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Effect of forms of B_2O_3–SiO_2 as an additive on magnetic properties of $SrFe_{12}O_{19}$ ferrites

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Strontium ferrites ($SrO \cdot 5.5Fe_2O_3$) were prepared using hot-rolled mill scale as a source of iron oxides. Calcination was performed at 1200 °C for 2 h. The fused B_2O_3–SiO_2, with various mole ratios of B_2O_3 to SiO_2, was added to the calcined ferrites during the milling stage. The ferrites were formed anisotropically. The fused additives are quite effective to enhance the magnetic properties; $(BH)_{max}$ can reach 3.0 MGOe for the ferrite sintered at 1220 °C for 2 h. In general, $(BH)_{max}$ is independent of the mole ratio of B_2O_3 to SiO_2 and dominantly influenced by the sintering temperature. The addition of 0.3 or 0.5 wt% fused additives showed no significant difference in the magnet quality. The quality of the magnet was decreased with increasing mole ratio of B_2O_3 to SiO_2 when unfused B_2O_3–SiO_2 was used under the same processing conditions.

1. Introduction

The quality of hard ferrites is evaluated in terms of $(BH)_{max}$ values. High remanence, B_r, and high coercivity, H_c, are generally required for quality magnets. The former can be obtained by densification and crystal orientation and the latter can be retained in fine-grain structures.

Gray and Routile [1] observed that the magnetic properties of strontium ferrites deteriorate on the addition of B_2O_3. Chien and Ko [2] found that the grain growth of the barium ferrites is dominantly influenced by the size of the silica added; coarse-grain (≈ 1 μm) silica tends to promote discontinuous grain growth which increases drastically with slightly increasing amounts of silica added in the range 0.15–0.50 wt% while fine-grain (≈ 0.013 μm) silica tends to retain fine-grain microstructures with the same increasing amount of silica on sintering at 1220 °C for 2 h.

The combined effect of H_3BO_3 and SiO_2 on the quality of hard ferrites was investigated by Harada [3]. He reported that the addition of SiO_2 at the mixing stage and H_3BO_3 at the milling stage is superior to the addition of H_3BO_3 at the mixing stage and SiO_2 at the milling stage for magnetic properties enhancement. However, adding both H_3BO_3 and SiO_2 at the milling stage for the preparation of hard ferrites has not been reported.

Adding B_2O_3 to hard ferrites either at the mixing or milling stage will cause inconvenience in material handling because B_2O_3 readily dissolves in water. The purpose of the present investigation was to add fused, as well as unfused, B_2O_3–SiO_2 to the strontium ferrites at milling stage and to find the effect of the forms of B_2O_3–SiO_2 as an additive on the magnetic properties of strontium ferrites.

2. Experimental procedure

2.1. Materials

The mill scale used in the present work was produced from the heavy steel plates during hot-rolling processes (Table I). The other raw materials included reagent-grade $SrCO_3$ and industrial-grade B_2O_3 and SiO_2. The dry mixes consisting of B_2O_3 and SiO_2 with B_2O_3/SiO_2 ratios 1:3, 1:2, 1:1, 2:1 and 3:1, were mixed in a ball mill for 6 h. These mixes were fused in a platinum crucible in an electric furnace at 1000 °C for 1 h. The fused B_2O_3–SiO_2 was ground in a ball mill for 16 h.

TABLE I Chemical composition of hot-rolled scale after leaching with water

Constituent	wt %
Total Fe	74.9
SiO_2	0.054
Al_2O_3	0.046
MnO	0.320
MgO	0.006
CaO	0.002
K_2O	0.060
Na_2O	0.024

2.2. Procedure

The amount of mill scale and strontium carbonate required for the preparation of strontium ferrite specimens was calculated in accordance with $n = 5.5$, where n is related to the chemical formula $SrO \cdot nFe_2O_3$. These powders in deionized water, together with a small amount of alcohol (≈ 1 wt % of the water added) as a dispersant, were ground in an attrition mill for 4 h.

