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Consolidation of hydrogenation–disproportionation–desorption–recombination processed Nd–Fe–B magnets by spark plasma sintering

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ABSTRACT

We have successfully consolidated hydrogenation–disproportionation–desorption–recombination (HDDR) processed Nd–Fe–Co–Zr–B–Ga powder by spark plasma sintering (SPS). The field compacted samples were sintered at different temperatures (T_S) from 550 to 600 °C with compressive pressure of 80 MPa for 20 min. Microstructural investigations by transmission electron microscopy indicated that the sintered specimen exhibits $Nd_2Fe_{14}B$ grains of ~300 nm with Nd-rich grain boundary phase. The optimum magnetic properties of B_r: 1.22 T, H_c: 928 kA/m, $_BH_c$: 600 kA/m, $(BH)_{max}$: 210 kJ/m^3 were obtained in the sample sintered at 550 °C. The strategy for further improving the coercivity and remanence is discussed based on the microstructure-property relationships.

1. Introduction

Hydrogenation–disproportionation–desorption–recombination (HDDR) process is well established to produce anisotropic fine grained $Nd_2Fe_{14}B$ magnetic powder [1]. Mainly, this process involves two steps, hydrogenation–disproportionation (HD) and desorption–recombination (DR). During HD step, the Nd–Fe–B powder of slightly Nd-rich composition with respect to $Nd_2Fe_{14}B$ reacts with H_2 at elevated temperatures (~750 °C) in the presence of hydrogen pressure to form a very finely divided crystalline mixture of NdH_2, Fe and Fe_2B. This confines to the original monocrystalline particle and recombines these phases to form strongly textured $Nd_2Fe_{14}B$ grains of ~200–300 nm during the DR process [1–4]. Li et al. reported that the grain boundaries of optimally processed HDDR powders were enriched with Nd, but the grain boundary phase was thought to be still ferromagnetic [5]. Although anisotropic HDDR powders are now used to produce anisotropic bonded magnet only [6], it can be excellent raw material for anisotropic sintered magnets as well from their very fine grain size that is close to the single domain size (~240 nm) of $Nd_2Fe_{14}B$. However, its coercivity is only in the range of 1000 kA/m, which is much smaller than that can be expected from nearly single domain sized magnetically isolated particles [1]. For such applications, this powder should be consolidated into the bulk form without substantial grain coarsening. The conventional liquid phase sintering is not viable for the consolidation of fine grained $Nd_2Fe_{14}B$ powder as it destroys the fine grain structure leading to inferior hard magnetic properties. Hence, non-equilibrium sintering techniques such as the current applied pressure-assisted (CAPA) process [7], hot-pressed processes followed by die-upset [8,9] and back extrusions [10] were adopted to fabricate highly dense bulk magnet.

Recently the spark plasma sintering (SPS) technique is widely used for sintering new kinds of materials especially to consolidate ultrafine grain [11], nanostructure [12] and nano-powders [13]. In the SPS process, pulsed electric current flows directly through the sintered materials, and generates local heating at the particle interfaces [13]. The specimens are sintered by the Joule's heat that was generated in the sintered materials and also by the heat transfer from the graphite dies and punches [14]. The SPS process has some advantages such as, rapid heating and cooling, lowers the sintering temperature and time, inhibits the grain growth and saves energy. Recently, Yue et al. applied the SPS process to sinter the coarse grained $Nd_2Fe_{14}B$ magnet. These magnets possess

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distinctive microstructure than conventional sintered magnet with very high corrosion resistance [15].

In the present study, we have applied the SPS process to consolidate fine grained Nd–Fe–B anisotropic magnetic powder prepared by the HDDR process to explore the possibility of processing ultrafine grained anisotropy sintered magnets. The microstructure and magnetic properties of this material was studied in detail.

2. Experimental

An alloy with a nominal composition of $Nd_{13.0}Fe_{64.36}Co_{16.0}B_{6.50}Zr_{0.09}Ga_{0.5}$ was induction melted and then homogenized at 1110 °C for 16 h. The ingot was crushed into powders ranging in size from 50 to 300 μm. The powders were first heated for 1 h at 840 °C with an argon flow of 2 l/min in a closed chamber. After holding for 15 min, hydrogen was introduced with a flow current of 2 l/min. The HD process took 4 h with the stable H_2 flow. Then the DR process was started at an argon atmosphere of 5.33 kPa. The field compacted powder was sintered with specially designed graphite die using the spark plasma sintering machine (Sumitomo Coal Mining Company Model 1050) in a vacuum of $<10^{-3}$ Pa. The SPS conditions were as follows: (i) applied pressure ~80 MPa, (ii) sintering temperature 550–600 °C, and (iii) sintering time 20 min and then furnace allowed to cool to ambient temperature. The compressive load was applied perpendicular to the magnetic orientation of the green compact. The surface of the sintered compact was removed by grinding with emery paper and then the density was measured by the Archimedes method using pure water as the liquid medium. In order to investigate the phases presented in sintered compact, X-ray diffraction (XRD) analyses were carried out with a Rigaku RINT-2500 X-ray diffractometer using Cu K_α radiation. Primary microstructural investigation at lower magnification was observed by SEM and more detailed microstructural studies were carried out by high resolution transmission electron microscopy (HRTEM) (FEI Tecnai F30). In order to investigate the elemental distribution in the matrix phase, grain boundary and triple junctions, energy-filtered images using electron energy loss spectroscopy were also observed using a Gatan Imaging Filter (GIF) installed on a Tecnai G2 F30 microscope. Nd, Fe, Co, B, Ga, Zr and O images were formed by the jump ratio method using Fe L edge (708 eV), Co L edge (779 eV), B K edge (188 eV), Ga L edge (1115 eV), Zr M edge (180 eV) and O K edge (532 eV), respectively. Exposure times of 5–40 s were used to acquire each energy-filtered image. TEM foils were prepared using a precision ion polishing system (PIPS). The magnetic properties were evaluated using a vibrating sample magnetometer of 1600 kA/m.

