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Norman F. Langley

DEPARTMENT OF
ENERGY, MINES AND RESOURCES
MINES BRANCH
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*VARIATIONS IN
THE CERAMIC AND MAGNETIC
PROPERTIES OF BARIUM HEXAFERRITE
SAMPLES MADE FROM IRON OXIDES
PREPARED BY DIFFERENT METHODS*

W. S. BOWMAN AND G. E. ALEXANDER
MINERAL SCIENCES DIVISION

J. M. JAWORSKI, G. A. INGHAM
NORTHERN PIGMENT COMPANY LIMITED, TORONTO 14, ONTARIO.

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Variations in the ceramic and magnetic properties of barium hexaferrite samples made from iron oxides prepared by different methods

J. M. Jaworski*, G. A. Ingham*, W. S. Bowmant and G. E. Alexander†

ABSTRACT. Physico-chemical properties of iron oxides produced by two different methods and the ceramic and magnetic properties of unoriented and oriented barium hexaferrite specimens prepared from these oxides are presented. The influence of calcination temperature on the grain growth of the polycrystalline barium hexaferrite during subsequent sintering is shown. Differences found in the reactivity, grain growth and magnetic properties suggest the use of different technological procedures for the production of barium ferrite from different iron oxides.

Introduction

The raw materials used in the manufacture of barium hexaferrite magnets are usually barium carbonate and iron oxide (Fe_2O_3). The purpose of this investigation was to determine the effect of the properties of the iron oxide on the ceramic and magnetic properties of the ferrite prepared from it.

The two iron oxides used in this study were designated R-21, which was produced by ferrous sulphate decomposition, and R-25, which was produced by direct precipitation. During production, R-21 was heated to over 1000°F , while R-25 underwent no heat treatment.

Experimental procedures

Characterization of iron oxides

The two iron oxides were subjected to chemical and spectrographic analysis. Various physical properties, including loose density, tap density, average particle size, porosity and surface area were measured. The samples were examined by XRD using $\text{CoK}\alpha$ radiation. Electron micrographs were prepared. $\text{BaCO}_3 - \text{Fe}_2\text{O}_3$ mixtures with a 1:5.5 molar ratio were prepared and heated in a thermobalance in order to compare the reactivity of the iron oxides.

Preparation of barium hexaferrite samples

A 2000-gram mixture of BaCO_3 and Fe_2O_3 with a molar ratio of 1:5.5 was prepared for each iron oxide. Each mixture was rotated in a glass mill without balls for 3 hours and was passed through a 40-mesh screen after each hour in order to ensure complete homogeneity.

Four 500-gram samples of each mixture were calcined for 2 hours in air at temperatures of 1880°F , 2060°F , 2300°F and 2410°F , respectively. The samples were heated at a rate of 300°F per hour and cooled at the natural cooling rate of the furnace. The average particle size of each calcine was measured using a Fisher sub-sieve sizer. The magnetization-per-gram, σ , was measured at room temperature on 0.2-gram samples of each calcine at a field strength of 18,000 oersted and at a gradient of 805 oersted per cm, using a simple transducer-type magnetic balance (1).

The calcines were wet-milled in a steel ball-mill for 32 hours in order to reduce the particles to micron size. The slurries obtained were evaporated and dried at 400°F for 24 hours. The powders were examined by XRD using $\text{CoK}\alpha$ radiation.

Unoriented 20-gram discs, 1.06 in. in diameter, were pressed at 8000 psi and sintered in air for 1 hour at temperatures of 2200°F and 2300°F . The discs were heated at a rate of 150°F per hour and cooled at the natural cooling rate of the furnace.

The remaining parts of the powders were re-slurried in alcohol, and oriented 1.5-in. diameter discs were prepared by pressing the slurries in a magnetic field of about 15,000

*Northern Pigment Company Limited, Toronto 14, Ontario.

†Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.

oersted at 5000 psi. The discs were demagnetized at 950°F and then sintered in air for 1 hour at temperatures of 2200°F and 2300°F with a heating rate of 125°F per hour and natural cooling.

The diametral shrinkage of all discs was measured. They were then lapped to form cylinders with faces parallel to within 0.0002 in. in order that accurate measurements of bulk density and magnetic properties could be made. The magnetic properties of the discs — coercive force (H_c), intrinsic coercive force (H_{ci}), remanent magnetization (B_r) and maximum energy-product $(BH)_{max}$ — were obtained by measuring the hysteresis loops by the "pole-coil method", as described by Steingroever (2).

Some oriented and unoriented discs were polished and etched in warm concentrated HCl for investigation of the grain structure.

Results and discussion

Table I shows that the two iron oxides under study have comparable degrees of chemical purity and similar physical properties. XRD analysis confirmed that both oxides contained pure alpha-hematite as the only detectable phase. Electron micrographs of the oxides (Figure 1) show that R-21 iron-oxide particles are essentially spherical in shape, while R-25 iron-oxide particles are irregular plates. Thermogravimetric analysis showed that iron oxide R-25 is more reactive than R-21 for the production of ferrites since the decomposition of $BaCO_3$ in admixture with R-25 occurred at a lower temperature than in admixture with R-21. The TGA results are shown in Figure 2.

XRD examination of the calcined samples revealed that the formation of barium hexaferrite was essentially

FIGURE 1
Electron micrographs of R-21 Fe_2O_3 (produced by ferrous sulphate decomposition) and R-25 Fe_2O_3 (produced by direct precipitation).

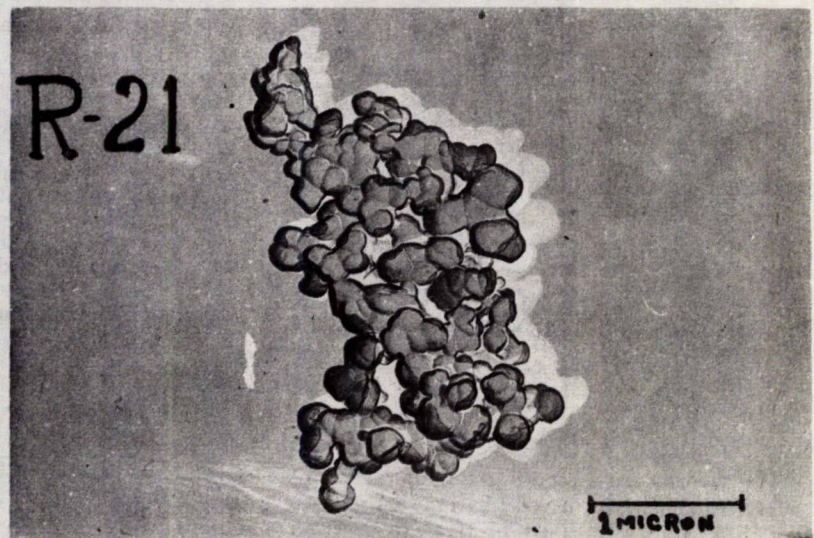


Table I. Physical-chemical properties of R-21 and R-25 iron oxides

Data	Unit	R-21 Fe ₂ O ₃ (produced by ferrous sulphate decomposition)	R-25 Fe ₂ O ₃ (produced by direct precipitation)
Fe ₂ O ₃	wt %	99.7	98.9
SiO ₂	"	0.08	0.04
CaO	"	0.02	0.04
Na ₂ O	"	0.03	0.01
Al ₂ O ₃	"	0.03	0.05
CuO	"	0.04	0.03
Cr ₂ O ₃	"	0.03	0.02
MgO	"	<0.01	<0.01
NiO	"	<0.01	<0.01
As ₂ O ₃	"	<0.01	<0.01
Loose density	g/cm ³	0.85	0.63
Tap density	"	1.34	1.30
Average particle size*	μ	0.77	0.53
Porosity*	%	60.4	68.7
Surface area	m ² /g	8.2	6.7
Density	g/cm ³	5.0	4.9

*Fisher sub-sieve sizer method.

complete at even the lowest calcination temperature since neither of the original constituents could be detected. As shown in Figure 3, the ferrite particles agglomerated as the calcination temperature increased, resulting in a growth in average particle size. Since the two mixtures started at approximately the same average particle size ($0.9 \pm 0.2\mu$), it can be seen from the results obtained that the R-21 mix exhibited agglomeration at a lower temperature than the R-25 mix.