The dried mixtures after attrition milling were calcined in an electric furnace at 1200 °C for 2 h. They were then crushed in a vibration mill to pass through a 0.147 mm screen and ground, together with either the fused or the unfused B_2O_3–SiO_2 powder, in an attrition mill for 4 h.

Discs, 22 mm diameter and $\geqslant 5$ mm thick, were anisotropically formed under a pressure of 200 MPa by die pressing dry powder in a magnetic field of 8 kG, parallel to the loading direction.

These disc specimens were sintered in an electric furnace at 1200–1250 °C for 2 h. The specimens were

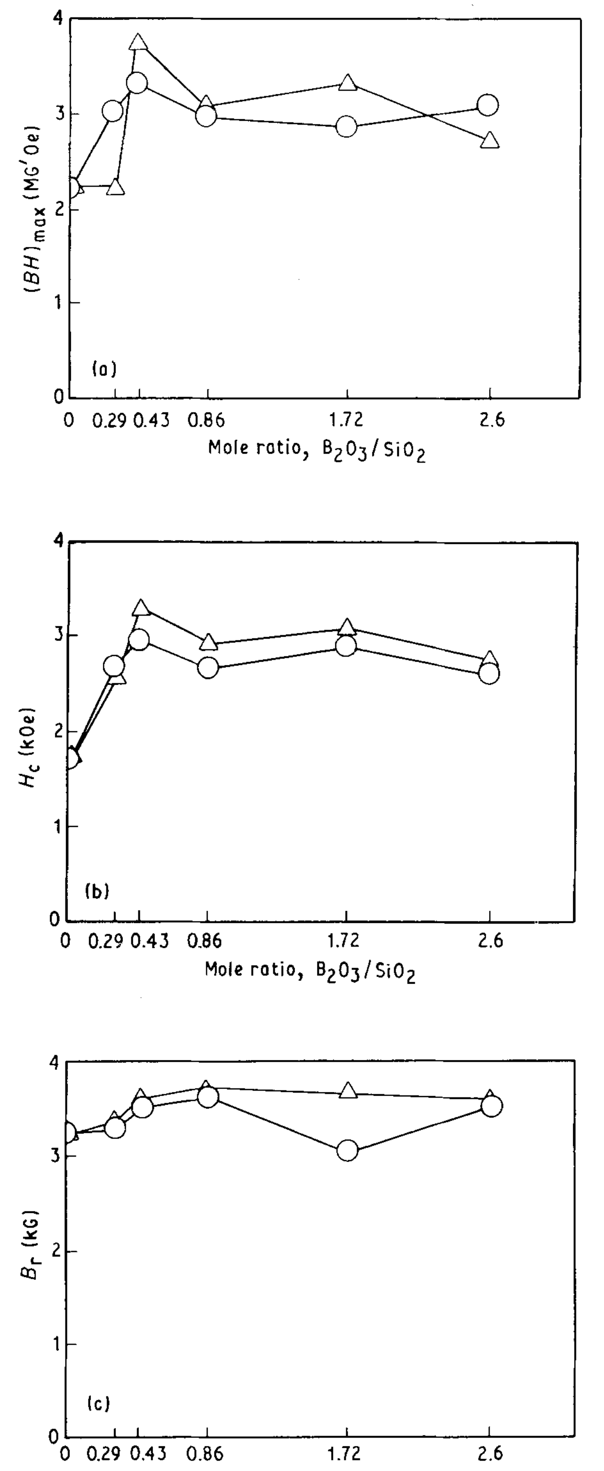

Figure 1 Effects of mole ratio and amount of fused additives on magnetic properties of strontium ferrites sintered at 1220 °C for 2 h. (a) $(BH)_{max}$, (b) H_c and (c) B_r. (△) 0.3 wt %, (○) 0.5 wt %.

