THE INFLUENCE OF COBALT CONTENT ON THE MAGNETIC PROPERTIES AND CORROSION OF PrFeCoCuNbB SINTERED MAGNETS

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Abstract

The effects of alloying additions upon the magnetic properties of PrFeB-based sintered magnets have been studied. The hydrogenation decrepitation process was employed to produce permanent magnets using a mixture of two alloys. The effect of cobalt content on the magnetic properties of these materials was investigated. A dramatic influence of additions on the magnetic properties of these praseodymium-based magnets has been shown.

1. Introduction

In the past, praseodymium-based sintered magnets with high intrinsic coercivity have been prepared with substitutions of Co, Al, Dy and Tb [1-4]. Moreover, it has been shown that magnets based on the compositions $Pr_{20.5}Fe_{bal}B_{3.7}Cu_2$ and $Pr_{16.9}Fe_{bal}B_4$ prepared using the hydrogen decrepitation (HD) process achieve high intrinsic coercivity after a post-sintering annealing [5-7]. Recently, HD PrFeBCoZrGa-based sintered magnets produced using a combination of two alloys has been investigated [8]. The influence of zirconium, gallium, copper and cobalt additions on their magnetic properties has also been studied. This paper reports the results of further work carried out on $Pr_{14}Fe_{bal}Co_xNb_{0.1}B_5$-type HD sintered magnets (x = 0, 4, 8, 10, 12, 16) prepared from a mixture of cast alloys. Thus, this investigation was undertaken to optimizes the cobalt content with respect to the magnetic properties and corrosion resistance of the HD Pr-based sintered magnets. Niobium free magnets have also been produced for a comparison. A $Pr_{16}Fe_{76}B_8$ HD sintered magnet has been used as a standard reference in the present work.

2. Experimental Procedure

Several commercial PrFeCoNbB alloys (14 at% Pr) in the annealed state (1100°C, 20 h) were used in this investigation. The chemical analyses of the as-cast alloys are given in Table 1. All the alloys contain about 0.1 wt% aluminium as an impurity (as per the supplier's specification). The study of the Co-containing alloys and the details of the preparation of the HD sintered magnets have already been described in previous papers [8-10]. In order to produce magnets from two alloys with distinct compositions [8] a praseodymium-enriched alloy ($Pr_{20.5}Fe_{bal}B_5Cu_2$), in the as cast condition, was used as sintering aid additive (16% in weight). Thus, the final composition of the sintered magnet is slightly richer in praseodymium (~15at% Pr) and contains a small amount of copper (~0.3 at% Cu). Hydrogenation of master and additive alloys (totalizing 15 g) was carried out simultaneously in a stainless steel vessel at a pressure of 1 bar and at 100°C. The decrepitated material was milled for 20 h using cyclohexane as the milling medium. The dried powder was then transferred to a small cylindrical rubber tube under a nitrogen atmosphere. This powder was aligned by pulsing three times to a 6 T magnetic field, pressed isostatically at 1000 kg cm^{-2} and then vacuum sintered for 1 h at 1030°C, followed by cooling inside the furnace. The $Pr_{16}Fe_{76}B_8$ standard magnet was prepared with the alloy in the as-cast condition, without any sintering aid and it was sintered at 1060° C. To evaluate the effect of additions only on sintering, no post-sintering heat treatment was

carried out. Magnetic measurements of the HD sintered magnets were performed in a permeameter after saturation in a pulsed field of 6 T. Corrosion test was carried out according to ASTM B-117 [11].

Table 1 Composition of the starting as-cast alloys.

Alloy nominal composition (at %)	Alloy analysed composition (wt%)					
	Pr	Fe	Co	B	Nb	Al/Cu
$Pr_{20.5}Fe_{bal}B_5Cu_2$	40.30	57.57	---	0.57	---	1.56
$Pr_{16}Fe_{78}B_8$	34.24	64.33	---	1.31	---	0.12
$Pr_{14}Fe_{80}B_6$	30.30	68.62	---	0.99	---	0.09
$Pr_{14}Fe_{79.9}B_6Nb_{0.1}$	30.11	68.68	---	0.97	0.14	0.10
$Pr_{14}Fe_{75.9}Co_4B_6Nb_{0.1}$	30.05	65.16	3.58	0.97	0.15	0.09
$Pr_{14}Fe_{71.9}Co_8B_6Nb_{0.1}$	30.29	61.36	7.15	0.96	0.15	0.09
$Pr_{14}Fe_{69.9}Co_{10}B_6Nb_{0.1}$	30.16	59.51	9.03	1.02	0.16	0.12
$Pr_{14}Fe_{67.9}Co_{12}B_6Nb_{0.1}$	30.14	57.80	10.83	0.98	0.15	0.10
$Pr_{14}Fe_{63.9}Co_{16}B_6Nb_{0.1}$	30.35	54.11	14.34	0.96	0.14	0.10

