

of heteropolar bonding than ZrO_2 , thus agreeing with our theory. I assume that this will be the case.

I agree with the interpretation of the various observations on the "region of transformation," and I am of the opinion that one can say something positive about inversion of zirconia only if particle size and degree of disorder are determined exactly.

Comments of Pol Duwez*

The authors should be congratulated for an interesting study of the complex subject of stabilization of zirconia. I agree completely with the conclusions presented in the paper. I would like to add, however, that if the compositions in the ternary system

Zr-Ti-O could be melted without contamination from crucible or atmosphere, many of the apparently contradictory results obtained on sintered specimens could be clarified.

I am glad to see that the stability of calcia-stabilized zirconia and the instability of magnesia-stabilized zirconia have been confirmed. The existence of the compound ZrTiO_4 also has been confirmed. The fact that this compound decomposes when heated in vacuum at 1180°C . means that under these conditions some of the oxygen is probably lost and the composition is not ZrTiO_4 any more.

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Phase Equilibrium Studies in the System Iron Oxide- Al_2O_3 in Air and at 1 Atm. O_2 Pressure

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Phase equilibrium data, obtained by using the quenching technique, are presented for the system iron oxide- Al_2O_3 in air and at 1 atm. O_2 pressure in the temperature interval 1085° to 1725°C . Stability ranges of the various phases are delineated, and approximate compositions of crystalline and liquid phases are determined. Special attention is focused on the phase Fe_2O_3 - Al_2O_3 (ss) and its stability relationships.

I. Introduction

THE study at high temperatures of phase equilibria in oxide systems is a profitable approach to an understanding of the performance of refractories in the many industrial operations where they are used. In a program of research sponsored by the American Iron and Steel Institute,* quaternary oxide systems are being studied which are particularly pertinent to problems of steel-plant refractories. In a recent review of this research,¹ seven quaternary systems which are being investigated are discussed. They are all parts of the very complicated seven-component system $\text{CaO-MgO-FeO-Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$. The work reported in this paper is

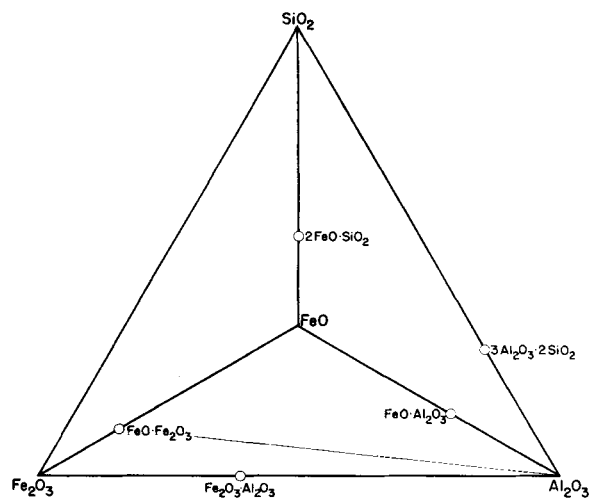


Fig. 1. Diagram representing the system $\text{FeO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ as an equilateral tetrahedron with one component at each apex. Compounds, with compositions given in terms of the oxide components, are plotted in weight per cent.

a part of this research program. It is one unit in the study of the system $\text{FeO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$.

In Fig. 1 this quaternary† system is portrayed as a regular tetrahedron. The left face of the tetrahedron is the system $\text{FeO-Fe}_2\text{O}_3\text{-SiO}_2$, for which a considerable amount of data has

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* This research program was initiated in the College of Mineral Industries, The Pennsylvania State University, October 1, 1949, upon recommendation of the Research Subcommittee of the Refractories Committee, American Iron and Steel Institute.

¹ E. F. Osborn, "Phase Equilibrium Studies of Steel Plant Refractories Systems"; pp. 145-77 of "Regional Technical Meetings," New York, 1954, American Iron and Steel Institute.

† The system $\text{FeO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ is part of the quaternary system Fe-Al-Si-O but is not in itself a completely quaternary system because metallic iron appears as a phase in certain composition-temperature ranges. However, quaternary relations obtain throughout most of the tetrahedron representing the system; hence for most purposes $\text{FeO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ may be considered quaternary.

been obtained.² Diagrams depicting high-temperature phase relations are available for the right face, the system $\text{FeO}-\text{Al}_2\text{O}_3-\text{SiO}_2$.³ Virtually no data have been published for the front face, where very high oxygen pressures obtain at liquidus temperatures. Little was previously known about the basal triangle, the system $\text{FeO}-\text{Fe}_2\text{O}_3-\text{Al}_2\text{O}_3$. This system has been studied in order to supply this missing information on phase relations among three of the most common of the oxides, and as a practical way of starting on the quaternary system $\text{FeO}-\text{Fe}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2$.

The system $\text{FeO}-\text{Fe}_2\text{O}_3-\text{Al}_2\text{O}_3$ is not entirely ternary because metallic iron appears as a phase in certain composition-temperature ranges. For present purposes, however, this can be ignored and the system treated as ternary. Because two of the components are oxides of the same element, this system differs fundamentally from the ordinary condensed ternary systems familiar to the ceramist. The gas phase must be considered in the present case. A certain partial pressure of O_2 of the gas phase, in equilibrium with the condensed phase, corresponds to each point within the triangle, at a certain temperature. Under strongly reducing conditions the compositions fall close to the join $\text{FeO}-\text{Al}_2\text{O}_3$. As the O_2 pressure is increased, the composition of the condensed phases changes in a manner which can roughly be described as a rotation of a straight line through the Al_2O_3 corner of the triangle, from the $\text{FeO}-\text{Al}_2\text{O}_3$ join toward the $\text{Fe}_2\text{O}_3-\text{Al}_2\text{O}_3$ join. The work of the present authors was accomplished at two different chosen atmospheric conditions of constant O_2 pressures, namely air (corresponding to 0.21 atm. O_2) and 1 atm. O_2 . Under these conditions the compositions of melts at liquidus temperatures fall approximately in the region indicated by the join $\text{FeO}-\text{Fe}_2\text{O}_3-\text{Al}_2\text{O}_3$ in Fig. 1. However, because the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio of the condensed phases is a complex function of O_2 pressure, temperature, and composition of the melt, the mixtures will not be located along straight lines across the triangle, but rather along irregularly curved lines. The phase relationships under these experimental conditions therefore should be discussed in terms of the ternary system rather than binary joins.

