

Enhanced Exchange Coupling of $\text{Nd}_2\text{Fe}_{14}\text{B}/\text{Fe}_3\text{B}$ Magnet Via Magnetic Field Treatment

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An externally applied magnetic field during heat treating the $\text{Nd}_2\text{Fe}_{14}\text{B}/\text{Fe}_3\text{B}$ based spring magnet was found to enhance the exchange coupling between the hard and soft magnetic grains. More than 30% increase in M_r/M_s values for melt-spun $\text{Nd}_4\text{Fe}_{73.5}\text{Co}_3(\text{Hf}_{1-x}\text{Ga}_x)\text{B}_{18.5}$ ($x = 0, 0.5, 1$) alloys was resulted from a uniform distribution of Fe_3B , $\alpha\text{-Fe}$ and $\text{Nd}_2\text{Fe}_{14}\text{B}$ phases, and also from a reduced grain size of those phases by 20%. The externally applied magnetic field induced a uniform distribution of fine grains. A study of Mössbauer effect also report that the enhancement of total magnetization of nanocomposite $\text{Nd}_2\text{Fe}_{14}\text{B}/\text{Fe}_3\text{B}$ alloys is attributed to an increased formation of Fe_3B after magnetic annealing.

1. Introduction

Nanocomposite spring magnets provide an alternate way to produce a high remanence magnetic materials which can be made into resin bonded magnets. Additional merit is in the cost reduction due to the less use of rare earth element. Basically the nanocomposite magnets have been studied on the composition of $\text{Nd}_2\text{Fe}_{14}\text{B}/\text{Fe}_3\text{B}$ [1, 2] and $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ [3, 4]. Although those magnetic materials showed M_r/M_s values (≤ 0.8) higher than the Stoner-Wohlfarth limitation ($M_r/M_s = 0.5$), the obtainable coercivity is still very low ranging over 2~4 kOe [5, 6].

According to the nanocomposite model proposed by Kneller & Hawig [7], the exchange coupling takes place when the critical particle size of both the soft (b_{cm}) and hard (b_{ck}) magnetic phases satisfies the relationship $b_{cm} = \pi (A_k/2K_k)^{1/2} = b_{ck}$ where A_k is anisotropic energy and K_k is anisotropic constant. The computed size resulted in 10 nm for $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ magnets. Realistically, however, the order of formation of $\text{Nd}_2\text{Fe}_{14}\text{B}$, Fe_3B and $\alpha\text{-Fe}$ is different, and the growth rate during phase separation is not the same. Despite the realistic fact, the previously reported studies were focussed on an interest in grain size reduction via a rapid solidification technique which has not guaranteed the effective exchange coupling yet. Recently, Fukunaga et al [8, 9]. reported results of computer simulation that there is an optimum grain size exhibiting a maximized energy product being dependent upon the volume fraction of soft (or hard) phase. The coupling force influences not only on the remanence magnetization but sometimes causes a decrease in coercivity below a certain grain size. In his computer simulation, however, the so called exchange energy parameter ($=SJ_c/6KV$)

was used on the assumption that the grains are with identical shape therefore disregarding the magnetostatic energy. S and V are the surface area and volume of $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains, respectively, and J_c is the exchange coupling constant.

The present study reports an additional result of Mössbauer effect on the nanocomposite magnets which showed a significantly enhanced remanence ratios induced by a uniform distribution of fine grains caused by the external magnetic field [10].

2. Experimental

Ingots of $\text{Nd}_4\text{Fe}_{73.5}\text{Co}_3(\text{Hf}_{1-x}\text{Ga}_x)\text{B}_{18.5}$ ($x = 0, 0.5, 1$) composition were prepared by plasma arc-melting the constituent elements in an argon atmosphere. 50~60 g pieces of ingot were melt-spun from a quartz tube, and spun onto a rotating wheel at a speed of 40 m/sec. The amorphous ribbons obtained were 20~30 μm thick and 10~15mm wide. These samples were annealed by furnace annealing as well as magnetic field annealing at 650~710 $^\circ\text{C}$ for 5 minutes. The applied field was fixed at 5 kOe along the direction of ribbon's long axis. X-ray diffraction of $\text{Cu K}\alpha$ radiation was used to identify the phases present, and microstructure and composition were checked by a transmission electron microscope. The hysteresis loops were measured in a vibrating sample magnetometer with a maximum field of 19 kOe along the long axis using appropriate demagnetization factors. Morphology of fracture surface image analysing were carried out using an image scanner attached in a scanning electron microscope. Additional thermomagnetic behaviors were examined using a thermogravimetric analyzer to identify the magnetic transformation of amorphous ribbons. Room temperature

