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Short-Loop Recycling Of Sintered NdFeB Magnets By Hydrogen Decrepitation

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Abstract

NdFeB permanent magnets are essential components for the rising green transition technologies including electric vehicles and wind turbines. These magnets contain critical Rare-Earth Elements involving strong supply risk and high environmental impacts. Their recycling is thus a key factor for a sustainable production.

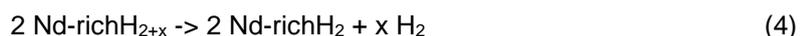
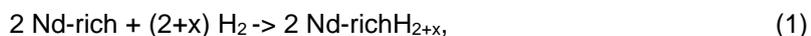
This study focuses on a short-loop recycling route based on the pulverization of end-of-life NdFeB magnets under hydrogen. The particle size distribution of the powders is affected by Hydrogen Decrepitation process conditions and is hereby proven to depend both on hydrogenation temperature and initial composition of the magnets. This study also emphasizes the interest of an appropriate thermal treatment on HD powders to recover their magnetic performances. It paves the way to a potential new recycling route of NdFeB permanent magnets for bonded magnets applications.

Introduction

NdFeB Permanent magnets are essential components for the rising green transition technologies including electric vehicles or wind turbines. They are used among a wide variety of applications like Hard Disk Drives (HDD), electrical motors, alternators, or electronic components. The demand for permanent magnets and Rare-Earth Elements (REE) will significantly rise in the next decade [1] and a secondary source should be set up to satisfy the forecast growth of these high-technology materials. NdFeB sintered magnets microstructure consists in hard ferromagnetic grains $\text{Nd}_2\text{Fe}_{14}\text{B}$ surrounded by a so-called Nd-rich phase [2]. This particular microstructure is responsible for their extrinsic magnetic properties and is obtained by a careful control of each step of their manufacturing process.

End Of Life (EOL) magnets could act as a sustainable secondary supply source for permanent magnets or rare-earth oxides [3]. Some magnets are actually reused by manufacturers. But since starting materials have often a very large range of composition, shapes, or properties, so called short-loop recycling routes have been implemented so far. They consist in obtaining NdFeB powders for instance by mechanical crushing but mainly by hydrogen-based reactions.

The Hydrogen Decrepitation (HD) process on EOL Permanent magnet will take place according to chemical reactions (1) - (2) typically at room temperature and under 1 bar hydrogen. Hydrogen is then desorbed under primary vacuum in three steps (3) - (4) – (5), respectively complete around 150, 300 and 700 °C [4].



Powder obtained can be reprocessed in the conventional powder metallurgy process which results in fully dense sintered magnets [4]–[10]. Waste NdFeB sintered magnets have also revealed to be very appropriate for the fabrication of bonded magnets throughout the HDDR process resulting in highly coercive anisotropic powder [11]–[15]. But this route also appears to be quite expensive. Only a few data can be found for bonded magnets fabricated with hydrogen decrepitated powders because of their quite low coercivity [16]. However, Li et al. [17] showed how anisotropic HD powders could be fabricated out of waste sintered NdFeB magnets. They emphasized the role of particle size on magnetic properties of HD powders. Later Michalski et al. [18] provided experimental data on the

influence of both hydrogenation temperature and pressure on the magnetic properties of the produced powders.

This study investigates the HD recycling route applied to EOL wind turbines magnets with different initial compositions, for bonded magnet applications. In a bonded magnets fabrication process typical particle size of the powders is around 100-200 μm . The particle size distribution of HD powders as a function of the hydrogenation temperature is therefore analysed. After the HD process, powders are non-coercive, however both remanence and coercivity can be strongly enhanced by an appropriate Thermal Treatment (TT) in what could be named a HD+TT process.

