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*THE EFFECT OF SOME OPERATIONAL  
VARIABLES ON THE PROPERTIES OF  
STRONTIUM HEXAFERRITE*

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# The effect of some operational variables on the properties of strontium hexaferrite<sup>\*</sup>

Sutarno, W. S. Bowman, G. E. Alexander and J. D. Childs

**ABSTRACT.** Strontium hexaferrite with the composition  $\text{SrO} \cdot 5.5 \text{Fe}_2\text{O}_3$  has been prepared by precipitating strontium carbonate in an iron-oxide slurry. The precipitated powders were calcined at various temperatures up to  $1300^\circ\text{C}$  and ball-milled for various lengths of time up to 32 hours. The resulting alcoholic slurries were pressed to discs under the influence of a magnetic field and then sintered at temperatures of  $1100$ – $1300^\circ\text{C}$ . The surface area of the powders, and the ceramic and magnetic properties of the discs were measured. It was found that the magnetic properties of strontium hexaferrite are sensitive, not only to the sintering temperature, but also to changes in calcination temperature and milling time. Under the most favourable combination of treatment conditions and composition, energy products of  $3.9 \times 10^6$  gauss-oersted have been achieved.

## Introduction

Hexaferrite compounds having the general composition  $\text{MO} \cdot n\text{Fe}_2\text{O}_3$ , where  $\text{M} = \text{Ba}, \text{Sr}, \text{Pb}$  (or a mixture of these) and  $n \approx 6$ , have been used as basic materials for ceramic permanent magnets. Until recently, the most widely used of this group of compounds was  $\text{BaO} \cdot n\text{Fe}_2\text{O}_3$ . However, arising from the spectacular results reported by Cocharde (1), the use of strontium ferrite has started to gain momentum. A strontium-ferrite-based permanent magnet has the advantages of being lighter in weight and of having a higher anisotropic energy than those of its barium and lead counterparts.

The merit of a permanent magnet is usually expressed by its maximum energy product,  $(\text{BH})_{\text{max}}$ . To increase the energy product, one must increase the remanent magnetization, while keeping the coercive force sufficiently high to retain its permanent-magnet quality. For a given degree of

particle orientation, the remanent magnetization of a ceramic permanent magnet depends on its density. The coercive force, on the other hand, depends strongly on the grain size of the ceramic specimen. In general, the smaller the grain size, the higher will be the coercive force. For the above reasons, the aims in making a good ferrite permanent magnet are to produce a well-oriented material in order to take the greatest advantage of its anisotropic property, and to attain the highest possible density and the smallest possible grain size.

There are numerous factors affecting the final magnetic properties of a ceramic ferrite permanent-magnet body. These factors can be divided into two major groups. Firstly, there are the chemical factors; these include the relative proportions of the major constituent oxides, and the amounts of the various possible doping elements. Secondly, there are the technological factors; these include the method of preparation, the temperature of calcination and the method of comminution.

In this work, the effects of three of these technological factors, namely, calcination temperature, milling time and sintering temperature, on the magnetic properties of the sintered ceramic body were investigated. Pure strontium ferrite (i.e., without doping) was chosen as the arbitrary composition for this investigation.

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## Experimental procedures

### A. General considerations

The work by Stuijts (2) on barium ferrite has indicated the importance of the non-stoichiometric composition (with  $n < 6$ ) in obtaining a high-sintered-density ceramic body. This behaviour was also found to be true in the case of strontium ferrite.

It is commonly accepted by the ferrite industry that the particle size and shape of the iron oxide used have a significant importance in ferrite formation. To minimize these effects for the purposes of this study, the samples were subjected to a relatively severe treatment. The raw materials were characterized only in terms of their chemical purity.

The surface area was used as the criterion for characterizing the calcined, milled powders. This method was used due to its simplicity. The coercive force of the powder (3) was not chosen, because of the danger of its dependence on such uncertain factors as lattice strain, etc.

