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Citation: *J. Appl. Phys.* **111**, 07A725 (2012); doi: 10.1063/1.3677761

View online: <http://dx.doi.org/10.1063/1.3677761>

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Properties of hydrogenation-disproportionation-desorption-recombination NdFeB powders prepared from recycled sintered magnets

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(Presented 3 November 2011; received 22 September 2011; accepted 16 November 2011; published online 8 March 2012)

The effects of the hydrogenation-disproportionation-desorption-recombination (HDDR) processing conditions on the microstructure and magnetic properties of NdFeB powders prepared from recycling sintered N42 grade magnets were evaluated. Temperatures below 840 °C and above 900 °C are deleterious to HDDR powders' properties. The hydrogen pressure, ranging from 60 to 135 kPa, has a major influence on the remanence compared to that on the intrinsic coercivity. The best magnetic properties ($J_r = 0.58$ T and $\mu_0 H_c = 1.15$ T) were obtained with $T_{recomb} = 860$ °C, $P_{H_2} = 135$ kPa, and $t_{recomb} = 330$ s. Such coercivity value corresponds to 93% of the starting material, not achieved yet by optimizing the HDDR process and without using Dy. © 2012 American Institute of Physics. [doi:10.1063/1.3677761]

I. INTRODUCTION

Ever since the NdFeB compound was reported^{1,2} the used amount of such material rises every year, achieving 691580 tons in 2008.³ Based on this number, it is imperative the reuse of the discarded material because of the high price of the rare earth elements.

Attempts to recycle NdFeB sintered pieces to prepare new magnets have been reported.⁴⁻⁶ The remanence (J_r) and intrinsic coercivity ($\mu_0 H_c$) of the recycled material are usually inferior to those of the starting material, although it still might represent a replacement choice of ferrites since the production cost is reduced.

The aim of the present work is the preparation and the characterization of NdFeB powders from recycled sintered pieces by the hydrogenation-disproportionation-desorption-recombination (HDDR) process without any additive and/or surface modifier with Dy which might preclude the magnet production.

II. EXPERIMENTAL

NdFeB sintered magnets (grade N42) without alloying elements with $J_r = 1.29$ T, $\mu_0 H_c = 1.23$ T, and $T_{Curie} = 310$ °C were used as a starting material. Firstly, the samples were thermally demagnetized and their coating was removed by grinding. Secondly, small pieces of the magnets (< 6 mm) were placed in a hydrogenation vessel that was evacuated to mechanical-pump pressure. Next, the HDDR processing parameters were changed in order to optimize the magnetic properties: temperature (800 °C $\leq T_{recomb} \leq 920$ °C) and hydrogen pressure (60 kPa (0.6 bar) $\leq P \leq 150$ kPa (1.5 bar)); the recombination step was carried out under vacuum (mechanical-pump pressure) with a constant time ($t_{recomb} = 330$ s)

for all samples. At the end of each run, a fast cooling was provided by a water-cooled coil on the vessel for 1 h.

(Micro) structural characterizations of the HDDR powders were carried out by high resolution scanning electron microscopy and X-ray diffraction (XRD) (Cr radiation). The magnetic properties of the powders were obtained by a vibrating sample magnetometer with a maximum applied field of 2 T at room temperature without prior magnetization. For remanence determination, it was considered $\rho_{NdFeB} = 7500$ kg/m³. No demagnetization correction was applied to the results.

III. RESULTS AND DISCUSSION

The desorption-recombination (DR) temperature was the first processing condition evaluated. Figure 1 depicts its influence on the magnetic properties of NdFeB powders for a constant hydrogen pressure ($P_{H_2} = 90$ kPa). The remanence and the intrinsic coercivity are enhanced with the temperature increase from 800 °C to 840 °C. However, a kink was identified in the second quadrant of the hysteresis loop of these powders (not shown); kinks were also observed in Nd₁₂Fe₈₂B₆ powders prepared by HDDR combined with mechanical milling.⁷ They are usually attributed to one (or even both) of the following reasons: (i) the presence of a soft magnetic phase together with the hard magnetic phase; and (ii) a bi-modal grain (crystallite) size distribution. However, due to the reduced temperature of the DR reaction of these powders (< 850 °C), the second possibility is discarded. Therefore, the probable reason for the observed kinks is an incomplete DR reaction. In order to confirm this assumption, Fig. 2 depicts the XRD pattern of the HDDR powder prepared with $T_{recomb} = 800$ °C. Four phases have been found: Nd₂Fe₁₄B, Nd, neodymium oxide, and Fe. The first phase was already expected where the second (Nd) might be related to the excess of it in the composition of the N42 sintered magnet to aid sintering as well as with the incomplete recombination reaction. Concerning the neodymium oxide, it

