

Study on the Rigidity of the Solid-HDDR Treated Nd-Fe-B-type Materials

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A non-coercive cast Nd-Fe-B-type material can be easily converted into a coercive one by employing HDDR process. Applying the conventional HDDR process to the Nd-Fe-B-type material generally leads to a powder-like material. HDDR treated material in a solid form can, however, be realized if the process is properly modified (solid-HDDR). In the present study, the change of rigidity (compressive strength) of the Nd-Fe-B-type material during the solid-HDDR has been investigated using a homogeneous sintered magnet with composition $\text{Nd}_{13.8}\text{Dy}_{0.7}\text{Fe}_{78.25}\text{Si}_{0.15}\text{Mn}_{0.6}\text{B}_{6.5}$. It has been found that the low strength of the hydrided material was improved by the subsequent disproportionation. The restoration of the strength was explained by the eutectoid-like disproportionation structure containing fine neodymium hydride rod embedded in tough iron matrix. The high strength of disproportionated material was reduced radically in earlier stage of recombination, and this was explained by the reduction of the disproportionated phase. The reduced strength was, however, recovered by further recombination, and this was explained by the fact that as the recombination continues the recombined grains adhere together. The optimally HDDR processed material has a comparable or even higher strength with respect to the initial sintered material prior to the solid-HDDR. The present study suggested that the rigidity of Nd-Fe-B-type material could be retained even after the solid-HDDR.

1. Introduction

An ordinary Nd-Fe-B-type ingot materials show no appreciable hard magnetic property, and this is due simply to the coarse $\text{Nd}_2\text{Fe}_{14}\text{B}$ matrix grain which is far greater than the critical single domain size ($\sim 0.3 \mu\text{m}$) of the compound. This coarse grain structure can easily be restructured into a fine microstructure with grain size comparable to the critical single domain size by employing HDDR process, thus the HDDR-processed ingot material can exhibit a considerable coercivity. The HDDR can, therefore, be said to be a unique process through which a non-coercive cast Nd-Fe-B-type material can be easily converted into a coercive one. Applying the HDDR process to the Nd-Fe-B-type ingot material generally leads to a powder-like material [1-6]. It has been reported, however, that material in a solid form can be obtained by the HDDR process if it is properly modified (solid-HDDR) [7-9]. Non-coercive Nd-Fe-B-type cast ingot material can, therefore, be converted into a magnet with a high coercivity in solid form using the solid-HDDR process, and a successful attempt has been reported by other group [5]. In order that the solid-HDDR

treated material can be utilized as a magnet, the material has to exhibit not only a high coercivity but also a sufficient rigidity. In the present study, the change of rigidity of the Nd-Fe-B-type material during the solid-HDDR has been investigated as a precursor to a study on preparation of a Nd-Fe-B-type cast magnet by solid-HDDR process.

2. Experimental Work

It is of importance to use a compositionally and structurally homogeneous material to monitor correctly the rigidity change during the solid-HDDR. As can be expected, an ordinary cast ingot material has a variety of inhomogeneity and structural flaws, and the cast ingot material is considered to be unsuitable for assessing the change of rigidity during the HDDR. In the present study, therefore, a sintered magnet rather than a cast ingot material was used because the sintered magnet could be considered to be more homogeneous in terms of composition and structure. The magnet used was an anisotropic and has chemical composition of $\text{Nd}_{13.8}\text{Dy}_{0.7}\text{Fe}_{78.25}\text{Si}_{0.15}\text{Mn}_{0.6}\text{B}_{6.5}$. Disc-shaped (13 mm ϕ , 3 mm thick) sample was subjected to a solid

-HDDR process. The sample was heated under vacuum up to around 650 °C of disproportionation starting temperature, at which hydrogen gas was introduced (0.2 bar). After introducing the hydrogen gas, the sample was heated rapidly (50 °C/min) toward the disproportionation temperature. The sample disproportionated for a given period was subsequently subjected to the desorption and recombination treatment under vacuum. The profile of solid-HDDR used in the experiment is shown in Fig. 1. The samples at each step were rapidly cooled down to room temperature to stop further process and then removed from the HDDR reactor. The rigidity of material at various conditions was assessed by measuring compressive strength. The compressive strength of the materials was measured using a universal testing machine. Dimension of the specimen used for the measurement of the compressive strength was $5 \times 5 \times 3 \text{ mm}^3$. Pressing was performed along the direction parallel to the aligning direction of the anisotropic sintered magnet with speed of 0.5 mm/min. Phase analysis of the material during the HDDR was performed by means of XRD (Cu K α radiation) and TMA (thermomagnetic analyzer).

