Properties enhancement and recoil loop characteristics for hot deformed nanocrystalline NdFeB permanent magnets

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Abstract. Nanocrystalline NdFeB magnets were prepared by spark plasma sintering (SPS) and SPS followed by HD using melt spun ribbons as the starting materials. The microstructure of SPSed and HDed magnets were analyzed. The effects of process including temperature and compression ratio on the microstructure and properties were investigated. High magnetic properties were obtained in anisotropic HDed magnets. The combination of Zn and Dy additions was successfully employed to improve the coercivity and thermal stability of the SPSed magnets. Open recoil loops were found in these magnets with Nd-rich composition and without soft magnetic phase for the first time. The relationship between the recoil loops and microstructure for SPS and HD NdFeB magnets were investigated. The investigations showed that the magnetic properties of SPS+HDed magnets are related to the extent of the aggregation of Nd-rich phase, which was formed during HD due to existence of porosity in SPSed precursor. Large local demagnetization fields induced by the Nd-rich phase aggregation leads to the open loops and significantly reduced the coercivity. By reducing the recoil loop openness, the magnetic properties of HDed NdFeB magnets were successfully improved.

1. Introduction
Anisotropic NdFeB magnets are generally prepared by two processes. One is pressing in a magnetic field followed by sintering; the other is inducing a c-axis orientation by plastic deformation, such as hot deformation (HD) like extrusion, compression or rolling. HDed NdFeB magnets have attracted much attention not only because of their high magnetic properties but also due to their exceptional corrosion resistance, thermal stability, and fracture toughness [1-3]. Up to now, the largest reported value of (BH)max for HDed magnets is 54.4 MGOe, achieved in a Nd₁₃.₅(Fe,Co)₈₀Ga₀.₅B₆ alloy[4]. The deformation mechanism, which is not capable of classic plastic flow through dislocation mechanism, is believed to be a combination of stress-assisted grain growth via mass transport and grain boundary sliding [5]. To achieve enhanced magnetic properties, the precursor and the hot deformation processing have to be well optimized for improving the grain structure.

The precursors for the hot deformed magnets are generally prepared by hot pressing or spark plasma sintering (SPS). SPS is known as one of the novel sintering techniques for preparing bulk materials with fine structure [6]. Low sintering temperature and short holding time make it possible to sinter nanocrystalline NdFeB powders into fully dense bulk magnet without significant grain growth [7]. This paper reports our systematic study on the preparation of SPSed and HDed NdFeB magnets. We also observed the open recoil loops in the HDed magnets with RE-rich compositions for the first
time. The relationships among the recoil loops, microstructure and coercivity were investigated in detail.

2. Experimental
Spark plasma sintering (SPS) was employed as the pre-process for obtaining nanocrystalline bulk NdFeB precursors from melt spun powders. Commercial melt spun ribbons with nominal composition of \(\text{Nd}_{13.5}\text{Co}_{6.7}\text{Ga}_{0.5}\text{Fe}_{73.5}\text{B}_{5.6}\) or \(\text{Nd}_{10.15}\text{Pr}_{1.86}\text{Fe}_{80.41}\text{Al}_{1.67}\text{B}_{5.91}\) were consolidated to dense isotropic magnets by SPS (SPS-825, Sojitz Machinery Co.) using the optimized processing parameters obtained previously (700 °C/5 min/50 MPa) \cite{8} if not stated otherwise. The SPSed magnets were subjected to hot deformation using a vacuum hot deformation facility (HP-12×12×12, Centorr Vaccum Industries, USA) at various temperatures and compression strain rates. The density for the magnets was measured based on the Archimedes principle. X-ray diffraction patterns were obtained with X-ray diffractometer (XRD, Philip X-pert) using Cu-K\(\alpha\) radiation. To characterize the microstructure, the SPSed and HDed magnets were carefully broken off manually from an indentation and the fracture was examined by SEM (Nano430, FEI). Magnetic properties were characterized by physical properties measurement system (PPMS-9 Quantum Design, USA) equipped with a 9T vibrating sample magnetometer.

3. Results and discussion

3.1 Process optimization for hot deformation
The XRD patterns of SPSed and HDed magnets obtained from the surface perpendicular to the pressing direction at the various compression ratios were shown in the Fig. 1. All XRD peaks are attributed to the tetragonal hard magnetic \(\text{Nd}_2(\text{FeCo})_14\text{B}\) phase. For the HDed magnets, enhanced (00l) peak densities indicate the c-axis crystallographic alignment. With increasing the compression ratio from 54 % to 80 %, the degree of c-axis orientation increases.

