Magnetic Properties, Curie Temperature and Microstructures of RFeB Based Magnets With Additives by Blending

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Abstract:

Since the invention of rare earth based magnets a great deal of research activity has been devoted to improve their magnetic properties by adding alloying elements. In the present study, rare earth based magnets (where R= Nd or Pr) were made with the combined additions of Co and Cu particles by conventional powder metallurgical process. However, the addition of these elements was made by a powder blending technique. The Cu level was kept at 0.25 at % while the Co content was varied. The Cu level was selected from the previous work on individual additions of Cu.
The paper describes the microstructure, magnetic properties and Curie temperature of the sintered blended magnets. The microstructures of the magnets produced were studied using a JEOL 6300 Scanning Electron Microscope (SEM). Phase compositions, in terms of elements with atomic number >12, were determined using a Link QX 2000 energy dispersive X-ray (EDX) spectrometer system fitted to the SEM. Curie points were determined using a magnetic pendulum balance system

1. Introduction

RFeB magnets provides the highest energy product of any magnetic material. These magnets are now responsible for a large fraction of the permanent magnet market due to high magnetocrystalline anisotropy and saturation magnetization of the $R_2Fe_{14}B$ phase [1]. The ternary alloy that forms the basic composition for most sintered magnets is approximately $R_{16}Fe_{76}B_8$. The properties of the ternary RFeB system can be improved upon by alloying additions. Alloy additions are traditionally made at the pre-casting stage [2]. This produce cast ingots of the final magnet composition. Recent developments in the magnet market have made the powder blending technique of more interest to industry. By blending powders prior to sintering a wide range of compositions can be assessed rapidly using only a small number of starting alloys. The number of devices using RFeB magnets is increasing rapidly. Many of these are of a short production run and a rapid turn around from the supplier is desired. Powder blending could potentially give a magnet producer the ability to keep a stock of basic alloy which is then blended with additives to yield the properties desired by a customer. This reduces the need to order in small alloy casts of a specific composition

In the present study the effects of making combined additions of Co and Cu particles by blending have been studied.

2. Experimental Details

The nominal compositions of the master alloys used (supplied by Rare Earth products, UK) in this work were $Nd_{16}Fe_{76}B_8$ and $Pr_{16}Fe_{76}B$. As preparation, the cast ingots were crushed to leave exposed surfaces as an aid to the hydrogen decrepitation process, which occurred under about 10 bars of hydrogen at room temperature. This was followed by roller ball milling the materials to a powder with particles size ~ 5 μm using cyclohexane as a milling medium. Powder blending was carried out in an air tight plastic pot of volume 250 cm^3 containing stainless steel balls of diameter 5mm using a ROTATOR DRIVE STR4 machine. After blending the powder was loaded into an isostatic press bag made of Neoprene rubber and was pulsed 5 times in a field of 4.5 Tesla to produce alignment. To lock the particles in orientation prior to sintering, the powder was isostatically pressed at 1400 kg cm^{-2}. The green compacts were then vacuum sintered at 1050 ^oC for 1 hour, followed by furnace cooling to room temperature. The densities of the sintered compacts were determined using the displacement method and a closed permeameter was used to measure the magnetic properties of the samples. The samples were magnetized in a magnetic field of 4.5 Tesla prior to the determination of the second quadrant demagnetization loop.

3. Results & Discussion

The microstructures of the Nd-based and Pr-based optimally heat-treated magnets produced by blending with 5 at % Co and 0.25 at % Cu are shown in Figures 1 and 2 respectively. EDX analysis of phases observed is shown in Table 1.

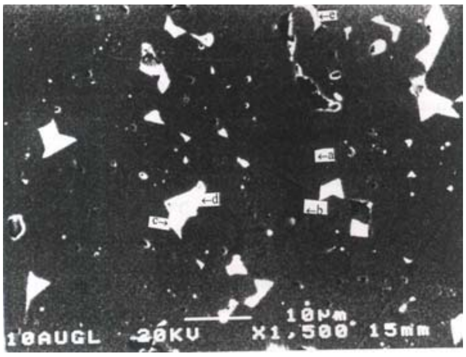

Fig. 1 Back scattered electron image of Nd-based magnet blended with 5 at % Co - 0.25 at % Cu. Lables indicate (a) $Nd_2Fe_{14}B$, (b) $NdFe_4B_4$, (c) Nd-rich, (d) Nd_3CoFe, and (e) Cu-rich

