Magnetic Properties of Ca-La-Co M-Type Ferrite Sintered Magnets with CaO and SiO₂ Inter-Additives

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Abstract

The effects of CaO and SiO₂ inter-additives on magnetic and physical properties of Ca-La-Co system ferrite sintered magnets were discussed. The results show that the maximum magnetization and remanence of the sintered magnets decrease with an increase in the ratio of SiO₂ to CaO inter-additives, because non-magnetic materials α -Fe₂O₃ are formed with an increase in the ratio. On the other hand, the coercivity H_{cJ} of Ca-La-Co system sintered magnets increase with an increase in the SiO₂ additives, because the average particle size of sintered magnets becomes smaller. Whereas, H_{cJ} of Ca-La-Co system sintered magnets decrease with an increase in the CaO inter-addition because the crystal growth of the sintered magnets occurred due to CaO inter-additive. Optimum magnetic properties and conditions in this experiment were as follows; inter-additives: 0.3 wt.% SiO₂ and 0.5 wt.% CaO, sintering temperature: 1200°C, B_r =0.429 [T], H_{cJ} =278 [kA/m], $(BH)_{max}$ =34.5 [kJ/m³].

Key Words: M-type ferrite, Magnetic properties, Ca-La-Co system, coercivity, inter-additives

I. INTRODUCTION

M-type ferrites are important hard-magnetic materials, which are being used in many applications, due to its high cost performance and high chemical stability. Recently, it has been reported that the Ca-La-Co system ferrite sintered magnets have high coercivity and magnetization [1]. Yet, we have many unknown contributing factors that enhance the magnetic properties of Ca-La-Co ferrite sintered magnets. The magnetic properties of ferrite sintered magnets have been affected not only by the specific physical properties such as the magnetic moment per unit cell and magnetocrystalline anisotropy, but also by nonspecific factors such as sintered states and grain size [2]. For better understanding of the contributing factors to enhance of Ca-La-Co ferrite sintered magnets, it is necessary that the effects of nonspecific factors be understood. This work was carried out to investigate the effects of CaO and SiO₂ inter-additives on magnetic and physical properties of Ca-La-Co system ferrite sintered magnets.

II. EXPERIMENTAL METHOD

The raw materials used in this experiment are CaCO₃, La₂O₃, α -Fe₂O₃, CoO and SiO₂ powders. The chemical composition was (Ca_{0.5}La_{0.5})_{1.1}Fe_{11.6}Co_{0.4}O₁₉. These raw materials were weighed and mixed with the total weight of the sample at 0.3 kg. Mixed samples were sintered to initiate a chemical reaction at 1250°C for 4 hrs in air. The reacting sintered samples were pulverized to under 150 μ m. The inter-additives of SiO₂ and CaO (using CaCO₃) were added to the pulverized powders. These powders along with the inter-additives were milled for 8 hrs using the stainless steel vibrating mill (wet method). The milled powder now in slurry form, was compacted into a cylindrical shape in the magnetic field. And these green compacts were sintered from 1160 to 1260°C for 1 hr in air. The magnetic properties of the sintered samples were measured with a DC Recording Fluxmeter. The average particle sizes of the samples were calculated from a Scanning Electron Microscope (SEM) photographs. The crystal structures and phases were examined by the X-ray Diffraction method using Cu-K α radiation.

III. RESULT AND DISCUSSION

A. Effects of SiO₂ Inter-additive on Magnetic and Physical Properties

First, only the effects of the SiO₂ inter-additive on magnetic and physical properties are discussed. Fig.1 shows the effect of SiO₂ inter-additive on coercivity H_{cJ} , maximum magnetization J_m , and the density of sintered magnets at 1160, 1200, 1240°C. J_m means magnetization of sintered magnets in the 960 kA/m magnetic field. In reference, the magnetic properties of the Sr-La-Co system ferrite sintered magnets produced with the same amount and kinds of inter-additives, and with the same milling conditions sintered at 1240°C in our laboratory are shown in Fig.1. As seen in Fig.1, the densities increased with an increase in the SiO₂ inter-addition, inversely, and maximum magnetization J_m decreased with

