Journal of University of Science and Technology Beijing
Volume 10, Number 3, June 2003, Page 26

Materials

Anisotropic characteristic in HDDR $Nd_{13}Fe_{80}B_7$

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(Received 2002-07-12)

Abstract: The function of disproportionation and desorption stages of hydrogenation-disproportionation-desorption-recombination (HDDR) process in the formation of magnetic anisotropy was studied. The results showed that degree of anisotropy (DOA) of $Nd_{13}Fe_{80}B_7$ induced by appropriate HDDR process is comparable with that of $Nd_{13}Fe_{80-x}B_7M_x$ (M=Co, Zr or Ga), however, the moderate coercive force of $Nd_{13}Fe_{80}B_7$ magnetic powder led to an undesirable $(BH)_{max}$ of 104 kJ/m^3 in bonded magnet. Experiments demonstrated that a relatively short disproportionation time, combined with a high desorption temperature and slow desorption rate, during HDDR process is beneficial to anisotropy attainment, but HDDR $Nd_{13}Fe_{80}B_7$ magnetic powder becomes isotropic if the disproportionation time is longer than a certain period. This phenomenon strongly indicated that the origin of anisotropy in NdFeB-type HDDR material is contributed by disproportionation stage. XRD (X-ray Diffraction) analysis and TEM (Transmission Electron Microscope) observation told that no other phase except NdH_2, α-Fe and Fe_2B has been found in the disproportionation step. The formation of HDDR $Nd_{13}Fe_{80}B_7$ anisotropy might be related to the early lamella disproportionation structure.

Key words: HDDR; anisotropy; isotropy; NdFeB;

[*This work was financially supported by the National Advanced Material Committee of China (NAMCC), (No. 2001AA324016).*]

The hydrogenation-disproportionation-desorption-recombination (HDDR) process is well known as an effective way for producing anisotropic NdFeB magnetic powders. In the early work, it was recommended that the additive such as Co, Zr or Ga was an important factor to induce anisotropy in the NdFeB magnetic powder [1-3], but the recent work showed that the ternary NdFeB possesses strong magnetic anisotropy as well [4,5], which brought much attention from both research and application point of view.

The early work [6] has been found that ternary $Nd_{13}Fe_{80}B_7$ powders treated by conventional hydrogenation-disproportionation-desorption-recombination (C-HDDR) process preserve a certain degree of anisotropy, but it is incomparable with one produced in modified $Nd_{13}Fe_{bal}Co_{16}Zr_{0.1}Ga_{1.0}B_7$ material. The purpose of this paper is to study the preparation of anisotropic ternary NdFeB and the origin of its anisotropy.

1 Experimental procedure

The alloys with a nominal composition of $Nd_{13}Fe_{80}B_7$ were melted under Ar atmosphere in vacuum induction furnace. The alloy ingots were homogenized at 1050℃ for 24 h and crushed into powders with a particle diameter size of 0.2 mm. The above as-cast powders were subjected to solid-disproportionation treatment (V-HD) [7] and slow desorption-recombination (S-DR) by altering the desorption rate [5] followed finally by a short desorption in high vacuum (this V-HD-S-DR process is shown schematically in **figure 1**). C-HDDR process has been carried out under 1.0×10^5 Pa hydrogen partial pressure and at a temperature range of 0-800℃ in order to obtain a reference material (this C-HDDR process is shown schematically in **figure 2**).

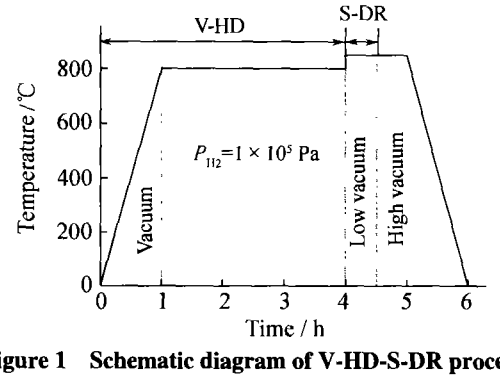

Figure 1 Schematic diagram of V-HD-S-DR process.

The components were analyzed by XRD. Microstructure changes were investigated by TEM. The HDDR-treated NdFeB magnetic powders were mixed with epoxy resin, and then molded into bonded mag-

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net in a magnetic alignment field of 1.5 T. Magnetic measurements were carried out on a B-H tracer. The degree of anisotropy (DOA) was calculated by the following equation,

$$DOA = (B_{r//}-B_{r\perp})/B_{r//} \quad (1)$$

Where $B_{r//}$ and $B_{r\perp}$ are the remanence of the sample parallel and perpendicular to the alignment field.