Mössbauer spectroscopy was carried out without applying a magnetic field using ⁵⁷Co (Rh) source for the ribbon samples to monitor the volume fraction of each phase formed during annealing.

3. Results and Discussion

A. The Typical Magnetic Properties After Furnace Annealing

When the spring magnets consisted of Fe₃B and /or α-Fe with the hard phase Nd₂Fe₁₄B are not heat treated properly, they always show hysteresis curves having a constriction at H = 0 as shown in Fig. 1. All the compositions used in this study

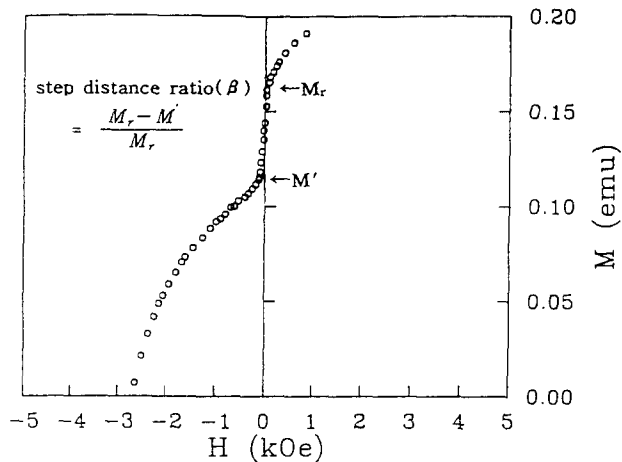


Fig. 1 The typical hysteresis loop of melt-spun Nd₄Fe_{73.5}Co₃Hf_{0.5}Ga_{0.5}B_{18.5} ribbons after annealing at 680 °C for 5 minutes without a magnetic field.

showed the same behaviors. This is due to the lack of full exchange coupling between the soft and hard phases leading to a low remanence magnetization. We have defined a “step distance ratio (STR)” as $(M_r - M') / M_r$ in this study for every samples, and plotted the STR and M_r / M_s as a function of annealing temperature as shown in Fig. 2. The STR increases with increasing annealing temperature for all the compositions, accordingly M_r / M_s shows decreases. Nd₄Fe_{73.5}Co₃Hf_{0.5}Ga_{0.5}B_{18.5} alloy shows the superior properties to those of others. Accordingly the effect of the addition of Hf and Ga was examined as plotted in Fig. 3. M_r / M_s ratio evidently increases with the addition of Ga and Hf at the same time exhibiting peak values for all the annealing temperatures at x (Ga) = 0.5, and decreases thereafter. At low annealing temperature except 705 °C, however, the STR shows relatively constant values. The addition of Ga is believed to enhance M_r / M_s values caused by the grain refinement. But the grain refinement by Ga may be superimposed on the effect of temperature at a low annealing range. This is why the STR values at lower temperature are relatively constant, and high M_r / M_s ratios are obtained by annealing at 628 °C for 5 minutes.

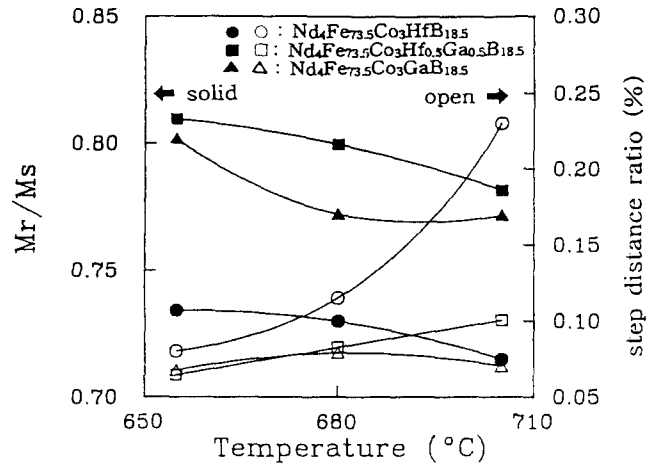


Fig. 2 Variation of reduced remanence (M_r / M_s) and step distance ratio ($(M_r - M') / M_r$) of the melt-spun Nd₄Fe_{73.5}Co₃Hf_{1-x}Ga_xB_{18.5} (x = 0, 0.5, 1) ribbons as a function of annealing temperature.

