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MÖSSBAUER STUDIES ON THE HYDROGEN DECREPITATION AND DESORPTION OF $Nd_{16}Fe_{76}B_8$ MAGNET

Yu Zhengfang (余正方), Zhang Jiangao (章建高) and Zheng Yufang (郑裕芳)

(Zhongshan University, Guangzhou 510275, China)

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ABSTRACT

Hydrogen decrepitation and desorption of the $Nd_{16}Fe_{76}B_8$ magnet are studied by X-ray diffraction analysis and ^{57}Fe Mössbauer spectroscopy. The results of the as-cast alloy samples treated under various hydrogen gas pressures at various temperatures are reported. A special hydrogenation-dehydrogenation treatment of the Nd-Fe-B cast alloy can produce excellent isotropic magnet powders and the treated sample has passed a hydrogenation-disproportion-recombination process. The effect of the presence of α-Fe in magnet powders is discussed.

Keywords: Mössbauer spectroscopy $Nd_{16}Fe_{76}B_8$ magnet Hydrogen decrepitation Desorption

1 INTRODUCTION

Harris *et al.*[1] reported that the hydrogen decrepitation (HD) process can be applied to the production of Nd-Fe-B type permanent magnets. Cadogan and Coey[2] studied the hydrogen absorption and desorption in $Nd_2Fe_{14}B$. The results indicate that primary absorption occurs in the range 473 – 573 K and results in the formation of a stable Nd-Fe-B hydride, and a dramatic absorption occurs at about 993 K followed by desorption up to 1273 K and results in the disproportionation of the material. McGuiness *et al.*[3] used the hydrogen decrepitation combined with jet milling (JM) to produce powder for the processing of permanent magnets. Takeshita and Nakayama[4] investigated the magnetic properties and microstructures of the Nd-Fe-B magnet powder produced by hydrogen treatment. They consider that the powder is made of very fine crystalline grains of the $Nd_2Fe_{14}B$ intermetallic compound. The aim of this work is to study the hydrogen decrepitation and desorption of $Nd_{16}Fe_{76}B_8$ alloy, especially the disproportionation and dehydrogenation process by Mössbauer spectroscopy.

2 EXPERIMENTAL

$Nd_{16}Fe_{76}B_8$ as-cast alloy samples in the form of small slabs were treated under various hydrogen gas presures (0.1 MPa··· 2.0MPa) at various temperatures (RT··· 1223 K), respectively. An individual sample of the as-cast alloy was heated at a rate of 50 K/min to a particular temperature within the range of 1023 - 1223 K while maintaining the hydrogen pressure at 0.2 MPa for 2 h. After holding the sample under vacuum condition at same temperature for 1h, it was then cooled slowly to room temperature. This is called "a special hydrogenation-dehydrogenation treatment" in the present paper.

XRD was carried out using a D/max-3A full automatic X-ray diffractometer with Cu *K* α radiation.

An MS-500 Mössbauer spectrometer with a ^{57}Co(Pd) source was used to measure the Mössbauer spectra. The isomer shift values are relative to α - Fe standard.

The magnetic properties of powders obtained by hydrogen treatments were measured by a vibrating sample magnetometer.

3 RESULTS AND DISCUSSION

X-ray diffraction and Mössbauer measurements confirm that the as-cast alloy is composed of an $Nd_2Fe_{14}B$ phase and a small amounts of $Nd_5Fe_{18}B_{18}$ phase.

For the samples treated at (or below) 923 K, their XRD patterns and Mössbauer spectra are not the same with those of $Nd_{16}Fe_{76}B_8$ unhydrogenated sample. Due to a non-uniform hydrogen concentration in the lattice as well as to a certain hydrogen-induced disturbance of the local atomic environment, hydrogen absorption favours the formation of a variety of local symmetries, leading to a broad anisotropy field distribution, although the overall crystal structure still appears to be preserved[5]. Two Mössbauer spectra of samples treated at 523 K and 823 K respectively, under 1.0 MPa hydrogen gas pressure are shown in Fig.1 (a, b). The spectra of hydrogenated samples are comprised of six magnetically split sextets corresponding to the six crystallographically inequivalent iron sites in the $Nd_2Fe_{14}BH_x$ tetragonal structure and a paramagnetic doublet corresponding to the $Nd_5Fe_{18}B_{18}$ phase[2,6]. The Mössbauer parameters and intensities of $Nd_2Fe_{14}BH_x$ are effected by the hydrogen treatment temperature, pressure and treatment time, but their values fall within a relatively narrow range. This indicates that a stable Nd-Fe-B hydride was formed. With respect to the unhydrogenated sample, the values of magnetic hyperfine field (H_i) and

Table 1

^{57}Fe Mössbauer parameters of sample treated at 1023 K

Phase	H_i (T)	QS (mm/s)	IS (mm/s)	Int (%)
α - Fe	33.0	0.00	0.01	76.0
Fe_2B	24.2	0.03	0.13	19.9
Doublet	0	0.55	0.05	4.1

isomer shift (IS) for the six inequivalent iron sites are both increase. The increase in H_i is due to an enhanced exchange interaction[7], and the increase in IS is due, in part, to the lattice expansion of about 1-2% caused by hydrogenation[2,8].

