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CANADA

DEPARTMENT OF ENERGY, MINES AND RESOURCES

OTTAWA

MINES BRANCH INVESTIGATION REPORT IR 67-46

FERRITES: PART III. CONSTRUCTION AND OPERATION OF A MAGNETIC ORIENTING PRESS FOR THE FABRICATION OF ANISOTROPIC FERRITE MAGNETS

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MINERAL SCIENCES DIVISION

D.R.B. PROJECT F.E. 200589
E.C.R.D.C. - C.73

COPY NO. 1

1867 1967

MAY 15, 1967

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SUMMARY OF RESULTS

The magnetic properties of a ferrite permanent magnet are greatly improved by orienting its particles into a crystallographically unidirectional arrangement. A press to be used for the fabrication of such anisotropic magnets has been constructed. The principles of the design of a magnetic orienting press are discussed. Its performance was tested by using barium hexaferrite powder prepared by a semi-coprecipitation method. Both X-ray diffraction and magnetic measurements were used to evaluate the products. It was shown that the degree of orientation increased with the magnetomotive force applied to the sample up to a certain point, and then remained constant as the field strength was further increased. It was found that the sintering of the specimen improved its texture.

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INTRODUCTION

The usefulness of hexagonal ferrite compounds of the type $MO.nFe_2O_3$, where M is Ba, Sr or Pb, or mixtures of them, and n is near to 6, as the basic material for permanent magnets, is mainly due to their strong crystalline anisotropy. The energy product $(BH)_{max}$ of these magnets can be increased by a factor of up to four times by orienting all the crystallites into a unidirectional array.

Several methods have been employed for orienting such specimens, with varying degrees of success. These methods are based either on mechanical forces or on magnetic forces, or on a combination of the two. The mechanical method of orientation utilizes the platelet shape of the ferrite crystals; the magnetic method makes use of the strong anisotropy of the material to effect the orientation of the domains.

The mechanical method was first employed by Stuijts et al (1). They filled a steel tube with the powder, welded both ends of the tube, and then hot-rolled it. The result was a specimen oriented with the c-axes of the crystallites perpendicular to the rolling plane. This method was modified by Bergstrom (2). In his technique, the powder was mixed with a certain binder to a convenient consistency. The mixture was then cold-rolled into thin sheets. By mounting these sheets together and pressing them at convenient pressures and temperatures, a piece of oriented specimen was obtained which was then ready to be sintered. This method, however, was reported to be successful only for the case of lead hexaferrite.

A method that has been reported (1) to be more successful is the magnetic-based method of orientation; this is the method that has been employed in this laboratory in the work to be described herein.

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(1) For references, see page 16.

PRINCIPLES OF MAGNETIC ORIENTATION

A. The Magnetic Orienting Press

According to the domain theory, in the absence of an external magnetic field, the resultant magnetic moment of a single-domain anisotropic particle will be directed along its direction of easy magnetization. In the case of the (Ba, Sr, Pb) hexaferrite crystals, this easy direction will be parallel to the c-axis.

When an external magnetic field, H, is applied to a single-domain particle, S, in the direction α_o from the c-axis (see Figure 1), the direction of the domain magnetization, M_s, will turn to an angle which is somewhat closer to the direction of H. In the equilibrium state, let the direction of M_s be at an angle α from the c-axis. Obviously, α is a function of both H and α_o.

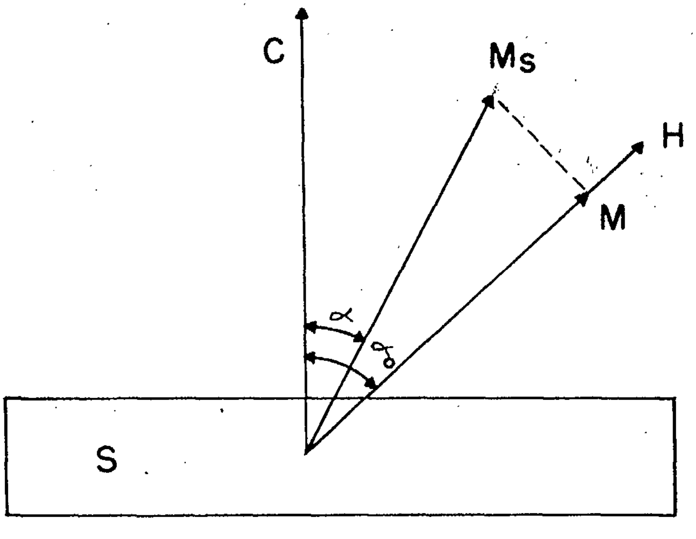

Figure 1. Schematic illustration of magnetic orientation mechanism applied to a single-domain particle.

