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Magnetic performance enhancement in La-Ca-Co doped SrFe$_{12}$O$_{19}$ ferrite permanent magnets via cold isostatic pressing

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Abstract

The crystallographic alignment, microstructure and magnetic properties were studied for La$_{0.6}$Ca$_{0.6}$Sr$_{0.1}$Fe$_{12.4}$Co$_{0.4}$O$_{19}$ ferrite permanent magnets prepared with standard ceramic method. The effect of cold isostatic pressing (CIP) and sintering temperature on the structural and magnetic properties of the magnets were investigated. The CIP significantly improves the density of the green compact and final magnets, but undermines the crystallographic alignment of the magnets simultaneously. As a result, the remanence of the magnet achieves optimal value under the compromise between the increased density and the degraded alignment. Moreover, the coercivity of the magnet increases linearly with the increment of the CIP pressure due the fact that CIP processed samples bear more uniform and finer grains in favor of high coercivity. Under optimal CIP pressure and sintering temperature, the magnet obtains best magnetic properties of $B_r$ of 0.439 T, $H_{cj}$ of 396 kA m$^{-1}$, $H_{cb}$ of 311 kA m$^{-1}$, and $(BH)_{max}$ of 35.8 kJ m$^{-3}$.

Introduction

Permanent magnetic materials including rare-earth permanent magnets (REPMs) and ferrite permanent magnets (FPMs) are indispensable fundamental materials in modern society that play a key role in many high-tech fields [1–10]. When compared to REPMs, FPMs bear much more economical fabrication cost and stronger chemical stability, leading to their wide application in motors, loudspeakers, etc. Moreover, as a kind of traditional permanent magnetic materials, FPMs have been continuously investigated during past decades to improve their magnetic properties [11–35]. To date, two main approaches have been applied for the improvement. Firstly, apart from the standard ceramic method, quite a few synthetic techniques such as chemical co-precipitation, sol-gel method, hydrothermal method, Pechini method, microwave induced combustion method, self-propagating high temperature synthesis, reverse micelle technique, and citrate precursor method have been developed and applied for FPMs [11–19]. Secondly, various cationic substitutions have been investigated. For instance, alkali metal ions, alkali-earth metal ions, transition metal ions, and rare earth metal ions have been applied to dope FPMs individually or jointly [20–34]. Specially, La-Ca-Co joint doping has been verified as an effective approach to remarkably enhance the overall magnetic properties of M-type Strontium ferrite (SrM ferrite) magnets [35–40].

Cold isostatic pressing (CIP) is a popular technique in conventional powder metallurgy technology. It can greatly enhance the densification of the green compact and lower the sintering temperature of the sample. In the previous research, Sagawa et al invented a modified CIP technique, namely the rubber isostatic pressing (RIP), for the fabrication of both sintered REPMs and FPMs [41]. For the sintered ferrite magnet, the remanence ($B_r$) and maximum energy density ($BH)_{max}$] has enhanced, while the coercivity has reduced after application of RIP. Nevertheless, the influence of the RIP to the crystallographic alignment and microstructure have never been investigated yet. More recently, Le et al introduced the CIP technique to the fabrication of Ni-Zn-Cu ferrite soft
magnets. They reported that CIP helped the densification of the magnets and led to an improvement of functional magnetic properties [42]. Moreover, CIP can significantly lower the sintering temperature of the magnets.

In current research, La–Ca–Co doped SrM ferrite magnets were prepared with standard ceramic technique, and CIP process was introduced right after conventional die pressing. The effects of CIP pressure as well as the subsequent sintering temperature on the crystallographic alignment, microstructure, and magnetic properties were studied and reported.

### Experimental details

SrM ferrite magnets with nominal composition of La$_{0.6}$Ca$_{0.6}$Sr$_{0.1}$Fe$_{12.4}$Co$_{0.4}$O$_{19}$ were prepared by standard ceramic method. In detail, La$_2$O$_3$, Co$_3$O$_4$, Fe$_2$O$_3$, SrCO$_3$, and CaCO$_3$ powders with their purity over 97.5% were dry mixed together with proper mass ratio. 30 wt% Polyvinyl alcohol (PVA) water was also added to the mixture, which was then pelletized and calcined at 1260 °C for 2 h in a muffle furnace. The as-sintered mixture bulk was crushed and grounded into coarse powder, which was then ball milled for 20 h with secondary additives of CaCO$_3$, SiO$_2$, H$_3$BO$_3$, and La$_2$O$_3$. The weight ratio of balls to powders to water is 20:1:2. After ball milling, the slurry was then compressed into cylindrical samples by wet press, applying 20 MPa pressure in a magnetic field of 1.2 T and the pressure holding time of 12 s. The green compacts were further compressed via cold Isostatic press machine at pressures of 60 MPa, 100 MPa, 140 MPa, 180 MPa and 220 MPa for 180 s. Finally, the compressed samples were sintered for 2 h in muffle furnace to obtain the magnets at sintering temperature ranging from 1175 °C to 1205 °C.