II. Previous Work

Although no complete phase diagram has been presented for the system iron oxide- Al_2O_3 in air, certain parts of the system have attracted the curiosity of various investigators. The fact that no complete series of solid solution exists between hematite (Fe_2O_3) and corundum (Al_2O_3) has been known for 25 years, but there is little quantitative agreement among reported data. Passerini⁴ reported the limits of solubility to be approximately 25 weight % Al_2O_3 in Fe_2O_3 and 20 weight % Fe_2O_3 in Al_2O_3 at 600°C., whereas Hansen and Brownmiller⁵ found 10 to 15 weight % Al_2O_3 in Fe_2O_3 and "very little" Fe_2O_3 in Al_2O_3 at 1200°C. The most extensive work

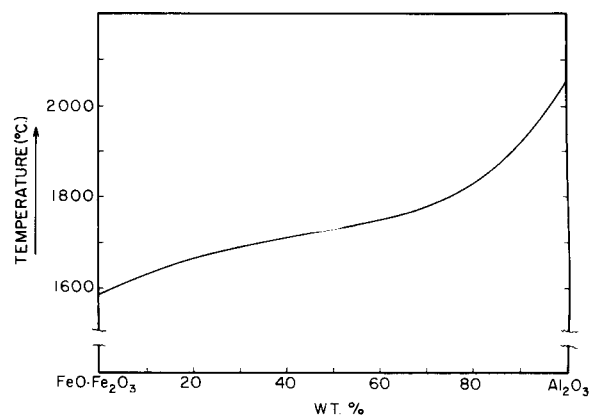


Fig. 2. Diagram illustrating "fusion temperatures" of iron oxide- Al_2O_3 mixtures in air, as reported by von Wartenberg and Reusch (footnote 9).

on phase equilibria in the system iron oxide- Al_2O_3 in air was carried out by Richards and White.⁶ These authors, although primarily interested in the sesquioxide-spinel* equilibrium, also gave figures, as follows, for the solid solubilities between Fe_2O_3 and Al_2O_3 : 16.5 weight % Al_2O_3 in Fe_2O_3 , 17.2 weight % Fe_2O_3 in Al_2O_3 at 1300° to 1370°C.

In their study of the decomposition of sesquioxides to spinels, Richards and White obtained results for the pure iron oxide end member which are in fair agreement with other data reported in the literature.⁷ Furthermore, Richards and White found that the decomposition temperature decreases slightly with the addition of Al_2O_3 , reaching a minimum of approximately 1370°C. at 20.0 weight % Al_2O_3 . Preliminary work carried out by the present authors confirmed the limited solubility between Fe_2O_3 and Al_2O_3 , in qualitative agreement with previous investigators, and in addition produced evidence for the existence of an intermediate phase $\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ (ss) between the two end members, not reported in previous literature. As this work neared completion, the authors learned that Richardson, Ball, and Rigby⁸ have identified this compound as one of the reaction products resulting from the attack of ferric oxide on aluminosilicate refractories.

Data for the system iron oxide- Al_2O_3 in air at liquidus temperatures were reported by von Wartenberg and Reusch.⁹ These authors presented a curve representing the "fusion temperatures" of iron oxide- Al_2O_3 mixtures as reproduced in Fig. 2.

⁵ W. C. Hansen and L. T. Brownmiller, "Equilibrium Studies on Alumina and Ferric Oxide, and on Combinations of These with Magnesia and Calcium Oxide," *Am. J. Sci.*, [5th Series], **15**, 225-42 (1928); *Ceram. Abstr.*, **7** [5] 320 (1928).

⁶ R. G. Richards and J. White, "Phase Relations of Iron Oxide-Containing Spinels: I, Relations in the System Fe-Al-O," *Trans. Brit. Ceram. Soc.*, **53**, 233-70 (1954).

* The term "spinel" is used here and subsequently to designate crystals with spinel structure. These crystals are members of the solid solution series between hercynite ($\text{FeO} \cdot \text{Al}_2\text{O}_3$) and magnetite ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$).

⁷ (a) J. W. Greig, E. Posnjak, H. E. Merwin, and R. B. Sosman, "Equilibrium Relationships of Fe_2O_3 , Fe_3O_4 , and Oxygen," *Am. J. Sci.*, [5th Series], **30**, 239-316 (1935); *Ceram. Abstr.*, **15** [2] 74 (1936).

(b) L. S. Darken and R. W. Gurry, "The System Iron-Oxygen: I, The Wüstite Field and Related Equilibria," *J. Am. Chem. Soc.*, **67**, 1398-1412 (1945).

⁸ H. M. Richardson, F. Ball, and G. R. Rigby, "Minerals Identified During Research on Refractories," *Trans. Intern. Ceram. Congr.* (Les Actes du congrès céramique international), **3d Congr.**, Paris, 1952 (published 1954); pp. 173-81 (in English).

⁹ H. von Wartenberg and H. J. Reusch, "Schmelz-diagramme Höchstfeuerfester Oxyde, IV" (Melting Diagrams of Highly Refractory Oxides: IV, Aluminum Oxide), *Z. anorg. u. allgem. Chem.*, **207** [1] 1-20 (1932); *Ceram. Abstr.*, **11** [11] 575 (1932).

² (a) R. Schuhmann, Jr., R. G. Powell, and E. J. Michal, "Constitution of the $\text{FeO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$ System at Slagmaking Temperatures," *J. Metals*, **5**, September 1953; *Trans. Am. Inst. Mining Met. Engrs.*, **197**, 1097-1104 (1953).

(b) Arnulf Muan, "Phase Equilibria in the System $\text{FeO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$," *J. Metals*, **7**, September 1955; *Trans. Am. Inst. Mining Met. Engrs.*, **203**, 965-76 (1955).

³ R. Hay, James White, and T. H. Caulfield, "The Ternary System $\text{FeO}-\text{Al}_2\text{O}_3-\text{SiO}_2$," *J. Soc. Glass Technol.*, **21** [85] 270-80T (1937); *Ceram. Abstr.*, **17** [9] 317 (1938).

(b) R. B. Snow and W. J. McCaughey, "Equilibrium Studies in the System $\text{FeO}-\text{Al}_2\text{O}_3-\text{SiO}_2$," *J. Am. Ceram. Soc.*, **25** [6] 151-60 (March 15, 1942).

(c) J. F. Schairer and Kenzo Yagi, "The System $\text{FeO}-\text{Al}_2\text{O}_3-\text{SiO}_2$," *Am. J. Sci.*, Bowen Volume, Part 2, 471-512 (1952).

⁴ L. Passerini, "Soluzioni solide isomorfismo e semimorfismo tra gli ossidi dei metalli trivalenti; sistemi $\text{Al}_2\text{O}_3-\text{Cr}_2\text{O}_3$, $\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3$, $\text{Cr}_2\text{O}_3-\text{Fe}_2\text{O}_3$ " (Solid Solutions, Isomorphism, and Symorphism Among Oxides of Trivalent Metals; The Systems $\text{Al}_2\text{O}_3-\text{Cr}_2\text{O}_3$, $\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3$, and $\text{Cr}_2\text{O}_3-\text{Fe}_2\text{O}_3$), *Gazz. chim. ital.*, **60**, 544-58 (1930).

III. Experimental Method

(1) General Procedure

Phase equilibria were determined by the quenching technique.* Weighed mixtures of chosen starting materials were held in platinum envelopes at constant temperature until equilibrium was reached among crystalline, liquid, and gas phases. The sample was then quenched to room temperature; the phases present were identified by X-ray and microscopic methods, and for the most significant runs composition was determined by chemical analysis.

(2) Materials

Many different starting materials were used; in all cases they were chemicals of the highest purity commercially available.

