

# The System Iron—Titanium—Oxygen at 1200°C. and Oxygen Partial Pressures Between 1 Atm. and $2 \times 10^{-14}$ Atm.

by A. H. WEBSTER and NORMAN F. H. BRIGHT

Mines Branch, Department of Mines and Technical Surveys, Ottawa, Ontario, Canada

The 1200°C. isotherm in the system Fe—Ti—O has been studied by equilibrating mixtures of iron oxide ( $\text{Fe}_2\text{O}_3$ ) and titanium oxide ( $\text{TiO}_2$ ) with atmospheres of controlled oxygen partial pressure. These atmospheres consisted of  $\text{CO}_2$ , air, oxygen, mixtures of  $\text{CO}_2$  and  $\text{H}_2$ , and mixtures of  $\text{CO}_2$  and CO. The resulting oxide mixtures were examined at room temperature by chemical analysis and by X-ray diffraction. The stability regions of the  $\alpha$ -oxides ( $\text{Fe}_m\text{Ti}_{2-m}\text{O}_3$ ), of the spinels, ( $\text{Fe}_n\text{Ti}_{3-n}\text{O}_4$ ), and of the orthorhombic oxides ( $\text{Fe}_p\text{Ti}_{3-p}\text{O}_5$ ) were determined. Some nonstoichiometry occurs in the spinels and in the  $\alpha$ -oxides. The oxygen partial pressures at which spinel is reduced to (iron +  $\alpha$ -oxides) and at which  $\alpha$ -oxide (ilmenite) is reduced to (iron + orthorhombic oxide) were determined as  $2.1 \times 10^{-13}$  and  $9.3 \times 10^{-14}$  atm., respectively. The orthorhombic solid solution series extends over the whole range of oxygen partial pressures studied.

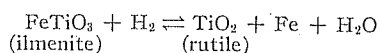
## I. Introduction

THE chemistry of the system iron—titanium—oxygen is of considerable interest because of the occurrence of large deposits of ilmenite which are becoming increasingly important as sources of pigment-grade titanium dioxide and, in some processes, as a source of iron. Titaniferous magnetite ores are also a source of iron but generally are less attractive than nontitaniferous materials. Studies of this system at controlled oxygen partial pressures should be useful in understanding certain features of the pyrometallurgical treatments for such titanium-bearing ores.

The temperature of 1200°C. was chosen chiefly for reasons of experimental suitability; equilibrium was attainable more rapidly than at lower temperatures, and attack on the refractory material (thoria), used to hold the test samples, was negligible at this temperature. This temperature also is within a range which has been considered for the solid-state reduction of ilmenite.<sup>1</sup>

A considerable amount of previous data has been published on the system Fe—Ti—O. The binary system Fe—O has been extensively studied, the description of this system given by Darken and Gurry being generally accepted.<sup>2</sup> The system Ti—O also has been extensively studied but has not been so well defined.<sup>3,4</sup> It is of interest to note that rutile deficient in oxygen ( $\text{TiO}_{2-x}$ ) exists under reducing conditions; the compositions of the nonstoichiometric rutile in equilibrium with  $\text{H}_2$ — $\text{H}_2\text{O}$  mixtures have been studied up to 1177°C. by Michaud and Pidgeon.<sup>4</sup>

The equilibrium



has been studied over the temperature range 950° to 1100°C. in two separate investigations, with good agreement in results.<sup>4, 5</sup>

Several studies on the system  $\text{FeO}$ — $\text{Fe}_2\text{O}_3$ — $\text{TiO}_2$  have been reported in the literature. MacChesney and Muan<sup>6</sup> investigated this system in air from 1400°C. to above the liquidus, and Karkhanavala and Momin<sup>7</sup> made a similar study from 620° to 1200°C. The phases stable in air at 1200°C. were reported to be hematite, pseudobrookite, and rutile. A study of this system at 1350°C. also has been reported by Schmahl and Meyer,<sup>8</sup> who used oxygen pressures down to about  $10^{-2}$  atm. Most of the studies, however, have been made without reference to the oxygen partial pressure.<sup>9,10</sup>