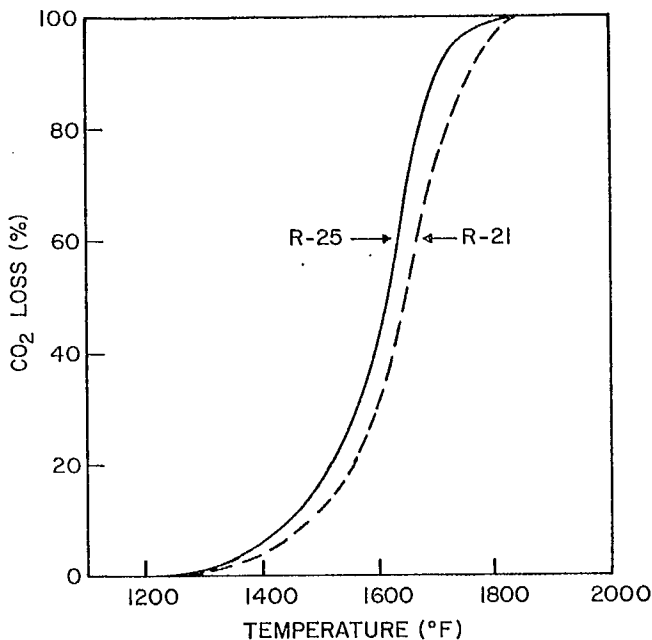


FIGURE 2. CO₂ loss from mixtures of BaCO₃ and Fe₂O₃ with a 1:5.5 molar ratio when heated in a thermobalance.

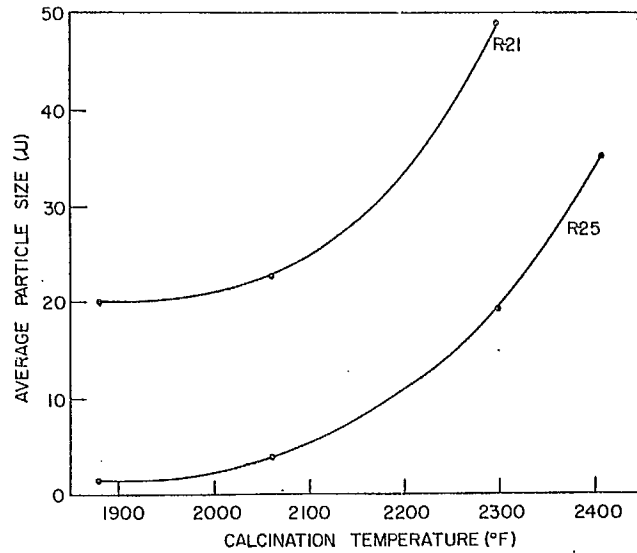


FIGURE 3. Average particle size of barium ferrite masses calcined at various temperatures for 2 hours, prepared from R-21 and R-25 iron oxides.

