Metal Injection Moulding of NdFeB Based on Recycled Powders

<u>*Philipp Imgrund*</u>[1]*, Oxana Weber*[1]*, Thomas Schlauf*[2]*, Karsten Pischang*[3]*, Lydia Pickering*[4]*, Allan Walton*[4]*, Joamin Gonzalez-Gutierrez*[5]*, Christian Kukla*[6]*, Carlo Burkhardt*[1]

[1] *OBE Ohnmacht & Baumgärtner GmbH & Co KG, Turnstraße 22, 75228 Ispringen, Germany*
[2] *2FOTEC GmbH, Viktor Kaplan-Strasse 2; A-2700 Wiener Neustadt / Austria*
[3] *PT+A GmbH, Fritz-Meinhardt-Str. 32, 01239 Dresden, Germany4*
[4] *School of Metallurgy & Materials, University of Birmingham, Edgbaston, Birmingham,B15 2TT, United Kingdom*
[5] *Montanuniversitaet Leoben, Department of Polymer Engineering and Science, Chair of Polymer Processing, Otto Gloeckel-Str. 2, 8700 Leoben, Austria*
[6] *Montanuniversitaet Leoben, Industrial Liaison Department, Peter Tunner Str. 27, 8700 Leoben, Austria*
Correspondence to: Philipp Imgrund (E-mail: pimgrund@obe.de)

ABSTRACT

Over the last ten years several groups have been carrying out research into metal injection moulding (MIM) of neodymium-iron-boron (NdFeB) powders to produce isotropic or anisotropic rare earth magnets with higher complexity than in the conventional press and sintering approaches. However, difficult processability due to the high affinity of the powder to oxygen and carbon pickup remains problematic in terms of obtaining sufficient remanence and coercivity. In this paper, a new approach to MIM of NdFeB magnets is presented. It is based on the use of powder obtained from recycling of used rare earth magnets by the hydrogen decrepitation (HD) process. Different types of binder systems have been used for producing mouldable MIM feedstock. Influence of debinding and sintering conditions on interstitial contents and magnetic properties of sintered MIM parts are presented and discussed. Magnets with a remanence of 570 mT, a coercivity of 970 kA/m and an energy product of 57 kJ/m³ could be produced without additional heat treatment.

INTRODUCTION

The production of magnets based on neodymium and other suitable metals, the so-called "rare earths", is a highly resource-intensive process, since their extraction from the ores involves using complex chemical processes involving harmful and toxic chemicals before the refined raw material, a metallic powder, is available for further processing. At the same time the global demand for these materials increases with the growing use of sensors, generators and electric motors in modern electric motors, energy generators and mobile electronics. From an economic perspective is particularly significant that over 90% of the global rare earth supply is being mined in China.

The objective of the present study is therefore to develop and evaluate the potential of using recycled neodymium-iron-boron (NdFeB) powders in the MIM process for the production of complex shaped isotropic and anisotropic magnets. This is done by preparing a recycled NdFeB powder from magnet scrap, which can be processed into new magnetic components by MIM. Since MIM is a near net shape process, complex magnets could be obtained with minimum post-processing operations while saving up to 30% raw materials and energy.

EXPERIMENTAL

Unlike many common MIM materials, NdFeB powder tends to pick up oxygen from the atmosphere even at room temperature. On the one hand this may strongly deteriorate the magnetic properties, on the other hand this also leads to safety issues due to increased risk of inflammation during processing. Another challenge is the control of carbon content in the material. Here the organic binder system is a source of contamination during thermal decomposition at about 500-600 °C. For instance carbon contents >1000 ppm are reported to cause significant losses in coercivity [1]. Therefore the main challenge of this work is to design the process chain according to the requirements of the recycled raw material, i.e. the adaption of injection moulding, debinding and sintering parameters with the aim of obtaining MIM magnets based on the recycled powder with properties comparable to magnets based on new powders.