3. Results

Fig. 1 shows XRD patterns of the sintered magnets at 550, 575 and 600 °C, respectively, with calculated tetragonal $Nd_2Fe_{14}B$ phase. One can clearly see that observed XRD patterns correspond to the $Nd_2Fe_{14}B$ phase and a small fraction of Nd-rich and $Nd_{1+\varepsilon}Fe_4B_4$ phases [16]. In order to check the degree of alignment of *c*-axis, the XRD patterns were measured for the magnet sintered at 550 °C in both perpendicular and parallel to the magnetic field direction. It can be observed from these XRD patterns that the large intensity of X-ray diffraction from (0 0 *l*) planes which inferred the anisotropic nature of the grains in sintered compact.

The magnetic hysteresis loops of the specimens measured along and perpendicular to the load direction are shown in Fig. 2.

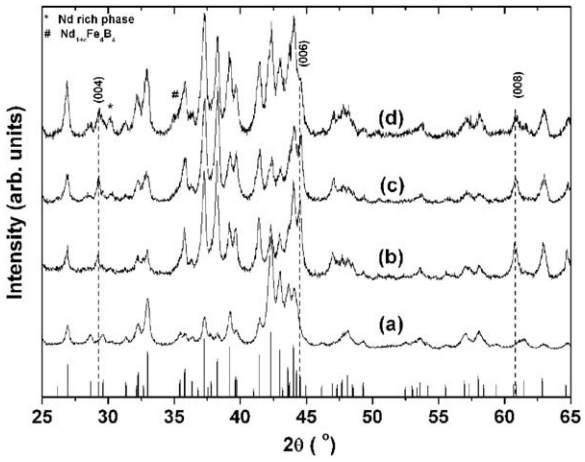

Fig. 1. XRD pattern of spark plasma sintered HDDR processed Nd–Fe–B magnets from plane parallel (a) 550 °C and plane perpendicular (b) 550 °C, (c) 575 °C and (d) 600 °C to the magnetic field orientation.

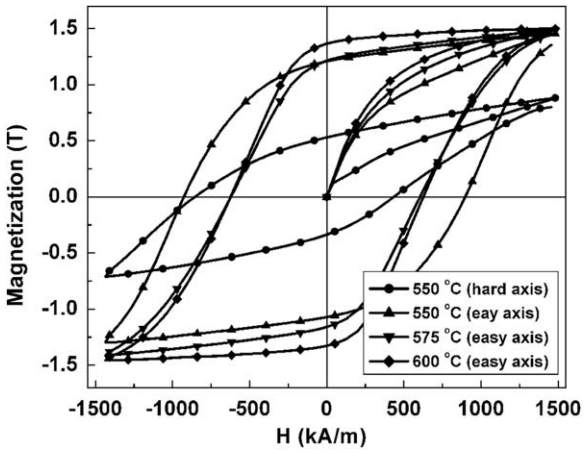

Fig. 2. Magnetization curves of the HDDR processed Nd–Fe–B magnets sintered at (a) 550 °C (hard axis) and (b) 550 °C, (c) 575 °C and (d) 600 °C (easy axis) by spark plasma sintering.

These sintered specimens exhibit anisotropic nature. The magnetic properties such as remnant magnetization (B_r), coercivity (H_c), energy product ($(BH)_{max}$) are evaluated from the hysteresis loop measurements as shown in Table 1. With an increase in the SPS temperature, remanence increased from 1.22 to 1.38 T, whereas the coercivity decreased from 928 to 622 kA/m. It would be due to the grain coarsening on sintering. The squareness of the demagnetization curves of the SPS specimens is lower than that of the sintered magnet [17]. It is due to the intrinsic nature of the HDDR powder particles that possess a maximum of 18° of dispersion in the solid angles made by the *c*-axis to that of parent monocrystalline particle [18]. Maki and Hirosawa studied the squareness in HDDR processed anisotropic Nd–Fe–B magnets and concluded that the inhomogeneity in its coercivity within the HDDR processed Nd–Fe–B particles is responsible for the lower squareness [19].

The density of the samples that are sintered at 550–600 °C with 80 MPa compressive pressure for 20 min is shown in Fig. 3(a). The density of the samples increased from 93% to 98.6% with increasing sintering temperature. It can be observed that the samples prepared by the SPS process at 600 °C are nearly fully dense (98.6%), whereas conventional liquid phase sintering generally requires the temperature above 1100 °C for 1–2 h [17].