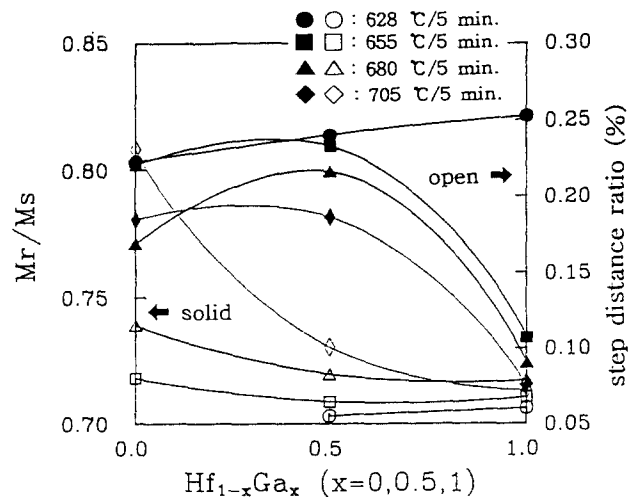


Fig. 3. Variation of reduced remanence (M_r / M_s) and step distance ratio ($(M_r - M') / M_r$) of the melt-spun Nd₄Fe_{73.5}Co₃Hf_{1-x}Ga_xB_{18.5} (x = 0, 0.5, 1) ribbons as a function of Hf content (x) after annealing.

B. Enhanced Magnetic Properties After Annealing In a Magnetic Field

Fig. 4 demonstrates the effect of external magnetic field on the enhanced remanence magnetization and energy product as well. Both the remanence magnetization and energy product values were obtained to be enhanced by 20~30% for all the compositions, though Nd₄Fe_{73.5}Co₃GaB_{18.5} alloys show the least effects, examined by applying an external field of 5 kOe during annealing the melt-spun alloys. Particularly the Nd₄Fe_{73.5}Co₃Hf_{0.5}Ga_{0.5}B_{18.5} alloy exhibits the energy product of 15.8 MGOe resulted from the high remanence (12.6 kG) and coercivity (2.8 kOe) as well at the annealing temperature of 680 °C. It is of interest to note that the coercivity values of Nd₄Fe_{73.5}Co₃Hf_{0.5}Ga_{0.5}B_{18.5} and Nd₄Fe_{73.5}Co₃HfB_{18.5} alloys show

the maximum values at 680 °C, and then tend to drop above that temperature.

Fukunaka et al. [8, 9] claimed that the magnetostatic energy does not play any influence on exchange coupling between two phases, and the coupling force increases with decreasing the grain size. However, they showed the behavior of coercivity as a function of grain size that the coercivity reach a maximum value when the exchange coupling parameter [9], $J_c S / K_u V$, drops just below 1. The parameter 1 corresponds to $(S/V)^{-1} = 20$ nm in his report for $Nd_2Fe_{14}B$ based composite. When $J_c S / K_u V > 1$, the coercivity was almost zero. He explained the behavior in terms of isotropic properties where the degree of isotropy increases with decreasing the grain size. Fig. 4 shows the identical trend with his simulation such that the magnetic annealing at 680 °C exhibited a peak coercivity of 2.83 kOe with the grain size of 22 nm. The coercivity drops above 705 °C seems to be caused by grain coarsening, while the low values in coercivity at 655 °C is due to too fine grain size.