3. Results and discussion

The variation in remanence and energy product of HD sintered magnets, produced from a mixture of Pr-based alloys, as a function of cobalt content, is shown in Figure 1. Good remanence values were achieved in all permanent magnets. The best remanence was observed in the $Pr_{14}Fe_{71.9}Co_4B_6Nb_{0.1}$ HD sintered magnet (1240 ± 25 mT). The $Pr_{14}Fe_{80}B_6$ sintered magnet also showed a good remanence value. The highest energy product (286 ± 6 kJ/m^3) was observed for the magnet containing 4 at.% cobalt and also for the $Pr_{14}Fe_{80}B_6$ magnet. The variation in coercivity of HD sintered magnets as a function of cobalt content is shown in Figure 2. High intrinsic coercivity [1191128 kA/m] was achieved in the sample prepared using the alloy with 4 at% cobalt. At higher Co contents this magnetic property decreased substantially. Previous investigation on $Pr_{15}Fe_{62.5}Co_{16}B_{5.5}Al_1$ sintered magnets reported a remanence of 1270 mT (12.7 kG) and an intrinsic coercivity of 764 kA/m (9.6 kOe) [2, 3]. For the present Pr-based HD sintered magnet with 16 at% Co a remanence of (1250 ± 25) mT and a coercivity of (637 ± 13) kA/m were observed.
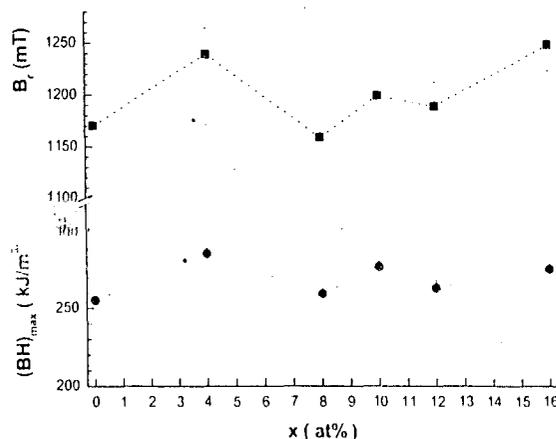
Fig. 1. Remanence and maximum energy product versus cobalt content for $Pr_{14}Fe_{bal}Co_xNb_{0.1}B_6$-type HD sintered permanent magnets.

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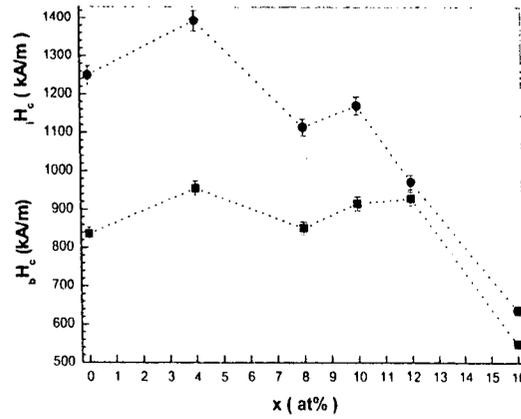
Fig. 2. Intrinsic and inductive coercivity versus cobalt content for $Pr_{14}Fe_{bal}Co_xNb_{0.1}B_6$-type HD sintered permanent magnets.