### B. Sample preparation and property measurements

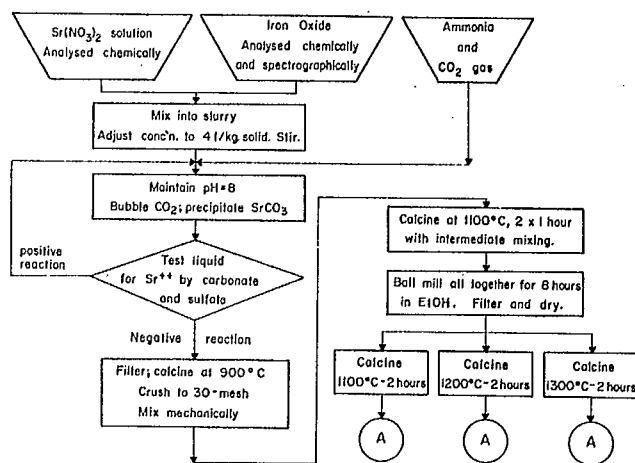
The sample-preparation procedure is illustrated by the flow charts in Figures 1(a) and 1(b). The strontium was precipitated as strontium carbonate in a slurry of iron-oxide particles at room temperature and at pH = 8. The mixed powder was then subjected to various treatments as illustrated in the flow charts. To prevent the dissolution of strontium, ethyl alcohol was used as the milling medium. The mass ratio of ferrite/alcohol/balls was 1/4/35. A mixture of 0.5 in.- and 0.375 in.-diameter steel balls was used in an 8-in.-diameter mill. The rotation speed was 72 rpm. The milling times were 8, 16, 24 and 32 hours. The samples were then stored in the form of alcoholic slurries ready for fabrication into discs. At this stage, the surface areas of the samples were measured using a Perkin-Elmer Sorptometer (based on the BET method) employing a nitrogen-helium mixture. Chemical analyses for the iron-strontium ratio were also carried out at this stage (4).

The ferrite slurries were pressed to 1.5-in.-diameter discs under the influence of a magnetic field (5). The magnetic field strength was estimated to be about 13,000 Oe. and the forming pressure was 5,000 psi. The discs were demagnetized by heating to 500°C and their green density was then measured.

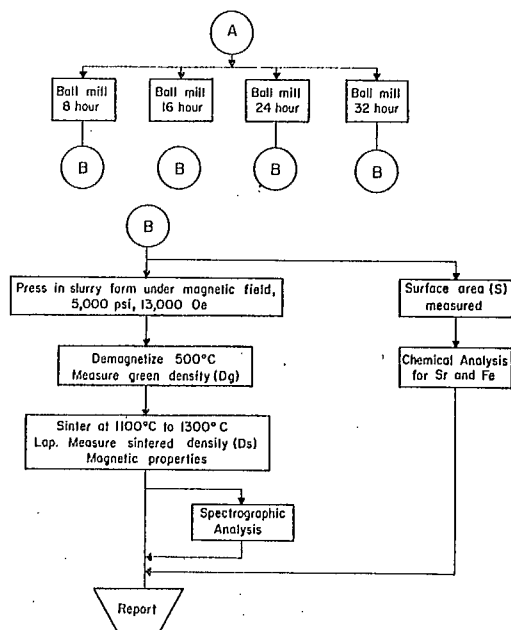
Sintering was carried out in a tube furnace under 1 atm of oxygen pressure. The heating rate was 200°C/hr and the soaking time was 2 hours; the specimens were cooled naturally in the furnace. The sintering temperature varied over the range 1100° to 1300°C.

The discs were lapped to produce cylinders with their faces parallel to within a tolerance of  $\pm 0.0002$  in. These parallel faces were ground using silicon-carbide grinding compound, grade 280. The sintered density,  $D_s$ , of the specimens was measured on these cylinders.

The magnetic properties of the specimen were then measured by the "pole-coil" method (6). (B-H) vs. H curves were plotted automatically and the magnetic quantities intrinsic coercive force ( $H_c$ ), remanent magnetization ( $B_r$ ) and maximum energy product  $(BH)_{max}$  were read from the curves or calculated graphically.



FIGURES 1a and 1b. Flowsheet of sample preparation.



## Results and discussion

The spectrographic analyses of both the iron-oxide raw material and a typical sintered ferrite disc are tabulated in Table I. The disc chosen was fabricated from a powder calcined at 1300°C and ball-milled for 24 hours. This represents a specimen that had been given severe treatment. It will be seen that the level of impurities in the ferrite disc, with the exception of barium, does not differ greatly from that found in the iron oxide. This indicates that the process employed in this investigation is acceptable from the point of view of purity control. The barium content in the ferrite disc, no doubt, originates from the "reagent-grade" strontium nitrate. Experience in this laboratory (7) has shown that the presence of barium at this

