

## A Study on the Magnetic Properties and Solid-HDDR Characteristics of Nd-Fe-B-type Alloys

S. W. Shon and H. W. Kwon

*Department of Materials Science and Engineering, The Pukyong National University, Pusan 608-739, Korea*

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A solid-HDDR characteristics of the Nd-Fe-B-type alloys and magnetic properties of the solid-HDDR treated materials have been investigated using three types of alloys;  $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$  (alloy A),  $\text{Nd}_{16}\text{Fe}_{75.9}\text{B}_8\text{Zr}_{0.1}$  (alloy B), and  $\text{Nd}_{12.6}\text{Fe}_{68.7}\text{Co}_{11.6}\text{B}_8\text{Ga}_{1.0}\text{Zr}_{0.1}$  (alloy C). It has been found that the four-components alloy B and six-components alloy C have showed higher hydrogenation temperatures than the ternary alloy A. The alloys A and B appeared to absorb more hydrogen gas more rapidly as well compared to the alloy C. The disproportionation temperature of hydrogenated materials was exhibited no significant difference among the alloys. The thermal stability of the hydrided materials of the three types of alloys was found to become more stable in order of number of components. The disproportionation and the recombination kinetics were significantly sluggish in the solid-HDDR manner with respect to the conventional manner. Some degree of anisotropic nature was found to exist in the ingot and this anisotropic nature was retained even after the solid-HDDR treatment. It was suggested the solid-HDDR treatment may possibly be used for a preparation of an isotropic or anisotropic Nd-Fe-B-type cast magnets.

### 1. Introduction

The Nd-Fe-B-type magnets are usually produced by the methods based on the traditional powder metallurgy [1, 2] or melt-spinning [3]. In these method, a handling of the highly reactive powder-form material is inevitable, thus the Nd-Fe-B-type powder should be treated under an inert gas atmosphere or vacuum throughout the whole manufacturing process. This causes a complication of production equipments and difficulty of process control, which eventually lead to a higher cost of the products. Thus, an alternative manufacturing process for the conventional methods, which can avoid the manufacturing and handling of a powder-form material, has long been desired. The most productive and cost-effective method which involves no powder-form material would be a production of cast magnet. Unfortunately, the Nd-Fe-B-type material has no appreciable hard magnetic properties at the state of cast ingot due to the excessively coarse grain size of the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  phase grains. It has been known, however, that the Nd-Fe-B-type cast ingot material can be easily transformed into a magnetically highly coercive material by means of a hydrogen treatment (HDDR) [4-6]. The feature associated with the conventional HDDR treatment is that the ingot material is usually converted into a powder form after the treatment, so this conventional method cannot be used for production of cast magnet [7-9]. However, if the HDDR treatment can be modified such that the ingot material would be mechani-

cally intact in a solid form even after the hydrogen treatment, the modified HDDR process can be utilised for a realisation of the Nd-Fe-B-type cast magnet. As a matter of fact, it has been reported that the ingot material can remain intact and the mechanical strength of the initial material can be restored even after the HDDR if it is properly modified (solid-HDDR) [10-12]. In order that the solid-HDDR treatment can be used as a mean of producing cast magnet, the HDDR treated material has to exhibit not only a sufficient mechanical strength but also a sufficient hard magnetic properties. The present authors group reported previously that the mechanical strength and shape of Nd-Fe-B-type cast ingot material can be retained after the solid-HDDR process [13]. In the present study, a solid-HDDR characteristics of Nd-Fe-B-type alloys has been investigated, and magnetic properties of the solid-HDDR treated materials has also been examined. The feasibility study of a Nd-Fe-B-type cast magnet using a solid-HDDR treatment is also included in this article.

