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The effect of silica characterization on the microstructure of $BaFe_{12}O_{19}$ ferrites

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The anisotropically formed $BaFe_{12}O_{19}$ ferrites were prepared from the hot-rolled mill scale and silica was added to the ferrite during fine milling in the range 0.15 to 0.50 wt%. These ferrites were sintered at 1220° C for 2 h. The grain growth of the ferrites is dominantly influenced by the sizes of the silica added. Coarse-grain ($\approx 1\,\mu m$) silica tends to promote discontinuous grain growth, which increases drastically with slightly increasing amounts of silica added, while fine-grain ($\approx 0.013\,\mu m$) silica tends to retain fine grain microstructures with the same increasing amount of silica. The average grain size of the ferrite without silica addition was 8 to 10 μm. The size was increased to as large as 30 μm on addition of 0.15% coarse-grain silica and the microstructure was full of extremely large grains on the addition of 0.50% coarse-grain silica.

1. Introduction

The quality of $BaFe_{12}O_{19}$ 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.

Broek and Stuijts [1] found that SiO_2 in the right amount ($\approx 1\%$) is an effective grain-growth inhibitor and its effectiveness ceases at higher temperatures. Müller and Heimke [2] reported that remanence and coercivity increased with increasing SiO_2 addition up to 1%. Gadalla and Schütz [3] observed that remanence and coercivity also increased with increasing SiO_2 addition up to 0.55%, and higher SiO_2 contents made the magnet's properties deteriorate.

Haberey and Kools [4] found that in the fine-grain strontium ferrite, secondary phases were not present in the grain boundaries, but were concentrated as crystalline pockets at some multiple grain junctions, and that silicon was enriched in the grain boundaries.

The quality of $BaFe_{12}O_{19}$ obtained from hot-rolled scale was investigated by Chien *et al.* [5].

It appears that the effect of the amount of SiO_2 added on the quality of magnets has been reported quite widely, but the effect of the characteristics of the SiO_2 has scarcely been mentioned. The purpose of the present investigation was to compare the quality of the magnets by adding SiO_2 of different sizes and forms.

2. Experimental details

2.1. Materials

The mill scale used in the present work was produced from the heavy steel plates during hot-rolling processes. The other raw materials included industrial-grade barium carbonate containing 98.5% $BaCO_3$ and two reagent-grade silicas. The chemical composition of the hot-rolled scale is given in Table I and the characterization of the SiO_2 is shown in Table II.

2.2. Procedure

The hot-rolled mill scale passed through a 2.362 mm opening screen was ground to −0.147 mm in a ball mill; −0.044 mm mill scale was subsequently obtained by milling in an attritor mill. The amount of mill scale and barium carbonate required for the preparation of barium ferrite specimens in the present work was calculated in accordance with $n = 5.6$, where n is related to the chemical formula $BaO \cdot nFe_2O_3$. These powders in deionized water, along with a small amount of alcohol (≈ 1 wt % of the water added) as a dispersant, were ground in an attritor mill for 4 h in accordance with the weight ratio of powders: deionized water: balls = 1 : 1 : 2.

The dried mixes after attritor milling were calcined in an electric furnace, which was heated at a rate of 6° C min^{-1} to 1200° C for 4 h. The calcined mixtures were crushed in a ball mill or vibration mill to pass through a 0.147 mm screen and ground with an attritor mill for 4 h. The same weight ratio of powders: deionized water: balls = 1 : 1 : 2 was maintained. The average particle size of the ground barium ferrite was 1.0 μm, which was determined by a Fisher Subsieve sizer.

TABLE I Chemical composition of hot-rolled scale

Constituent	wt %
Total Fe	74.6
SiO_2	0.043
Al_2O_3	0.048
MnO	0.282
MgO	0.012
CaO	0.029
K_2O	0.0038
Na_2O	0.14

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TABLE II Characterization of silica

SiO_2 type	SiO_2 content (wt %)	Specific surface area ($m^2 g^{-1}$)	Particle size (μm)	Crystal form
Coarse	99.6	0.56	10.5*	Quartz
Fine	96.46	171	0.0132†	Amorphous

* The mean value measured with Fisher Subsieve sizer.
† $D_{BET} = 6/\varrho_s S_w$, where $\varrho_s = 2.65\,g\,cm^{-3}$, and $S_w = 171\,m^2\,g^{-1}$.

Barium ferrite powders were thoroughly mixed with SiO_2 powders and lubricants during the fine milling for 4 h in an attritor mill. Discs, 22 mm diameter and $\geqslant 5$ mm thick, were anisotropically formed under a pressure of 1.0 ton cm^{-2}. The latter was formed by die pressing dry powder in a magnetic field of 6000 Oe, parallel to the loading direction.