At this stage, the component, M of M_s in the direction of H will have a magnitude given by:

$$M = M_s \cos(\alpha_o - \alpha) \qquad \text{---} \qquad \text{(Eq. 1)}$$

The anisotropic energy* of a hexagonal crystal can be expressed(3) as:

$$E_k = K_1 \sin^2\alpha + K_2 \sin^4\alpha + K_3 \sin^6\alpha + \qquad \text{---} \qquad \text{(Eq. 2)}$$

where α is the angle between the direction of magnetization and the c-axis, and K_1, K_2, K_3, --- are the anisotropic constants. In order to simplify the calculation, all terms but the first of Eq. 2 are neglected; hence:

$$E_k = K_1 \sin^2\alpha \qquad \text{---} \qquad \text{(Eq. 2a)}$$

The torque acting on each unit volume of crystal is equal to the rate of change of energy density with angle

$$T = \frac{\partial E_k}{\partial \alpha} = K_1 \sin 2\alpha \qquad \text{---} \qquad \text{(Eq. 3)}$$

T will be a maximum when $\alpha = 45°$.

The equilibrium value of α can be computed by minimizing the total magnetic energy with respect to α. This energy, E, consists of anisotropic energy and magnetization energy; the latter is equal to $HM_s \cos(\alpha_o - \alpha)$ (see Eq. 1). Thus:

$$E = K_1 \sin^2\alpha - HM_s \cos(\alpha_o - \alpha) \qquad \text{---} \qquad \text{(Eq. 4)}$$

At equilibrium (4):

$$\frac{\partial E}{\partial \alpha} = 2K_1 \sin\alpha \cos\alpha - HM_s \sin(\alpha_o - \alpha) = 0 \qquad \text{---} \qquad \text{(Eq. 5)}$$

$$\frac{HM_s}{2K_1} = \frac{\sin\alpha \cos\alpha}{\sin(\alpha_o - \alpha)} = \frac{H}{H_a} \qquad \text{---} \qquad \text{(Eq. 6)}$$

where $H_a = \dfrac{2K_1}{M_s}$

For $\alpha_o = 90°$,

$$\frac{H}{H_a} = \sin\alpha \qquad \text{---} \qquad \text{(Eq. 7)}$$

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* The anisotropic energy is defined as the magnetic energy, $\int H\,dM$, required to turn the vector from a preferred direction into a so-called difficult direction (3).

If $H = H_a$, then $\alpha = 90°$. Therefore, H_a is the anisotropic field, that is, the field required to turn the magnetization vector into the direction perpendicular to its original easy direction.

In a powder, the directions of the c-axis of the individual particles are randomly distributed; hence α_o varies from 0 to 180°. From Eq. 6, it is shown that there is no value of H that will exert maximum torque on all the particles ($\alpha = 45°$) simultaneously. Among the various particles, presumably, the most difficult ones to orient will be those with $\alpha_o = 90°$. Therefore, it is profitable to design a press with a magnetic field capable of exerting a maximum torque on the particles with $\alpha_o = 90°$.

For $\alpha_o = 90°$, Eq. 6 becomes:

$$H = H_a \sin\alpha$$

α will be 45° if $H = \frac{1}{2} H_a \sqrt{2}$.

For $(Ba,Sr,Pb)O.6.0Fe_2O_3$, this value of H is about 13,000 oersteds.

B. The Degree of Orientation

There are two basic methods of expressing the degree of orientation for a given specimen. The first is by measuring the ratio of the remanent magnetization in the direction perpendicular to the direction of easy magnetization, $B_{R\perp}$, to the remanent magnetization parallel to the easy direction, $B_{R//}$. Thus,

$$\frac{B_{R\perp}}{B_{R//}} = 0 \text{ for a completely oriented specimen}$$

and $$\frac{B_{R\perp}}{B_{R//}} = 1 \text{ for a completely randomly-oriented specimen.}$$

The second method is by using X-ray diffraction parameters. If a completely oriented specimen is exposed to an X-ray beam in such a way that the plane perpendicular to the easy direction of magnetization is the reflecting plane, then only (00ℓ) reflections will appear in the diffracted beam. Based on this principle, the following considerations can be used to define the degree of orientation.

(a) Lotgering expression (5)

The degree of orientation of a specimen is expressed by the quantity f, which is defined as:

$$f = \frac{(P - Po)}{(1 - Po)} \qquad \text{---} \qquad \text{(Eq. 8)}$$

where $P = \frac{\Sigma I_{(00\ell)}}{\Sigma I_{(hk\ell)}}$ for an oriented specimen of degree of orientation f,

$Po = \frac{\Sigma I_{(00\ell)}}{\Sigma I_{(hk\ell)}}$ for a completely random specimen,

$I_{(hk\ell)}$ = intensity of $(hk\ell)$ reflection,

and $I_{(00\ell)}$ = intensity of (00ℓ) reflection.