![Figure 1. XRD patterns for the SPSed (a) and HDed magnets at various temperatures and compression ratios: (b) 750°C-54%; (c) 750°C-68%; (d) 800°C-73%; (e) 800°C-80%](image)

Two distinct zones with different grain sizes were noticed in SPSed NdFeB magnets as shown in the Fig. 2 (a) and (b). The coarse grain zones correspond to the particle boundary area of ribbons and the fine grain zones correspond to the interior of the particles. The formation mechanism of the two-zone structure was discussed in our previous paper \cite{8}. The microstructure of the coarse grain zones and fine grain zones are consisted of equiaxed grains for SPSed isotropic magnets. For HDed anisotropic magnets, the two-zone microstructure still exists, as shown in the Fig. 2 (c). It is observed that the microstructure of the fine grain zones consists of small platelet-shaped \(\text{Nd}_2\text{Fe}_{14}\text{B}\) grains due to the deformation of the grains, as shown in the Fig. 2(c) and (d). Within each grain the crystallographic c-axis, which is the magnetic easy axis, is perpendicular to the platelet. However, in the coarse grain zones, the microstructure of equiaxed grains was maintained, as shown in the Fig. 2 (c), indicating that large grains are hard to be deformed. The reason can be explained as follows. Compared to the large
grains, the fine grains need a shorter diffusion distance for preferential growth of Nd$_2$Fe$_{14}$B grains. A larger driving force exists for the growth of small grains [9]. The results imply that the microstructure with large grain size is not beneficial to obtain anisotropic magnet by plastic deformation.

![Figure 2. Microstructure of typical SPSed magnet (a, b) and HD magnet (c, d)](image)

Fig.3 shows the microstructure of HD magnets obtained at various deformation conditions. The coarse grain zones in Fig.3 (a), (c), (e), and (g) correspond to the particle boundary area of ribbons and the fine platelet-shaped grain zone correspond to the interior of the particles [8]. With the increase of compression ratio from 54% to 80%, the average width of the coarse grain area increases from ~3.9 to ~5.4 µm, and the average width of the fine grain area decreases from ~11.2 to ~4.1 µm.

![Figure 3. Microstructure of HD magnets parallel to the pressing direction at various compression ratios: (a), (b) 750°C-54%; (c), (d) 750°C-68%; (e), (f) 800°C-73%; (g), (h) 800°C-80%; the insets are the microstructure of HDed magnets perpendicular to the pressing direction respectively](image)

Fig. 4 shows the dependences of the average widths of the fine and coarse grain zones on the compression ratios. The width of the coarse grain zone clearly increases with increasing compression ratio. The increase of deformation time and temperature are responsible to the slight increase of coarse grain area width. The preferential growth of Nd$_2$Fe$_{14}$B grains under stress perpendicular to the
pressing direction is contributed to the decrease of the fine grain area width. The mean dimensions of grain perpendicular and parallel to the pressing direction, defined as $w$ and $h$ (Fig.4 inset), respectively, in the fine grain zone for HD magnets prepared at various compression ratios are plotted in Fig. 5. Both $w$ and $h$ increase with the increasing compression ratio, indicating an increasing grain volume due to mass diffusion. The increase value of $w$ is attributed to the increasing compression ratio and time. Large compression ratio can enhance grain rotation and deformation. Increase of deformation time leads to more mass transportation caused by diffusion [5]. Both of them can enhance the preferential growth of Nd$_2$Fe$_{14}$B grains under stress along perpendicular to the pressing direction, consistent with the XRD results. This microstructure characteristic has an important effect on the magnetic properties.

Fig.5 shows magnetic hysteresis loops at 300K of the SPSed and HDed magnets parallel and perpendicular to the pressing direction at various deformation conditions. As listed in the Table 1, the degree of texture, indicated by the remanence along two directions ($J_r^\parallel/J_r^\perp$), for SPSed magnet is only 0.012, indicating an isotropic behavior. For the magnetic properties of HDed magnets parallel to the pressing direction, with increasing compression ratio from 54% to 80%, the remanence $J_r$ increases from 1.19 T to 1.34 T, indicating the increase of the orientation degree of c-axis texture. At the same time, the coercivity $J_H$ decreases from 1239 kA/m to 731 kA/m. The different dependences of remanence and coercivity on the compression ratio lead to a maximum of energy product at compression ratio of 73%. The optimal combination of the magnetic properties are $J_r = 1.32$ T, $J_H = 847$ kA/m, and $(BH)_{\text{max}} = 303$ kJ/m$^3$. With the formation and enhancement of c-axis texture, the remanence along the direction perpendicular to the pressing direction decreases from 0.39 T to 0.23 T.

