HDDR Characteristics and Magnetic Properties of $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ (x = 0-0.6) Alloys

H. W. Kwon*

School of Materials Science and Engineering, Pukyong National University, Nam-Gu, Pusan 608-739, Korea

HDDR characteristics and magnetic properties of $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ (x = 0-0.6) alloys were investigated. The effect of applying magnetic field during the recombination step on the anisotropic nature of the HDDR-treated material was also examined. The $Nd_2(Fe,Co)_{14}B$ phase in the Nd-Fe-B alloys with high Co-substitution alloy had remarkably enhanced phase stability. The $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ alloys with high Co-substitution could be HDDR-treated successfully by only using high pressure hydrogen. However, these alloys had no appreciable coercivity. The poor coercivity of the HDDR-treated $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ alloys with high Co-substitution was attributed to the $Nd(Fe,Co)_2$ phase in the alloys. The magnetic filed applied during the recombination step had little effect on the anisotropic nature of the HDDR-treated powder.

Key words : HDDR, Hydrogenation, Disproportionation, Desorption, Recombination, NdFeCoB

1. Introduction

High coercivity Nd-Fe-B powder is produced mainly by two techniques, the melt-spinning [1] and HDDR (hydrogenation, disproportionation, desorption, and recombination) [2, 3] processes. In both processes, fine grain structure is developed, and this is considered as a key to the achievement of high coercivity. In the HDDR process, in particular, the recombination stage is considered to be the most crucial step in determining the final grain size. Lower recombination temperature is, of course, beneficial to obtain an even and fine grain structure. Many research efforts have been made to find an effective way of reducing the recombination temperature via chemical substitution, and it was found that the Co-substitution for Fe in the Nd-Fe-B alloy was effective in reducing the recombination temperature of $Nd_2Fe_{14}B$ phase, thus improving the magnetic properties of HDDR-treated Nd-Fe-B materials [4-7]. In this article, a particular emphasis was placed on the investigation of HDDR characteristics and magnetic properties of the Nd-Fe-B alloy with high Co-substitution. The effect of applying magnetic field during the recombination step on the anisotropic nature of the HDDR-treated material was also examined.

*Corresponding author: Tel: +82-52-620-1641, e-mail: hwkwon@pknu.ac.kr

2. Experimental procedure

The $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ (x = 0-0.6) alloys were prepared by induction melting of the high purity constituent elements. The alloy ingots were annealed for 3 days at 1050 °C, and then pulverized into powder with particle size of around 100 μm. The powder materials were used for the HDDR treatment under various conditions. The reaction between the material and hydrogen gas was investigated by DTA with heating rate of 7 °C/min under various hydrogen pressures from 1 to 10 kgf/cm². The phase changes of the material during the HDDR process were examined by XRD with Cu-K_α radiation. The magnetic characterization of the HDDR-treated materials was performed by VSM. Prior to the VSM measurement, the powder sample was wax-bonded and magnetized with pulsing field of 4.5 Tesla. For some samples the desorption and recombination step were undertaken under magnetic field (1 kOe) in order to see the effect of magnetic field on the anisotropic nature of the HDDR-treated powder material. The anisotropic nature of the powder was examined using an aligned sample. The powder was aligned under a magnetic filed of 10 kOe, and then wax-bonded. The demagnetization curves of the aligned sample were measured along the aligning direction and perpendicular to it after pulse magnetizing (4.5 Tesla) along each direction. The anisotropic nature of the powder was evaluated by comparing the

remanence values along the parallel and transverse directions.