Experimental

Starting Material

Three types of wind turbine Permanent magnets (M1, M2, M3) were collected and used as starting materials. They were subjected to a demagnetizing thermal treatment at 350°C and a sandblasting step in order to remove the surface coating layer. Their composition analysed by Inductively Coupled Plasma (ICP) and their magnetic properties measured with an Hysteresigraph system are given in Table 1 and Table 2. These magnets were systematically decrepitated under 2 bar of H_2 and temperatures ranging from 50 to 200 °C. Desorption of hydrogen was operated at 250 and 550 °C steps until vacuum reached 10^{-1} mbar. After HD, desorption and sieving some powders were subjected to a thermal treatment at 900°C – 500°C with 2 hours steps under secondary vacuum atmosphere.

Table 1: Composition of the three wind turbine magnets used analysed by ICP (± 0.1 wt %)

Initial Magnet	B	Al	Fe	Co	Cu	Ga	La	Ce	Pr	Nd	Gd	Dy	%REE
M1	1	0.7	68	0.1	-	-	0.9	1.5	6	19	2.9	-	30.3
M2	1	0.5	66.8	1.5	0.2	-	-	-	0.9	27.2	-	3.8	31.9
M3	1	0.2	66.3	0.5	0.1	0.1	-	-	6	24.8	-	1.4	32.2

Table 2: Magnetic properties of initial magnets

Magnet	Coercivity (kA/m)	Remanence (T)
M1	993 \pm 20	1.22 \pm 0.02
M2	1451 \pm 30	1.22 \pm 0.02
M3	1377 \pm 22	1.35 \pm 0.02

Characterization

Particle size distribution was analysed by sieving in a N_2 controlled atmosphere glovebox at 1000, 800, 500, 300, 200 and 100 μm . Magnetic properties of the powders have been measured on resin compressed magnets. Cylindrical samples of 10 mm diameter and 7 mm height have been prepared with approximately 86 wt% of powder and 14 wt% of paraffin wax. The mixture is done on a hot plate at 180°C in a compression matrix. Oriented magnet samples are produced by aligning in a field of ~ 1.8 T. Remanence of powders is extrapolated using the volume ratio of magnetic powders by measuring the relative density of the obtained bonded magnets with the Archimedes' method. Microstructures are analysed using high resolution Scanning Electron Microscope (SEM) on polished samples with diamond papers down to 0.25 μm . Microstructures are given in Secondary Electrons (SE) and in Back Scattered Electrons (BSE) modes.

Results and discussion

Particle size distribution of HD magnetic powders

The particle size distributions of powders obtained after HD are plotted in Figure 1. The hydrogenation temperature has a clear influence on particle size distribution for the three type of magnets. Indeed, reaction (1) is activated with the rising temperature and complete around 150°C [19]. But when temperature rises, solubility of hydrogen in the NdFeB matrix also decreases resulting in a lower volume expansion of the phases, a lower fracturation stress and hence coarser particles [4]. For each

kind of magnets there is an optimum temperature to obtain a higher ratio of fine particle sizes (100 °C for M3, 150°C for M1 and M2). This temperature depends on the composition of the magnet and the amount of Rare-Earth Elements (REE). So initial magnet influences the particle size distribution of the recycled powders which also influences the magnetic properties of the obtained powders [17], [18]. It is worth noting that obtained particles are very brittle and friable. An additional deagglomeration step would get finer particles. But for the process implemented in this study particle size distribution is only influenced by the conditions of hydrogen decrepitation: hydrogenation temperature and pressure as a higher pressure results also in finer powders obtained [20]. Note also that powders obtained from sintered magnets are also finer compared to powders obtained from strip cast alloys [20]. This would imply that waste sintered magnets would be even more appropriate for bonded magnets fabrication processes.