Table I. Semi-quantitative spectrographic analysis of  $\text{Fe}_2\text{O}_3$  (raw material) and  $\text{SrO} \cdot 5.5 \text{Fe}_2\text{O}_3$ \*

Element	Percentage by weight†		Element	Percentage by weight†	
	$\text{Fe}_2\text{O}_3$	$\text{SrO} \cdot 5.5 \text{Fe}_2\text{O}_3$		$\text{Fe}_2\text{O}_3$	$\text{SrO} \cdot 5.5 \text{Fe}_2\text{O}_3$
Sr	ND	PC	Bi	ND	ND
Ba	ND	0.1–0.2	Al	0.006	0.02
Mn	0.06	0.06	V	ND	ND
Sb	ND	ND	Zr	ND	ND
Mg	0.04	0.09	Cu	0.01	0.03
Mo	ND	ND	Ag	ND	0.002
W	ND	ND	Zn	ND	ND
Pb	ND	ND	Ti	ND	0.007
Sn	ND	ND	Ni	0.03	0.03
Cr	ND	0.07	Co	ND	ND
Si	0.03	0.04	Na	ND	ND
Fe	PC	PC			

\*Sintered specimen, made from powder calcined at  $1300^\circ\text{C}$  and ball-milled for 24 hours.

†ND = non-detectable; PC = principal constituent.

level does not greatly alter the magnetic properties of the strontium ferrite.

The analyzed composition of this sample was  $\text{SrO} \cdot 5.7 \text{Fe}_2\text{O}_3$ . If the barium content is included in the composition, then the formula becomes  $(\text{Sr}_{0.95}\text{Ba}_{0.05})\text{O} \cdot 5.6 \text{Fe}_2\text{O}_3$ . This small change from the nominal composition of  $\text{SrO} \cdot 5.5 \text{Fe}_2\text{O}_3$  was caused by pick-up of iron from the mill. A similar situation occurred in a sample with an intended composition of  $\text{SrO} \cdot 5.7 \text{Fe}_2\text{O}_3$ ; the analyzed composition in this case was found to be  $\text{SrO} \cdot 6.0 \text{Fe}_2\text{O}_3$ .

Table II and Figure 2 show that the surface area of the powders was independent of the calcination temperature but increased with milling time. An average surface area of  $14 \text{ m}^2/\text{g}$  was obtained by ball-milling the samples for 32 hours.

The discs fabricated from the powders ball-milled for 32 hours were found to have a lower green density than those fabricated from the coarser powders. However, these discs sintered at lower temperatures than the others.

Table II. Surface area in  $\text{m}^2/\text{g}$  of  $\text{SrO} \cdot 5.5 \text{Fe}_2\text{O}_3$  (Calcined at various temperatures and ball-milled for various times)

Calculation temp. ( $^\circ\text{C}$ ) (Soaked for 2 hours)	Ball-milling time (hours)			
	8	16	24	32
1100	3.7	7.5	10.8	12.9
		10.2	11.0	15.9
		8.3	10.2	
1200	3.6	7.2	11.6	13.1
		9.8	14.0	14.0
		9.2	10.5	
1300	4.4	7.9	10.2	14.3
		7.3	10.2	13.4
		8.0	10.5	
Average	3.9	8.4	11.0	13.9
Standard Deviation	$\pm 1.4$	$\pm 1.1$	$\pm 1.2$	$\pm 1.1$

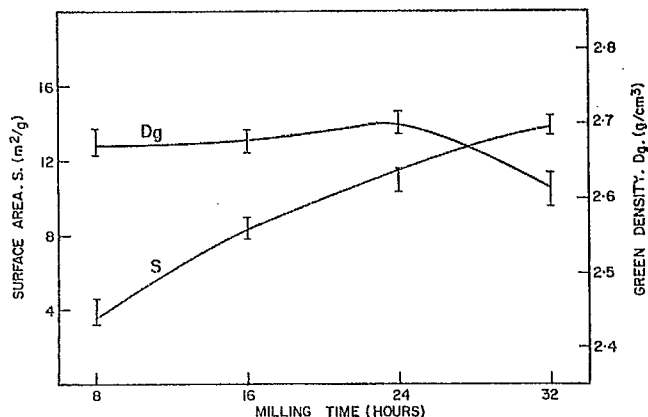


FIGURE 2. Surface area and green density vs. ball-milling time for  $\text{SrO} \cdot 5.5 \text{Fe}_2\text{O}_3$ .