Ignited oxides (Fe_2O_3 heated at 400°C . for 24 hours, Al_2O_3 at 1300°C . for 24 hours) were used in a few cases, but because of the sluggishness of reactions among these oxides, they proved to be poor starting materials. In the case of mixtures with relatively low Al_2O_3 contents (less than 30 weight %) the oxide mixtures could be successfully melted in a gas-air combustion furnace at 1650°C . Platinum crucibles containing the mixtures were essentially saturated with iron under the conditions prevailing in the furnace so that loss of iron to the platinum of the crucible could be kept at a minimum. Although this liquid was very fluid and gave rise to dendritic crystals formed during quenching, it was still a favorable starting material. The mixtures used for the determination of liquidus and solidus temperatures (quenched liquids as well as ignited oxides) were held at a temperature slightly below solidus at least 24 hours. It is essential that this step be followed in order to establish the equilibrium ratio between Fe^{2+} and Fe^{3+} in the crystalline phases before the liquidus and solidus temperature determinations are carried out. The most successful starting materials for runs in the subsolidus region, from the standpoint of reactivity, were coprecipitated nitrate mixtures. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in various proportions were dissolved in water, which was evaporated rapidly. Upon careful drying and ignition of this material, an oxide mixture was obtained yielding only very weak X-ray lines of hematite(ss) and corundum(ss). A few starting mixtures were prepared similarly by pouring the nitrate solution into excess base, giving a coprecipitate of $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$, which was subsequently dried and ignited.

(3) Furnaces

Vertical tube furnaces with windings of platinum or 80% platinum 20% rhodium were used for most of the quenching experiments. Runs at 0.21 atm. O_2 were made in an open furnace with air circulating through; runs at 1 atm. O_2 were made by leading commercial tank oxygen through the furnace from below. Quenching runs at temperatures above 1650°C . were made with a modified Roberts and Morey¹⁰ strip furnace, using strip resistors of a 60% platinum 40% rhodium alloy. Runs were made in air and at 1 atm. O_2 . In the latter case a gastight hood was placed over the strip furnace; the hood was evacuated and then filled with O_2 gas at 1 atm.

(4) Temperature Control and Measurement

Temperatures in the platinum-wound furnace were measured before and after each run with a platinum-platinum-10% rhodium thermocouple frequently calibrated at melting points defined as follows: Au, 1063°C .; $\text{CaMgSi}_2\text{O}_6$, 1391.5°C .; CaSiO_3 , 1544°C . Literature values for temperatures on the Geophysical Laboratory scale are used without correction up to 1550°C ., the upper limit of the original scale. Temperatures above 1550°C . are adjusted to the 1948 International Scale using the correction data tabulated by Corruccini¹¹ and by Sosman.¹² Furnace temperature was controlled by a second thermocouple inserted close to the heating element and connected through compensating lead wires to a Celestray controller. The temperature gradient at the hot spot did not exceed 1°C . over 1 in. at 1450°C . Temperatures on the strip furnace were measured with an optical pyrometer calibrated at melting points defined as follows: CaSiO_3 , 1544°C .; CaO 10% SiO_2 90%, 1708°C .; Pt, 1769°C .

(5) Identification of Phases

The phases present were identified by examination under the microscope, using mostly transmitted light and occasionally reflected light. Identification was further confirmed by X-ray techniques, using Co or Fe radiation with a General Electric XRD-3 diffractometer. Considerable difficulty was encountered in phase determinations in the liquidus temperature region. Because of the high fluidity of iron oxide-rich liquids, dendritic crystals readily formed during quenching, causing microscopic identification to be difficult and X-ray methods to be useless as tools for determining liquidus temperatures. The polishing of sections for examination under reflected light was difficult to carry out for mixtures high in Al_2O_3 because of the extreme hardness of corundum. Approximate solidus temperatures could be determined by observing the sintering temperature of samples previously kept just below the solidus for a period long enough to permit the equilibrium ratio $\text{Fe}^{2+}/\text{Fe}^{3+}$ to be attained in the sample. The liquidus temperatures as determined on the strip furnace are based on the direct observation of the complete flow of the sample. In the present case, the solidus and liquidus curves are relatively close together in the temperature range studied, and the liquidus temperature can be determined fairly accurately.

Determination of the composition of crystalline phases was accomplished by accurate d -spacing measurements and comparison with standards of known composition. The same X-ray unit was used for these measurements as above, but the X-ray diffraction patterns were run at a rate of $1/5^\circ$ 2θ per minute as compared to 2° 2θ per minute for identification purposes.

(6) Method of Chemical Analysis

The total iron content was determined by the Zimmermann-Reinhardt method.[†] The crushed sample was brought into solution by fusion with $\text{K}_2\text{S}_2\text{O}_7$ and subsequent treatment with H_2SO_4 . Fe^{3+} was reduced to Fe^{2+} with SnCl_2 , excess SnCl_2 was precipitated with HgCl_2 , and the solution was titrated with 0.1 N KMnO_4 .

A simple gravimetric method was used to determine divalent iron. The preweighed sample containing an unknown amount of FeO was heated in air at approximately 1200°C . for 48 hours, thereby converting all iron to trivalent iron.

* This technique was originally described by E. S. Shepherd, G. A. Rankin, and F. E. Wright ("Binary Systems of Alumina with Silica, Lime, and Magnesia," *Am. J. Sci.*, [4th Series], **28**, 293-333 (1909)) and has been redescribed in many papers emanating from the Geophysical Laboratory of the Carnegie Institution of Washington and from this laboratory.

¹⁰ H. S. Roberts and G. W. Morey, "Micro-Furnace for Temperatures Above 1000°C ," *Rev. Sci. Instr.*, **1**, 576-79 (1930); *Ceram. Abstr.*, **10** [5] 374 (1931).

¹¹ R. J. Corruccini, "Differences Between the International Scales of 1948 and 1927," *J. Research Natl. Bur. Standards*, **43** [2] 133-36 (1949); RP 2014; *Ceram. Abstr.*, **1950**, May, p. 1066.

¹² R. B. Sosman, "Temperature Scales and Silicate Research," *Am. J. Sci.*, Bowen Volume, Part 2, 517-28 (1952).

[†] This method is described in detail in standard textbooks on quantitative inorganic analysis.

