Curie temperature determination of $Pr_{14}Fe_{79.9-x}Co_xB_6Nb_{0.1}$ permanent magnet alloys

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Abstract: This paper reports the results of investigations carried out to determine the Curie temperature (T_c) of some annealed praseodymium-based alloys represented by the formula $Pr_{14}Fe_{79.9-x}Co_xB_6Nb_{0.1}$. The Curie temperature of these permanent magnet alloys increase linearly with the cobalt content at about (10.2±0.3) ^{o}C/at%. $Pr_{14}Fe_{80}B_6$ and $Pr_{14}Fe_{79.9}B_6Nb_{0.1}$ magnetic alloys with a T_c of 290^{o}C have been used as a standard reference. Magnets were prepared from the alloys using the hydrogenation, disproportionation, desorption and recombination (HDDR) process.

Introduction

In the past, Pr-Fe-B HDDR bonded magnets with high anisotropy have only been produced with substitutions of Co, Zr and Nb [1-5]. Recently, it has been shown the influence of the cobalt and niobium content on the magnetic properties of PrFeCoBNb-type HDDR magnets [6, 7]. The microstructures of these alloys also changed considerably with the addition element content [6]. The Curie temperature of the Nd-based alloy (310^{o}C) is slight higher than that of the Pr-based alloy (290^{o}C) [5]. Cobalt-containing alloys and magnets have a higher Curie temperature in comparison to the conventional Nd-Fe-B or Pr-Fe-B materials due to the substitution of Co for Fe in the matrix phase. It has been reported that the Curie temperature of the $Nd_2Fe_{14}B$ phase increases linearly with the Co content at about 11^{o}C per at% [5, 8]. Similar increase in T_c has also been reported for $Nd_{13.7}Fe_{63.5}Co_{16.7}B_6Zr_{0.1}$ (T_c=485^{o}C) and $Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Zr_{0.1}$

(T_c=465°C) alloys [5]. This paper reports the results of further work carried out on $Pr_{14}Fe_{79.9-x}Co_xB_6Nb_{0.1}$-type alloys and HDDR magnets (where x = 0, 4, 8, 10, 12, 16). This investigation was undertaken to systematically determine the Curie temperature of these materials as a function of the cobalt content and also to verify if a similar linear increase of 11°C/at% applies to the Pr-Fe-Co-B-Nb based materials.

Materials and Methods

Various commercial alloys in the homogenized state were studied. Homogenisation heat treatment was carried out by annealing the as-cast alloys in vacuum at 1100°C for 20 h. The details of the preparation of the HDDR bonded magnets, alloy annealing and magnetic measurements have all been described in previous papers [1-6]. A susceptibility analyser was employed for thermomagnetic analysis (TMA) of the alloys in order to investigate their susceptibility versus temperature behaviour over the temperature range 50-500°C. A magnetic field of low amplitude (333 Hz) and a heating rate of 1°C/min were employed in this study. Permeameter measurements were performed after saturation in a pulsed field of 6.0 T. Remanence values have been normalized assuming 100% density for the HDDR sample, and by also considering a linear relationship between density and remanence.

Results and Discussion

The variation in Curie temperature of the annealed Pr-based alloys as a function of cobalt content is shown in Fig. 1. The calculated or theoretical Curie temperature of the Pr-Fe-B-Nb alloys with Co additions, plotted as a solid line, was based on a $Pr_2Fe_{14}B$ phase with a Curie temperature of 290°C increasing 11°C per at% Co (assuming the same behaviour as the Nd-based materials). The Curie temperature of the $Pr_2Fe_{14}B$ matrix phase without addition of cobalt, determined previously by differential thermal analysis (DTA), was around 290°C [9]. This value was slightly higher than that determined in the same study using TMA (282°C). This phase also has various reported Curie temperatures such as 303°C [10], 290°C [11] and 284°C [12]. Thus in the present study the chosen reference temperature for the $Pr_2Fe_{14}B$ phase was 290°C. Good agreement was obtained between the measured and the calculated values. A linear fit for the TMA measured values showed that the Curie temperature of the $Pr_2Fe_{14}B$ phase increases linearly with the Co content at about 10.2^{o}C per at%. Therefore, not only the Curie temperature of Pr-based is inferior to that of Nd-based materials but also the rate of increase with cobalt content. The thermomagnetic curves showing the Curie temperature for the $Pr_{14}Fe_{79.9-x}Co_xB_6Nb_{0.1}$-type alloys in the annealed condition are presented in Fig. 2. Very well defined susceptibility variation is observed in all the magnetic alloys on the Curie temperature.