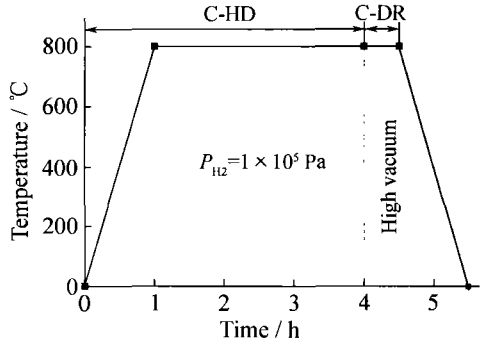

Figure 2 Schematic diagram of C-HDDR process.

2 Results and discussion

The effects of HDDR treatment condition on magnetic properties of $Nd_{13}Fe_{80}B_7$ alloys were examined systematically. The results showed that ternary $Nd_{13}Fe_{80}B_7$ alloys treated by appropriate V-HD-S-DR process is able to obtain anisotropy, and its DOA is comparable with that of $Nd_{13}Fe_{80-x}B_7M_x$ (M=Co, Zr or Ga), as seen in **table 1**. However, being the moderate coercive force of the HDDR $Nd_{13}Fe_{80}B_7$ alloys, the corresponding bonded magnet merely has an undesirable $(BH)_{max}$ of 104 kJ/m^3.

It was also found that disproportionation time, desorption temperature and desorption rate are of three important factors to induce the magnetic anisotropy in ternary NdFeB type alloys. The detailed HDDR process for $Nd_{13}Fe_{80}B_7$ involves heating the material in hydrogen at temperature of 800℃ for 3 h with a partial pressure of 0.1 MPa, followed by a slow desorption rate under 2.0×10^{-3}m^3/min at 850℃ for 45 min and a short desorption in high vacuum.

Table 1 Comparison of magnetic characteristics measured from bonded samples with different composition

Alloy composition	Magnetic characteristics			
	B_r / T	$_iH_c$ /(kA·m^{-1})	$(BH)_{max}$ / (kJ·m^{-3})	DOA
$Nd_{13}Fe_{80}B_7$	0.8	717.6	104	0.50
$Nd_{13}Fe_{bal}B_7Co_{18}Ga_{1.0}Zr_{0.1}$[7]	0.86	930	124	0.54

2.1 Dependence of disproportionation on anisotropy

Curve (a) in **figure 3** shows the dependence of $Nd_{13}Fe_{80}B_7$ anisotropy on solid disproportionation time. With the prolonged disproportionation time, the anisotropy of $Nd_{13}Fe_{80}B_7$ bonded magnet decreases monotonically. When the disproportionation time is greater than 14 h, HDDR $Nd_{13}Fe_{80}B_7$ bonded magnet becomes almost isotropic. The result seemed to show that the disproportionation stage is vital for anisotropy inducement.

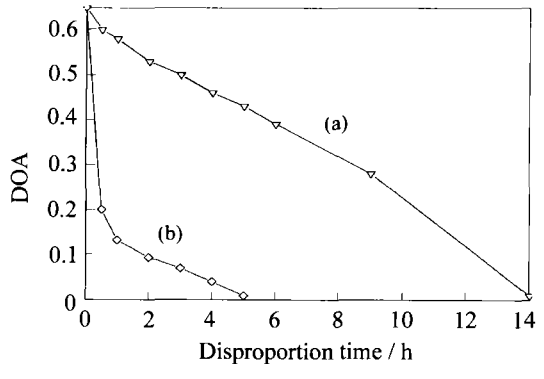

Figure 3 Effects of disproportionation time on anisotropy of $Nd_{13}Fe_{80}B_7$ materials treated by (a) V-HD-S-DR and (b) C-HDDR process.

To further understand if the disproportionation stage is the key to formation of HDDR NdFeB anisotropy, the dependence of disproportionation time on anisotropy processed by conventional HDDR was examined. The results exhibited a similar regulation with V-HD-S-DR process, as is seen from curve (b) in figure 3. However, there exist two differences, i) a lower degree of anisotropy (DOA); ii) a shorter in disappearing time of anisotropy, compared with V-HD-S-DR process.

Based on above statement, it might be concluded that the origin of anisotropy in NdFeB-type HDDR material is contributed by disproportionation stage. The following section of desorption parameters is merely important for enhancement of anisotropy.

