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Study of Hopkinson Effect in the HDDR-treated Nd-Fe-B-type Material

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Abstract

Hopkinson effect in the HDDR-treated $Nd_{15}Fe_{77}B_8$ alloy was examined in detail by means of a thermomagnetic analysis with low magnetic field (600 Oe). The emergence and magnitude of maximum in magnetisation in the thermomagnetic curve due to the Hopkinson effect was correlated to the grain structure and coercivity of the HDDR-treated material. The HDDR-treated materials showed clear Hopkinson effect (maximum in magnetisation just below the Curie temperature of the $Nd_2Fe_{14}B$ phase) on heating in the thermomagnetic curve. Magnitude of the magnetisation rise due to the Hopkinson effect became smaller as the recombination time increased. The magnetisation recovery at room temperature on cooling from above the Curie temperature became smaller as the recombination time increased. The HDDR-treated materials with shorter recombination time, finer grain size and higher coercivity showed larger magnetisation maximum due to Hopkinson effect in the thermomagnetic curve.

1. INTRODUCTION

The Hopkinson effect [1] generally means the phenomenon that an initial susceptibility of a magnetic material increases with increasing temperature and exhibits a sharp maximum just below its Curie temperature (T_c). Because of the increased susceptibility a peculiar magnetisation maximum is usually observed just below the Curie temperature in a thermomagnetic curve, and this is also referred to as a Hopkinson effect. Some magnetically hard materials with very fine microstructure have been reported to show the obvious Hopkinson effect in a low field thermomagnetic curve [2-5]. It has also been not uncommon to observe the peculiar magnetisation maximum just below the Curie temperature of $Nd_2Fe_{14}B$ phase in the thermomagnetic curve of the HDDR-treated Nd-Fe-B-type materials, and this has been considered to be due to the Hopkinson effect. A key advantage of the

HDDR (hydrogenation, disproportionation, desorption and recombination) [6,7] is that the coarse-grained ingot material can be converted easily into a material with fine grain structure simply by hydrogen absorption and desorption treatment. Thus, the HDDR-treated material has very high coercivity due to the fine grain structure which is comparable to the critical single domain size (d_c = 0.3 μm) of the $Nd_2Fe_{14}B$ phase in the Nd-Fe-B-type material. In the present article, the Hopkinson effect in the H DDR-treated Nd-Fe-B-type is examined in detail by means of a thermomagnetic analysis with low magnetic field. The emergence and magnitude of maximum i n magnetisation in the thermomagnetic curve due to the Hopkinson effect in the HDDR-treated Nd-Fe-B-type material is related to the grain structure and coercivity of the material.

2. EXPERIMENTALS

$Nd_{15}Fe_{77}B_8$ alloy used in the present study was prepared by an induction melting of the high purity constituent metals under Ar gas. The prepared alloy ingot was homogenised at 1000 °C for 5 hrs. The homogenised alloys were milled into a powder with particle size of 40 – 60 μm, and then subjected to an HDDR-treatment. The HDDR conditions used were tabulated in Table 1.

Table 1. HDDR condition used

Hydrogenation	**D**isproportionation	**D**esorption and **R**ecombination
Heating the alloy under H_2 gas (p = 1.2 kgf/cm^2) up to 750 °C with rate of 7 °C/min.	Holding the hydrogenated material at 750 °C under H_2 gas (p = 1.2 kgf/cm^2) for 1 hour.	Holding the disproportionated material under vacuum for required period (30 – 150 min) and then furnace cooled.

Magnetic characterisation of the materials was undertaken using a VSM. For the VSM measurement powder samples were wax-bonded and magnetised prior to the measurement using a pulse magnetiser with magnetic field of 4.5 T. Thermomagnetic analysis of the HDDR-treated materials was performed by Sucksmith-type magnetic

balance with magnetic field of 600 Oe. Grain structure of the HDDR-treated material was examined by observing the fracture surface of the milled powder by means of high resolution SEM (HRSEM). Magnetic domain structure of the annealed material was examined by Kerr image.

3. RESULTS AND DISCUSSION

Fig. 1 shows the x-ray diffraction spectra for the $Nd_{15}Fe_{77}B_8$ materials at annealed (before the HDDR) or HDDR-treated (recombination time: 30 min.) state. The x-ray diffraction spectra for the HDDR-treated materials with longer recombination times than 30 min were also examined, and those were found to be identical with that of the material HDDR-treated with recombination time of 30 min. It can be seen that the material HDDR-treated in the present study has been nicely recombined into an initial phase state.

