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The objective of this project is to conduct research towards the development of satisfactory permanent magnet materials without the use of critical alloying elements through fine powder techniques.

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ABSTRACT

This report describes the techniques and initial results of investigations on fine particle permanent magnet materials.

The greater part of the investigations reported herein were on iron powders produced by thermal reduction of commercial rouge. For these powders, studies were made to determine the influence of variations in the conditions of reduction for loose powders and of variations in the pressing and sintering conditions for compacted powders. The data reported include metallic iron content, density, and magnetic properties, as related to the conditions of preparation.

Preliminary investigations are also reported on powders produced from ferrous formates and from mixed formates, including investigations on the characteristics of powders reduced from formates produce in various shapes and sizes. In general, the formate powders appear to be more easily reduced and to yield better magnetic properties than the oxide powders.

The best properties obtained to date have been by reduction of a ferrous formate powder containing 0.066% magnesium which yields a $B \times H_{max}$ of approximately 0.7×10^6. Indications are that by careful variations of the production techniques, this value may be appreciably improved.

INTRODUCTION

Purpose and Scope:

The objective of this project is to study the production and properties of fine particle permanent magnet materials.

This report covers in addition to the results of the past year's work, which it must be emphasized should be considered in the nature of a progress report rather than a terminal report, methods and techniques the development of which has extended for over two years. Much of this work was undertaken, or at least initiated prior to the granting of the contract, but it is deemed necessary and appropriate to report on it here in order that the techniques used in the work be fully known.

In view of the extended coverage of the report, it is divided into three sections:

I - General Statement of Aims

II - Equipment and Techniques

III - Experimental Results to Date

Personnel:

The personnel of the project have included, in addition to the principal investigator, Mr. Ananthanarayanan, Dr. J. F. Libsch, (Project Director); Dr. A. C. Zettlemoyer (Advisor on chemical matters); Dr. G. P. Conard II (Assistant Director of Magnetics Projects); Mr. A. V. Fraioli (Investigator); and Mr. Edward Stewart (Investigator).

I - GENERAL STATEMENT OF AIMS

The first concern of this project has been with studies of the various means of producing fine ferromagnetic powders and the effect of variations in the production processes on the magnetic properties of these powders in both the loose and the compacted form.

Among the variables to be controlled in connection with the particle production are size, shape, orientation, composition and surface condition of the powder. The first four factors are of importance for both loose and compacted powders, while the fifth variable might prove of primary importance in its influence on the properties of the compacted powders.

In addition to the variables within the powder production itself, when a satisfactory powder is obtained, it is necessary to investigate means of compacting and bonding this powder to provide satisfactory solid magnets.

To date, the investigations have been concerned primarily with the production of iron powder by three methods: (1) reduction of the oxide; (2) reduction of the formate; and (3) chemical precipitation; and with the characteristics of pressed and sintered compacts of powders obtained by methods (1) and (2) as related to the production and pressing and sintering conditions.

II - EQUIPMENT AND TECHNIQUES

(A) Preparation of Ultra-Fine Ferromagnetic Powders

Introduction:

Several methods show promise for the production of ultra-fine iron and other ferromagnetic powders (1-6). These include:

1. Low temperature reduction of compounds with a reducing gas (1, 2).
2. Direct precipitation of the metals from an aquoous solution of their salts (3).
3. Electrolysis of salt solutions in the presence of grain growth inhibitors (4,5).
4. Low temperature decomposition of the carbonyls or other methods of deposition of the metals from their vapor (6).

Of these methods, the first was chosen for the routine production of iron powders. The raw materials used were either Jewelers' rouge (commercial grade of Fe_2O_3 - approximately 98% Fe_2O_3, balance primarily SiO_2, particle size approximately 1 μ and finer) or ferrous formate and mixed formate powders produced as described below:

Lot I:

Plastiron (annealed electrolytic iron of -100 mesh) powder was dissolved in hot dilute formic acid. Ferrous formate was precipitated by chilling the solution to room temperature. The formate crystals produced were washed in alcohol, dried and stored in a vacuum for future use. The crystals obtained by this means were hexagonal platelets

(50 μ to 100 μ in size).

Lot II:

The coarse crystals of Lot I were redissolved in dilute formic acid and recrystallized by the addition of an equal volume of 95% ethyl alcohol (7). By allowing the precipitation to take place in a tall vessel, fine elongated crystals of an average size of 15 μ x 5 μ x 5 μ along with star-like clusters about 10 μ in diameter were obtained.

Lot II - Ground:

A batch of Lot II was ground by a single pass through a three roll mill used for dispersion of paint or ink pigments. The rolls were 4" dia. x 8" wide and were set at a force of 5 pounds per linear inch between rolls. This grinding broke up the star-like clusters and some of the needles and resulted in particles of approximately 10 micron size.

Lot II - Ball-Milled:

Another batch of Lot II was ball-milled in an inert atmosphere until the crystals were crushed to 1 micron or finer.

Lots A, B and C:

Three batches of formate were next prepared by recrystallizing Lot I formate to which varying amounts of magnesium formate had previously been added, the technique for precipitation being the same as for Lot II. The co-precipitated mixtures of ferrous and magnesium formates

were analyzed for their magnesium contents. The batches were designated Lots A, B and C in the descending order of their magnesium content:

Lot A: 2.5% Mg in the formate
Lot B: 0.29% Mg in the formate
Lot C: 0.066% Mg in the formate

The sizes of the crystals in all of these batches were comparable to those of Lot II.

Reduction of Powders:

The powders were reduced with hydrogen. As the reduced powders are pyrophoric, it was first necessary to devise techniques and construct equipment so that reduction of the powders and subsequent handling could be readily performed without bringing the loose powders into contact with the air.

The equipment used is illustrated schematically in Figure 1. Ten grams of the compound to be reduced, contained in a stainless steel boat (h), were placed in the heated combustion chamber (j) through which a regulated stream of purified hydrogen at approximately 1.5 cu. ft./hr./gm. of powder was passed. The reduction was carried out for times ranging from 30 to 900 minutes and at temperatures of from 500-1100°F. Helium was then introduced into the combustion tube, the whole system flushed with helium, and the boat containing the powder was placed under the Kjeldall joint (k). Acetone was then dripped into the boat until the reduced powder was well covered.

The helium flow was stopped and the slurry of powder and acetone transferred to a suitable container.

B - Particle Size Studies

Attempts were then made to study the particle size (and shape) of the powders produced by the following methods:

(1) Electron microscope studies *
(2) X-ray line broadening **
(3) Nitrogen adsorption***

For the first technique, electron micrographs were made from specimens obtained by dispersing the powders in dilute solutions of perlodion in amyl alcohol. The perlodion powder mixture was well rubbed out on a glass plate to the consistency of a thick paste, a drop of which was next cast into a film on the surface of brine contained in a large pan. The film was lifted off in a frame, refloated on water to remove all traces of brine, and small portions were selected and mounted on the specimen holder of an RCA electron microscope having a resolution of 100 Angstrom Units or better. The specimens were examined at magnifications varying from 1250-45,000 X.

It became clear that with this technique, dispersion

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* The electron microscope studies were made at the New Jersey Zinc Co., Palmerton, Pa., with the kind assistance of the members of their staff.
** The X-ray work was done by Prof. H. V. Anderson, Chemistry Department, Lehigh University.
*** The nitrogen adsorption measurements were made by Mr. A. V. Fraioli and Miss Yung-Fang Yu, Chemistry Department, Lehigh University.

of the particles was not satisfactory. The powders tended to group together in rings of magnetic closure (Fig. 2). Of several variations tried to overcome this deficiency, one did show some promise. A magnetic field was applied by waving a U-shaped Alnico magnet under the glass plate holding the rubbed-out specimen just prior to casting the film. In some areas of the field, good dispersion was observed (Fig. 3), while in others the particles became aligned in strings, indicating the possibility of magnetically aligning the powders (Fig. 4). This experiment, though crude in nature, suggests a possible method of adequately dispersing the particles to obtain electron micrographs suitable for particle size and distribution determinations. Recently, other investigators (8) have found that by applying an alternating magnetic field to the suspension while it is being rotated, even the larger aggregates can be broken up. If the magnetically agitated suspension of proper consistency is quickly cast into films the dispersed particles do not have time to reaggregate into ringlets by mutual attraction because the viscous resistance of the medium would hinder their ready motion towards one another.

The second technique actually measures grain or crystallite size, but for these fine particles, it is presumed that each particle is a single crystal.

The pyrophoric nature of the powders called for special techniques in the preparation of the X-ray specimens. The

slurry of the powder and acetone was laid on several layers of filter paper to absorb most of the acetone. The powder, slightly moist with acetone, was removed to another filter paper where it was gently mixed with a trace of non-diffracting grease. Satisfactory specimens could be made from such a mixture without any oxidation during the experiment. Only the strongest line, viz. the (110) line, was recorded on a G.E. XRD 3 X-ray recording spectrometer unit with cobalt radiation. The same line was also recorded under conditions yielding sharpest resolution by using a sample of annealed iron-powder having coarse particles. In this respect, the technique used differs from the conventional method of mixtures described by Warren (9). The angular widths of the recorded lines were measured at points of half-maximum intensity and the thickness of the particles in the (110) direction was calculated from the formula -

$$D_{(110)} = \frac{0.89\lambda}{\sqrt{B^2 - b^2} \cdot \cos\theta}$$

where -

$D_{(110)}$	=	particle thickness along a direction normal to the (110) planes.
λ	=	wavelength of X-radiation used.
B	=	angular width of (110) line in radians for the powder sample.
b	=	angular width of the sharp (110) line.
and θ	=	Bragg angle of diffraction.

These calculations assume no strain in the powders. It is felt that this assumption may be justified in view of the method of obtaining the powders and preparing the specimens.

In the third technique, the mean particle size was determined from the surface area measurements obtained by nitrogen monolayer adsorption and the presence or absence of desorption hysteresis was used as an indication of the presence or absence, respectively, of pores.

C - Magnetic Testing of Powders (and Compacts)

The magnetic properties of loose aggregates of the powders and of the compacts obtained by pressing them at pressures varying from 20-100 tons per square inch were measured, using a Sanford-Bennett Permeameter (10).*

The specimens used for measurements on loose powders consisted of moist powder gently rammed into a 1-3/4 inch long, 6 m.m. outside diameter, 1 m.m. wall thickness pyrex glass tube and held in place by stoppers at the ends of the tube.

D - Pressing and Sintering of Powders

The pressing of the test bars was done in a single action die on a Baldwin-Southwork testing machine at pres-

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* Earlier measurements were made by our investigators at Bell Telephone Laboratories, Murray Hill, N. J., with the kind assistance of their personnel, while the later measurements were made at the Franklin Institute, Philadelphia, with the facilities provided by Dr. A. D. Franklin.

sures of from 20-100 tons per square inch.