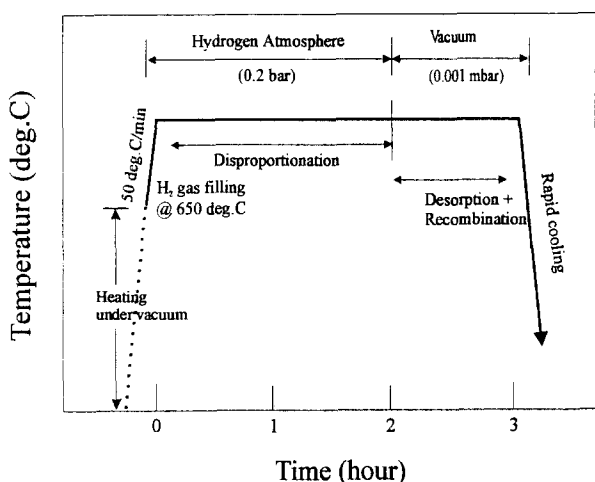


Fig. 1. The profile of solid-HDDR process.

3. Results and Discussion

The hydrogenated sample showed very friable character and no appreciable strength was measured. The low strength of the hydrided material was enhanced by disproportionation. In order to see the variation of the rigidity of the sample during the solid-HDDR, the compressive strength of the sample disproportionated under various conditions was measured. Fig. 2 represents the variation of the compressive strength as a function of the disproportionation temperature for the samples disproportionated for 2 hrs at each temperature. As can be seen in the Fig. 2, the compressive strength of the sample disproportionated at low temperature of 650 °C appears to be very low compared to the initial strength (85 kgf/mm²) prior to the HDDR. The strength of the disproportionated sample appears to increase with increasing the

disproportionation temperature up to 800 °C, and then levels off above 800 °C. Of particular note is that the compressive strength of the fully disproportionated material has been found, unexpectedly, to be higher than that of the initial sintered magnet. The low strength of the sample disproportionated at 650 °C may be explained by the presence of significant amount of brittle hydride phase. At lower temperatures the disproportionation reaction may be slow and not be completed within the given period of 2 hrs. Most of the phases in the sample may still remain as brittle hydrides which have been formed during the hydrogenation. As the disproportionation temperature increases more disproportionation reaction may proceed for the given period and the remaining hydride may be lessened. It has been reported that the disproportionation of the Nd₂Fe₁₄BH_x and the NdFe₄B₄H_x phases leads to a particular eutectoid-like microstructure, consisting of fine neodymium hydride rods embedded in a tough iron matrix [9-12]. The disproportionated phases are, therefore, expected to have a considerable rigidity because of the particular structure containing a lot of tough iron. The gradual increase in the compressive strength with increasing the temperature observed at the temperature range below 800 °C may, thus, probably be explained by the gradual increase in the amount of disproportionated phases. At higher temperatures above 800 °C, however, it can be expected that most of the hydride phases may have been disproportionated for the given period, and this may explain the level-off of the strength increase. It is notable that the compressive strength of the fully disproportionated material is higher than that of the initial material.

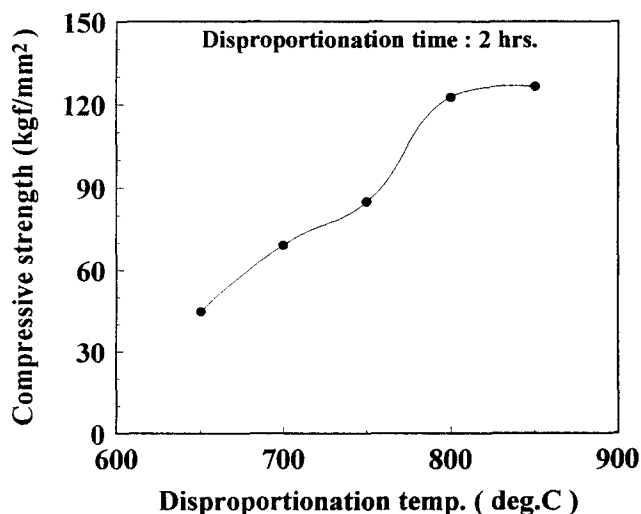


Fig. 2. Variation of the compressive strength as a function of disproportionation temperature for the hydrogenated material.