The particle size and the phase composition of the ball milled powder was examined by laser particle size analyzer (LPSA) and X-ray diffractometer (XRD) with Cu-K$_\alpha$ radiation, respectively. The crystallographic alignment and microstructure of the magnets were studied with XRD and scanning electron microscopy (SEM), respectively. The magnetic properties of the magnets were tested with B-H tracer. The density of the green compacts and magnets was evaluated by the ratio of the mass to the volume of the magnets.

### Results and discussion

Figure 1 shows the XRD patterns of as-calcined powders before and after alignment as well as the SrM ferrite sintered magnet. The indexation of the peaks in the pattern of powders before alignment affirmed the single-phase hexagonal crystal structure without any heterogeneous phase, and the prominence of diffraction peaks of (006), (107), (114), (203), and (2,0,11) in the pattern indicates that powders are randomly distributed in the measured sample. After alignment, peaks of (006), (008), and (0,0,14) become dominant, suggesting the single crystal nature of the powder, whose average particle size is 0.7 μm given by LPSA examination. Moreover, peaks
of (006), (008), and (0,0,14) are also dominant in the pattern of the sintered magnet, demonstrating that the c-axis crystallographic alignment was well preserved after compressing and sintering process. The good alignment is crucial for strong magnetic anisotropy of the magnets. Nevertheless, note that the c-axis crystallographic alignment of the final magnet is a little weaker than that of the aligned powders due to the fact that pressing process may undermine the alignment of the initial powders.

Figure 2(a) shows the density of green compacts as a function of CIP pressures. Note that sample of 0 MPa means that sample never undergoes the CIP after die pressing. As the pressure increases from 0 to 180 MPa, the density of the compacts almost increases linearly from 2.45 g cm$^{-3}$ to 3.12 g cm$^{-3}$. Further enhancement of the pressure to 220 MPa only results in little increment of the density to 3.14 g cm$^{-3}$. Nevertheless, the 28.2% growth rate of the density was expected to have remarkable influence to the structural and magnetic properties of the final magnets. Figure 2(b) shows the density of SrM ferrite sintered magnet as a function of CIP pressures, and the sintering temperature of the magnets is 1175 °C. As the pressure increases from 0 to 100 MPa, the density of the compacts almost increases slightly from 5.00 g cm$^{-3}$ to 5.01 g cm$^{-3}$. After that, the density increases faster to 5.07 g cm$^{-3}$ when the pressure arrives to 180 MPa. The maximum growth rate of the density of the magnet via CIP is 1.4%. We also noticed that the maximum density growth rates are 1.6%, 1.8% and 1.2% for the magnets sintered at 1185 °C, 1195 °C, and 1205 °C, respectively. The density increment may contribute to higher remanence of the magnets.

Figure 3(a) shows the XRD patterns of SrM ferrite sintered magnets with and without CIP processing, and the sintering temperature of the magnets is 1175 °C. The measured surface of the magnets is perpendicular to the c-axis of the magnets. Note that all samples exhibit strong crystallographic alignment. Nevertheless, the intensity ratio of $I_{(008)}/I_{(107)}$ which demonstrates the degree of alignment that drops with the application of CIP (figure 3(b)). In detail, the $I_{(008)}/I_{(107)}$ value of the magnet without CIP is 2.76, while the value drops to under 1.75 for all of the samples with CIP. It is therefore concluded that CIP will undermine the alignment of the green compact and subsequent of the sintered magnets. Similar results were also reported by Sagawa et al previously [41].

Based upon above investigation, it is found that CIP contributes to density enhancement but undermines crystallographic alignment of the magnets simultaneously. Therefore, the effect of CIP to the magnetic
properties of the magnets was further studied, as shown in figure 4. Figure 4(a) shows the remanence of the magnets as a function of CIP pressure. It indicates that under different sintering temperature, the remanence ($B_r$) shows increasing trend with increased pressure. Moreover, with the application of CIP, the magnetic coercive force ($H_{cb}$) increases substantially for magnets sintered under 1175–1195 °C (figure 4(b)). Moreover, it is found that application of CIP is benefit to the squareness of the demagnetization curve of the magnet, and the higher pressure the better squareness factor of the curve, as shown in figure 5. As a result, the maximum energy product ($BH_{max}$) shows increasing trend with increased pressure, demonstrating that the advantage of CIP processing unambiguously outweighs its disadvantage with regard to the magnetic properties of the magnets.