The sintering of the pressed compacts was accomplished in the equipment shown in Figure 1. The specimen to be sintered was first placed in the furnace tube. The tube was evacuated with a standard Cenco Hyvac vacuum pump (boosted for some runs by a mercury diffusion pump). The atmosphere to be used for sintering (hydrogen or helium) was then admitted and the furnace heated to the required temperature. Sintering experiments were performed at temperatures of 450 to 1700°F for times of 2 to 16 hours.

E - Analysis of Compacts

The compacts were analyzed for metallic iron by hydrogen evolution and for total iron by potassium permanganate titration.

F - Density Measurements

The average dimensions of the specimens were measured with a micrometer correct to 1/100 millimeter. The specimens were next evacuated and weighed and the average densities were calculated.

III - EXPERIMENTAL RESULTS OBTAINED TO DATE

A. - Powders Produced by Reduction of Rouge

Several batches of powders were produced from rouge as described in Section II, with reduction in the temperature range 600°-900°F and times of 100, 200 and 900 minutes.

Size and Shape of Powder Particles

Electron Microscopy:

As mentioned earlier, the lack of dispersion in most of the micrographs and the relatively low magnification in the single micrograph of Figure 3, having adequate dispersion, did not permit any particle size measurements. From preliminary results, however, three significant observations may be mentioned:

a. Firstly, that the particles could be satisfactorily dispersed and size counts could probably be made by using the method of magnetic dispersion.

b. Secondly, that the particles could also be aligned in a magnetic field, when they are suspended in a medium.

c. Lastly, that the particles are not far from spherical in shape and as such do not have any appreciable shape anisotropy.

This last result is equally important from the practical standpoint of making permanent magnets from these powders because, in this connection, large shape anisotropy of the powder particles is highly desirable in order to attain large coercive force values.

The present experiments appear to indicate that the

thermal reduction process of powder preparation does not produce powders of high shape anisotropy and is therefore incapable of producing powders with the high coercive forces that have been predicted by Neel (11), and by Stoner and Wohlforth (12).

X-Ray Diffraction and N_2 Adsorption:

Particle sizes of powders prepared at temperatures ranging from 650-900°F as determined by the X-ray diffraction and nitrogen adsorption methods are given in Figure 5. It will be noticed that the values obtained by the two methods are of the same order of magnitude. In addition, the pore volume results are given in Figure 6. The relative insensitivity of surface area and particle size measurements to increased reduction temperature, when considered with further evidence to be given in subsequent sections, is believed to indicate that the reduction of the rouge has been incomplete in all cases, even at 900°F.

The lack of any appreciable hysteresis in the adsorption-desorption cycle appears to indicate that if appreciable porosity is present in the individual particles it must be on a scale smaller than the size of the N_2 molecule and therefore would be of the nature of the atomic scale porosity predicted by earlier investigators (2). The gradual decrease of pore volume with increasing reduction temperature is interpreted as an indication of sintering taking place during the reduction.

Magnetic Properties of "Loose" Powders and of Powder Compacts

The magnetic properties of loose aggregates of the powders and of the compacts obtained by pressing them at pressures varying from 20-100 tons per square-inch were measured, using a high H permeameter of the Senford-Bennett type.

Loose Powders:

The coercive forces of powders prepared at various temperatures for 100, 200 and 900 minutes of reduction and a hydrogen flow of approximately 1.5 cu. ft./hr./gm. of oxide are shown graphically in Figure 7.

Some general features may be observed from these curves:

(a) All the curves are approximately parabolic in shape, thus exhibiting a maximum coercive force for an intermediate temperature of reduction.

(b) The coercive force values for the 200 minutes of reduction time are uniformly higher than those for 100 minutes of reduction time, while the 900-minute curve is displaced so that it crosses both the shorter time curves.

(c) The maximum coercive force occurs at lower temperatures for longer reduction times.

(d) The maximum coercive forces actually obtained are reasonably high, 520 oersteds for 100 minutes' reduction time, 640 oersteds for 200 minutes' reduction time, and 580 oersteds for 900 minutes' reduction time. From the trends of the curves it appears that a coercive force as high as 650 oersteds may be obtainable with the 900-minute reduction.

The parabolic nature of the curves may be readily

understood by considering the well-known effects of crystal size on coercive force theoretically derived by Neel (11, 13) and experimentally verified by Bertaut (14) on the one hand, and the effect of oxygen content of the powders recently reported by Lihl (15) on the other. At the low temperatures of reduction, extremely fine particle size and the excessive oxygen content of the powders together work against the development of a high coercive force. At the higher temperatures of reduction, the growth of the metal particles into poly-domains would tend to offset the beneficial effects of the decreased oxygen content in these powders. The balance between the effects of particle size and of oxygen content would thus tend to give a maximum point on the coercive force vs. temperature of reduction curve. The shift of the point of maximum coercive force to the lower temperatures for the higher times of reduction is also understandable on the same basis. For the higher times of reduction, the balance between the particle size and O_2 content effects must evidently obtain at a lower temperature of reduction. Thus, the increased time appears to be more effective in the reduction of the oxide than it is in the sintering of these powders. According to Lihl (15), in formate reduced iron powders, the maximum coercive force is obtained when the powder contains about 65% metallic iron, the actual value of this maximum being the greater the lower the temperature of reduction. The metallic iron data available for the powders which yielded high coer-

cive force values are shown in Table I. It would appear that some definite correlation between metallic iron content and the coercive force exists in the rouge-reduced powders as well. The maximum coercive force occurs at approximately 55-60% metallic iron, a value somewhat below that reported by Lihl for the formate reduced powders. The point at which the maximum H_c is obtained might perhaps also be used as an index of comparing the reducibility of different grades of oxide, from which the Fe powder may be prepared.

Powder Compacts:

Figures 8 and 9 show the variation of coercive force and of B_s and B_r, respectively, of the compacts as a function of compacting pressure. As the coercive force decreases gradually with increasing pressure, the B_s and B_r values show a corresponding increase. It may be noted that the B_s and B_r values are generally far lower ($B_s \sim 5000$, $B_r \sim 2000$) than those expected for pure iron.

The rate of decrease of coercive force with increasing pressure seems to be dependent on the initial powder characteristics. For example, the compacts from the powders reduced at 600°F for 200 minutes, which evidently contained more residual oxygen, show a more gradual decrease of coercive force with pressure than the powders prepared at higher temperatures. None of the powders, however, show a marked decrease in coercive force.

In Figure 10, the densities of compacts prepared from

powders reduced at 750°F for 100 minutes and powders reduced at 800°F for 200 minutes are plotted as a function of compacting pressure. The densities obtained are low, even at the highest compacting pressure used, viz., 100 t.s.i. This may be due to a high oxygen content in the powders.

The high coercive forces, the low saturation and low remanence values, as well as the low densities of the compacts, are indicative of incompleteness of reduction.

According to Neel (11), the coercive force of compacts should follow the law -

$$H_c \propto 1 - \frac{d}{d_o}$$

where -

H_c = coercive force
d = density of compact
d_o = density of iron in bulk.

$1 - \frac{d}{d_o}$ values for the above compacts vs. the corresponding compacting pressures are shown in Figure 11.

When the coercive force is plotted against $1 - \frac{d}{d_o}$ (Fig. 12), it is found that all of the points for compacts from two different batches of powder fall approximately on the same straight line. When this curve is extrapolated to $1 - \frac{d}{d_o} = 1$ (infinite dilution of the ~~pores between~~ particles), a coercive force value of 780 oersteds is obtained. This value is only about half the theoretical value of 1400 calculated by Neel (11) and also shown in the figure It is to be noted, however, that no correction has been

made for the oxygen content of the powders and the 'd' values are at best only average density values. It should be further noted that the data for compacts from powder reduced at 700°F for 900 minutes of reduction time lie on a straight line of greater slope extrapolating to a value of 860 oersteds at $1 - \frac{d}{d_o} = 1$, a value closer to Neel's theoretical value. This trend is in the right direction as the latter powders contained more metallic iron than either of the other two.

Studies on Sintering

Powders prepared at 700°F for 200 minutes of reduction time (H_2 flow 1.5 cu.ft./hr.gm.) were pressed into bars approximately 1¼" x 1/8" x 1/8" and sintered at various temperatures for 2, 4 and 16 hours. The variation of H_c, B_s and B_r, as well as the density, metallic iron and total iron of some of the compacts thus obtained was determined and the results are assembled in Tables II, III and IV. The magnetic data are also shown graphically in Figure 13.

The coercive force results appear to indicate that for the times investigated, the formation of domain boundaries takes place in all cases over a range from approximately 1,000 to 1600°F. At higher temperatures, further sintering and densification is observed as the result of contraction of the pores between sintered particles.

It is also noted that further reduction of the residual oxide takes place during the sintering as indicated

by the increase in metallic and total iron contents. In view of this observation, experiments are being undertaken on sintering under non-reducing conditions.

If, as a first approximation $(B \times H)_{max}$ is assumed to be $(1/3\ B_r \times H_c)$, the maximum energy product obtained for these sintered compacts is approximately 0.5×10^6 obtained from powders reduced for 900 minutes.

B-Powders Produced by Reduction of Formates

The investigation undertaken to date on the formate reduced powders have been of an exploratory nature only and the data are in many respects incomplete. It should, therefore, be borne in mind that more complete data may in some cases subsequently alter some of the trends indicated in this section and that in some areas the data are so sketchy as to preclude the possibility of drawing sound conclusions therefrom. This work is being continued, and it is planned to fill in the data in those areas which show promise of yielding either valuable information or magnetic materials with desirable properties.

The formates were reduced in a stream of purified dry hydrogen for a period of 30 or 60 minutes at temperature ranging from 550°F to 1100°F. The hydrogen flow was kept at 1.5 cu. ft./hr./gm of the salt in all cases. The techniques and precautions used for preventing the powders from oxidizing were identical with those described in Part II.

Magnetic Properties of Formate-Reduced Iron Powders and Powder Compacts

Loose Powders and Powder Compacts from Lot I and Lot II:

The coercive force values of loose aggregates of the iron powders obtained from Lot I formate for 30 minutes and 60

minutes of H_2 reduction at various temperature are shown in the curves of Figure 14.

The parabolic nature of all of the curves is similar to that obtained with the rouge-reduced powders treated in III-A of this report. The H_c max. for Lot I powders after 30 minutes reduction time appears to occur at a higher temperature of reduction than for the same type of powder after 60 minutes reduction time. This is in agreement with the data reported by Lihl (15), previously mentioned in Section III-A. His work indicates that the H_c max. points on both of these curves probably correspond to the same degree of reduction and the powder prepared at the lower temperature would be expected to show the higher coercive force.

It should also be noted that the H_c max. points themselves occur at very much lower temperatures than for rouge-reduced powders. Thus, the formates are more easily reduced than the oxides.

The coercive force vs. temperature of reduction curve of the iron powders from the finer formate of Lot II shows the H_c max. point at a very much lower temperature than that obtained from the coarser formate of Lot I. The H_c max. value appears to be correspondingly much higher. The curve for Lot II is also seen to intersect both of the curves for Lot I.