The result shown in Fig. 2 suggested that the compressive strength of the disproportionated sample seemed to be closely related to the extent of disproportionation. Therefore, it is very important to examine the phases presenting in the sample disproportionated under various conditions. Phase analysis for the samples disproportionated for 2 hrs at 650 °C or 800 °C was

performed using an XRD and the obtained diffraction spectrum are presented in Fig. 3. It appears that the sample disproportionated at 650 °C for 2 hrs has a significant amount of $Nd_2Fe_{14}BH_x$ phase which has not been disproportionated. On the other hand, it can be seen that for the sample disproportionated at 800 °C for 2 hrs the $Nd_2Fe_{14}BH_x$ phase has been disproportionated almost fully and no evidence for the presence of the hydride phase can be found. These results support that the lower compressive strength obtained from the sample disproportionated at lower temperature may be due to the presence of undisproportionated hydride phase which is very brittle. The higher compressive strength observed from the samples disproportionated at higher temperatures seems to be related to the full disproportionation of the hydride phases.

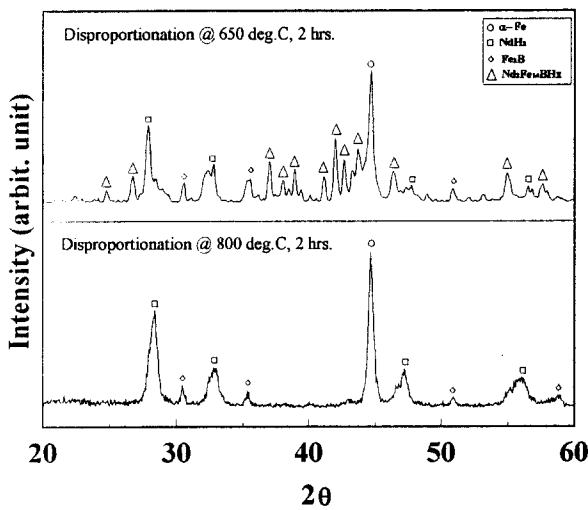


Fig. 3. X-ray diffraction spectrum for the material disproportionated at 800 °C.

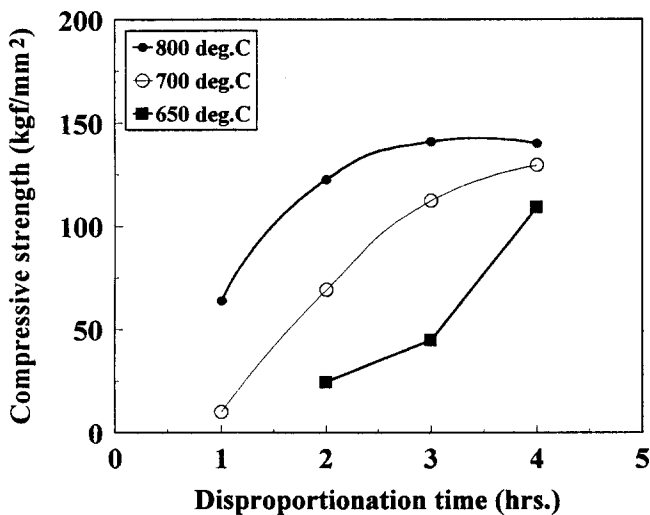


Fig. 4. Variation of the compressive strength as a function of disproportionation time at various temperature for the hydrogenated material.