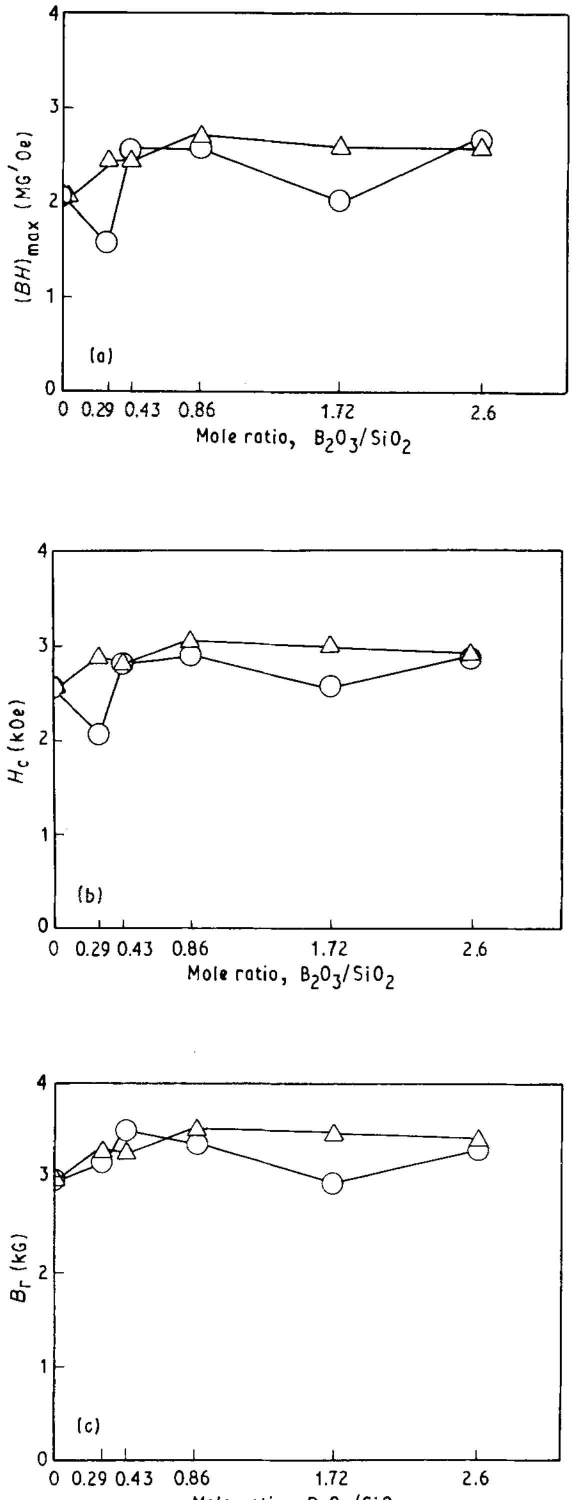

Figure 2 Effects of mole ratio and amount of fused additives on magnetic properties of strontium ferrites sintered at 1200 °C for 2 h. (a) $(BH)_{max}$, (b) H_c and (c) B_r. (△) 0.3 wt %, (○) 0.5 wt %.

TABLE II Summary of the effects of sintering temperature and the amount of additives on the quality of the magnets

Fused B_2O_3–SiO_2 (wt %)	Sintered at 1200 °C $(BH)_{max}$ (MGOe)		Sintered at 1220 °C $(BH)_{max}$ (MGOe)	
	Mean value $\bar{x}$	Standard deviation $\bar{\sigma}$	Mean value $\bar{x}$	Standard deviation $\bar{\sigma}$
0.3	2.5792	0.1042	3.0470	0.4943
0.5	2.3328	0.4548	3.0648	0.1479

removed from the furnace after normal furnace cooling to room temperature.

The sintered specimens were polished for the various magnetic properties measurements. The microstructures were observed with scanning electron microscopy (SEM) using the polished section technique after the specimens had been thermally etched at 1050 °C for 45 min.