Figure 15a shows the coercive force of compacts pressed at 60 t.s.i. from iron powders prepared at various temperatures from Lot I and Lot II formates for the same hydrogen flow and for the same reduction time of 60 minutes and Figure 15b shows the corresponding B_s and B_r values.

The rate of decrease of coercive force with temperature of reduction for Lot I appears to be less than that for Lot II though, as only two points were obtained for Lot I, the coercive force for this powder may not follow the approximate linear trend observed for Lot II. The B_s values appear to increase with increasing temperature of reduction, at a rate almost proportional to the rate of decrease of coercive force, but the differences in rates of increase of B_s between the two powders are less than the differences for H_c. The B_r values at first increase slowly, but afterwards, at least for the Lot II powder, appear to attain a steady value. These data may be interpreted as a reflection of the higher reducibility of the finer formates. Lastly, the B_s increases more rapidly than B_r with increasing temperature of reduction.

Comparison Between Lot II, Lot II-Ground and Lot II-Ball-Milled:

Figure 16 shows the coercive force vs. reduction temperature for iron powders from formates of Lot II, Lot II-Ground and Lot II-Ball-Milled, while Figures 17a and 17b show the H_c, and B_s and B_r values for compacts pressed at 60 t.s.i.

It may be seen from Figure 16 that only the right-hand side of the parabolas appear to be be obtained. The Hc max. points probably fell either at 500°F (the lowest temperature investigated) or lower. There is not much difference between Lot II and Lot II-Ground, but the much finer

ball-milled Lot II shows lower values of H_c throughout the temperature range studied.

This might indicate either that the whole H_c curve is shifted to the left, with perhaps a higher peak value of H_c at lower temperatures than those investigated, as the result of higher reducibility of the finer powders, or that the coercive force is merely depressed at the higher temperatures because of a greater tendency of the fine powders to sinter.

The coercive force values of compacts of these powders (Fig. 17) show a linear decrease with increasing temperature, as before, but the lines for all powders have substantially the same slope.

From Fig. 17b, it may be noticed that the Bs values increase somewhat with increasing fineness of the formate. This trend would be expected whether the effect of fineness were to increase reduction or sintering rate. The B_r values also show a corresponding increase which is very slight (excluding those where there were cracks in the specimens).

Effect of Small Additions of Magnesium Formate:

A comparison of the magnetic behavior of iron powders from Lot II formate and Lot A and Lot C formates containing 2.5% and 0.066% Mg, respectively, is shown in the coercive force vs. temperature of reduction curves of Fig. 18 (for a constant hydrogen flow of 1.5 cu. ft./hr./gm. and constant reduction time of 60 minutes). From the trend of the curves,

it may be seen that addition of magnesium (presumably present as MgO) tends to increase the H_c max. value when such addition is not appreciable. Thus, the H_c max. value with 0.066% Mg is the highest obtained, about 650 oersteds, nearly 25% greater than that for the straight Lot II.

Although the data are insufficient for a close comparison, there seems to be no doubt that when the magnesium addition to the formate is small enough to not decrease the reducibility appreciably, a substantial increase in coercive force values may be expected, probably because the MgO formed during the reduction is finely dispersed in the iron powder, providing diffusion barriers between the iron particles and thus preventing appreciable sintering of these fine powders. Figures 19a and 19b show the H_c, and B_s and B_r values, respectively, for compacts from Lot II (0% Mg) and Lot C (0.066% mg). (Cracks in specimens did not permit B_s and B_r values to be calculated for Lots B and A). The presence of magnesium in the formate tends to produce compacts with higher coercive force from low temperature reduced powder, but at the higher temperatures of reduction, no clear difference is observed in the coercive force.

In contrast to the coercive force behavior, however, the B_s values do not differ markedly at low temperature, but the B_s for the compacts containing magnesium does not increase linearly with increasing temperature but tends to increase more slowly at the higher temperatures than that for the

pure iron powder. The B_r values for the Lot C are, however, slightly increased over those for Lot II. This increase though of the order of 20% may not be really significant and may arise from sampling.

It appears, in general, that judicious additions of Mg to the formate can cause marked improvement in the H_c without being detrimental to the B_s and B_r to any considerable extent.

A study of these data indicates a rather sharp peak in the H_c max. for small amounts of added magnesium and indicates the advisability of a more thorough survey of the effects of magnesium additions in the range from zero to approximately 1/2 per cent. If, as a first approximation, $B \times H_{max.}$ is assumed to be 1/3 ($B_r \times H_c$), the maximum energy product obtained for the formate reduced compacts is that of $.675 \times 10^6$ obtained for the powder reduced from the formate containing 0.066% Mg as magnesium formate.

From the trends of the data obtained to date, it appears advisable to investigate the effect of lower reduction temperatures and longer reduction times on the straight and the mixed formate powders. One technique which might permit extremely low reduction temperature would be to transform the formate to FeO by short time, high temperature treatment. The FeO powder should then be reducible to iron powder at very low temperatures.

C - Summary of Results on Reduced Formate and Oxide Powders

The results of the investigations to date may be summarized as follows:

(1) The thermal reduction process by itself appears to be incapable of producing powders with a high degree of shape anisotropy.

(2) Increased reduction times permit reduction at lower temperatures with a relative increase of reduction rate compared to sintering rate, thus providing the possibility of producing powders with higher coercive force.

(3) The results agree with those of Lihl (15) on the decrease of temperature of reduction for maximum coercive force with increased reduction times.

(4) Ferrous formate powders reduce at a lower temperature than commercial rouge, probably because of the lack of impurities and because the formate appears to decompose directly to the ferrous oxide early in the reduction, while the rouge is in the ferric state. As the result of the considerations mentioned in (2), therefore, the formate powders may be generally capable of producing higher coercive force iron powders than the commercial rouge.

(5) MgO in proper amounts may provide a further increase in the coercive force through interfering with sintering during reduction.

(6) Increased fineness of salts may permit obtaining increased coercive force through an increase in reduction rates and consequent possibility of reduction at lower tem-

peratures. It may, however, also tend to decrease the coercive force through increasing the sintering rate.

(7) The rate of variation of the coercive force with compacting pressure is appreciably influenced by the powder characteristics; for example, the amount of oxides or other impurities present.

(8) From the point of view of coercive force, the maximum sintering effect when pressed bars are reheated (multidomain formation), appears to take place over a narrow range of temperatures, while the saturation induction and remanence values tend to start a gradual increase somewhat before the sharp drop in coercive force. This indicates that by careful control of the sintering techniques, higher B x $H_{max.}$ values may be obtainable.

(9) Increased sintering times tend to decrease the temperature at which the coercive force drops sharply. In these experiments, this change was small, perhaps because of the impurities in the powder.

(10) While the highest B x $H_{max.}$ obtained in these investigations was approximately 0.7×10^6 for the magnesium containing formate reduced powders and was approximately 0.5×10^6 for the rouge reduced powders, these values should be capable of improvement. In the case of the oxide powders at least the low B x $H_{max.}$ product is probably due in part to a low remanence, as a result of impuri-

tion present. The value may therefore be improved by magnetic separation of non-ferromagnetic impurities after the reduction. In addition, careful variations of reduction, pressing and sintering techniques and alignment of particles in magnetic fields may well be capable of producing powders of sufficient quality to find application in the permanent magnet field.

TABLE I

Metallic Iron Content of Powders Reduced From Rouge For Various Times at Temperatures Yielding Large Coercive Force Values

Reduction Temperature in °F	Reduction Time in Minutes	Coercive Force in Oersteds	Metallic Iron Content %
750	100	520	51
800	100	500	57
700	200	560	50
750	200	640	56
800	200	530	59
600	900	580	56
700	900	580	60
800	900	504	65

TABLE II

Magnetic Properties of Sintered Iron Compacts - Compacts Pressed at 40 t.s.i. From Powders Reduced from Rouge at 700°F For 200 Minutes and Sintered 2 Hours In Hydrogen

Sintering Temperature °F	Coercive Force-Oersteds	Intrinsic Induction (at H = 4000 Oersteds) - Gauss	Remanence Gauss
---	530	3750	1720
450	520	3820	1790
700	504	4110	1945
1000	480	4352	2111
1200	390	5590	2185
1400	200	4846	1400
1600	72	5743	3283
1700	32	5500	---

TABLE III

Magnetic Properties and Density of Sintered Iron Compacts - Compacts Pressed at 40 t.s.i. From Powders Reduced from Rouge at 700°F for 200 Minutes and Sintered 4 Hours in Hydrogen

Sintering Temperature °F	Coercive Force-Oersteds	Intrinsic Induction (at H = 4000 Oersteds) - Gauss	Remanence Gauss	Density Gms./c.c.
---	514	4015	2000	3.04
800	478	4710	2405	3.19
1000	430	5220	2676	3.0
1200	204	6352	2680	3.38
1400	50	7338	2290	3.75
1600	5	7730	3680	4.48

TABLE IV

Magnetic Properties, Density, Metallic Iron Content and Total Iron Content of Sintered Iron Compacts - Compacts Pressed at 40 t.s.i. From Powders Reduced from Rouge at 700°F for 200 Minutes and Sintered 16 Hours in Hydrogen

Sintering Temperature °F	Coercive Force-Oersteds	Intrinsic Induction (at H = 4000 Oersteds) - Gauss	Remanence Gauss	Density Gms./c.c.	Metallic Fe%	Total Iron %
---	500	4600	2400	3.14	50	76.1
600	430	4940	2560	3.06	57.3	78.2
800	400	5520	2960	3.15	63.8	80.8
1000	382	5900	3080	3.10	68	79.7
1200	192	6280	3140	3.36	76	78.2
1400	48	7750	2780	3.88	80.9	83.2
1600	5	11500	4900	5.50	88.4	87.8