These disc specimens were sintered in an electric furnace at 1220° C for 2 h. The heating rate was 6° C min^{-1} up to 1000° C and 4° C min^{-1} above 1000° C. The specimens were removed from the furnace after normal furnace cooling to room temperature.

Sintered specimens were polished for the measurement of diameter and thickness. A *B–H* curve was produced for the disc specimen by a magnetic hysterisis loop tracer. Coercivity (H_c) and maximum energy product $(BH)_{max}$ were obtained from the *B–H* curve.

The microstructures were observed with a reflected light microscope after the polished section had been subjected to coarse and fine grindings and thermal etching at 1100° C for 30 min.

3. Results and discussion

Table III summarizes the effect of the amount and type of silica added on the quality of the anisotropically formed magnets. Figures 1 and 2 show that the values of H_c and $(BH)_{max}$ decreased drastically for the magnets with the coarse-grain silica addition and those of H_c and $(BH)_{max}$ varied very little for the magnets with fine-grain silica addition when the amount of silica addition was slightly increased. The shrinkages of the magnets with the coarse-grain silica addition were slightly higher than those with the fine-grain silica, as shown in Fig. 3.

Figure 4 shows a micrograph of the barium ferrite without silica addition; the grain sizes are in the range 8 to 10 μm. Figure 5 demonstrates that discontinuous grain growth occurred in the barium ferrites with the coarse-grain silica addition and it increased rapidly with slightly increasing silica addition; the grain sizes of the barium ferrite added with 0.15 and 0.30% coarse-grain silica were as large as 30 and over 50 μm, respectively, and the extremely exaggerated grains were absolutely dominant in the microstructure of the barium ferrite with 0.5% coarse-grain silica addition. However, a uniform fine grain (5 to 6 μm) structure was retained by adding 0.3% fine grain silica to the barium ferrite as shown in Fig. 6. Of course, the lower values of H_c and $(BH)_{max}$ are related to the discontinuous grain growth as shown in Figs 1 and 2.

TABLE III Magnetic properties of the magnets added with various amounts of silica

Type	Additive		H_c (Oe)	B_r (G)	$(BH)_{max}$ (10^6 Oe G)	Shrinkage (%)
	Coarse silica (wt %)	Fine silica (wt %)				
α5	0	0	1902	3396	2.22	14.2
α5I1	0.15	0	2002	3038	1.89	15.8
α5I3	0.30	0	1248	3062	1.22	16.6
α5I5	0.50	0	576	3098	0.59	16.3
α5II	0	0.15	2119	3342	2.36	15.2
α5IIII	0	0.30	2294	3258	2.47	15.1
α5IIV	0	0.50	2237	3256	2.32	15.0

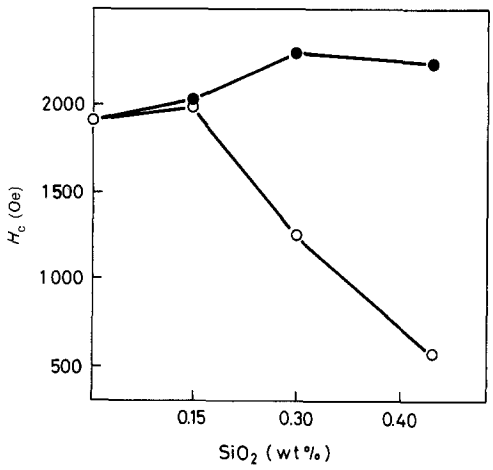


Figure 1 The effect of the size of the silica added on coercivity. (○) Coarse silica, (●) fine silica.

Table II shows that the average particle size was 10.5 μm for the coarse-grain silica and 0.0132 μm for the fine-grain silica, respectively. It is assumed that the coarse-grain silica and the barium ferrite powders had a similar size of ≈ 1 μm after milling; the coarse grain silica was dispersed in the barium ferrite while the barium ferrite was coated by the fine-grain silica. The shrinkage of the ferrites added with coarse-grain silica was $\approx 1\%$ higher than that with fine-grain silica, as shown in Fig. 3. Higher shrinkage is an indication of a higher liquid-phase content once present in the ferrite during the sintering. It is suggested that the SiO_2-enriched liquid phases caused by the dispersion of SiO_2 in the barium ferrite promotes discontinuous grain growth, while the thin liquid film containing silica, which surrounds the ferrite particles and is

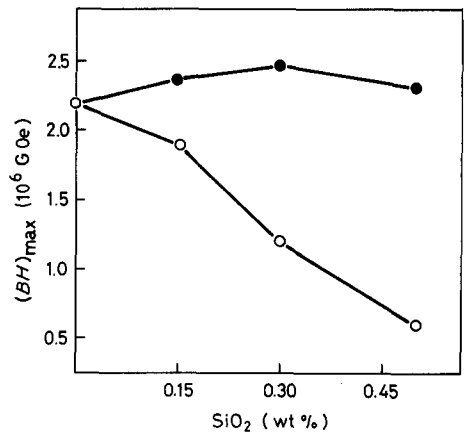


Figure 2 The effect of the size of the silicon added on maximum energy product. (○) coarse silica, (●) fine silica.