3. Results and discussion

The magnetic properties of the strontium ferrites with added fused B_2O_3–SiO_2 are shown in Figs 1 and 2. As can be seen from Figs 1a and 2a, the addition of the fused B_2O_3–SiO_2 as an additive is quite effective to enhance the quality of the strontium ferrites; there were irregularities in the $(BH)_{max}$ values when the mole ratio of B_2O_3 to SiO_2 was 0.29; the irregularities were most probably caused by experimental errors. In general, the $(BH)_{max}$ values are independent of the mole ratio of B_2O_3 to SiO_2. It is believed that the fused B_2O_3–SiO_2 reacted with the strontium ferrite to form a liquid at the elevated temperatures; only a fixed amount of B_2O_3 could be held in the liquid and the remainder evaporated during sintering, regardless of the fused B_2O_3–SiO_2 containing different amounts of B_2O_3 due to different mole ratios.

The effects of sintering temperature and the amount of additive on the quality of the strontium ferrites are summarized in Table II. Apparently, the $(BH)_{max}$ values are dominantly influenced by the sintering temperature and the addition of 0.3 or 0.5 wt % fused B_2O_3–SiO_2 showed no significant difference in the magnet quality. Apparently, sintering at 1220 °C is favoured over sintering at 1200 °C.

The viscosity of the liquid phase decreases as the temperature increases. The lower viscosity facilitates a more uniform distribution of the liquid phase among the grains and results in a uniform and fine-grain microstructure (Fig. 3). However, a slightly higher temperature could produce a lower viscosity liquid phase and result in discontinuous grain growth and degradation in magnet quality (Fig. 4). In summary, for the strontium ferrites to which fused B_2O_3–SiO_2 was added, the optimum sintering temperature was 1220 °C, and 1200 °C was too low while 1250 °C was too high.

The magnetic properties of the strontium ferrites to which unfused B_2O_3–SiO_2 was added during the milling stage are shown in Fig. 5. In general, the

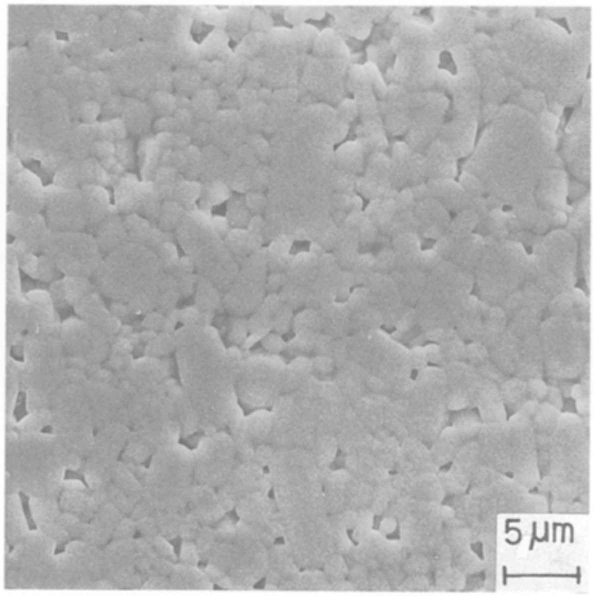

Figure 3 Scanning electron micrograph of strontium ferrite to which 0.3 wt % fused B_2O_3–SiO_2, mole ratio 1.72, was added, and sintered at 1220 °C for 2 h: $(BH)_{max}$ = 3.32 MGOe, H_c = 3000 Oe and B_r = 3680 G.