The value of f will be zero for a completely random specimen and unity for a completely oriented specimen.

(b) Gillam expression (6)

The Lotgering expression does not take account of the magnitude of the deviation from the correct alignment of those crystals giving Bragg reflections with indices other than (00ℓ); for example, a crystal that contributes to the (107) reflection is much closer to the correct alignment, (00ℓ), than are those that contribute to the (110) reflection. Since the contribution of each single-domain particle to the resultant magnetization is proportional to the cosine of the angle between the c-axis and the magnetization direction, Gillam introduced a cosine term into his expression. The expression thus becomes:

$$q = \frac{\Sigma I_{(hk\ell)} \cos \Phi_{(hk\ell)}}{\Sigma I_{(hk\ell)}} \qquad --- \qquad \text{(Eq. 9)}$$

where $\Phi_{(hk\ell)}$ is the angle of deviation from the correct alignment of a particular particle, which is equal to the angle between the $(hk\ell)$ and (00ℓ) planes; $I_{(hk\ell)}$ is the intensity of $(hk\ell)$ reflection.

(c) The quantity, q, in the Gillam expression will have a value of unity for a completely oriented specimen and somewhat less than one for a randomly- or partly-oriented specimen. This expression should be corrected by those factors that affect the intensity of certain reflections but are not related to the degree of orientation of the particle itself, such as the factors dependent only on the intra-crystalline angles for example, the Lorentz polarization factors. Without such corrections, this expression will give more weight to the very low angle reflections, than to those of medium angle due to the differences in the Lorentz polarization factors.

The intensity of a given $(hk\ell)$ reflection is proportional to the number of $(hk\ell)$ planes that happen to be in the right position to give the appropriate Bragg reflection. The ratio, $R_{(hk\ell)}$, of the intensity of a given reflection of an oriented specimen to that of the same reflection for a completely random specimen, therefore represents the ratio of the number of such planes in the right position. Thus, $R_{(hk\ell)}$ represents the relative number of particles in the particular position in the oriented specimen with respect to the random one.

$$R_{(hk\ell)} = \frac{I_{(hk\ell)} \text{ oriented}}{I_{(hk\ell)} \text{ random}} \quad --- \quad \text{(Eq. 10)}$$

The plot of $R_{(hk\ell)}$ vs. $\cos \Phi_{(hk\ell)}$ thus respresents the distribution function of the position of all the particles in the specimen. From this plot, the expected value of $\cos \Phi_{(hk\ell)}$ can be computed.

$$\overline{\cos \Phi}_{(hk\ell)} = \frac{\sum\limits_{hk\ell} \left\{ R_{(hk\ell)} \cos \Phi_{(hk\ell)} \right\}}{\sum\limits_{hk\ell} R_{(hk\ell)}} \quad --- \quad \text{(Eq. 11)}$$

The value of $\overline{\cos \Phi}_{(hk\ell)}$ from Eq. 11 can be used as an expression of the degree of orientation of the specimen.

CONSTRUCTION OF THE PRESS

For practical reasons it would be desirable to have the ferrite specimen in the form of a disk with a final diameter of about 1-inch and a thickness of about 0.25 inch. Taking account of the shrinkage occurring during sintering and subsequent lapping, the "green" disk diameter should preferably be about 1.5 inch.

There is no easy way to find out the permeability of a ferrite powder during pressing. It will probably be sufficient to assume that the reluctance of the volume occupied by the ferrite during pressing is equivalent to a 3 cm air gap, and that the reluctance of the rest of the circuit is negligible, since it is made from a high-permeability, magnetically-soft steel. The magnetomotive force required to produce a field strength of 13,000 oersted is about 31,000 amp.-turns.

The mould must be made from a non-magnetic material in order to prevent the flux from by-passing the powder. The plunger must be as soft as possible magnetically to prevent the specimens from sticking to them due to their residual magnetization.

The following factors were taken into consideration in the design of the press described in the present report:

(1) A pneumatic press, capable of delivering a total force of up to 30 tons with a 6-inch stroke, was available.

(2) A d.c. power supply with an output of up to 40 V and capable of delivering currents up to 500 amp. was also available.

(3) A means of dissipating the heat produced during the pressing had to be provided.

(4) The geometrical limitations dictated by the above-mentioned press had to be observed.

From the above considerations, it will be seen that the magnetic coil was required to have at least 150 turns and to be capable of carrying 200 amp., supplied from the available power supply.