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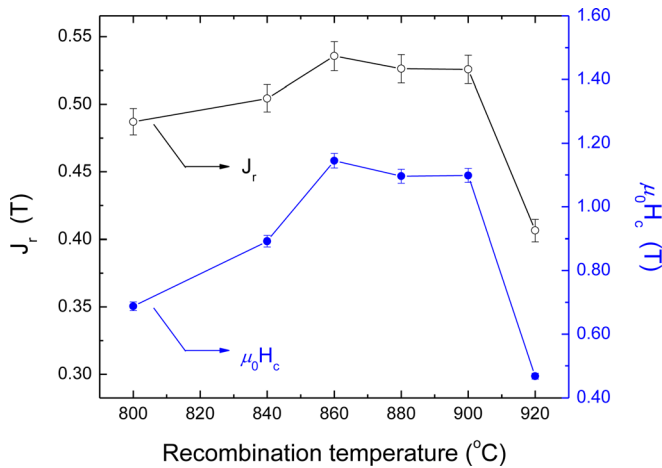


FIG. 1. (Color online) Influence of the HDDR recombination temperature on the magnetic properties of NdFeB powders. The H_2 pressure is constant (90 kPa). Error bars = 2%.

is present as a function of the affinity of the oxygen with Nd during the preparation of the samples (which will be more evident in low-vacuum procedures), leading to the formation of free-Fe phases and, consequently, to the reported kink in the demagnetization curve. During the DR stage, the minimum obtained pressure is about 10 Pa (10^{-4} bar) for the powder with the best magnetic properties; for comparison, the DR reaction was carried out under a pressure of about 10^{-3} Pa in Ref. 8.

In the temperature range $860^\circ\text{C} \leq T_{\text{recomb}} \leq 900^\circ\text{C}$, the magnetic properties of the HDDR powders are approximately constant ($J_r \sim 0.53$ T and $\mu_0 H_c \sim 1.10$ T) although a dropping trend can be identified. This fact indicates that, under such temperature and hydrogen pressure conditions, no significant microstructural changes should be expected. Regarding J_r , the obtained values are 15% inferior to that previously reported for NdFeB powders without alloying elements prepared by HDDR (about 0.61 T in Ref. 8). However, it was already suggested that NdFeB alloys with

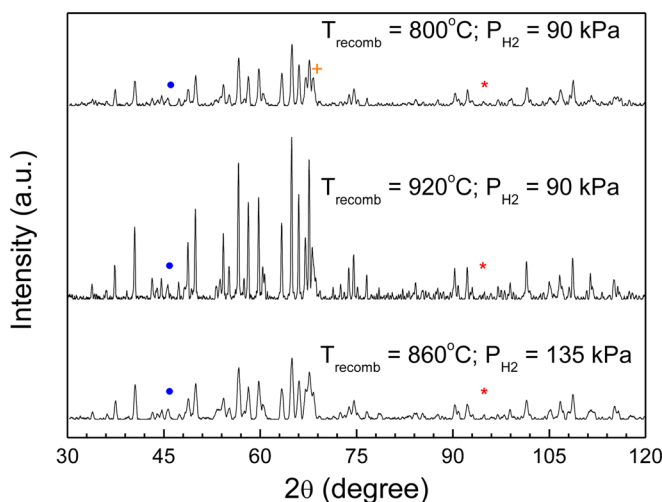


FIG. 2. (Color online) X-ray diffraction patterns of HDDR powders prepared under distinct conditions. The neodymium oxide (\bullet), Nd ($*$), and Fe ($+$) peaks are identified in the pattern. The non-identified peaks refer to the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase.

no alloying elements are isotropic after the HDDR treatment. This fact was attributed to a higher degree of sensibility of such alloys to H_2 , indicating a possible existence of a quite narrow processing window in order to obtain anisotropic powders.⁸