The following three principal solid-solution series have been described as existing in the system  $\text{FeO}$ — $\text{Fe}_2\text{O}_3$ — $\text{TiO}_2$ :

(1)  $\alpha$ - $\text{Fe}_2\text{O}_3$  to  $\text{FeTiO}_3$  (i.e.,  $\text{Fe}_m\text{Ti}_{2-m}\text{O}_3$ ), referred to in this paper as " $\alpha$ -oxides." Hematite and ilmenite have limited solid solubility in each other at low temperatures,

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The writers are, respectively, scientific officer and head, Physical Chemistry Section, Mineral Sciences Division, Mines Branch, Department of Mines and Technical Surveys.

<sup>1</sup> R. H. Walsh, H. W. Hockin, D. R. Brandt, P. L. Dietz, and P. R. Girardot, "Reduction of Iron Values of Ilmenite to Metallic Iron at Less Than Slagging Temperatures"; in press, *Trans. Am. Inst. Mining Met. Petrol. Engrs.*

<sup>2</sup> (a) L. S. Darken and R. W. Gurry, "The System Iron—Oxygen: I, The Wüstite Field and Related Equilibria," *J. Am. Chem. Soc.*, 67 [8] 1398–1412 (1945).

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

<sup>3</sup> (a) R. C. DeVries and Rustum Roy, "Phase Diagram for the System Ti— $\text{TiO}_2$  Constructed from Data in the Literature," *Am. Ceram. Soc. Bull.*, 33 [12] 370–72 (1954).

(b) Sten Andersson, Bengt Collén, Ulf Kuylenstierna, and Arne Magnéli, "Phase-Analysis Studies in the Titanium—Oxygen System," *Acta. Chem. Scand.*, 11, 1641–52 (1957).

(c) N. F. H. Bright, "X-Ray Studies in the Ti—O System"; in press, *Proc. Ann. Conf. Applications of X-Ray Analysis, Ninth Conf.*, 1960. Published by the University of Denver.

<sup>4</sup> G. G. Michaud and L. M. Pidgeon, "Selective Reduction of Iron in Ilmenite and the Oxygen Pressure of  $\text{TiO}_{2-x}$  (Rutile)," *Trans. Can. Inst. Mining Met.*, 57, 187–89 (1954).

<sup>5</sup> C. H. Shomate, B. F. Naylor, and F. S. Boericke, "Thermodynamic Properties of Ilmenite and Selective Reduction of Iron in Ilmenite," *U. S. Bur. Mines Rept. Investigations*, No. 3864, 19 pp. (1946); *Ceram. Abstr.*, 1946, October, p. 182.

<sup>6</sup> J. B. MacChesney and Arnulf Muan, "Studies in the System Iron Oxide—Titanium Dioxide," *Am. Mineralogist*, 44 [9/10] 926–45 (1959).

<sup>7</sup> M. D. Karkhanavala and A. C. Momin, "Subsolidus Reactions in the System  $\text{Fe}_2\text{O}_3$ — $\text{TiO}_2$ ," *J. Am. Ceram. Soc.*, 42 [8] 399–402 (1959).

<sup>8</sup> N. G. Schmahl and Günter Meyer, "Iron Titanate in Region of Directly Measurable Oxygen Pressure," *Metall.*, 13 [12] 1114–15 (1959).

<sup>9</sup> Emile Pouillard, "Sur le comportement de l'alumine et l'oxyde de titane vis-à-vis des oxydes de fer" (On the Behavior of Alumina and of Titanium Oxide with Respect to Iron Oxides), *Ann. chim.*, [12], 5, 164–214 (1950).

<sup>10</sup> G. D. Nicholls, "Mineralogy of Rock Magnetism," *Advances in Phys.*, 4 [14] 113–90 (1955).

but form a complete solid-solution series at higher temperatures. The consolute temperature is reported to be in the region 950° to 1050°C.<sup>10</sup> This solid-solution series has a hexagonal (rhombohedral) structure.