Note that the intrinsic coercive force ($H_{ci}$) of the magnets sintered under 1175 °C and 1185 °C increases with the CIP pressure, while the $H_{ci}$ of the magnets sintered under 1195 °C exhibits opposite trend. It is reported that the initial density of the green compact has not negligible influence to the optimal sintering temperature, and the higher of the density the lower of the optimal sintering temperature [Le]. It is therefore expected that 1195 °C may too high for the green compacts with higher density by CIP processing. We also noticed that for the magnets sintered under 1205 °C, the $H_{cb}$, $H_{ci}$, and $(BH)_{max}$ not only deteriorate substantially compared with the magnets with lower sintering temperature (1175–1195 °C), but also drop fast with the enhanced CIP pressure (not shown here). It is therefore concluded that the final magnetic properties of the magnets were decided by the combined influences of CIP pressures and sintering temperatures.

To clarify the combined influences of CIP pressures and sintering temperatures to the magnetic properties of the magnets, the microstructure of the magnets with different processing conditions was observed with SEM, as shown in figure 6. Figures 6(a)–(c) show morphologies of SrM ferrite magnets sintered under 1175 °C, 1185 °C, and 1195 °C with CIP of 60 MPa, respectively. It shows that the cavities in the microstructure reduce gradually from 8.29% to 4.14% as the sintering temperature increases (table 1), suggesting that under same CIP condition, increment of sintering temperature can accelerate densification of the magnet. The densification will improve the density and thus the magnetization saturation as well as the remanence of the magnets.
Nevertheless, grain growth was found simultaneously. In detail, as the temperature increases from 1175 °C to 1185 °C, the grains become more uniform with minor increment of the average grain size and such typical microstructure is expected to bear higher coercivity. As the temperature increases to 1195 °C, however, excessive grain growth was observed. Some adjacent grains combine into big ones due to the high sintering temperature.

Table 1. Cavity ratios of SrM ferrite sintered magnets shown in figure 6.

| Samples | (a)  | (b)  | (c)  | (d)  | (e)  | (f)  |
|---------|------|------|------|------|------|------|
| Cavity ratio (%) | 8.29 | 7.10 | 4.14 | 5.47 | 3.19 | 2.93 |

Figure 5. Demagnetization curves of SrM ferrite sintered magnets as a function of CIP pressures with sintering temperature of 1185 °C.

Figure 6. SEM morphology of SrM ferrite sintered magnet: (a) with CIP of 60 MPa & sintered under 1175 °C, (b) 1185 °C, (c) 1195 °C, and (d) with CIP of 220 MPa & sintered under 1175 °C, (e) 1185 °C, (f) 1195 °C, all of the observed surface of the magnet is perpendicular to the c-axis of the magnet.
resulting into bimodal distribution of the grain size, which will undermine the coercivity of the magnets. Figures 6(d)–(f) show morphologies of SrM ferrite magnets sintered under 1175 °C, 1185 °C, and 1195 °C with CIP of 220 MPa, respectively. Compared with their counterparts in figures 6(a)–(c), i.e., magnets sintered under same temperature but lower CIP pressure of 60 MPa, the cavities in the microstructure is even, suggesting that under same sintering temperature, increment of CIP pressure also accelerates densification of the magnet (table 1). The variance of the grain size and size distribution in the magnets in figures 6(d)–(f) is similar to those of the magnets in figures 6(a)–(c). It is well known that the magnetic hardening process of FPMs is single domain reversal mechanism, microstructure with fine and uniform grains is responsible for high coercivity. In our case, magnet of figure 6(d) exhibits highest coercivity in all samples, and together with good remanence it also yields the highest maximum energy product. Figure 6(f) shows morphology of the magnet with CIP of 220 MPa & sintered under 1195 °C, it shows that the cavities in the microstructure is also rare, corresponding to the high remanence of the magnet. Nevertheless, bimodal grain size distribution was observed, that is, the microstructure contains excessive growth grains, which may result from the combination of high sintering temperature and CIP process. The magnet therefore bears poor coercivity. It is thus suggested that proper combination of sintering temperature with CIP processing may yield ideal microstructure and thus magnetic properties. Moreover, it is worth to note that application of CIP leads to higher density of green compact, which in turn lower the optimal sintering temperature. Our observation results have good agreement with those reported by Le et al in ferrite soft magnets [42].

Conclusion

In conclusion, effect of CIP processing on the crystallographic alignment, microstructure, and magnetic properties of La-Ca-Co doped SrFe12O19 ferrite permanent magnets was studied. CIP can improve the density of the green compact and subsequent the final magnets, but slightly destroy the crystallographic alignment of the green compact and the magnets. Nevertheless, the advantage of CIP outweighs its disadvantage in terms of the overall magnetic properties of the magnets. Specially, the coercivity of the magnet increases linearly with the increment of the CIP pressure due the fact that CIP processed samples bear more uniform and overall magnetic properties of the magnets. Specially, the coercivity of the magnet increases linearly with the increment of the CIP pressure due the fact that CIP processed samples bear more uniform and fine grains in favor of high coercivity. With combination of optimal CIP pressure and sintering temperature, we obtain the magnet bearing magnetic properties of Br of 0.439 T, Hc of 396 kA m−1, Hcb of 311 kA m−1, and (BH)max of 35.8 kJ m−3.

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