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Study of Carbon Influence on Magnetic Properties of Metal Injection Molding Nd-Fe-B based Magnets

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Abstract: In this work, Metal Injection Molding (MIM) process was applied to manufacture Nd-Fe-B magnets, where carbon residues were quantified. In a separated test, controlled additions of carbon were added prior to sintering in the conventional processing of Nd-Fe-B magnets, aiming to simulate the binder residues with more accuracy. The carbon contents in the sintered magnets were related to final magnetic properties such as remanence and coercivity. It was found that the rare-earth content in the alloy influence the threshold where further additions of carbon will degrade coercivity. This study gives directions on developing binder systems and debinding processes, focusing on reaching adequate carbon levels to maximize final magnetic properties.

Introduction

The applications of Nd-Fe-B based magnets are nowadays experiencing an expressive diversification, as more technologies are making use of them aiming efficiency and miniaturization. Despite of the trends in broadening the gamut of shapes and sizes, the production methods for all of them are essentially the same, based on uniaxial or isostatic pressing, sintering and machining. Given the complex machinability of this material, parts with more complex geometries tend to be expensive. The Metal Injection Molding (MIM) is a process that emerges as an alternative for manufacturing complex parts with high productivity, hence reducing the cost per part.

Nevertheless, on MIM, one must deal with proper binder extraction and, consequently, lower carbon residues, especially when processing Nd-Fe-B that is sensitive to the presence of this element [1-4]. In this situation, carbon could potentially react with alloy constituents forming carbides [1,2]. These carbides could subtract neodymium from Nd2Fe14B if there is not enough rich phase or elements which carbides are more stable, decomposing the phi-phase and affecting magnetic properties. When disproportionation takes place alpha-Fe can be formed [3], what will reduce the coercivity significantly, being a soft magnetic phase that will act as a reverse-domain nucleation site. Another study showed the tendency of carbon to be concentrated preferentially on the rich-Nd phase [4], so the amount of the latter (given by Rare-Earth content) should play some role on the carbon effect.

Earlier studies reporting MIM for Nd-Fe-B [5-8] relate the concern with the carbon content but did not varied the alloy composition, focusing on the development of a most efficient binder and its proper extraction. So it was conceived what would be the impact of alloy composition in the magnetic properties of magnets produced by MIM, given that this process will generally contaminate the material with carbon.

However, it is complex to keep constant the carbon content by MIM parameters, making difficult to compare its effect of different alloys. Therefore in this study, firstly MIM process was applied to manufacture magnets with one type of Nd-Fe-B alloy, in order to quantify the carbon levels reminiscent after sintering and final magnetic properties. This carbon level will indicate the scenario that the material is subjected during processing.

Later, conventional PM process was applied to produce magnets with different Rare-Earth amounts and carbon was added in controlled quantities, simulating binder residues, and magnetic properties were evaluated. It was also a goal of this work to evaluate if the artificially added carbon behaves in the same fashion as the carbon residue of binder systems, by the comparison of magnetic properties.

Experimental Procedure

Powder preparation

Nd-Dy-Co-Fe-B alloys with different Rare-Earth amounts were chosen for this study. These alloys were transformed into powder by HD (hydrogen decrepitation) followed by a fine milling step in a planetary ball mill. The HD was processed in an average temperature from 160°C to 180°C and hydrogen gas at 1 bar. After the HD, the alloy was ball milled under hexane with a rotational speed of 230 rpm for 2 hours. The ball-to-powder ratio used was 10 to 1.

Feedstock Preparation

The feedstock for injection molding was prepared with the powder manufactured by the previous item for the alloy Nd17Dy2B12Co8Fe61. The binder system (representing 8 wt% of the feedstock) was composed by paraffin wax (55%), high density polyethylene (30%) and ethylene-vinyl acetate (15%). For the feedstock mixture, paraffin wax and ethylene-vinyl acetate were previously dissolved in a small quantity of hexane and mixed together with the milled powder. In order to get a better powder coating, this pre-mixture was agitated during 30 minutes in the planetary mill with a rotational speed of 230 rpm. The solvent was then pumped out in order to get a dry mixture of the binders and the powder. This pre-mixture was then filled into HDPE bags, which would be eventually part of the feedstock, and then fed to a shear mixer flushed by argon to avoid oxidation. The feedstock mixture was carried out at 150 °C for 30 minutes. In order to manufacture anisotropic testing samples, a magnetic field in form of pulses (4,5 T max.) was applied during the feedstock pressing, this being hot pressed at 160 °C with 130 MPa.

Debinding and Sintering

Binder removal was carried out by a chemical debinding followed by a thermal debinding. The chemical debinding was performed by immersing the samples in heated hexane with an average temperature between 45°C to 55°C. Thermal debinding and sintering step were carried out in the same cycle, described in the Fig. 1. During the thermal debinding hydrogen flow was applied and sintering was done under high vacuum.