(2)  $\text{Fe}_3\text{O}_4$  to  $\text{Fe}_2\text{TiO}_4$  (i.e.,  $\text{Fe}_x\text{Ti}_{3-x}\text{O}_4$ ), referred to as "spinel" in this paper. Magnetite and ulvöspinel ( $\text{Fe}_2\text{TiO}_4$ ) are reported to form a continuous solid-solution series at sufficiently high temperatures. The consolute temperature is probably about 600°C.<sup>11</sup> This solid-solution series has the cubic spinel structure.

(3)  $\text{Fe}_2\text{TiO}_5$  to  $\text{FeTi}_2\text{O}_5$  (i.e.,  $\text{Fe}_p\text{Ti}_{3-p}\text{O}_5$ ), referred to as "orthorhombic oxides" in this paper. Pseudobrookite and ferrous dititanate form a continuous solid-solution series at 1150°C.<sup>12</sup> Members of this series have an orthorhombic structure.

Other phases encountered in the course of this investigation were rutile ( $\text{TiO}_2$ , tetragonal), wüstite ( $\text{Fe}_{1-x}\text{O}$ , cubic, NaCl-type structure), and metallic iron (face-centered cubic at 1200°C. but body-centered cubic when examined at room temperature).

The system "FeO-TiO<sub>2</sub>" has been reported by Grieve and White<sup>13</sup> to contain the compounds "FeO,"  $\text{Fe}_2\text{TiO}_4$ ,  $\text{FeTiO}_3$ , and  $\text{TiO}_2$ . The orthorhombic compound  $\text{FeTi}_2\text{O}_5$ , however, apparently was not recognized in that investigation.

## II. Experimental

The general procedure used in the present study was to equilibrate pellets of appropriate mixtures of  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$ , at the desired temperature, with an atmosphere of known composition. The pellets were then cooled rapidly to room temperature, generally in an inert gas, and examined by X-ray diffraction and by chemical analysis. Fisher Certified Reagent ferric oxide and Baker Analyzed reagent titanium dioxide (anatase) were used as starting materials.

### (1) Apparatus

A 60:40 Pt:Rh alloy, internally wound furnace, controlled by a Brown controller-pyrometer, was used with a horizontal, closed-end, mullite working tube 1 1/4 in. in inside diameter. The sample pellets were held in a thoria boat which lay on an alumina boat. An alumina block, acting as a radiation shield, was placed in front of the alumina boat. A platinum draw-wire was attached to the alumina boat; this wire enabled the pellets to be withdrawn to the cool end of the furnace tube, without exposure to air, at the conclusion of the equilibration period. The gas being used as the controlling atmosphere entered through an inlet tube, which was arranged to carry the preheated gas to the closed end of the working tube. The temperature of the furnace was measured by a shielded Pt-Pt-10% Rh thermocouple placed above the pellets. The temperatures reported represent those of the pellets, probably to within  $\pm 10^\circ\text{C}$ .

### (2) Atmospheres

The atmospheres used to give the controlled oxygen partial pressures were oxygen and air at 1-atm. pressure, air at 1-cm. Hg pressure,  $\text{CO}_2$ ,  $\text{CO-CO}_2$  mixtures, and  $\text{CO}_2\text{-H}_2$  mixtures. The theory governing the use of such atmospheres has been discussed by Muan.<sup>14</sup> Oxygen partial pressures were calculated using the data summarized by Coughlin.<sup>15</sup> Gas mixtures were prepared by transferring appropriate quantities of gas from commercial cylinders into a smaller cylinder, which served as a reservoir to supply the gas as required. Argon was added to the  $\text{CO-CO}_2$  and  $\text{CO}_2\text{-H}_2$  mixtures to reduce thermal diffusion.<sup>16</sup> The gases were passed over Drierite and, when appropriate, over copper at 500°C., before use. For all atmospheres except air and oxygen, heating and cooling of the samples were conducted in an inert atmosphere.