It was found that quarter-inch copper tubing was suitable for this job. This tubing was insulated with a Teflon sleeve. About 300 ft. of tubing was used and produced 198 turns. The resistance of this coil was such that the power supply was capable of delivering 375 amp. through it. The maximum magnetomotive force of this arrangement was thus about 75,000 amp. turn. The coil was connected to a water supply having a pressure sufficient to give enough flow of water to dissipate the heat produced during normal operation.

It has been mentioned in the previous section of this report that the mould should be made from a non-magnetic material. Brass was first tried, but it was found to be mechanically too soft for satisfactory use. Stainless steel No. 304 was then used to replace the brass sleeve and worked satisfactorily. The plunger was made of mild steel. A non-magnetic spacing piece, placed between the mild steel part of the plunger and the specimen, was found to be necessary in order to break the magnetic attraction between sample and plunger during the removal of the oriented specimen.

For orienting the specimen, it was necessary to press the sample in the form of slurry. To remove the liquid during compaction, the plunger was perforated along its length and connected to a vacuum system, the excess liquid being removed by suction.

A set of mild steel yokes was installed between the top and bottom plunger to close the magnetic circuit. The modified press is illustrated in Figure 2.

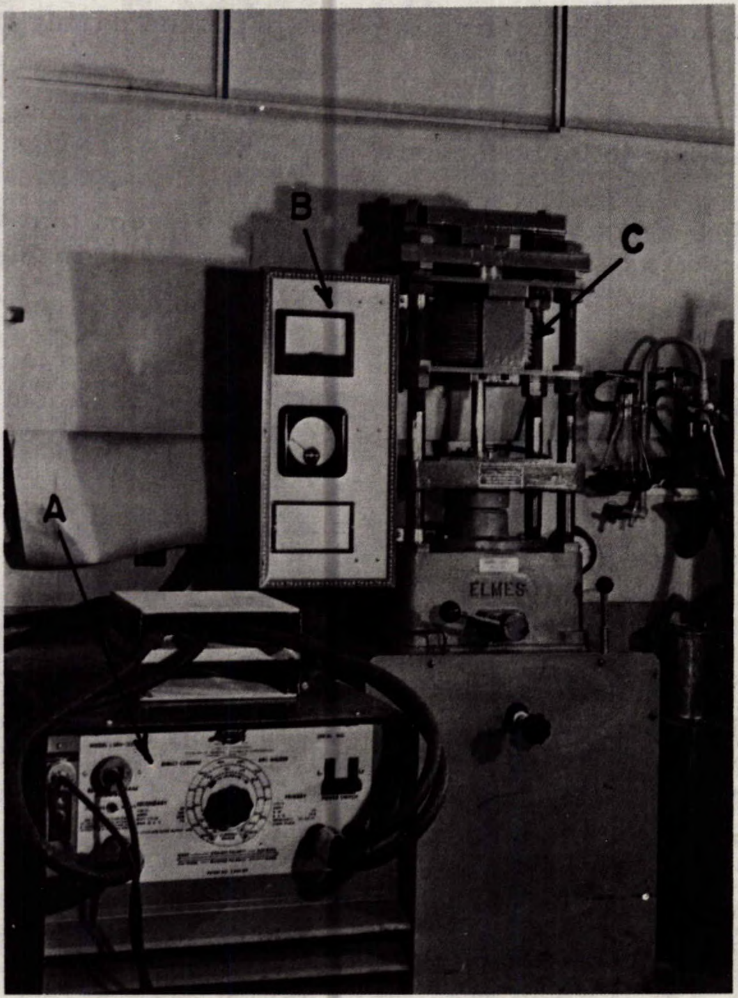

Figure 2. Magnetic Orienting Press and Power Supply.
A. Power supply; B. Control panel; C. Magnetic coil.

EXPERIMENTAL METHOD OF OPERATION

A. Suspected Variables

A number of variables is suspected to affect the quality of the oriented disks produced by this press. These variables are:

(1) Both the magnitude and the profile of the current flowing through the magnetic coil.

(2) The speed of movement of the plunger; this will affect the rate of the closing of the gap and, hence, the profile of the magnetic field applied to the particles.

(3) The forming pressure.

(4) The consistency of the powder; that is, whether dry- or wet-pressing is used.

Due to the limitations of the existing press, some of the above variables, such as the speed of the plunger, and the minimum reproducible pressure were invariant.

B. Operational Test

Barium ferrite powder, with the nominal composition of $BaO.5.5\,Fe_2O_3$, was used as the raw material for this test. The powder was prepared by depositing barium carbonate on a suspended iron oxide slurry at room temperature. The precipitate was calcined twice for one hour at 1100°C and then once at 1300°C for two hours. This well-calcined sample was then ball-milled in alcohol for 16 hours and dried at about 110°C.