3. Results and Discussion

Fig. 1 shows the intrinsic coercivity variation with the Co-content in the $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ alloys HDDR-treated at the same condition. The hydrogenation and disproportionation was carried out by heating the alloys up to 750 °C and holding there for 30 min under 1 kgf/cm^2 hydrogen gas. The desorption and recombination were carried out at 750 °C for 30 min under vacuum. As can be seen, the coercivity of the HDDR-treated $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ materials shows remarkably different values depending on the Co-content. The materials with Co-substitution less than x = 0.2 have reasonably high coercivity. On the contrary, the materials with higher Co-contents (x = 0.4 and 0.6) exhibit rather poor coercivity. Various HDDR conditions were applied to the alloys with higher Co-
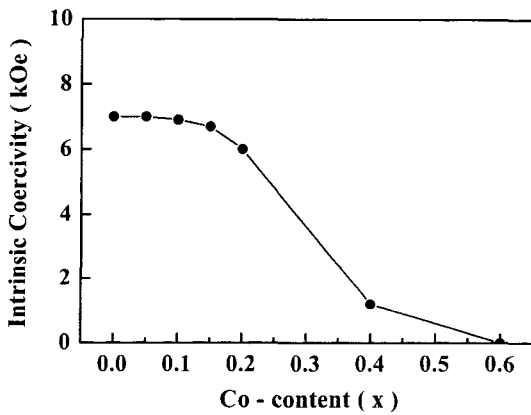
Fig. 3. Variation of intrinsic coercivity as a function of recombination time for some HDDR-treated $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ alloys.

substitution, and the coercivity was found to be still negligibly low as shown in Fig. 2 and Fig. 3. For comparison, coercivity variation of the $Nd_{15}Fe_{77}B_8$ alloy without Co-substitution is also included in the Fig. 2 and Fig. 3.

It is of interest to understand the reason for the poor coercivity of $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ alloys with higher Co-contents. One possible explanation would be related to the enhanced stability of the $Nd_2Fe_{14}B$-type phase by the Co-substitution for Fe. The stability of $Nd_2Fe_{14}B$ phase under hydrogen atmosphere is enhanced significantly by the Co-substitution as can be seen from the DTA result (Fig. 4) performed under hydrogen (1 kgf/cm^2) for the alloys with/without Co-substitution. It can be seen that, for the $Nd_{15}Fe_{77}B_8$ alloy without Co-substitution, two sharp reaction exotherms representing the hydrogenation and disproportionation are visible at around 70 °C and 720 °C, respectively. For the $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ alloys with high Co-substitution (x = 0.4 and 0.6), broad hydrogenation exotherm is visible at higher temperature above 200 °C. It is noted that the exotherm for the disproportionation appears to be broad for the x = 0.4 alloy and, even more

Fig. 1. Variation of intrinsic coercivity as a function of Co-content in the HDDR-treated $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ alloys.
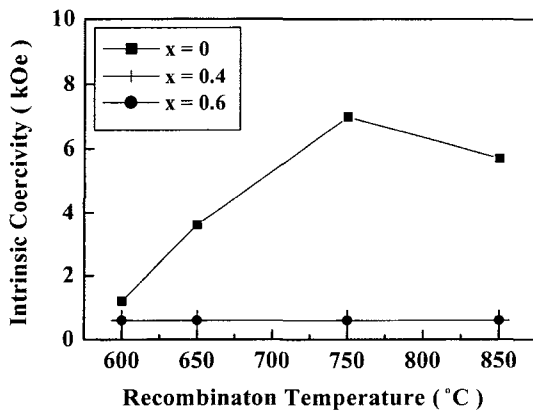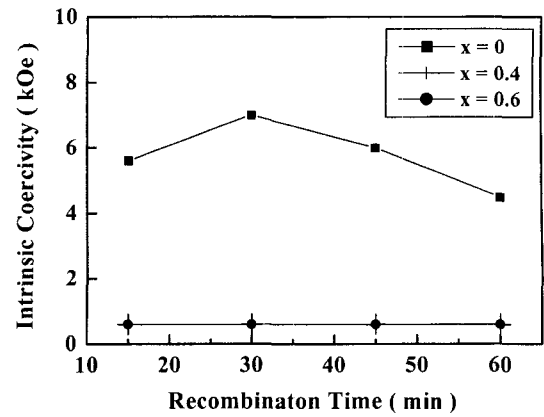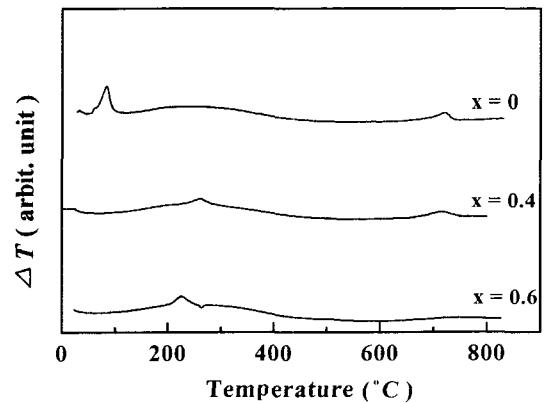
Fig. 2. Variation of intrinsic coercivity as a function of recombination temperature for some HDDR-treated $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ alloys.