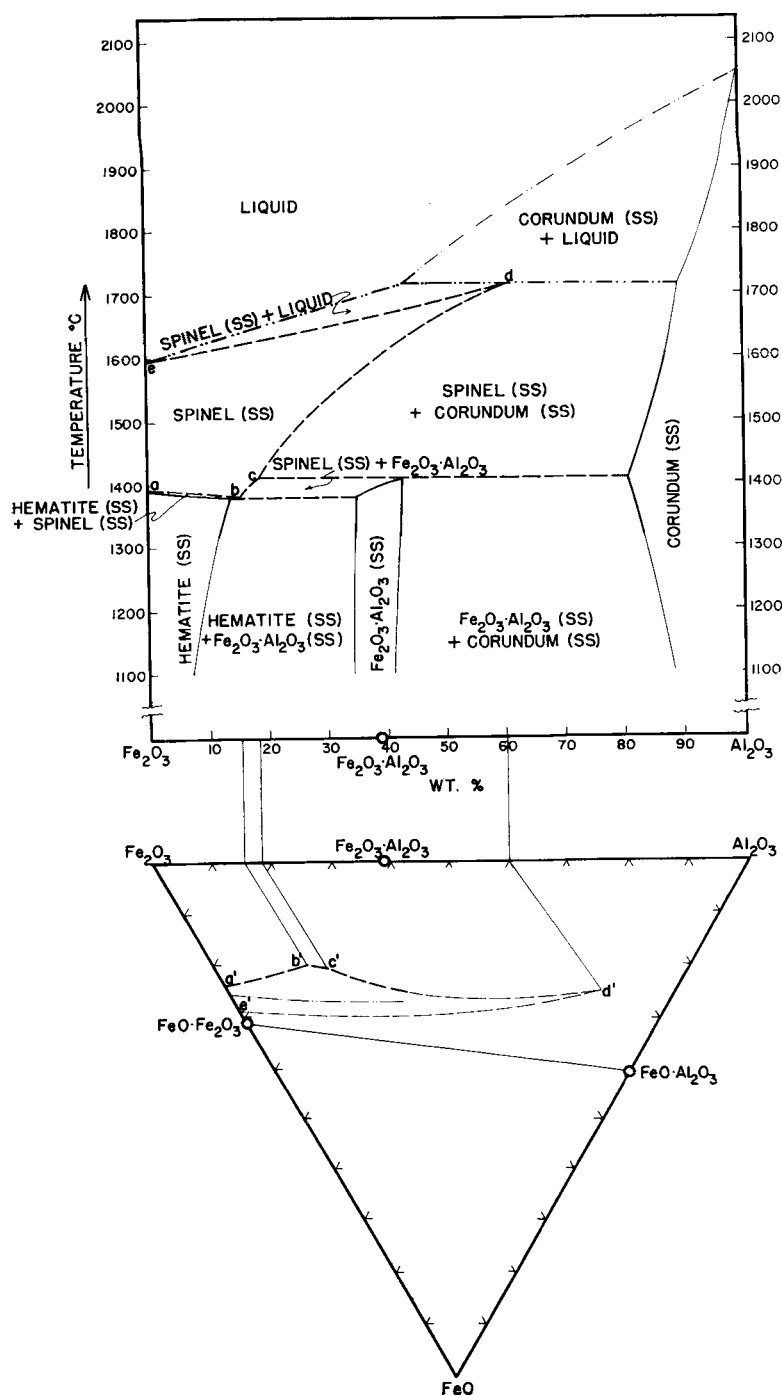


Fig. 3. Diagrams to show phase relationships in the system iron oxide- Al_2O_3 in air. The upper half of the figure is a pseudo-binary plot illustrating the phases present, as labeled on the diagram, as a function of temperature in $^{\circ}\text{C}$. Heavy lines are phase boundaries. These lines are solid where the relations are binary. Dashed lines indicate those portions of the system where spinel is the only condensed phase whose composition is off the join $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$. Dash-dot lines are used where a liquid phase is present. The boundary curves are drawn as light lines in areas where reliable data were not obtained. The lower triangular diagram shows curves representing compositions of phases in equilibrium along boundary curves. Line symbols used are the same as in the upper pseudo-binary diagram. Composition lines are drawn as light lines where no data are available. Light, straight, solid lines between the two diagrams are projection lines connecting corresponding phases in the two diagrams, as described in the text.

¹³ L. S. Darken and R. W. Gurry, "The System Iron-Oxygen: II, Equilibrium and Thermodynamics of Liquid Oxide and Other Phases," *J. Am. Chem. Soc.*, **68** [5] 798-816 (1946); *Ceram. Abstr.*, 1947, February, p. 50g.

Small crucibles made from silica tubing were used as containers for the samples. These crucibles maintained constant weight during the experiment. The amount of FeO present in the initial sample was calculated from the weight increase.

IV. Results

The results of the quenching experiments for the determination of phase boundaries are given in Tables I and II,* for runs in air (= 0.21 atm. O_2) and at 1 atm. O_2 , respectively. On the basis of these data, as well as data available in the literature, phase equilibrium diagrams were constructed as shown in Figs. 3 and 4, for air and 1 atm. O_2 , respectively. Because of complications arising from the change in the oxidation state of iron, and in order to illustrate the relationships as clearly as possible, two different representations are used in each of these figures. In the upper half of each figure the data are presented in a diagram which has the appearance of a binary system, Fe_2O_3 and Al_2O_3 being chosen as components. This portion of the figures shows the phase assemblages, as labeled on the diagram, as a function of temperature, the latter plotted in $^{\circ}\text{C}$. along the vertical axis. Because the system is not binary, the composition of the phases cannot be read from such a diagram. Therefore, supplementary diagrams, showing curves representing compositions of phases in equilibrium along boundary curves, are presented in the lower part of Figs. 3 and 4. To represent the phase relationships in the upper diagram in terms of the two chosen components Fe_2O_3 and Al_2O_3 , a method must be selected for projecting the true compositions in the ternary system $\text{FeO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ upon the binary join $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$. The actual compositions have been projected along straight lines pointing to the O corner of the large triangle representing the system Fe-Al-O , of which $\text{FeO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ is a part. This choice of projection method is not an arbitrary one. In a system of this kind, by reacting with the atmosphere, as the temperature is changed, O_2 is added to, or subtracted from, the condensed phases concomitant to a proportional change in ratio between divalent and trivalent iron. The change in composition caused by such a reaction is described by straight lines through the O corner of the triangle representing the system Fe-Al-O . These are analogous to the iso-silica lines introduced to describe paths of equilibrium crystallization in the system $\text{FeO-Fe}_2\text{O}_3\text{-SiO}_2$.^{2(b)}

The temperatures determined for the decomposition of Fe_2O_3 to $\text{FeO}\cdot\text{Fe}_2\text{O}_3$ are in satisfactory agreement with those reported.^{2(b), 6, 7} The melting point of $\text{FeO}\cdot\text{Fe}_2\text{O}_3$ reported by Darken and Gurry¹³ and of Al_2O_3 by von Wartenberg and Reusch⁹ have been used.

Chemical analyses were not carried out on samples equilibrated above 1650°C ., because only very small samples can be used in strip-furnace runs. The curves representing compositions of the spinel phase in the lower triangular diagrams

* See pages 212 and 213.