With  $\text{CO-CO}_2$  and  $\text{CO}_2\text{-H}_2$  atmospheres, the samples were generally held at the desired temperature for two periods, each 3 to 4 hours, with crushing and repelleting between

heating cycles. One equilibration period of 18 to 20 hours was used with the other atmospheres.

### (3) Chemical Analyses

The following procedures were used for analysis of the samples:

(a) Total iron and total titanium: After fusion with  $\text{KHSO}_4$ , the sample was dissolved in 10%  $\text{H}_2\text{SO}_4$  and made up to a known volume. Iron was determined on an aliquot portion by reduction with stannous chloride, followed by titration with  $\text{KMnO}_4$ . Titanium was determined colorimetrically after the addition of hydrogen peroxide.

(b) Total reducing capacity (i.e., combined Fe(II) and Ti(III)): After crushing the samples in an inert atmosphere, they were dissolved in  $\text{H}_2\text{SO}_4$  containing standardized vanadate solution. Hydrofluoric acid was added to aid dissolution. After the sample had dissolved, the solution was diluted, boric acid and phosphoric acid were added, and the residual vanadate was titrated with ferrous ammonium sulfate. For a few samples, solution was effected by heating the sample, sealed in a Pyrex-brand glass tube, with HCl; the reducing capacity was then determined by permanganate titration.

In some instances, the Fe/(Fe + Ti) atom ratios in the samples were assumed to be as given by the proportions of  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  used in preparing the samples, but in other cases they were determined by chemical analysis. The root-mean-square difference between determined and prepared Fe/(Fe + Ti) ratios was 0.014.

### (4) X-Ray Diffraction

X-ray diffraction patterns were determined on the samples at room temperature, using a 57.3-mm.-diameter Debye-Scherrer powder camera and  $\text{CoK}\alpha$  radiation.

### (5) Microscopical Examination

Microscopical examination of polished sections for phase determinations in the equilibrated pellets was made difficult by the high porosity of the samples and by the similarity in color of certain of the phases encountered. The technique was of little value except in the detection of iron metal.

## III. Results

### (1) General Results

At 1200°C., over the region of oxygen partial pressures investigated, no liquid phases were found in the system Fe-Ti-O. The stable phases at 1200°C., as determined by X-ray diffraction on samples cooled to room temperature, are indicated in Fig. 1 as functions of the Fe/(Fe + Ti) atom ratio in the total solid and of the logarithm of the oxygen partial pressure ( $\log p_{\text{O}_2}$ ). It should be noted that this diagram gives no direct indication of the oxygen contents of the condensed phases. The stability regions of the iron oxides containing no titanium, plotted on the left-hand side of Fig. 1, were taken from the data of Darken and Gurry.<sup>2</sup> In general,

<sup>11</sup> E. A. Vincent, J. B. Wright, R. Chevallier, and Suzanne Mathieu, "Heating Experiments on Some Natural Titaniferous Magnetites," *Mineralog. Mag.*, 31 [239] 624-55 (1957).

<sup>12</sup> S. Akimoto, T. Nagata, and T. Katsura, "The  $\text{TiFe}_2\text{O}_5\text{-Ti}_2\text{FeO}_5$  Solid Solution Series," *Nature*, 179 [4549] 37-38 (1957).

<sup>13</sup> J. Grieve and J. White, "System FeO-TiO<sub>2</sub>," *J. Roy. Tech. Coll. (Glasgow)*, 4 (Part 3) [1] 441-48 (1939); *Ceram. Abstr.*, 18 [9] 257 (1939).

<sup>14</sup> Arnulf Muan, "Phase Equilibria at High Temperatures in Oxide Systems Involving Changes in Oxidation States," *Am. J. Sci.*, 256 [3] 171-207 (1958).

<sup>15</sup> J. P. Coughlin, "Data on Theoretical Metallurgy: XII, Heats and Free Energies of Formation of Inorganic Oxides," *U. S. Bur. Mines Bull.*, No. 542, 80 pp. (1954).

