Magnetic and microstructural properties of (Nd,Pr)-(Tb,Dy,Gd)-(Fe,Co,Al,Cu)-B type magnets

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Abstract (Nd,Pr)-(Tb,Dy,Gd)-(Fe,Co,Al,Cu)-B magnets were heat treated in two different ways and investigated in the temperature range 4.2 to 400 K. After optimal heat treatment intrinsic coercive field $_iH_c = 1640$ and 5040 kA/m for room temperature and 10 K was obtained and the temperature coefficient of remanence $\alpha = -0.01$ for temperature range 80 to 375 K was found. On basis of magnetic measurements and ^{57}Fe Mössbauer spectroscopy, the possible reasons for the increase of $_iH_c$ during multi-step heat treatment are discussed.

Keywords NdFeB · Magnetization · ^{57}Fe Mössbauer · Heat treatment · Rare earth magnets · Permanent magnets

From the different kinds of NdFeB magnets those with small temperature coefficient α got high interest in recent years as there are new applications even at cryogenic temperatures [1]. Beside low α, spin reorientation (at 135 K in pure $Nd_2Fe_{14}B$), which weakens magnetism because of spin canting, has to be shifted to lower T values. This is obtained by partial substitution of Nd by Pr, because $Pr_2Fe_{14}B$ shows no spin reorientation down to 4.2 K [2].

In recent years we have shown that a multi-step heat treatment provides low α and rather high coercive field and energy product, whereas single-step heat treatment results in poorer magnetic properties [3–5]. However, up to now the reason for this

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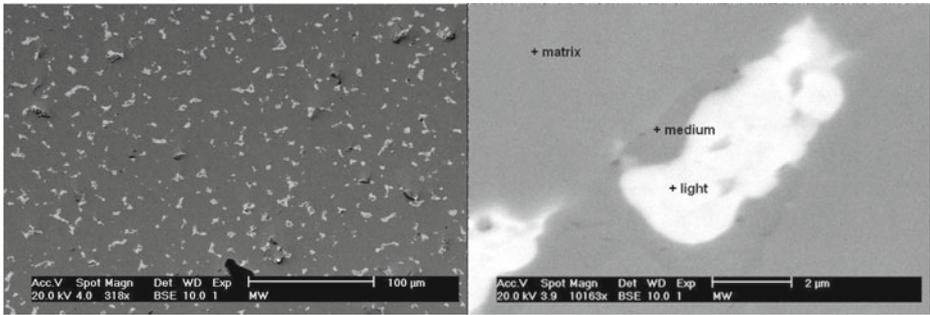
**Fig. 1** SEM micrographs of sample A. Three different regions (matrix, medium and light) are identified

Table 1 Remanence B_r, coercive field $_iH_c$, demagnetizing field H_k, defined where M_r is reduced by 10 %, energy product $(BH)_{max}$ for 300 K, Curie temperature T_c, reversible temperature coefficient $\alpha = (\Delta B_r/B_r)/\Delta T \cdot 100$ and $\beta = (\Delta_i H_c /_i H_c)/\Delta T \cdot 100$ in temperature range 80–375 K

| Sample	B_r(T)	$_iH_c$(kA/m)	H_k(kA/m)	$(BH)_{max}$ (kJ/m^3)	T_c(K)	α (%/K)	β (%/K)
A	0.93	1280	1170	168	753	−0.01	−0.28
B	0.93	1640	1360	168	764	−0.01	−0.27

improvement is unclear. It is the aim of this work to investigate magnetic properties and microstructure on two identical samples, heat treated in different way.

$Nd_{2.9}Pr_{3.22}Dy_{5.92}Tb_{0.89}Gd_{0.95}Co_{15.77}Fe_{62.57}Al_{0.20}Cu_{0.03}B_{7.55}$ sintered permanent magnets were heat treated in two ways: (a): 1175 K (2 h) + cooling to RT with average cooling rate of 1 K/s (sample A), and (b) 1175 K (2 h) + cooling (0.02 K/s) to 675 K (2.8 h) + increase to 775 K (1 h) + cooling to RT with average cooling rate of 1 K/s (sample B). Samples with this composition were chosen, because they fulfil best above mentioned goal to reach both low α and high $_iH_c$. Microstructure was investigated by optical microscopy, SEM, and local X-ray analysis (LXA). Magnetic measurements were performed at RT up to 3 T on large cylinders (Ø 40 mm, $h = 8$ mm) in hysteresisgraph, and at 10 to 400 K up to 9 T on smaller samples ($\sim$2 × 2 × 2 and $\sim$1 × 1 × 2 mm^3) in a QD-PPMS-VSM. ^{57}Fe Mössbauer spectra were recorded between 4.2 K and RT. Spectra were analysed by solving the full Hamiltonian, for both electrostatic and magnetic interactions. Possible differences in f-factor for the different Fe sites were not taken into account.

