Journal of Magnetism and Magnetic Materials 323 (2011) 1152–1155

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Production and corrosion resistance of NdFeBZr magnets with an improved response to thermal variations during sintering

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ARTICLE INFO

Article history:
Received 25 May 2010
Received in revised form
11 November 2010
Available online 29 December 2010

Keywords:
NdFeB
Magnetic property
Sintering temperature
Corrosion resistance

ABSTRACT

This study describes an attempt to produce NdFeB magnets that are insensitive to the sintering temperature. It was found that addition of Zr to NdFeB magnets significantly augmented the thermal stability of this magnetic material during sintering at high temperature even at industrial scale. The best sintered magnets were produced by jet-milling the powder (to achieve an average 3.4 μm particle size), and then aligned, pressed and sintered under argon at 1100 °C for 3 h followed by appropriate heat treatment. The magnetic properties of the resulting magnets were: $(BH)_m$=403.8 kJ m^{-3} ($\pm$4.7 kJ m^{-3}), B_r=1430 mT ($\pm$9 mT) and $_iH_c$=907 kA m^{-1} ($\pm$12 kA m^{-1}). Large grain growth, in excess of 100 μm in the Zr-free magnets, was observed during sintering at 1100 °C. This did not occur in the presence of Zr. These observations imply that the sensitivity of this class of magnets to high sintering temperatures is greatly reduced by Zr addition. Corrosion resistance of NdFeB was therefore significantly improved by the addition of small amounts of Zr.

1. Introduction

Since their discovery in 1983 [1], demand for sintered NdFeB magnets has greatly increased, due to their superior magnetic properties. Total output of sintered NdFeB magnets in China reached 52,400 tons in 2008 [2] and is still growing. The sintering temperature plays an important role in the magnetic properties of the final material, especially during industrial scale production. An optimum sintering temperature has to be applied, accompanied by appropriate heat treatment, in order to densify the green NdFeB compacts and achieve the best magnetic properties. Generally more than 250 kg of the material is loaded into an industrial furnace during mass production. This material is then sintered by heat radiation. Typical problems with heat distribution during the sintering stage often result in sintered magnets being over- or under-sintered in the outer or central regions of the bulk material, respectively, due to this uncontrolled temperature variation. Therefore the magnetic properties of the NdFeB magnets produced in this way often display significant fluctuations. Quality control of these sintered magnets is thus a problematic and time consuming part of industrial magnet production. Theoretically, reducing the sensitivity of the magnetic material to sintering temperatures could solve this problem. It was decided to achieve this by fine tuning magnet composition to obtain more uniform properties of the resulting sintered magnets.

It was previously reported that a ZrB_2 [3] phase emerged upon Zr addition to the PrFeB magnetic system, resulting in a material that displayed improved coercivity and a classical square shape during the demagnetising loop. It was also established that during preparation of nano-composite NdFeB, addition of Zr had an impact on the grain size [4,5] and its distribution. Other researchers have investigated the effects of various elemental additions of Dy, Nb, Al, Cu and Co and preparation techniques on the properties of NdFeB magnets [6–8]. In this paper we now demonstrate how optimum additions of Zr can significantly reduce the influence of sintering temperature on the final magnetic properties of NdFeB sintered magnets produced at industrial scale.

2. Experimental

The starting materials employed in sample preparation were of 99.9 wt% purity for Nd, Fe, Al, Dy, Zr, Ga and an FeB alloy (20 wt% B). The magnets, with approximate compositions of $Nd_{13.3}Dy_{0.48}Fe_{bal}B_{5.75}$ and $(NdDy)_{12.99}(Fe)_{bal}B_{5.9}$ (at%) with additions of Al, Ga and Zr, were prepared by a strip casting technique, with a line speed of 2 m/s produced by the Zhongbei Shenyang company. These alloys were subjected to a standard hydrogen decrepitated (HD) treatment, followed by jet-milling to produce fine powders with an average particle size of 3.4 μm. The powders were aligned by applying a 1.8 T magnetic field and then

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doi:10.1016/j.jmmm.2010.12.029

isostatically pressed at a pressure of 6 MPa, to produce green compacts. These compacts were heated under argon at a rate of 5 °C/min followed by sintering at 1065–1105 °C for 3 h in furnace made by the ULVAC vacuum furnace (Shenyang) Co. Ltd. Sintered magnets were quenched to room temperature under Ar gas to prevent oxygen pick up. This was followed by heat treatment, again under Ar, for 2 h at 900 °C and then for 3 h at 600 °C, followed by quenching to room temperature.

The magnetic properties reported in this work were obtained by averaging the results from a number of samples analysed using *B–H* tracer (model AMT-4); three samples were obtained from outer region and two samples from central region of the bulk magnetic material obtained from an industrial furnace after sintering. The microstructure was investigated using a JEM-2010 transmission electron microscope and by optical microscopy (OLYMPUS-MX50). Corrosion properties were measured by the PCT-30-2 high pressure acceleration life tester at 121 °C under 2 atm for 48 and 96 h.

