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AN INVESTIGATION OF THE PERMANENT MAGNETS $Nd_{15}(Fe, Co)_{77}B_8$ WITH Dy AND Al ADDITIVES

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ABSTRACT

Nd-(Fe, Co)-B alloys with Dy and Dy-Al additives have been studied by the Mössbauer effect and X-ray diffraction. The results indicate that the alloys consist of a tetragonal phase, a B-rich phase and a Nd-rich phase. The average magnetic moment of Fe atoms in the tetragonal phase has been determined. The variation of remanence due to Dy and Dy-Al additives has been derived from the Mössbauer data and found to agree with the results of magnetic measurements. The site substitutions of Dy and Al in the alloys are also discussed.

Keywords: Mössbauer spectroscopy Permanent magnet Additives Magnetic moment

1 INTRODUCTION

Nd-Fe-B alloys exhibit superior properties for use of permanent magnets. However their Curie temperature is relatively low which gives a rise to unsatisfactory thermal stability. Addition of Co raises the Curie temperature but leads to a decrease in coercivity. Incorporation of small amounts of Dy and Dy-Al causes an increase in the Curie temperature and thus improves the thermal stability and the coercivity with little reduction of the remanence.[1-3]

2 EXPERIMENTAL

The alloys investigated were prepared by arc melting in an argon atmosphere. The ingots were crushed and ground into powders which were then pressed in a magnetic field before being sintered at about 1080°C. A S-570 Scanning Electron Microscope equipped with EDS-PV 9900 were used for microstructural observation and microanalysis of composition. The magnetic properties were measured by CL6-1 Magnetometer to test static magnetic properties (Table 1). The X-ray diffraction measurements were carried out in a X-ray diffractometer Rigaku D/Max-RB with Cu K_α radiation. The Mössbauer spectra were taken at room temperature with a ^{57}Co(Pd) source.

Table 1

Magnetic properties of $Nd_{15}(Fe, Co)_{77}B_8$ with Dy and Al additives

Sample No.	Additives	$B_r^{1)}$(T)	$H_{cj}^{2)}$(kA/m)	$H_{cb}^{3)}$(kA/m)	$1/2(BH)_m^{4)}$ (kJ/m^3)
A_1	1 wt.% Dy	1.14	262.6	234.9	57.30
B_1	2 wt.% Dy	1.08	469.7	437.9	100.67
C_1	2 wt.% Dy+0.5 wt.%Al	1.05	1154.5	756.4	101.46

1) Remanence 2) Coercivity ($M=0$) 3) Coercivity ($B=0$) 4) Maximum energy product

3 RESULTS

The X-ray diffraction patterns show that the alloys consist of a phase of tetragonal structure and two minor phases (see Fig.1). By SEM observation, one of the minor phases is Nd-rich phase in which the content of the Nd varies from 85 at% to 96 at%. The other minor phase may be B-rich phase from comparing with diffraction pattern of Ref.[4]. The Co content in tetragonal phase is about 16 at%. The Mössbauer spectra shown in Fig.2 are composed of six sets of sextets, one doublet and one singlet, corresponding to the six inequivalent Fe sites in tetragonal phase[4], B-rich phase and Nd-rich phase, respectively (see Teble 2).

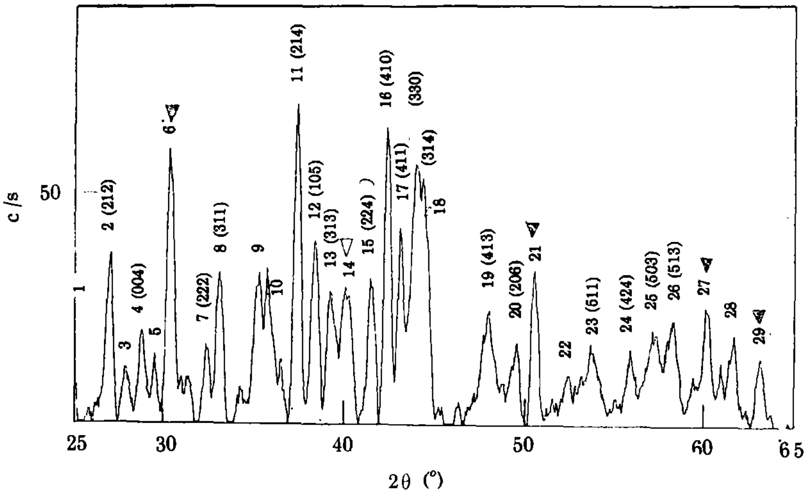

Fig.1 The X-ray diffraction pattern of $Nd_{15}(Fe, Co)_{77}B_8$ with Dy-Al (sample C_1) additives