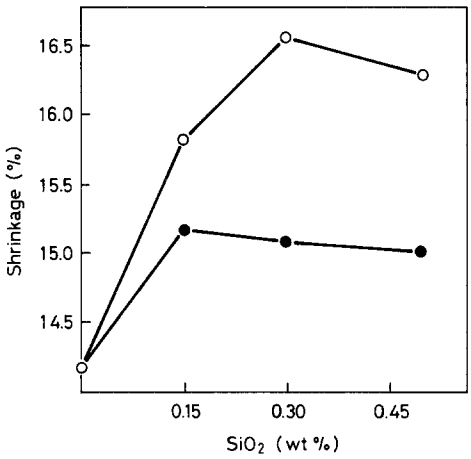
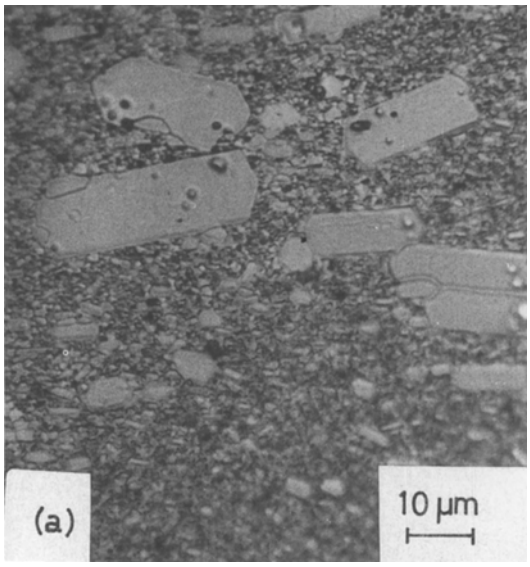
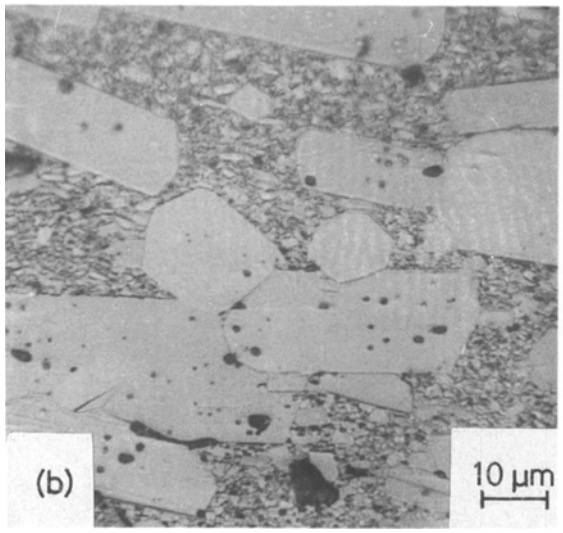


Figure 3 The effect of the size of the silica added on the firing shrinkage. (○) Coarse silica, (●) fine silica.

caused by the more uniform distribution of SiO_2 particles, impedes grain-boundary movement. The present work seems to echo Haberey and Kool's finding that silicon enriched in the grain boundaries plays a role in grain-growth inhibition [4].

Two mixtures, one containing 10% ferrite +90% fine-grain silica and the other containing 10% ferrite





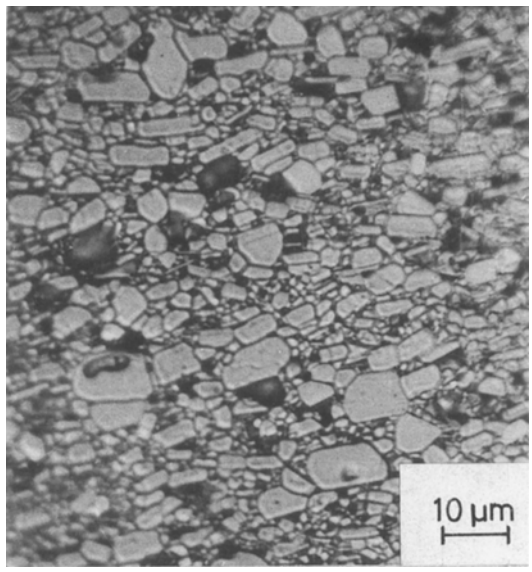


Figure 4 A reflected light micrograph of the $BaFe_{12}O_{19}$ magnet without silica addition.