For the samples treated at above (or about) 973 K, the results have shown that heating in hydrogen rather than in a vacuum caused the disproportionation of the alloy yielding α-Fe, iron-boride and neodymium hydride. Fig.1 (c) and Table 1, respectively, show the Mössbauer spectrum and Mössbauer parameters of a sample treated at 1023 K. The dominant phase is α-Fe (76.0%). The others are Fe_2B (19.9%) and a paramagnetic doublet with QS = 0.55 mm/s and IS = 0.05 mm/s (4.1%). XRD confirms the presences of iron-boride and neodymium hydride.

Fig.1 (d) shows a Mössbauer spectrum of sample which has passed a special hydrogenation-dehydrogenation treatment at 1093 K. The fitting results of this Mössbauer spectrum indicate that it is comprised of $Nd_2Fe_{14}B$ phase, $Nd_5Fe_{18}B_{18}$ phase, and α-Fe (about 3% of the total spectrum). This means that the vacuum annealing treatment at around 1093 K would result in the removal of the hydrogen from neodymium hydride and the subsequent recombination of the α-Fe, iron-boride and neodymium to form the original alloy. Further experiments show that both the content of α-Fe and intrinsic coercivity H_{ci} are related to the hydrogenation-dehydrogenation temperature (T). This is consistent with the results obtained by McGuiness *et al.*[9]. The presence of α-Fe in magnet powders would seriously prevent the development of high coercivities. The elimination of α-Fe in the treated sample is an important thing in producing Nd-Fe-B type magnet powders. In our present work, when T = 1113 K, the α-Fe

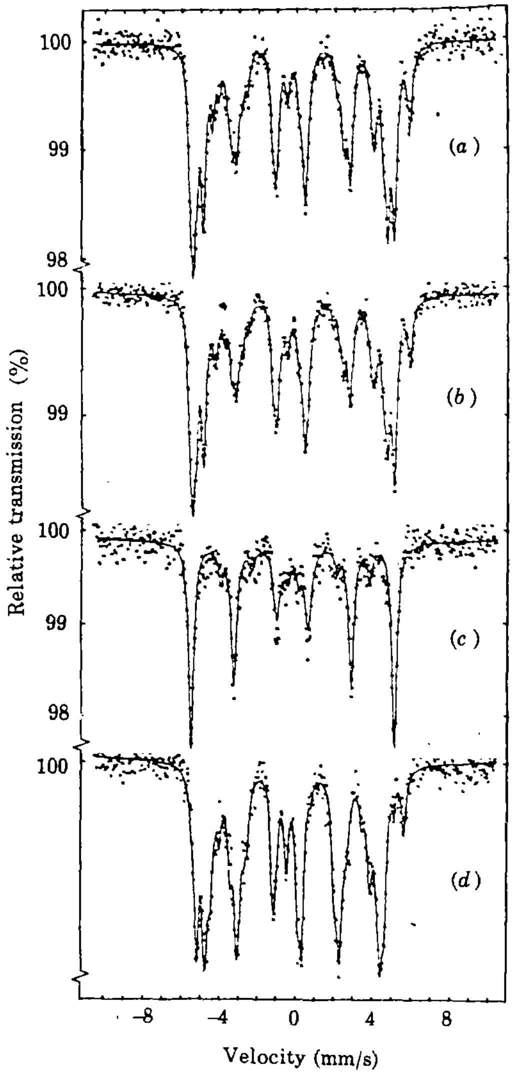

Fig.1 ^{57}**Fe Mössbauer spectra of** $Nd_{16}Fe_{76}B_8$ **at room temperature**

(a) Hydrogenated at 523 K (b) Hydrogenated at 823 K (c) Hydrogenated at 1023 K (d) Hydrogenation-dehydrogenation treatment at 1093 K phase disappears and the intrinsic coercivity H_{ci} is more than 8.75×10^5A/m.

4 CONCLUSIONS

The main conclusions from the results mentioned above can be summarized as follows:

a. The hydrogen decrepitation of the Nd-Fe-B type as-cast alloys is an effective method for the powder production of the Nd-Fe-B type permanent magnets.

b. When the samples were treated at (or below) 923 K, hydrogen absorption results in the formation of a stable Nd-Fe-B hydride. When the treated temperature is higher than 973 K, the results show that heating in hydrogen caused the disproportionation of the alloy yielding α-Fe, iron-boride and neodymium hydride.

c. A special hydrogenation-dehydrogenation treatment of the Nd-Fe-B as-cast alloy at a particular temperature within the range of 1023-1223 K can produce excellent isotropic magnet powders and the treated sample has passed a hydrogenation-disproportionation-recombination process.

d. The content of α-Fe and intrinsic coercivity in magnet powders are related to the hydrogenation-dehydrogenation temperature T. In order to obtain the superior intrinsic coercivity, it is necessary to choose an optimum treated temperature.

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