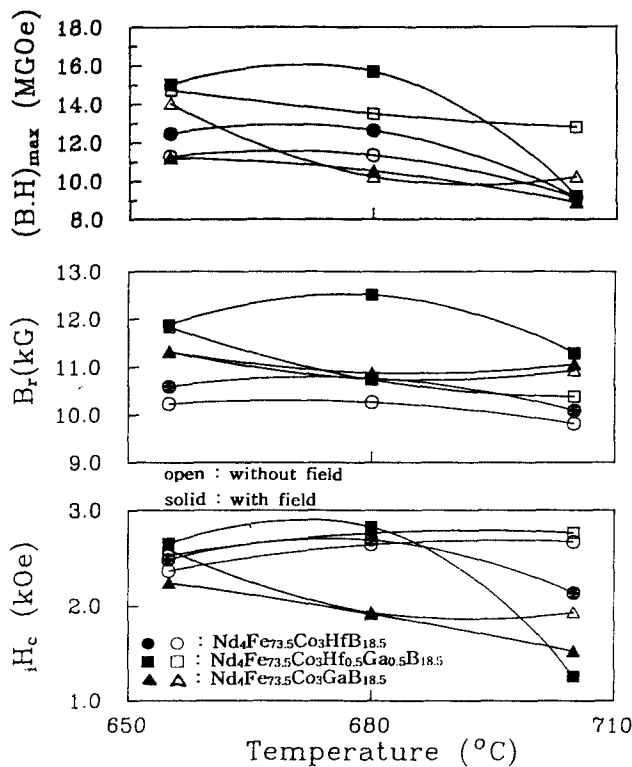


Fig. 4 Variation of magnetic properties of the melt-spun $Nd_4Fe_{73.5}Co_3Hf_{1-x}Ga_xB_{18.5}$ ($x=0, 0.5, 1$) ribbons as a function of annealing temperature with and without a magnetic field.

Fig. 5 shows the typical hysteresis curves before and after the magnetic annealing where the enhancement in M_r/M_s is prominent. The enhanced properties are plotted in Fig. 6 where all the three composition demonstrates a 20~30% increase in M_r/M_s values. The $Nd_4Fe_{73.5}Co_3Hf_{0.5}Ga_{0.5}B_{18.5}$ alloys always exhibited M_r/M_s values more than 0.82 which is considerably hard to obtain by conventional ways. Besides the M_r/M_s of that alloy was

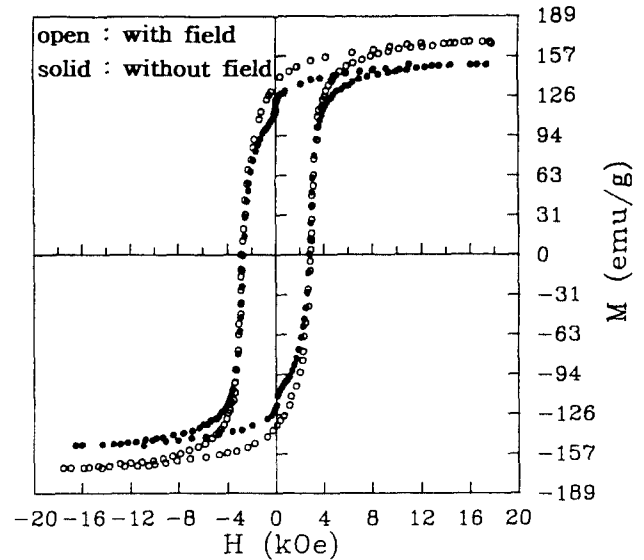


Fig. 5 The typical hysteresis loops of melt-spun $Nd_4Fe_{73.5}Co_3Hf_{0.5}Ga_{0.5}B_{18.5}$ ribbons after annealing with and without a magnetic field.