### 2. Experimental Procedures

The alloys used for the present study were produced by an induction melting of the constituent elements with high purity. Three types of alloys were used;  $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$  (alloy A),  $\text{Nd}_{16}\text{Fe}_{75.9}\text{B}_8\text{Zr}_{0.1}$  (alloy B), and  $\text{Nd}_{12.6}\text{Fe}_{68.7}\text{Co}_{11.6}\text{B}_8\text{Ga}_{1.0}\text{Zr}_{0.1}$  (alloy C). The ternary alloy A is a typical "Neomax" composition alloy, which is known to exhibit an iso-

tropic HDDR character. The isotropic HDDR means that recombined small grains have no crystallographic orientation relation with their parent grain, thus each recombined grain has a random orientation and the material becomes magnetically isotropic. In the four-components alloy B ( $\text{Nd}_{16}\text{Fe}_{75.9}\text{B}_8\text{Zr}_{0.1}$ ) some of the Fe was substituted by a small amount of Zr. The small addition of Zr has been known to induce an anisotropic HDDR character. The anisotropic HDDR means that recombined small grains have more or less the same crystallographic orientation with that of their parent grain, thus each recombined grain has the same orientation with each other and the material becomes magnetically anisotropic. The six-components alloy C ( $\text{Nd}_{12.6}\text{Fe}_{68.7}\text{Co}_{11.6}\text{B}_8\text{Ga}_{1.0}\text{Zr}_{0.1}$ ) is featured with a multiple addition of Co, Ga, and Zr. This composition is known to show a good anisotropic HDDR character and high permanent magnetic properties. Compositions of the alloys used in the present study are tabulated in Table 1. The as-cast alloys were homogenised at  $1000^\circ\text{C}$  under Ar gas atmosphere (for 3 days for alloy A and B, and for 9 days for alloy C). Specimens with dimension of  $10 \times 10 \times 2 \text{ mm}^3$  were cut from the homogenised alloys and then subjected to a solid-HDDR treatment (see reference [14] for details of solid-HDDR profile). The HDDR characteristics of alloys (in a conventional or solid manner) were examined by means of a TPA (Thermopiezic analyser), a DTA (Differential thermal analyser), and an XRD (Cu-K $\alpha$  radiation). A variation of intrinsic coercivity during the desorption and recombination was also used for examining the HDDR characteristics. Magnetic characterisation of the materials was performed by means of a VSM. For the VSM measurements the samples were previously magnetised by a pulse magnetic field of 4.5 Tesla.

### 3. Results and Discussion

Fig. 1 represents DTA traces showing a reactivity of the alloys for the three types of alloys undertaken under a hydrogen gas with hydrogen gas. It can be seen that two exothermic peaks appear during heating up to around  $800^\circ\text{C}$ . The exothermic event at lower temperature may be correspond to the hydrogen absorption mainly by the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  phase and the event at higher temperature to the disproportionation of the hydrogenated  $\text{Nd}_2\text{Fe}_{14}\text{BH}_x$  material into a mixture of  $\alpha\text{-Fe}$ ,  $\text{NdH}_2$ , and  $\text{Fe}_2\text{B}$ . It also appears that compared to the ternary alloy A the four component alloy B and six component alloy C have higher hydrogenation

Table 1. The chemical composition of alloys used in the present study (at.%)

	Nd	Fe	Co	B	Ga	Zr
Alloy A	15	77		8		
Alloy B	16	75.9		8		
Alloy C	12.6	68.7	11.6	6	1.0	0.1

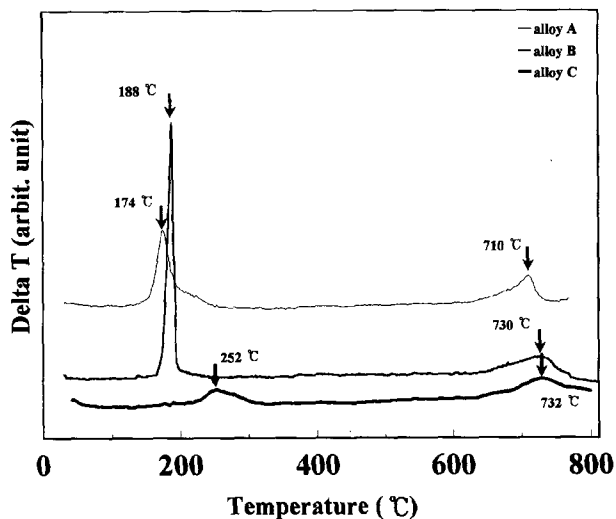


Fig. 1. DTA traces for the alloys under hydrogen gas.