an increase in the SiO₂ inter-addition. If compared to Sr-La-Co ferrite made in our laboratory, it was found that the densities of the Ca-La-Co ferrite sintered magnets, those without SiO₂, and those with few SiO₂ additives, were greatly different from that of the Sr-La-Co ferrite. Additionally, the decrease of J_m with an increase in the SiO₂ inter-addition of Ca-La-Co system ferrite sintered magnets showed different behavior from that of the Sr-La-Co system sintered magnets. The phase analyses of Ca-La-Co ferrite sintered magnets with several amounts of SiO₂ inter-additive are shown in Table 1. The M-Type single phase was obtained from the samples sintered at over 1240°C without SiO₂ additives, M-type and α -Fe₂O₃ multi phases were obtained from other samples. Furthermore, it was found from the intensity of the XRD spectra that the α -Fe₂O₃ increased with an increase in the amount of SiO₂ inter-addition. Moreover, all the SiO₂ inter-additional samples of the Sr-La-Co system ferrite sintered magnets were M-type single phase. From these results, it is thought that the inter-addition of SiO₂ achieve high density in the Ca-La-Co ferrite sintered magnets, however, the magnetizations of sintered magnets decrease due to the generating of the impurity phase α -Fe₂O₃. Moreover, the coercivity H_{cJ} of Ca-La-Co system ferrite increased with an increase in the amount of SiO₂ inter-additive. The effects of the amount of SiO₂ additives on the average particle size of Ca-La-Co sintered at 1160, 1200 and 1240°C magnets are shown in Fig.2. The average particle sizes decrease with an increase of SiO₂ inter-additives, but increase with sintering temperature. It is considered that these effects on particle size produced an increase of H_{cJ} . Fig.3 shows the relation between the average particle size and the density of Ca-La-Co sintered magnets with SiO₂ inter-additive. As seen in Fig.3, it was learned that small particles and high density sintered magnets were obtained by increasing SiO₂ inter-additive.

Table I Phase analysis of Ca-La-Co system ferrite sintered magnets with SiO₂ inter-additive.

SiO ₂ [wt.%] \ sintering temp. [°C]	1160	1180	1200	1220	1240	1260
0	M α	M α	M α	M α	M	M
0.1	M α	M α	M α	M α	M α	M
0.2	M α	M α	M α	M α	M α	M
0.3	M α	M α	M α	M α	M α	M α

B. Effects of SiO₂ and CaO Inter-Additives on Magnetic and Physical Properties

Second, the effects of SiO₂ and CaO inter-additives on magnetic and physical properties are discussed. Fig.4 shows the effect of the SiO₂ and CaO inter-additives on coercivity H_{cJ} , maximum magnetization J_m and the density of sintered magnets at 1160, 1200, 1240°C. In reference, the magnetic properties of the Sr-La-Co

Fig. 1 Effect of SiO₂ inter-addition on the magnetic properties and densities of sintered magnets.

Fig. 2 Effect of SiO₂ addition weight on the particle size of Ca-La-Co system ferrite sintered magnets.

Fig. 3 Relationship between density and particle size of Ca-La-Co system ferrite sintered magnets with SiO₂ inter-additive.