2.2 Influence of desorption temperature and rate on anisotropy

Table 2 shows the effects of desorption temperature on the anisotropy of HDDR $Nd_{13}Fe_{80}B_7$ bonded magnet. It is seen that high desorption temperature is surely helpful for the improvement of HDDR $Nd_{13}Fe_{80}B_7$ anisotropy. However, this is only true of short disproportionation time. When the disproportionation time is greater than 14 h, high temperature

desorption treatment can not make HDDR $Nd_{13}Fe_{80}B_7$ bonded magnet gain anisotropy.

Table 2 Effects of desorption temperature on the anisotropy of $Nd_{13}Fe_{80}B_7$ by V-HD-S-DR

DOA of various desorption temperature	Disproportionation time (750℃) / h				
	3.0	5.0	14.0	21.0	30.0
DOA (750℃)	0.1	0.00	0.00	0.00	0.00
DOA (850℃)	0.31	0.23	0.10	0.06	0.01

Although Nakamura reported that high desorption temperature can make ternary NdFeB alloys get anisotropy [4], it is suspected that this was merely a result of the treatment in much shorter hydrogen treatment time of 2 h in the disproportionation step.

Table 3 shows the effects of desorption rate on the anisotropy of HDDR $Nd_{13}Fe_{80}B_7$ bonded magnet. It can be seen a lower desorption rate is beneficial for anisotropy enhancement. Again, the slow desorption treatment cannot also make $Nd_{13}Fe_{80}B_7$ alloys obtain anisotropy as the disproportionation time is longer than 14 h.

Table 3 Effects of desorption rate on the anisotropy of HDDR $Nd_{13}Fe_{80}B_7$ bonded magnet made by V-HD-S-DR powder

DOA of various desorption rate	Disproportionation time (750℃) / h					
	0.5	1.5	3.0	6.0	9.0	14.0
DOA (2.0×10^{-3} m^3/min)	0.33	0.26	0.20	0.16	0.10	0.00
DOA (2.0×10^{-4} m^3/min)	0.47	0.44	0.41	0.33	0.22	0.01

2.3 Observation on microstructures of disproportionation stage

Four samples with disproportionation time of 5 min, 15 min, 3 h and 14 h were studied respectively by XRD and TEM.

The changes in X-ray diffraction patterns with the disproportionation time are shown in **figure 4**. It is seen that the disproportionation rate of $Nd_{13}Fe_{80}B_7$ as-cast powder with hydrogen is very quick. When disproportionation time was 5 min, No $Nd_2Fe_{14}B$ phases were observed. It is also found that the diffraction peaks of Fe_2B phase just appear in the late stage of disproportionation. In fact, there exists Fe_2B phase in the early stage of disproportionation (viewed in **figure 5**). However, some reported the formation of the Fe_2B is delayed behind those of NdH_2 and α-Fe [8]. When the disproportionation time is prolonged, the fine Fe_2B grains (50 nm) in the early stage of disproportionation would coarsen, and indicate a stripe-contrast. So the diffraction peaks of Fe_2B phase covered by that of α-Fe phase would be obviously observed in the late stage of disproportionation. Besides this, no other phases except NdH_2 α-Fe and Fe_2B are observed by the present X-ray diffraction measurements.

In order to clarify the origin of HDDR NdFeB anisotropy, the samples were further investigated by TEM, the results are showed in **figure 6**. It is found that great changes in the microstructure had happened during the disproportionation reaction. When the disproportionation time is shorter (30 min), the corresponding microstructure mainly has the lamella characteristic. With the prolonged disproportionation time (3 hours), some of the early lamella structure have coarsened, and even transformed into spherical morphology. As the disproportionation time is approaching to 14 h, the early microstructure is entirely converted into spherical morphology. The results exhibited that the lamella disproportionation structure is beneficial to the attainment of anisotropy. Further identification work for this is under taking.

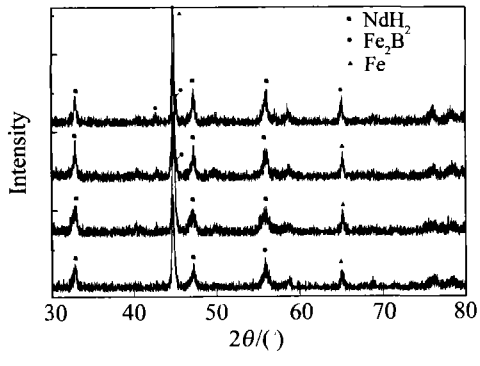

Figure 4 X-ray powder diffraction pattern for the HD process of $Nd_{13}Fe_{80}B_7$ alloys. The powder specimen were obtained by heating in 0.1 MPa H_2 from 5 min to 14 h at 800℃ and immediately quenched to room temperature.