▼ and ▽ show two minor phases

It can be seen that the hyperfine fields of the six inequivalent sites of Fe in the tetragonal major phase are reduced with increase of the Dy and Al contents and this indicates that Dy and Al cations enter into the tetragonal phase. The average hyperfine field is[4]

$$<H> = \Sigma_i H_i S_i / \Sigma_i S_i$$

where H_i and $S_i/\Sigma S_i$ are the hyperfine field and the relative area of the subspectra of the *i*th Fe crystal site in the tetragonal phase respectively. The influence of the Al additive on $<H>$ of the tetragonal phase is much stronger than that of Dy.

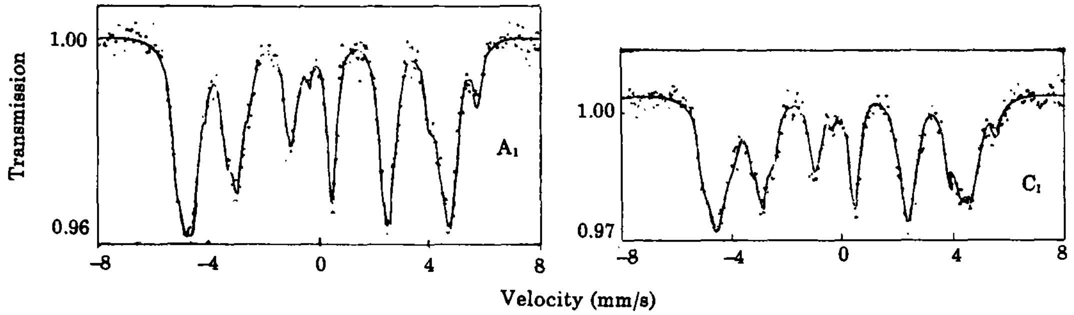

Fig.2 The Mössbauer spectra of $Nd_{15}(Fe, Co)_{77}B_8$ with Dy (sample A_1) and Dy— Al (sample C_1) additives

Table 2

Mössbauer parameters of $Nd_{15}(Fe,Co)_{77}B_8$ with Dy and Dy— Al additives

No.	Mössbauer parameters	Tetragonal phase						B-rich phase	Nd-rich phase
		J_2	k_2	j_1	k_1	e	c		
A_1	IS (mm/s)	0.11	-0.16	-0.20	-0.01	-0.04	-0.06	0.13	0.51
	QS (mm/s)	0.66	0.19	0.11	0.25	-0.08	0.11	0.81	
	H (T)	33.01	31.13	28.41	28.62	25.99	24.78		
	S (%)	14.1	21.2	17.2	29.1	7.1	8.1	2.7	0.4
B_1	IS (mm/s)	0.09	-0.13	-0.21	-0.02	-0.12	-0.17	0.10	0.49
	QS (mm/s)	0.70	0.14	0.07	0.24	0.11	0.01	0.58	
	H (T)	32.54	31.03	28.19	28.41	25.52	24.31		
	S (%)	14.4	21.6	12.5	33.2	6.1	7.5	4.4	0.3
C_1	IS (mm/s)	0.07	-0.14	-0.20	-0.02	-0.07	-0.06	0.14	0.36
	QS (mm/s)	0.60	0.21	0.09	0.28	0.07	0.21	0.81	
	H (T)	32.32	30.91	27.93	28.08	25.26	23.34		
	S (%)	13.8	10.9	17.1	28.3	15.0	11.4	2.7	0.9

4 DISCUSSION

Using the empirical ratio between the average hyperfine field and the average Fe atomic magnetic moment, 14.7 T/μ_B[5], the average Fe moment in undoped $Nd_2Fe_{14}B$ is estimated to be $\mu_{Fe} = 2.02\ \mu_B$ with $<H> = 29.6$ T. Since the molecular magnetic moment of $Nd_2Fe_{14}B$ is $\mu = 32.1\ \mu_B$[6], the average magnetic moment of Nd atom is

$$\mu_{Nd} = (\mu - 14\mu_{Fe})/2 = 1.91\ \mu_B$$

Assuming all cobalt are in tetragonal phase and neglecting the effect of atomic moment of small Dy content, a molecular magnetic moment μ of the tetragonal phase in the present samples can be evaluated by

$$\mu = 2\mu_{Nd} + 14\mu_{Fe}(1-0.16) + 14\times 0.16\mu_{Co}$$

where μ_{Fe} is determined from the average hyperfine field $<H>$ of Fe and changes with the additives. The atomic moment of cobalt is taken as 1.30 μ_B[4]. The values of μ and μ_{Fe} are given in Table 3.