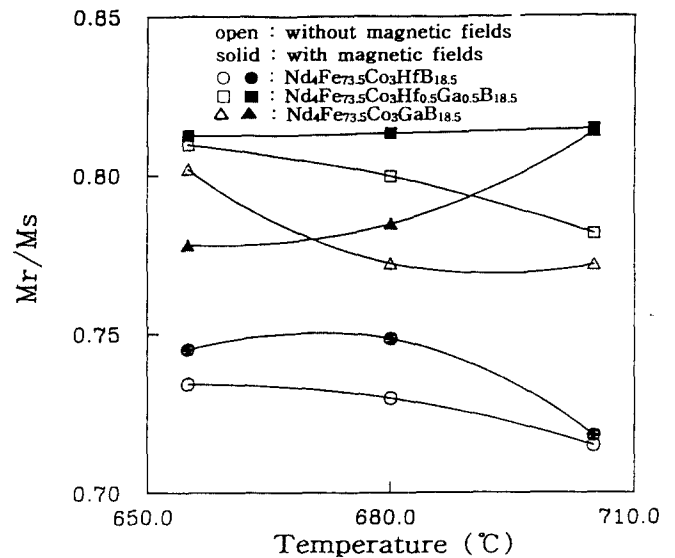


Fig. 6 Variation of reduced remanence (M_r/M_s) of the melt-spun $Nd_4Fe_{73.5}Co_3Hf_{1-x}Ga_xB_{18.5}$ ($x=0, 0.5, 1$) ribbons as a function of annealing with and without a magnetic field.

found not to be influenced by a high annealing temperature.

Taking into account the X-ray diffraction patterns of $Nd_4Fe_{73.5}Co_3Hf_{0.5}Ga_{0.5}B_{18.5}$ in Fig. 7, one will realize that considerable changes took place for α -Fe and Fe_3B phases after the annealing without and with a magnetic field. (110) and (200) peaks of α -Fe can be seen to be diffused with a shortened height after the annealing with a magnetic field. This is the same for (301), (311), (321), (302) and (411) of Fe_3B . On the other hand no change is observed for $Nd_2Fe_{14}B$ peaks. The observed lattice parameters of each phase are $a = 2.8779$ for α -Fe, $a = 8$.

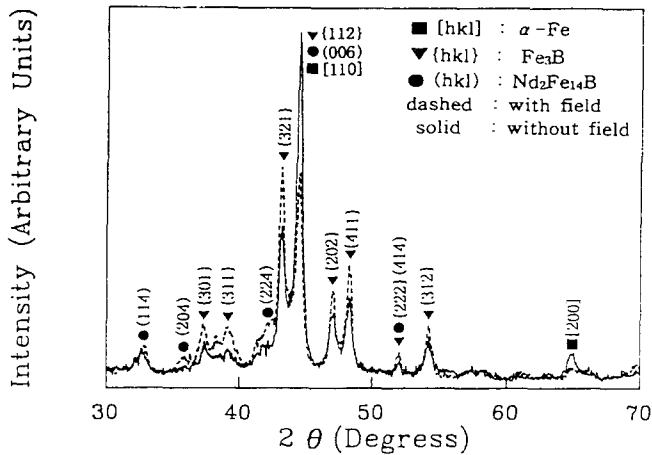


Fig. 7 X-ray diffraction patterns of melt-spun Nd₄Fe_{73.5}Co₃Hf_{0.5}Ga_{0.5}B_{18.5} ribbons after annealing with and without a magnetic field.

6832 and $c=4.2835$ for Fe₃B and $a=8.7875$ and $c=12.21 \text{ \AA}$ for Nd₂Fe₁₄B, respectively. The Nd₄Fe_{73.5}Co₃Ga_{0.5}B_{18.5} and Nd₄Fe_{73.5}Co₃Hf_{0.5}B_{18.5} alloys also showed the identical patterns indicating that grains become finer by applying the external field. In order to relate this change in patterns with microstructures, we confirmed the grain refinement by scanning 1000 grains using the transmission electron microscopy and an image analyzer attached in a scanning electron microscope as shown in Fig. 8 and Fig. 9, respectively. Magnetic annealing without a field as shown in Fig. 8 (a) and (b) introduced abnormally coarse α -Fe (particles appearing black) and Fe₃B grains with an average grain size of 30 nm. After the magnetic annealing, however,