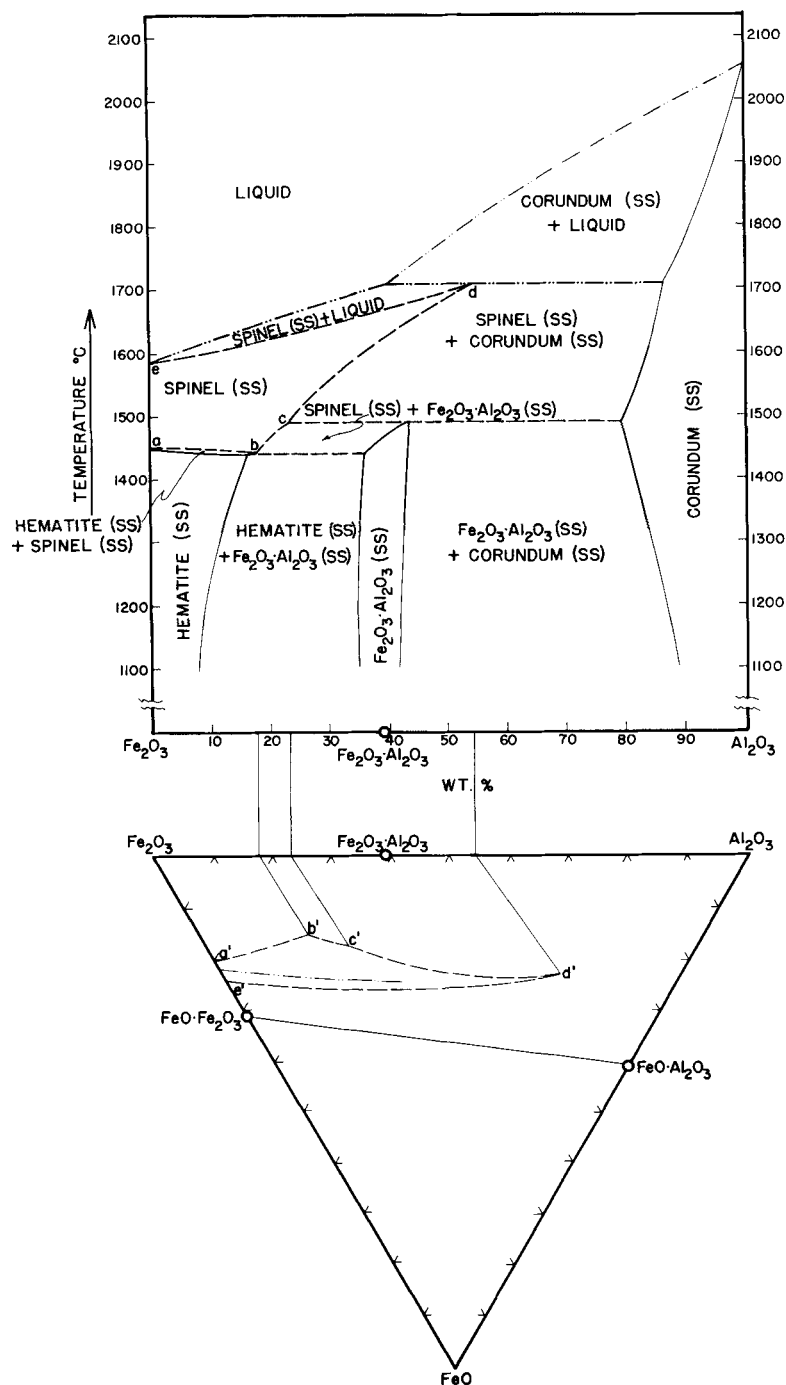


Fig. 4. Diagrams to illustrate phase relationships in the system iron oxide- Al_2O_3 at 1 atm. O_2 pressure. The line symbols used are the same as in Fig. 3.

in Figs. 3 and 4 were drawn on the basis of data given by Richards and White,⁶ as well as those obtained in the present study. The reproducibility of analytical results for divalent iron content was very poor for these mixtures, and the location of the composition lines shown in Figs. 3 and 4 should be considered only approximate. The rate of quenching is probably very critical in this system, and the method used by Richards and White,⁶ namely, weighing the samples in the furnace, is probably more advantageous. The light lines representing the compositions of liquid and spinel phases above 1650°C. are only rough qualitative extrapolations of the results obtained at lower temperatures.

The compositions of the solid solution phases hematite(ss), corundum(ss), and $\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ (ss) were determined by X-ray

diffraction measurements. This procedure requires standard curves relating d -spacing to composition for samples of known compositions. As an example of such a standard curve, Fig. 5 shows the d -spacing in angstrom units versus composition in mole per cent for the solid solution series Fe_2O_3 - Al_2O_3 . Similarly, the rate of change of d -spacing as a function of composition by the substitution of Al^{3+} for Fe^{3+} in the phase $\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ (ss) was determined from standards made up at close composition intervals in the one-phase field of $\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ (ss).

The most important features of the phase relationships are as follows: In air (Fig. 3) the only phases present below 1380°C. (the temperature of point *b*) are hematite(ss), corundum(ss), and $\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ (ss). The phase $\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ (ss) was not found by Richards and White⁶ in their excellent work on sesquioxide-spinel equilibria recently published. The present data prove conclusively, however, that this phase is stable relative to hematite(ss) + corundum(ss) above 1318°C. We have not been able to synthesize the phase below this temperature, although, once formed, it fails to decompose to hematite(ss) + corundum(ss) at lower temperatures. Because of the sluggishness of the reactions and the consequent uncertainty as to equilibrium relationships below 1318°C., the phase boundaries are drawn as light lines below this temperature. The compositions of the phases below 1380°C. are represented by points along the join Fe_2O_3 - Al_2O_3 ; hence this part of the diagram in Fig. 3 has been drawn as solid lines.

As the temperature is increased, a point is reached where ferric oxide starts dissociating to ferrous oxide plus oxygen, and a spinel phase forms in addition to the other phases. This decomposition, in air, takes place at approximately 1390°C. for the pure Fe_2O_3 end member, and the decomposition temperature decreases slightly as Al_2O_3 is added. The 1:1 phase decomposes to spinel and corundum at 1410°C. (temperatures of point *c*, Fig. 3). At the temperature of the appearance of spinel as a phase, the system ceases to be binary. The composition of the spinel phase along a boundary curve at any temperature within its range of stable existence can be found by following the projection lines to points on the corresponding dashed composition lines in the lower triangular diagram. For instance, the compositions of spinels along the boundary curve *c-d* in the upper diagram vary along the dashed curve *c'-d'* in the lower diagram.

When the temperature becomes high enough for a liquid phase to develop, a new situation arises inasmuch as an additional phase with a composition outside the binary join Fe_2O_3 - Al_2O_3 is present.

Liquidus temperatures increase as Al_2O_3 is added to Fe_2O_3 (from 1594° for the pure iron end member¹³ to approximately 2050°C. for Al_2O_3) with spinel as the primary phase in the iron oxide-rich melts and corundum as the primary phase in the more Al_2O_3 -rich melts.

