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Anisotropic powder from sintered NdFeB magnets by the HDDR processing route

R.S. Sheridan, R. Sillitoe, M. Zakotnik, I.R. Harris, A.J. Williams*

School of Metallurgy and Materials, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

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ABSTRACT

Sintered NdFeB-based scrap magnets were recovered and processed using the HD and HDDR routes. The effects of varying the HDDR processing temperature were investigated (over the range 835–930 °C). The disproportion was carried out with a pressure ramp to a maximum of 1000 mbar hydrogen pressure with a 1 h hold time at each step and the optimum recombination conditions were set at 100 mbar with a 20 min hold time. Anisotropic NdFeB powder was produced in all cases with the best magnetic properties achieved at a processing temperature of 880 °C, producing powder with a remanence of 1.10($\pm$ 0.02) T and an intrinsic coercivity of 800 ($\pm$ 16) kA m^{-1} and giving a $(BH)_{max}$ of 129($\pm$ 2.5) kJ m^{-3}.

1. Introduction

Since their development in 1984 [1], neodymium iron boron magnets have found extensive use in personal computers mostly in the voice coil motors of hard disk drives and also in the CD and DVD-ROM drives. Due to the short lifetime of personal computers there is now a large amount of scrap sintered NdFeB magnets that are currently going into landfill or recycled along with other iron-based scrap. Recent large increases in the price of rare earth elements and concerns over the security of supply are making it increasingly attractive to recycle these magnets. Although each hard disk drive uses only a small amount of magnet (~15–20 g) [2] there are other applications using much larger volumes of magnets that will be available in the near future. One example is the Toyota PRIUS, which uses about 2 kg of sintered NdFeB magnets in each vehicle in the electric motor and in the generator employed in regenerative braking.

Recently reports have been made on the use of hydrogen for the recycling of NdFeB sintered magnets [2]. The hydrogen decrepitation (HD) process has been used to turn the magnets into a demagnetised powder [3]. Potentially, this provides a means of separating the NdFeB magnets from any protective coating as well as from other scrap materials [4]. The powders can be reprocessed into sintered magnets with properties comparable to those of the starting material [2,5]. Alternatively, the powder can be used in the production of resin bonded magnets either by degassing the hydrogen under vacuum at ~750 °C [2] and mixing with an appropriate binder or by further processing of the powder by the Hydrogenation Disproportionation Desorption Recombination (HDDR) route [6,7]. The HD degassed powder is anisotropic but due, in part, to the small number of grains per particle it is susceptible to corrosion and degradation of the magnetic properties [8]. The HDDR process leads to a significant refinement of the grain size to approximately 0.3 μm [9–11] and therefore the powder particles consist of many more grains than the HD powder. This results in the HDDR powder being far more stable to corrosion than the HD powder but as the refined grains are usually isotropic, there is a significant reduction in the remanence. To date, there have been reports of isotropic powder produced by only the HDDR processing of sintered NdFeB magnets [8].

There are many reports on the production of anisotropic HDDR powder from cast NdFeB-based alloys. Initially this was achieved by the use of additions such as cobalt, gallium, zirconium or niobium [9], which have been demonstrated to alter the kinetics of the HDDR process. It has also been shown that additions are not required in order to achieve magnetic anisotropy [11]. Careful control of hydrogen pressure during the HDDR heating cycle can be used to control the rates of reaction that, under certain circumstances, can lead to the production of anisotropic powder [12]. After the initial HD process, the NdFeB alloy is heated in vacuum to the processing temperature at which hydrogen is introduced to the degassed material to cause disproportionation at a slower rate than in conventional isotropic HDDR processing. This has been termed the v-HD treatment [13,14]. After disproportionation is complete, desorption and recombination are induced by a "slow" reduction of the hydrogen pressure by flushing the hydrogen from the system with a flow of argon gas

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* Corresponding author. Tel.: +44 121 414 3959.
E-mail address: a.j.williams@bham.ac.uk (A.J. Williams).

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prior to evacuation with a rotary pump. This has been termed the s-DR process [13,14]. The entire cycle has been referred to as dynamic HDDR or d-HDDR [15]. In this case rather than a vacuum, low hydrogen pressure is applied during the heating cycle and a slow reduction of the pressure at the start of the recombination stage has been used instead of flushing with argon. The work presented in this paper processes scrap sintered magnets using the v-HD process to prevent disproportionation occurring until the hold temperature has been reached whereas the slow recombination is induced by reducing the hydrogen pressure without the introduction of argon, as used in the d-HDDR process.