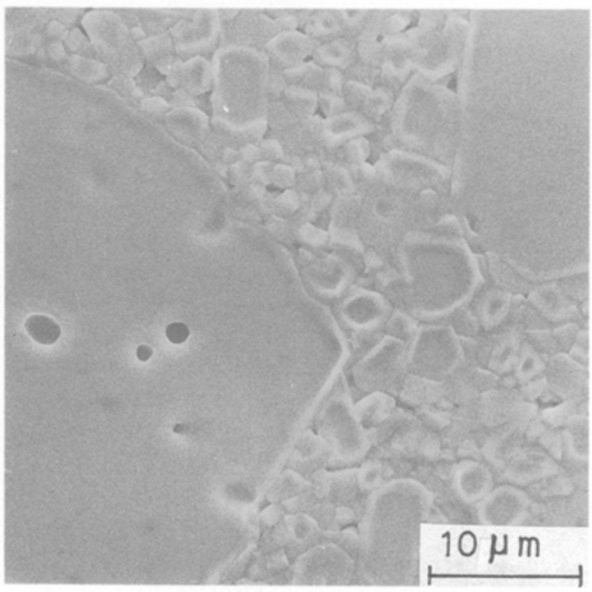

Figure 4 Scanning electron micrograph of strontium ferrite to which 0.5 wt % fused B_2O_3–SiO_2, mole ratio 1.72, was added, and sintered at 1250 °C for 2 h, $(BH)_{max}$ = 1.55 MGOe, H_c = 1700 Oe and B_r = 3142 G.

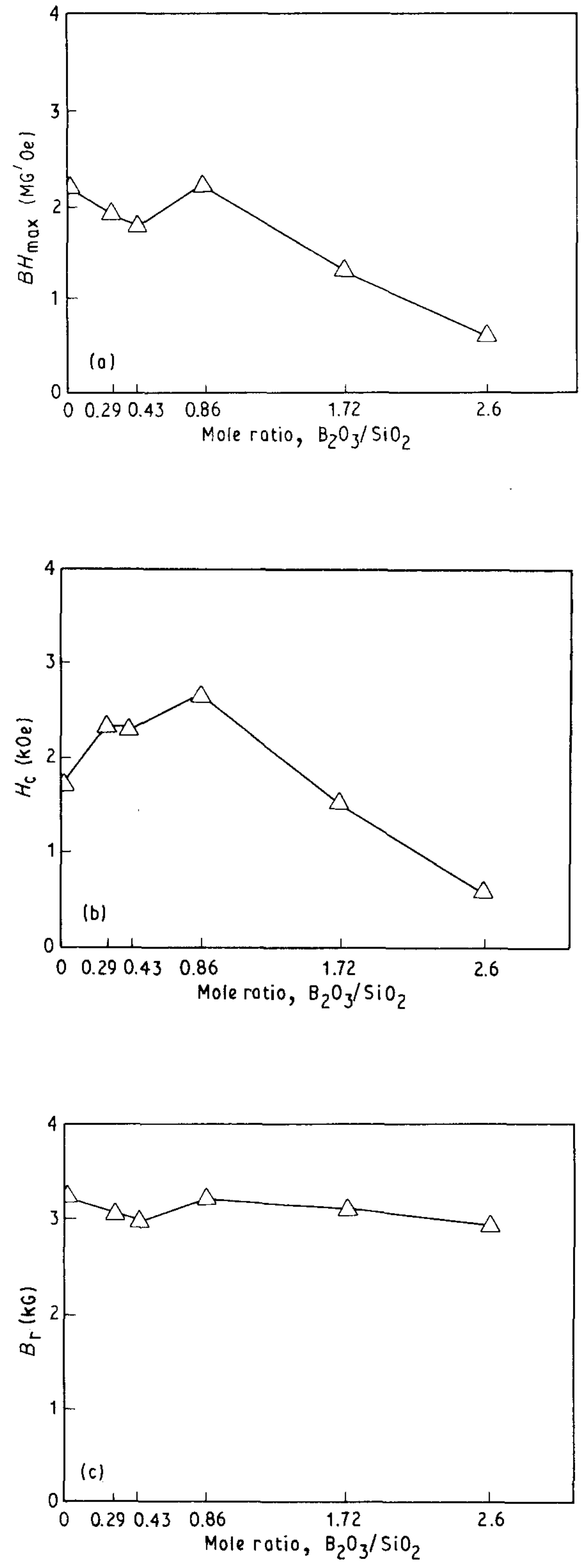

Figure 5 Effects of mole ratio and amount (0.5 wt %) of unfused additives on magnetic properties of strontium ferrites sintered at 1220 °C for 2 h. (a) $(BH)_{max}$, (b) H_c and (c) B_r.

