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Interim Report
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PERMANENT MAGNET MATERIALS

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ABSTRACT

Comparison of the diameters of iron oxide crystallites before reduction with those of the iron particles produced at reduction temperatures less than about 200°C indicates that each oxide crystallite produces one iron particle. At higher temperatures, sintering of the iron particles occurs. These results suggest that for low-temperature reduction, nucleation of the new phase may be much slower than growth.

1. INTRODUCTION

The recent development of single-domain ferromagnetic particles [1,2,3,4,5,6] has focussed attention upon the low-temperature reduction of metal oxides to produce metallic particles. Theoretical work [7,8] has indicated that control over particle shape would be desirable in order to produce prolate particles. However, in the results available in the literature [3,6,9,10,11,12,13] on work on this type of reaction, there appears no study of the essential factors controlling the geometry of the final metal particles. It is well known that finer particles are produced at lower reduction temperatures, but the question of the relation between the geometric properties of the initial oxide and of the final metal remains unexplored. This report presents the results of a study of the particle and crystallite sizes of some iron oxides and of the iron particles produced by reduction of these oxides at temperatures between 125 and 450°C

2. EXPERIMENTAL

Most of the oxides used were formed by thermal decomposition of ferrous formate:

$$Fe\ (COOH)_2 \cdot 2H_2O \longrightarrow Fe\ (COOH)_2 + 2H_2O$$

$$Fe\ (COOH)_2 \longrightarrow FeO + 2CO + H_2O.$$

This reaction is not so clean as these simple equations would indicate. There are several side reactions, which produce CH_4 [14], solid carbon [6], various carbon oxides [3,14], and variable amounts of ferric ion. Further, the oxide formed is not simple, but apparently is a mixture of Fe_3O_4 and metallic Fe (cf. Report F-2236, dated 31 December 1953, from this project). However, the crystallite size of the Fe_3O_4 phase above may be determined from x-ray line broadening, and compared to the iron crystallite sizes in the final powder, without interference from the impurities. The presence of the free iron in the initial oxide should be only slightly disturbing, since the precision of the measurements is inherently low.

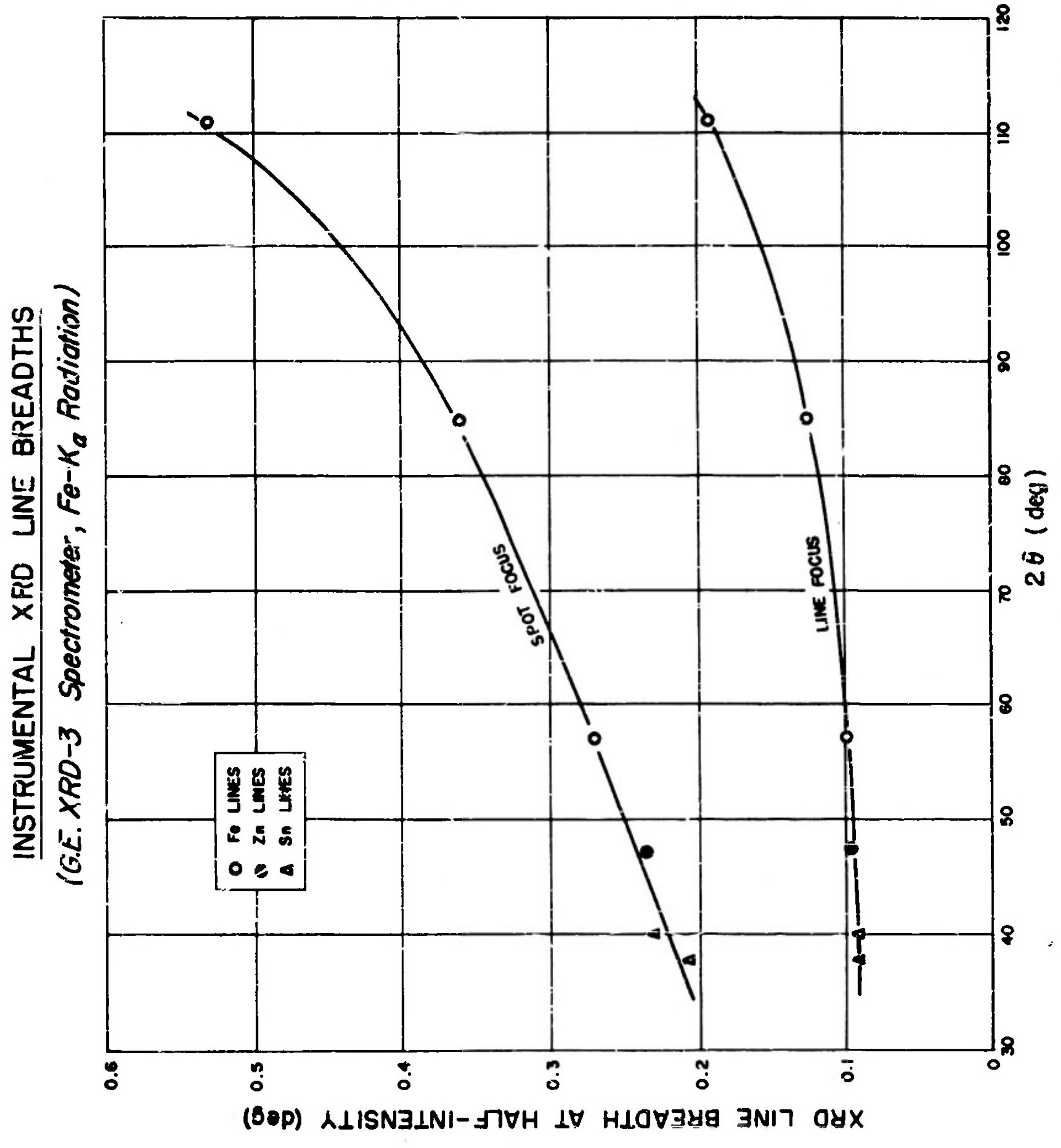
Several other oxides were used as well. These were a sample of Fe_3O_4 with acicular particles approximately 0.5 μ x 3 μ, γ -Fe_2O_3 with approximately the same particle dimensions, and α -Fe_2O_3 with a diameter of roughly 3 μ.