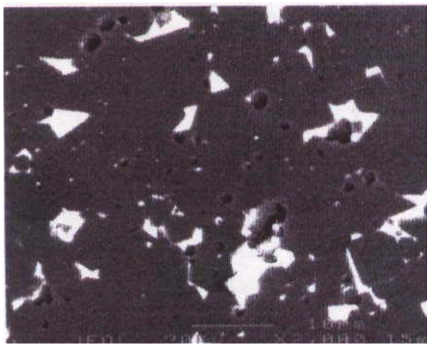

Fig. 2 Back scattered electron image of Pr-based magnet blended with 5 at % Co-0.25 at % Cu. Lables indicate (a) $Pr_2Fe_{14}B$, (b) $Pr_6Fe_{13}Cu$ (c) $PrFe_4B_4$, (d) Pr_3 (Co,Fe)

The effects of Co-Cu additions on remanence and coercivity of the magnets are shown in Figs. 3 and 4 respectively. The Nd-based magnets were heat treated either at 500 ^oC for 1 hour, 630 ^oC for 1 hour or 8 hours at 900 ^oC, furnace cooled and then heat treated at 500 ^oC for 1 hour followed by rapid cooling . Pr based magnets were also heat treated for 8 hours at 900 ^oC, furnace cooled and then heat treated at 500 ^oC for 1 hour followed by rapid cooling. Low temperature heat treatment of the Pr-based magnets did not improve the coercivity of sintered magnets. Both in the Nd and Pr-based magnets, the grain boundary phase was mainly modified to $Nd_3(Co,Fe)$ and $Pr_3(Co,Fe)$ phase respectively and was found to be inhomogeneous. None or only trace quantities of copper was identified in the matrix phase while cobalt was found to be present mainly in the matrix phase. These results are consistent with previous work [2,3,4]. In all Pr-based heat-treated magnets, a $Pr_6Fe_{13}Cu$ type phase was identified. The enhancement of H_{ci} in these magnets after a two step heat treatment can be attributed to the formation of this phase which presumably provides magnetic isolation between the 2:14:1 grains [4].

The results indicate that in both sets of alloys, the presence of copper increased the amount of Co that could be incorporated before the coercivity drops significantly. With the heat-treated Nd-based magnets (at 630 °C for 1 hour), an addition of 3.5 at % Co caused a loss of 364 kA/m when added alone and 120 kA/m when added in combination with 0.25 at % copper. Even this loss has been fully recovered after two step heat treatment. With Pr-based magnets an addition of 3.5 at % Co caused a loss of 190 kA/m when added alone and non when added in combination with 0.25 at % copper. These results are consistent with the previous work of Kim [5]. who reported that combined additions of both copper and cobalt can yield magnets with higher remanence and coercivities than those with either addition on its own.

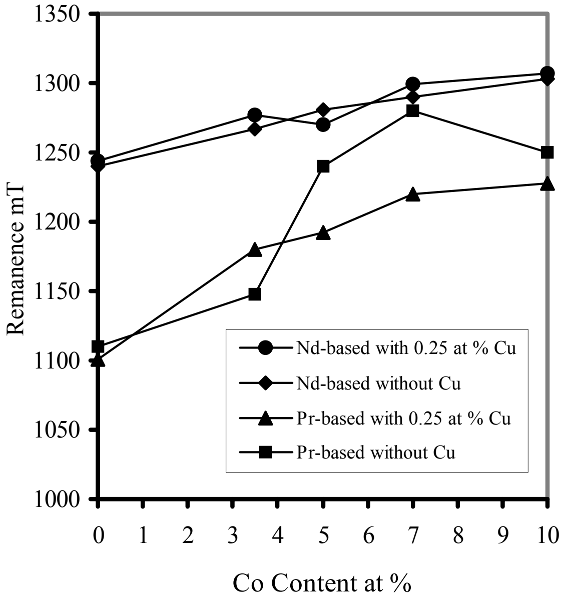

Fig. 3 Effect of cobalt content on the remanence of magnets containing 0.25 at % Cu

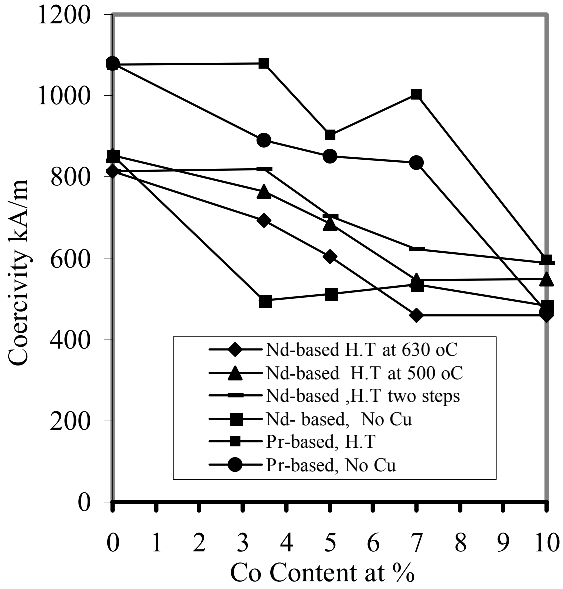

Fig.4 Effect of cobalt content and heat treatment temperature on the coercivity of magnets containing 0.25 at % Cu