Fig. 4. DTA results performed under 1 kgf/cm^2 hydrogen gas for some HDDR-treated $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ alloys.

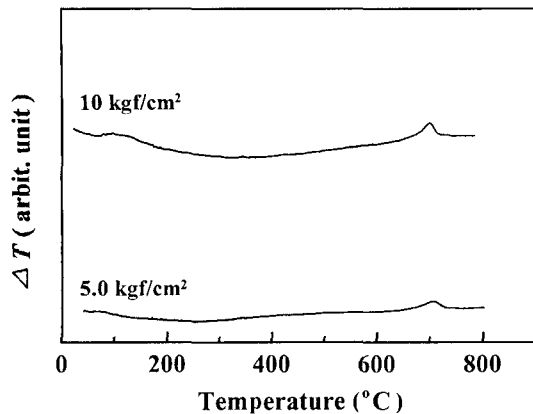Fig. 5. DTA results performed under high pressure hydrogen gas for the $Nd_{15}(Fe_{0.4}Co_{0.6})_{77}B_8$ alloy.

Fig. 6. XRD spectrum of the $Nd_{15}(Fe_{0.4}Co_{0.6})_{77}B_8$ alloy heated up to 800 °C under 10 kgf/cm² hydrogen gas.

remarkably, this disappears for the x = 0.6 alloy. This result indicates that $Nd_2Fe_{14}B$ phase without Co-substitution can be disproportionated at an elevated temperature under 1 kgf/cm² hydrogen. However, $Nd_2Fe_{14}B$ phase is stabilized by the Co-substitution, and can not be disproportionated easily under 1 kgf/cm² hydrogen even at high temperature. Therefore, the $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ alloys with high Co-substitution can not be successfully HDDR-treated under the atmospheric hydrogen pressure, and no appreciable coercivity can be achieved.