Variation of the compressive strength of the samples as a function of disproportionation time at different temperatures was examined and the result is shown in Fig. 4. It is apparent that the compressive strength at each temperature increases as the disproportionation time increases and then levels off. The general trend of the increase in strength at various temperatures seems to be similar except that as the temperature increases the strength increases more rapidly. For the sample disproportionated at low temperature the strength has not reached the peak value within the period used in the present study and still increases. The gradual increase in the compressive strength is due, needless to say, to the increase in the amount of the disproportionated phase as the time goes on.

It should be interesting to know whether the high compressive strength observed from the fully disproportionated sample can be maintained when it is subjected to a subsequent recombination. The fully disproportionated sample (disproportionated at 800 °C for 2 hrs) was subjected to recombination under vacuum at various temperatures for 1 hr. The strength of the recombined sample was measured and the variation of the strength as a function of the recombination temperature is shown in Fig. 5. It appears that the compressive strength of the samples recombined at temperatures lower than 800 °C still show relatively high strength over 70 kgf/mm². On the other hand, the samples recombined at higher temperature above 850 °C have significantly low strength around 30 kgf/mm². The high strength observed in the samples recombined at lower temperature may be due to the presence of significant amount of the tough disproportionated phases which have not been recombined. As the temperature increases the recombination reaction may proceed more rapidly, and greater amount of

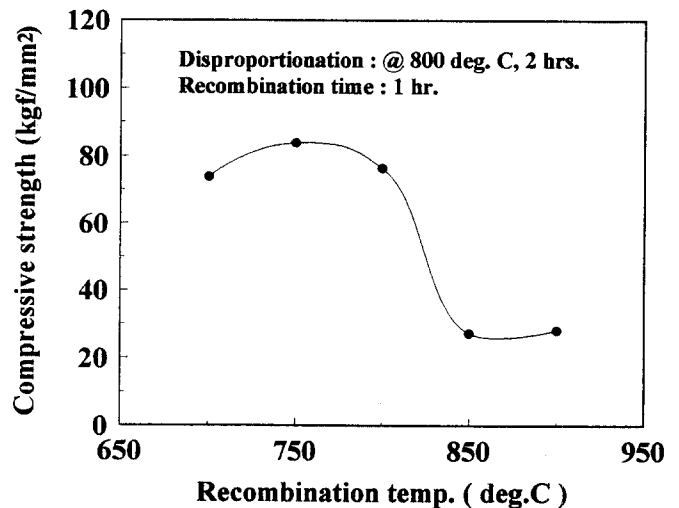


Fig. 5. Variation of the compressive strength as a function of recombination temperature for the fully disproportionated material.

the recombined grains may be formed. The lower strength of the samples recombined at higher temperature may, therefore, be ascribed to the reduction of the tough disproportionated phases. Phase analysis of the samples recombined under various conditions supported this explanation. Phases in the samples recombined at 800 °C for 1 hr or 5 hrs were analyzed by TMA, and the results are shown in Fig. 6. As can be seen, for the sample recombined for 1 hr only one magnetic phase with Curie temperature of 760 °C is found, corresponding to the disproportionated α -Fe phase. This result indicates that most of the disproportionated phases remain unrecombined and the recombination reaction has been hardly achieved. Phase analysis for the sample recombined for 5 hrs is also included in Fig. 6. In addition to the α -Fe, another magnetic phase with Curie temperature of 315 °C is observed, corresponding to the recombined

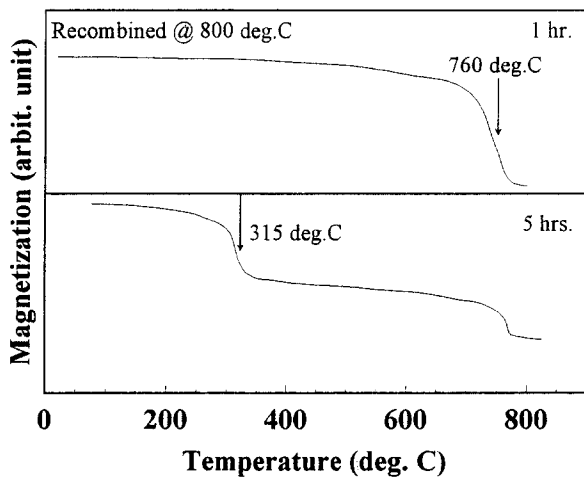


Fig. 6. TMA traces for the material recombined at 800 °C.