The powders ball-milled for 8 hours (having a surface area  $\approx 4 \text{ m}^2/\text{g}$ ) were sufficiently fine for orientation purposes. However, the sintered discs produced from these powders showed magnetic properties that were inferior to those of discs produced from the finer powders. For this reason, only powders milled for 16, 24 and 32 hours were investigated completely.

Figures 3, 4 and 5 show the magnetic properties of the sintered discs as functions of sintering temperature. The remanent magnetization and the density increase with increasing temperature up to the point when it was observed optically that secondary grain growth started to occur. The coercive force decreases with increasing sintering temperature up to this point. Beyond the point when secondary grain growth started to occur, the remanent magnetization, density and coercive force remain constant up to  $1225^\circ\text{C}$ .

Tests made outside of the sintering temperature range reported in Figures 3, 4 and 5 showed that the remanent magnetization, density and coercive force drop off at higher sintering temperatures (see Figure 6, Curve D). It is also worthy of note in Figure 6 that the coercive force of an unsintered specimen is relatively low (Curve A), indicating that it must first increase and then decrease with increasing sintering temperature.

As is shown in Figures 3 to 5, samples calcined at  $1100^\circ\text{C}$  have higher maximum  $(\text{BH})_{\text{max}}$  values than those calcined at higher temperatures. Among these samples, those ball-milled for 24 hours have the highest energy product. The peaks of these energy products occurred at a sintering temperature of about  $1200^\circ\text{C}$ , except that, for samples milled for 32 hours, the peak occurred  $25^\circ\text{C}$  lower. Samples calcined at  $1200^\circ\text{C}$  show similar trends in properties to those calcined at  $1100^\circ\text{C}$ , except that the actual values were at a lower level. Samples calcined at  $1300^\circ\text{C}$  have about the same properties as those calcined at  $1200^\circ\text{C}$ , with the exception of those samples ball-milled for 24 hours. For some unknown reason, this particular group of samples behaved rather strangely. The whole curve seems to be shifted to higher temperatures and the sintering rate seems to be much faster than for the rest of the samples. The explanation for this behaviour is not understood at present.

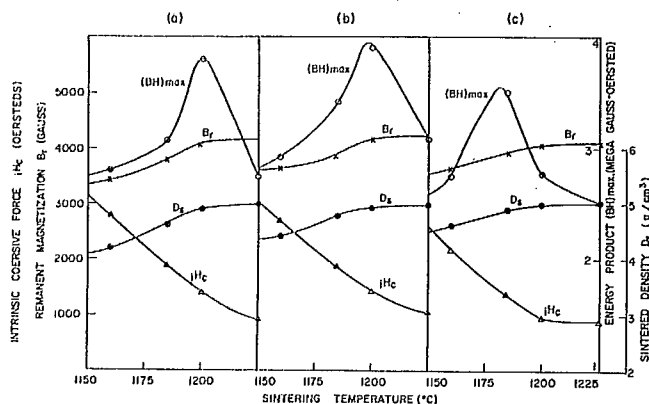


FIGURE 3. Magnetic properties vs. sintering temperature for  $\text{SrO.5.5 Fe}_2\text{O}_3$ , calcined at  $1100^\circ\text{C}$  for 2 hours. Ball-milled for (a) 16 hours, (b) 24 hours, (c) 32 hours.

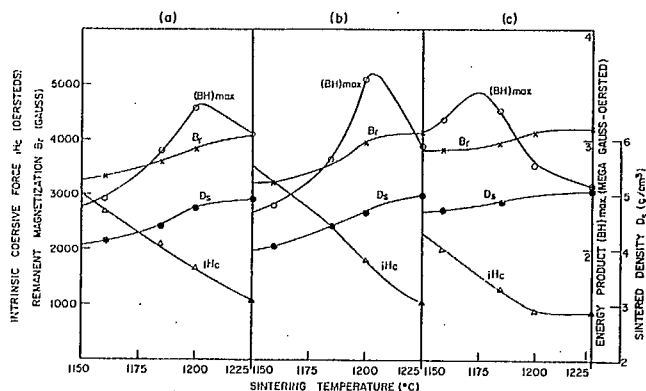


FIGURE 4. Magnetic properties vs. sintering temperature for  $\text{SrO.5.5 Fe}_2\text{O}_3$ , calcined at  $1200^\circ\text{C}$  for 2 hours. Ball-milled for (a) 16 hours, (b) 24 hours, (c) 32 hours.