Figure 3 shows the demagnetisation curves of the $Pr_{14}Fe_{71.9}Co_4B_6Nb_{0.1}$ HD sintered magnet prepared from a mixture of cast alloys. The addition of 4 at% Co in the alloy improved substantially the intrinsic coercivity and somewhat the remanence of the HD sintered magnet but also yielded a pronounced kink on the second quadrant curve. The $Pr_{14}Fe_{79.9}B_6Nb_{0.1}$ HD sintered magnet also showed such a kink, but much less pronounced. This kink was not observed in the $Pr_{16}Fe_{78}B_8$ and $Pr_{14}Fe_{80}B_6$ HD magnets. For magnets prepared with higher cobalt contents (8, 10, 12 and 16 at%) the kink disappeared and a progressive decrease in coercivity was observed with increasing concentration of cobalt in the sintered magnets. This behaviour has been attributed to the presence of $Pr_3(FeCo)$ and $Pr(FeCo)_2$ phases in the Co-containing magnets. All these Co-containing phases have been reported previously for Nd-based magnets [12-15]. Table 2 gives the composition determined by EDX in the hard magnetic matrix phase, the Pr-rich phase and cobalt-containing phases found on the HD sintered magnets. The $Pr(FeCo)_2$ and $Pr_3(FeCo)$ phases were also observed in these $Pr_{14}Fe_{bal}Co_xNb_{0.1}B_5$ alloys and have been reported in details elsewhere [10]. Figures 4-11 show backscattered electron images of all Pr-based HD sintered magnets analyzed by EDX.
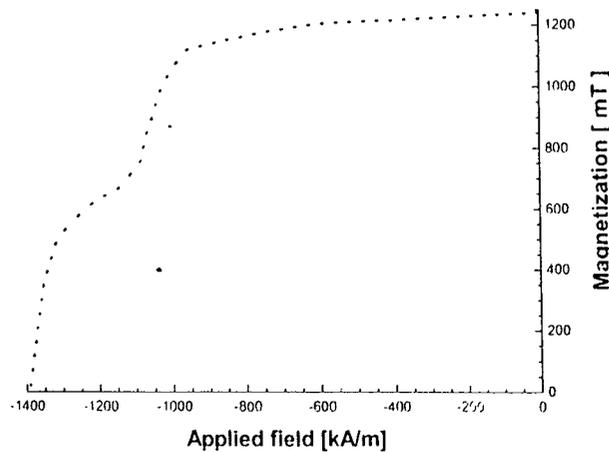
Fig. 3. Demagnetization curve of the $Pr_{14}Fe_{71.9}Co_4B_6Nb_{0.1}$ HD sintered magnet.

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A summary of the magnetic properties and the increase in mass due to corrosion of these magnets is shown in Table 3. It is worth noting that niobium addition in the alloy increased the intrinsic coercivity in the HD sintered magnets from (1050 ± 21) to (1249 ± 25) kAm^{-1}. In contrast, the remanence and squareness factor decreased with the addition of this element. It is also worth noting that the best squareness factor (SF=0.90 ± 0.02) was achieved in the magnet containing 10 at% Co. It is appropriate to mention that the combined addition of Co and Cu to NdFeB-type magnets (produced by powder blending) allowed the addition of higher Co contents to sintered magnets without a dramatic loss of coercivity. Measurements of Curie temperature on the magnetic alloys showed an increase of 11°C per at% Co. Similar increase in Curie temperature has been obtained with Nd-based magnets [12]. Niobium and cobalt additions improved the corrosion resistance of these copper-containing Pr-based HD-sintered magnets. The $Pr_{16}Fe_{76}B_8$ HD sintered permanent magnet processed under the same conditions and using the cast alloy in the as-received condition showed the highest mass variation (increase) due to corrosion $(310\pm15$ mg$)$. This was expected since the rare earth content of this alloy, with the "neomax" composition, is the highest among the tested alloys.

Table 2 Composition determined by EDX in the hard magnetic matrix phase (ϕ) and the various phases found in the Pr-based HD sintered magnets (All results are average of three measurements, individual readings showed scatter of up to ± 5 %. The boron concentration cannot be detected by EDX and hence it is the concentration ratio of the metallic components regarded as significant).