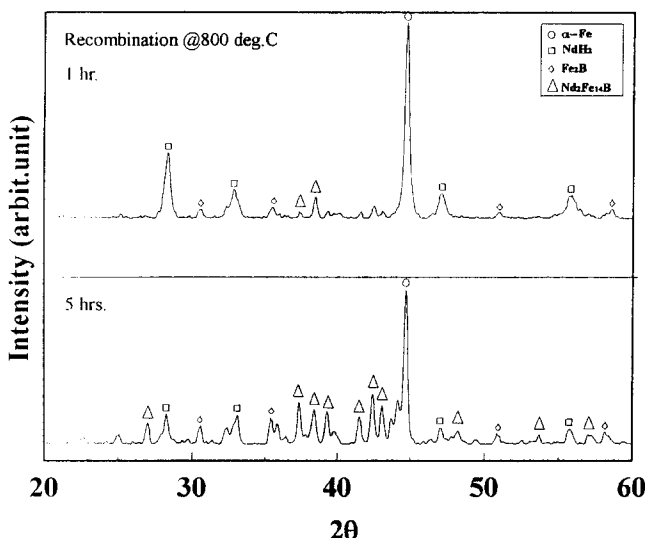


Fig. 7. X-ray diffraction spectrum for the material recombined at 800 °C.

Nd₂Fe₁₄B phase. This result indicates that recombination has taken place to some extent. Similar results are also confirmed by XRD as shown in Fig. 7. Meanwhile, for the sample recombined at higher temperature (900 °C) a significant degree of recombination has been achieved even for the period of 1 hr as confirmed by TMA (Fig. 8) and XRD (Fig. 9). Although a significant amount of recombined phase has been formed in the samples recombined at higher temperatures, the recombined grains may be distributed discontinuously throughout the sample and no significant adhesion between the grains may have been achieved. This may possibly explain the low strength observed from the samples recombined at higher temperatures.

It should be interesting to see whether the low strength of the sample recombined at higher temperatures observed in the previous result can be enhanced by a further recombination. The change of compressive strength with the recombination time at 900 °C was examined and the result is shown in Fig. 10. It is apparent that the strength increases as the recombination time increases, and then levels off after 4 hrs. The low strength observed from the samples recombined shorter periods may be attributed to the reduction of tough disproportionated phases. As the time increases the recombination may continue, thus resulting in further reduction of the disproportionated phases and at the same time, greater formation of the recombined Nd₂Fe₁₄B phase. It should be emphasized, here, that the recombined grains may begin to distribute more continuously throughout the sample and adhere together. The strength of the sample may, therefore, be recovered, and this explains the gradual increase in the strength with recombination time. The saturation of the strength enhancement observed from the samples recombined longer than 4 hrs may be due to the completion of the recombination. The completion of the recombination at 900 °C for 4 hrs can be confirmed by the TMA (Fig. 8) and XRD (Fig. 9). The investigation of the structural development during the recombination by TEM is underway using a cast ingot material. Along with the structural investigation, the change of

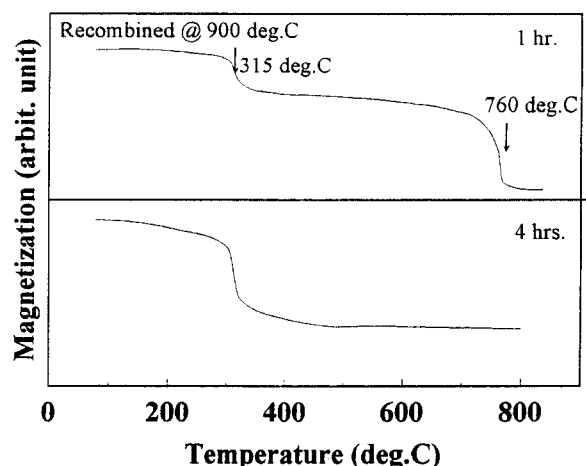


Fig. 8. TMA traces for the material recombined at 900 °C.