Table 3

The calculated average moment of Fe atom and the molecular moment of the tetragonal phase in the present samples

Sample No.	A_1	B_1	C_1
$<H>$ (T)	29.2	29.1	28.0
μ_{Fe} (μ_B)	2.00	1.98	1.91
μ (μ_B)	30.3	30.0	29.2

μ_{Co} is taken as 1.30μ_B and μ_B is the Bohr magneton

μ_{Fe} and μ change little with variation of the Dy content. Since both Dy and Nd are trivalent, the electron transfer effect in the Fe band has little effect. The Curie temperature of $Dy_2Fe_{14}B$ is close to that of $Nd_2Fe_{14}B$[7]. However, small amount of Al additive causes a relatively large change of μ_{Fe} and μ due to the substitution of the Al cations in the Fe sites. The electron transfer in the Fe band and the dilution of the exchange coupling lead to the decrease of μ_{Fe} at room temperature.

The X-ray diffraction shows that the lattice parameters of the tetragonal phase in the three samples are found to be close to each other. Neglecting the small change of the unit cell volume V_T, the saturation magnetization of the tetragonal phase was calculated by $M_s = 4\times 3.14\times 9.273\times 10^{-25}\times 4\,\mu / V_T$ (T). The remanence of the sample is $B_r = M_s X \cos\theta$. Where X is the volume fraction of the tetragonal phase in the sample and θ is the average orientation angle of the c-axis in the sample. Assuming the values of θ are the same for the three samples the ratio between the remanence of two samples is

$$B_{r1}/B_{r2} = (M_{s1}\times X_1)/(M_{s2}\times X_2) = (\mu_1 \times X_1)/(\mu_2 \times X_2) \qquad (1)$$

The area S_i of the subspectrum of the ith phase is proportional to the total number of Fe atoms in the phase which in turn is proportional to the volume fraction of the phase X_i. Thus $X_i = K_i \cdot S_i$. where $i = 1,2,3$ represent the tetragonal phase, B-rich and Nd-rich phases respectively. The proportional constant K_i varies for different phases. By using the experimental results of the alloy $Nd_{17}(Fe_{0.8}Co_{0.2})_{75}B_8$[4] the values of K in tetragonal phase was evaluated. The volume fractions of tetragonal phase was calculated and the result is listed in Table 4. Substituting the above values into equation (1) the remanence ratio between the different samples based on the Mössbauer study are $B_r(A_1)/B_r(B_1)=1.03$, $B_r(B_1)/B_r(C_1)=1.02$, while the values from magnetic measurements are $B_r(A_1)/B_r(B_1)=1.06$, $B_r(B_1)/B_r(C_1)=1.02$. They agree relatively well.

Table 4

The calculated volume fractions of the tetragonal phases

Samples No.	A_1	B_1	C_1
K	0.84	0.84	0.84
X	81.4	80.0	80.8

5 CONCLUSIONS

a. The variation of the Dy content does not induce much change in the magnetization of the tetragonal phase for the $(Dy, Nd)_{15}(Fe, Co)_{77}B_8$ alloy. The change of the relative volume fraction of non-magnetic phase is the main reason for the decrease of remanence.

b. A further decrease of the remanence by the addition of Al is mainly caused by the reduction in the average magnetic moment of Fe atoms in the tetragonal phase.

c. With increase in the Dy content the hyperfine fields of Fe at the j_2, e, and c sites experience the largest reduction. It is suggested that Dy atoms may substitute Nd atoms in the f site mainly since the f site of Nd atom has a relatively short distance from the j_2, e and c sites[8].

d. On the addition of Al, the hyperfine fields of Fe at k_1 and c sites experience the largest reduction. The near neighbours of the k_1 site are the e, c and k_2 sites, and the nearest neighbour of the c site is the k_2 site as well as the hyperfine field of Fe atom at k_2 has the smallest reduction. Thus it is suggested that Al atoms mainly substitute Fe atoms in the k_2 site.

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