temperatures. It is notable that the exothermic peaks for the hydrogenation of the alloy A and B (in particular alloy B) are featured with a narrow temperature range and high heat output with respect to the alloy C, and are indicating that those alloys are hydrogenated more rapidly. Meanwhile, the disproportionation temperatures of hydrogenated material appear to exhibit no significant difference among the alloys.

The hydrogenation and disproportionation behaviours of the alloys were examined in more detail using a TPA, and the results are shown in Fig. 2. As can be seen, on heating up to  $800^\circ\text{C}$  under hydrogen gas in a closed chamber two pressure drops appear for each alloy. Needless to say, the pressure drop appearing at lower temperature may be due to hydrogen absorption (hydrogenation) mainly by  $\text{Nd}_2\text{Fe}_{14}\text{B}$  phase, while the pressure drop at higher temperature may be due to the disproportionation of the  $\text{Nd}_2\text{Fe}_{14}\text{BH}_x$  hydride, which absorbs hydrogen additionally. It is notable that alloy A and B (in particular alloy B) show a greater hydrogen pressure drop on the hydrogenation compared to the alloy

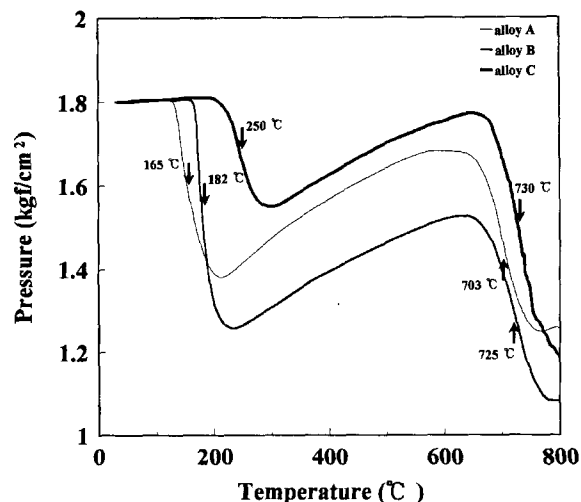


Fig. 2. TPA traces for the alloys under hydrogen gas.

C. The greater pressure drops for the alloy A and B indicate that these alloys absorb more hydrogen. More rapid and greater pressure drops on hydrogenation for the alloy A and B appear to be consistent well with the previous DTA results, which showed narrower and higher exothermic peak for the hydrogenation of the alloy A and B.

It is also notable that the hydrogen pressure drop due to the disproportionation of the hydrogenated alloys appears to stop at higher temperature for alloy B compared to alloy A, indicating that the hydride of four component alloy B has higher thermal stability than the ternary alloy A hydride. It seems that the hydrogen pressure drop due to the disproportionation of the hydrogenated six component alloy C still continues even at 800°C, which is the highest temperature available from the TPA rig. This indicates that the hydride of six component alloy C has even higher thermal stability.

For an effective HDDR treatment in a conventional or solid reaction, a full disproportionation of the hydride phase is essential. It is, therefore, interesting to examine the disproportionation character of the hydrogenated alloy in the solid manner and compare it to that of the conventional manner. For this purpose the alloy C was selected as the previous DTA and TPA results showed that this alloy exhibited the highest thermal stability among the alloys. The alloy C fully hydrogenated in a conventional or solid manner was subjected to a disproportionation at 800°C for 1 hour. Phase analysis of the materials disproportionated under the same condition was performed using an XRD, and the obtained spectra are shown in Fig. 3. The material disproportionated for 1 hour in a conventional manner appears to be fully disproportionated and  $\alpha$ -Fe and  $\text{NdH}_2$  phases are dominantly observed. On the other hand, the material disproportionated for 1 hour in a solid manner appears to have still not-disproportionated hydride phase.