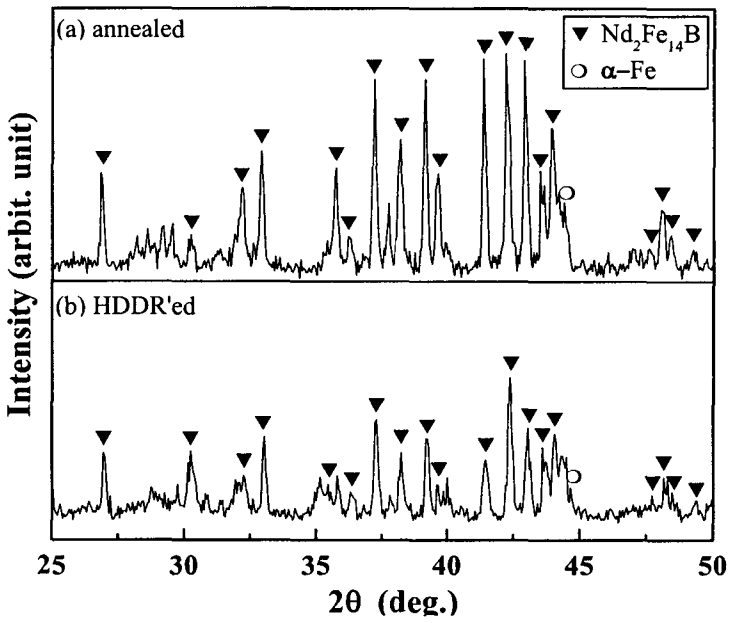


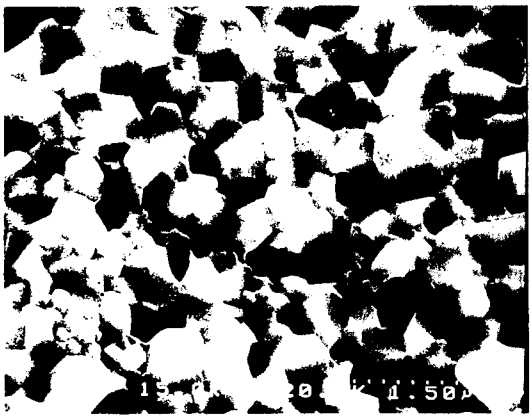
Fig. 1.X-ray diffraction spectra for the $Nd_{15}Fe_{77}B_8$ materials at (a) annealed or (b) HDDR-treated state (R=30 min.).

Fig. 2 shows the surface morphology of the HDDR-treated $Nd_{15}Fe_{77}B_8$ material powders. The materials have been HDDR-treated with various recombination times and then briefly milled. These photos show the fracture surface of the recombined

grains caused by the brief milling. It seems that the fracture took place through a so-called inter-granular crack along the grain boundaries between the recombined grains, thus the grain structure of the HDDR-treated materials can be clearly examined using this fracture surface morphology. As can be seen, the microstructure of the material HDDR-treated with 30 min of recombination time consists of very fine grains with grain size of 0.2 - 0.3 μm (Fig. 2(a)). It is notable that this grain size is comparable to the critical single domain size (0.3 μm) of the $Nd_2Fe_{14}B$ phase and it has very uniform distribution. The grain size of the recombined grains appears to increase as the recombination time increases, and its distribution becomes wide as can be seen in Fig. 2 (b) - (e).

(a) 30 min

(b) 60 min



(c) 90 min

(d) 120 min

(e) 150 min

Fig. 2. High resolution SEM photographs showing the microstructure of the $Nd_{15}Fe_{77}B_8$ materials HDDR-treated with different recombination time.

Fig. 3 shows the thermomagnetic analysis curve of the $Nd_{15}Fe_{77}B_8$ materials HDDR-treated with different recombination time. Also included in Fig. 3 is the thermomagnetic analysis curve of the bulk $Nd_{15}Fe_{77}B_8$ material at annealed condition for comparison. As can be seen, on heating the magnetisation of HDDR-treated materials remains almost constant or slightly increases up to a certain temperature, and then increases (this trend is more obvious for the materials with shorter recombination times) and shows maximum just below the Curie temperature of the $Nd_2Fe_{14}B$ phase. The constant or slightly increasing magnetisation at lower temperature range on heating may be closely related to the microstructure and magnetic domain structure of the recombined grains. As seen in Fig. 2, the recombined grains in HDDR-treated materials have grain size comparable to or larger than critical single domain size of $Nd_2Fe_{14}B$ phase. It is, thus, thought almost certainly that some recombined grains, of which easy magnetisation axes orient randomly, may have domain walls inside them. When these materials are heated under a weak applied field, the mobility of domain wall may be enhanced as the temperature increases and the walls may be displaced easily along the applied field direction. This domain wall displacement may lead to an increase in magnetisation, which may be predominant in competition with the magnetisation decrease due to a thermal agitation. This may give an explanation for the constant or slightly increasing magnetisation at lower temperature range on heating.

