Effect of Na₂O and SrO Addition on Magnetic Properties of Anisotropic SrZn₂ System W-Type Hexagonal Ferrite Magnets.

Hiroshi Yamamoto and Masahiro Chono

School of Science and Technology, Meiji University

1-1-1, Higashimita, Tama-ku, Kawasaki 214-71, Japan

ABSTRACT—This experiment was carried out to investigate the effect of Na₂O and SrO additives on the magnetic and physical properties of SrZn₂-W type hexagonal ferrite. The specimens were prepared by the conventional manufacturing methods without the atmosphere control. It was found that the magnetic properties of SrO · 2ZnO·8Fe₂O₃ were considerably improved on adding 1.33wt% Na₂O and 0.67wt% SrO after semisintering treatment. The optimum condition of making magnet with suitable properties are as follows : chemical analysis composition: $\text{Sr}^{2+}_{0.953}\text{Zn}^{2+}_{1.595}\text{Na}^{+}_{0.271}\text{Fe}^{2+}_{0.080}\text{Fe}^{3+}_{16.157}\text{O}_{27}$; semisintering condition : 1300°C x 1h in air ; sintering condition : 1250°C x 0.5h in air. The magnetic properties are : $J_m = 0.415 \text{ T}$, $J_r = 0.375 \text{ T}$, $H_c = 123.4 \text{ kA/m}$, $H_{cb} = 118.6 \text{ kA/m}$, $(\text{BH})_{\text{max}} = 22.8 \text{ kJ/m}^3$, $T_c = 361^\circ\text{C}$, $H_A = 1084 \text{ kA/m}$, $K_A = 2.25 \times 10^3 \text{ J/m}^3$ and $n_B = 33.8\mu\text{B}$. The magnetic properties of this compound powder heated at 1100 °C after milling are $\sigma_s = 82.9 \times 10^{-6} \text{ Wb}\cdot\text{m/kg}$ and $H_c = 199 \text{ kA/m}$, and they are useful as the bonded magnet material.

I. INTRODUCTION

Research on the magnetic properties of Ba and Sr W-type ferrite magnets with the atmosphere control were reported by Lotgering et al.[1] in 1980. Recently, Toyota[2] reported SrFe₂-C W-type ferrite sintered in N₂ gas atmosphere having the excellent magnetic properties. However, there are a few studies of W-type ferrite sintered magnet without atmosphere control. Yamamoto et al.[3] synthesized Sr-Zn system W-type hexagonal ferrite without using any special atmosphere to achieve the considerably improved and reproducible magnetic properties.

This experiment was carried out to investigate the effect of Na₂O and SrO additives on the magnetic and physical properties of SrZn₂-W type hexagonal ferrite without atmosphere control.

II. EXPERIMENTAL METHODS

The raw materials used in this experiment were SrCO₃, ZnO, α -Fe₂O₃, Na₂CO₃ powders. Using these raw materials, the basic composition was SrO·2ZnO·8Fe₂O₃, the compound whose total weight was 0.3kg was prepared. The raw materials were homogeneously mixed under alcohol using ball milling for 3h. This mixed powder was dried up, and then pressed at a pressure 49MPa to form a columnar shaped samples 36mm diameter x 7mm. These formed samples were semisintered at 1300°C for 1h in air. Those semisintered clinkers were ground less than 150 μm , and then SrO(0~1.5wt%) and Na₂O(0~1.5wt%) were added to be the suitable added contents and added ratios. Here, SrCO₃ was used to obtain SrO, similarly Na₂CO₃ was used to obtain Na₂O. They were pulverized using a stainless vibration mill(by wet method) for 8h. These pulverized powders were pressed at a pressure 294MPa to form a columnar shape of 13mm diameter x 11~13mm under magnetic field of 800kA/m along the pressing direction, and then sintered at 1200~1300 °C in air for 0.5h.

The magnetic properties were measured by a high

sensitivity self-recording fluxmeter, and Curie temperature and temperature dependence were measured by a vibrating sample magnetometer(VSM). A density was examined by Archimedes principle, the crystal structure was analyzed by X-ray diffraction. Microstructure of these samples was observed by SEM.