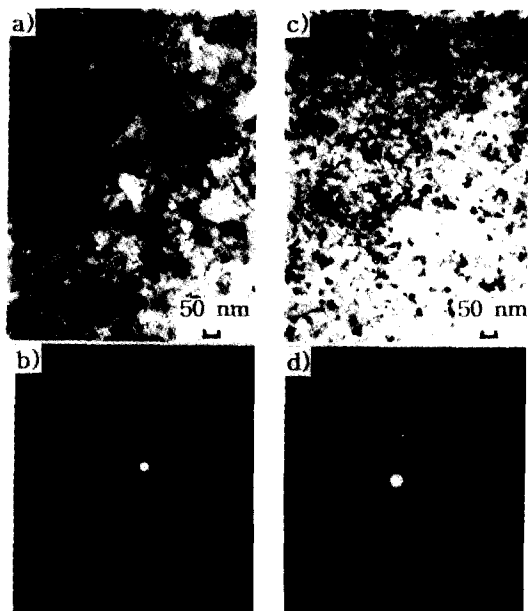


Fig. 8 TEM micrographs showing the grain aspect of the annealed Nd₄Fe_{73.5}Co₃Ga_{0.5}Hf_{0.5}B_{18.5} ribbons (a) without a magnetic field and its (b) selected area diffraction pattern, (c) with a magnetic field and its (d) selected area diffraction pattern.

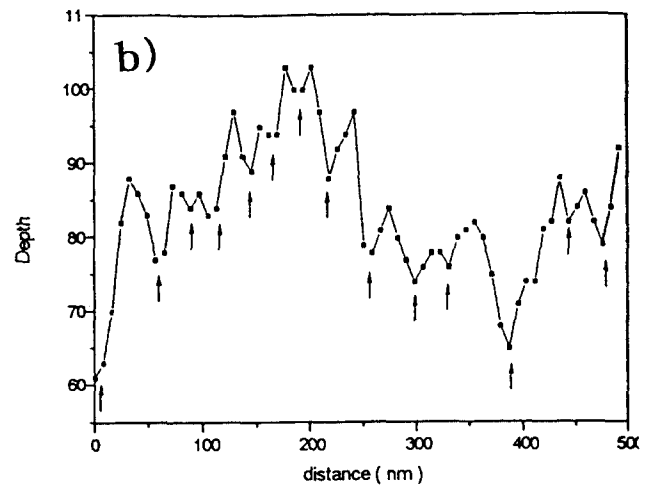
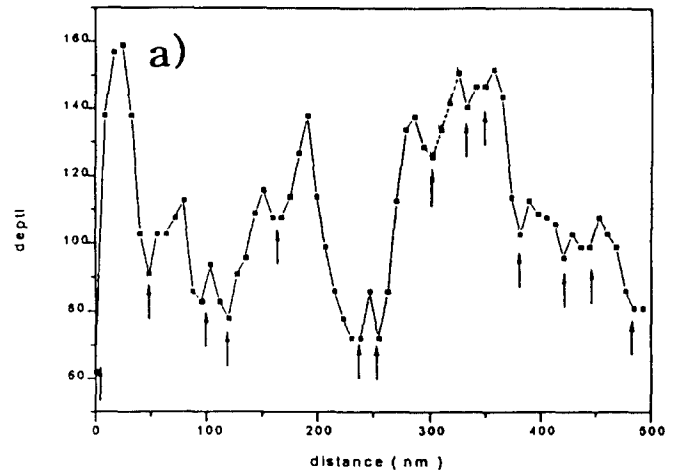


Fig. 9 Grain size distribution for the annealed ribbons (a) without a magnetic field, and (b) with a magnetic field corresponding to Fig. 8.

very uniform distribution of fine grains were obtained being evident in Fig. 8 (c) and (d). The uniformity of grains for each case is identified by scanning 1000 grains and shown in Fig. 9 (a) and (b). The grain irregularity (size scattering) of 70~160% was measured before the magnetic annealing, while the irregularity of 60~100% was obtained after the annealing. Considering the enhancement in M_r/M_s values, X-ray patterns and the results of grain aspect, applying an external field during annealing induces not only the grain refinement but causes a uniform distribution of the grains at the same time. Presently the exact mechanism of grain refinement is not known yet.