POWDER PREPARATION

The basis for recycling of magnetic components to powder is the high reactivity of neodymium with hydrogen (H_2), which facilitates the process dramatically [2], see Figure 1a. For instance, if a computer hard drive is placed in a closed reactor under hydrogen atmosphere tumbled in a rotating drum, then after a short time the NdFeB powder can be collected and removed in its hydrogenated form after pumping out the hydrogen (Figure 1b). After removal of corrosion coatings such as electroplated nickel layers, MIM processing can be carried out with the powder obtained.
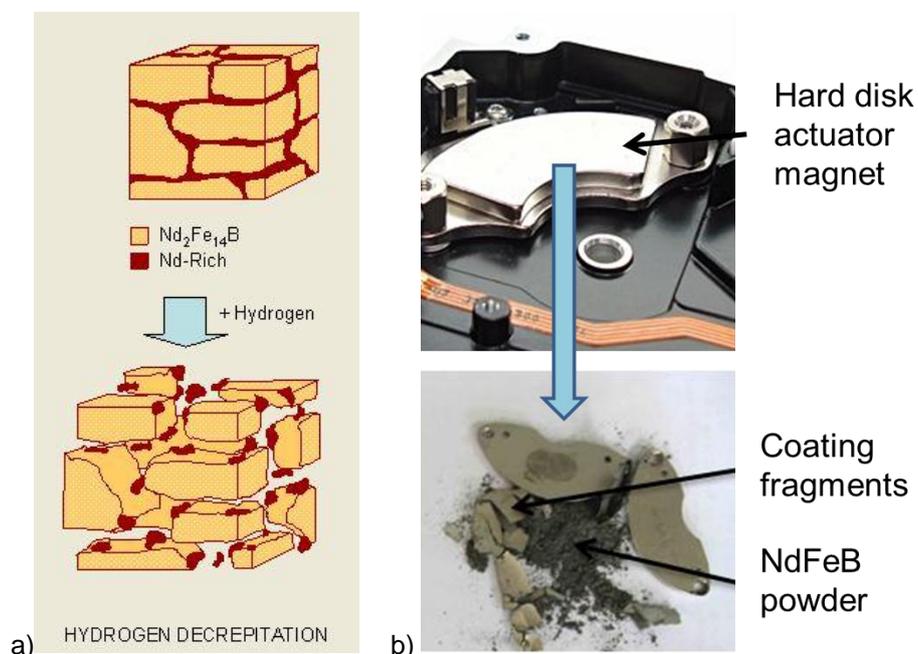

Figure 1: Schematic illustration of the hydrogen decrepitation (HD) process [2; 3]

FEEDSTOCK PREPARATION

Feedstock was prepared from the recycled powders using three different types of binder systems. The first two were proprietary binder systems which can be debinded in a suitable solvent and thermal debinding process. The components of these systems were kept the same, but the amount of backbone polymer was higher in the first system. The third binder was based on a different wax-polymer system and required a different solvent for pre-debinding.

The first two feedstocks were compounded with the powder without further precautions in atmosphere, keeping the exposition of the NdFeB powder to air within the time frame of a few seconds. Feedstocks 1 and 2 were received in vacuum sealed bags and further processed as received. For the third feedstock, the powder and binder systems were compounded in a three-step procedure under inert atmosphere. Table 1 gives an overview of the feedstock systems under investigation.