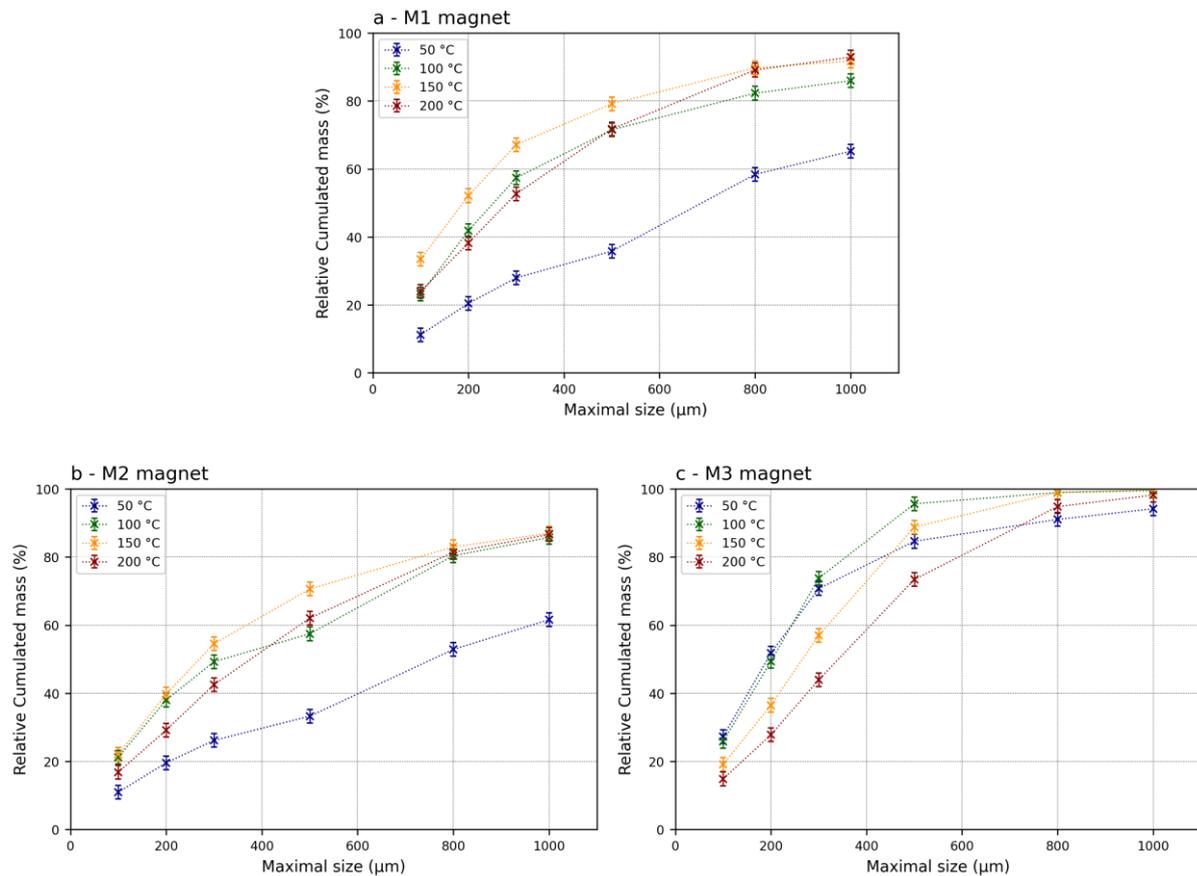


Figure 1. Particle size distribution of M1 (a), M2 (b) and M3 (c) magnets.

Microstructure of HD powders

Microstructure of Hydrogen decrepitated powders obtained from M1 magnet is shown Figure 2. HD reaction is strongly exothermic and results in a significant stress. Powders are hence very brittle, porous and friable. Figure 2b shows that polishing protocol was strong enough to remove some of the fractured grains. Transgranular cracks are also visible on Figure 2d, and Nd-rich phase initially surrounding each magnetic grain of $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase is no longer present. As mentioned in section 3, powder obtained is hence non coercive because of its brittle structure demagnetizing itself during orientation step. In a conventional powder metallurgy process such a microstructure is interesting because it allows an efficient milling process. But as such, these powders cannot be used for bonded magnet.