Optical microscopy gives grains sizes of 10 to 20 μm. SEM micrographs (Fig. 1) and LXA show that 92–94 % of samples consist of $Nd_2Fe_{14}B$ type (2-14-1) phase (*matrix*). *Light* particles have Rare Earth to metal ratio RE/M > 9, whereas in *medium* region M/RE $\sim$2.5 to 3. Table 1 summarizes main magnetic parameters at 300 K. Whereas the structure sensitive properties like coercive ($_iH_c$) and de-magnetizing field (H_k), as well as Curie temperature (T_c) are higher for sample B, remanent magnetization (M_r) and energy product (BH)$_{max}$ are the same. Figure 2a shows hysteresis loops at selected temperatures. Dips at low negative fields, present at all T are due to degradation of surface layers by mechanical treatment during preparation. They are more pronounced for smaller samples and fully absent for the largest ones. Similar effect was observed by Uestuener et al. [1]. At 10 and 20 K
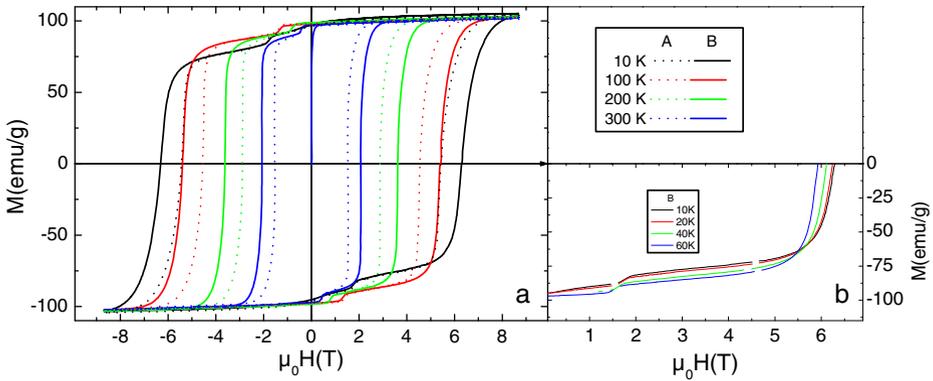
Fig. 2 (color online) **a** hysteresis loops at selected temperatures for sample A and B. **b** enlargement of dip at lowest temperatures for sample B
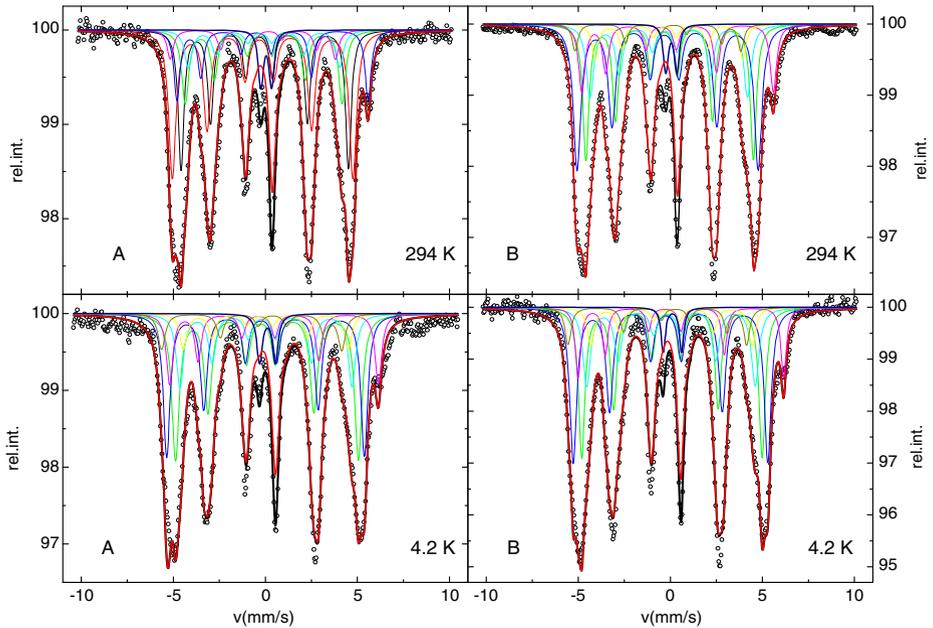
Fig. 3 (color online) ^{57}Fe Mössbauer spectra for both sample A and B at 4.2 and 294 K. Thick black line corresponds to calculated spectrum, red line is sum of six subspectra (*thin lines*) corresponding to the 2-14-1 phase and thick dark blue doublet corresponds to 1.1-4-4 phase