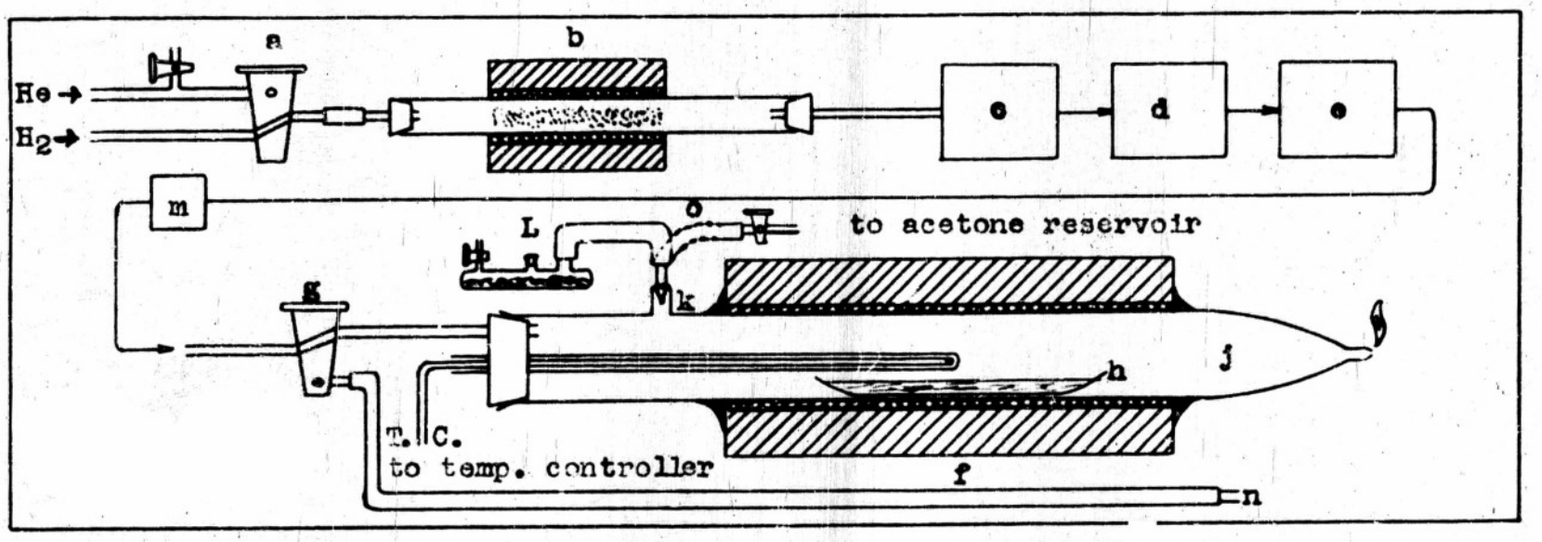

Fig. 1. Apparatus Used for the Reduction of Powders and for the Sintering of Powder Compacts.

a: Selector stop-cock for hydrogen or helium.
b: Hydrogen deoxidizer consisting of either palladium catalyst or heated Cu shot.
c: Two silica gel drying towers.
d: Dry ice trap.
e: Two phosphorus pentoxide drying flasks.
m: Glass-wool filter.
g: Stop-cock to reverse flow of gas in reduction or sintering chamber whenever necessary through the rubber hose "n".
f: Heating furnace. h: Stainless steel boat containing compound to be reduced or compact to be sintered.
j: Reduction or sintering chamber. k: Kjeldahl joint.
L: Phosphorus pentoxide tube with stop-cock at one end.
o: Alternate connection between Kjeldahl joint "k" and acetone reservoir.
T.C.: Control thermocouple.

Fig 2. Electron Micrograph of Rouge Reduced Iron Powder (Reduction Temp. 900°F; Reduction Time 200 Minutes). Arrows Show Formation of Rings of Magnetic Closure.

Fig 3. Electron Micrograph of Rouge Reduced Iron Powder (Reduction Temp. 750°F; Reduction Time 100 Minutes) Showing Dispersion of Particles Obtainable by Proper Use of a Magnetic Field.

Fig 4. Electron Micrograph of Rouge Reduced Iron Powder (Reduction Temp. 750°F; Reduction Time 100 Minutes) Showing Alignment of Particles in a Magnetic Field.

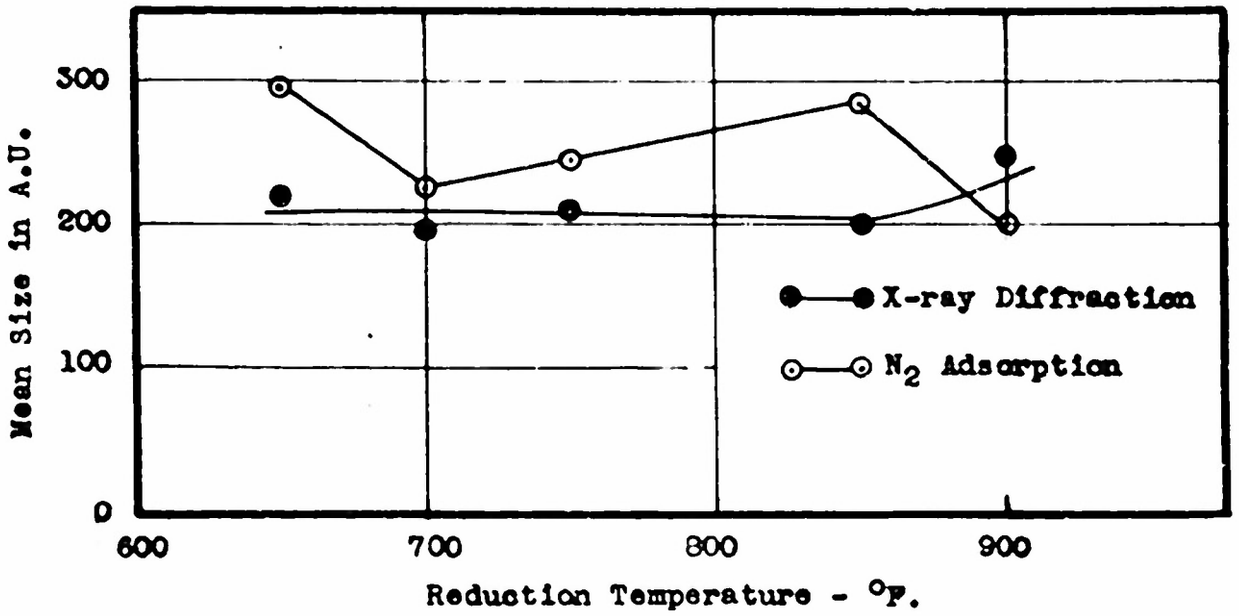

Fig. 5. Mean Crystallite or Particle Size of Powders Reduced from Ferric Oxide (Rouge), by X-ray Diffraction and N_2 Adsorption Methods.

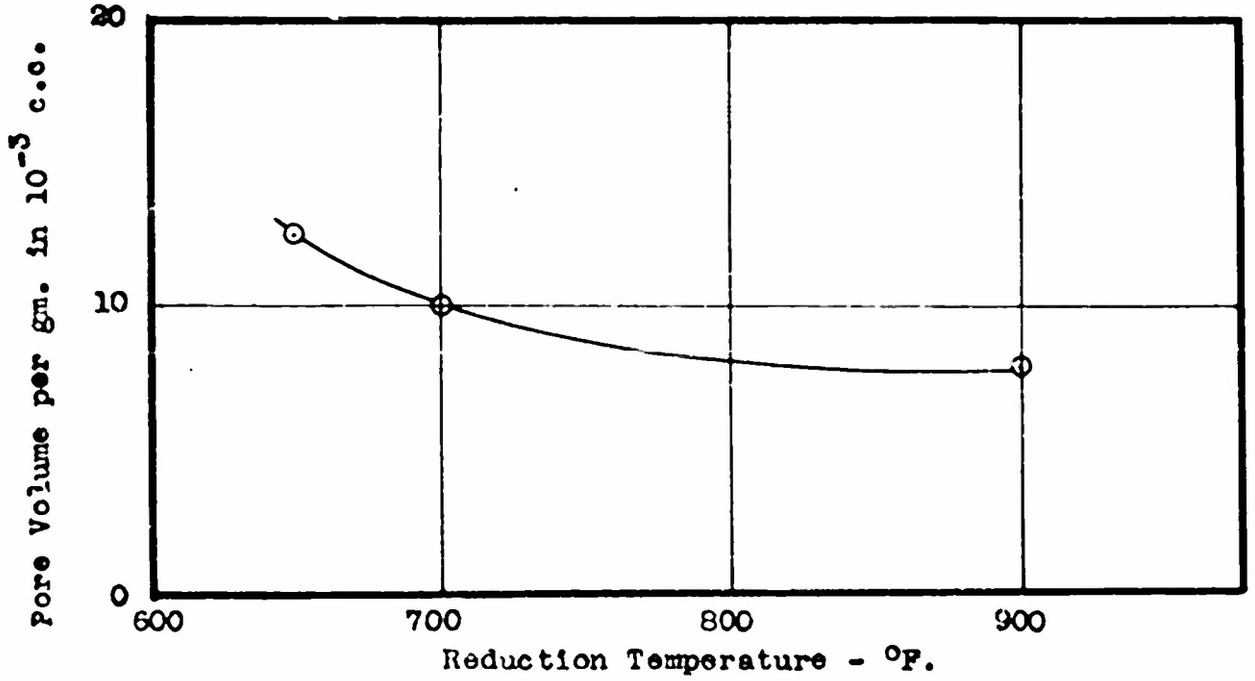

Fig. 6. Pore Volume per gm. of Powders Reduced from Ferric Oxide (Rouge), by Nitrogen Desorption.

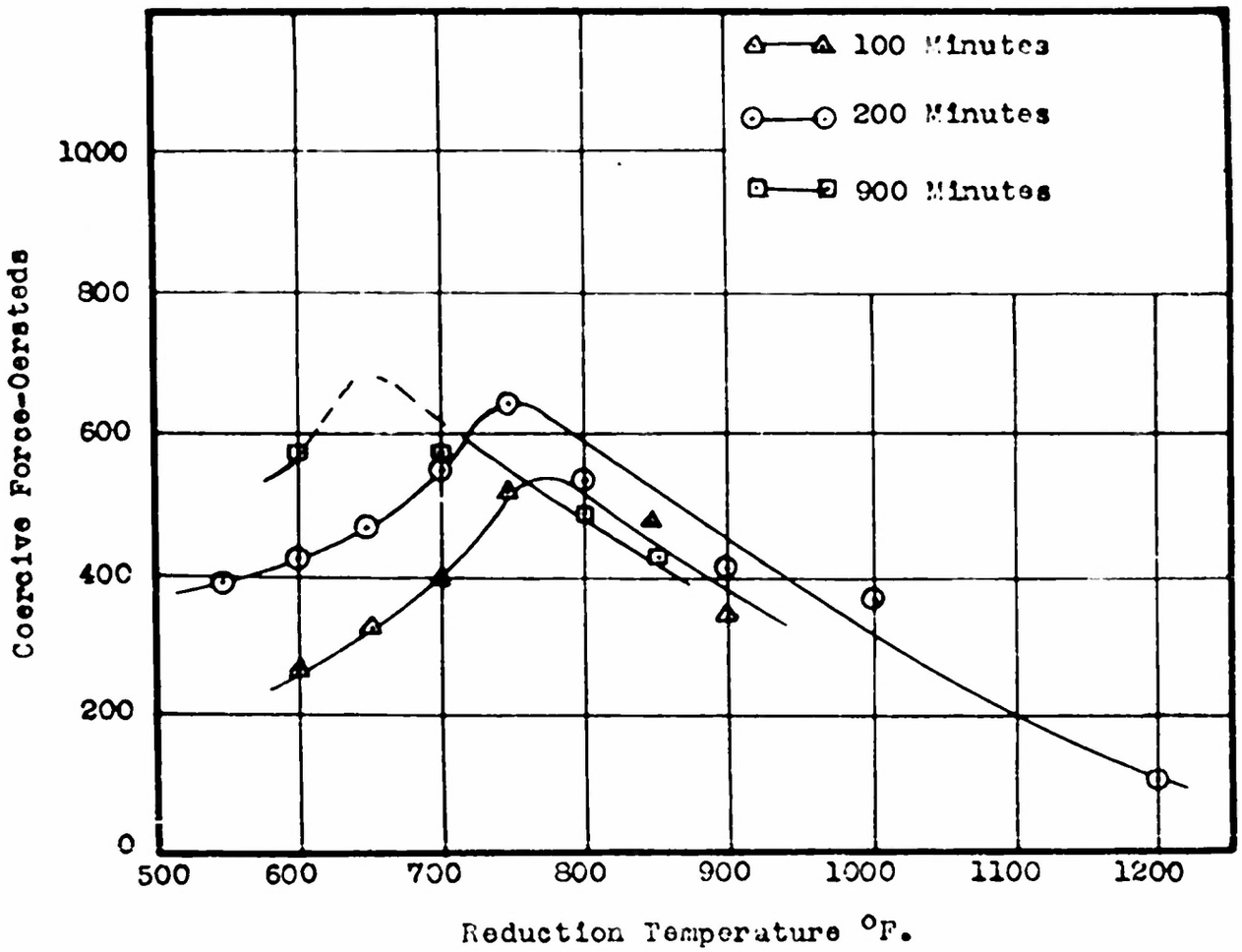

Fig. 7. Variation of Coercive Force with Temperature of Reduction of Iron Powders Prepared from Rouge for Various Reduction Times.