III. RESULTS AND DISCUSSION

The authors reported about the effect of Na₂O additives on the magnetic and physical properties of SrZn₂-W type hexagonal ferrite formerly[4]. As the result of these, it was found that magnetic properties improved as for 1.5% Na₂O addition for SrZn₂-W type hexagonal ferrite. So, this experiment was carried out to investigate the effect of Na₂O and SrO additives on the magnetic and physical properties of SrZn₂-W type hexagonal ferrite.

Fig.1 shows the magnetic properties of SrO·2ZnO·8Fe₂O₃ compounds in addition with 0~1.5wt% SrO and 1.5wt% Na₂O after semisintering treatment at various sintering temperatures. These samples were semisintered at 1300°C. The value of J_m , J_r , H_{cj} , H_{cb} and $(\text{BH})_{\text{max}}$ were determined from J-H curve measured by the high sensitivity self-recording fluxmeter in the magnetic field up to 800kA/m. In this figure, J_m is the flux density at 800kA/m. S.S.C. and S.C. are semisintering condition and sintering condition, respectively. As seen this figure, the values of H_{cj} and H_{cb} did not change until SrO addition from 0 to 1.0wt%, and then decreased sharply. The values of J_m and J_r increased with increasing SrO addition. The value of $(\text{BH})_{\text{max}}$ increased with increasing SrO addition from 0 to 0.75wt%, however this trend was slightly different in every sintering temperature. The best value of $(\text{BH})_{\text{max}}$ was obtained with a sample added with 1.5wt% Na₂O and 0.75wt% SrO sintered at 1250 °C.

From a result of Fig.1, it was found to be obtained good magnetic properties when the ratio of addition of Na₂O and SrO was 2:1. Fig.2 shows effect of the total quantity of Na₂O and SrO additives on magnetic properties of

SrO·2ZnO·8Fe₂O₃ compounds. As indicated this figure, the value of H_{cJ} and H_{cB} increased with increasing the total quantity, on the other hand, the value of J_m and J_r increased with increasing the total quantity from 0 to 1.5wt%, and then almost kept constant. The best value of $(BH)_{max}$ was obtained with the sample added with 2.0wt% total quantity (1.33wt% Na₂O and 0.67wt% SrO) sintered at 1225 °C .

Fig.1 Effect of SrO addition on magnetic properties of SrO·2ZnO·8Fe₂O₃ compounds in addition with Xwt% SrO and 1.5wt% Na₂O after semisintering at various sintering temperatures.

Fig.2 Effect of the total quantity of Na₂O and SrO additives on magnetic properties of SrO·2ZnO·8Fe₂O₃ compounds. The ratio of addition of Na₂O and SrO at 2:1 .

Fig.3 shows the X-ray diffraction patterns of SrO·2ZnO·8Fe₂O₃ compounds added with the total contents (0~2.25wt%) of Na₂O and SrO at the addition ratio of 2:1. These samples were semisintered at 1300 °C and sintered at 1225°C . As shown this figure, in the sample without additives, multiphases(W-phase and α -Fe₂O₃ phase) revealed, and the other samples was a W-type single phase.

Fig.4 shows the effect of sintering temperatures on magnetic properties of SrO·2ZnO·8Fe₂O₃ compounds added with Xwt% Na₂O and Ywt% SrO after semisintering

Fig.3 X-ray diffraction patterns of SrO·2ZnO·8Fe₂O₃ compounds added with the total quantity (0~2.25wt%) of Na₂O and SrO additives at the addition ratio of 2:1. s.s.c.:1300°Cx1h in air. s.c.:1225°Cx0.5h in air.

Fig.4 Effect of sintering temperature on magnetic properties of SrO·2ZnO·8Fe₂O₃ compounds in addition with Xwt% Na₂O and Ywt% SrO after semisintering treatment.

treatment. As shown this figure, it was found that the best magnetic properties were obtained by semisintering at 1300 °C for 1h followed by final sintering at 1225 °C for 0.5h in the sample added with 1.33wt% Na₂O and 0.67wt% SrO after semisintering treatment. The resulting magnetic properties are $J_m=0.415$ T, $J_r=0.375$ T, $H_{cJ}=123.4$ kA/m, $H_{cB}=118.6$ kA/m, $(BH)_{max}=22.8$ kJ/m³. The magnetic anisotropic field H_A of these samples was determined based on two magnetization curves by applying field up to 1600 kA/m parallel and perpendicular to the alignment axis(c axis) and using extrapolation method for ten different samples (7 x 7 x 7mm³). K_A was estimated by $K_A=J_m \cdot H_A/2$. As a result , K_A is 2.25×10^5 J/m³ and H_A is 1084kA/m, these values are larger than those of SrO·2ZnO·8Fe₂O₃ single crystal reported by Greatch[5]. And the average grain size of these samples is about 2.0 μ m.