**Table 1: Feedstock types under investigation**

	Binder	**Compounding**	**Debinding**
Feedstock 1	Reference	Single-step, air	Solvent 1
Feedstock 2	Modified backbone component	Single-step, air	Solvent 1
Feedstock 3	Modified backbone and wax component	Three-step, inert atmosphere	Solvent 2

INJECTION MOULDING

Injection moulding was carried out using an Arburg Allrounder 270 U injection moulding machine, see Figure 2a. In the case of feedstock 3, injection moulding was performed while flooding the funnel and

injection moulding screw with Argon (Ar), to prevent oxygen pickup of the feedstock at elevated temperatures, Figure 2b. All feedstock variants were injection moulded to disc-shaped samples of 23.7 mm diameter and 6 mm height, see Figure 2c. The geometry was chosen to suit subsequent characterization needs, especially determination of magnetic properties.
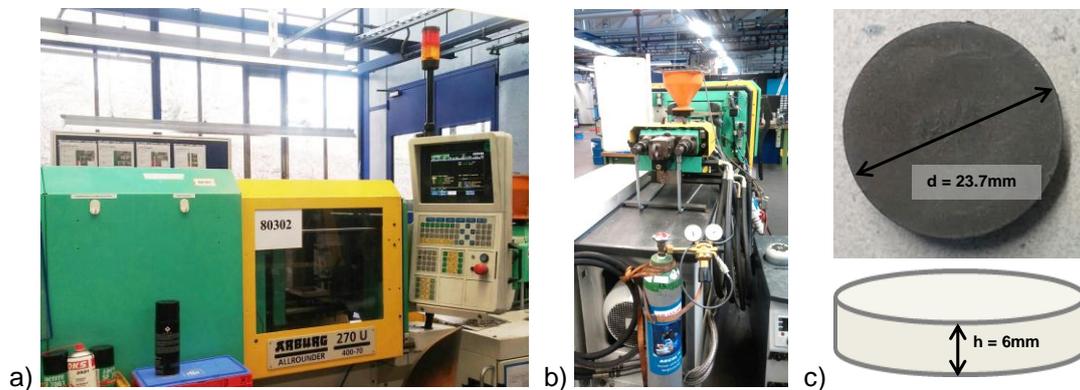
Figure 2: Injection moulding machine, (a) side view; (b) rear view, with Ar supply; c) sample dimensions

SOLVENT DEBINDING

Solvent debinding was done in a LÖMI EBA 200 debinding vessel for feedstock 1 and 2, Figure 3a. For feedstock 3, a laboratory debinding equipment as depicted in Figure 3b was used. In both cases, green parts were placed on perforated stainless steel plates. All samples were debinded for 24h at temperatures of 50 °C (feedstock 1 and 2) and 60 °C (feedstock 3).
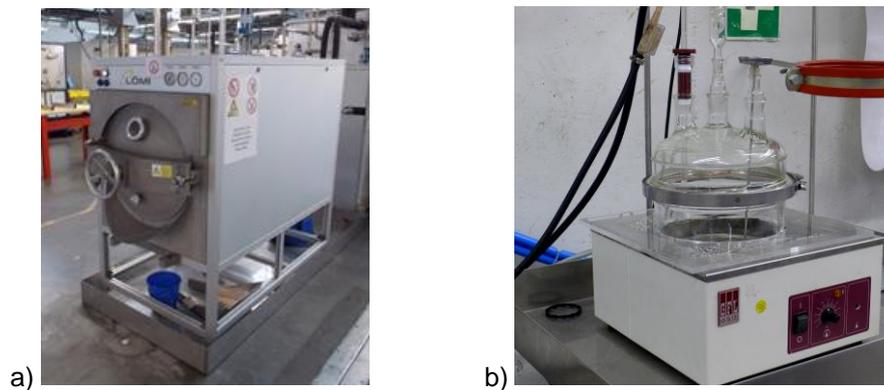
Figure 3: Solvent debinding equipment: (a) LÖMI vessel; (b) laboratory equipment

THERMAL DEBINDING AND SINTERING

Thermal debinding and sintering were done in an Elnik MIM furnace (type MIM 3045T). All parts were placed on Molybdenum plates without using getter material. Different thermal debinding and sintering conditions were evaluated with special attention to control carbon and oxygen contamination. The main parameters that were varied were heating rates and temperatures of thermal debinding, as well as sintering temperatures. Debinding was done in a reducing atmosphere, while sintering was carried out under inert gas conditions. Table 2 gives an overview of debinding and sintering parameters varied during process development. The sintered parts were characterized for oxygen and carbon content as well as magnetic properties (B-H-demagnetisation curves).