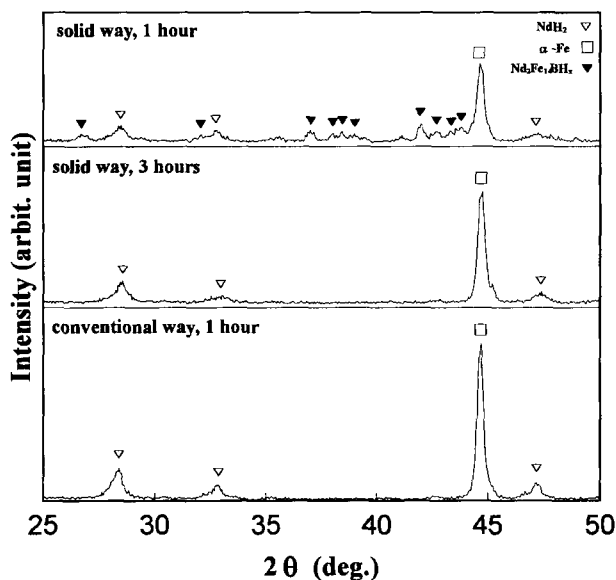


Fig. 3. XRD patterns for the alloy C hydrogenated and then disproportionated at 800°C.

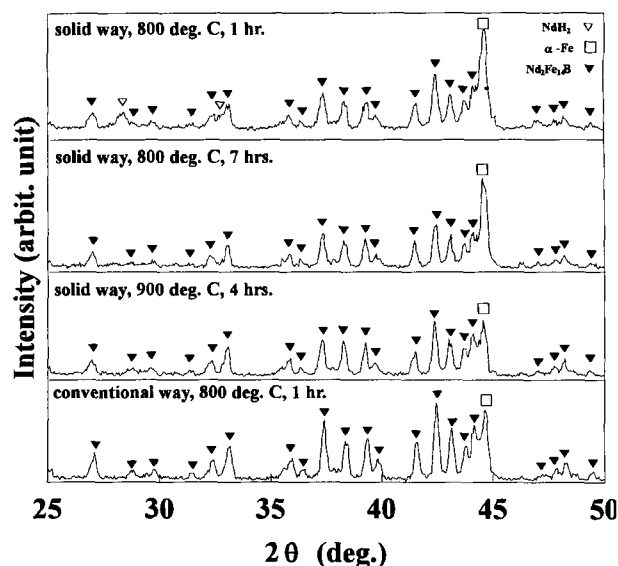


Fig. 4. XRD patterns for the alloy C recombined under various conditions.

The amount of not-disproportionated hydride phase decreased as the disproportionation time was extended, and as can be seen in Fig. 3. The not-disproportionated hydride phase disappeared after 3 hours and full disproportionation was confirmed. This result indicates that the disproportionation kinetics is significantly sluggish in the solid-HDDR manner with respect to the conventional manner, and this is probably due to the poor diffusion kinetics of hydrogen atom into the solid form sample.

The samples fully disproportionated in different ways were subjected to a desorption and recombination treatment at 800°C or 900°C under vacuum, and its development was traced by a phase analysis using an XRD. As can be seen in Fig. 4 the sample recombined for 1 hour in a conventional manner shows no presence of  $\text{NdH}_2$  phase and the recombined  $\text{Nd}_2\text{Fe}_{14}\text{B}$  phase is dominant, although some of the free iron is still observed. However, it is found that the sample recombined under the same condition in a solid-manner still had showed a significant amount of uncombined  $\text{NdH}_2$  and  $\alpha$ -Fe. The recombination in a solid manner was so sluggish that the uncombined phases were still observed even after the treatment at 800°C for 7 hours. In order to complete the recombination within a practical time period the recombination temperature was raised to 900°C, and the development was monitored using an XRD. It was found that the disproportionated  $\text{NdH}_2$  phase disappeared after 4 hours as shown in Fig. 4. These results indicate that the recombination kinetics in the solid manner is considerably sluggish with respect to the conventional manner.