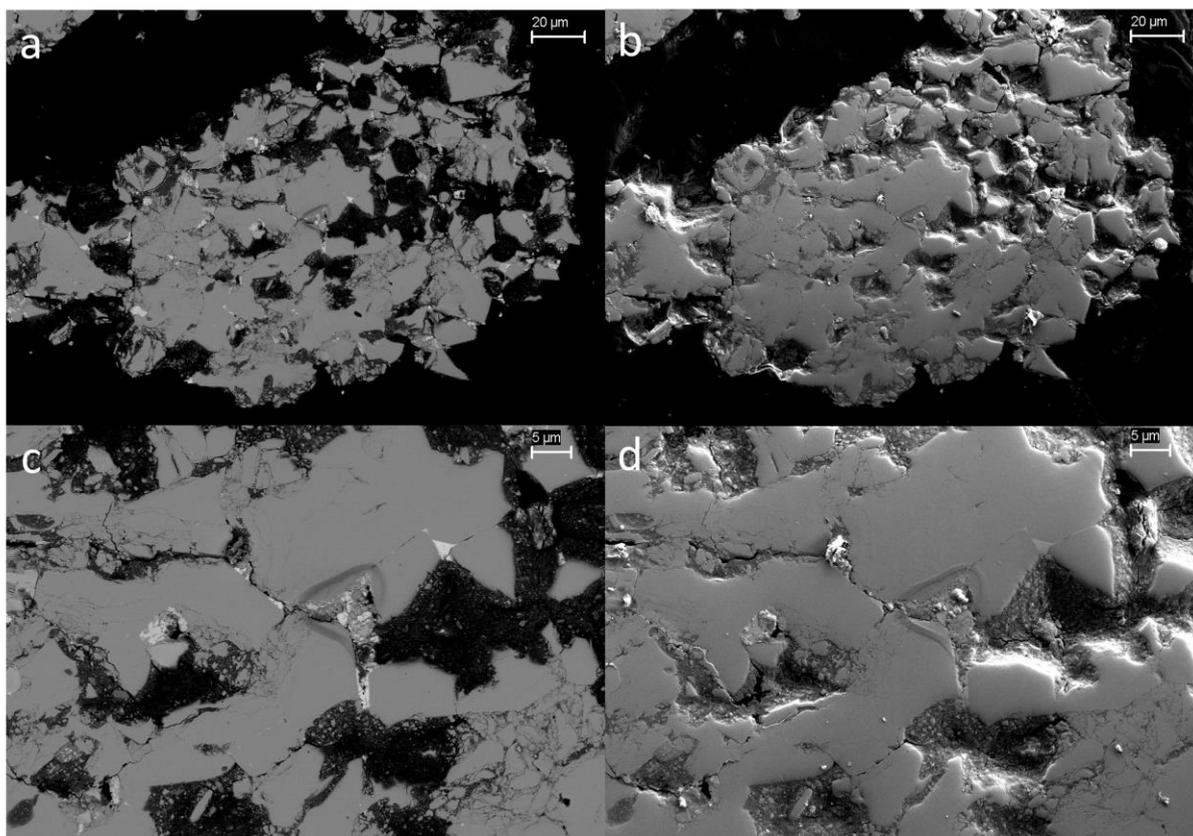


Figure 2. Microstructure of powders obtained from M1 magnet after HD at 100 °C observed in BSE (a&c) and in SE (b&d). In BSE gray contrast correspond to hydride main $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase and white contrast to remaining Nd-rich phase.

Effect of a thermal treatment on magnetic properties

Magnetic properties of powders with a 100-200 μm grain size, obtained after HD and dehydrogenation at 550°C, for M1 and M2 magnets are plotted on Figure 3, dotted lines. As explained in section 2 powders obtained are non-coercive due to their microstructures. Coercivity is a microstructure related property, which is given by an effective magnetic decoupling of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnetic grains, by the Nd-rich grain boundary phases. Remaining hydrogen in the powder, especially in the Nd-rich phases, also explains these poor properties. Indeed, partial dehydrogenation was performed at 550°C as the complete dehydrogenation occurs at around 700°C.