![Figure 4](image1.png)

**Figure 4.** The widths of fine grain zone and coarse grain zone (a) and the mean magnitude in the fine grain zone perpendicular and parallel to the pressing axis (b) for HD magnets at various compression ratios: (a) 750°C-54%; (b) 750°C-68%; (c) 800°C-73%; (d) 800°C-80%

![Figure 5](image2.png)

**Figure 5.** Magnetic hysteresis curves of the SPSed and HDed magnets parallel to the pressing direction (a) and perpendicular to the pressing direction (b)
The magnetic properties are directly related to the microstructure. The dimension $w$ of the platelet-shaped grain is related to the remanence and coercivity. Larger values of $w$ result in higher remanence, as shown in Table 1. This can be attributed to the improved anisotropy. Table 1 also shows that with the increase of compression ratio, $J_{Hc}$ decreases. Since the increase of the platelet-shaped grain diameter enhances the irregular degree of grain, which possibly increases the stray field acting on the grains. Therefore, the increased of stray field is one possible reason for the reduction of the coercivity.

### Table 1. Magnetic properties and degree of texture of SPSed and HDed magnets parallel and perpendicular to the pressing direction

| Process of sample | $J_r$ (T) | $J_{Hc}^\parallel$ (kA/m) | $J_{Hc}^\perp$ (kA/m) | $(BH)_{max}^\parallel$ (kJ/m$^3$) | $(BH)_{max}^\perp$ (kJ/m$^3$) | $J_{r}^\parallel$ - $J_{r}^\perp$ |
|-------------------|------------|-----------------|----------------|-----------------|----------------|----------------|
| 700°C-SPS         | 0.82       | 0.81            | 1516           | 1517            | 116            | 113            | 0.012           |
| 750°C-54%         | 1.19       | 0.39            | 1239           | 1095            | 259            | 25             | 0.670           |
| 750°C-68%         | 1.29       | 0.30            | 995            | 773             | 293            | 14             | 0.768           |
| 800°C-73%         | 1.32       | 0.24            | 847            | 638             | 303            | 9              | 0.820           |
| 800°C-80%         | 1.34       | 0.23            | 731            | 585             | 285            | 8              | 0.823           |

3.2 Compositional modification for SPS magnets

It is still not possible to completely avoid the grain coarsening during SPS, which leads to inevitable decrease in coercivity for SPSed magnets. Hence, maintaining a high coercivity is particularly important for SPSed NdFeB magnets. To improve coercivity, the magnetic powders can be mixed with some metal powders (such as Zn and Cu powders). During SPS, the metal powders can react with the magnetic matrix and presumably diffuse into the neodymium-rich phase surrounding the Nd$_2$Fe$_14$B grains at high temperature and pressure required for densification, which has been confirmed by electron microprobe analysis [10]. By this method, the enhancement of coercivity has been achieved by Cu and Zn additions. It was found that both elements increased the coercivity of hot-pressed magnets by ~37%. For die-upset magnets, coercivity was increased by ~91% for Zn addition, which is higher than ~75% by Cu addition [11]. Another effective way to enhance coercivity and maintain the low concentration of high cost rare earth element Dy is the development of a core-shell microstructure, which is formed by segregation of Dy along the grain boundary area, by the addition of powdered Dy compounds (oxides, fluorides, or hydride) [12-14]. It was reported that adding 4 wt.% Dy$_2$O$_3$ enhanced the coercivity by 37.9% (from 11.6 to 16.0kOe) for sintered Nd$_{15}$Fe$_{77}$B$_8$ magnet [12].

### Table 2. Room temperature magnetic properties, density and temperature coefficients for SPSed Nd$_{10.15}$Pr$_{1.86}$Fe$_{80.41}$Al$_{1.67}$B$_{5.91}$ magnets with the optimal powder additions

| SPSed Samples | $J_r$ (T) | $J_{Hc}$ (kA/m) | $(BH)_{max}$ (kJ/m$^3$) | Density (g/cm$^3$) | $\alpha$ (K$^{-1}$) | $\beta$ (K$^{-1}$) |
|---------------|-----------|----------------|-------------------------|-------------------|-------------------|----------------|
| Nd-Fe-B       | 0.77      | 953            | 96                      | 7.43              | -0.145            | -0.518         |
| Nd-Fe-B+0.6 wt.% Zn | 0.76  | 1054           | 97                      | 7.38              | -0.135            | -0.454         |
| Nd-Fe-B+2wt.% Dy$_2$O$_3$ | 0.74  | 1098           | 92                      | 7.23              | -0.132            | -0.488         |
| Nd-Fe-B+0.6 wt.% Zn+2wt.% Dy$_2$O$_3$ | 0.73  | 1142           | 91                      | 7.22              | -0.133            | -0.462         |