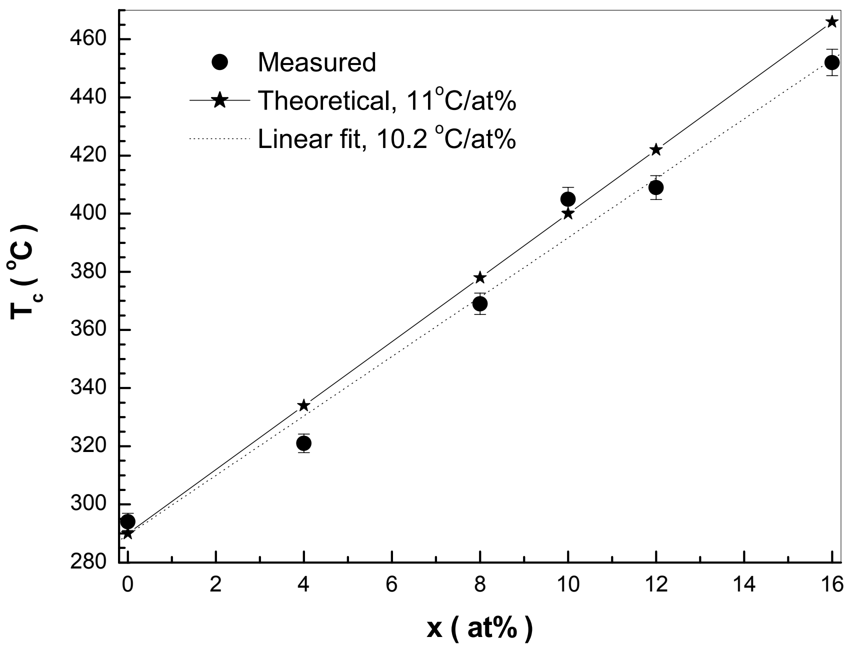

Fig.1 - Curie temperature versus cobalt content for $Pr_{14}Fe_{79.9-x}Co_xB_6Nb_{0.1}$-type HDDR magnets.