A dehydrogenation step at 750°C was applied on these powders followed by a thermal treatment at 900°C-2h and another plateau at 500°C-2h. Table 3 shows that a very significant gain can be observed on magnetic properties (remanence and coercive field) due to both a complete dehydrogenation and a recombination of the Nd-rich phase thanks to the thermal treatment close to typical sintering and annealing temperatures of NdFeB fully dense magnets. Coercivity of powders obtained from M2 magnets are higher than those for M1 magnets, which is related to the presence of Dy in the M2 magnet. Decent magnetic properties are obtained and could probably fit some applications. However, remanence, coercivity and rectangularity of the demagnetization curve are still significantly low compared to those of the initial magnet and could be furthermore improved by an optimized annealing.

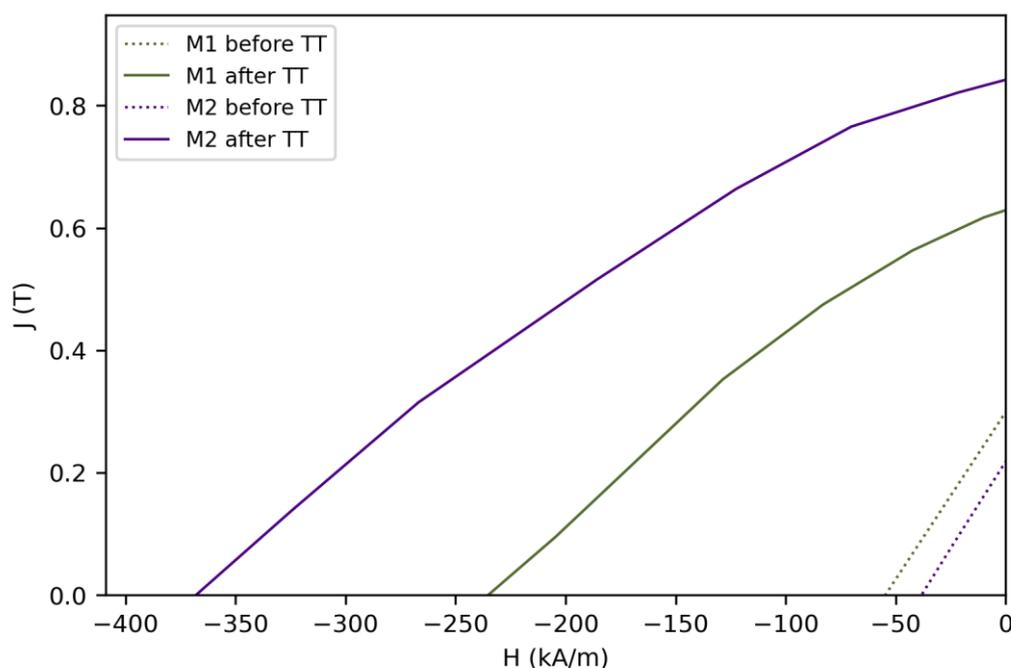


Figure 3. Demagnetization curves of HD powders from M1 and M2 magnets sieved at 100-200 μm . Both powders were also dehydrogenated at 750°C and then subjected to a thermal treatment at 900°C-500°C.

Table 3: Magnetic properties of HD powders before and after a Thermal Treatment (TT) at 900°C-500°C

Initial magnet	Before TT		After TT	
	Jr (T)	Hcj (kA/m)	Jr (T)	Hcj (kA/m)
M1	0.16	26	0.64 (+300%)	225 (+765%)
M2	0.21	48	0.84 (+300%)	354 638%

Conclusion

Three types of wind turbine EOL magnets were analysed during a HD+TT process aiming at producing bonded magnets. Particle size distribution of powders obtained after HD showed a clear dependence on hydrogenation temperature which itself depends on initial composition of the magnets. This suggests that the composition of the initial magnets affects the performances of the recycling process. After HD, powders obtained were proven to be non-coercive and impossible to use as it in a bonded magnet. Nevertheless the interest of a thermal treatment to recover the microstructure of the magnet has been emphasized. Obtained powders have poor magnetic properties compared to what could be achieved out of a HDDR treatment. However they could probably fit some applications asking only for low performance magnets. Further work is currently ongoing in order to investigate the effect of this additional thermal treatment and evaluate the feasibility of such a process for bonded magnets applications.

Acknowledgements

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