We investigated the effects of separated and combined Dy$_2$O$_3$ and Zn additions on the magnetic properties, microstructure and thermal stability of SPSed nanocrystalline NdFeB magnets. The magnetic properties of the magnets with different additions are listed in Table 2. The magnets with 0.6 wt.% Zn and 2 wt% Dy$_2$O$_3$ additions have $J_{Hc}$ values about 11% and 15% higher than that of the additive free magnet, respectively. To further improve the properties, the
combination of 2 wt.% Dy$_2$O$_3$ and 0.6 wt.% Zn additions were employed. The magnetic properties for the magnet with Dy$_2$O$_3$+Zn addition are also shown in Table 2. The combined addition considerably increases the magnetic properties, which produced a ~20% increase in coercivity. An optimal combination of $J_r=0.73$ T, $J_H=1142$ kA/m, and $(BH)_{max}=91$ kJ/m$^3$ were obtained. Importantly, the thermal stability of the doped magnets is also improved, demonstrated by the reduced temperature coefficients of remanence ($\alpha$) and coercivity ($\beta$) in Table 2. These SPSed samples can not only work as the isotropic permanent magnets but also can be employed as the ideal precursors for hot deformed anisotropic NdFeB magnets.

3.3 Recoil loop characteristics

As a series of magnetic characteristic curves, recoil loops, measured by removing and reapplying an increased successively reversed field on a previously positively saturated magnetic sample, can provide physical insight into magnetization reversal mechanism. In practice, open recoil loops can cause working point change for permanent magnets. The energy loss associated with the open recoil loops is not negligible, which is disadvantageous to the application of permanent magnets. It is commonly accepted that the open recoil loops results from the exchange decoupled soft phase in the nanocomposite alloys [15]. Generally, single phase alloys have narrow and even closed loops [16]. Recently, McCallum [15] pointed out that the enclosed area in the loops is related to the mean field interaction strength, the distribution of coercivity, and the volume fraction of the soft phase. From the experimental studies, the open recoil loops was also found to be related to the unstable magnetic moments caused by thermal fluctuation [17], strong exchange coupling due to the nanostructure [18], and the inhomogeneity in the magnetic anisotropy [19]. Here we investigated the relationship between the recoil loops and microstructure for hot deformed NdFeB magnets.

For the experiments, SPS was carried out at various temperatures with a pressure of 50 MPa for 5 min. HD was carried out at 750°C for 20 min under a uniaxial stress of 350 MPa. As expected, the density of SPSed magnets increases with increasing SPS temperature. The magnet SPSed at 700 °C has a density of 7.33 g/cm$^3$, while the density of that SPSed at 650°C is only 7.03 g/cm$^3$. The low magnification images for these two samples are shown in Fig.6a and Fig.6b. Some pores can be clearly observed for the low density magnet (Fig.6a). Reduced porosity is evident in Fig.6b. The microstructure of SPSed magnet consists of uniform equiaxed grains (insets in Figs.6a and 6b).

Above mentioned two samples were subjected to HD at 750°C, and the microstructures after HD are shown in Figs.6c and 6d. Platelet-shaped Nd$_2$Fe$_{14}$B grains due to deformation are formed. Some strip-
shaped grains can be observed, indicated by the arrows. The Fe/Nd atomic ratios detected by EDS indicate that these grains are Nd-rich phase. The existence of porosity in SPSed precursor is considered to be the main reason for Nd-rich phase aggregation in HDed magnets. It can be assumed that liquid Nd-rich phase aggregated in the pores at high temperature during the early stage of HD, and it was squeezed to form some strip-shaped grains under the uniaxial stress during deformation. Comparing Fig.6a with Fig.6b, higher SPS temperature led to an improved density and less porosity, and therefore, it reduced Nd-rich phase aggregation in SPS+HDed magnets, as shown in Fig.6c and Fig.6d. To confirm above assumption, a low porosity SPS magnet with high density close to the theoretical value of 7.50 g/cm³ was prepared by optimal process and raw powders. After hot deformation, no Nd-rich phase aggregation was observed, as presented in Fig.7a, which is attributed to the elimination of the porosity in the SPSed precursor. Hence, the results demonstrated that the Nd-rich phase aggregation results from the existing porosity in SPSed precursor and the reduced porosity in SPS precursor is beneficial to eliminate Nd-rich phase aggregation.