**Table 2: Parameter sets used for thermal debinding and sintering experiments**

	HR [°C/min]	T_{th} [°C]	T_S [°C]
Sintering run 1	1	360 / 640	1100
Sintering run 2	0.5	300 / 700	1100
Sintering run 3	0.5	300 / 700	1080
Sintering run 4	0.5	300	1100

HR   heat-up rate during thermal debinding;
T_{th} temperature plateaus during thermal debinding;
T_S sintering temperature.

RESULTS AND DISCUSSION

POWDER AND FEEDSTOCK CHARACTERISATION

The powder morphology can be seen from the SEM image in Figure 4. As expected from the process, an angular shaped powder was obtained. The mean particle size measured by laser granulometry amounted to 26.3 µm. The chemical composition is listed in Table 3 and shows high Dysprosium contents of about 4.3-4.4 wt.% and acceptable interstitial levels of oxygen (0.68 wt.%) and carbon (0.097 wt.%).
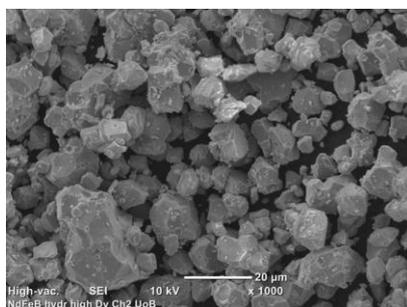
Figure 4: Recycled NdFeB powder obtained by the HD process

Table 3: Chemical composition of the recycled powder

B	Co	Dy	Fe	Nb	Nd	Pr	O	N	C	S
wt.%										
1.05	3.3	4.33	63.45	1.17	27.28	0.29	0.680	0.034	0.097	<0.01

All feedstock variants proved processable using melt temperatures between 110 °C (feedstock 1 and 2) and 150 °C (feedstock 3). Changeover pressures ranged between 500-600 bar (feedstock 1 and 3) and 1000 bar (feedstock 2). Tool temperatures were moderate at 20-30 °C for all feedstock types.

RESULTS OF SOLVENT DEBINDING

Table 4 shows the results of solvent pre-debinding trials with the three feedstock types. It can be seen that feedstock 1 and 2 reached the theoretical debinding rates given by the supplier and more than 93 % of the soluble constituents could be removed. In contrast, for feedstock 3, only 78.1 % of the soluble constituents were removed in the solvent debinding step.

Table 4: Mass loss and binder removal rates

	Calculated mass loss [wt.%]	Actual mass loss [wt.%]	Removal rate [%]
Feedstock 1	5.67 – 6.3	5.86	> 93.0
Feedstock 2	6.48 – 7.11	6.69 – 6.74	> 94.0
Feedstock 3	4.75	*3.71 – 3.75*	*> 78.1*

RESULTS OF THERMAL DEBINDING AND SINTERING

Due to the insufficient pre-debinding results of feedstock 3 a relatively large amount of residual binder remained in the samples and caused some cracks or bulges after sintering, see Figure 5. About one third of the samples was affected by such defects and further trials with different solvent debinding agents and prolonged debinding times are envisaged to further improve the process.
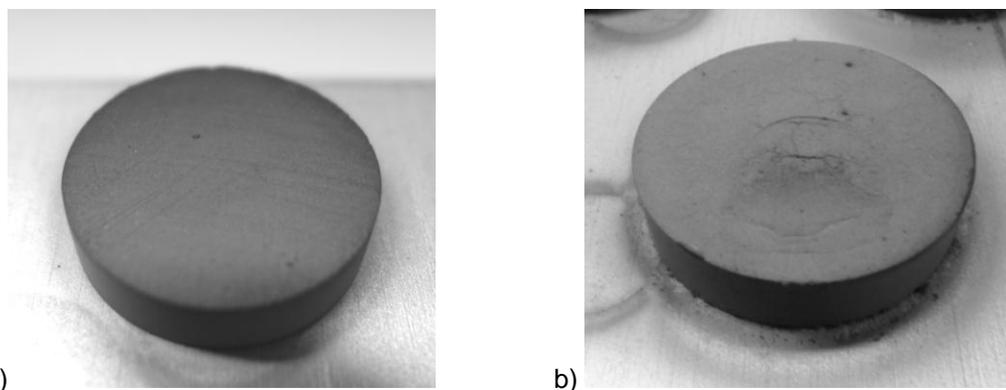

