

Fabrication of Sub-Micron Near Stoichiometric NdFeB Magnetic Powder through HDDR Processing Route

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Abstract—Homogenized Near-Stoichiometric NdFeB alloys of composition $Nd_{12.7}Fe_{81.3}B_{6.0}$ and $Nd_{12.2}Fe_{81.2}B_{5.9}Zr_{0.1}$ were hydrogenated and disproportionated at 850°C for 30 minutes. All $Nd_2Fe_{14}B$ phase were fully converted into NdH_3 , Fe_3B and Fe . The recombination process produces sub-micron sizes ($\sim 0.3 \mu m$) of $Nd_2Fe_{14}B$ grains at an optimum temperature of 880°C. Zr-addition into the NdFeB alloy inhibits grain growth during the recombination process.

Index Terms—Near Stoichiometry NdFeB, HDDR, isotropic powder

I. INTRODUCTION

The hydrogenation disproportionation desorption and recombination (HDDR) process is a promising new processing route for the production of NdFeB powder. When NdFeB-type alloys are heated in hydrogen to above 650°C, the $Nd_2Fe_{14}B$ matrix phase disproportionates into a mixture of NdH_3 , Fe and Fe_2B [see for example 1, 2]. It is possible to recombine such a disproportionated mixture by heating under vacuum, thus producing a fine-grained of $Nd_2Fe_{14}B$. The powders produced by the HDDR process commonly are isotropic. McGuinness et al [3] pointed out that addition of Zr can induce magnetic anisotropy for the HDDR NdFeB powders, hence improves the hard magnetic properties of bonded magnets. The additions, such as Co, Ga or Zr, used to produce anisotropy in earlier work have been shown not to be necessary. Highly coercive isotropic and anisotropic powder can be produced using the ternary alloy by controlled HDDR treatment. The processing conditions, such as temperature and pressure, have a significant effect on anisotropy inducement. Sugimoto et al [4] have presented that anisotropic powders can be prepared from the ternary NdFeB alloy by controlling the rate at which the hydrogen pressure decreases in disproportionation stage and raising the vacuum temperature to higher than 800°C.

In this work, the near stoichiometric compositions of Nd-

Fe-B were selected as they contained high proportion of $Nd_2Fe_{14}B$ phase. Zirconium (0.1 at %) was added into the near stoichiometric NdFeB alloy to reduce the formation of Fe dendrites during casting [5]. The correlation between magnetic properties and the grain structure of $Nd_2Fe_{14}B$ produced in recombination stage was investigated.

II. TECHNICAL WORK PREPARATION

The composition of the studied alloys was $Nd_{12.7}Fe_{81.3}B_{6.0}$ and $Nd_{12.2}Fe_{81.2}B_{5.9}Zr_{0.1}$. The alloys were prepared by induction melting followed by high temperature homogenization. Homogenization has to take place due to the high proportion of Fe dendrites within the $Nd_2Fe_{14}B$ phase. The homogenized ingots were broken-up into small pieces and decrepitated at 120°C prior to the HDDR treatment. A schematic treatment pattern for the HDDR process is shown in Fig. 1. The disproportionation process was carried out at 850°C for 30 minute under 1 bar hydrogen pressure. The desorption and recombination process were carried out by evacuating the furnace tube until it reached a vacuum of 10^{-1} mbar and hold at temperature range of 790°C to 920°C for another 30 minutes. Cooling to room temperature with a cooling coil round the furnace tube was implemented.

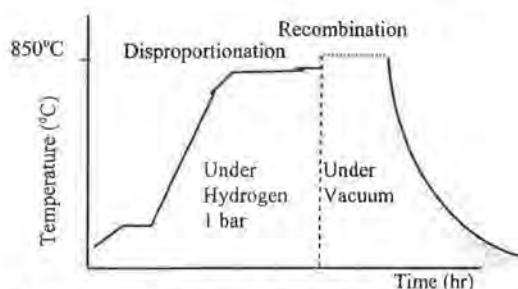


Fig. 1. Schematic illustration of the HDDR pattern used in this study.

The magnetic properties were measured using a VSM with a maximum field of 1.1T after applying a pulsed field of 1.4T to the aligned and fixed powders inside sample holder. (The magnetic measurement techniques used have been described in detail elsewhere [6]). The degree of anisotropy (DOA) was calculated by the following equation:

$$DOA = (Br_{\parallel} - Br_{\perp}) / (Br_{\parallel}) \quad (1)$$

where Br_{\parallel} and Br_{\perp} were the remanence of the sample parallel and perpendicular to the alignment field.

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Microstructures changes were observed using an optical microscope and high resolution SEM. The chemical components of the sample were analyzed by the X-ray diffractometer (XRD).