<sup>16</sup> M. N. Dastur and John Chipman, "Elimination of Thermal-Diffusion Error in Studies of Gas-Metal Equilibrium," *Discussions Faraday Soc.*, 1948, No. 4, pp. 100-108.

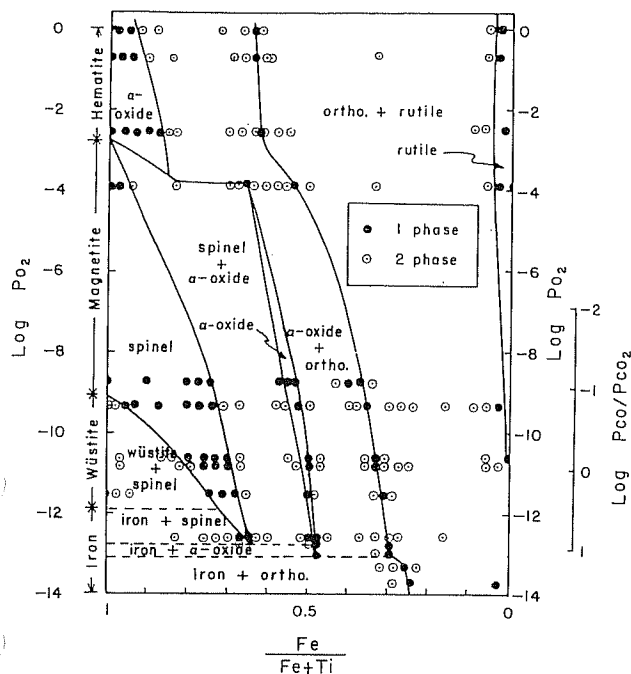


Fig. 1. Phases present in the system Fe-Ti-O at 1200°C. as a function of the Fe/(Fe + Ti) atom ratio and the oxygen partial pressure. At approximately  $\log p_{O_2} = -4$ , it will be noted that a region is shown in which a small variation in oxygen partial pressure is accompanied by a large change in the composition of the  $\alpha$ -oxide solid solution. This condition is represented by an almost horizontal line (not necessarily straight) which slopes slightly downward toward the lower right-hand side of the diagram. The  $\alpha$ -oxide field in this region will have a very small, but undetermined, width. The line separating the (ortho. + rutile) and ( $\alpha$ -oxide + ortho.) fields similarly represents the ortho-oxide solid-solution series of small, but finite, width. (Ortho. = orthorhombic oxide.)

the positions of the phase boundaries are probably correct to within  $\pm 0.02$  in the ratio Fe/(Fe + Ti). Equilibrium oxidation-reduction paths would be represented by lines parallel to the  $\log p_{O_2}$  axis on this plot, the iron and titanium metals and oxides being essentially nonvolatile at the temperature of the investigation.

Note that, with increasing titanium content, the stability region of any given type of oxide structure is shifted to lower oxygen partial pressures. The various solid-solution series are now discussed with reference to Fig. 1.

(a)  $\alpha$ -Oxide solid solution: The  $\alpha$ -oxide was observed to exist as a single phase over a range of Fe/(Fe + Ti) ratios, at a given oxygen partial pressure, in two different regions of the diagram, as shown in Fig. 1. Conversely, in these regions, for a given Fe/(Fe + Ti) ratio, a single-phase  $\alpha$ -oxide was stable over a considerable range of oxygen partial pressures.

In the region Fe/(Fe + Ti) = 0.85 to 0.65, at about  $\log p_{O_2} = -4$  a small variation in oxygen partial pressure was accompanied by a large change in the Fe/(Fe + Ti) ratio of the stable member of the  $\alpha$ -oxide solid-solution series. Unfortunately, it was experimentally inconvenient to supply atmospheres in the oxygen partial pressure region of interest. Hence, the following procedure was used to estimate the position of the phase boundary in this region: Samples were equilibrated with 1-atm. pressure of  $CO_2$  at various temperatures between 1120° and 1180°C. and were examined by X-ray diffraction after cooling to room temperature. The results are shown in Fig. 2(a), in which the phases present are indicated as functions of the atom ratio Fe/(Fe + Ti) and of the temperature. A similar plot over the temperature range 1050° to 1090°C., for an argon- $CO_2$  atmosphere, giving a  $CO_2$  partial pressure of 0.63 atm., is shown in Fig. 2(b). From these plots, the values of  $\log p_{O_2}$  for the  $\alpha$ -oxide solid solution