Fig. 10 (a) and (b) show the Mössbauer spectra at room temperature for the Nd₄Fe_{73.5}Co₃Hf_{0.5}Ga_{0.5}B_{18.5} samples annealed without and with a magnetic field. The curves of solid circles are as measured, and the curves of different colors correspond to resolved fits of each atomic site of existing phases. One can find that both the spectra of annealed sample without and with a magnetic field are fitted well with subspectra for each α -Fe, Fe₃B, and Nd₂Fe₁₄B. The amorphous samples annealed without or with a field at 680 °C for 5 minutes, which is the optimal

condition to obtain the best hard magnetic properties, consist of mainly bct-Fe₃B (67~82 vol. %), and then α-Fe (6~19 vol. %), and small amount of Nd₂Fe₁₄B (12~14 vol. %). These volume contents of soft and hard magnetic phases in the Nd₄Fe_{73.5}Co₃Hf_{0.5}Ga_{0.5}B_{18.5} alloy are very close to those of simulated model proposed by Kneller and Hawig [7] who proposed 10 vol. % of hard magnetic phase when the critical grain size for each soft and hard magnetic phase is identical to obtain the appropriate exchange coupling.

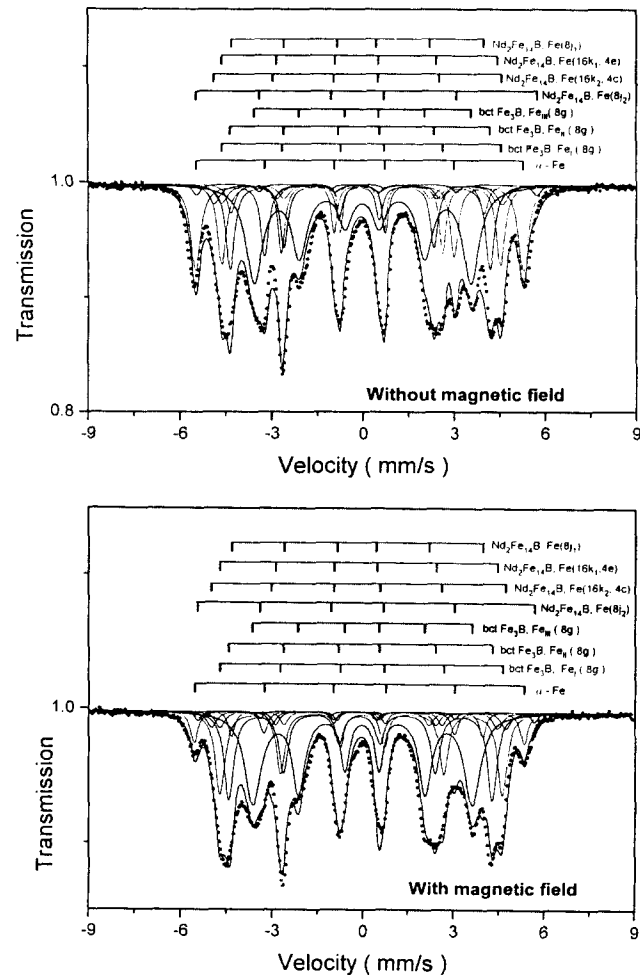


Fig. 10 The resolved curve fits of α-Fe, Fe₃B and Nd₂Fe₁₄B phases of Mössbauer spectroscopy for (a) the alloys annealed without a magnetic field, and (b) with a field.

The result of Mössbauer spectroscopy is summarized in Table I. Basically the changes in hyperfine field (HF), isomer shift (IS), and quadrupole splitting (QD) for each phase in the sample annealed without and with a magnetic field are not prominent. In general, however, a reduced IS and QD, and an increased HF are obtained by annealing the samples at a magnetic field. This result implies that magnetically treated nanocomposite alloys induced a well developed long range ordering in Fe₃B and Nd₂Fe₁₄B structures taking into account the increased HF and reduced IS/QD for Fe₃B particularly. Most of all, it is worthy to note that the volume fraction of Fe₃B

B increases from 67.21% to 82.08% while that of α-Fe decreases from 18.94% to 6.22%. The formation of Nd₂Fe₁₄B phase slightly decrease from 13.85 to 11.72 vol. %. Therefore it is proposed that the enhancement in reduced remanence ($M_r/M_s=0.82$) in this alloy was induced also by the increased formation of Fe₃B phase in addition to the effect of grain refinement during the magnetic annealing. The tetragonal Fe₃B consisting of 8 formula units of trigonal prism has three inequivalent Fe sites Fe_I (8g), Fe_{II} (8g) and Fe_{III} (8g) at the vertices of trigonal prism [11]. The Fe_I (8g) was reported to have an atomic moment of 2.03 μ_B, and also has 10 nearest neighbors. Accordingly one can claim that the increased formation of Fe₃B contribute to the enhancement of total magnetization of the nanocomposite magnets. From the present Mössbauer spectroscopy average HF of the Fe_I (8g) atoms was measured to be 28.99 Tesla which is quite similar to that of Mao's report [12], but smaller than that of single phase Fe₃B [13].