III. RESULTS AND DISCUSSIONS

A. Effects of disproportionation time on the near stoichiometric alloy

Disproportionation of $Nd_2Fe_{14}B$ was found difficult to complete. As presented in Fig. 2(a) coexisting diffraction peaks from initial 2-14-1 phase and the newly formed disproportionated mixture i.e. NdH_2 , $\alpha-Fe$ and Fe_2B [see for example 7,8] were detected on the alloy after disproportionate at $850^\circ C$ for 30 minutes. It is probably due to minimal amount of grain boundary phase and a large initial grain size. It is much more difficult in the Zr-containing alloy due to the existence of the ZrB_2 phase that acted as a barrier limiting hydrogen diffusion [9]. All 2-14-1 peaks were disappeared only after 60min in disproportionation stage.

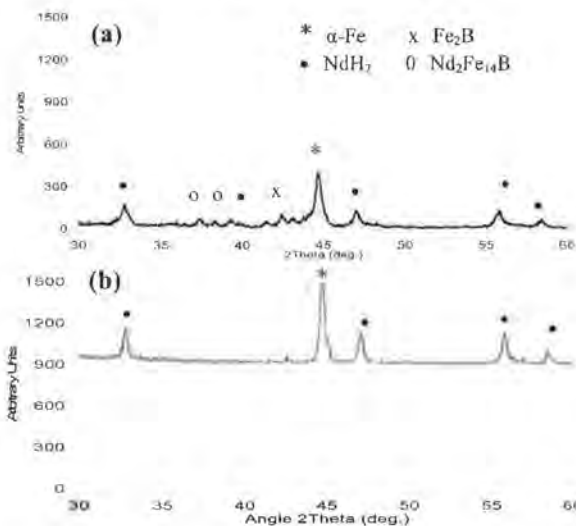


Fig. 2. XRD traces for $NdFeBZr$ alloy disproportionated (a) 30 and (b) 60 minutes at $850^\circ C$.

The initiation of the disproportionation reaction (Fig. 3) divides the original 2-14-1 grains into two regions; fine disproportionated regions (in darker gray) and non-disproportionated regions (in much lighter gray). The details of the fine disproportionated regions, that appeared in the TEM as fine rods of NdH_2 embedded in the Fe matrix [10] cannot be seen in the micrograph at this magnification.

At relatively low temperatures, the decomposed structure is acicular but on further heating or for longer holding times at high temperature, it was found that this acicular structure tends to form a more spherical-like structure (Fig. 4). The existence of the coarsened acicular structure at a prolong disproportionation times caused the powder to become fully isotropic and will exhibit a low kinetic reaction for recombination [11].

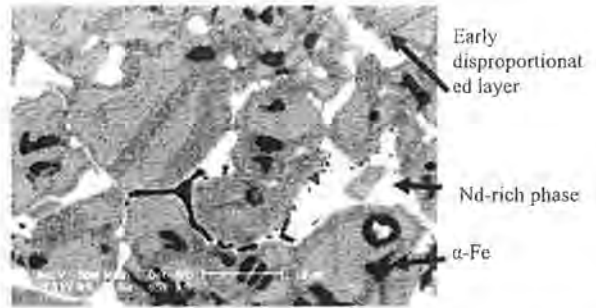


Fig. 3. A Backscattered SEM image for the non-Zr containing alloy at an early stage of the disproportionation reaction at $850^\circ C$.

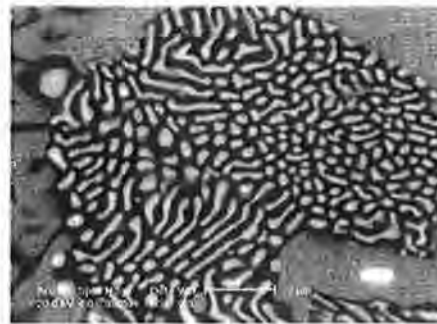


Fig. 4. A backscattered SEM image showing the coarse acicular structure in non-Zr containing sample after 2 hours in the disproportionation stage ($850^\circ C$)

B. Effects of recombination temperature on magnetic properties of the hddr powder

A typical XRD trace for the non-Zr and Zr-containing sample recombined at $850^\circ C$ are displayed in Fig. 5. All the diffraction lines were indexed according to the $Nd_2Fe_{14}B$ phase, indicating that all the disproportionated mixture had fully recombined to $Nd_2Fe_{14}B$.

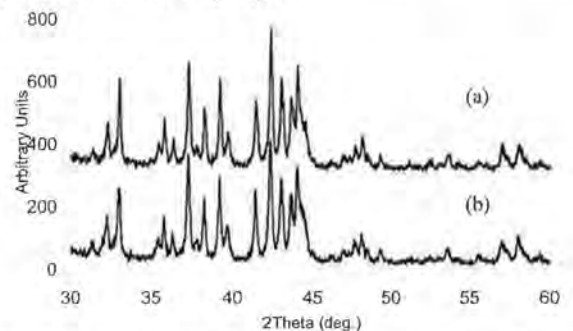


Fig. 5. XRD traces of (a) Zr- and (b) non-Zr containing powders after recombination at $880^\circ C$

Fig. 6 shows the demagnetisation curves for the recombined non-Zr and Zr-containing powder, measured in the easy direction (labelled as //). For clarity, the magnetic responses recorded in the hard direction (labelled as \perp) are not shown in the figure but the associated magnetic properties derived from the curves for these samples are listed in Table 1.