Conventional PM process with carbon additions

In order to test the effect of carbon on the magnetic properties, carbon amounts were added in controlled proportions to the powder and then, conventional PM process was employed to manufacture the magnets. The milled powder described in item 3.1 and carbon powder (99,9% purity) were mixed in a glove-box in three different proportions, resulting in mixtures with 0%, 0,25% and 0,50% of carbon. Alloys with two different RE amounts were tested, with compositions Nd17Dy2B12Co8Fe61 and Nd15Dy2Co5B12Fe66. The powders were uniaxially pressed in a cylindrical die with diameter of 10 mm. Magnetic field in form of pulses (4,5 T max.) were applied during the pressing step in order to obtain a cristalographic texture. The sintering step was carried out under high vacuum, following the cycle described in Fig. 2. The hydrogen removal is performed during sintering keeping constant temperature around 260 °C and 605 °C, which are the temperatures where hydrogen is released from the 2:14:1 and rich phase, respectively. The sintering is performed at 1080 °C.

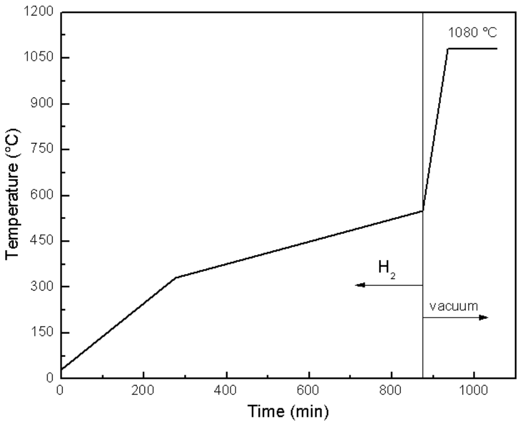

Figure 1 – Thermal debinding and sintering cycle, developed in the same furnace, being the debinding under hydrogen flux, and the sintering developed under high vacuum.

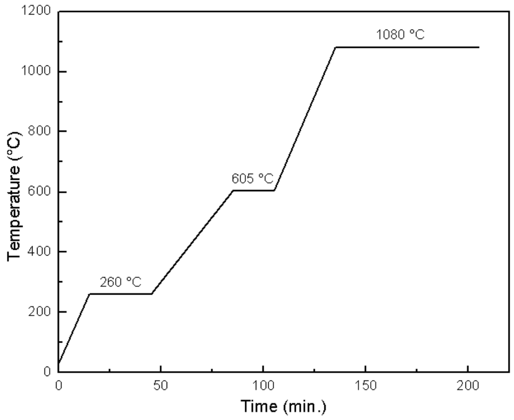

Figure 2 – Conventional sintering cycle, with two stages for hydrogen releasement, developed entirely under high vacuum.

Results and Discussion

Metal Injection Molded Magnets

In the MIM samples, the chemical debinding developed a weight loss showed in Fig. 3. After thermal debinding and sintering, the magnets were pulse magnetized under a field of 4.5 T, and magnetically characterized. Table 1 shows the main properties reached in these magnets in comparison to a reference magnet, which was crafted from the same powder employed on the feedstock, but sintered without any polymer in the cycle described in Fig. 2. The demagnetization curves of both magnets are showed in Fig. 4.

Comparing both magnets it can be seen that the MIM samples had the coercivity reduced by 30 %. This difference could be attributed to the carbon residues of polymers. The carbon content in the sintered sample produced by MIM varied from 0,10-0,15 %. The samples processed by the conventional process showed a carbon level of 0,06 %, which source is thought to be from the solvent used during wet milling and not extracted during thermal cycle. The remanence was also lower in the MIM samples, mainly by the lower density achieved after sintering, what could also be an effect of carbon, which form neodymium carbides with higher melting points, consuming the rich-phase responsible for the liquid phase during sintering.

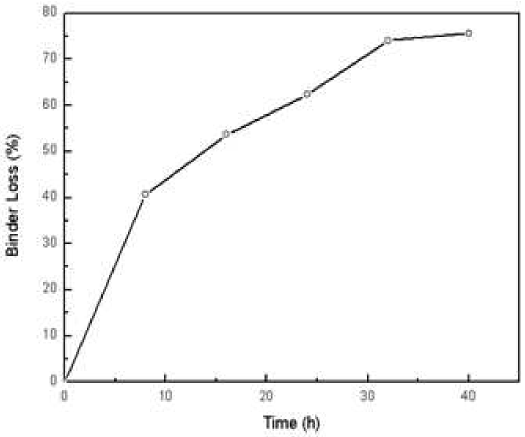

Figure 3 – Weight loss of polymer during monitored chemical debinding under hexane. Debinding was interrupted after removing 75% of soluble binder components, which took 40 h.

Table1 – Main data of samples produced by MIM and a reference produced by conventional PM process. Samples are isotropic.