Reduction of these oxides at temperatures from 125 to 440°C was performed using the CaH_2 technique described previously (P-2236-10, 30 June 1953). At the lower temperatures, several days were required for appreciable degrees of reduction.

Crystallite sizes were determined by an approximate method using the broadening of x-ray diffraction lines. The experimental data was for the most part taken with a G. E. XRD-3 spectrometer, with Fe-K_α radiation. The observed line breadth was corrected for $\alpha_1 - \alpha_2$ broadening using Jones' [15] method, and for instrumental broadening using Warren's [16] approximation. The instrumental broadening was determined using well-annealed Armco iron, polished and etched, and polished and etched Zn and Sn. The line breadths observed with these specimens are shown as a function of 2 θ in Figure 2-1 for both line and spot focus tubes. These data fall on smooth curves. For intermediate values of 2θ, the appropriate line breadth was obtained by interpolation from these curves.

This approximate method of obtaining crystallite sizes is not highly accurate.[17] However, where particle size and shape distributions are expected to remain approximately constant, it should afford a reliable comparison between the products and reactants of such a reaction as the reduction of the oxides studied here.

Rough comparison with electron microscope sizes indicated that for the FeO and Fe particles involved the particle and crystallite sizes were roughly the same. This was not true for the three extra oxides, the Fe_3O_4, γ-Fe_2O_3, and α -Fe_2O_3 specimens. For them, the crystallites were considerably smaller than the particles. Each particle contained



INSTRUMENTAL XRD LINE BREADTHS

(G.E. XRD-3 Spectrometer, Fe-K_α Radiation)

FIGURE 2-1

on the order of 5000 crystallites.

The degree of reduction of a given powder was usally determined by measuring the volume of H_2 released when a sample of the product was dissolved in dilute acid. It had previously been shown (Report P-2236-10, 30 June 1953) that the degree of reduction determined in this way agrees well with that expected from the amount of H_2 produced during the CaH_2 reduction. Both measurements give lower limiting values.

Pressed bars were prepared of most of the powders produced, and their magnetic properties determined in the Sanford-Bennett[18] permeameter. The coercive forces reported here have been "corrected" to infinite dilution according to the equation

$$_{\infty}H_c = \frac{_IH_c}{1-v}$$

where $_IH_c$ is the observed value of the intrinsic coercive force, and v is the volume fraction of specimen occupied by powder. This latter was estimated from the saturation magnetization:

$$v = \frac{I_s}{PI_o}$$

where I_s is the observed saturation magnetization, I_o that for pure Fe, 1707 gauss/cm^3, and P the degree of reduction. This correction procedure very crudely allows for differences in pressing in intercomparing coercive forces.

