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Highly oriented NdFeB nanocrystalline magnets from partially recombined compacts with ultrafine grain size by reactive deformation under low pressure

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Abstract: The partially recombined compacts with ultrafine grain size were taken advantage of preparing anisotropic nanocrystalline magnets with full density and homogenous microstructure and texture by reactive deformation under low pressure. Because of the ultrafine grain size of the precursors, the partially recombined phases could quickly achieve recombination. The results suggested that the newly recombined $Nd_2Fe_{14}B$ grains with fine grain size could undergo deformation immediately during the desorption-recombination reaction, and then an obvious anisotropy and uniform alignment would be obtained. The magnetic properties, $(BH)_{max}$=214 kJ/m^3, B_r= 1.26 T, H_{cj}=463 kA/m, were obtained after being treated for 5 min at 820 ºC in high vacuum under low pressure less than 26 MPa. Microstructures of the magnets were analyzed using X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) respectively. Magnetic measurements were carried out using a vibrating sample magnetometer (VSM) with the maximum field of 2.88 T. Accurate phase contents were measured by a Mossbauer spectrometer.

Keywords: $Nd_2Fe_{14}B$; nanocrystalline; HDDR; deformation; anisotropy; rare earths

High performance NdFeB magnets have attracted far-ranging attention due to their broadening significance in various engineering applications, such as generators, motors, computer devices, etc.[1–5] The market and consumption for NdFeB magnets are rapidly growing, especially when their properties and cost-effectiveness are drastically improved. Particularly outstanding magnetic properties can be obtained in anisotropic NdFeB magnets due to the high saturation magnetization of $Nd_2Fe_{14}B$ phase and the large magnetocrystalline anisotropy energy. Anisotropic NdFeB magnets are mainly prepared by HDDR (hydrogenation-disproportionation- desorption-recombination) and hot press-hot deformation from quenched powders[6,7], HDDR treated powders[8,9], or amorphous bulks[10]. Although the typical maximum energy product of the highest grade commercial anisotropic NdFeB magnets is about 398 kJ/m^3, there is plenty of scope for its growth up to the theoretical value (509 kJ/m^3). It is widely known that the magnetic properties strongly depend on the process routing, and consequently on the ultimate microstructure. Thus there is still a core issue needed to be solved how to obtain the microstructure with consistent orientation, homogeneous and fine grain size for the fabrication of high performance anisotropic nanocrystalline NdFeB magnets. It is strict in the mold and experimental conditions for withstanding high pressure under high temperature by hot press—hot deformation process[11–13]. And using HDDR method also has its own limitations to prepare anisotropic NdFeB magnets. Namely, the magnetic properties of anisotropic NdFeB magnet can be significantly fluctuant due to the difficulty to accurately control the important reaction parameters and to its own exothermic and endothermic phenomenon accompanied in the HDDR reactions[14–17].

Based on these studies, we put forward an overall new thinking of the combination of hot deformation and dehydrogenation-recombination process for hydrogen disproportionation products to prepare anisotropic nanocrystalline NdFeB magnets. We have already studied the reactive deformation of complete disproportionation and partially recombined green compacts, but the magnets finally obtained is with poor grain orientation[18], or with large grain size[19]. And in this investigation, anisotropic nanocrystalline NdFeB magnets with uniform texture were prepared by applying the reaction *in-situ* hot deformation to partially recombined (PR) NdFeB cold compacts, based on the homogeneous alignment effect of recombined $Nd_2Fe_{14}B$ nucleation from PR phases with ultrafine grain size under low pressure (<26 MPa). The microstructure and magnetic properties of the magnets during the reactive deformation (RD) process were investigated.

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1 Experimental

Commercial melt-spun ribbons with nominal composition of $Nd_{13.5}Fe_{73}Co_{7.5}B_6$ were used as raw material. PR treatment was performed by heating the raw material at 800 ºC for 5 min in pure H_2 atmosphere for hydrogen-disproportionation, and then isothermally heat-treated at the same temperature for 2 min in vacuum. Then PR ribbons were compacted to cold cylindrical shapes (10 mm in diameter and 10 mm in height). These green compacts were spark plasma sintered in vacuum for up to 30 min at 820 ºC, under a constant uniaxial stress of 2 kN (P_{RD}<26 MPa), with compression ratio about 75%. The microstructure and phase constitutes of samples were measured by X-ray diffraction (XRD) with Cu Kα radiation and room temperature transmission Mössbauer spectrometry (MS) with a ^{57}Co/Pd source. The microstructure of PR phases was studied by a transmission electron microscope (TEM). The fracture surface of magnets was observed by field-emission scanning electron microscope (FESEM). The magnetic properties of the magnets were examined using a Lake Shore vibrating sample magnetometer (VSM).