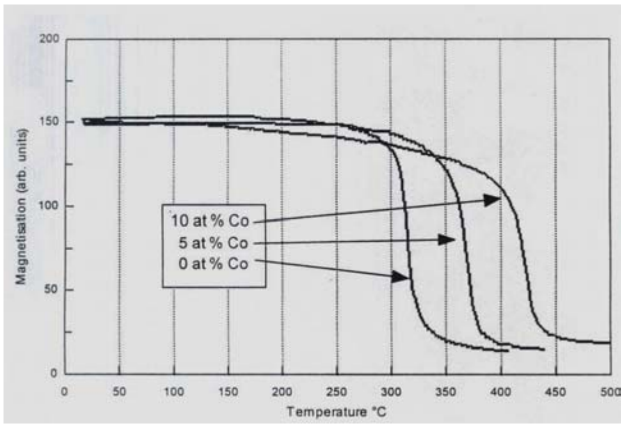

Fig. 5 Effect of cobalt content on the Curie temperature of Nd-based magnets with 0.25 at % copper

In both alloys there was a trend towards increased remanence with cobalt content. The cobalt substitutes for iron in the matrix phase; hence during sintering, reactions between the cobalt particles and the liquid have resulted in an increased proportion of the matrix phase. This is in good agreement with the results for the magnets made with no addition of copper [6]. The addition of 0.25 at % copper is small enough that there is no apparent effect on the remanence due to the new phases reducing the proportion of matrix material. However the remanence of Pr-based magnets after combined Co-Cu additions is lower than the magnets made with cobalt additions alone. This can be attributed to the fact that full density was not achieved in these magnets.

The Curie points of the magnets were measured using a pendulum balance. The results are shown in Figure 5. There is a rise in Curie temperature with the increase in Co concentration. The small copper additions did not influence this property. The Curie points of both Pr-based and Nd-based magnets were in excellent agreements with those for singular additions of cobalt [3,6,7].

Table 1. EDX Analysis of the phases observed

Magnet Sample	Phase	RE(at %)	Fe(at %)	Co (at %)	Cu (at %)
Nd-based heat treated 5 at % Co, 0.25 at % Cu	$Nd_2Fe_{14}B$	13	82	5	0
	$NdFe_4B_4$	23	77	0	0
	Nd rich	96	4	0	0
	$Nd_3(Co,Fe)$	75	3	16	6
	Nd_2FeCo	64	17	14	5
	Copper rich	50	20	18	12
Pr-based heat treated 5 at % Co, 0.25 at % Cu	$Pr_2Fe_{14}B$	14.5	80.50	5.0	0
	$PrFe_4B_4$	21.5	74.6	4.0	4.6
	$Pr_6Fe_{13}Cu$	30.5	59.5	5.0	5.0
	$Pr_3(Co,Fe)$	73.0	7.0	15.0	5.0
	$Pr_2(Co,Fe)$	63.0	16.0	16.5	4.5

4. Conclusions:

Blending is an effective way of adding Co and Cu to RFeB magnets. Blending additions of Co to these magnets result in an increase in Curie point and remanence, but a decrease in coercivity. The addition of a very small amount of Cu, by blending, has significant beneficial effects on the coercivity and heat treatment characteristics of sintered magnets. The combined addition of copper and cobalt allows more cobalt to be added without drastic loss in coercivity. The microstructure is apparently refined by the addition of copper; non of which is detected in the matrix phase.

References

[1] M. Sagawa, S. Fujimura, N. Togawa, H. Yamamoto and Y. Matsuura, Journal of Applied Physics, 55(6) (1984) p2023.

[2] A. Kianvash, Proceedings of 13th International Workshop on RE Magnets & their Applications, Birmingham, 1994, p 913-921.

[3,] R.S. Mottram and I.R. Harris, Proceedings of the 15th International Workshop on Rare Earth Magnets and their Applications, Dresden, (1998) p473-479.

[4] G.J. Mycock, R.N. Faria and I.R. Harris, J. Alloys & Compounds; 201 (1993) p23-28.

[5] A.S. Kim, Proceedings of 3rd ISPMM, Korea (19950) p646.

[6] A. Ahmad, R.S. Mottram and I.R. Harris, Materials Science Forum, Trans Tech Publications, Switzerland, Vol. 373-376 (2001) p325-328.

[7] Y. Matsuura; S. Hirosawa; h. Yamamoto, S. Fujimura and M. Sawga, Applied Physics Letters 46(3) (1985) p308.