Recombination behaviour of the disproportionated material in different manners was also examined using a variation of intrinsic coercivity during the recombination, and the results were presented in Fig. 5. The coercivity variation for the sample treated in a solid manner shows a peak (around 6 kOe) at around 4 hours and then rapidly

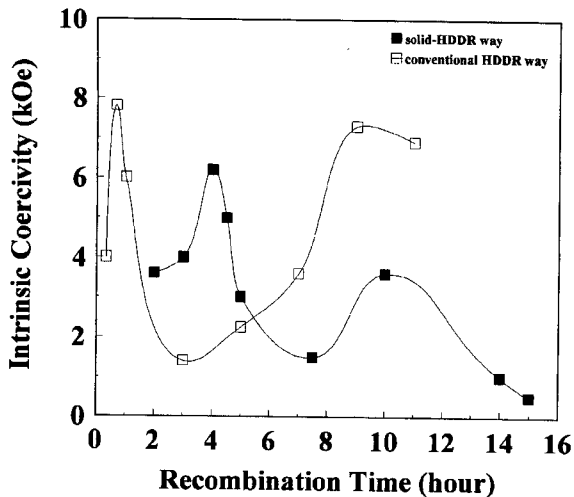


Fig. 5. Variation of the intrinsic coercivity as a function of prolonged recombination time for the solid-HDDR or conventional HDDR treated alloy C.

decreases. This development seems to be consistent well with the X-ray phase analysis results in Fig. 4. The coercivity development in a conventional manner appears to be much faster, and the peak coercivity also has higher value (around 8 kOe). It is notable that in both the conventional and solid manner the degraded coercivity after showing the peak is restored to some extent on prolonged recombination. This behaviour was also observed previously in a different alloy system ( $\text{Nd}_{12.6}\text{Fe}_{\text{bal}}\text{B}_8$ ,  $\text{Nd}_{12.6}\text{Fe}_{\text{bal}}\text{B}_6\text{Zr}_{0.1}$ , and  $\text{Nd}_{12.6}\text{Fe}_{\text{bal}}\text{Co}_{11.6}\text{B}_6\text{Ga}_{1.0}\text{Zr}_{0.1}$ ), and it was accounted for in terms of the development of well-defined smooth grain boundary between the recombined grains on prolonged recombination [15].

In order that the solid-HDDR treated material can be used as a magnet it has to have an isotropic and anisotropic features according to an application requirements as the conventional sintered or bonded magnets do. For an isotropic solid-HDDR magnet no particular crystallographic relation in the cast ingot state is required. However, if the solid-HDDR treated materials is to be used as an anisotropic magnet two major requirements must be fulfilled: First, the initial ingot alloy has to have an anisotropic nature in which the easy magnetisation direction (c-axis) of the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  magnetic phase grains are pointing a certain direction. Secondly, the anisotropic nature in the initial ingot must be retained even after the HDDR treatment (anisotropic HDDR). In the present article, in an attempt to examine the feasibility of solid-HDDR treated anisotropic magnet those two requirements were examined. The presence of anisotropic nature in the initial ingot was also examined by means of an XRD. A specimen in cubic shape was cut from the ingot in such a way that one plane is parallel to the mould wall as shown in Fig. 6. The X-ray spectra obtained from the two different planes are shown in Fig. 7. Also included in Fig. 7 is the spectrum for an isotropic powder sample for a comparison. It appears that compared to the isotropic