If we assume that the poor coercivity of the HDDR-treated $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ materials with high Co-substitution would be related to the difficult disproportionation due to the enhanced $Nd_2Fe_{14}B$ phase stability, the HDDR-treated materials would exhibit an appreciable coercivity provided that it can be disproportionated by any means. The easiest way to obtain a fully disproportionated material may be to apply a high pressure hydrogen gas. The alloy with high Co-substitution (x = 0.6) was heated under high pressure hydrogen gas (5 and 10 kgf/cm²), and the reaction was monitored by DTA (Fig. 5). A sharp and clear exotherm is visible at around 700 °C, and this corresponds to a complete disproportion of the 2 : 14 : 1 phase. It is noted that no obvious exotherm for the hydrogenation is visible in these high pressure hydrogen DTA results, and this may be attributed to the fact that the material has been hydrogenated already under high pressure hydrogen gas even at room temperature before heating. The DTA sample heated up to 800 °C under 10 kgf/cm² hydrogen gas was phase-analyzed by XRD, and the result is shown in Fig. 6. This XRD analysis also indicates that the matrix $Nd_2(Fe,Co)_{14}B$ phase is no longer existed, but instead a mixture consisted of mainly NdHx and Fe(Co) resulting from the disproportionation of the $Nd_2(Fe,Co)_{14}B$ phase is found. The $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$
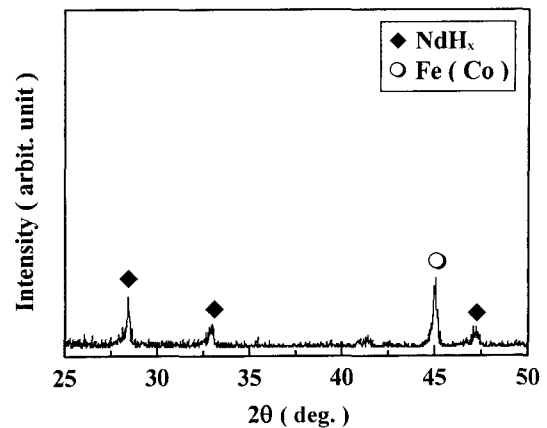
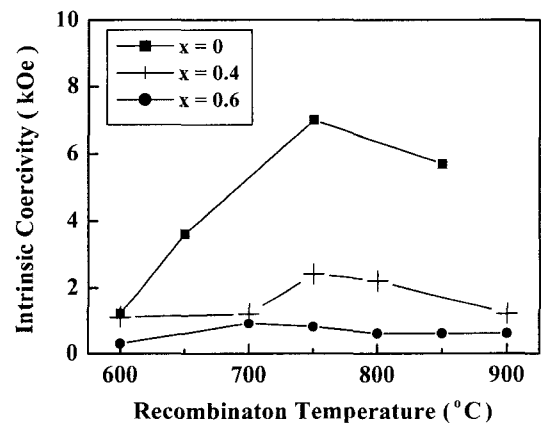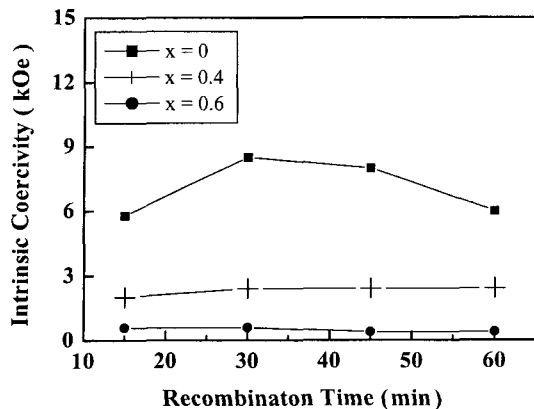Fig. 7. Variation of intrinsic coercivity as a function of recombination temperature (for 30 min) for some HDDR-treated $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ alloys. The alloy with x = 0 was treated with 1 kgf/cm² hydrogen, and the alloys with x = 0.4 and 0.6 with 10 kgf/cm² hydrogen.

(x = 0.4, 0.6) alloys fully disproportionated by using high hydrogen pressure (10 kgf/cm²) were subjected to the desorption and recombination at various conditions. These alloys exhibit slightly higher coercivity compared to that of the alloys treated with 1 kgf/cm² hydrogen. However, these coercivities are still drastically poor compared to those of the $Nd_{15}Fe_{77}B_8$ alloy without Co-substitution as shown in Fig. 7 and Fig. 8. The $Nd_{15}Fe_{77}B_8$ alloy here was HDDR-treated with 1 kgf/cm² hydrogen gas. Based on the above result, it can be said that the poor coercivity of the $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ alloys with high Co-substitution is not attributed to the incomplete disproportionation, but other explanation may prevail.