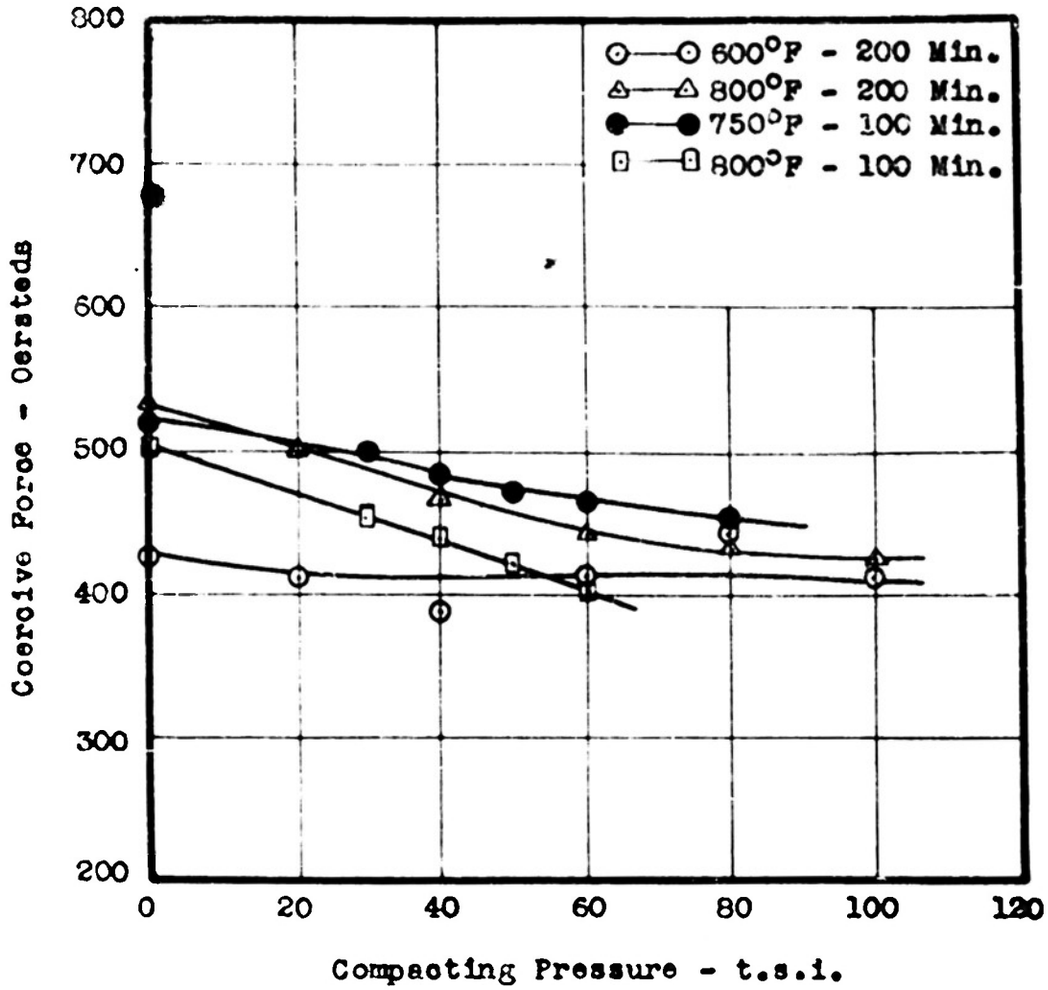

Fig. 8. Variation of Coercive Force with Compacting Pressure of Compacts of Iron Powders Prepared from Ferric Oxide (Rouge Reduced at Temperatures and for Times Indicated).

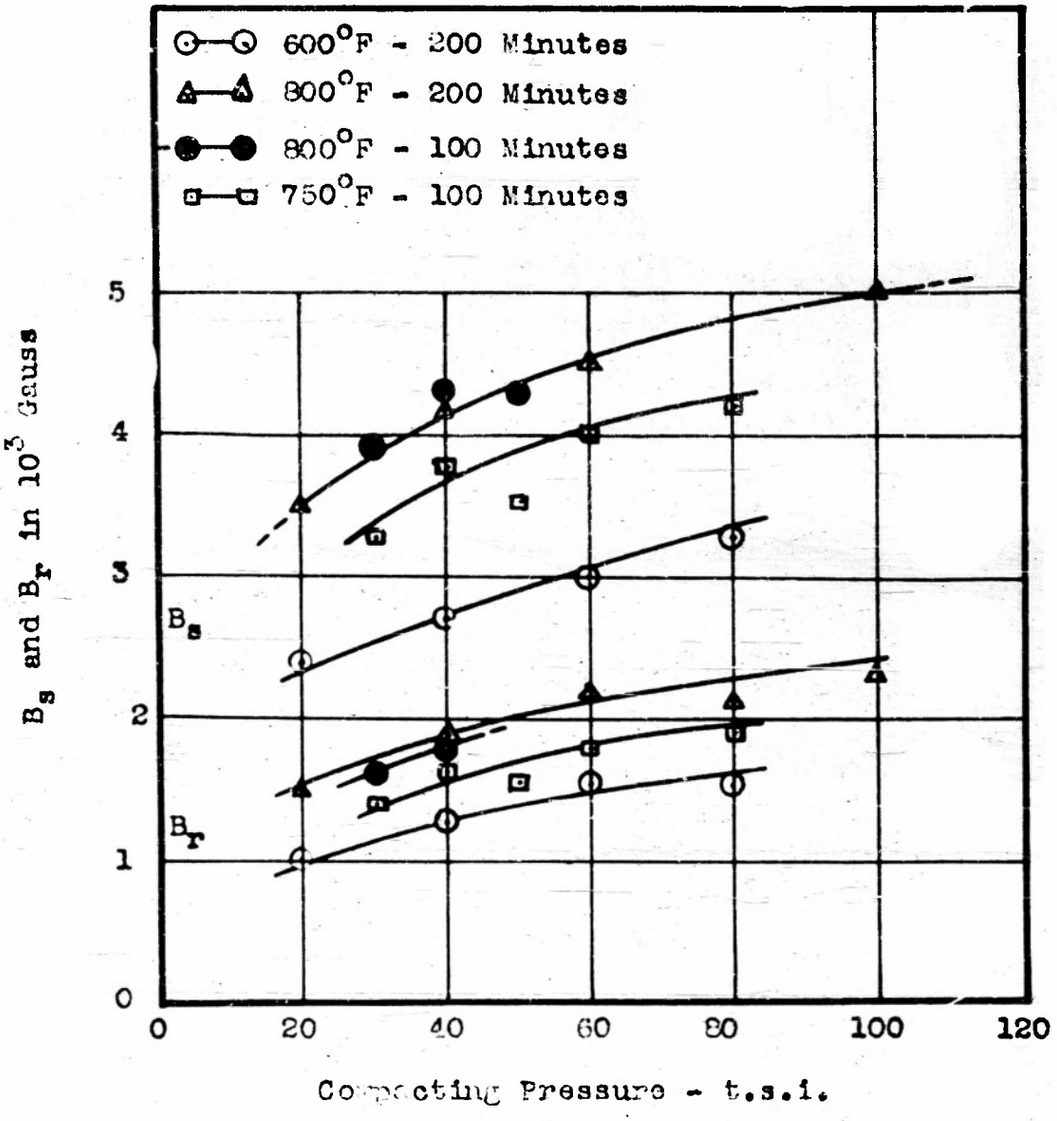

Fig. 9. Influence of Compacting Pressure on the Intrinsic Induction at H = 4000 Oersteds (B_s) and Remanence (B_r) of Compacts Prepared from Iron Powders Reduced from Ferric Oxide (Rouge Reduced at Temperatures and for Times Indicated).

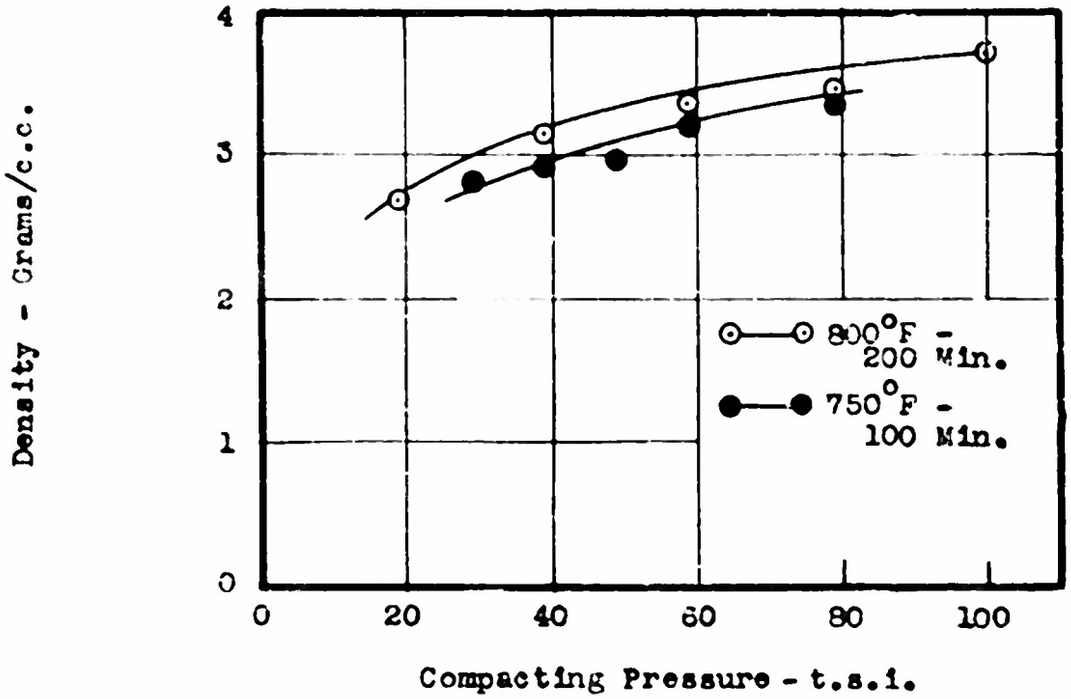

Fig. 10. Influence of Compacting Pressure on the Density of Compacts from Iron Powders Reduced from Ferric Oxide (Rouge Reduced at Temperatures and Times Indicated).