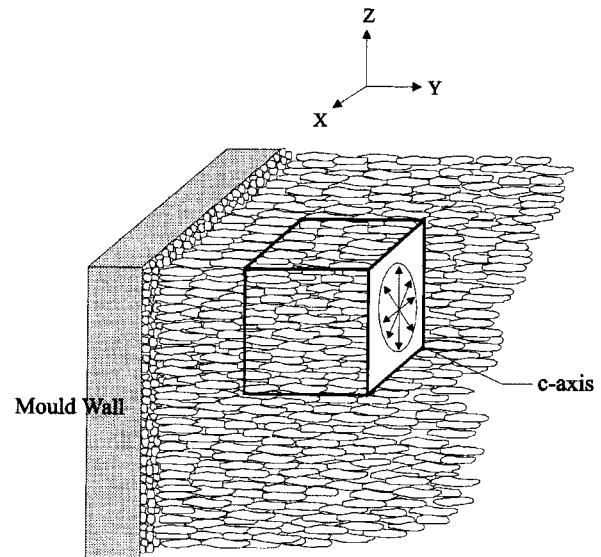


Fig. 6. Schematic diagram showing the details of specimen cut from the ingot.

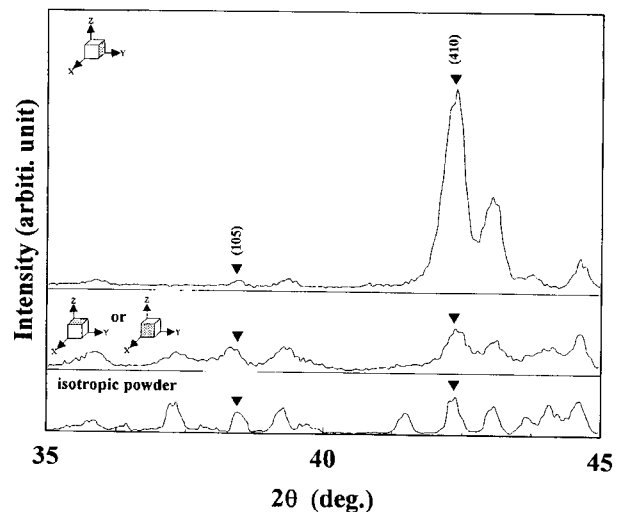


Fig. 7. XRD patterns for the different planes of specimen (annealed alloy C).

powder sample the spectrum from XZ-plane is featured to have disproportionately high intensity of the (410) plane and disproportionately low intensity of the (105) plane. This result indicates that c-axes of the grains are placed more or less in the XZ-plane, and this seems to be consistent well with that from the magnetic domain image observation.

It is of most importance that the anisotropic nature existing in the ingot must be retained even after the solid-HDDR treatment for a realisation of the anisotropic cast magnet. This requires that an anisotropic HDDR must be guaranteed during the solid-HDDR treatment. The retention of initial anisotropic nature after the solid-HDDR was examined by means of XRD and magnetic characterisation using the alloy C. This alloy contains some additives, Co, Ga, and Zr, which are known to cause an anisotropic HDDR in the conventional manner. A plate-like specimen with dimension of  $10 \times 10 \times 2 \text{ mm}^3$  was cut from the ingot being parallel to

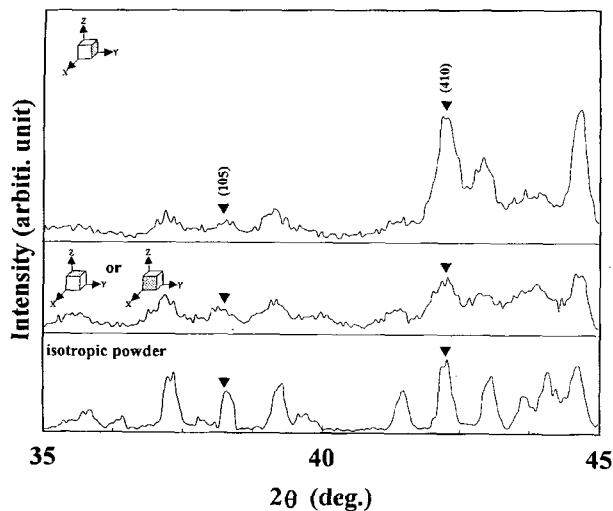


Fig. 8. XRD patterns for the different planes of specimen (solid-HDDR-treated alloy C).