At 1 atm. O_2 (Fig. 4) the picture is very similar to that in air. The composition lines in the lower diagram are displaced somewhat farther toward the Fe_2O_3 - Al_2O_3 join as compared with the situation in air. It is also evident that the

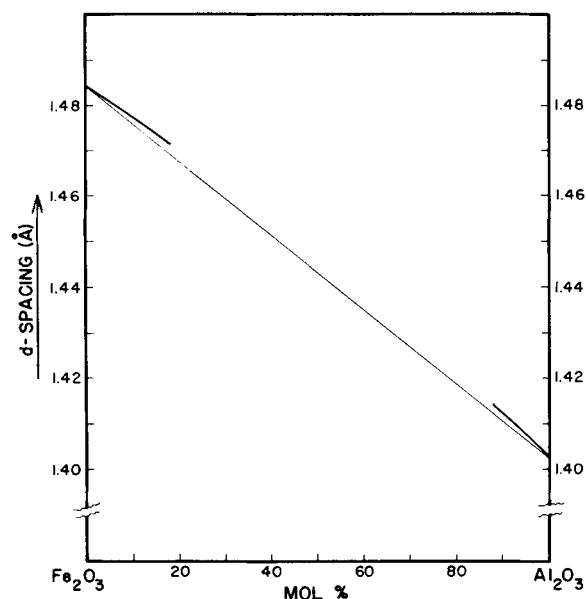


Fig. 5. Diagram showing change in d -spacing with composition for [124] reflection in Fe_2O_3 - Al_2O_3 mixtures. Heavy lines were determined and are compared with a straight line joining the values for the pure oxides.

temperatures at which the sesquioxides decompose to spinel are somewhat higher than in air. The result is that the field of stable existence of the 1:1 phase is enlarged upward by approximately 80°C . The increase in O_2 pressure from that of air to 1 atm. has only a minor effect on liquidus temperatures.

V. Discussion

In any high-temperature investigation of systems with iron oxide as a component, obtaining a suitable container for the sample is a major problem. The use of platinum envelopes as containers in the present study requires some explanation, in view of the ease of alloying of metallic iron with platinum. Actually, in air and at 1 atm. O_2 this reaction does not disturb the equilibrium investigation. One is dealing with equilibria among oxide phases, liquid as well as crystalline, and a gas phase. These equilibria, at a chosen temperature, are influenced by platinum only if the latter enters one or more of the phases involved. There is no evidence of substitution of platinum ions in any of the crystalline structures encountered under the experimental conditions of this study. Furthermore, Darken and Gurry¹³ found that iron oxide liquids under experimental conditions similar to the present ones dissolved only very small amounts of platinum. Finally, the vapor pressure of platinum at the temperatures of the present investigation is negligible. The alloying of iron with platinum can disturb these phase equilibrium studies only if the amount of iron going into the platinum of the envelope is large enough to change appreciably the total composition ($\text{FeO} + \text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ ratio) of the samples. Such a possibility is not in conflict with the statement made above. Even if a significant change in total composition takes place, the positions of the equilibria are not changed; the change observed in such a case is only in the relative amounts of the phases present in equilibrium. In an atmosphere of air, or at 1 atm. O_2 , the amount of iron which goes into the platinum of the envelope is so small that its effect on the total composition of the oxide sample can be neglected. This conclusion, based on chemical analysis of a few critical samples, is in agreement with observations made by Larson and Chipman.¹⁴

Table I. Results of Quenching Experiments ($p_{\text{O}_2} = 0.21$ Atm. (Air))

Starting materials	Composition (wt. %)		Temp. of quenching run ($^\circ\text{C}$.)	Phases present*
	Fe_2O_3	Al_2O_3		
Hematite	100	0	1387	Hem.
			1393	Magn.
			1589	Magn.
			1599	Liq.
Nitrates	95	5	1085	Hem.(ss)
			1385	Hem.(ss)
			1392	Spin.(ss)
Nitrates	90	10	1115	Hem.(ss) + tr. Cor.(ss)
			1273	Hem.(ss)
			1386	Hem.(ss) + Spin.(ss)
			1397	Spin.(ss)
Spinel(ss)	90	10	1385	Hem.(ss) + Spin.(ss)
			1393	Spin.(ss)
			1610	Spin.(ss)
			1625	Liq.
Nitrates	85	15	1115	Hem.(ss) + Cor.(ss)
			1273	Hem.(ss) + Cor.(ss)
			1367	Hem.(ss) + tr. 1:1(ss)
			1378	Hem.(ss) + tr. 1:1(ss)
			1383	Spin.(ss)
Quenched Liq.	80	20	1111	Hem.(ss) + Cor.(ss)
			1210	Hem.(ss) + Cor.(ss)
			1302	Hem.(ss) + Cor.(ss)
			1395	Spin.(ss) + 1:1(ss)
			1414	Spin.(ss) + Cor.(ss)
			1439	Spin.(ss) + tr. Cor.(ss)
			1445	Spin.(ss)
			1660	Liq.
Nitrates	80	20	1349	Hem.(ss) + 1:1(ss)
			1378	Hem.(ss) + 1:1(ss)
			1383	Spin.(ss) + 1:1(ss)
Spinel(ss)	80	20	1620	Spin.(ss)
			1640	Spin.(ss) + Liq.
			1650	Liq.
Quenched Liq.	70	30	1111	Hem.(ss) + Cor.(ss)
			1210	Hem.(ss) + Cor.(ss)
			1251	Hem.(ss) + Cor.(ss)
			1310	Hem.(ss) + Cor.(ss)
			1326	Hem.(ss) + 1:1(ss)
			1347	Hem.(ss) + 1:1(ss)
			1510	Spin.(ss) + tr. Cor.(ss)
			1523	Spin.(ss)
Nitrates	70	30	1345	1:1(ss) + Hem.(ss)
			1382	1:1(ss) + Spin.(ss)
			1399	1:1(ss) + Spin.(ss)
			1408	1:1(ss) + Spin.(ss)
			1414	Spin.(ss) + Cor.(ss)
Spinel(ss)	70	30	1650	Spin.(ss)
			1685	Liq.
Nitrates	66	34	1345	1:1(ss) + Hem.(ss)
			1382	1:1(ss) + Spin.(ss)
			1534	Spin.(ss) + Cor.(ss)
			1557	Spin.(ss)
Nitrates	63	37	1111	Hem.(ss) + Cor.(ss)
			1292	Hem.(ss) + Cor.(ss)
			1316	Hem.(ss) + Cor.(ss)
			1320	1:1(ss)
			1345	1:1(ss)
			1382	1:1(ss)
			1399	1:1(ss) + Spin.(ss)
Nitrates	59	41	1415	Spin.(ss) + Cor.(ss)
			1345	1:1(ss)
			1573	Spin.(ss) + Cor.(ss)
			1603	Spin.(ss)
Spinel(ss)	59	41	1675	Spin.(ss) + Liq.
			1685	Spin.(ss) + Liq.
			1710	Liq.

* Abbreviations in Tables I and II have the following meanings: Liq. = liquid. Magn. = crystals of magnetite. Hem.(ss) = crystals of hematite with corundum in solid solution. Cor.(ss) = crystals of corundum with hematite in solid solution. 1:1(ss) = crystals of $\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ (ss). Spin.(ss) = crystals of spinel. tr. = trace.

¹⁴ H. R. Larson and John Chipman, "Activity of Iron in Iron-Platinum Solid Solutions," *Acta Met.*, 2, 1-2 (1954).