3. RESULTS

In Table 3-1 are listed the data for reduction of the various FeO specimens. T_1 is the temperature for thermal decomposition of the ferrous formate to produce the FeO, and d_1 is the resulting FeO crystallite (and particle) diameter. T_2 is the temperature of reduction, and d_2 the resulting Fe crystallite (and particle) diameter. P is the degree of reduction, expressed as the weight % of free metal present. $_{\infty}H_c$ is the coercive force of the iron powder compact, "corrected" to infinite dilution as described above.

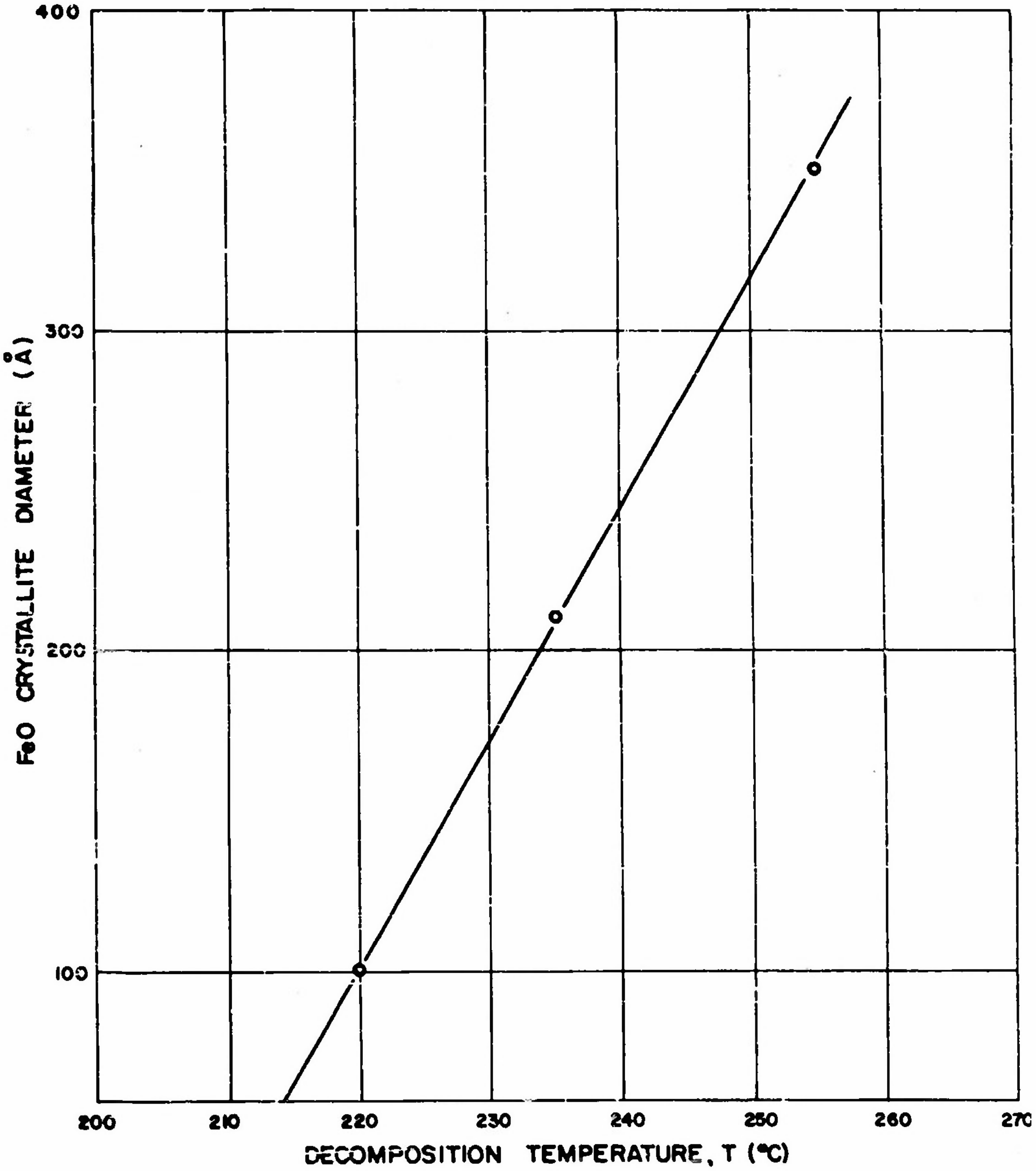
Table 3-1

Reduction of FeO Powders

Substance	T_1	d_1	T_2	d_2	P	∞H_c
FeO-1	255°C	350 Å	400°C	536 Å	0.95	133 Oe
			300	382	.75	407
			220	275	.82	701
			205	250	.92	641
			150	250	.91	640
FeO-2	235	210	350±10	300	.80	855
			285	255	.70	662
			285	260	.68	885
			260	230	.72	975
			220	195	.80	970
			200	174	.60	1030
			185	165	.68	1080
			150	170	.85	---
FeO-3	220	100	450	440	.72	255
			300	265	.86	770
			200	145	.62	846
			150	130	.70	---
			125	95	.68	---

In Figure 3-1, the crystallite (particle) diameter of the FeO is plotted as a function of the temperature at which the ferrous formate was decomposed. Figure 3-2 contains the iron crystallite (particle) diameter as a function of the temperature of reduction of the FeO. The data for each FeO size are plotted separately. The dotted lines leading in from the left show the expected iron crystallite (particle) diameters if each FeO crystallite produced one iron crystallite. Figure 3-3 shows the coercive forces plotted against the iron crystallite diameters. The solid lines were taken from the thesis of Bertaut[3] for loose powders.