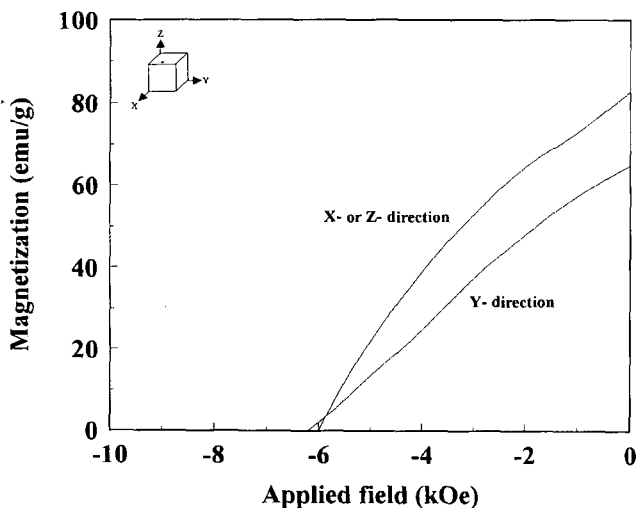


Fig. 9. Demagnetisation curves measured along different directions of the solid-HDDR treated alloy C.

XZ-plane, and subjected to a solid-HDDR treatment. X-ray spectrum was taken from the XZ-plane after the solid-HDDR, and the result is shown in Fig. 8. Also included in Fig. 8 is the spectrum from an isotropic powder sample for a comparison. As can be seen, compared to the isotropic powder sample the intensity of (410) plane of the solid-HDDR treated sample appears to be still disproportionately high, indicating that the anisotropic nature existing in the initial ingot has been retained to a great extent after the solid-HDDR. The retention of anisotropic nature was also examined by means of magnetic characterisation using a VSM. A specimen in a cubic shape with dimension of  $2 \times 2 \times 2 \text{ mm}^3$  was cut from the plate-like sample used for the X-ray diffraction, and the remanence was measured along two different directions X (or Z) or Y in Fig. 6. The measured demagnetisation curves are shown in Fig. 9. It appears that the remanence along the X- or Z- direction is somewhat higher than that along the Y- direction, indicating a presence of some degree of anisotropic nature.

Table 2. Magnetic properties of the solid-HDDR treated alloy C

$H_c$ (kOe)	$B_r$ (kG)	$(BH)_{max}$ (MGOe)
6.2	7.9	8.2

The best permanent magnetic properties obtained so far from the solid-HDDR treated alloy C are tabulated in Table 2. It seems that those properties are not good enough for a commercialisation of the cast magnets, and further improvement of the properties by an appropriate means, such as an optimisation of the process, variation of alloy composition or improving the texture in cast ingot, is required. It is found obviously, however, that the solid-HDDR treatment to the Nd-Fe-B-type ingot material can give rise to an appreciable coercivity and also retain the anisotropic nature existing in the initial ingot materials. This fact suggests that the solid-HDDR treatment may possibly be used for a preparation of an isotropic or anisotropic Nd-Fe-B-type cast magnets.

#### 4. Conclusions

A solid-HDDR characteristics of three different types of alloys has been examined, and it has been found that compared to the ternary alloy A the four-components alloy B and six-components alloy C have higher hydrogenation temperatures. The alloy A and B appeared to absorb more hydrogen gas and more rapidly compared to the alloy C. The disproportionation temperature of hydrogenated materials was found to exhibit no significant difference among the alloys. It was also found that the hydride of four-components alloy B has higher thermal stability than the ternary hydride and the hydride of six-components alloy C has even higher thermal stability. The disproportionation and the recombination kinetics were significantly sluggish in the solid-HDDR manner with respect to the conventional manner. It was found that some degree of anisotropic nature existed in the ingot and this anisotropic nature was retained even after the solid-HDDR treatment. It was suggested the solid-HDDR treatment may possibly be used for a preparation of an isotropic or anisotropic Nd-Fe-B-type cast magnets.

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