a)   b)

Figure 5: Examples of samples after sintering 3: a) feedstock 1; b) feedstock 3

Carbon and oxygen contents

For all sintering runs indicated in Table 2, carbon and oxygen content were measured by hot gas extraction. Results are given in Figure 6.
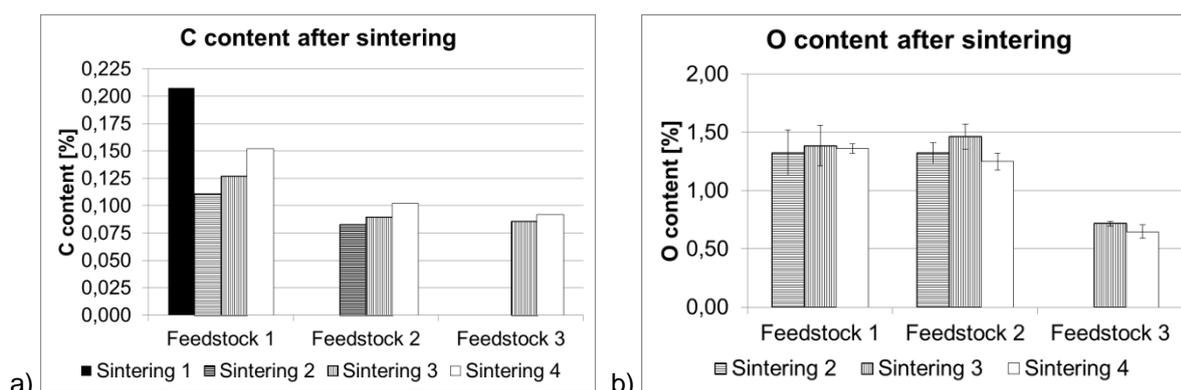

a)   b)

Figure 6: a) Carbon; b) oxygen content of sintered NdFeB parts

In run 1, in which the heating rate was 1 °C/min in the debinding cycle, a carbon content of 0.21 wt.% was recorded for feedstock 1. In the subsequent sintering runs, carbon contents were significantly reduced for all feedstocks. Feedstock 2 and 3 showed the lowest values at 0.09 wt.% in sintering runs 3 and 4. In line with the findings of other authors, this can be attributed to the reduction of the heating rate from 1 °C/min to 0.5 °C/min in the thermal debinding cycle [4]. Furthermore, modification of the backbone polymer in feedstock 2 compared to feedstock 1 also lead to a significant decrease in carbon content, i.e. reduced pickup from the binder system.

In terms of oxygen content, no influence of the processing route could be detected for feedstock 1 and 2. In both systems, significant oxygen contamination in the range of 1.4 wt.% was recorded for sintering runs 2, 3 and 4. In contrast, feedstock 3 showed oxygen contents of only 0.72 wt.% and 0.65 wt.% for sintering 3 and 4, respectively. As all feedstock variants were processed in the same furnace runs, the near-complete suppression of oxygen pickup along the process chain can be attributed to the three-step compounding route under inert atmosphere used for preparation of this feedstock.