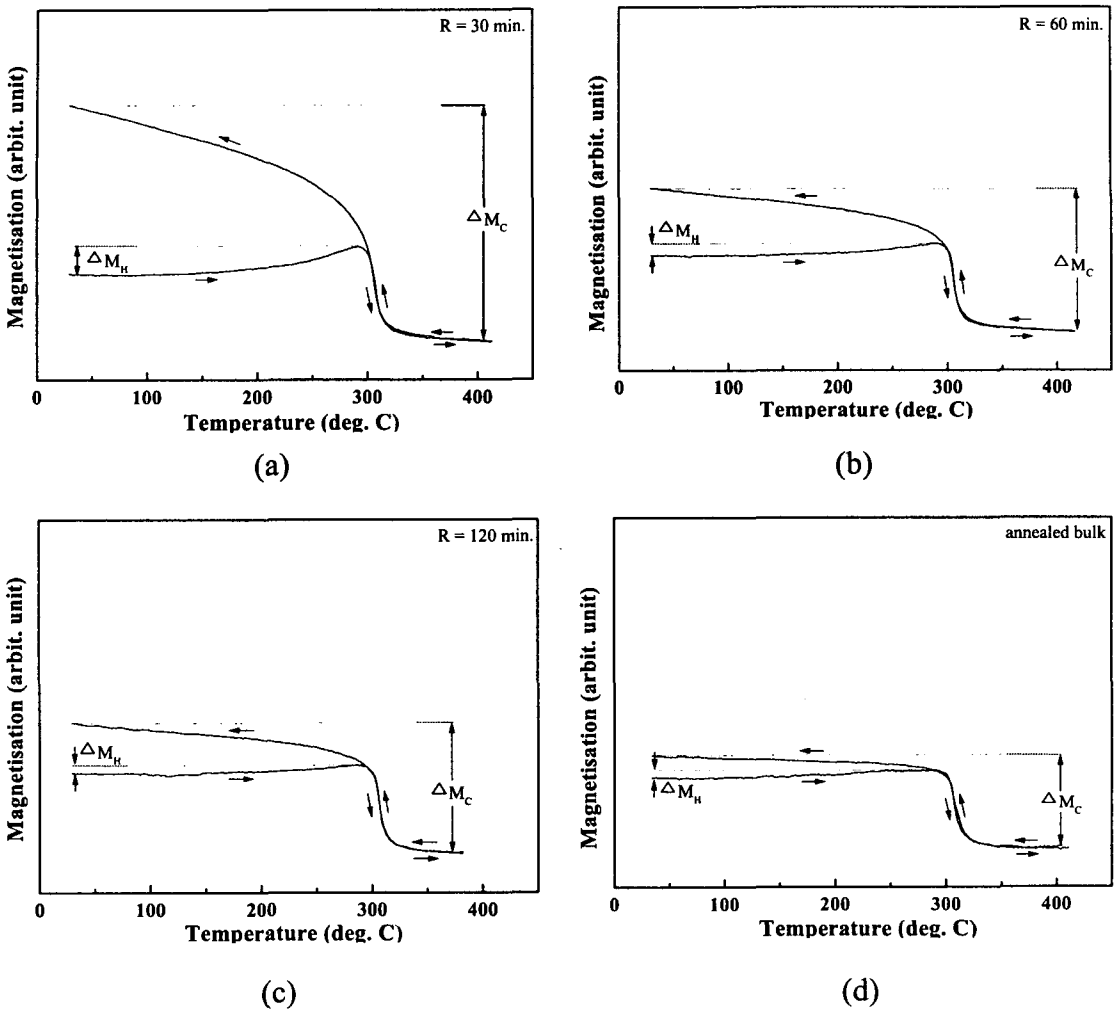


Fig. 3. Thermomagnetic curves of the bulk or HDDR-treated $Nd_{15}Fe_{77}B_8$ materials with different recombination time.