(i) Dry-pressing

Because of the difficulty of pressing a slurry encountered during the earlier test period, the performance of this press was first tested under dry-pressing conditions.

Samples of about 20 g of ferrite powder were ground in an agate mortar to break the agglomerates, and then pressed at 10,000 psi. Currents of various magnitudes from 75 to 275 amp. were applied suddenly before the pressing was started and kept constant until a few seconds after the final pressure was applied. The current was turned off before the pellet was ejected from the mould. A clear lacquer spray was applied to the disks in order to give them enough "green" strength for subsequent handling.

X-ray diffractometer charts were prepared using filtered CoK radiation with the face of the "green" disk as the reflecting plane. The speed of scanning was 0.25° 2θ per minute and the range of 2θ examined was from 5° to 60°. The peak areas were measured by means of a planimeter.

(ii) Wet-pressing

It was shown, in the preliminary results, that the dry-pressed specimens were not fully oriented. It was also shown that the degree of orientation increased with increasing field current up to about 150 amp. From then on, increasing the current further did not improve the degree of orientation. For this reason, the wet-pressing method was then tried. This method has a number of advantages compared with the dry-pressing technique. Firstly, the calcined powder was wet ball-milled to single-domain particles before pressing. Upon drying, these particles have a tendency to agglomerate. This agglomeration will increase the resistance of the particles to rotation by the field. The presence of the liquid reduces the tendency to agglomerate. Secondly, the buoyancy effect of the liquid makes the ferrite particles relatively lighter and, hence, easier to rotate in the field. A slurry containing about 20% solids was found to be most convenient in use. Thirdly, between the ball-milling and the pressing operations, the ferrite material can be stored and handled in the form of a slurry. In a large-scale production operation, this would simplify the materials-handling problems.

Based on the preliminary results of the dry-pressing technique, the field current was applied intermittently with the maximum of 175 amp., except when the full forming pressure was being applied when the field current was maintained steady at its maximum value. The forming pressure was 5,000 psi. For the convenience of the pressing operation, alcohol was used to make the slurry. It was found that no binder was necessary to form a reasonably strong "green" disk.

RESULTS AND DISCUSSION

The degree of orientation of the specimens can be expressed by both Equation 8 (the Lotgering expression) and by Equation 11.

The results with the dry-pressed specimens are plotted in Figure 3. Both expressions show that increasing the field current, I_f, will increase the degree of orientation only up to $I_f \approx 150$ amp. From then on, further increase of the current has no effect in increasing the degree of orientation of the sample. The maximum degree of orientation for the dry-pressed specimens was found to be about 0.36, using the Lotgering expression, and about 0.89 in terms of $\overline{\cos \Phi}$ (see Equation 11). It must be noted here that there is not a linear correspondence between any of these figures and the degree of perfection of orientation; however, they are useful as figures of merit.

It was found also that sintering of the specimens improved their degree of orientation. A specimen dry-pressed at $I_f = 175$ amp. had $\overline{\cos \Phi} = 0.88$ in the "green" state; after it had been sintered at 1270°C for 40 min; the $\overline{\cos \Phi}$ value was then 0.91. The current was applied intermittently in order to shake the particles magnetically. The wet-pressed disks showed a higher degree of orientation than the dry-pressed specimens. The values of $\overline{\cos \Phi}$ were found to be 0.96 for "green" disks and 0.98 for the sintered specimens. The f factors were found to be 0.64 and 0.80, respectively.

Figure 4A shows the diffractometer trace of a barium hexaferrite powder; Figure 4B shows the trace of the same powder wet-pressed at $I_f = 175$ amp. and sintered at 1270°C for 30 minutes.

The improvement of the texture of the specimens on sintering can also be seen in the improvement of the squareness of the hysteresis loop observed with the "green" disk by comparison with that of the sintered disk (see Figure 5).