CRYSTALLITE DIAMETERS OF FeO PRODUCED BY THERMAL DECOMPOSITION OF FERROUS FORMATE



FIGURE

EFFECT OF REDUCTION TEMPERATURE ON DIAMETER OF IRON PARTICLES

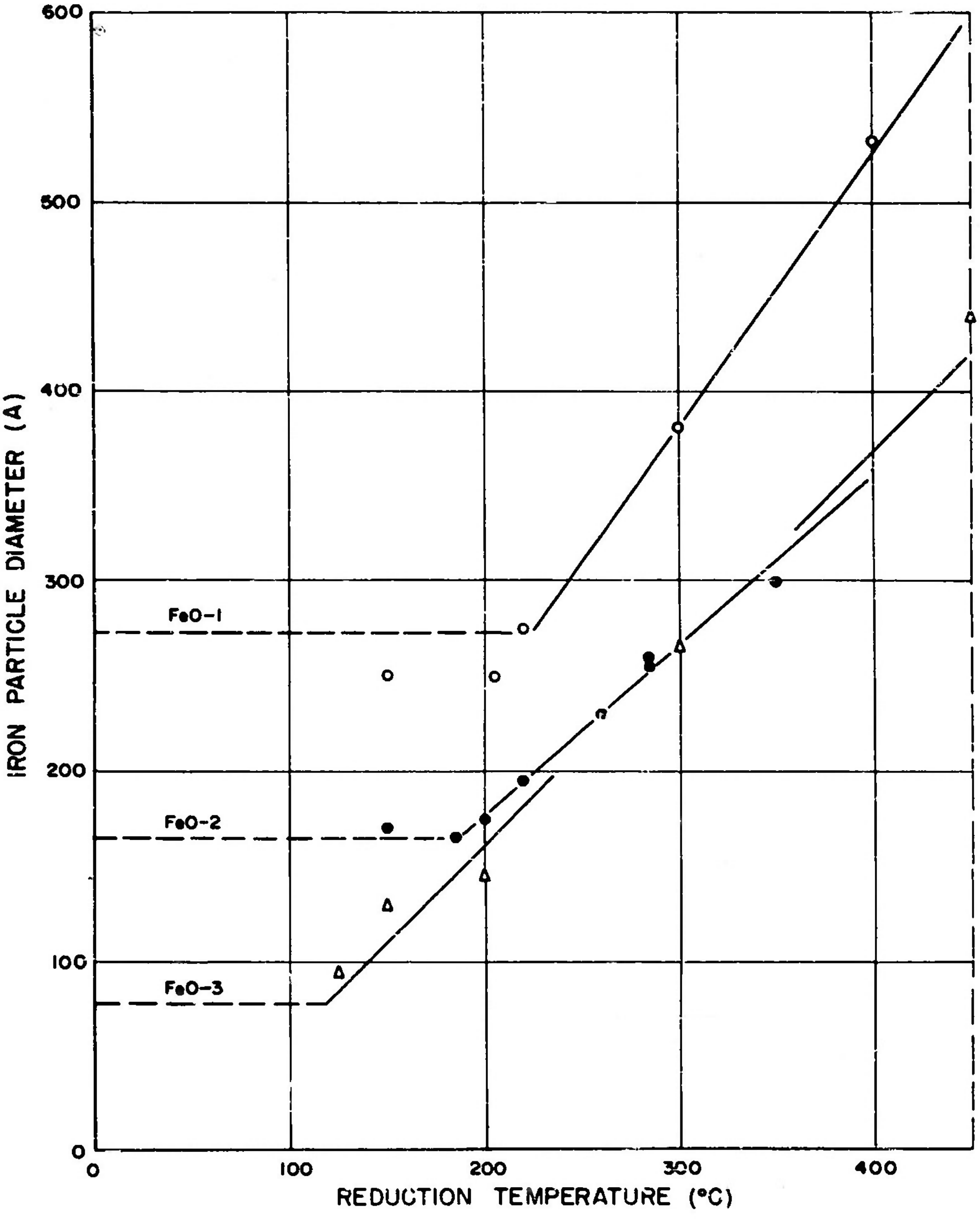


FIGURE 3-2

VARIATION OF "INFINITE-DILUTION" COERCIVE FORCE OF FINE IRON POWDERS WITH PARTICLE SIZE

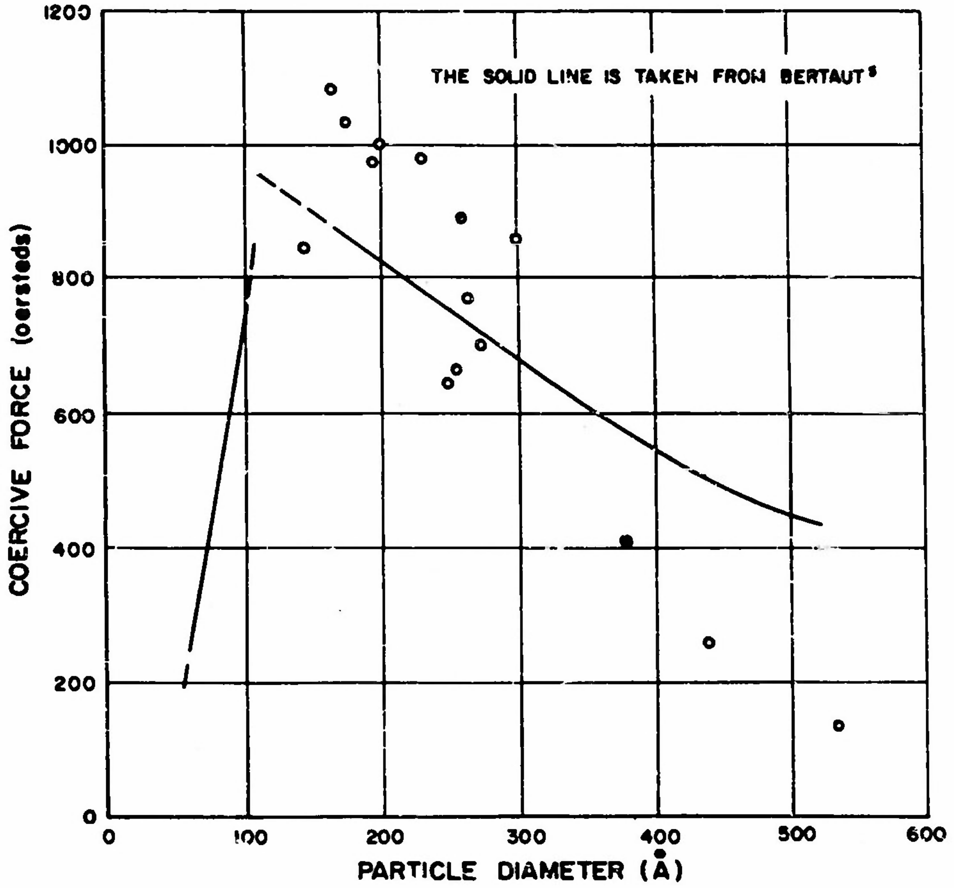


FIGURE 3-3

4. DISCUSSION

As Figure 3-1 shows, the crystallite size of the FeO, formed by thermal decomposition of ferrous formate, was very sensitive to the decomposition temperature. The nature of the ferrous formate (crystallite size, etc.) seemed to have little influence on the FeO produced. This is the sort of behavior to be expected when nucleation of the new phase is quite rapid, so that the density of nuclei formed is independent of the size of the parent crystal.