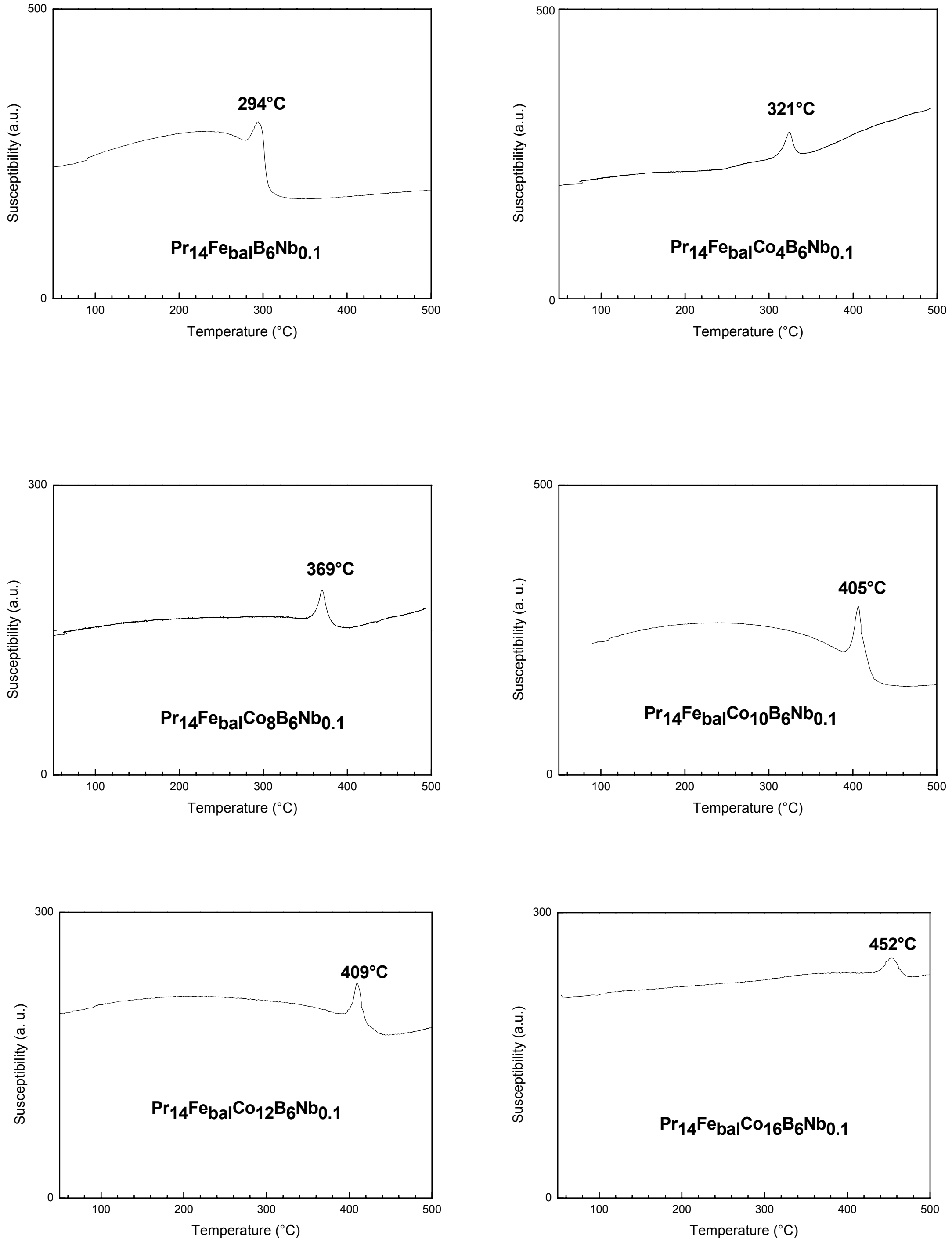

Fig.2 - Thermomagnetic curves for the $Pr_{14}Fe_{79.9-x}Co_xB_6Nb_{0.1}$-type alloys in the annealed condition (x = 0, 4, 8, 10, 12, 16).

The variation in remanence and intrinsic coercivity of HDDR magnets, produced from annealed Pr-based alloys, as a function of cobalt content is shown in Figure 3. Good remanence values were achieved in samples prepared from annealed Co-containing alloys. In the presence of 8.0 at.% Co, the remanence increased from 0.79 to 0.84 T, which was the highest remanence value. Higher Co contents produced a slight decrease in remanence. In the presence of 4.0 at.% cobalt, a magnet with the best intrinsic coercivity (0.97 MA/m) was obtained. At higher Co contents this magnetic property decreased substantially. It was also noted that the HDDR magnet produced using the Co-free alloy in the annealed condition presented good intrinsic coercivity (0.92 MA/m).

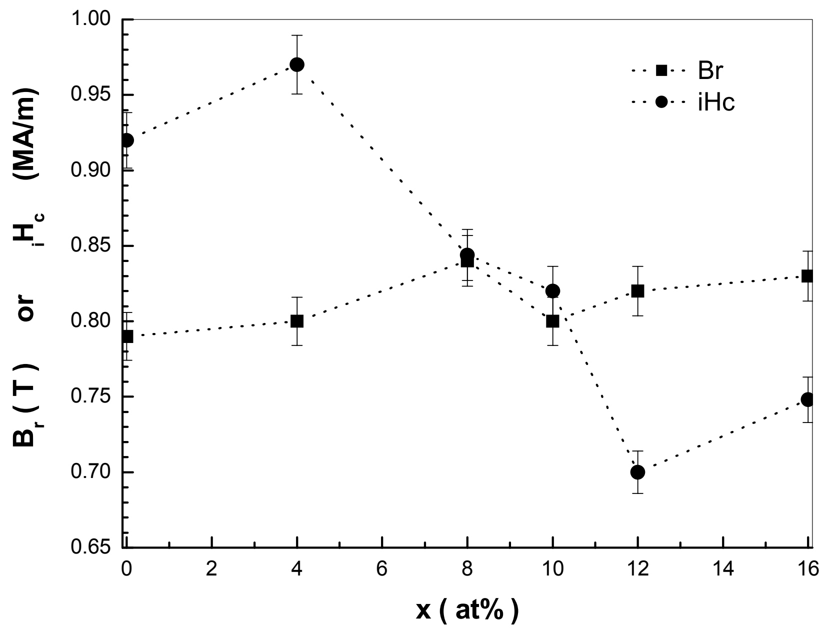

Fig.3 - Remanence and intrinsic coercivity versus cobalt content for $Pr_{14}Fe_{79.9-x}Co_xB_6Nb_{0.1}$-type HDDR magnets produced from annealed alloys.