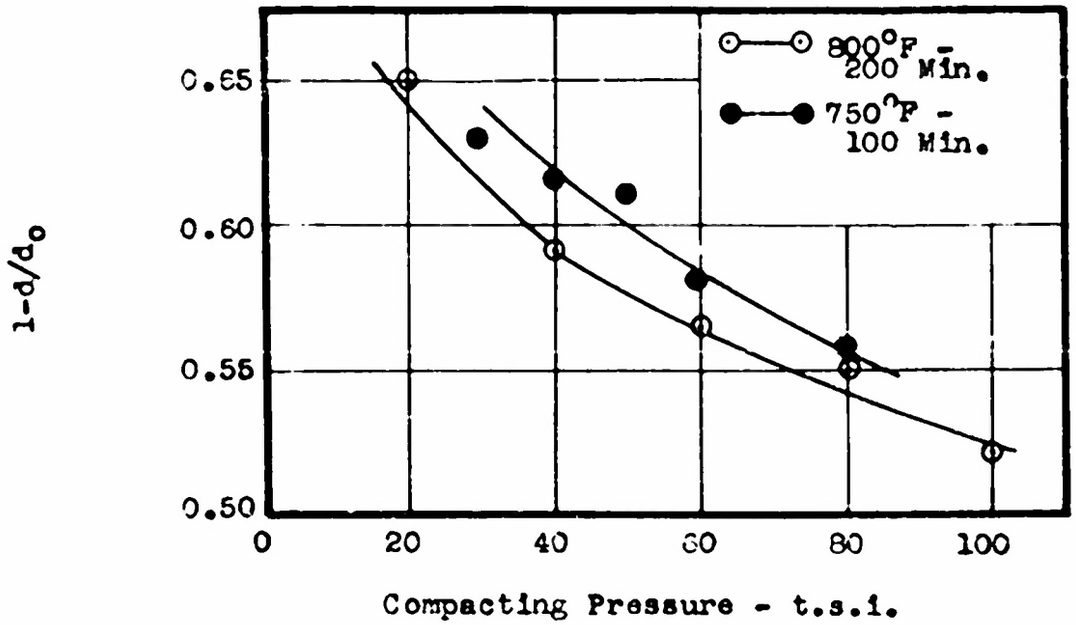

Fig. 11. $1-d/d_o$ Versus Compacting Pressure for Compacts from Iron Powders Reduced from Ferric Oxide (Rouge Reduced at Temperatures and for Times Indicated).

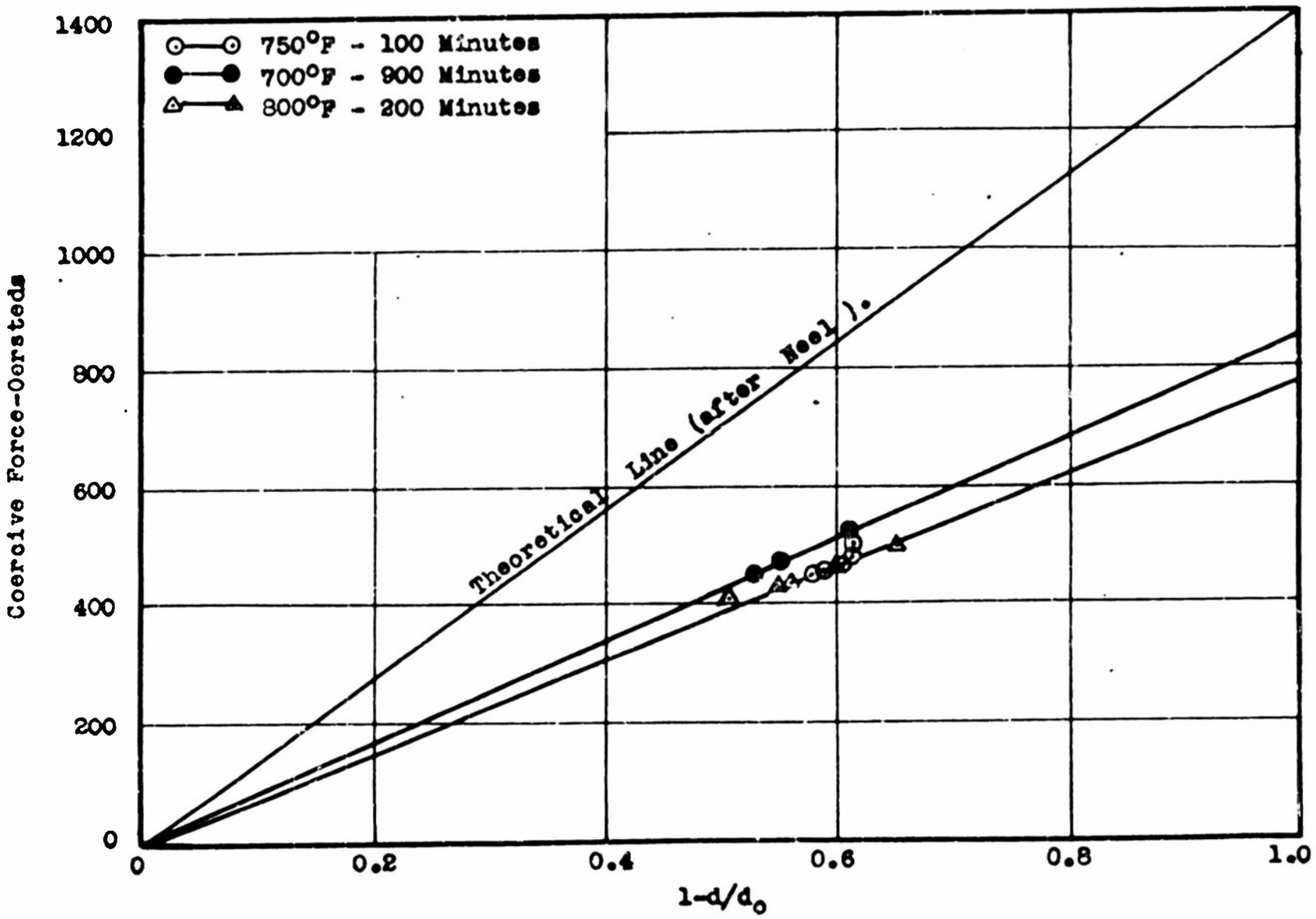

Fig. 12. Coercive Force Versus $1-d/d_o$ for Compacts of Iron Powders Reduced from Ferric Oxide (Rouge Reduced at Temperatures and for Times Indicated).

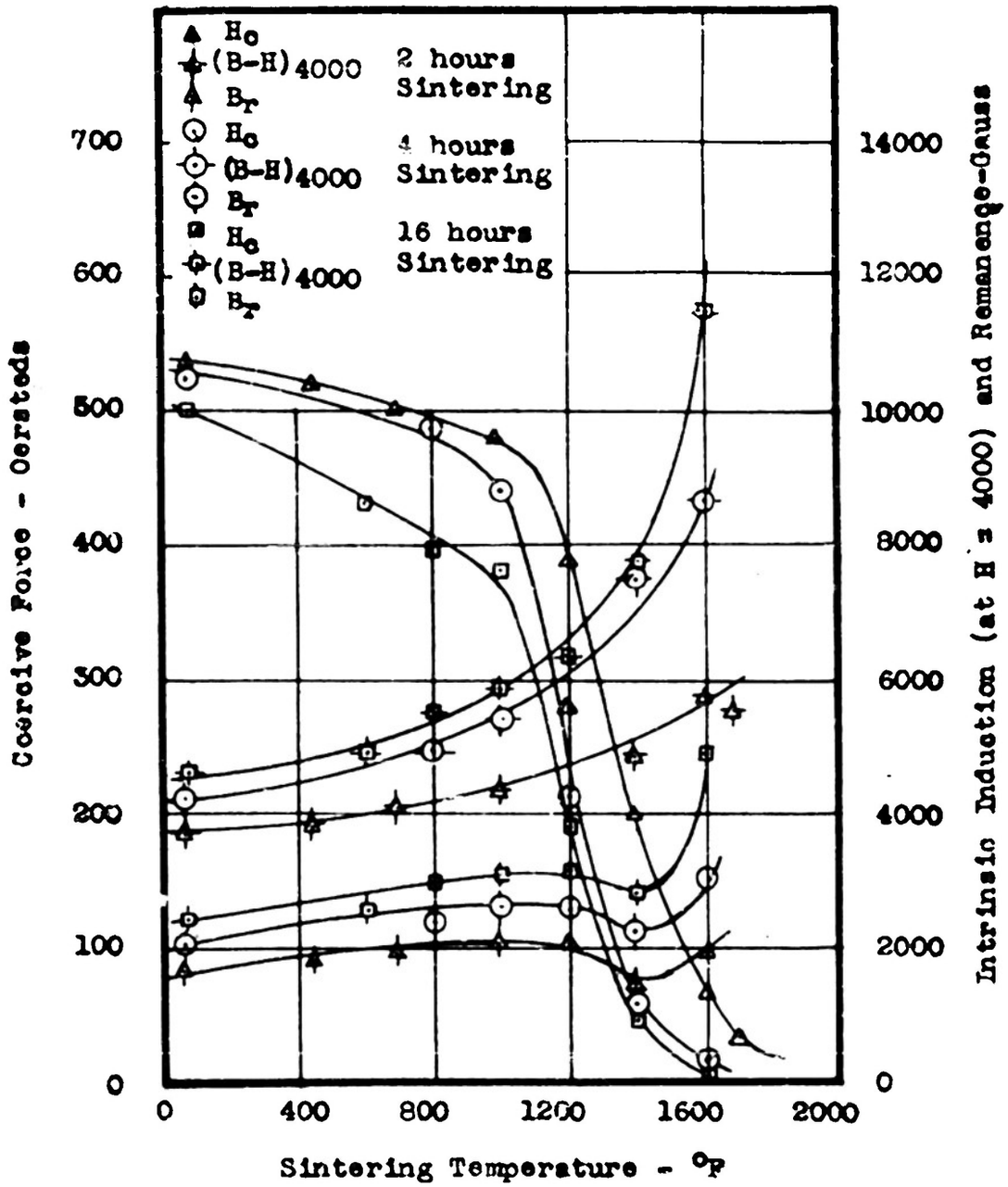

Fig. 13. Influence of Sintering Temperature and Sintering Time on the Magnetic Properties of Compacts Pressed at 40 t.s.i. from Iron Powders Reduced from Ferric Oxide (Rouge Reduced at 700°F for 20C Minutes).