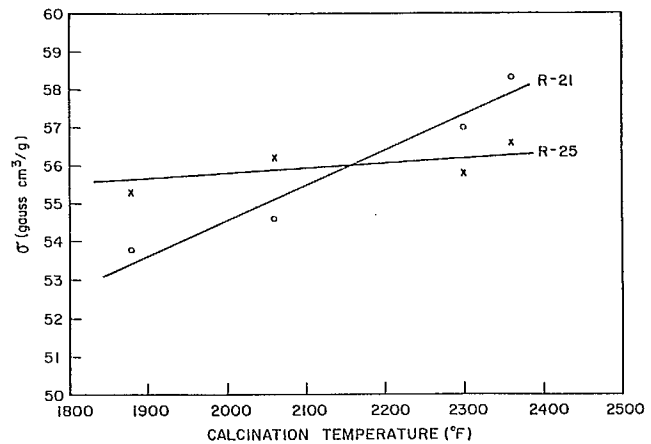


FIGURE 4. Magnetization-per-gram values vs. calcination temperature of the ferrite calcines prepared from R-21 and R-25 iron oxides.

The magnetization-per-gram values obtained in this investigation were about 20% lower than the published saturation magnetization-per-gram of barium hexaferrite, viz. 72 gauss cm³ per gram (3). This seems to indicate that the field applied was not sufficient to achieve saturation in the polycrystalline agglomerates. As the calcination temperature was raised, σ increased due perhaps to crystallite growth (see Figure 4).

Diametral shrinkage and sintered density values of discs are presented as functions of calcination temperature in Figure 5: Generally, diametral shrinkage values decreased with increasing calcination temperature from 1880°F to 2300°F. Higher values were noted at a temperature of 2410°F. The sintered density of unoriented discs followed the same trend. The sintered density of oriented discs did not vary in the same manner. This is understandable in

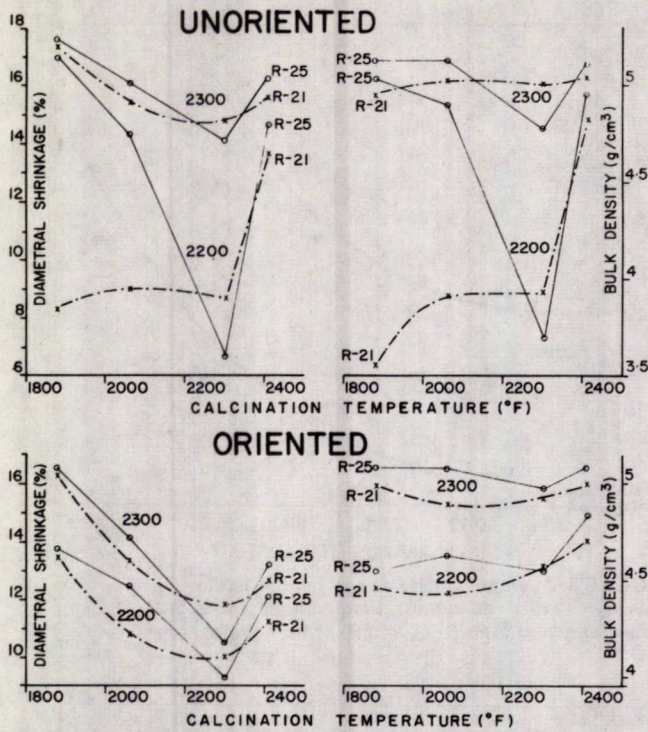


FIGURE 5. Diametral shrinkage and bulk density of unoriented and oriented barium ferrite discs prepared from R-21 and R-25 iron oxides sintered 2200°F and 2300°F for 1 hour.

view of the highly anisotropic nature of the shrinkage for oriented discs, whereas, in unoriented discs, the shrinkage is predominantly isotropic. Generally, the values of diametral shrinkage and sintered density were lower for the discs prepared from R-21 oxide than for those prepared from R-25 oxide.

The magnetic properties of the discs are shown as functions of calcination temperature in Figure 6. With sintering of both oriented and unoriented pellets for 1 hour at 2200°F, B_r and $(BH)_{max}$ values were generally higher for discs made from R-25 oxide than from R-21 oxide. The reverse was true of H_{c1} values. With firing for 1 hour at 2300°F, there was an increase in $(BH)_{max}$ and B_r , accompanied by a decrease in H_{c1} . Discs made from R-21 oxide showed a greater change in properties under these firing conditions than those made from R-25 oxide. The values presented were not obtained under the best sintering conditions. Superior values were obtained with a few samples that were prepared with shorter firing times, as is shown in Table II.