further weakening of magnetization is present (Fig. 2b), indicating either appearance of spin reorientation or ordering of a possible present $R_{1.1}M_4B_4$ phase.

As starting parameter set for analysis of MB spectra for the six different iron sites model (c) of Onodera et al. [6] for pure $Nd_2Fe_{14}B$ was used. Whereas the intensity ratio for sites k_1, j_1, e, and c were hold fix, they were allowed to change for sites k_2 and j_2, where Co [7] and Al [8] preferentially go. The thus obtained spectra (Fig. 3)

Table 2 Mean hyperfine field B_{hf}, mean quadrupole splitting $QS = eQV_{zz}/4$, mean center shift CS relative to ^{57}Co**Rh**, mean half line width $\Gamma/2$ and relative intensity of phases 2-14-1 and 1.1-4-4 at 4.2 and 294 K for both sample A and B

Phase	T(K)	Sample	B_{hf}(mm/s)	QS (mm/s)	CS(mm/s)	$\Gamma/2$(mm/s)	Rel.int.
2-14-1	4.2 K	A	31.7(1)	0.125(3)	−0.080(1)	0.230(5)	0.96(1)
		B	31.1(2)	0.126(3)	−0.074(4)	0.218(5)	0.97(1)
	294 K	A	29.0(1)	0.129(2)	−0.190(1)	0.215(3)	0.96(1)
		B	29.1(1)	0.133(2)	−0.190(1)	0.213(3)	0.96(1)
1.1-4-4	4.2 K	A	0	0.425(4)	0.115(2)	0.178(5)	0.04(1)
		B	0	0.497(4)	0.115(5)	0.139(5)	0.03(1)
	294 K	A	0	0.289(3)	0.051(2)	0.143(4)	0.04(1)
		B	0	0.297(3)	0.053(2)	0.125(4)	0.04(1)

explain 96 % of the measured one. 3 to 4 % of the spectra can be fitted by doublet with $QS = 0.43$ ($\sim$0.29) mm/s and CS (rel.^{57}Co**Rh**) = 0.115 (−0.52) mm/s at 4.2 K (294 K). From these values it is concluded that this phase is most probably the η-phase $Nd_{1.1}Fe_4B_4$ [9], which fits well to findings from microstructure investigations. The remaining less than 2 % of the spectrum could not be identified unequivocally. Within measuring accuracy no difference between both samples, neither at high nor low temperature is present (Fig. 3). Table 2 contains the obtained mean hyperfine parameters.

According to literature several reasons can be responsible for the higher coercive field of sample B. First, second step of heat treatment might cause soft magnetic boundary phases, which are mainly formed at triple joints of grains, to become paramagnetic. This possibility can be ruled out, as beside the η-phase no other nonmagnetic component is present in the Mössbauer spectra of sample B. Further explanation could be rearrangement of Co on the Fe sites during slow cooling from 1175 to 675 K, thus leading to elastic stresses [3]. This can favor diffusion of excess Nd (Pr) to the grain boundaries forming phases that improve the magnetic separation of the grains. This also would lead to higher $_iH_c$. Within the accuracy of the analysis no indication for different Fe/Co occupation on 16 k_2 and 8 j_2 for the two samples is evidenced by Mössbauer investigation. Another reason for increased stress can be the formation of nano-precipitates during ageing at lower temperatures. As no separate phase is found by Mössbauer spectroscopy in sample B, these nano-phases cannot consist of Fe containing material.

In conclusion, we can exclude changes in structure of 2-14-1 phase. Reason for higher $_iH_c$ values after second heat step is better magnetic separation of grains by increased Nd (Pr) diffusion to grain boundaries, triggered by stresses, which are not caused by rearrangement of Co and Fe, but probable by formation of nano-phases not consisting of Fe.

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