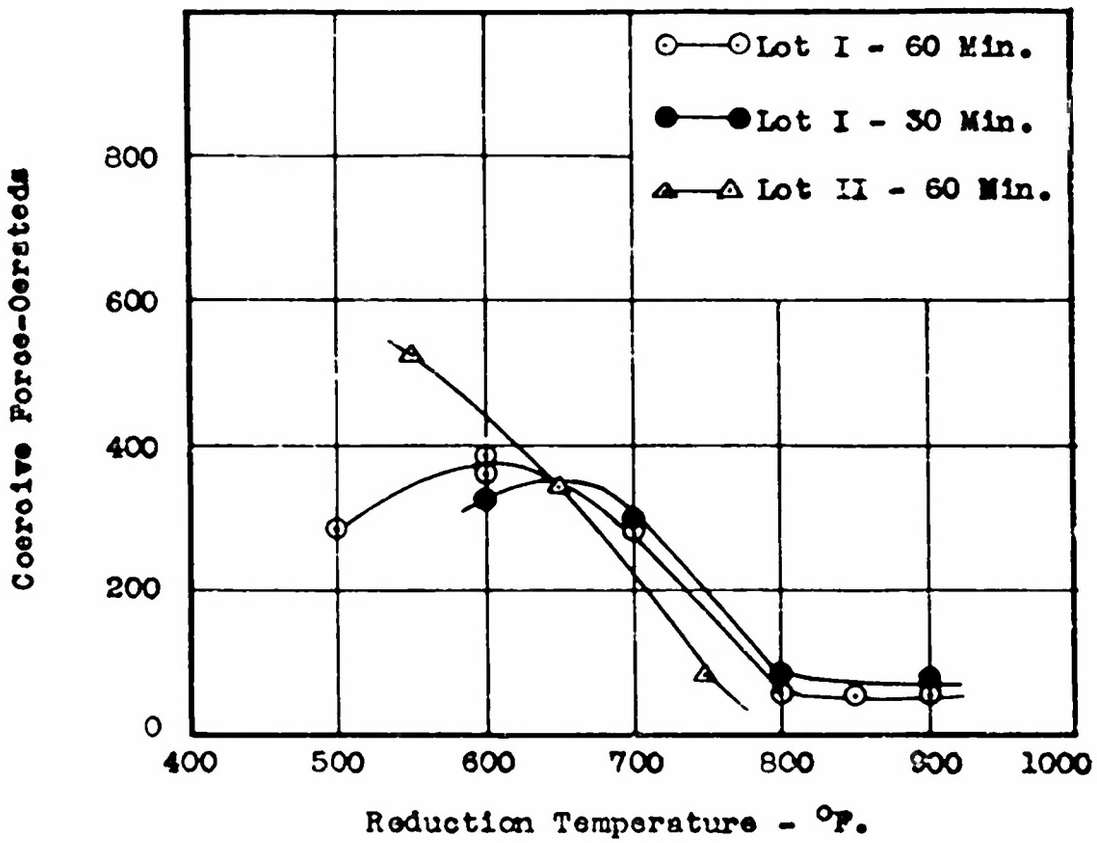

Fig. 14. Coercive Force Versus Reduction Temperature for Iron Powders Prepared from Lot I and Lot II Ferrous Formates for Reduction Times Indicated.

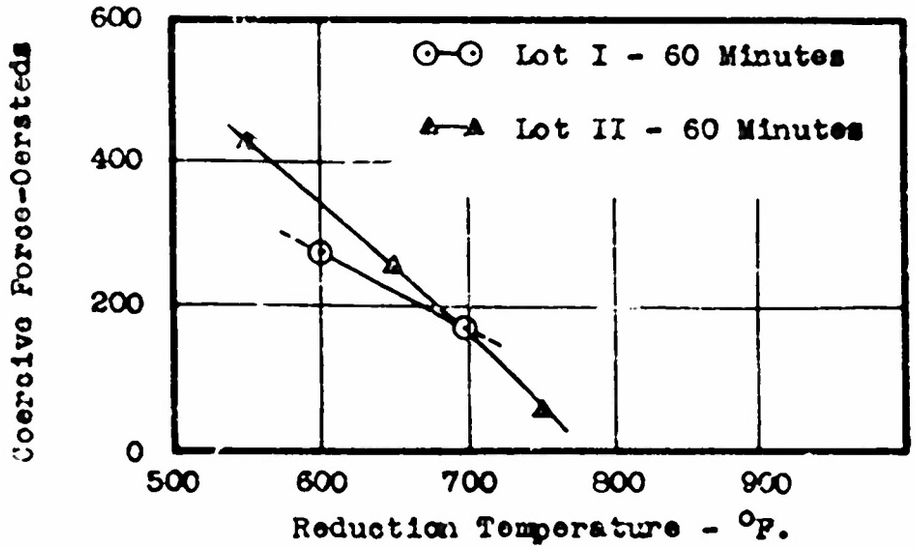

Fig. 15-a. Coercive Force of Iron Powder Compacts Pressed at 60 t.s.i., from Powders Reduced from Ferrous Formates (Lots I and II) at Various Temperatures for 60 Minutes.

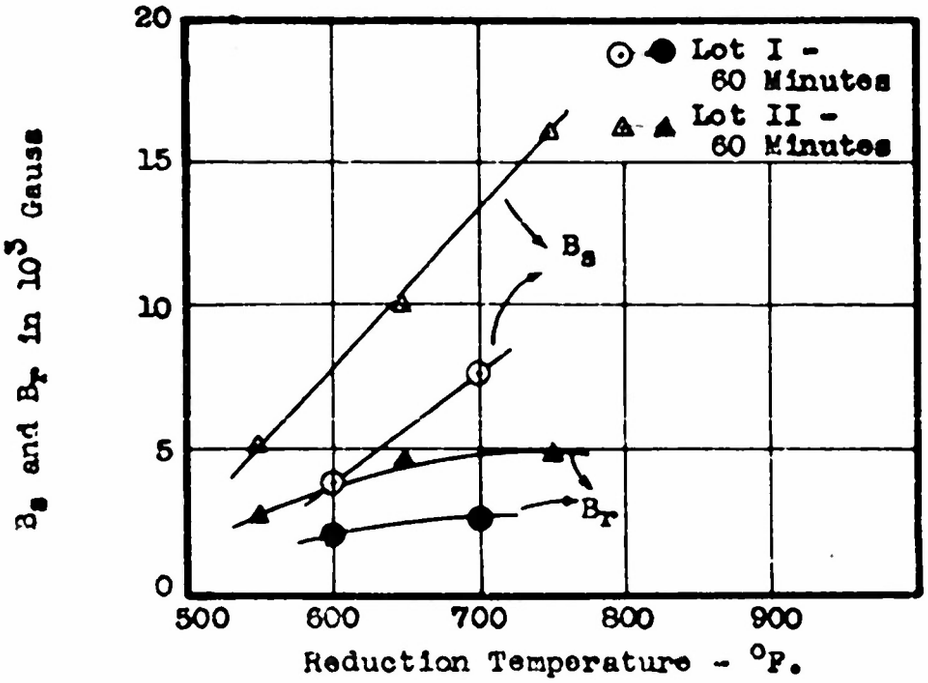

Fig. 15-b. Intrinsic Induction at H = 4000 (B_s) and Remanence (B_r) of Iron Powder Compacts Pressed at 60 t.s.i., from Powders Reduced from Ferrous Formates (Lots I and II) at Various Temperatures for 60 Minutes.

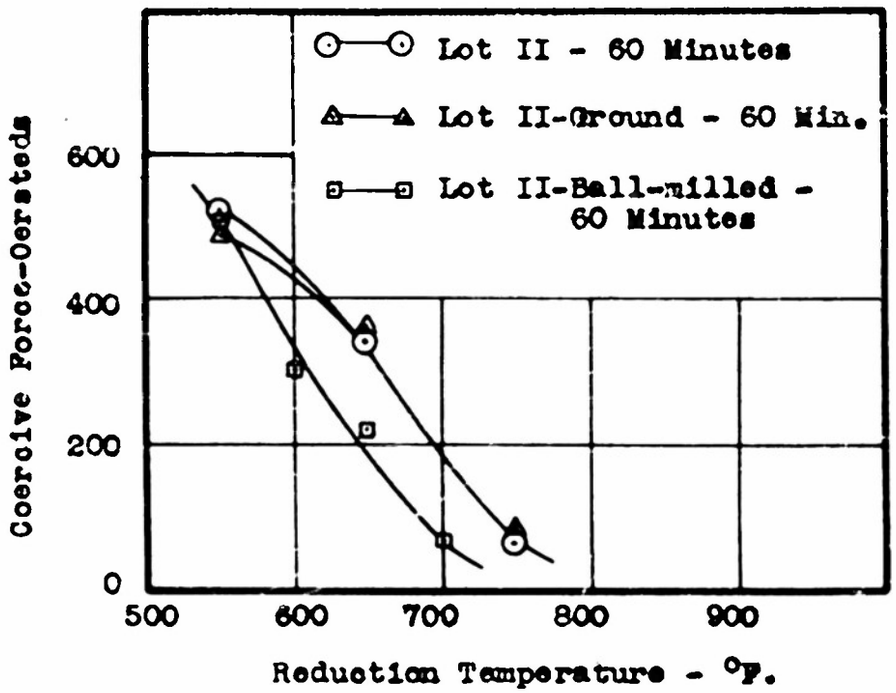

Fig. 16. Coercive Force Versus Temperature of Reduction of Iron Powders Obtained from Lot II Ferrous Formates of Various Sizes (Reduction Time - 60 Minutes).