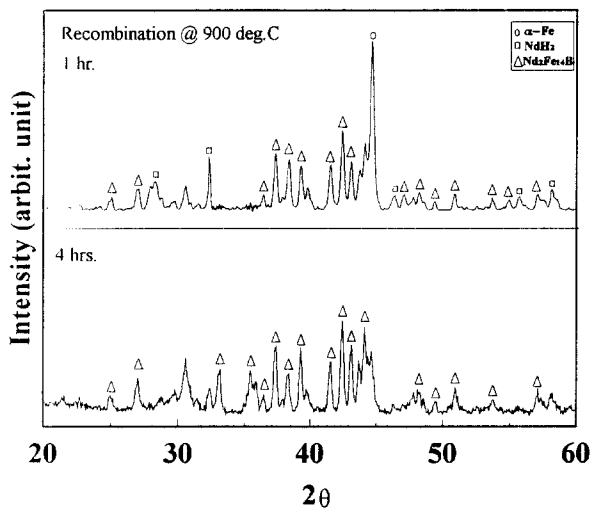


Fig. 9. X-ray diffraction spectrum for the material recombined at 900 °C.

magnetic properties of the material during HDDR is also under investigation using the cast ingot material. The results of these investigations will be correlated with each other and it will be reported elsewhere. It is worth noting that as can be seen in the Fig. 10, the fully recombined sample has a comparable or even higher strength with respect to the initial sintered magnet prior to the solid-HDDR. The present study, thus, indicates clearly that a properly controlled solid-HDDR process can lead to a material in a solid form with a sufficient rigidity. Morphology of the solid-HDDR treated sample is shown in Fig. 11 and compared with that of the initial material or the conventionally HDDR treated sample. It is apparent that the sample solid-HDDR treated under optimum condition remains intact after the treatment. As can be seen, the sample conventionally HDDR treated transformed into a powder-like material.

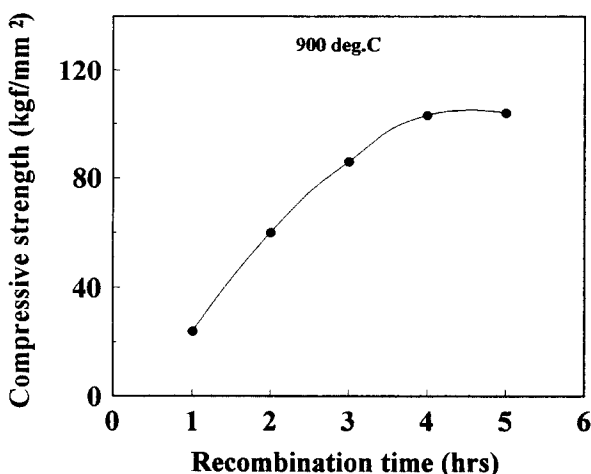


Fig. 10. Variation of the compressive strength as a function of recombination time at 900 °C for the fully disproportionated material.

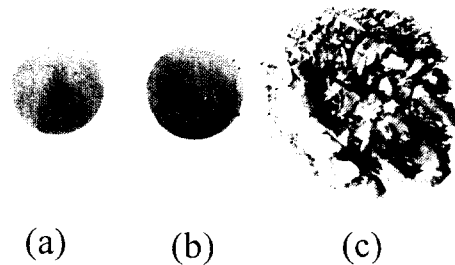


Fig. 11. Morphologies of the samples under various conditions.

- (a) before HDDR
- (b) solid-HDDR treated
- (c) conventional HDDR treated

4. Conclusions

The compressive strength of the solid-HDDR material was measured for the sintered magnet under various HDDR conditions, and it has been found that the low strength of the hydrided material was improved by the subsequent disproportionation. The restoration of the strength was explained by the eutectoid-like disproportionation structure containing fine neodymium hydride rod embedded in tough iron matrix. The high strength of disproportionated material was reduced radically in earlier stage of recombination, and this was explained by the reduction of the disproportionated phase. The reduced strength was, however, recovered by further recombination. The optimally HDDR processed material has a comparable or even higher strength with respect to the initial sintered material prior to the solid-HDDR. The present study suggested that the rigidity of Nd-Fe-B-type material could be retained even after the solid-HDDR.

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