The samples that were sintered at 2200°F for 1 hour were characterized by grain sizes down to the limit of resolution of the microscope. The largest grains did not exceed 3.5μ . No significant differences were observed between grain structures of discs prepared from the different iron oxides or from the different calcines. With sintering at 2300°F for 1 hour, discs prepared from iron oxide R-25 were generally characterized by discontinuous grain structure, containing some giant grains. Discs prepared from

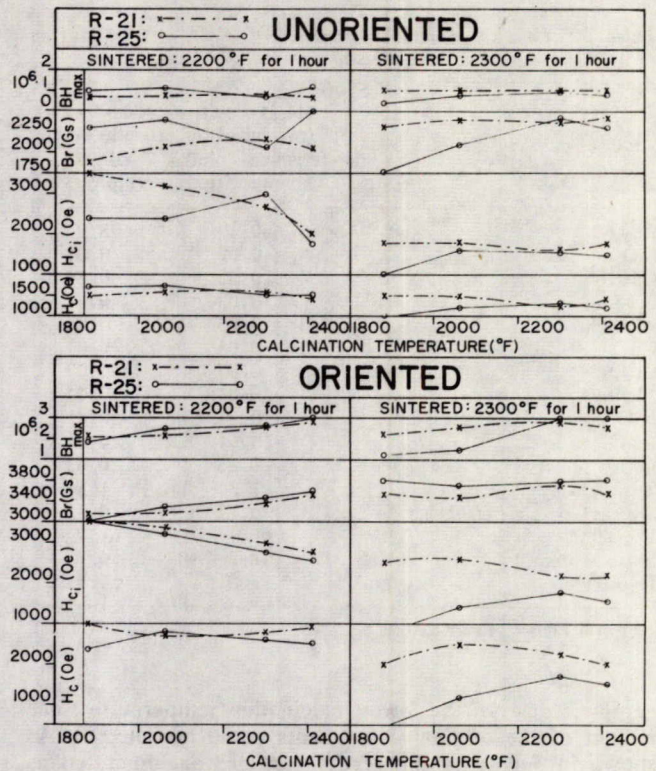


FIGURE 6. Magnetic properties of unoriented and oriented barium ferrite discs prepared from R-21 and R-25 iron oxides sintered at 2200°F and 2300°F for 1 hour.

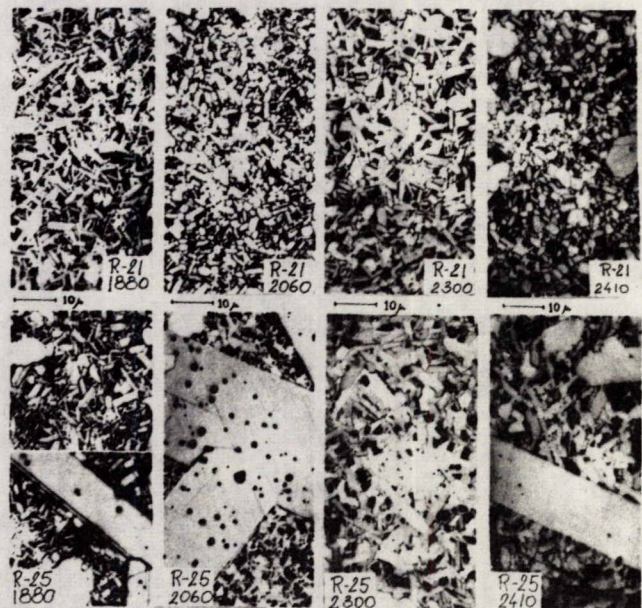


FIGURE 7. Grain structure of unoriented barium ferrite discs prepared from R-21 and R-25 iron oxides sintered at 2300°F for 1 hour (various calcination temperatures).