system ferrite sintered magnets produced with the same amount and kinds of inter-additives, and with the same milling conditions sintered at 1240°C in our laboratory are shown in Fig.4. The density of sintered magnets at 1200 and 1240°C gradually decrease with an increase in the CaO inter-additive, and the density of sintered magnets at 1160°C decreases rapidly with an increase in the CaO inter-additive. The J_m of sintered magnets at 1200 and 1240°C increase with an increase in the CaO inter-additive from 0 to 0.5wt%, and then decrease. The phase analyses of Ca-La-Co system sintered magnets with SiO₂ and CaO inter-additives from XRD spectra are shown in Table 2. It was learned that the M-type single phase was obtained by the inter-addition of a large amount of CaO. From both results, it is worth considering that α -Fe₂O₃ impurity phase disappears by an increase of CaO inter-additive; the magnetization decreases due to a lowering of density with an increase of CaO inter-addition in the region of M-type single phase. Meanwhile, both properties of density and magnetization of Sr-La-Co ferrite sintered magnets have the same characteristics, and the M-type phases were obtained from all the inter-added samples. On the one hand, the H_{cJ} of Ca-La-Co system ferrite sintered magnets at 1160°C gradually decreases with an increase in the CaO inter-addition. On the other hand, the H_{cJ} of sintered magnets at 1200 and 1240°C, comparatively speaking, rapidly decreases with an increase in the amount of CaO inter-additive. Fig.5 shows the effect of CaO inter-addition on the average particle size of Ca-La-Co system ferrite sintered magnets. The sizes of sintered magnets grow to a large size with an increase in the amount of CaO inter-additive. It is considered that the decrease of coercivity with an increase of CaO inter-additive is caused by this phenomenon. The relationship between density and average particle size is shown in Fig.6. It is shown that the inter-addition of CaO promotes the growth of particles with densification.

Table II Phase analysis of Ca-La-Co system ferrite sintered magnets with SiO₂ and CaO inter-additives.

sintering temp. [°C]		1160	1180	1200	1220	1240	1260
SiO ₂ , CaO [wt.%]							
0.3	0	M α	M α	M α	M α	M α	M α
0.3	0.3	M α	M α	M α	M α	M	M
0.3	0.5	M	M	M	M	M	M
0.3	0.7	M	M	M	M	M	M

IV. CONCLUSION

In this research, the effects of SiO₂ and CaO inter-addition on magnetic properties of Ca-La-Co system ferrite sintered magnets were discussed. Concluding remarks are shown as follows.

(1) The density of Ca-La-Co system ferrite sintered magnets increase with an increase in the SiO₂ additives, however, magnetization

Fig. 4 Effects of CaO inter-addition on the magnetic properties and densities of sintered magnets.

Fig. 5 Effect of CaO addition weight on the particle size of Ca-La-Co system ferrite sintered magnets.

Fig. 6 Relation between density and particle size of the Ca-La-Co system ferrite sintered magnets with SiO₂ and CaO inter-additives.

decreases with an increase in the SiO₂ additives because α -Fe₂O₃ impurity phase was formed by SiO₂ inter-addition. In contrast to this, magnetization was increased by a suitable amount of CaO inter-addition. This occurred because the α -Fe₂O₃ impurity phase was less formed by CaO, although density was lowered with the addition of too much CaO.

(2) The coercivity H_{cJ} of the Ca-La-Co system sintered magnets increase with an increase in the amount of SiO₂ inter-additive due to the average particle size of sintered magnets becoming smaller. Whereas, the H_{cJ} of the Ca-La-Co system sintered magnets decrease with an increase of the CaO inter-addition because the average particle size of sintered magnets were grown by CaO inter-additive.

The preparation condition and the magnetic properties of Ca-La-Co system ferrite sintered magnet with the maximum value of the maximum energy product in this experiment were as follows; inter-additives are 0.3 wt.% SiO₂ and 0.5 wt.% CaO, sintering condition were 1200°C×1h in air, $J_m=0.444$ [T], $B_r=0.429$ [T], $H_{cJ}=278.1$ [kA/m], $(BH)_{\max}=34.5$ [kJ/m³]

REFERENCES

- [1] Y. Kobayashi, S. Hosokawa, E. Oda and Y. Toyoda, *J. Jpn. Soc. Powder Powder Metallurgy*, **55**, 541 (2008).
- [2] Y. Kaneko, S. Amamoto and A. Hamamura, *J. Jpn. Soc. Powder Powder Metallurgy*, **34**, 169 (1987).