Magnet	Phase	Pr (at%)	Fe (at%)	Co (at%)
$Pr_{14}Fe_{bal}Co_{16}B_6Nb_{0.1}$	$Pr_2(FeCo)_{14}B$	13.4	72.0	14.6
	Pr-rich	85.3	14.7	-
	Pr(FeCo)	57.0	37.0	6.0
$Pr_{14}Fe_{bal}Co_{12}B_6Nb_{0.1}$	$Pr_2(FeCo)_{14}B$	13.5	76.6	9.9
	Pr-rich	87.8	12.2	-
	$Pr_3(FeCo)$	74.8	21.4	3.8
	Pr(FeCo)	59.4	35.4	5.2
	$Pr_{1.9}FeCo)_4B_4$	27.2	60.3	12.5
$Pr_{14}Fe_{bal}Co_{10}B_6Nb_{0.1}$	$Pr_2(FeCo)_{14}B$	14.2	76.4	9.4
	Pr-rich	85.3	14.7	-
	$Pr_3(FeCo)$	81.8	15.5	2.7
	$Pr(FeCo)_2$	66.3	12.0	21.7
	Pr(FeCo)	51.8	42.3	5.9
$Pr_{14}Fe_{bal}Co_8B_6Nb_{0.1}$	$Pr_2(FeCo)_{14}B$	14.4	77.9	7.7
	Pr-rich	82.8	15.0	2.2
	Pr(FeCo)	52.8	33.2	14.0
$Pr_{14}Fe_{bal}Co_4B_6Nb_{0.1}$	$Pr_2(FeCo)_{14}B$	13.5	82.6	3.9
	Pr-rich	84.1	15.9	-
	$Pr_3(FeCo)$	69.9	28.9	1.2
	Pr(FeCo)	55.1	43.0	1.9
$Pr_{14}Fe_{bal}B_6Nb_{0.1}$	$Pr_2Fe_{14}B$	13.8	86.2	-
	Pr-rich	81.6	18.4	-
	PrFe	50.3	49.7	-
$Pr_{14}Fe_{bal}B_6$	$Pr_2Fe_{14}B$	13.6	86.4	-
	Pr_3Fe	69.2	30.8	-
$Pr_{16}Fe_{76}B_8$	$Pr_2Fe_{14}B$	13.6	86.4	-
	Pr_3Fe	75.2	24.8	-
	$Pr_{1.1}Fe_4B_4$	21.4	78.6	-

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Table 3 Magnetic properties and mass gain due to corrosion of Pr-based HD sintered magnets (error: ±2%).

Alloy used in the magnet's production	B_r (mT)	$_iH_c$ (kA/m)	$_bH_c$ (kA/m)	$(BH)_{máx}$ (kJ/m³)	SF (ratio)	Increase in mass (g)
$Pr_{16}Fe_{78}B_8$	1140	1289	867	249	0.87	0.31
$Pr_{14}Fe_{80}B_6$	1230	1050	851	286	0.78	0.13
$Pr_{14}Fe_{79.9}B_6Nb_{0.1}$	1170	1249	836	255	0.68	0.10
$Pr_{14}Fe_{71.9}Co_4B_6Nb_{0.1}$	1240	1393	955	286	0.68	0.08
$Pr_{14}Fe_{75.9}Co_8B_6Nb_{0.1}$	1160	1114	851	259	0.81	0.05
$Pr_{14}Fe_{69.9}Co_{10}B_6Nb_{0.1}$	1200	1170	915	277	0.90	0.07
$Pr_{14}Fe_{67.9}Co_{12}B_6Nb_{0.1}$	1190	971	928	263	0.87	0.04
$Pr_{14}Fe_{63.9}Co_{16}B_6Nb_{0.1}$	1250	637	549	276	0.75	0.04

Fig. 4 Backscattered electron image of $Pr_{14}Fe_{bal}Co_{10}B_6Nb_{0.1}$ magnet.