Table II. Magnetic properties of oriented barium ferrite samples prepared from R-21 and R-25 iron oxides and fired at 2200°F and 2300°F for 30 min.

Iron oxide used	Temp. of calcination (°F for 2 hours)	Firing: 2200°F for 30 min.				Firing: 2300°F for 30 min.			
		B_r (Gs)	H_c (Oe)	H_{ci} (Oe)	$(BH)_{max}$ ($\times 10^6$ Gs.Oe)	B_r (Gs)	H_c (Oe)	H_{ci} (Oe)	$(BH)_{max}$ ($\times 10^6$ Gs.Oe)
R-21	1900	3190	2700	3780	2.3	3320	2700	3300	2.3
R-25		3000	2600	3960	2.1	3400	1650	2200	2.0
R-21	2100	3200	2600	3400	2.4	3400	2710	2940	2.6
R-25		3400	2800	3180	2.5	3500	2250	2400	2.6
R-21	2300	3300	2850	3130	2.4	3630	2480	2540	2.9
R-25		3210	2690	2900	2.3	3630	2160	2250	2.9
R-21	2400	3540	2730	2780	2.8	3720	2240	2290	3.1
R-25		3550	2520	2600	2.9	3600	1900	1990	2.8

iron oxide R-21 were generally characterized by continuous small grain structure. These grain structures are shown in Figures 7 and 8.

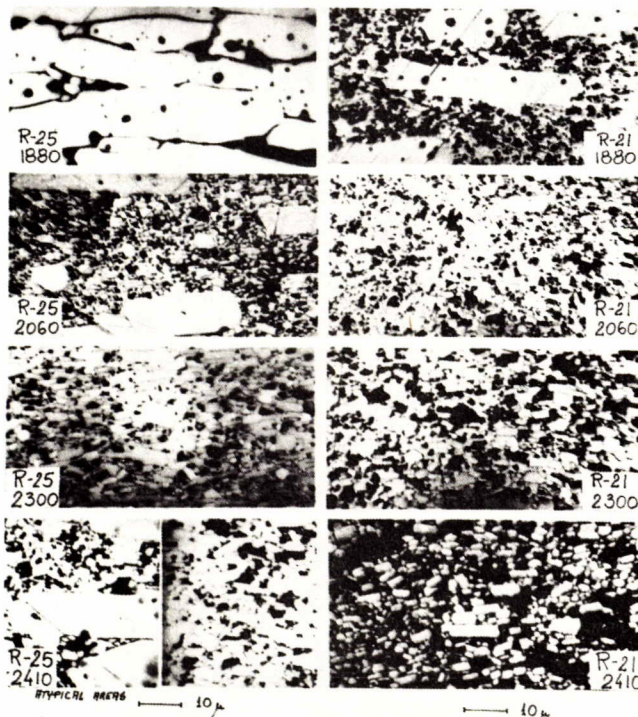


FIGURE 8. Grain structure of oriented barium ferrite discs prepared from R-21 and R-25 iron oxides sintered at 2300°F for 1 hour (various calcination temperatures).

Conclusions

It is clear that R-21 iron oxide, prepared by ferrous sulphate thermal decomposition, and R-25 iron oxide, prepared by direct precipitation, produce different ceramic behaviour and magnetic properties in the ferrites prepared from them. Barium ferrite samples made from R-21 oxide agglomerate to a larger extent during calcination at a given temperature than do samples prepared from R-25 oxide. On the other hand, there is a higher density, greater shrinkage and larger grain size in the discs prepared from R-25 oxide. There is less difference in ceramic behaviour between samples made from R-21 oxide and R-25 oxide in oriented discs than in unoriented discs. Both oxides give larger grains in oriented ferrites than they do under comparable conditions in unoriented discs.

The differences between samples made from the two iron oxides can be minimized by employing higher calcination temperatures and shorter sintering times.

Acknowledgments

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