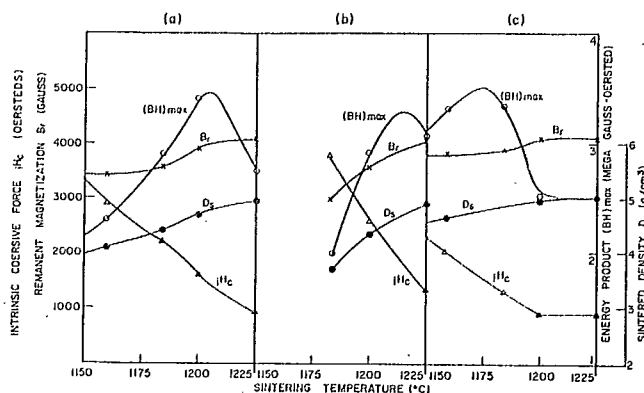


FIGURE 5. Magnetic properties vs. sintering temperature for  $\text{SrO.5.5 Fe}_2\text{O}_3$ , calcined at  $1300^\circ\text{C}$  for 2 hours. Ball-milled for (a) 16 hours, (b) 24 hours, (c) 32 hours.

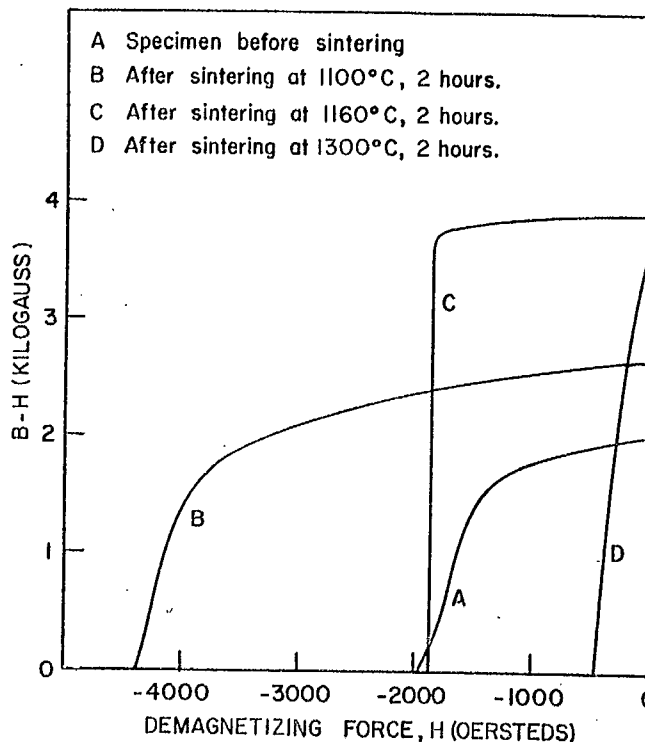


FIGURE 6. Comparative demagnetizing curves for strontium ferrite at various sintering stages.

### Conclusions

From the foregoing discussion, it can be concluded that both calcination temperature and ball-milling time are important variables affecting the properties of strontium ferrite. The following detail effects were observed:

1. The surface area of the milled ferrite powder is dependent only on the milling time, and is independent of calcination temperature.
2. The green density of the specimen is independent of the calcination temperature, and depends only on the milling time for the samples with high surface area (i.e., those milled for 32 hours).
3. The calcination temperature has a very strong effect on the magnetic properties of strontium ferrite. Ferrites calcined at  $1100^\circ\text{C}$  give a higher maximum  $(\text{BH})_{\text{max}}$  value than those calcined at  $1200^\circ\text{C}$  or  $1300^\circ\text{C}$ .
4. The ball-milling time has a less dramatic effect on the magnetic properties. The ferrites milled for 32 hours sintered at a slightly lower temperature than those milled for shorter times. The best milling time seems to be between 16 and 24 hours.
5. The magnetic properties are strongly dependent on the sintering temperature. The highest  $(\text{BH})_{\text{max}}$  values occur at temperatures between  $1160$ – $1225^\circ\text{C}$ .
6. The samples calcined at  $1100^\circ\text{C}$  and ball-milled for 24 hours gave the best magnetic properties. The peak of  $(\text{BH})_{\text{max}}$  was  $3.9 \times 10^6$  gauss-oersted and occurred at a sintering temperature of  $1200^\circ\text{C}$ .

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