3. Results and discussion

The starting material for this study was $Nd_{13.3}Dy_{0.48}Fe_{bal}B_{5.75}Al_{0.24}Ga_{0.1}Zr_y$; the addition of Al was to improve wettability of the grain boundary material whilst small additions of Ga and Dy were designed to improve the coercivity of the resulting magnets. It was then decided that small additions of Zr might be required to suppress grain growth at higher sintering temperatures. In order to optimise the procedure and densify the powders into sintered magnets, a range of sintering temperatures was selected from 1065 to 1105 °C. The low temperature (1065 °C) seems to be associated with reduced grain growth during the furnace sintering. However higher sintering temperatures (1100 °C) are associated with the best magnetic properties and good densification to the sintered magnet. The results are presented in Table 1, which summarise the magnetic properties for the sintered magnets. Nearly full densification (about 98 vol%) was achieved for material sintered at temperatures $\geq$1100 °C. The result for the best magnet composition is shown in Fig. 1. The variations in magnetic properties indicate that the $(NdDy)_{13.32}Fe_{bal}B_{5.75}Al_{0.24}Ga_{0.1}Zr_{0.07}$ composition sintered at 1100 °C was found to show optimum magnetic properties. Further this is accompanied by a slight fall in the coercivity, possibly indicating that a high temperature oxidation corrosion happened.

In order to understand this variation in properties, magnets of the base composition, with and without addition of Zr, were sintered at the indicated temperatures and the resulting material sectioned and its microstructures studied by optical microscopy. It is worth noting that grain growth in excess of 100 μm occurred in the Zr-free containing magnets at the higher sintering temperature (1100 °C) shown in Fig. 2b. It is clear from Fig. 2 that the sintered material without Zr addition (Fig. 2b) displays an increased grain size compared with that of the Zr-containing magnets (Fig. 2c and d) and also evidence of porosity. Both these observations are consistent with the decrease in the magnetic properties observed in Fig. 3. Thus, the Zr addition of 0.07% and 0.43% to the $(NdDy)_{13.32}Fe_{bal}B_{5.75}Al_{0.24}Ga_{0.1}Zr_x$ composition decreased the average grain size, from 10.6 to 8.7 μm, respectively. During the sintering process Zr segregates on the grain boundary, which suppresses the grain growth and is associated with the observed reduced temperature sensitivity of the sintering process.

The TEM microstructures of the sintered magnets are shown in Fig. 4. The microstructure shows evidence of a ZrB_2 precipitated phase in the $Nd_2Fe_{14}B$ grains, which has been ascribed [9,10] to the presence of Zr additions. This Zr addition is suggested to inhibit of grain growth. This addition of the Zr made these magnets insensitive to sintering temperature and hence more suitable for production scale magnet preparation using equipment with weak temperature control. Adding the appropriate amounts of the Zr to the base composition is therefore a good method of producing magnets on a large scale with consistent properties.

The effects of Zr additives on weight loss are presented in Table 2. It can be seen that the magnets without Zr additions, sintered at 1065 and 1100 °C, resulted in a material that displays rapid weight loss up to 48 h exposure. During more extended exposure, corrosion products become more apparent in the Zr-free material. These products detached from the rest of the magnetic phase may explain the increased weight loss observed for Zr-free magnets when compared to that of the Zr-containing magnets. This would indicate that good corrosion resistance for Zr-containing magnets probably results from an increased density of sintered magnets produced from this alloy.

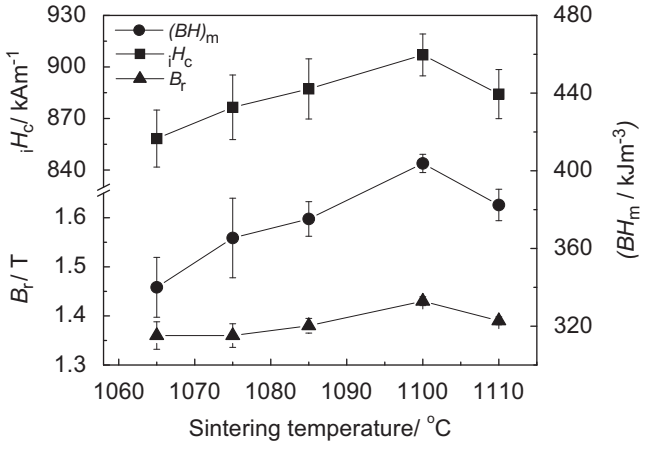

Fig. 1. Summary of the magnetic properties versus sintering temperature for the $(NdDy)_{13.32}Fe_{bal}B_{5.75}Al_{0.24}Ga_{0.1}Zr_{0.07}$ sintered magnet.

Table 1
Properties of sintered magnets.

Magnet content (at%)	Sintered (°C)	B_r (T)	$_iH_c$ (kA/m)	$(BH)_m$ (kJ/m^3)	Density (g/cm^3)
$(NdDy)_{12.99}Fe_{bal}B_{5.9}$	1065	1.37	626	314	7.53
$(NdDy)_{12.99}Fe_{bal}B_{5.9}$	1085	1.40	526	276	7.58
$(NdDy)_{12.99}Fe_{bal}B_{5.75}Al_{0.24}Ga_{0.1}$	1065	1.36	741	332	7.53
$(NdDy)_{12.99}Fe_{bal}B_{5.75}Al_{0.24}Ga_{0.1}$	1085	1.39	560	298	7.58
$(NdDy)_{12.99}Fe_{bal}B_{5.75}Al_{0.24}Ga_{0.1}Zr_{0.07}$	1085	1.36	846	363	7.58
$(NdDy)_{12.99}Fe_{bal}B_{5.75}Al_{0.24}Ga_{0.1}Zr_{0.07}$	1100	1.42	865	401	7.60
$(NdDy)_{12.99}Fe_{bal}B_{5.75}Al_{0.24}Ga_{0.1}Zr_{0.07}$	1105	1.43	857	403	7.60