All powders are considered to be isotropic as indicated by low values of DoA (0% is a fully isotropic state). Powders processed at $850^\circ C$ and $880^\circ C$ contain only ~15 to 30% of the possible full alignment of 2-14-1 grains. The DoA values

increase with the operating temperature, probably because the disproportionation and recombination reaction becomes completed. A much lower degree of DoA was observed in the Zr-containing alloy, as Zr retards the completion of the disproportionation reaction.

TABLE I.
MAGNETIC PROPERTIES OF THE NON-ZR AND ZR-CONTAINING HDDR TREATED POWDER

Non-Zr containing powder				
Temp (°C)	790°C	850°C	880°C	920°C
Br // (T)	0.65	0.78	0.74	0.64
iHc (kA/m)	485	470	550	440
Br ⊥ (T)	0.54	0.56	0.51	0.60
iHc⊥ (kA/m)	500	480	545	500
DoA (%)	17	28	31	6
Zr-containing powder				
Temp (°C)	790°C	850°C	880°C	920°C
Br // (T)	0.76	0.80	0.80	0.84
iHc (kA/m)	525	450	560	470
Br ⊥ (T)	0.74	0.68	0.62	0.65
iHc⊥ (kA/m)	525	450	560	480
DoA (%)	3	15	21	23

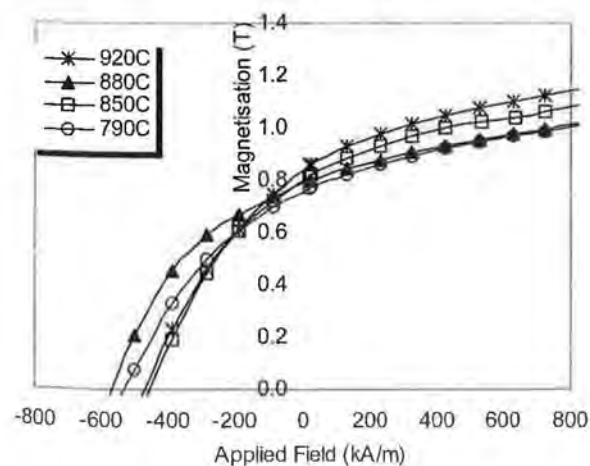
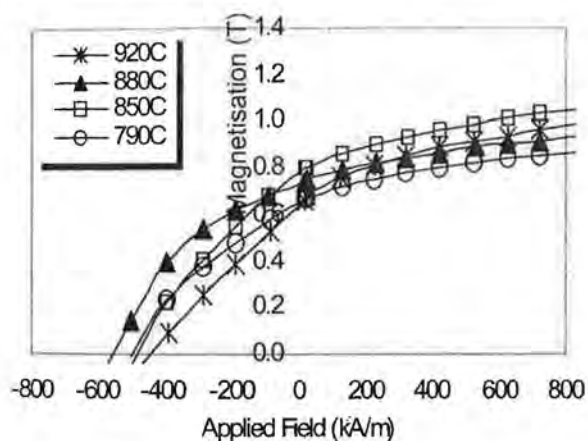


Fig. 6. Demagnetization curves of (a) non-Zr (b) Zr-containing NdFeB HDDR treated powder

The microstructure of the Zr- and non-Zr containing NdFeB HDDR treated powders recombined for 30 minutes at 920°C are shown in Fig. 7 and Fig. 8 respectively. As observed in the micrographs, the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain sizes were in the submicron range (below 300nm). Some grains are elongated in shape (~500nm), typical of over processed material, particularly in the non-Zr containing powder when processed at 920°C. The presence of such grains results in a decrease in the resistance to demagnetisation, which reduces the coercivity of the powder. The grain growth explains why a lower coercivity has been observed when the powder is treated at higher temperature (920°C). Powder treated at this temperature had the lowest coercivity (~440kA/m). The highest coercivity is only in the range of 550kA/m for the powder treated at 880°C, with also exhibits a low remanence (~0.8T).



Fig. 7. The HRSEM micrograph of the Zr- containing powders, recombined for 30 minutes at 920°C

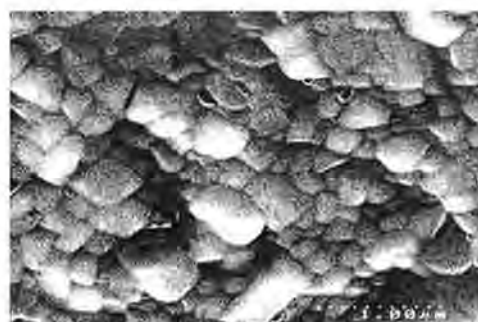


Fig. 8. The HRSEM micrograph of the non-Zr containing powders, recombined for 30 minutes at 920°C

IV. CONCLUSION

The production of anisotropic Zr-containing Near Stoichiometric NdFeB powder was practically difficult using the conventional HDDR. The optimum recombination temperature in the HDDR treatment was found to be 880°C. The addition of Zr prevents grain growth and allowed the coercivity to be enhanced.

V. ACKNOWLEDGMENT

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