2. Materials and methods

Scrap sintered magnets, supplied by Arnold Magnetics Ltd, were used throughout this study. Ion coupled plasma (ICP) analysis determined the magnets to have a composition: $Nd_{13.4}Dy_{0.8}Al_{0.7}Nb_{0.3}Fe_{78.5}B_{6.3}$ (atomic%) and an oxygen content of 4300 ppm, with remanence of 1.36 T, intrinsic coercivity of 860 $kA\,m^{-1}$ and maximum energy product of 340 $kJ\,m^{-3}$ as measured using a permeameter (no demagnetization factor). The sintered magnets were hydrogen decrepitated at room temperature under 5 bar of hydrogen pressure. The powder was then stored under argon in a glovebox. HDDR processing was performed on 15 g batches of the powder, in an Inconel tube furnace. A computer-controlled system was constructed in order to accurately control the hydrogen pressure within the tube, using mass flow controllers. The powder was first heated under vacuum (rotary pump, $\sim 10^{-1}$ mbar), at a ramp rate of 800 °C h^{-1}, to a temperature T, which, for these studies, was varied between 835 and 930 °C. When the sample reached the set temperature the hydrogen pressure in the chamber was increased at a rate 16 mbar min^{-1} to a pressure of 1000 mbar. This pressure was then held for a further hour, after which the hydrogen pressure was reduced to 100 mbar at a rate of 100 mbar min^{-1}. After a 20 min hold at 100 mbar the pressure was further reduced at a rate of $\sim$10 mbar min^{-1} until the pressure was reduced to that of the rotary pump vacuum. At this point the powder was cooled quickly by rolling the furnace off the Inconel tube; cooling of the powder to below 500 °C occurred in less than 5 min. The processing conditions are shown schematically in Fig. 1. Powder samples of $\sim$30 mg were mixed with wax, heated to melt the wax and then aligned in a field of 1.5 T while the wax was allowed to solidify. The samples were then pulse magnetized in a field of 6 T, prior to measurement of the magnetic properties in the alignment direction using a Lakeshore 7300 VSM. The samples where then remagnetised in the pulsed field at 90° to the alignment direction and then measured in that direction. The specific magnetisation values from the VSM were converted to polarization using a theoretical density of 7.5 g cm^{-3}. There was no attempt to predict a self-demagnetization factor for the measurements of the samples due to the unpredictable particle shapes and sizes and so the magnetic properties remained uncorrected.

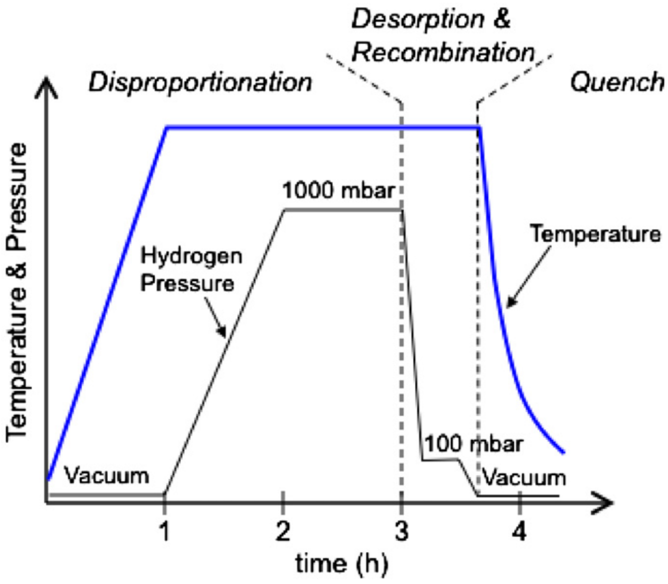

Fig. 1. Schematic showing the variation of temperature and pressure during the HDDR process.

3. Results and discussion

The pressure of hydrogen and the input flow rate into the chamber during disproportionation at 890 °C are shown in Fig. 2. In the first 10 min, as pressure increases there is a peak in the input flow rate of hydrogen, peak A in Fig. 2, which corresponds to the absorption of hydrogen by the Nd-rich phase, as shown in Eq. (1) (where $x \sim 1$, and is dependent on temperature and pressure). The Nd-rich phase has been reported to contain $\sim$5 at% iron [16], which may be forced out of solution when hydrogen is absorbed [17], although for simplicity this is ignored in Eq. (1). In the example shown in Fig. 2, this lower pressure reaction is seen as a double peak; however, this is not reproducible and in some cases it is a single peak and in other cases more than two peaks. This may relate to variations in surface oxidation, which could affect the time needed to initiate hydrogen absorption. As pressure increases more hydrogen is introduced into the system; the data is not corrected for the amount of hydrogen needed to fill the reaction vessel so an input flow of hydrogen does not necessarily equate to a reaction taking place. At higher pressure, in this case at around 600 mbar (after $\sim$40 min), the input flow rate starts to increase and another peak is observed—peak B in Fig. 2. This peak relates to the disproportionation of the $Nd_2Fe_{14}B$ phase as shown by the reaction in Eq. (2):

$$Nd + xH_2 <-> NdH_{2x} \tag{1}$$

$$Nd_2Fe_{14}B + 2xH_2 <-> 2NdH_{2x} + 12Fe + Fe_2B \tag{2}$$

The pressures at which these reactions begin provide an indication of the equilibrium pressure of these reactions, i.e. the pressure above which the reaction proceeds to the right and below which the reaction proceeds to the left. These reactions have this equilibrium point because the Gibbs free energy of metal hydrides (in this case neodymium hydride) decreases, i.e. becomes more stable, with increasing hydrogen pressure, resulting in the right hand side exhibiting a lower Gibbs free energy with increasing hydrogen pressure, while the left hand side is relatively unaffected. As a consequence, with increasing pressure above the equilibrium pressure, the composition of the neodymium hydride will become richer in hydrogen, i.e. x in Eqs. (1) and (2) will increase. Metal hydrides are also unstable with increasing temperature, making the right hand side of the equations less stable, and thus, the equilibrium pressure increases with increasing temperature. This can be seen in Fig. 3, which plots the onset of the disproportionation reaction against temperature. The dotted line indicates the predicted trend with increasing disproportionation pressures as performed at 930 °C. Using the existing experimental set-up and conditions used it was not possible to determine any increase in the pressure related to the onset of absorption by the Nd-rich phase, which in all cases appeared to occur immediately on input of hydrogen to the system. The data in Fig. 3 indicate slightly higher onset pressures than those previously reported [11,14,18]; however, this could be