Fig. 9 shows the XRD spectrum of the $Nd_{15}(Fe_{0.4}Co_{0.6})_{77}B_8$ alloy, which has been fully disproportionated using high hydrogen pressure (10 kgf/cm²) and then recombined at 750 °C for 30 min. As can be seen, most of the material
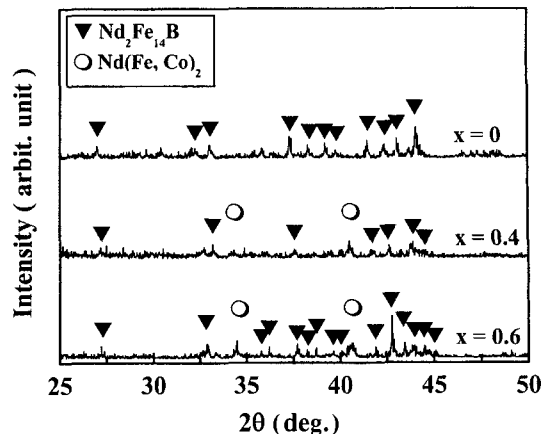
Fig. 8. Variation of intrinsic coercivity as a function of recombination time (at 750 °C) for some HDDR-treated $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ alloys. The alloy with x = 0 was treated with 1 kgf/cm² hydrogen, and the alloys with x = 0.4 and 0.6 with 10 kgf/cm² hydrogen.
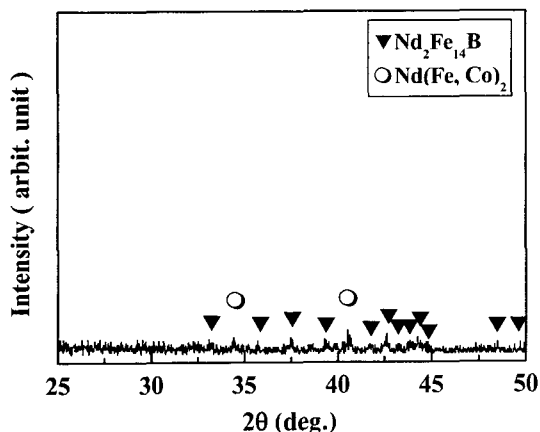
Fig. 9. XRD spectrum of the $Nd_{15}(Fe_{0.4}Co_{0.6})_{77}B_8$ alloy fully disproportionated using high hydrogen pressure (10 kgf/cm²) and recombined at 750 °C for 30 min.

Fig. 10. XRD spectra of some $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ alloys before HDDR.

has been converted into the $Nd_2(Fe,Co)_{14}B$ phase. It is noted, however, that in addition to the 2 : 14 : 1 phase a significant amount of $Nd(Fe,Co)_2$ phase also presents. This $Nd(Fe,Co)_2$ phase also existed in the $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ alloys with x = 0.4, 0.6 before the HDDR-treatment as shown in Fig. 10. The $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ alloys with lower Co-substitution of x = 0 0.2 contained no or little $Nd(Fe,Co)_2$ phase before and after the HDDR treatment. Other research group [8] also reported the 1 : 2 phase existing as an intergrannular phase in the Nd-Fe-Co-B alloy. The $Nd(Fe,Co)_2$ phase is known to be a magnetic phase at room temperature [9]. Therefore, under a demagnetizing field, a reverse domain may be nucleated easily at the boundary between the 2 : 14 : 1 matrix phase and 1 : 2 phase and/or at the interior of the 1 : 2 phase itself. This may lead to a poor coercivity. It can be said, there-

fore, that the poor coercivity of the HDDR-treated $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ alloys with high Co-substitution may be closely related to the presence of the 1 : 2 phase.

Aims of the present work also include, in part, examining the effect of magnetic field on the anisotropic nature of the HDDR treated material. The fully disproportionated $Nd_{15}Fe_{77}B_8$ and $Nd_{15}(Fe_{0.8}Co_{0.2})_{77}B_8$ alloys were recombined under a magnetic field (1 kOe). These HDDR-treated powders were aligned and wax-bonded, and the demagnetization curves were measured along the directions parallel and perpendicular to the aligning direction. As can be seen in Fig. 11, for the both alloys the remanence along the aligning direction and transverse direction shows similar values regardless of the application of magnetic field during the recombination. This indicates that the application of magnetic filed during the recombination step has little effect on the anisotropic nature of the HDDR-treated powder. It is noted that the coercivity of the both alloys recombined under magnetic field is consistently higher than that of the alloys recombined without magnetic field. Precise explanation for this enhanced coercivity by the magnetic field during the recombination is not fully understood at the present time.