Quite a different situation is observed for the reduction of the FeO. Here the diameters of the iron crystallites formed are all about equal to or larger than what would be expected if each FeO crystallite produced one iron crystallite. In this case the rate of nucleation is very low compared to the rate of growth. Once a nucleus is formed in an FeO crystallite, rapid growth uses up the entire crystallite before a second nucleus can form. If the temperature be too high, sintering occurs, and the iron particles contain more iron, on the average, than in one average FeO crystallite.

This picture explains why the curves in Figure 3-2 level off at a low temperature, the level value coinciding with the expected value. In the case of FeO-3, the level portion was approached but not quite reached. The break in each curve, above which the crystallite (and particle) diameter increases rapidly with reduction temperature, marks the onset of sintering.

That oxide crystallite, rather than particle, diameter is important is shown in Table 4-1. Here reduction data at temperatures low enough to avoid sintering are shown for all the oxides. d_1 is the oxide crystallite diameter, and d_2 (obs) is that observed for the iron.

COURSE OF REDUCTION REACTION

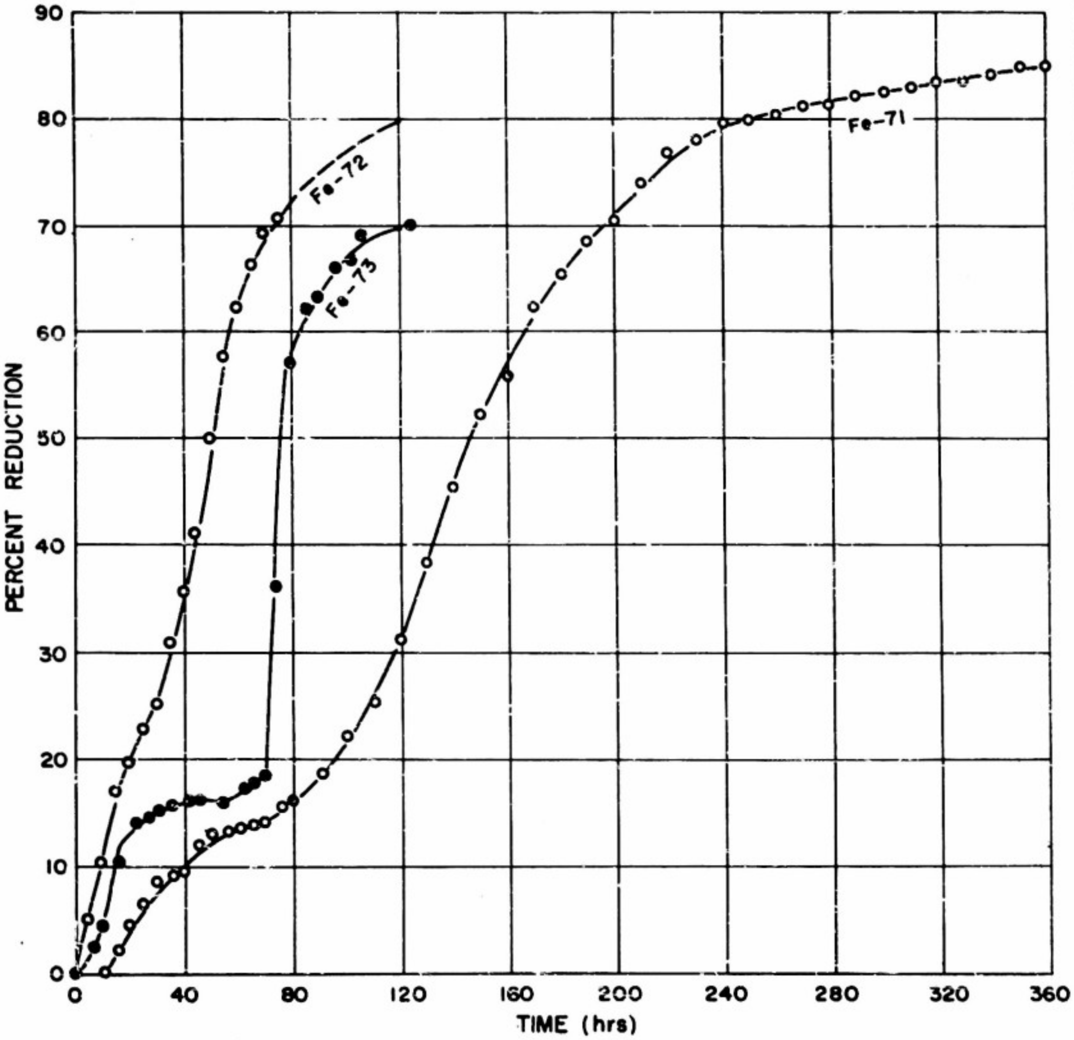


FIGURE 4-1

Table 4-1

Reduction of Various Iron Oxides

Substance	d_1	d_2(obs.)	d_2(calc.)	Oxide Density
FeO-1	350 Å	250 Å	273	4.8 g/cm^3
FeO-2	210	165	164	"
FeO-3	100	95	78	"
Fe_3O_4	280	200	221	5.2
γ-Fe_2O_3	356	275	264	4.6
α-Fe_2O_3	430	330	331	5.2

d_2 (calc.) is the expected value based on the assumption that each oxide crystallite produces one iron crystallite without change of shape. In these calculations, the density of iron was taken at 7.9 g/cm^3. The densities for the oxides are listed in Table 4-1, column 5.

Even with the large, polycrystalline iron oxide particles, a good correspondence exists between oxide and iron crystallite sizes.

The picture of slow nucleation followed by rapid growth is borne out by kinetic data for this system. Figure 4-1 shows the extent of reduction as a function of time for three typical runs. (This figure is reproduced from Report P-2236-10) A long induction period is followed by a sudden period of rapid reaction, and then a long "tail". At somewhat higher temperatures (350 to 600°C). Tatievskaya[19] et el also found the rate of reaction to be a maximum part way through the reaction. The induction period apparently corresponds to the slow formation of nuclei, and the period of rapid reaction to the rapid growth of the new phase.