Magnetic properties

The magnetic properties of the samples were analyzed with a Brockhaus Hystograph HG 200 and Metis HyMPulse pulse field magnetometer at room temperature, respectively, following pulse magnetisation to 5 T. Analyses were not performed following sintering 1, as the high carbon content

suggested deterioration of magnetic properties beforehand. Table 5 shows the values of remanence and coercivity obtained. Both values remained unsatisfactory for feedstock 1 and 2 processed by sintering runs 2, 3 and 4. This can be attributed to excess oxygen content in the samples (see Figure 2b), which suppresses the formation of Nd-rich phase typical of a NdFeB magnet.

Feedstock 3, which features good carbon and oxygen levels, showed low Br and jHc values for sintering 3 as well. However good magnetic properties with a remanence of 0.57 T and coercivity of 970 kA/m were recorded for this feedstock following sintering 4.

Table 5: Magnetic properties of MIM samples from recycled powders

	Feedstock 1		Feedstock 2		Feedstock 3	
	B_r [T]	jHc [kA/m]	B_r [T]	jHc [kA/m]	B_r [T]	jHc [kA/m]
Sintering run 2	0.26	40	0.21	41	-	-
Sintering run 3	0.26	146	0.25	141	0.15	33
Sintering run 4	0.15	15	0.12	16	**0.57**	**970**

Figure 7 shows the demagnetisation curve of feedstock 3 after sintering 4. The improvement is obviously related to the adjustement of thermal debinding conditions, as indicated in Table 2.
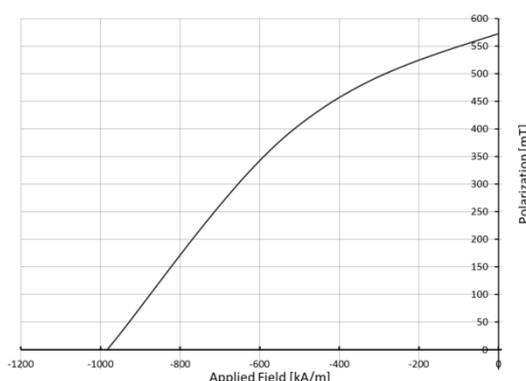
Figure 7: Demagnetisation curve of feedstock 3 following sintering 4

CONCLUSION AND OUTLOOK

The feasibility of a MIM process using 100% recycled NdFeB powder has been successfully demonstrated. It has been shown that proper selection of the binder system, feedstock preparation route, debinding rates and sintering temperatures are of major importance to control density, oxygen and carbon levels and to thus obtain desirable hard magnetic properties. The magnetic properties found for feedstock 3 in sintering run 4 are well in the range of isotopic NdFeB magnets processed by MIM using fresh non-recycled materials [1; 4]. Considering the similar level of C contents in feedstock 2 and 3, compounding of feedstock 2 under protective atmosphere may lead to similar interstitial levels and potential for magnet production as found for feedstock 3. Further research will be conducted with respect to feedstock compounding and MIM processing conditions to optimise magnetic properties. Furthermore development of a processing route for anisotropic NdFeB magnets based on recycled powders is envisaged.

Acknowledgements

REFERENCES

[1] T. Hartwig, L. Lopes, P. Wendhausen, N. Ünal, Metal Injection Molding (MIM) of NdFeB Magnets; EPJ Web of Conferences 75, 04002 (2014); DOI: http://dx.doi.org/10.1051/epjconf/20147504002

[2]: M. Degri: The Processing and Characterisation of Recycled NdFeB-type Sintered Magnets. PhD thesis, School of Metallurgy and Materials, College of Engineering and Physical Sciences, University of Birmingham, 2014
[3] URL: http://www.petervis.com/gallery/hard/Hard%20Drive%20Recovery/Hard%20Drive%20Recovery%20Voice%20Coil%20Assembly.html [4 May 2016]
[4] C. Weck, T. Hartwig: Sintern von spritzgegossenen NdFeB-Magneten. Workshop Magnetwerkstoffe – Vom Design zum Recycling. Fraunhofer IFAM, Bremen, 20.5.2015