In conclusion, an external magnetic field during annealing the melt-spun Nd₄Fe_{73.5}Co₃(Hf_{1-x}Ga_x)B_{18.5} (x=0, 0.5, 1) alloys was found to induce a grain refinement about 20% and enhances

Table I. The result of Mössbauer spectroscopy

phase/site		HF (T)	I. S (mm/sec)	Q. D (mm/sec)	Vol. fraction(%)
α-Fe	without field	33.43	-0.114	0.010	18.94
	with field	33.85	-0.116	0.009	6.22
bct Fe ₃ B	without field	28.43	-0.046	-0.012	67.21
	with field	28.99	-0.037	-0.015	
Fe _I (8g)	without field	26.45	-0.122	0.042	82.08
	with field	26.98	-0.103	0.046	
bct Fe ₃ B	without field	22.12	-0.0301	0.021	82.08
	with field	22.52	-0.027	0.023	
Nd ₂ Fe ₁₄ B	without field	34.73	-0.033	0.310	13.854
	with field	34.51	-0.032	0.303	
Nd ₂ Fe ₁₄ B	without field	28.21	-0.165	0.121	11.72
	with field	28.51	-0.182	0.120	
Nd ₂ Fe ₁₄ B	without field	29.41	-0.192	0.071	11.72
	with field	30.21	-0.161	0.082	
Nd ₂ Fe ₁₄ B	without field	25.82	-0.192	0.033	11.72
	with field	25.80	-0.194	0.03	

remanence/energy product values by 30%. The magnetic field also causes a uniform distribution of α -Fe and Fe₃B grains, and an increased formation of Fe₃B phase during annealing. The alloys at $x = 0.5$ exhibited the remanence magnetization of 12.5 kG and $(B \cdot H)_{\max}$ of 15.8 MGOe with a coercivity of 2.83 kOe. At this composition the grain size was observed to be 22 nm.

References

- [1] R. Coehoorn, D. B. De Mooij and C. De Waard, J. Magn. Mater. **80** (1989) 101.
- [2] J. Ding, P. G. McCormick and R. Street, J. Magn. Mater. **124** (1993) 1.
- [3] A. Manaf, R. A. Buckely and H. A. Davies, J. Magn. Mater. **128** (1993) 302.
- [4] J. Wecker, K. Schnitzke and H. Cerva, Appl. Phys. Lett. **67** (4) (1995) 563.
- [5] L. Withanawasam and G. C. Hadjipanayis, J. Appl. Phys. **76** (10) (1994) 7065.
- [6] J. M. Yao, T. S. Chin and S. K. Chen, J. Appl. Phys. **76** (10) (1994) 7071.
- [7] E. F. Kneller and R. Hawig, IEEE Trans. on Mag. **27** (4) (1991) 3588.
- [8] H. Fukunaga and H. Inoue, Jap. J. Appl. Phys. **31** (1992) 1347.
- [9] N. Kitajima and H. Fukunaga, Proc. 3rd Inter. Symposium on Phys. of Mag. Mater., ed. by C. S. Kim and T. D. Lee, (The Korean Magnetic Society, Seoul, Korea, Aug. 21-25, 1995), p. 652-655.
- [10] C. J. Yang and Y. B. Park, *ibid*, p. 675-678.
- [11] Y. D. Zhang J. I. Budnick, J. C. Ford and W. A. Hines, J. Magn. Mater. **100** (1991) 13.
- [12] M. Mao, C. Yang and F. Li, J. Phys.: Condens. Matter. **4** (1992) 9147.
- [13] C. L. Chien, D. Musser, F. E. Luborsky and J. L. Water, Phys. Rev. B **20** (1979) 283.