This result of a one-to-one relationship between oxide crystallite and iron crystallite (particle) may be important for efforts to control the shape of the iron particles. At sufficiently low temperatures, where sintering does not take place, it would seem reasonable that acicular iron oxide crystallites should give rise to acicular iron particles. It is planned in this Laboratory to study the possibility of producing such oxide crystallites, and the reduction process involved with them.

Sintering of these iron particles apparently occurs at remarkably low temperatures. For the finest particles, the break in the curve in Figure 3-1 will occur near 100°C. This temperature is much lower than those observed by Ananthanarayanan and Libsch[10]. For a compact of particles with diameters near 200 to 250 Å, they found the coercive force to decrease suddenly on baking at temperatures above about 540°C. Since the coercive force is a measure of particle size, this would seem to be a valid measure of sintering. They pointed out that their powder contained some 2% SiO_2 in the original oxide, and that this could retard sintering. On the other hand, Wheeler[20] has reported sintering in evaporated iron and nickel films at temperatures below 100°C.

The coercive force-particle size curve in Figure 3-3 is qualitatively similar to the curve given by Bertaut.[3] The one given here appears to be steeper, but this must be influenced by the sample preparation method and by the correction to infinite dilution.

5. CONCLUSION

These reduction studies have given the following definite conclusions regarding the low temperature reduction of Fe_3O_4, γ-Fe_2O_3, and α-Fe_2O_3:

1. Each oxide crystallite produces one primary iron crystallite (particle).
2. Sintering among the iron particles begins at temperatures as low as 200°C, the exact temperature depending upon the particle size.
3. The one-to-one relationship between oxide and iron crystallites indicates that nucleation of the new phase is much slower

than growth. This is borne out by the data on the kinetics of the reaction.

4. For the thermal decomposition of the ferrous formate, the situation is different. Each formate crystallite produces many (thousands of) FeO crystallites (particles). The FeO size is determined primarily by the temperature of thermal decomposition, and not influenced strongly, if at all, by the size of the formate crystallites. Apparently nucleation is rapid in this reaction.
5. The coercive force of these fine iron particles behaves with decreasing particle size in the same fashion as has already been given by Bertaut.[3]

Alan Franklin Alan D. Franklin

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