Figure 7. Microstructure and recoil loops for SPS+HDed magnets prepared with 68% deformation ratio using high density (7.50 g/cm³) SPS precursors

The recoil loops for SPSed and SPS+Hded magnets were obtained. All SPSed magnets had closed loops, similar to the normal single phase NdFeB magnet and RE-rich sintered microcrystalline NdFeB magnets. Interestingly, the recoil loops of hot deformed magnets with same composition are open, as shown in the Fig.6e and 6f, although there is no soft magnetic phase detected by XRD. This type of open recoil loops for Nd-rich NdFeB magnets has never been reported before and is worthy of investigation. On the other hand, the maximum openness of recoil loops does not take place at the coercive field, which is different from that of nanocomposite NdFeB alloys.[20]

Considering the microstructure and magnetic properties, we suggested that strip-shaped Nd-rich phase with dimension up to several micrometers, as shown in Figs.6c and 6d, generate non-negligible local demagnetizing fields. Large demagnetizing factor induced by the Nd-rich phase aggregation along pressing direction (c axis) produces a large demagnetization field. The Nd-rich phase aggregation with various sizes, larger than grains, leads to non-uniform distribution of local demagnetizing fields. These demagnetization fields can reduce the local pinning field and lead to the inhomogeneity of magnetic anisotropy. This variation of local magnetic anisotropy in the magnets should be responsible for the formation of open recoil loops. In other words, the open recoil loops arise from the difference in local reversal field due to non-uniform distribution of large local demagnetization fields. Since there exists non-uniformly distributed demagnetization fields, the reverse fields at different parts of the magnets are different, which eventually results in open recoil loops.
Table 3. A summary of the process, density, Nd-rich aggregation, recoil loop characteristics and coercivity for SPS+HDed magnets

| SPS process          | HD process              | SPS precursor density, g/cm³ | Nd-rich phase aggregation | Recoil loops openness | \( j_{Hc} \), kA/m |
|----------------------|-------------------------|-----------------------------|--------------------------|-----------------------|---------------------|
| 650°C-50MPa-5min     | 750°C-20 min-350 MPa    | 7.03                        | Serious                  | large                 | 226                 |
| 700°C-50MPa-5min     | 750°C-20 min-350 MPa    | 7.33                        | Medium                   | Medium                | 288                 |
| Optimal process and raw powders | 750°C-20 min-350 MPa | 7.50                        | Not observed             | No                    | 995                 |

Above explanation has been verified by experiments. As shown in Figs.6c and 6d, with increasing SPS temperature from 650 to 700°C, Nd-rich phase aggregation was reduced in SPS+HDed magnets. Correspondingly, the openness of recoil loops is also reduced, as presented in Figs.6e and 6f. Furthermore, for the HDed magnets without Nd-rich phase aggregation, the recoil loops is found to be fully closed (Fig.7b). These results confirmed that the openness of recoil loops arises from the aggregation of Nd-rich phase. A more serious distribution of local demagnetization field contributes to the more open recoil loops. The characteristics of recoil loops and magnetic properties for SPS and HDed magnets are summarized in Table 3. The clear relationships between Nd-rich phase aggregation, recoil loops openness and coercivity have been demonstrated. Distribution of large local demagnetization fields not only leads to reduced coercivity, but also results in open recoil loops.

4. Conclusions
Anisotropic nanocrystalline magnets were prepared by SPS followed by hot deformation. Excellent magnetic properties were obtained by optimized process. The microstructure evolution and its influences on the magnetic properties were investigated. Fine and regular grain microstructure is beneficial to deformation and improving coercivity. The increase of stray field is responsible for the decrease of coercivity with increasing compression ratio. Zn and Dy\(_2\)O\(_3\) additions have been successfully employed to improve the coercivity and thermal stability of SPSed magnets. The aggregation of Nd-rich phase not only leads to low coercivity, but also results in open recoil loops. The openness of recoil loops is related to the local demagnetization fields induced by Nd-rich phase aggregation. The reduction of the Nd-rich phase aggregation is beneficial to achieve deformation anisotropy and high magnetic properties.

5. Acknowledgements
This work is financially supported by the Natural Science Foundation of China (Grant No. 51174094), Guangdong Provincial Science and Technology Program (Grant No. 2012B091000005), and the State Key Laboratory for Advanced Metals and Materials (Grant No. 2011-ZD05).

6. References
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