	Green Density	Sintered Density	Carbon After Sintering	Remanence	Coercivity	Energy Product
MIM Process	4,5g/cm³	6,23g/cm³	0,10 - 0,15%	0,714 T	647,3 kA/m	92,1 kJ/m³
Reference	4g/cm³	7,02g/cm³	0,06%	0,799 T	916,6 kA/m	120,7 kJ/m³

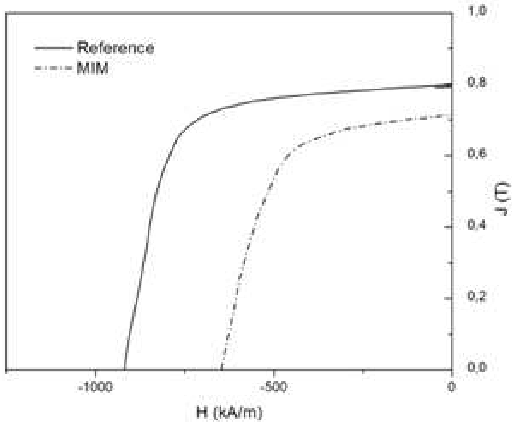

Figure 4 – Comparison of demagnetization JH curve for magnets produced by MIM and reference magnets fabricated with the same powder but by the conventional PM process.

Carbon influences on Magnetic Properties

The intentional addition of carbon, which simulates the binder residues that are in the surroundings of the alloy during sintering, is expected to behave differently depending on the alloy composition. Firstly, on Fig. 5, the magnetic properties of anisotropic magnets made with the alloy Nd17Dy2B12Co8Fe61 was measured for the pure alloy and the additions of 0,25 and 0,5% of carbon. It can be noticed the effect of carbon reducing the coercivity as the addition increases. Nevertheless, the addition of 0,25% of carbon, higher than could be reached in MIM (around 0,15%), dropped the coercivity only by 13%, in contrast with the 30% drop evaluated in the actual MIM process (Fig. 4).

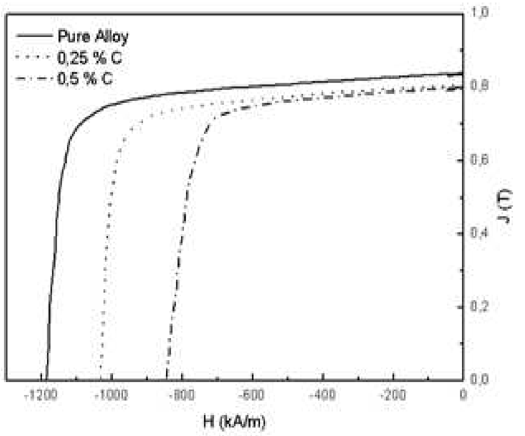

Figure 5 – Demagnetization curves for Nd17Dy2B12Co8Fe61 magnets with different carbon additions. Coercivity drops as the carbon content increases.

In Fig. 6, it can be seen the magnetic properties of anisotropic magnets made with the alloy Nd15Dy2Co5B12Fe66. This alloy showed higher coercivity than the previous in the pure state, but with 0,25% carbon addition, a remarkable drop of coercivity could be noticed. The addition of 0,5% of carbon is not indicated, as the coercivity was too low to be correctly measured by the equipment. The remanence is also reduced, mainly by the softening of the magnet. This expressive drop (85%) could be explained by the decreased tolerance to carbon presence, manly by the lower rich phase amount. As rare-earths reacts with carbon, less liquid phase is formed, impairing the microstructure development and reducing magnetic hardness. Also, carbon in contact with Nd2Fe14B phase could lead to decomposition of this compound, releasing free iron, which also reduces coercivity being a soft magnetic phase.

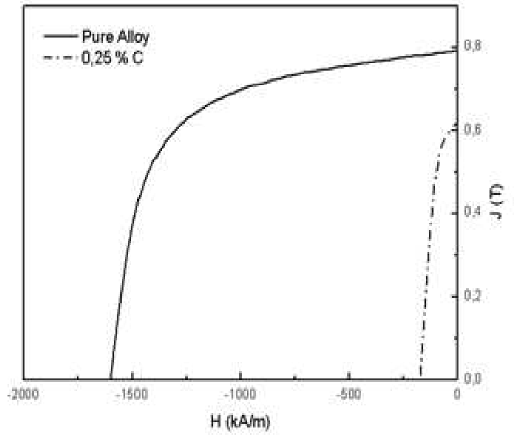

Figure 6 – Demagnetization curves for Nd15Dy2Co5B12Fe66 magnets, with and without carbon additions. The coercivity drops noticeably, even with small carbon additions, indicating the lower tolerance of the less rich alloy.

Conclusions

In MIM of NdFeB based materials, carbon levels from 0,10 to 0,15 % were reached. Magnetic properties of the MIM processed alloy was inferior to alloy produced by conventional process, being the coercivity affected. The artificially addition of carbon in the conventional PM samples showed less influence in the magnetic properties then the carbon left by the MIM process, given the higher impact on the magnetic properties of the latter even with smaller amounts. Different alloys compositions behave differently in carbon presence. Alloys with higher amount of rare-earths, consequently with more RE-rich phase, showed more tolerance to carbon presence, being less affected by carbon than lower RE alloys.

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