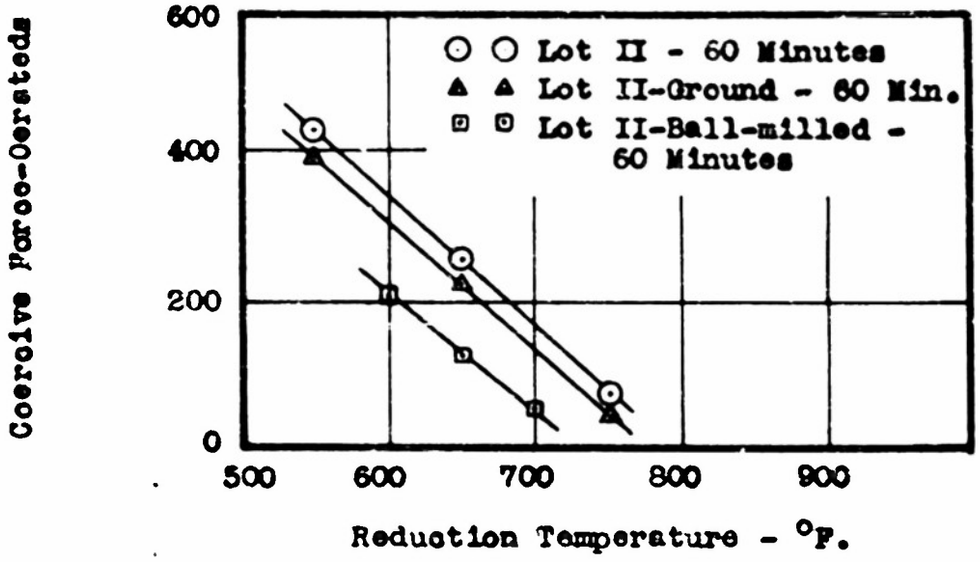

Fig. 17-a. Coercive Force of Iron Powder Compacts Pressed at 60 t.s.i., from Powders Reduced at Different Temperatures for 60 Minutes, from Lot II Ferrous Formates of Various Sizes.

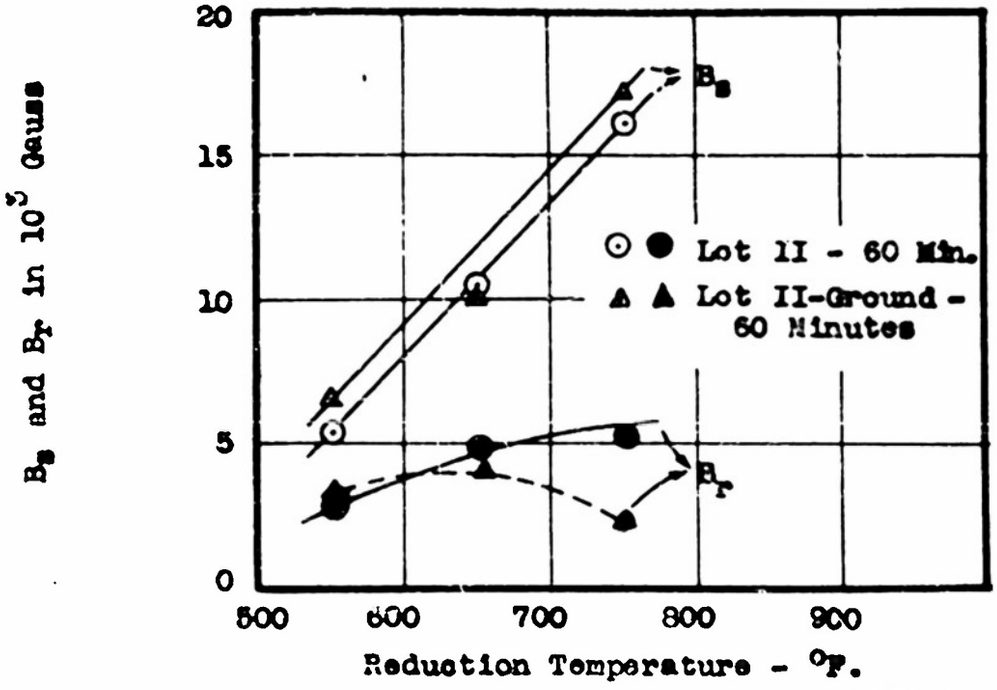

Fig. 17-b. Intrinsic Induction at H = 4000 (B_s) and Remanence (B_r) of Iron Powder Compacts Pressed at 60 t.s.i., from Powders Reduced from Lot II Ferrous Formates of Various Sizes at Temperatures and for Times Indicated.

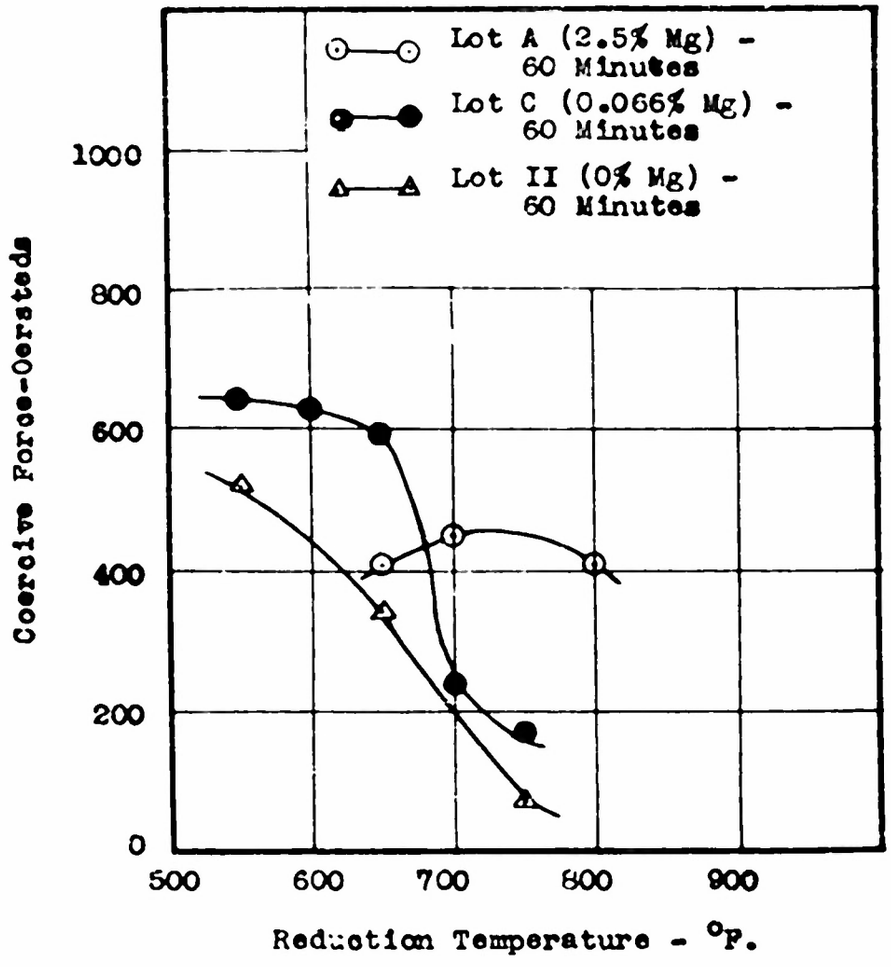

Fig. 18. Influence of Magnesium Content on the Coercive Force of Iron Powders Obtained by Reduction of Mixtures of Ferrous and Magnesium Formates at Various Temperatures for 60 Minutes.

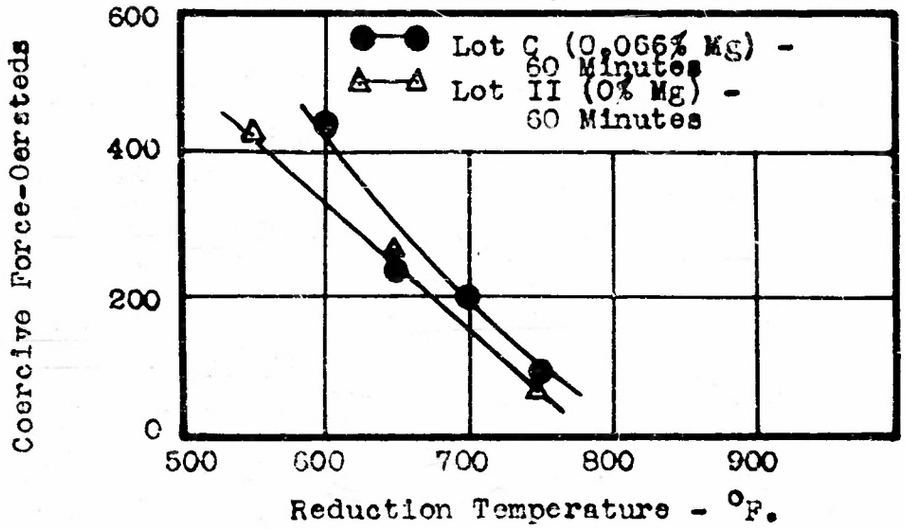

Fig. 19-a. Influence of Magnesium Content on the Coercive Force of Iron Powder Compacts Pressed at 60 t.s.i., from Powders Reduced from the Formates at Various Temperatures for 60 Min.

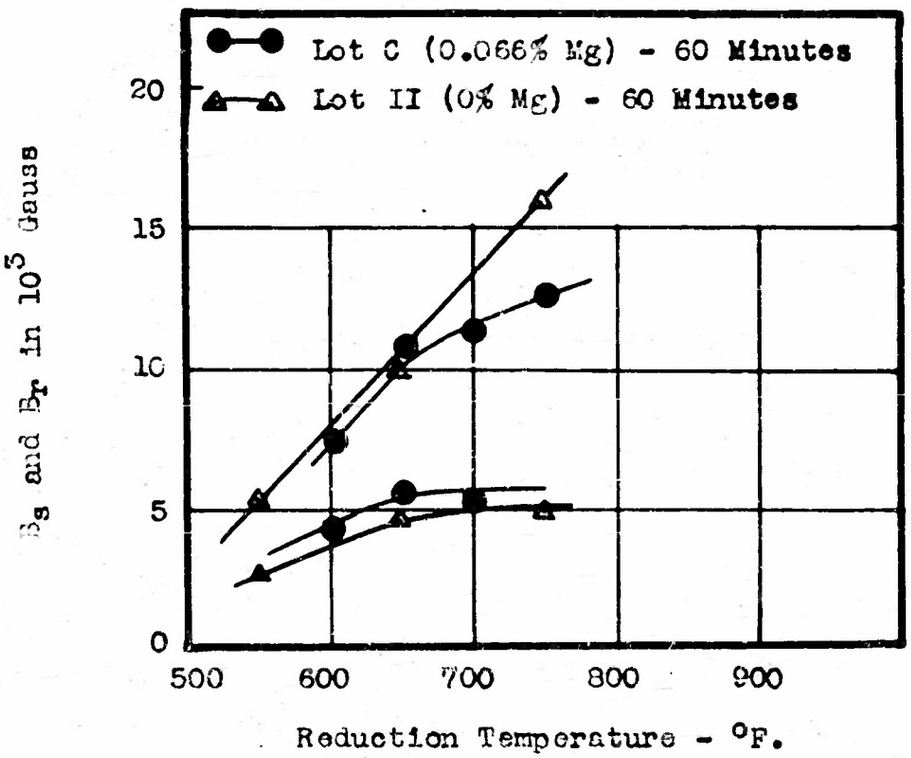

Fig. 19-b. Influence of Magnesium Content on the Intrinsic Induction at H = 4000 (B_s) and Remanence (B_r) of Iron Powder Compacts Pressed at 60 t.s.i., from Powders Reduced from the Formates at Various Temperatures for 60 Min.

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