperature and the peritectic temperature during the following 10 seconds when the microgravity con-

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^{*2}Graduate Student, Chiba Institute of Technology.

Fig. 1 Cooling curves of $\text{Nd}_2\text{Fe}_{14}\text{B}$ alloy ingots solidified under microgravity conditions ($9.8 \times 10^{-5} \text{ m s}^{-2}$), along with the data of $\text{Nd}_2\text{Fe}_{14}\text{B}$ alloy ingots solidified under 9.8 m s^{-2} conditions. The duration when the microgravity was achieved was indicated by the arrow.

ditions was achieved. Although the obvious recalescence is not seen in the cooling curve, the samples are expected to be solidified in microgravity conditions. The cooling rate of the sample solidified under microgravity conditions is about 60 K s^{-1} . Virtually the same cooling rate is obtained from the sample solidified under 9.8 m s^{-2} conditions. This indicates that the gravity conditions does not affect the cooling rate of the sample.

Figure 2 shows the cross sectional microstructures of Nd-Fe-B alloy ingots solidified under microgravity conditions and 9.8 m s^{-2} conditions. The upper, middle, and bottom parts of the cross sections of the samples were observed. The microstructures of the sample solidified under 9.8 m s^{-2} conditions show equiaxed grains throughout the entire sections. Similar equiaxed grains are observed in the microstructure of the sample solidified under microgravity conditions, indicating that the gravity condition does not significantly affect the microstructure of the alloy ingots. When an alloy solidifies under 9.8 m s^{-2} conditions, the expected microstructure is not so homogeneous due to the heat convection and the gravity segregation. Such a heat convection and a gravity segregation can be neglected when an alloy solidifies under microgravity conditions.¹⁰⁾ As a result, the alloy solidified under microgravity conditions is expected to have a very homogeneous microstructure.

In order to clarify the small difference in the microstructures of the samples, the average sizes of these grains were measured. The average sizes of grains in the microstructures of the samples are summarized in Table 1. Except for the gravity conditions, the samples were melted and solidified in the same conditions. The average grain size of the sample solidified under 9.8 m s^{-2} conditions varies from $5.7 \mu\text{m}$ of

Fig. 2 The cross-sectional microstructures of $\text{Nd}_2\text{Fe}_{14}\text{B}$ alloy ingots: (a) upper, (b) middle, and (c) bottom parts of the sample solidified under 9.8 m s^{-2} conditions, (d) upper, (e) middle, and (f) bottom parts of the sample solidified under microgravity conditions ($9.8 \times 10^{-5} \text{ m s}^{-2}$).

Table 1 Average grain sizes of upper, middle, and bottom parts of Nd-Fe-B alloy ingots solidified under microgravity conditions ($9.8 \times 10^{-5} \text{ m s}^{-2}$) and 9.8 m s^{-2} conditions.

	Nd-Fe-B alloy ingots solidified under microgravity conditions	Nd-Fe-B alloy ingots solidified under 9.8 m s^{-2} conditions
Upper parts of the sample	$6.0 \mu\text{m}$	$7.2 \mu\text{m}$
Middle parts of the sample	$5.8 \mu\text{m}$	$8.1 \mu\text{m}$
Bottom parts of the sample	$5.5 \mu\text{m}$	$5.7 \mu\text{m}$

the bottom part of the sample to $8.1 \mu\text{m}$ of the middle part of the sample. On the other hand, the average grain size of the sample solidified under microgravity conditions varies from $5.5 \mu\text{m}$ of the bottom part of the sample to $6.0 \mu\text{m}$ of the upper part of the sample. This indicates that the sample solidified under microgravity conditions has a very homogeneous microstructure as expected for the alloy solidified under microgravity conditions.

In the production of the stoichiometric $\text{Nd}_2\text{Fe}_{14}\text{B}$ alloy ingots, the main problem is the formation of the $\alpha\text{-Fe}$ phase.⁸⁾ The existence of the $\alpha\text{-Fe}$ phase deteriorates the hard magnetic properties of Nd-Fe-B alloys and results in the formation of Nd-rich phase, which is very sensitive to be attacked by the oxidation environments. Therefore, a long time homogenization at elevated temperatures is required to reduce the amount of the primary $\alpha\text{-Fe}$ phase in the $\text{Nd}_2\text{Fe}_{14}\text{B}$ alloy ingots.¹¹⁾ The detailed microstructural studies are carried out to investigate the existence of the primary $\alpha\text{-Fe}$ phase and

Nd-rich phase in the $\text{Nd}_2\text{Fe}_{14}\text{B}$ alloy ingots. Figure 3 shows the SEM micrograph of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ alloy ingots solidified under microgravity conditions and the corresponding x-ray mappings of neodymium and iron. Iron and neodymium are detected in the matrix phase, as expected for the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase. No neodymium is detected in the dendritic phase where iron is enriched. Neodymium is enriched in the grain boundary regions. This indicates that the sample contains both iron phase and Nd-rich phase. The XRD studies of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ alloy ingots solidified under microgravity conditions showed the diffraction peaks from α -Fe phase and $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase. These results suggest that the sample solidified under microgravity conditions contained some α -Fe phase together with the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase as is the case for the $\text{Nd}_2\text{Fe}_{14}\text{B}$ alloy ingots solidified under 9.8 m s^{-2} conditions. No clear diffraction peaks from the Nd-rich phase were found in the XRD pattern because of the small fraction of the Nd-rich phase. The primary α -iron phase is often detected together with either $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase or the amorphous phase in the alloys produced by rapid solidification processing.¹²⁾

It is known that the nucleation and growth of the peritectic phase will be allowed thermodynamically when the liq-

uid phase is undercooled far below the peritectic temperature.¹³⁾ The crystallization of the properitectic phase can be suppressed and the crystallization of the peritectic phase may dominate the solidification process. In the Nd-Fe-B system alloys, the peritectic phase is the hard magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase and the properitectic primary phase is the soft magnetic α -Fe phase. Thus, the large undercooling may be required to achieve the direct crystallization of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase in the solidification of the stoichiometric $\text{Nd}_2\text{Fe}_{14}\text{B}$ alloy ingots. Nagashio *et al.* have been reported that the direct nucleation of a peritectic phase can be obtained by quenching the undercooled melts onto a copper plate.¹⁴⁾ Such a large undercooling of melts may be achieved in the solidification under microgravity conditions due to the none of heat convection and gravity segregation. Thus the quenching of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ melts would lead to the formation of homogeneous microstructures without the primary α -Fe phase.

4. Conclusion

Nd-Fe-B alloy ingots with the stoichiometric composition of $\text{Nd}_2\text{Fe}_{14}\text{B}$ were melted and superheated by an electric furnace. The super heated melt was quenched under microgravity conditions of $9.8 \times 10^{-5} \text{ m s}^{-2}$ for 10 seconds achieved by dropping the furnace into a 500 m long shaft. The temperature of the melt reached below the peritectic temperature during the microgravity conditions. The resultant alloy ingots consisted mostly of equiaxed $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains as was the case for the alloy ingots solidified under 9.8 m s^{-2} conditions. However, the grain size distribution in the alloy ingots solidified under microgravity conditions was smaller than that in the alloy solidified under 9.8 m s^{-2} conditions. The α -Fe and Nd-rich phases were noticed in the grain boundary regions of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains in the alloys solidified under microgravity conditions.

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Fig. 3 Scanning electron micrograph of $\text{Nd}_2\text{Fe}_{14}\text{B}$ alloy ingots solidified under microgravity conditions and the corresponding x-ray mappings of iron and neodymium.

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