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

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**The 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 with the grain structure and coercivity of the HDDR-treated material. The HDDR-treated materials showed a clear Hopkinson effect (maximum in magnetisation just below the Curie temperature of the $Nd_2Fe_{14}B$ phase) on heating. The 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 the Hopkinson effect in the thermomagnetic curve.**

## 1. Introduction

The Hopkinson effect [1] generally means the phenomenon that the 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 an 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 a HDDR (hydrogenation, disproportionation, desorption and recombination) treatment [6, 7] is that the coarse-grained ingot material can be converted easily into a material with fine grain structure simply by a 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 mm) of the $Nd_2Fe_{14}B$ phase in Nd-Fe-B-type material. In the present article, the Hopkinson effect in the HDDR-treated Nd-Fe-B-type material is examined in detail by means of thermomagnetic analysis with low magnetic field. The emergence and magnitude of maximum in 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. Experimental

The $Nd_{15}Fe_{77}B_8$ alloy used in the present study was prepared by induction melting of 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 mm, and then subjected to an HDDR-treatment. The HDDR conditions used are given in Table 1.

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 (TMA) of the HDDR-

Table 1. HDDR condition used

| Hydrogenation | Disproportionation | Desorption and Recombination |
|---|---|---|
| heating the alloy under $H_2$ gas ($p$=1.2 kgf/cm$^2$) up to 750 °C at 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 the required period (30~150 min.) and then furnace cooled. |

treated materials was performed using a Sucksmith-type magnetic balance with a magnetic field of 600 Oe. Mass of the specimen for TMA was 120 mg for all measurements. 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 using the Kerr effect.

## 3. Results and Discussion

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

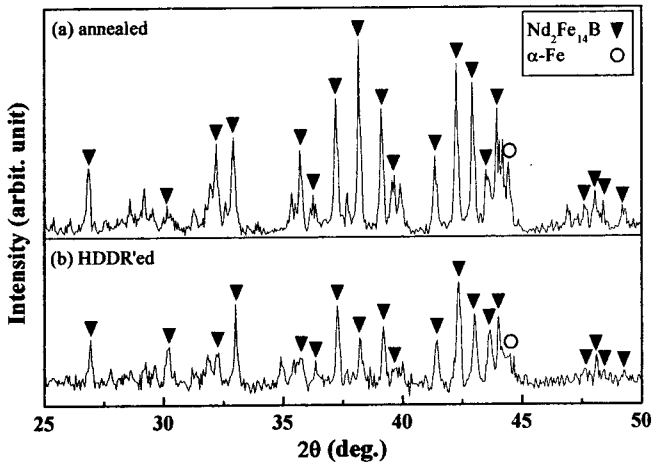


Fig. 1. X-ray diffraction spectra for $Nd_{15}Fe_{77}B_8$ materials in (a) annealed or (b) HDDR-treated state (R=30 min.).

Fig. 2 shows the surface morphology of the HDDR-treated $Nd_{15}Fe_{77}B_8$ 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 by intergranular fracture 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 in the figure, the microstructure of the material HDDR-treated with 30 min of recombination time consists of very fine grains of 0.2~0.3 $\mu$m diameter (Fig. 2(a)). It is notable that this grain size is comparable to the critical single domain size (0.3 $\mu$m) of the $Nd_2Fe_{14}B$ phase, and the size distribution is very uniform. The grain size of the recombined grains appears to increase as the recombination time increases, and its distribution becomes uneven as can be seen in Fig. 2(b)~(e).

Fig. 3 shows the thermomagnetic analysis curve of the $Nd_{15}Fe_{77}B_8$ materials HDDR-treated with different recombination times. Also included in Fig. 3 is the thermomagnetic analysis curve of the bulk $Nd_{15}Fe_{77}B_8$ material in the 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