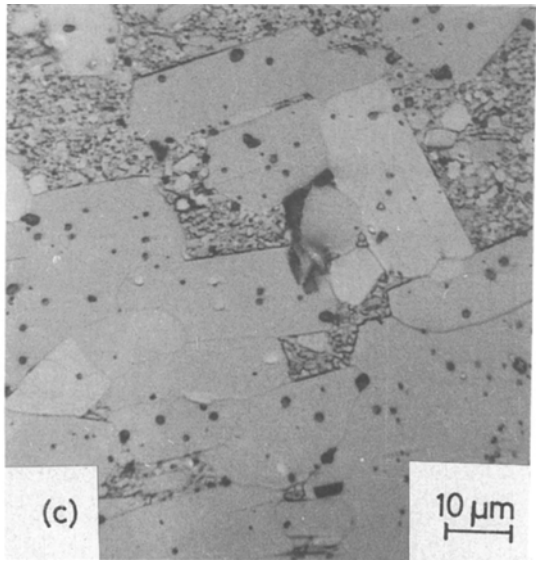
+90% coarse-grain silica were heated in air for 0.5 h at 1050° C, the temperature at which the structural alteration of silica occurs. The X-ray diffraction indicates that quartz was converted to cristobalite and amorphous silica was converted to quartz at 1050° C. Apparently, the microstructure of the ferrites is affected by the particle sizes of silica instead of the forms of silica in the present work.

Table III shows that the values of B_r for the ferrites added with the coarse-grain silica were slightly lower than those added with fine-grain silica. Figures 4 to 6 show that there are more pores in the discontinuous grain growth ferrite particles than fine-grain particles. More pores in the particles are attributed to deterioration of B_r values.

4. Conclusion

The anisotropically formed $BaFe_{12}O_{19}$ ferrites were prepared from hot-rolled mill scale and silica was

Figure 5 Reflected light micrographs of the $BaFe_{12}O_{19}$ magnets with the addition of (a) 0.15%, (b) 0.30%, (c) 0.50% coarse-grain silica.



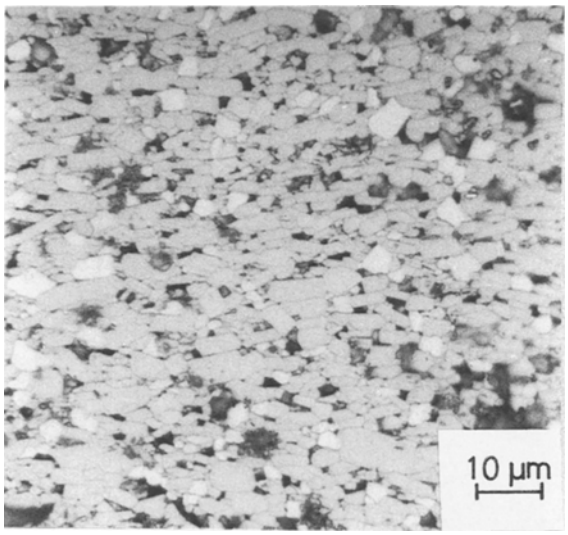


Figure 6 A reflected light micrograph of the $BaFe_{12}O_{19}$ with the addition of 0.3% fine-grain silica.

added to the ferrites during fine milling in the range 0.15 to 0.50 wt %. These ferrites were sintered at 1220° C for 2 h. The grain growth of the ferrites is dominantly influenced by the sizes of the silica added. Coarse grain ($\approx 1\,\mu$m) silica tends to promote discontinuous grain growth, which increases drastically with slightly increasing amounts of silica added, while fine-grain (0.013 μm) silica tends to retain fine-grain structures with the same increasing amount of silica. The average grain size of the ferrite without silica addition was 8 to 10 μm. The size was increased to as large as 30 and over 50 μm, respectively, on addition of 0.15 and 0.30% coarse-grain silica and the microstructure was almost full of extremely large grains after addition of 0.50% coarse silica. The values of $(BH)_{max}$ and H_c varied very little and were maintained at an average of 2.33×10^6 Oe G and 2200 Oe, respectively, for the ferrite added with increasing amounts of fine-grain silica, but the values were down from 1.89 to 0.59×10^6 Oe G and from 2000 to 576 Oe for the ferrites added with the same amount of coarse-grain silica.

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