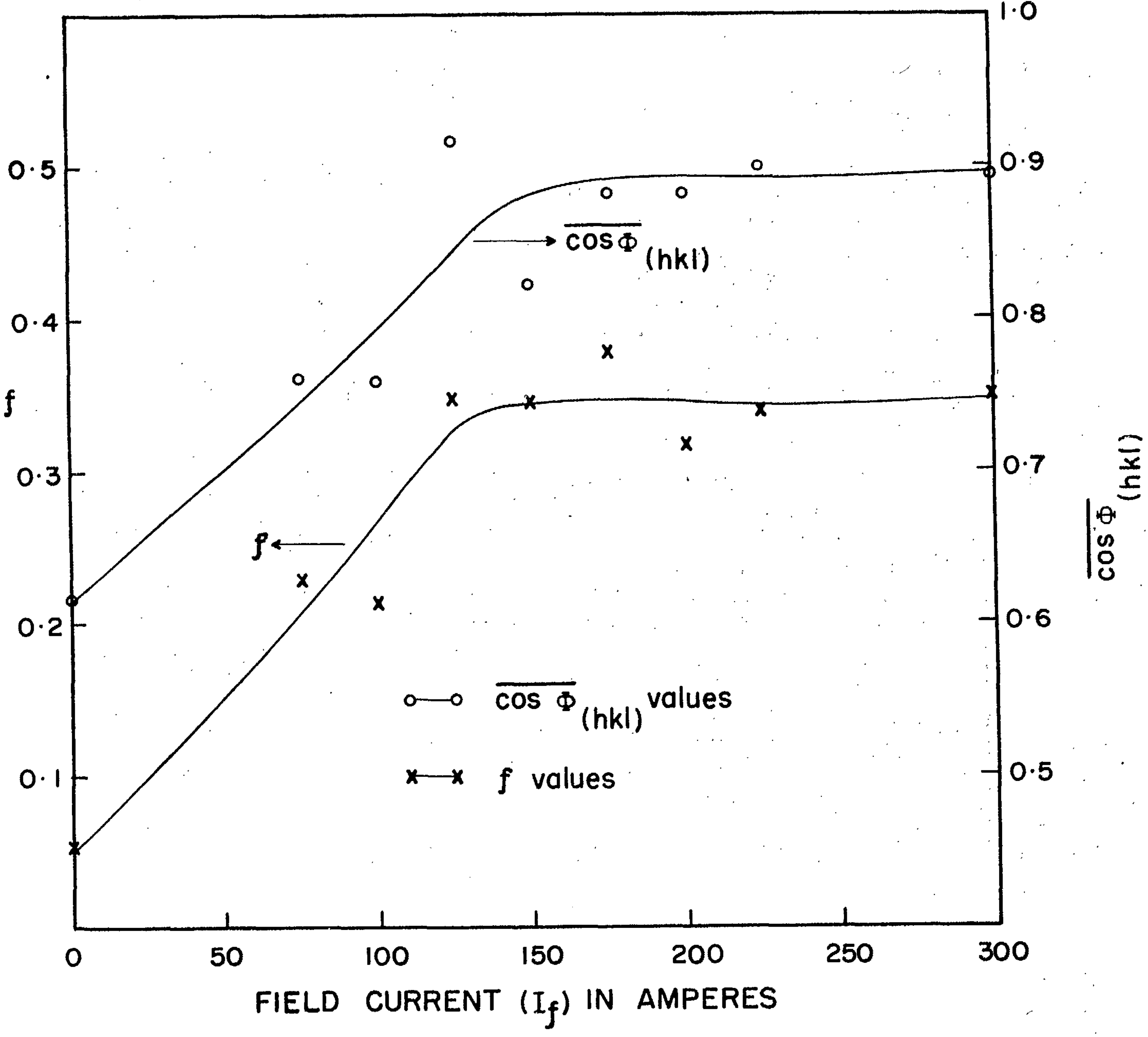

Figure 3. Degree of orientation vs. maximum field current, I_f, applied during pressing. (Weight of specimens about 20g.)