Increasing the DR temperature to 920°C the magnetic properties are strongly reduced despite the DR time is short compared to other HDDR cycles reported in literature.^{9,10} Compared to the best magnetic properties (obtained at 860°C), $\Delta J_r = -18\%$ and $\Delta \mu_0 H_c = -55\%$. For this specific case, the grain (crystallite) size growth can be pointed as the main source for such reduction in the magnetic properties, although the presence has also been verified of the neodymium oxide phase (no kinks in the demagnetization curve have been observed). An estimation carried out by high resolution scanning electron microscopy (HRSEM) images showed that the grain size of this HDDR powder is larger than 600 nm, twice the mono-domain particle size of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase.¹¹ This large grain size is also qualitatively evidenced by the XRD pattern in Fig. 2; it is clear that the peaks of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnetic phase of this powder are sharper compared to the material treated at 800°C .

The influence of the hydrogen pressure on the magnetic properties of the NdFeB HDDR powders was also evaluated at the temperature at which the best magnetic properties were previously determined (860°C), and is presented in Fig. 3. Both final magnetic properties are minimum with $P_{H_2} = 60$ kPa and are improved with the increase of the hydrogen pressure to 90 kPa. For pressures up to 150 kPa, J_r and $\mu_0 H_c$ follow distinct behaviors: the former reaches its maximum at 135 kPa (0.58 T), which corresponds to the pressure at which the recombination of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase seems to be maximized and the highest magnetic properties are obtained, whereas the latter is independent of the H_2 pressure. Concerning the intrinsic coercivity, its behavior is in qualitative agreement with previous results reported for the $\text{Nd}_{12.6}\text{Fe}_{81.4}\text{B}_6$ alloy powder,⁸ although the $\mu_0 H_c$ absolute value in the present work is 30% superior. Its XRD pattern is comparable to that of the powder prepared at 800°C

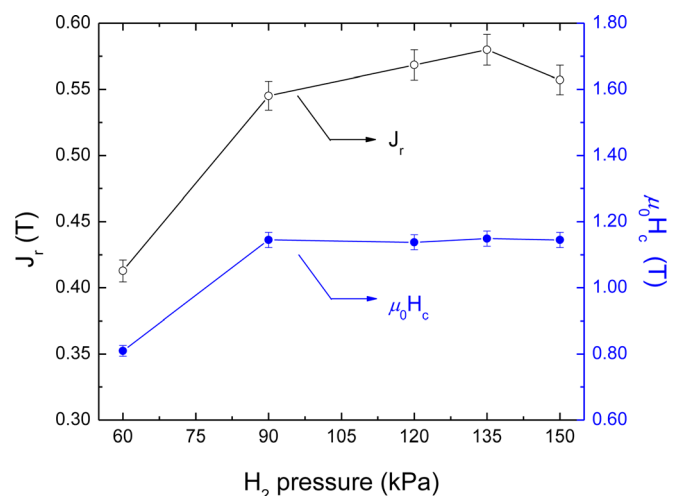


FIG. 3. (Color online) Influence of the H_2 pressure on the magnetic properties of NdFeB powders. The recombination temperature is constant (860°C). Error bars = 2%.