quality of the magnet decreased with increasing mole ratio of B_2O_3 to SiO_2. The reflected light micrograph revealed that the deterioration of the quality of the magnet was caused by discontinuous grain growth (Fig. 6). Moreover, the appearance of large hexagonal crystals is an indication of the existence of a considerable amount of liquid phase during sintering. B_2O_3 alone could react much more readily with the strontium ferrites at the sintering temperature to produce a considerable amount of liquid phase, which is related to the discontinuous grain growth. The B_2O_3 in the fused B_2O_3–SiO_2 is believed to be less reactive with the strontium ferrites at the same sintering temperature, and less liquid was produced.

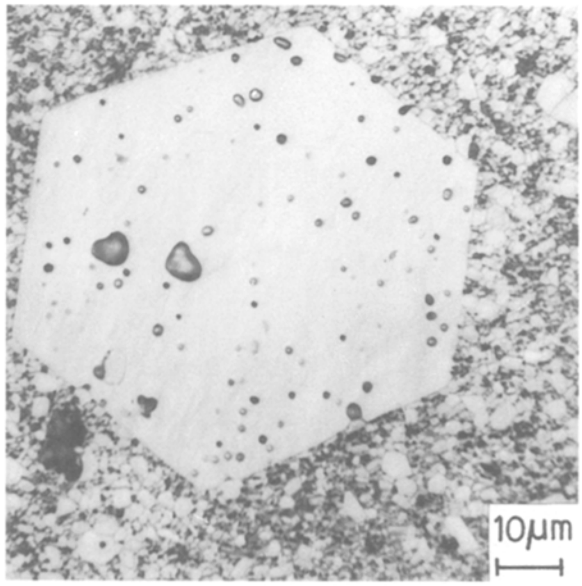

Figure 6 Reflected light micrograph of Sr-ferrite added with 0.5 wt % unfused B_2O_3–SiO_2 of mole ratio 1.72 and sintered at 1220 °C for 2 h, $(BH)_{max}$ = 1.30 MGOe, H_c = 1500 Oe, and B_r = 3100 G.

4. Conclusion

Strontium ferrites ($SrO \cdot 5.5Fe_2O_3$) were prepared by using hot-rolled mill scale as a source of iron oxides. Calcination was made at 1200 °C for 2 h. 0.3 or 0.5 wt % fused B_2O_3–SiO_2 with B_2O_3/SiO_2 ratios of 1:3, 1:2, 1:1, 2:1 and 3:1 were added to the calcined ferrites during the milling stage. These ferrites were formed anisotropically and sintered at 1200 and 1220 °C, respectively. The fused additives are quite effective to enhance the magnet quality. The $(BH)_{max}$ values can reach 3.0 and 2.5 MGOe for the ferrites sintered at 1220 and 1200 °C for 2 h, respectively. In general, $(BH)_{max}$ values are independent of the mole ratio of B_2O_3 to SiO_2 and dominantly influenced by the sintering temperature. The optimum sintering temperature was 1220 °C. 1200 °C was too low while 1250 °C was too high. The addition of 0.3 or 0.5 wt % fused B_2O_3–SiO_2 showed no significant difference in the magnet quality. The quality of the magnet was decreased with increasing mole ratio of B_2O_3 to SiO_2 when unfused B_2O_3–SiO_2 was used under the same processing conditions.

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