2 Results and discussion

Fig. 1 displays the XRD patterns of raw material and partially recombined (PR) magnetic powder. The XRD studies present that almost all peaks for raw material are attributed to the tetragonal hard magnetic $Nd_2Fe_{14}B$ phase, while for PR sample, $Nd_2Fe_{14}B$ phase coexists with NdH_x and α-Fe phases, indicating that the $Nd_2Fe_{14}B$ phase in PR sample is newly recombined from part of the disproportionate phases.

TEM investigation was recorded to monitor the grain size and phases for the PR magnetic powder, as shown in Fig. 2. In the sample after PR treatment newly recombined $Nd_2Fe_{14}B$ phase is detected, coexisting with disproportionated phases, which is consistent with XRD results above. Moreover, the grains in Fig. 2 are quite uniform in crystalline size with about 20 nm.

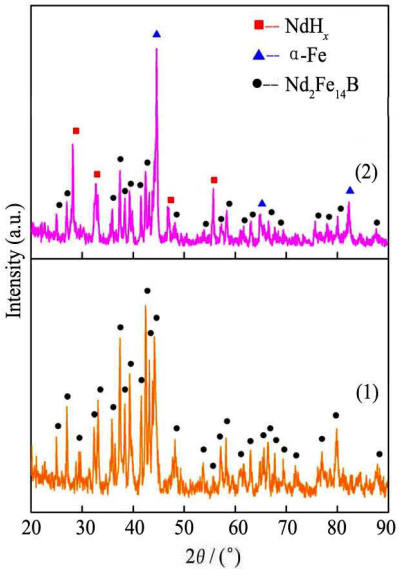

Fig. 1 XRD patterns of raw material (1) and PR magnetic powder (2)

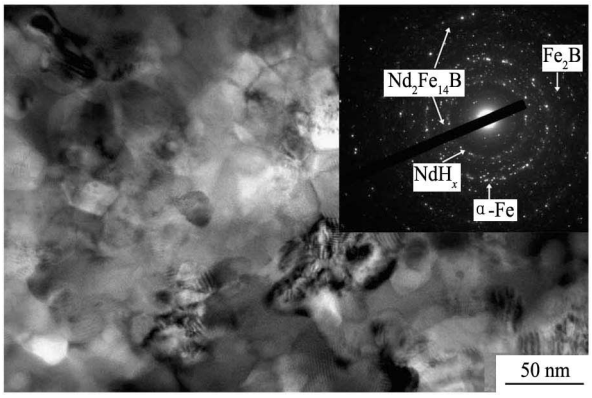

Fig. 2 TEM investigation of microstructure and phases for the PR magnetic powder

Mössbauer spectra in Fig. 3 are obtained from PR magnetic powder and the powders by crushing the magnets treated by RD process to understand the evolution of phase constitutes in the magnets during the RD process. The relative intensity of $Nd_2Fe_{14}B$ contributions increases while that of Fe_2B and α-Fe decreases remarkably after RD treatment at the beginning. Furthermore, calculated by the spectra, the spectra area ratios corresponding to $Nd_2Fe_{14}B$ phase for RD treated samples are approximately 40% (0 min), 86.3% (1 min), 88.3% (5 min), 90.7% (15 min), and 100% (30 min), respectively. The results suggest that the fraction of $Nd_2Fe_{14}B$ phase increases with great rapidity at the beginning, and confirm that a full recombination was achieved by 30 min treatment with pressure. Due to the ultrafine grain size of the partially recombinated precursors, the atoms are relatively more active and the biggish specific surface area offers dehydrogenation products abundant nucleation

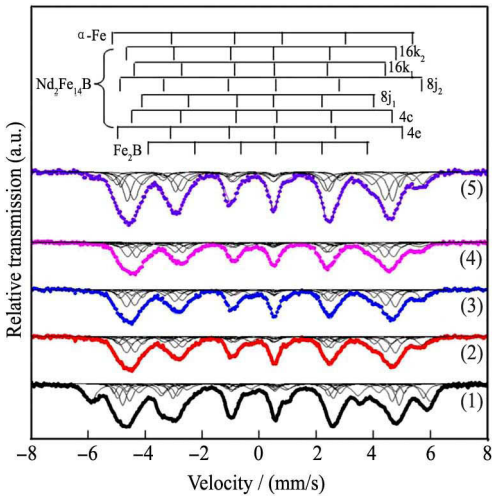

Fig. 3 Mössbauer spectra of PR compacts treated by RD at 820 ºC for various time: (1) PR powder; (2) RD 1 min; (3) RD 5 min; (4) RD 15 min; (5) RD 30 min (4c, 4e, $8j_1$, $8j_2$, $16k_1$, and $16k_2$ corresponding to 6 positions occupied by 56 Fe atoms of $Nd_2Fe_{14}B$ crystal)