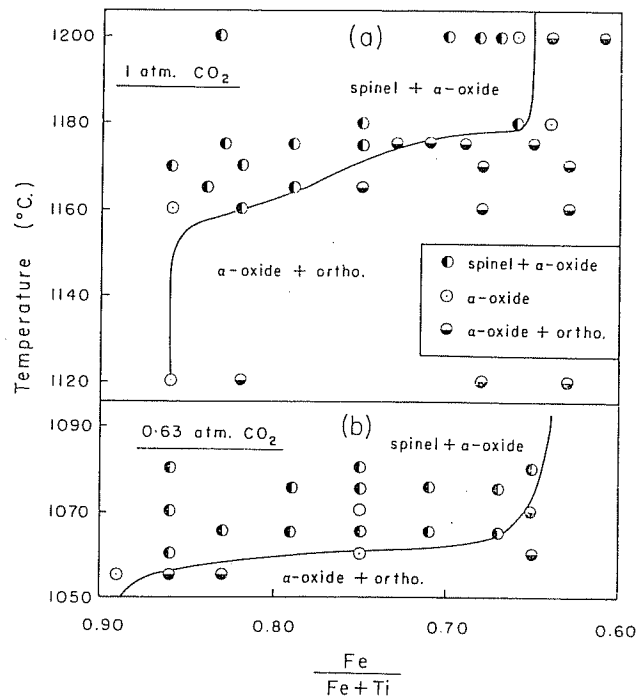


Fig. 2. Phases in equilibrium with (a)  $CO_2$  and (b) 63%  $CO_2$  in argon, as a function of temperature and the Fe/(Fe + Ti) ratio. (Ortho. = orthorhombic oxide.)

were determined at two temperatures for a series of Fe/(Fe + Ti) ratios. These  $\log p_{O_2}$  values were plotted against  $1/T^\circ K.$  and extrapolated to give  $\log p_{O_2}$  values at 1200°C. for each of the Fe/(Fe + Ti) ratios.

The small change in  $\log p_{O_2}$  with changes in the proportion of iron in the  $\alpha$ -oxide solid solution is to be expected just above the consolute temperature of the miscibility gap reported by previous investigators<sup>9, 10</sup> to exist in the  $\alpha$ -oxide solid-solution series. Across the miscibility gap the two solid solutions on either side of the gap would have the same oxygen partial pressure.

In Fig. 3, which is the lower portion of Fig. 1 shown on an expanded partial pressure scale, it is seen that the X-ray diffraction results indicated the coexistence of three solid phases at  $\log p_{O_2} = -13.04$ . These phases were metallic iron,  $\alpha$ -oxide, and orthorhombic oxide. According to the phase rule, this should not be so for a three-component system at a fixed temperature, except for one unique oxygen partial pressure. This observation was probably due to a non-equilibrium condition caused by the slow reduction of the  $\alpha$ -oxide in atmospheres of oxygen partial pressures only slightly lower than those at which this phase is stable. On this basis, the limit of  $\alpha$ -oxide solid solution was determined to be  $p_{O_2} = (9.3 \pm 0.2) \times 10^{-14}$  atm. (i.e.,  $\log p_{O_2} = -13.03$ ).

(b) Orthorhombic solid solution: The orthorhombic solid solution was, as far as could be determined, continuous over the whole range of atmospheres studied. Two regions, in which quite small variations in oxygen partial pressure were accompanied by quite large changes in the Fe/(Fe + Ti) ratio of the orthorhombic phase, were noted at about  $\log p_{O_2} = -3.5$  and  $-13.1$  (see Fig. 1). These inflections may indicate the existence of some discontinuities in the solid-solution series at lower temperatures.