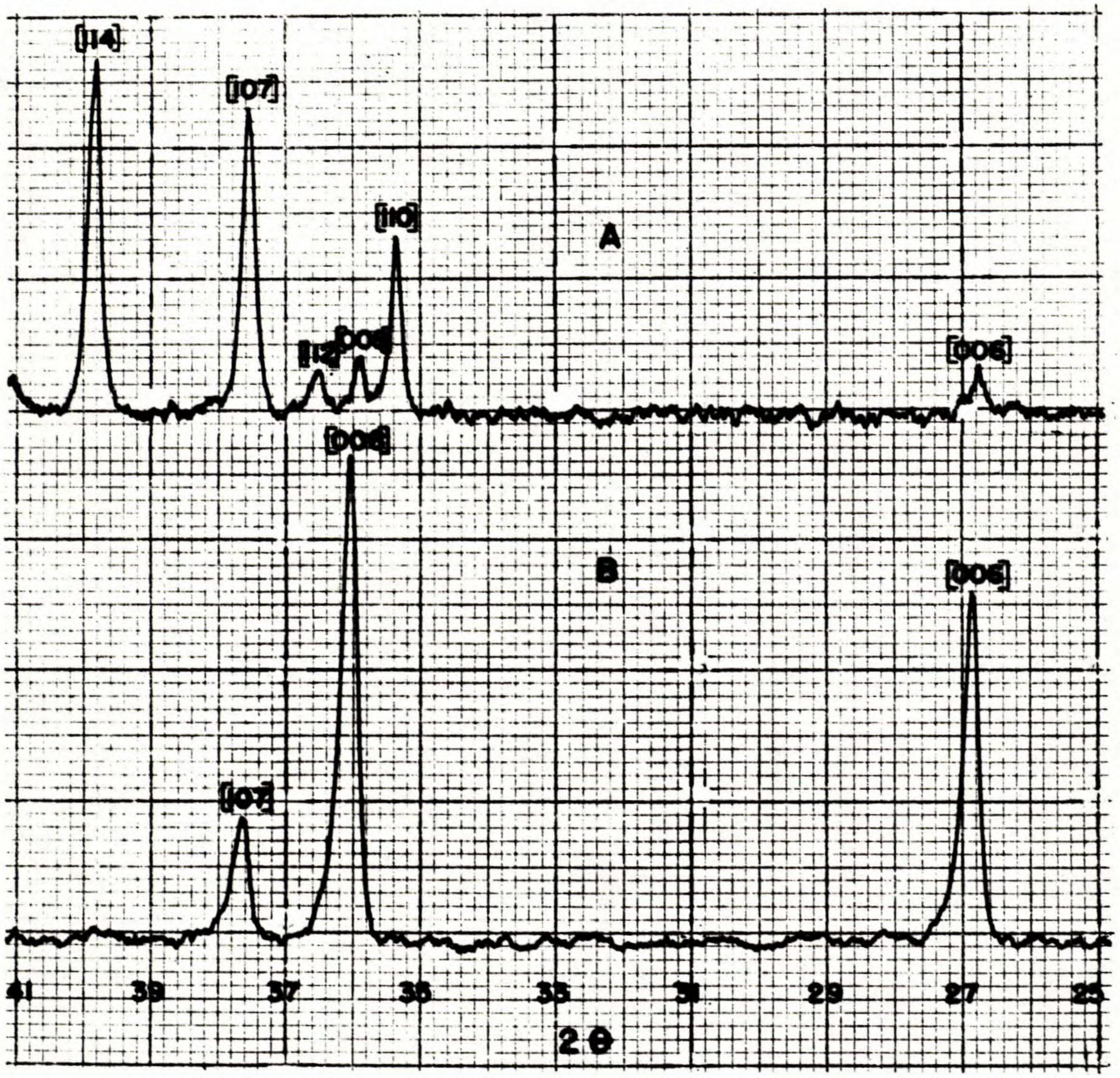

Figure 4. Diffractometer pattern of barium ferrite using filtered CoK radiation.