When the material is heated further toward the Curie temperature the magnetocrystalline anisotropy may become increasingly weak. The reduced magnetocrystalline anisotropy may result in an easy rotation of magnetisation of the grains along the applied field, thus leading to an increase in magnetisation. At the same time, there may, of course, be a decrease in magnetisation due to thermal agitation. The magnetisation increase due to the easy magnetisation rotation and the magnetisation decrease due to the thermal fluctuation may compete with each other. The former may probably be predominant in competition in the temperature range approaching the Curie temperature. This may lead to a steep increase in

magnetisation. Further heating may demagnetise the material and the magnetisation decreases sharply to zero at the Curie temperature. This may explain the appearance of a maximum in magnetisation just below the Curie temperature in the thermomagnetic curve. It can be said that this Hopkinson effect is essentially a competition effect between the applied magnetic field and magnetocrystalline anisotropy.

It is notable that the magnitude of maximum (ΔM_H) for the HDDR-treated material is closely related to the recombination time. The magnitude of maximum in magnetisation just below the Curie temperature becomes smaller as the recombination time increases. This can be explained as follows. There may be a good deal of domain wall to move easily in larger grains (in the materials with longer recombination time) under a given applied field, and the domains favourably oriented with respect to applied field may occupy majority of volume in the larger grains. Thus, most of the volume magnetisation of the grains may be more or less parallel to the applied field. Under this circumstance, the contribution to magnetisation increase due to magnetisation rotation (Hopkinson effect) just below the Curie temperature may result mainly from the magnetisation rotation of the unfavourably oriented small domains. This contribution may probably be small, thus the magnetisation rise due to Hopkinson effect may become smaller for the materials HDDR-treated with longer recombination time. This interpretation may be applicable to the explanation of thermomagnetic curve of the annealed bulk material. The bulk material may have very large grain size and each grain may have great domain walls (see Fig. 4), so that negligible magnetisation rise due to the Hopkinson effect just below the Curie temperature is expected as shown in Fig. 3(e).

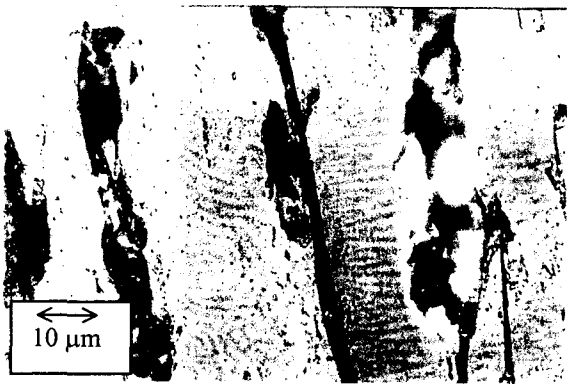


Fig. 4. Kerr image showing the magnetic domain structure of $Nd_2Fe_{14}B$ grains in $Nd_{15}Fe_{77}B_8$ bulk material.

It is also notable in Fig. 3 that the HDDR-treated materials which showed a magnetisation maximum on heating show no magnetisation maximum during cooling and instead show typical ferromagnetic behaviour featuring with monotonous increase of magnetisation below the Curie temperature. This thermomagnetic behaviour on cooling can be accounted for as follows. When the sample is cooled down and crosses the Curie temperature under applied field, the magnetic moment of randomly oriented recombined fine grains may be aligned along the direction of applied field because the magnetocrystalline anisotropy of the grains may be very weak near the Curie temperature. The applied field may be predominant in determining the direction of magnetic moment of the grains just below the Curie temperature. As the temperature decreases further the magnetic moment of each grain tends to reorient toward its easy magnetisation axis which is nearest to the applied field. This indicates that the magnetic moments of all grains in the sample may orient more or less in favourable fashion with respect to the applied field. This alignment of magnetic moment of the grains may be maintained on further cooling down to room temperature. Under this circumstance, only the magnetisation increase may appear on cooling due to the reduced thermal agitation. As a result, no magnetisation maximum or Hopkinson effect may be observed during cooling and instead a monotonous increase of magnetisation may be monitored. It is worth noting that the magnetisation recovery (ΔM_C) at room temperature on cooling may be influenced by the grain size of the HDDR-treated material. For the materials with longer recombination time, the recombined grains may be larger, and these may be multi-domain grains. Thus, in the temperature range below Curie temperature on cooling, reverse domains may develop and grow in each grain as the temperature decreases. This presence of reverse domains may lead to lower magnetisation recovery at room temperature. It is expected, therefore, that the larger grain size (or the longer recombination time) in the HDDR-treated material is the smaller magnetisation recovery may be. This expectation is verified clearly by the cooling curves as shown in Fig. 3.