4. Conclusion

The $Nd_2(Fe,Co)_{14}B$ phase in the $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ alloys with high Co-substitution had remarkably enhanced phase stability, and the phase could not be successfully disproportionated by heating it under an atmospheric hydrogen pressure. Therefore, the HDDR-process of the alloys with high Co-substitution could not be undertaken successfully, and no appreciable coercivity could be achieved. However, the stabilized $Nd_2(Fe,Co)_{14}B$ phase in
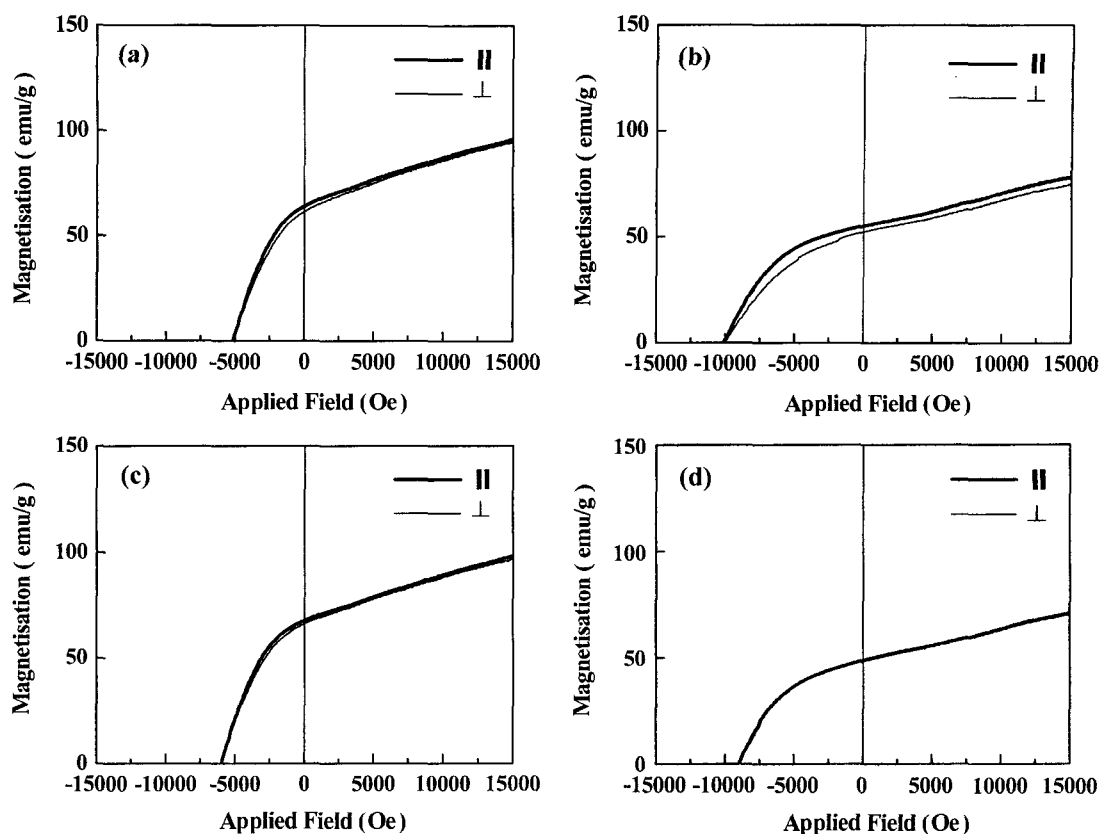
Fig. 11. Demagnetization curves measured along different directions for the HDDR-treated $Nd_{15}(Fe_{1-x}Co_x)_{77}B_8$ alloys recombined with/without magnetic field. (a) x = 0, without field, (b) x = 0, under field, (c) x = 0.2, without field, and (d) x = 0.2, under field.

the Nd-Fe-B alloy with high Co-substitution could be fully disproportionated by heating under high pressure hydrogen gas (10 kgf/cm^2), and the disproportionated phases were successfully recombined into the 2 : 14 : 1 phase. Nonetheless the material exhibited no appreciable coercivity after HDDR. The poor coercivity of the HDDR-treated Nd-Fe-B alloys with high Co-substitution was attributed to the $Nd(Fe,Co)_2$ phase. The magnetic filed applied during the recombination step was found to have little effect on the anisotropic nature of the HDDR-treated powder.

Acknowledgement

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