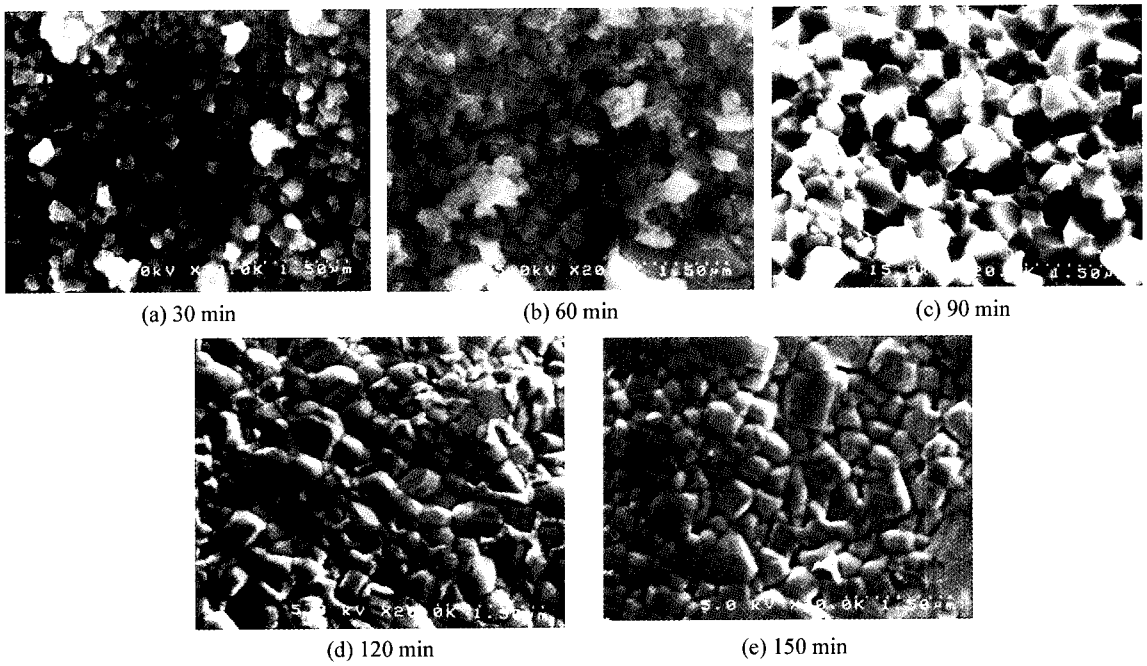


Fig. 2. High resolution SEM photographs showing the microstructure of $Nd_{15}Fe_{77}B_8$ materials HDDR-treated with different recombination timesa.