Fig. 5 Backscattered electron image of $Pr_{14}Fe_{bal}Co_{12}B_6Nb_{0.1}$ magnet.
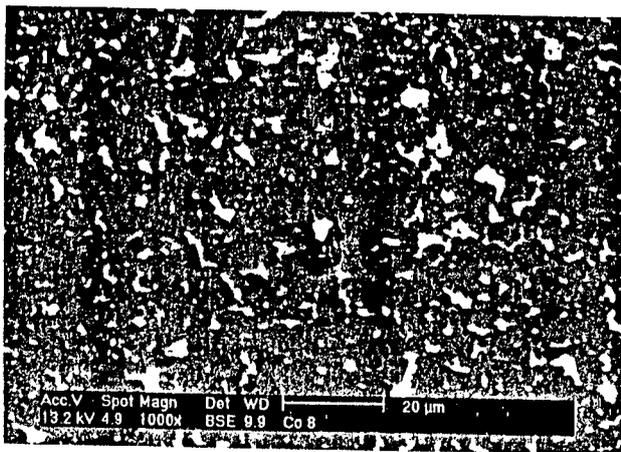
Fig. 6 Backscattered electron image of $Pr_{14}Fe_{bal}Co_{10}B_6Nb_{0.1}$ magnet.
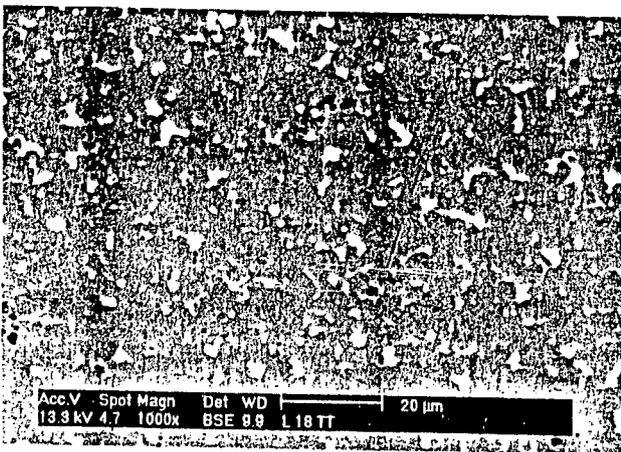
Fig. 7 Backscattered electron image of $Pr_{14}Fe_{bal}Co_8B_6Nb_{0.1}$ magnet.
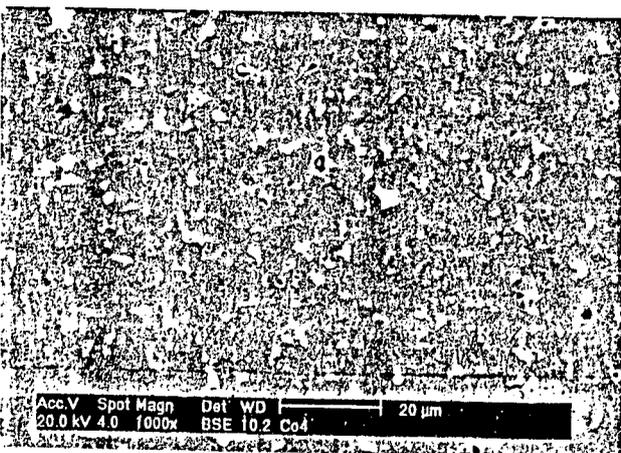
Fig. 8 Backscattered electron image of $Pr_{14}Fe_{bal}Co_8B_6Nb_{0.1}$ magnet.
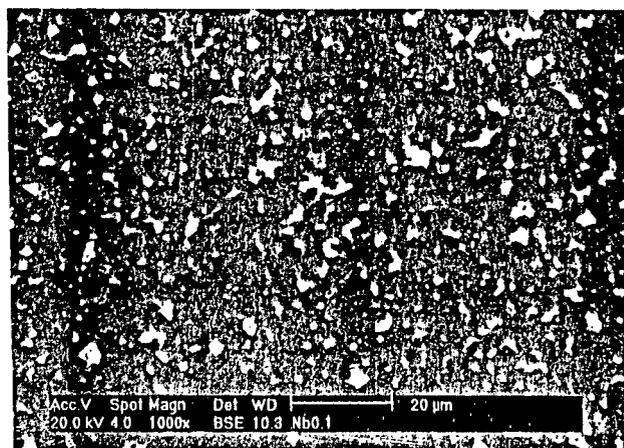
Fig. 9 Backscattered electron image of $Pr_{14}Fe_{bal}B_6Nb_{0.1}$ magnet.
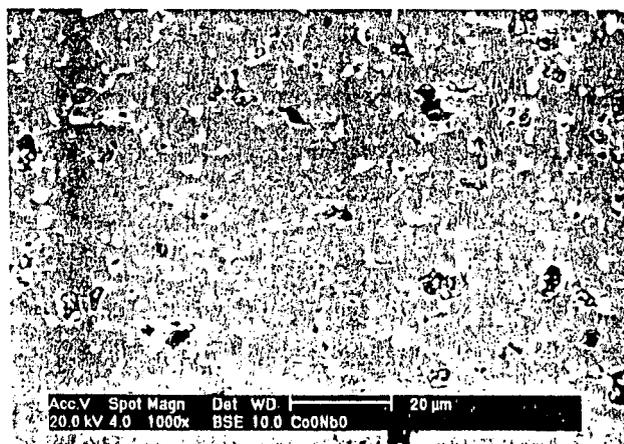
Fig. 10 Backscattered electron image of $Pr_{14}Fe_{bal}B_6$ magnet.
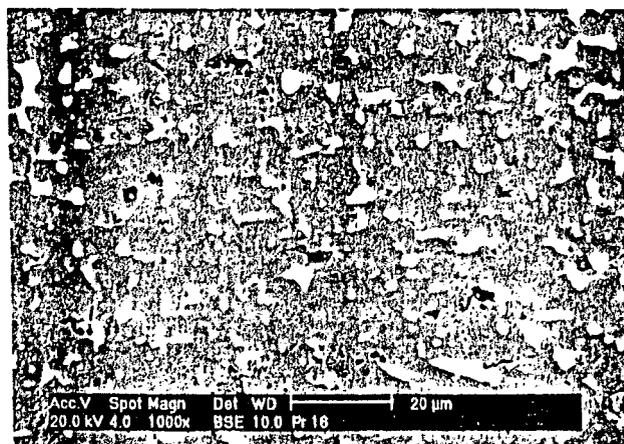
Fig. 11 Backscattered electron image of $Pr_{16}Fe_{bal}B_6$ magnet.