A. Completely random specimen (prepared from powder)

B. Oriented specimen (prepared from sintered disk)

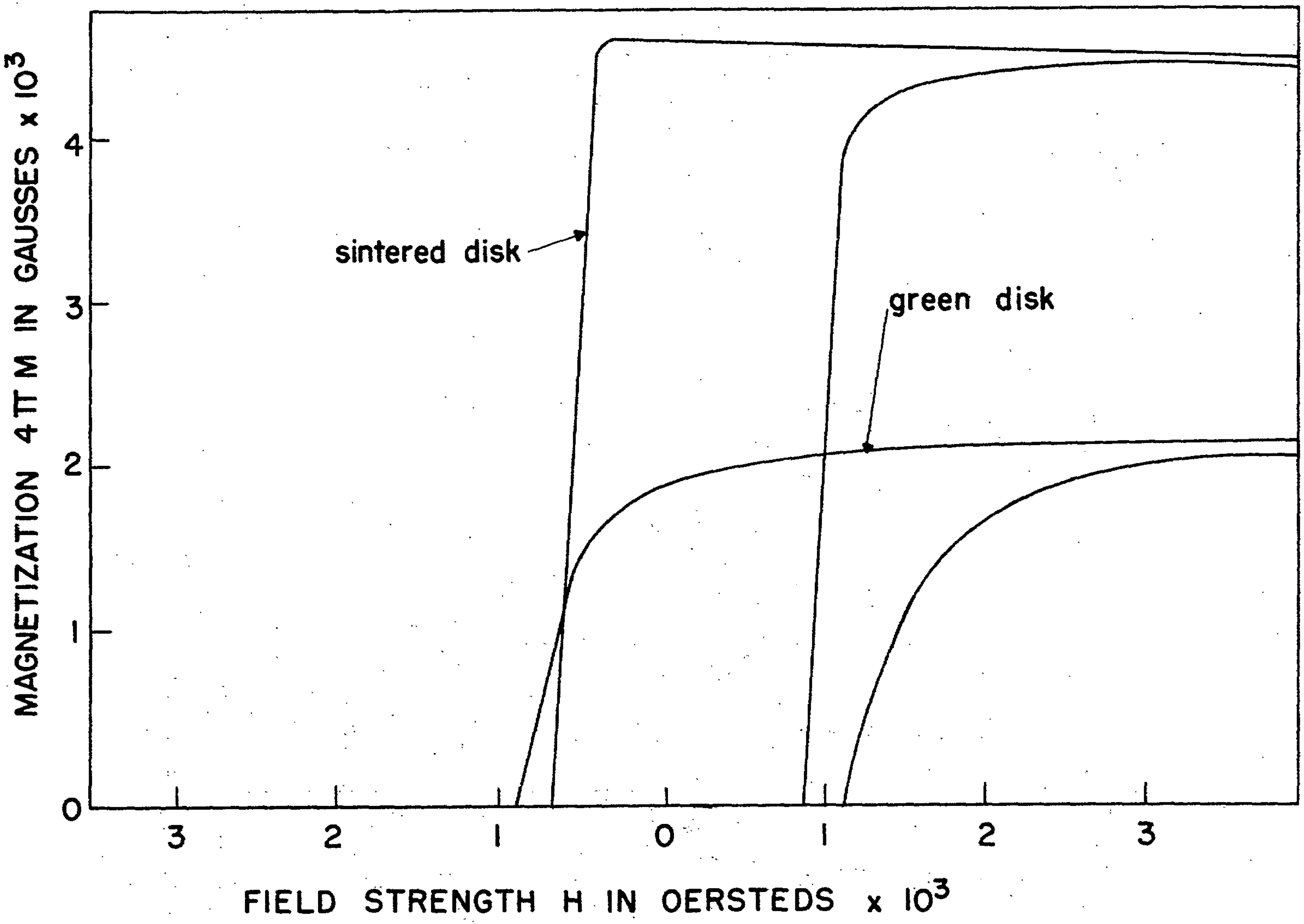

Figure 5. Hysteresis curve of barium hexaferrite, showing the effect of sintering on the squareness of the loop.

CONCLUSIONS

From the foregoing discussion, it can be concluded that:

a) The modified press is capable of producing ferrite specimens with a high degree of anisotropy.

b) The wet-pressing method using a slurry, having a consistency of about 20% solids, was found to be far superior to the dry-pressing method.

c) The use of a magnetomotive force of at least 30,000 amp. turns was required to produce oriented specimens weighing about 20 g and having 1.5 in. diameter.

d) The use of higher fields did not further increase the degree of orientation of the specimens.

e) The texture of the specimens was improved by sintering.

ACKNOWLEDGEMENTS

This investigation was conducted under the direction of Dr. N.F.H. Bright, Head, Physical Chemistry Section and Mr. I. F. Wright, co-ordinator of the Mines Branch Electronic Ceramics Programme, and was supported by the Defence Research Board under E.C.R.D.C. Contract C-73.

The authors are indebted to Dr. A.H. Webster for his valuable consultation throughout the work.

All parts of the modified press were fabricated by the Technical Services Division staff under the direction of Mr. D.M.Norman. The X-ray examinations were conducted by Mr. E.J. Murray, Technician.

The D.C. power supply was supplied on extended loan from the Physical Metallurgy Division.

The authors would also like to thank Mr. G.A.C. Wills, Technician, for his assistance throughout the work.

The above-mentioned personnel, with the exception of Mr. I.F.Wright (Mineral Processing Division) and Mr. D.M. Norman (Technical Services Division), are all members of the staff of the Mineral Sciences Division, Mines Branch.

REFERENCES

1. A.L. Stuijts, G.W. Rathenau and G.H. Weber, "Ferroxdure II and III, Anisotropic Permanent Magnet Materials", Philips Tech. Rev., 16, [5-6], 141-180 (1954).

2. J.W. Bergstrom, "General Motors Ferriroll Process", Paper presented at the Annual Meeting of the Canadian Ceramic Society, February, 1967.

3. J. Smit and H.P.J. Wijn, "Ferrites", Published by John Wiley and Sons, New York, (1959) p. 48.

4. R.M. Bozorth, "Ferromagnetism", Published by D. Van Nostrand Company, Inc., Toronto, (1951) p. 577.

5. F.K. Lotgering, "Topotactical Reactions with Ferrimagnetic Oxides Having Hexagonal Crystal Structure: I.", Journ. Inorg. Nucl. Chem., 9, 113-123 (1959).

6. E. Gillam and E. Smethurst, "The Orientation Texture and Magnetic Properties of Polycrystalline Barium Hexaferrite", Proc. Brit. Ceram. Soc., 2, 129-137 (1964).

APPENDIX III

ELECTRONIC CERAMICS

ECRDC RESEARCH PROJECT C 73

Identification of Mines Branch Personnel

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Dr. A.H. Gillieson, MSD	Spectrographic analyses
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EMD - Extraction Metallurgy Division
MSD - Mineral Sciences Division

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