Table I (concluded)

Starting materials	Composition (wt. %)		Temp. of quenching run (°C.)	Phases present
	Fe_2O_3	Al_2O_3		
Nitrates	54	46	1345	1:1(ss) + tr. Cor.(ss)
			1382	1:1(ss) + tr. Cor.(ss)
			1408	1:1(ss) + tr. Cor.(ss)
			1414	Spin.(ss) + Cor.(ss)
			1619	Spin.(ss) + Cor.(ss)
Spinel(ss)	54	46	1652	Spin.(ss)
			1665	Spin.(ss)
			1685	Spin.(ss) + Liq.
			1695	Spin.(ss) + Liq.
			1715	Liq.
Nitrates	43.8	56.2	1345	1:1(ss) + Cor.(ss)
			1382	1:1(ss) + Cor.(ss)
			1408	1:1(ss) + Cor.(ss)
			1414	Spin.(ss) + Cor.(ss)
Spinel(ss)	43.8	56.2	1700	Spin.(ss)
			1725	Cor.(ss) + Liq.
Nitrates	33	67	1315	Hem.(ss) + Cor.(ss)
			1322	1:1(ss) + Cor.(ss)
			1401	1:1(ss) + Cor.(ss)
			1420	Spin.(ss) + Cor.(ss)
Nitrates	20	80	1114	Cor.(ss) + Hem.(ss)
			1221	Cor.(ss) + Hem.(ss)
			1273	Cor.(ss) + Hem.(ss)
			1364	Cor.(ss) + tr. 1:1(ss)
			1530	Cor.(ss) + Spin.(ss)
			1603	Cor.(ss) + Spin.(ss)
Nitrates	15	85	1114	Cor.(ss) + Hem.(ss)
			1280	Cor.(ss)
			1530	Cor.(ss)
Nitrates	10	90	1603	Cor.(ss) + Spin.(ss)
			1221	Cor.(ss)

A notable feature of the diagrams in Figs. 3 and 4 is the region of stable existence of the phase $\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3(\text{ss})$. The structure of this phase was found to be analogous to $\kappa\text{-Al}_2\text{O}_3$, in agreement with the observation of Richardson, Ball, and Rigby.⁸ This structure is not confined to the stoichiometric 1:1 composition but permits solid solution toward Fe_2O_3 and Al_2O_3 to an amount of 3 or 4 weight % each. Although kinetic relationships were not studied systematically in this investigation, the question of reaction rates cannot be bypassed in discussing the stability of the phase $\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3(\text{ss})$. As pointed out previously, starting with Fe_2O_3 and Al_2O_3 , it was impossible to synthesize $\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3(\text{ss})$ until a temperature of 1318°C. was reached, whereas, once formed, the 1:1 phase failed to decompose to the oxide components at lower temperatures. In other words, equilibrium is not obtained among these phases at temperatures below 1318°C. The data establish conclusively the stability of the 1:1 phase relative to hematite(ss) + corundum(ss) at least down to 1318°C., and it *may* be stable below this temperature, perhaps even to room temperature. One is confronted with the problem of deciding which of the following two interpretations is correct. The first alternative is that 1318°C. actually represents the lower limit of stable existence of $\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3(\text{ss})$ and that the decomposition of the phase below this temperature is so sluggish as to prevent its breaking down to the equilibrium products. The second possibility is that the phase has a stability range extending to much lower temperatures, but its formation from the oxide components is too slow for observation within a reasonable period of time until a temperature of 1318°C. is reached. This type of problem is often encountered in ceramic and synthetic mineral research, and no direct method is available to decide which of the above-mentioned possibilities prevails. A means often resorted to in such a case is the introduction of

Table II. Results of Quenching Experiments ($p_{\text{O}_2} = 1 \text{ Atm.}$)

Starting materials	Composition (wt. %)		Temp. of quenching run (°C.)	Phases present
	Fe_2O_3	Al_2O_3		
Hematite	100	0	1450	Hem.
			1456	Magn.
Nitrates	90	10	1451	Hem.(ss)
			1453	Hem.(ss) + Spin.(ss)
			1459	Spin.(ss)
Nitrates	85	15	1252	Hem.(ss) + Cor.(ss)
			1306	Hem.(ss) + Cor.(ss)
			1316	Hem.(ss) + Cor.(ss)
			1322	Hem.(ss) + tr. 1:1(ss)
			1351	Hem.(ss) + tr. 1:1(ss)
			1443	Hem.(ss)
			1450	Hem.(ss) + Spin.(ss)
Spinel(ss)	85	15	1456	Spin.(ss)
			1443	Hem.(ss)
Quenched Liq.	80	20	1443	Hem.(ss) + 1:1(ss)
			1455	Spin.(ss)
Quenched Liq.	70	30	1315	Hem.(ss) + Cor.(ss)
			1322	Hem.(ss) + 1:1(ss)
			1345	Hem.(ss) + 1:1(ss)
			1443	Hem.(ss) + 1:1(ss)
			1450	Spin.(ss) + 1:1(ss)
			1449	Spin.(ss) + 1:1(ss)
			1463	Spin.(ss) + 1:1(ss)
Spinel(ss)	70	30	1474	Spin.(ss) + 1:1(ss)
			1660	Spin.(ss) + Liq.
Nitrates	66	34	1322	Hem.(ss)
			1441	Hem.(ss) + tr. 1:1(ss)
			1465	Spin.(ss) + tr. 1:1(ss)
			1479	Spin.(ss) + 1:1(ss)
			1487	Spin.(ss) + 1:1(ss)
			1494	Spin.(ss) + Cor.(ss)
			1315	Hem.(ss) + Cor.(ss)
			1323	1:1(ss)
Nitrates	57	43	1460	1:1(ss)
			1487	Spin.(ss) + 1:1(ss)
			1512	Spin.(ss) + Cor.(ss)
			1316	Hem.(ss) + Cor.(ss)
			1324	1:1(ss) + Cor.(ss)
			1354	1:1(ss) + Cor.(ss)
			1465	1:1(ss) + Cor.(ss)
Nitrates	33	67	1479	1:1(ss) + Cor.(ss)
			1487	1:1(ss) + Cor.(ss)
			1494	Spin.(ss) + Cor.(ss)
			1479	1:1(ss) + Cor.(ss)
Spin.(ss) + Cor.(ss)	33	67	1495	Spin.(ss) + Cor.(ss)
			1695	Spin.(ss) + Cor.(ss)
			1715	Cor.(ss) + Liq.

hydrothermal conditions to increase the rate of the solid-state reactions involved. An excellent review of the principles and applications of this method to subsolidus equilibrium studies in synthetic mineral systems has been given by Osborn.¹⁵ Unfortunately, in the present case hydrothermal runs were of no help. Runs made in a silver-lined bomb at 470°C. and 10,000 lb. per sq. in. water pressure produced magnetite(ss) and corundum(ss). Another, more indirect, approach is as follows: At the hypothetical temperature t at which $\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3(\text{ss})$ decomposes to hematite(ss) and corundum(ss), there is only one composition of the 1:1 phase which is in equilibrium with the two other phases. The sketch in Fig. 6 shows the hypothetical equilibria among these phases as labeled in the diagram. The two lines AB

¹⁵ E. F. Osborn, "Subsolidus Reactions in Oxide Systems in Presence of Water at High Pressures," *J. Am. Ceram. Soc.*, **36** [5] 147-51 (1953).