Fig.5 Temperature dependence on magnetic properties of $\text{SrO} \cdot 2\text{ZnO} \cdot 8\text{Fe}_2\text{O}_3$ compounds in addition with 1.33wt% Na_2O and 0.67wt% SrO after semisintering treatment.

Fig.5 shows the temperature dependence of saturation magnetization and intrinsic coercivity of $\text{SrO} \cdot 2\text{ZnO} \cdot 8\text{Fe}_2\text{O}_3$ compound added with 1.33wt% Na_2O and 0.67wt% SrO after semisintering treatment. The spherical sample was prepared in order to make a correction of demagnetizing factor. The value of σ_s was calculated by the extrapolation method using $1/H^2$. As the temperature decreases, σ_s exhibits a linear increasing tendency, the H_{cj} increases up to about 200°C , and then decreased sharply. These trend is very similar to M-type ferrite magnets. Extrapolation from the data in the figure indicated that the σ_s at $0\text{K}(-273^\circ\text{C})$ is $154.5 \times 10^{-6}\text{Wb-m/kg}$, and the molecular weight of this sample, $MW=1532.8$, was obtained by chemical analysis. As a result, the magnetic moment per formula unit of this compound was calculated to be $n_B=33.8 \mu\text{B}$ (without any correction for 4.2% non-magnetic impurities expected by chemical analysis). This value is lower than that of a single crystal[5].

Fig.6 Curie temperature of $\text{SrO} \cdot 2\text{ZnO} \cdot 8\text{Fe}_2\text{O}_3$ compounds in addition with the total quantity (0~2.25wt%) of Na_2O and SrO additives at the addition ratio of 2:1.

Fig.6 shows Curie temperature of $\text{SrO} \cdot 2\text{ZnO} \cdot 8\text{Fe}_2\text{O}_3$ compounds added with the the total quantity (0~2.25wt%) of Na_2O and SrO additives at the addition ratio of 2:1. As shown this figure, Curie temperature decreased up to 2.0 wt%, and kept nearly constant for 2.0wt compound addition and above. It appeared that there are a range of Na_2O and SrO solubility in $\text{SrZn}_2\text{-W}$ ferrite. The T_c of the sample added with 1.33wt% Na_2O and 0.67wt% SrO (total content

is 2.0wt%) having the best magnetic property was 361°C .

Fig.7 shows the effect of annealing temperature on magnetic properties of $\text{SrO} \cdot 2\text{ZnO} \cdot 8\text{Fe}_2\text{O}_3$ compound powder in addition with 1.33 wt% Na_2O and 0.67wt% SrO after semisintering treatment. As shown this figure, the values of σ_s and H_{cj} increase with increasing of annealing temperature. The typical properties of these samples is $\sigma_s=82.9 \times 10^{-6}\text{Wb-m/kg}$ and $H_{cj}=199 \text{ kA/m}$, and they are useful as the bonded magnet material.

Fig.7 Effect of annealing temperature on magnetic properties of $\text{SrO} \cdot 2\text{ZnO} \cdot 8\text{Fe}_2\text{O}_3$ compound powder in addition with 1.33 wt% Na_2O and 0.67wt% SrO after semisintering treatment.

IV. CONCLUSION

In Sr-Zn system W-type hexagonal ferrite magnets, the effect of Na_2O and SrO addition after semisintering treatment on magnetic and physical properties were investigated, it was found that magnetic properties of this compound were significantly improved by adding SrO and Na_2O after semisintering treatment. Particularly, intrinsic coercivity is about 70% larger than that of without any additives. The best magnetic properties is obtained by adding with 1.33wt% Na_2O and 0.67wt% SrO (total content is 2.0wt%) in this system, and the best value of $(BH)_{\max}$ indicated 22.8kJ/m^3 , which was 95% larger than that of without any additives. These results indicate a potential industrial use of the W-type ferrite magnets.

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