A summary of the magnetic properties and Curie temperature of all the magnets produced with the praseodymium-based alloys in the annealed condition are shown in Table 1. The best energy product (121 kJ/m^3) was observed in the magnet containing 8 at.% cobalt. Niobium addition increased the remanence from 0.68 to 0.79 T in HDDR magnets prepared from annealed Co-free alloys but had no effect on coercivity. The highest intrinsic coercivity (0.97 MAm^{-1}) was observed in the HDDR magnet containing only 4 at.% cobalt.

Table 1 - Magnetic properties and Curie temperature of Pr-type magnets.

Composition	B_r (T)	$_iH_c$ (MA/m)	$(BH)_{max}$ (kJm^{-3})	T_c (^oC)
$Pr_{14}Fe_{80}B_6$	0.68±0.01	0.92±0.02	81±2	299±1.5
$Pr_{14}Fe_{79.9}B_6Nb_{0.1}$	0.79±0.02	0.92±0.02	114±2	294±1.5
$Pr_{14}Fe_{75.9}Co_4B_6Nb_{0.1}$	0.80±0.02	0.97±0.02	111±2	321±1.6
$Pr_{14}Fe_{71.9}Co_8B_6Nb_{0.1}$	0.84±0.02	0.84±0.02	121±2	369±1.8
$Pr_{14}Fe_{69.9}Co_{10}B_6Nb_{0.1}$	0.80±0.02	0.82±0.02	107±2	405±2.0
$Pr_{14}Fe_{67.9}Co_{12}B_6Nb_{0.1}$	0.82±0.02	0.70±0.01	113±2	409±2.0
$Pr_{14}Fe_{63.9}Co_{16}B_6Nb_{0.1}$	0.83±0.02	0.75±0.01	101±2	452±2.3
$Pr_{14}Fe_{64.0}Co_{16}B_6$	0.70±0.01	0.75±0.01	80±2	456±2.3

4. Conclusions

The Curie temperature of the $Pr_{14}Fe_{79.9-x}Co_xB_6Nb_{0.1}$ permanent magnet alloys increase linearly with the cobalt content at about (10.2±0.3)^{o}C/at%, rate which is slightly inferior to that reported for neodymium-iron-boron-based materials (11^{o}C per at%). Bonded magnets produced with these magnetic alloys exhibited a non-linear behaviour as far as remanence and intrinsic coercivity are concerned. Only $Pr_{14}Fe_{75.9}Co_4B_6Nb_{0.1}$ and $Pr_{14}Fe_{71.9}Co_8B_6Nb_{0.1}$ HDDR powders produced from annealed alloys yielded magnets with good overall magnetic properties. The former exhibited better intrinsic coercivity (0.97 MAm^{-1}) and the latter an improved remanence (0.84 T).

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References

[1] Y. B. Kim, W. Y. Jeung, J. Appl. Phys., 83 (1) (1998) 6405
[2] R.N. Faria, A.J. Williams, I.R. Harris, J. Alloys and Comp. 287 (1999) L10-L12.
[3] R.N. Faria, A.J. Williams, I.R. Harris, J. Magn. Magn. Mater 202 (1999) 349
[4] R.N. Faria, D.N. Brown, I.R. Harris, J. Alloys and Comp. 296 (2000) 219
[5] R.N. Faria, B. E. Davies, D.N. Brown, I.R. Harris, J. Alloys and Comp. 296 (2000) 223
[6] L. P. Barbosa, H. Takiishi and R.N. Faria, J. Magn. Magn. Mater., 268 (2004) 132.
[7] L. P. Barbosa, H. Takiishi, L. F. C. P. Lima and R.N. Faria, J. Magn. Magn. Mater., 283 (2004) 263.

[8] R. S. Mottram, PhD. Thesis, University of Birmingham, (1998) 109

[9] R.N. Faria, X. J. Yin, J. S. Abell and I.R. Harris, J. Magn. Magn. Mater 129 (1994) 263

[10] 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 (1988) 5510

[11] J. Jinghua, H. Yiying and L. Jingkui, Scientia Sinica (Series A) V-XXX (1987) 607

[12] N. Takahashi, H. Nakamura, C. R. Paik, S. Sugimoto, M. Okada and M. Homma, Matter. Trans. Jpn. Inst. Metals 32 (1991) 90