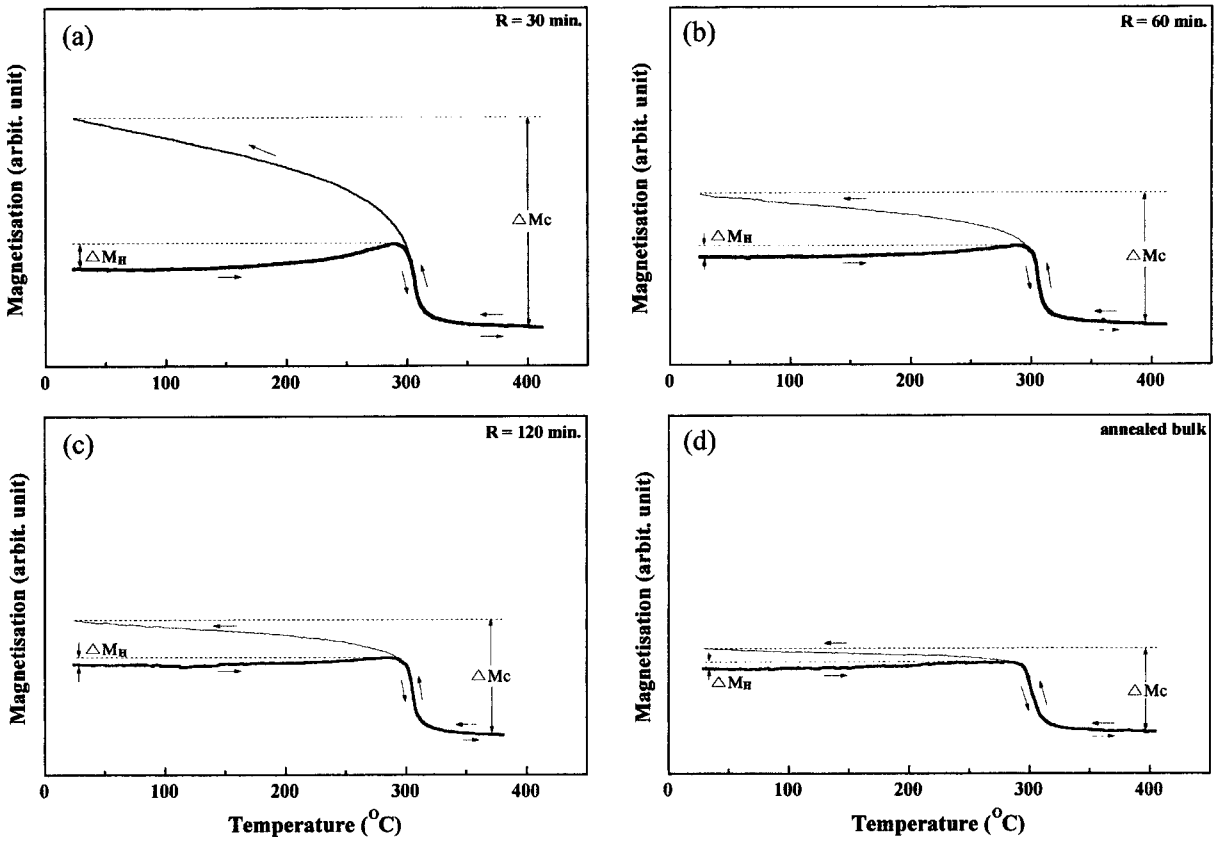


Fig. 3. Thermomagnetic curves of the bulk and HDDR-treated $Nd_{15}Fe_{77}B_8$ materials with different recombination time.

temperature, and then increases (this trend is more obvious for the materials with shorter recombination times) and shows a 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 shown 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, with random orientation of the easy magnetisation axes, may have domain walls inside them. When these materials are heated in a weak applied field, the mobility of the domain walls 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 larger than the magnetisation decrease due to a thermal agitation. This may explanae the constant or slightly increasing magnetisation in the lower temperature range on heating.

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 towards 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 compete with each other. The former may probably be predominant in the temperature range approaching the Curie temperature. This may lead to a steep increase in magnetisation. Further heating will 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 the magnetocrystalline anisotropy, as the anisotropy changes with temperature.

It is notable that the magnitude of maximum $\Delta M_H$ for the HDDR-treated material is closely related to the recombination time. The magnitude of the 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 the applied field may occupy most of the 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 the magnetisation increase due to mag-

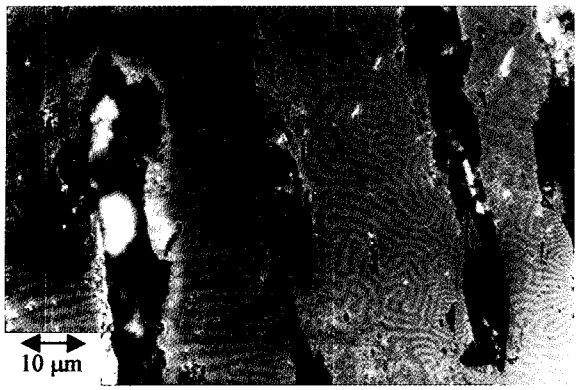


Fig. 4. Kerr image showing the magnetic domain structure of $Nd_2Fe_{14}B$ grains in $Nd_{15}Fe_{77}B_8$ bulk material.

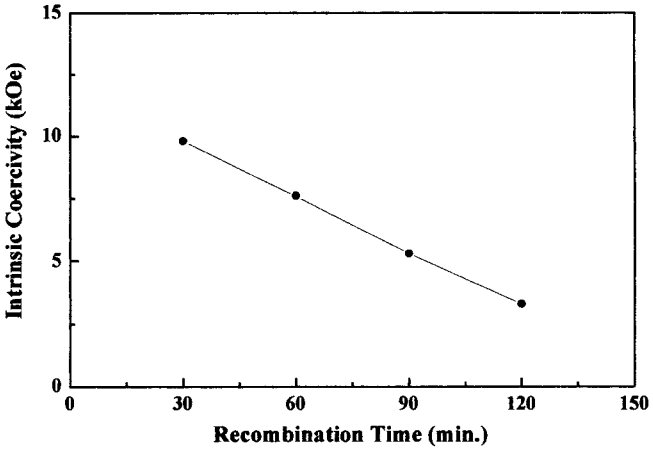


Fig. 5. Variation of the intrinsic coercivity of the HDDR-treated $Nd_{15}Fe_{77}B_8$ materials as a function of recombination time.

netisation rotation 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 the thermomagnetic curve of the annealed bulk material. The bulk material usually has very large grain size and each grain has many 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(d).

It is also notable in Fig. 3 that the HDDR-treated materials which showed the magnetisation maximum on heating show no magnetisation maximum during cooling and instead show typical ferromagnetic behaviour 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 in an 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 is 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 alignment with 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 a 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 monotonic increase of magnetisation may be found. It is worth noting that the magnetisation recovery $\Delta M_C$ 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 the 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 the grain size (or the longer recombination time) in the HDDR-treated material, the smaller the magnetisation recovery. This expectation is verified clearly by the cooling curves as shown in Fig. 3.

It may be interesting to examine the correlation between the Hopkinson 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 $\mu$m) 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.

## 4. Conclusion

The heating thermomagnetic curve of HDDR-treated materials showed a maximum in magnetisation due to the

Hopkinson effect just below the Curie temperature of the $Nd_2Fe_{14}B$ phase. The 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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