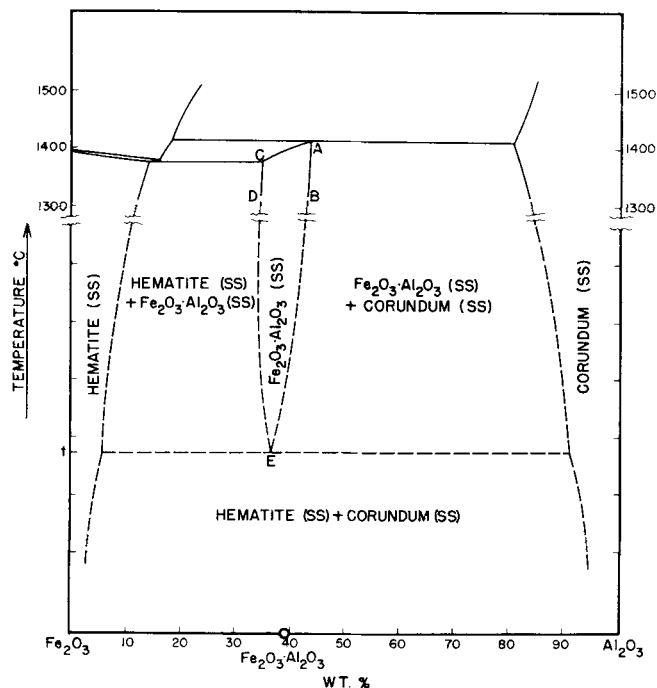


Fig. 6. Sketch presented to illustrate possible equilibrium relationships among the phases hematite (ss), corundum (ss), and $\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ (ss) at temperatures where equilibrium is not attained experimentally. Heavy lines are boundary curves. The lines AB and CD, representing outlines of the $\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ (ss) field, are extended as dashed lines to the hypothetical point E corresponding to the hypothetical temperature t , as discussed in the text.

and CD, representing compositions of $\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ (ss) in equilibrium with hematite(ss) and corundum(ss), respectively, must meet at one point E at temperature t . Whether this point is located at the exact 1:1 stoichiometric composition, or not, is unknown but irrelevant to the problem. Also, the two lines AE and CE, as well as the slopes of these two lines, must be continuous functions of temperature as long as no phase transformations take place in the crystalline phases which are in equilibrium along these boundary curves. The d -spacing measurements indicate very little decrease in width of the $\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ (ss) field as temperature is lowered toward 1318°C. In other words, point E in Fig. 6 must be located at a temperature below 1318°C. It is tentatively concluded from this observation that the phase $\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ (ss) is stable relative to hematite(ss) + corundum(ss) also at temperatures below 1318°C.

The determination of d -spacing as a function of composition in the solid solution phases hematite(ss) and corundum(ss) (Fig. 5) indicates a considerable positive deviation from the straight line connecting the d -spacing values for the two end members. Vegard's law¹⁶ was originally postulated as a good approximation in a continuous solid solution series when the two ions replacing each other are very similar in crystal chemical behavior. In the present case, however, the large gap in solubility points to significant differences between the two ions Fe^{3+} and Al^{3+} , and the deviation from linearity is not unexpected. The determination of compositions of spinels in the magnetite-hercynite ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$ - $\text{FeO} \cdot \text{Al}_2\text{O}_3$) series by means of X-ray methods is not simple. It would be a straightforward problem if the compositions of the spinel phase were located exactly along the join $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ - $\text{FeO} \cdot \text{Al}_2\text{O}_3$ (see Fig. 3). This is equivalent to postulating that the ratio of divalent ions (here Fe^{2+}) to trivalent ions (here

$\text{Fe}^{3+} + \text{Al}^{3+}$) remains constant and equal to one-half at all temperatures at constant O_2 pressure and at different O_2 pressures at constant temperature. If such were the case, one could prepare standard samples with varying Al_2O_3 contents, and a single curve, presumably closely approximating a straight line, would result when d -spacing was plotted versus composition, the latter expressed in mole per cent. Unfortunately, the true relationship is more complicated, as demonstrated experimentally and ably described by Richards and White.⁶ The spinel compositions fall on the Fe_2O_3 - Al_2O_3 side of the join $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ - $\text{FeO} \cdot \text{Al}_2\text{O}_3$. This can be expressed crystallographically by stating that there is a certain amount of solid solution between spinel and γ - Fe_2O_3 and γ - Al_2O_3 , the latter two being modifications of Fe_2O_3 and Al_2O_3 with fundamentally the same structure as spinel. (For a good discussion of these structures the reader is referred to a paper by Verwey.¹⁷) Because of this possibility, the ratio $\text{Fe}^{2+}/\text{Fe}^{3+}$ will vary with temperature as well as with O_2 pressure. Hence, in order to determine spinel compositions by X-ray methods, it would be necessary to have a large number of standard curves available showing the variation of d -spacing with composition (iron oxide/ Al_2O_3 ratio) and with the two other variables, temperature and O_2 pressure, as well. We do not have such curves. The boundaries limiting the spinel area in the present investigation (Figs. 3 and 4) were determined by direct observation, under the microscope, of the first appearance or disappearance of one of the two phases present at the boundary. However, as a check, enough standards were made up in a narrow temperature range of 1420° to 1440°C. in air for the X-ray determination of spinel compositions in mixtures close to the spinel boundary of the field where spinel and corundum(ss) are in equilibrium.

VI. Summary

Phase equilibria have been determined in the system iron oxide- Al_2O_3 in air and at 1 atm. O_2 , in the temperature range 1085° to 1725°C. The following crystalline phases are encountered in this study: hematite with corundum in solid solution, corundum with hematite in solid solution, a 1:1 phase ($\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ (ss)), and finally a spinel phase, essentially a solid solution between magnetite ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$) and hercynite ($\text{FeO} \cdot \text{Al}_2\text{O}_3$) with some excess Fe_2O_3 and/or Al_2O_3 .

The system is binary if hematite(ss), corundum(ss), and $\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ (ss) are the only phases present. As the temperature is increased, a point is reached where the ferric oxide starts to dissociate to ferrous oxide plus oxygen, and a spinel phase forms in addition to the other phases present. For the pure Fe_2O_3 end member, this decomposition takes place at 1390°C. in air and at 1455°C. in 1 atm. O_2 , and the decomposition temperature decreases slightly as Al_2O_3 is added. The 1:1 phase decomposes to spinel and corundum(ss) at 1410°C. and at 1490°C. in air and at 1 atm. O_2 , respectively. With spinel present as a phase the system is ternary rather than binary.

Liquidus temperatures increase as Al_2O_3 is added to iron oxide. In air the pure iron oxide end member melts at 1594°C., and Al_2O_3 at approximately 2050°C. Spinel is the primary phase in the iron oxide-rich melts, whereas corundum(ss) is the primary phase in the more Al_2O_3 -rich melts. The increase in O_2 pressure from that of air to 1 atm. has only a minor effect on liquidus temperatures.

Acknowledgments

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¹⁶ L. Vegard, "Die Konstitution der Misch-kristalle und die Raumerfüllung der Atome," *Z. Physik*, **5**, 17 (1921).

¹⁷ E. J. W. Verwey, "Crystal Structure of γ - Fe_2O_3 and γ - Al_2O_3 ," *Z. Krist.*, **91**, 65-69 (1935)(in English); *Ceram. Abstr.*, **15** [1] 43 (1936).