3 Conclusions

(1) $Nd_{13}Fe_{80}B_7$ alloys treated by appropriate HDDR process may obtain anisotropy, which is comparable with that of $Nd_{13}Fe_{80-x}B_7M_x$ (M=Co, Zr or Ga). HDDR $Nd_{13}Fe_{80}B_7$ anisotropic bonded magnet shows an undesirable $(BH)_{max}$ of 104 kJ/m^3, this is caused by its moderate coercive force.

(2) The key to the formation of HDDR NdFeB anisotropy lies in the disproportionation step. When the disproportionation time is longer, the HDDR NdFeB bonded magnet shows isotropy. High desorption temperature and slow desorption treatment are merely a guarantee to obtaining strong anisotropy for $Nd_{13}Fe_{80}B_7$ alloys.

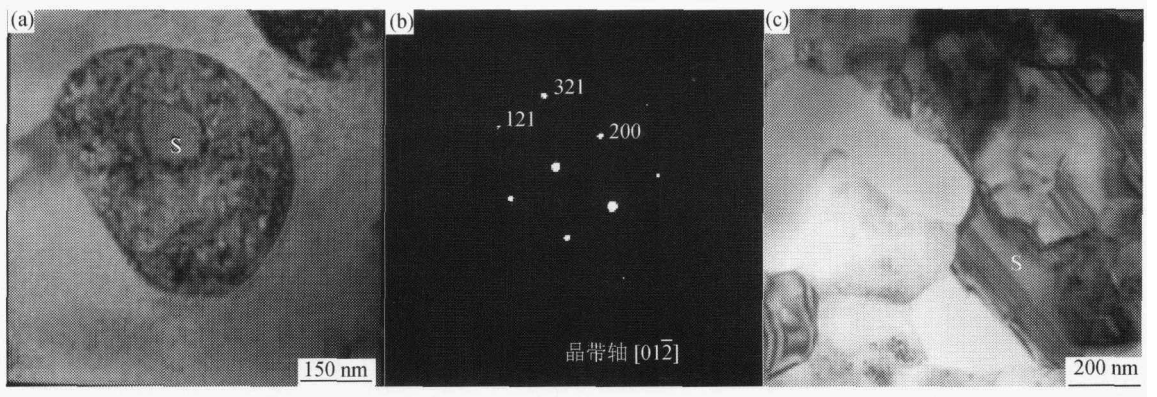

Figure 5 TEM images of typical Fe_2B grain existing in the spherical NdH_2 region. The disproportionation samples of (a) 30 min and (c) 14 h, (b) diffraction pattern taken from the area *S*.

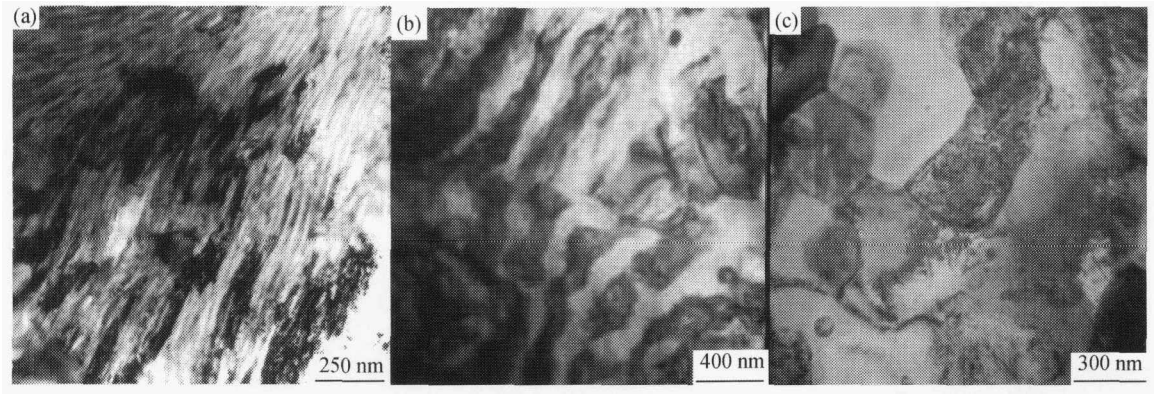

Figure 6 Series of TEM bright field micrographs showing the solid-disproportionation stages of the $Nd_{13}Fe_{80}B_7$ alloy 15 min (a), 3 h (b) and 14 h (c) of annealing in hydrogen at 800℃. The black and white areas are NdH_2 and α-Fe respectively.

(3) No other phases except NdH_2, α-Fe and Fe_2B are found in the disproportionation step. The formation of HDDR $Nd_{13}Fe_{80}B_7$ anisotropy may be related to the lamella microstructure in the early stage of disproportionation.

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