Chemical analysis of samples heated at low oxygen partial pressures indicated directly that the orthorhombic oxide solid-solution series extends beyond the ferrous dititanate composition toward the composition  $Ti_3O_5$ . This result can also be inferred from Fig. 1.

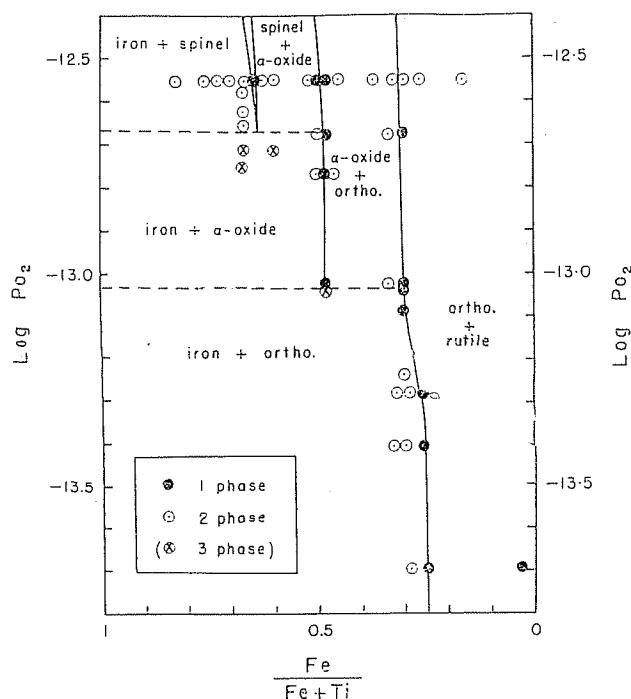


Fig. 3. Phases present in the system Fe-Ti-O at 1200°C. and oxygen partial pressures from  $3 \times 10^{-13}$  to  $2 \times 10^{-14}$  atm. (Ortho. = orthorhombic oxide.)

The orthorhombic oxides are shown in Fig. 1 as existing as a single phase at only one value of the Fe/(Fe + Ti) ratio for a given atmosphere. No significant variation in lattice spacings could be observed in passing from the orthorhombic phase in equilibrium with  $\alpha$ -oxide to the orthorhombic phase in equilibrium with rutile at a given oxygen partial pressure. The width of the stability region for the orthorhombic phase is thus probably less than 0.03 in the ratio Fe/(Fe + Ti) at any given oxygen partial pressure.

(c) *Spinel solid solution*: The spinel structure is stable over a substantial range of oxygen partial pressures for any given Fe/(Fe + Ti) ratio above approximately 0.7.

The limit of the spinel solid-solution series at low oxygen partial pressures occurs at  $p_{O_2} = (2.1 \pm 0.2) \times 10^{-13}$  atm. (i.e.,  $\log p_{O_2} = -12.6$ ), as indicated in Fig. 3. Here, as in the case of the  $\alpha$ -oxide series, three solid phases (metallic iron, spinel, and  $\alpha$ -oxide) were found to occur over a narrow range of oxygen partial pressures. This again was assumed to be due to nonequilibrium conditions, as discussed previously.

(d) *Rutile*: Titanium oxide, exposed to an atmosphere of low oxygen partial pressure ( $\log p_{O_2} = -10.60$ ) at 1200°C. for a total of 9 hours, was found to be slightly oxygen-deficient, analyzing as  $TiO_{1.989}$ . No significant differences in lattice parameters were observed, however, among samples heated at various oxygen partial pressures. The solid solubility of iron oxide in rutile is probably quite limited at 1200°C., since, at the higher oxygen partial pressures, a second phase was observed with Fe/(Fe + Ti) as low as 0.06, and, at lower oxygen partial pressures, with values as low as 0.03. No change in the rutile lattice spacings was observable in any sample.