It may be interesting to examine the correlation between the Hopkins effect, microstructure and intrinsic coercivity of the HDDR-treated material. Fig. 5 shows the variation of intrinsic coercivity of the HDDR-treated $Nd_{15}Fe_{77}B_8$ materials as a function of recombination time. As can be seen, the coercivity increases as the recombination time increases and then decreases gradually. The material recombined 30 min was found to have grain size comparable to the critical single domain size (0.3 μm) of the $Nd_2Fe_{14}B$ phase as seen in Fig. 2(a). This may lead to high coercivity in the material. As the recombination time increases the grains may over-grow, and this

may lead to deterioration of the coercivity. As the coercivity in the HDDR-treated material is closely related to the grain size, there may be a close relation between the coercivity, grain size and magnetisation maximum (Hopkinson effect). The material with finer grain size and higher coercivity may exhibit higher magnetisation maximum (more obvious Hopkinson effect) in the thermomagnetic curve (heating). This is clearly verified by the results shown in Fig. 2, Fig. 3 and Fig. 5.

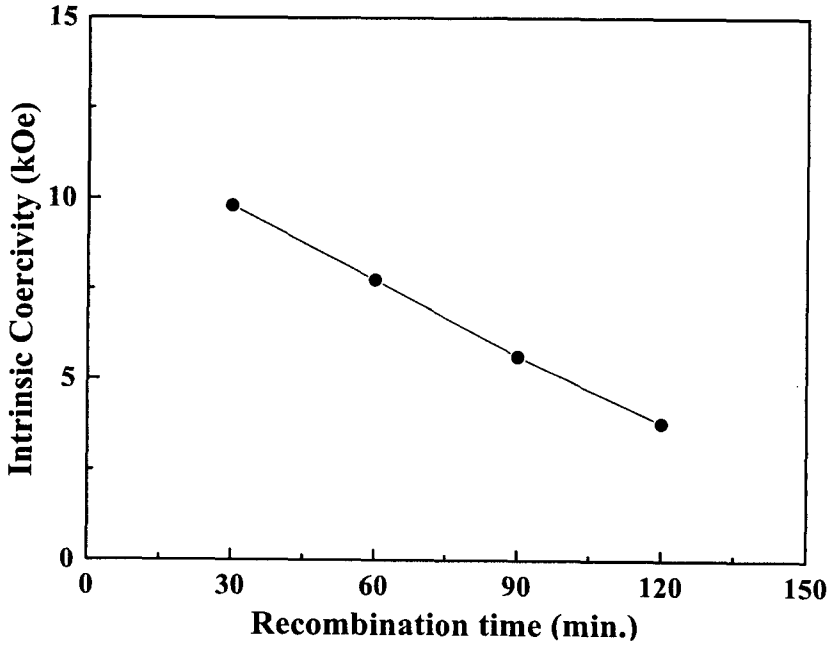


Fig. 5. Variation of the intrinsic coercivity of the HDDR-treated $Nd_{15}Fe_{77}B_8$ materials as a function of recombination time.

4. CONCLUSION

The heating thermomagnetic curve of HDDR-treated materials showed maximum in magnetisation due to the Hopkinson effect just below the Curie temperature of the $Nd_2Fe_{14}B$ phase. Magnitude of the maximum became smaller as the recombination time increased. The magnetisation recovery at room temperature on cooling had a close relation to the recombination time. The magnetisation recovery became smaller as the recombination time increased. There was a close relationship between the coercivity, grain size and magnetisation maximum (Hopkinson effect) of the HDDR-treated material. The material with finer grain size and higher coercivity showed larger magnetisation maximum in the thermomagnetic curve.

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References

1. S. Chikazumi, Physics of Ferromagnetism (2nd Ed.),Oxford University Press Inc., New York, 486 (1997)
2. G. C. Hadjipanayis and Y. F. Tao, J. de. Phys. **46**, C6-237 (1985)
3. Popov and M. Mikhov, J. Magn. Magn. Mat., **75**, 135 (1988)
4. H. W. Kwon, Yoon B. Kim, and W. Y. Jeong, Proc. 15th International workshop on Rare-Earth Magnets and Their Applications, 583 (1998) or H. W. Kwon, Yoon B. Kim, and W. Y. Jeong, Journal of Magnetics, **4**, 26 (1999)
5. N. S. Gajbhiye, S. Prasad, and G. Balaji, IEEE Trans. **MAG-35**, 2155 (1999)
6. T. Takeshita and R. Nakayama, Proc. 10th International workshop on Rare-Earth Magnets and Their Applications, 551 (1989)
7. R. Harris, Proc. 12th International workshop on Rare-Earth Magnets and Their Applications, 347 (1992)