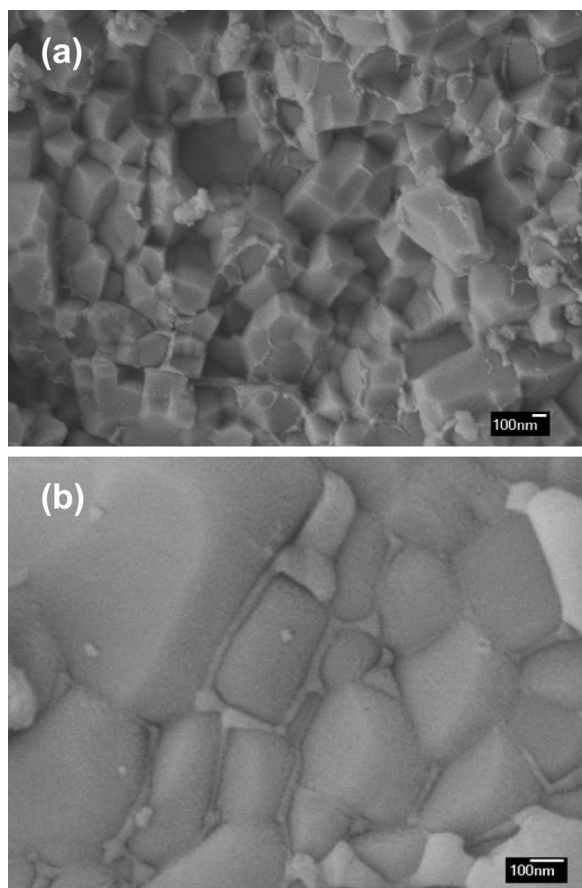


FIG. 4. SEM/FEG images of the HDDR optimized powder: (a) fracture surface and (b) one particle surface.

previously discussed (see also Fig. 2), although no soft magnetic phases have been found and, consequently, no kinks have been observed as shown later. Regarding its microstructure, the HDDR magnetic optimized powder has particles with irregular surface and flat edge grains with a size ranging between 250 and 400 nm, shown in Figs. 4(a) and 4(b). It is worth pointing out that to the best of our knowledge, this is the first time that the coercivity of a NdFeB powder prepared from recycling sintered NdFeB magnets was almost fully recovered (over 93% compared to that of the starting material) only optimizing the HDDR processing conditions and without using Dy. Besides, both final magnetic properties of the HDDR optimized powder are in the same order of magnitude (as $\mu_0 H_c$) or even superior (as J_r) compared to those reported for SmCo-based samples prepared by HDDR.¹²

The demagnetization curve of the HDDR optimized powder at room temperature is shown in Fig. 5. The reduced squareness is attributed to the low degree of crystallographic orientation of the recombined Nd₂Fe₁₄B phase. However, it is possible to use this HDDR optimized powder to prepare bonded magnets. Assuming the powder density is 7500 kgm⁻³ with a loading of 80% (in vol.) of magnetic particles in the magnet, a bonded magnet with $J_r \sim 0.48$ T and $\mu_0 H_c \sim 1.15$ T is expected. These values are higher compared to those of any known ferrite magnet (about 0.45 T either for J_r or $\mu_0 H_c$) and might be considered a low cost replacement choice of magnetic oxides because the starting

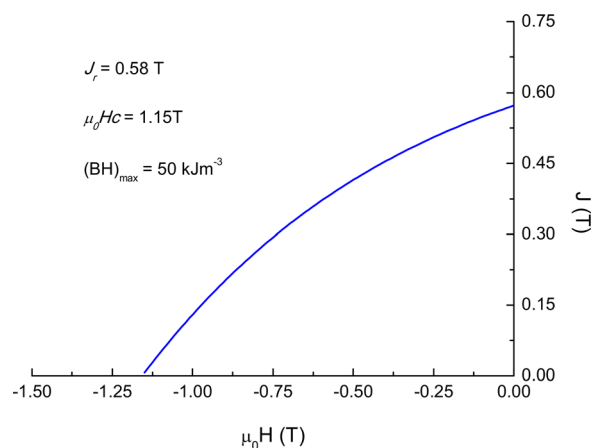


FIG. 5. (Color online) Demagnetization curve of the HDDR powder with the best magnetic properties: $T_{recomb} = 860$ °C, $P_{H2} = 135$ kPa, and $t_{recomb} = 330$ s.

material has already been discarded and no further process, except the HDDR and the binder addition, are needed.

IV. CONCLUSIONS

NdFeB isotropic powders were prepared from recycling N42 sintered magnets by the HDDR process. The best magnetic properties ($J_r = 0.58$ T and $\mu_0 H_c = 1.15$ T) were obtained with $T_{recomb} = 860$ °C, $P_{H2} = 135$ kPa, and $t_{recomb} = 330$ s.

The short recombination time is an advantage for large scale production. Furthermore, the obtained magnetic results might have a beneficial economical (and ecological) impact because the magnetic properties of the bonded magnets prepared with such powders will be superior to those of any known ferrite, using a discarded material with a lower cost and without Dy.

ACKNOWLEDGMENTS

The authors thank IPT and IPEN for their facilities. E.A. Périgo also thanks FAPESP for the partial financial support of this investigation (proc. 2010/08018-8).

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