4. Conclusions

These results show that the addition of 4 at% Co to Pr-based magnets although convenient to improve the intrinsic coercivity, corrosion resistance and Curie temperature causes the appearance of a kink on the demagnetization loop. Cobalt additions superior to 4 at% on the Pr-based permanent magnets causes a diminution of the intrinsic coercivity. This behaviour has been attributed to the presence of Co-containing soft ferromagnetic phases with Curie points above room temperature in HD sintered magnets. Niobium addition in the alloy increased the intrinsic coercivity in the HD sintered magnets but at the expenses of the remanence, energy product and squareness factor.

Acknowledgements

References

[1] F. Pourarian, S. G. Sankar and W. E. Wallace, J. Magn. Magn. Mat. 74 (1988) 177.
[2] S. Y. Jiang, H. Y. Chen, S. F. Cheng, E. B. Boltich, S. G. Sankar, D. E. Laughlin and W. E. Wallace, J. Appl. Phys. 64 (10) (1988) 5510.
[3] S. Y. Jiang, J. X. Yan, B. M. Ma, S. G. Sankar and W. E. Wallace, Proc. 10th International Workshop on Rare-Earth Magnets and Their Applications, Kyoto, Japan, May 1989, p. 457.
[4] S. Y. Jiang, J. X. Yan, F. S. Li and C. L. Yang, Proc. 10th International Workshop on Rare-Earth Magnets and Their Applications, Kyoto, Japan, May 1989, p. 409.
[5] R.N. Faria, J. S. Abell and I.R. Harris, J. Alloys and Comp. 177 (1991) 311.
[6] R.N. Faria, J. S. Abell and I.R. Harris, J. Alloys and Comp. 185 (1992) 81.
[7] R.N. Faria, X. J. Yin, J. S. Abell and I.R. Harris, J. Magn. Magn. Mat. 129 (1994) 263.
[8] R. N. Faria, H. Takiishi, L. F. C. P. Lima and I. Costa, J. Magn. Magn. Mater. 237 (2001) 261.
[9] H. Takiishi, L. F. C. P. Lima, R.N. Faria, Powder Technology 127 (2002) 223.
[10] L. Barbosa, H. Takiishi and R. N. Faria, J. Magn. Magn. Mater. 268 (2004) 132.
[11] ASTM B-117   Methods of salt-spray (Fog) testing. March 29, 1973. In : 1973 Annual book of ASTM Standards- V. 03.02 p. 1-12.
[12] R. S. Mottram, A. J. Williams and I. R. Harris, J. Magn. Magn. Mater 217 (2000) 27.
[13] R. S. Mottram, A. J. Williams and I. R. Harris, J. Magn. Magn. Mater 234 (2001) 80.
[14] J. C. S. Onelly, A. P. Tschiptschin, F. J. G. Landgraf, in: Eight International Symposium on Magnetic Anisotropy and Coercivity in Rare-Earth Transition Metal Alloys, Birmingham, September (1994) 261.
[15] J. Fidler, IEEE Trans. Mag. 21 (1985) 1955.