(e) *Wüstite*: No evidence was found in this investigation for solid solubility of TiO in wüstite, since no changes were observed in the wüstite cell parameter; also, at Fe/(Fe + Ti) = 0.97, a second phase (spinel) was observable.

Table I. Attainment of Equilibrium and Reproducibility of Results

(a) 1-cm. Hg air ( $\log p_{O_2} = -2.56$ )		
Fe/(Fe + Ti) atom ratio	Phases detected by X-ray diffraction	
	24-hr. heating; no preliminary reduction	20-hr. heating; preliminary reduction
0.93	$\alpha$ -oxide	(1) $\alpha$ -oxide only (2) $\alpha$ -oxide + tr. spinel
0.87	$\alpha$ -oxide + minor ortho.	$\alpha$ -oxide
0.85		$\alpha$ -oxide + ortho.
0.83	$\alpha$ -oxide + ortho.	$\alpha$ -oxide + ortho.
0.64	Ortho.	Ortho. + tr. $\alpha$ -oxide
0.63		Ortho.
0.62	Ortho. + tr. rutile	Ortho. + tr. rutile
(b) CO/CO <sub>2</sub> = 0.157 ( $\log p_{O_2} = -9.32$ )		
Fe/(Fe + Ti) atom ratio	Phases detected by X-ray diffraction	
	2 heating periods; total, 6 1/2 hr.	3 heating periods; total, 25 hr.
1.00	Wüstite + spinel	Wüstite + spinel
0.97	Spinel + sl. tr. wüstite	Spinel + some wüstite
0.96	Spinel only	
0.71	Spinel + sl. tr. $\alpha$ -oxide	Spinel + sl. tr. $\alpha$ -oxide
0.31	Ortho. + tr. $\alpha$ -oxide	Ortho. + tr. $\alpha$ -oxide

Ortho. = orthorhombic oxide, tr. = trace, sl. tr. = slight trace.

## (2) Reproducibility of Results

Two regions of this investigation in which satisfactory results were difficult to obtain are discussed in some detail:

(a) In air at 1-cm. Hg pressure, particularly at high iron contents, the results showed rather poor reproducibility. As shown in Table I(a), at Fe/(Fe + Ti) = 0.93 two results indicated one phase, and one result indicated two phases. The data of Darken and Gurry<sup>2</sup> indicate that hematite ( $\alpha$ -oxide) is the stable phase in the system Fe-O at the oxygen partial pressure given by this atmosphere. Hence, the single-phase results were accepted. The low-iron boundary of the  $\alpha$ -oxide region is also somewhat uncertain for this particular atmosphere.

(b) Results obtained on samples subjected to two different equilibration procedures in a carbon monoxide-carbon dioxide mixture (CO/CO<sub>2</sub> = 0.157) are reported in Table I(b). All the X-ray diffraction patterns obtained were identical except for the proportion of wüstite observed for the composition with Fe/(Fe + Ti) = 0.97. The data of Darken and Gurry<sup>2</sup> indicate, however, that, in the system Fe-O under this atmosphere at 1200°C., wüstite is the stable phase. The observed spinel in the "all-iron" sample shown in Table I(b) must therefore have been formed by the disproportionation of the wüstite during cooling. The agreement of the results at the lower iron contents was good.

## (3) The System FeO-Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>

The system FeO-Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> at eight different oxygen partial pressures at 1200°C. is shown in Figs. 4(a) and 4(b). The compositions, plotted in mole %, were determined by chemical analysis after equilibration with the atmosphere under consideration. The three parallel straight lines on each composition triangle denote the stoichiometric compositions of the three principal solid-solution series: spinel,  $\alpha$ -oxide, and orthorhombic oxide. As would be expected, the proportion of ferrous iron with respect to ferric iron increases as the oxygen partial pressure decreases. At the lowest oxygen partial pressure plotted, viz.,  $2.9 \times 10^{-12}$  atm., the oxygen isobar leaves the FeO-Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> composition triangle. This can be attributed to the presence of trivalent titanium in the orthorhombic phase.

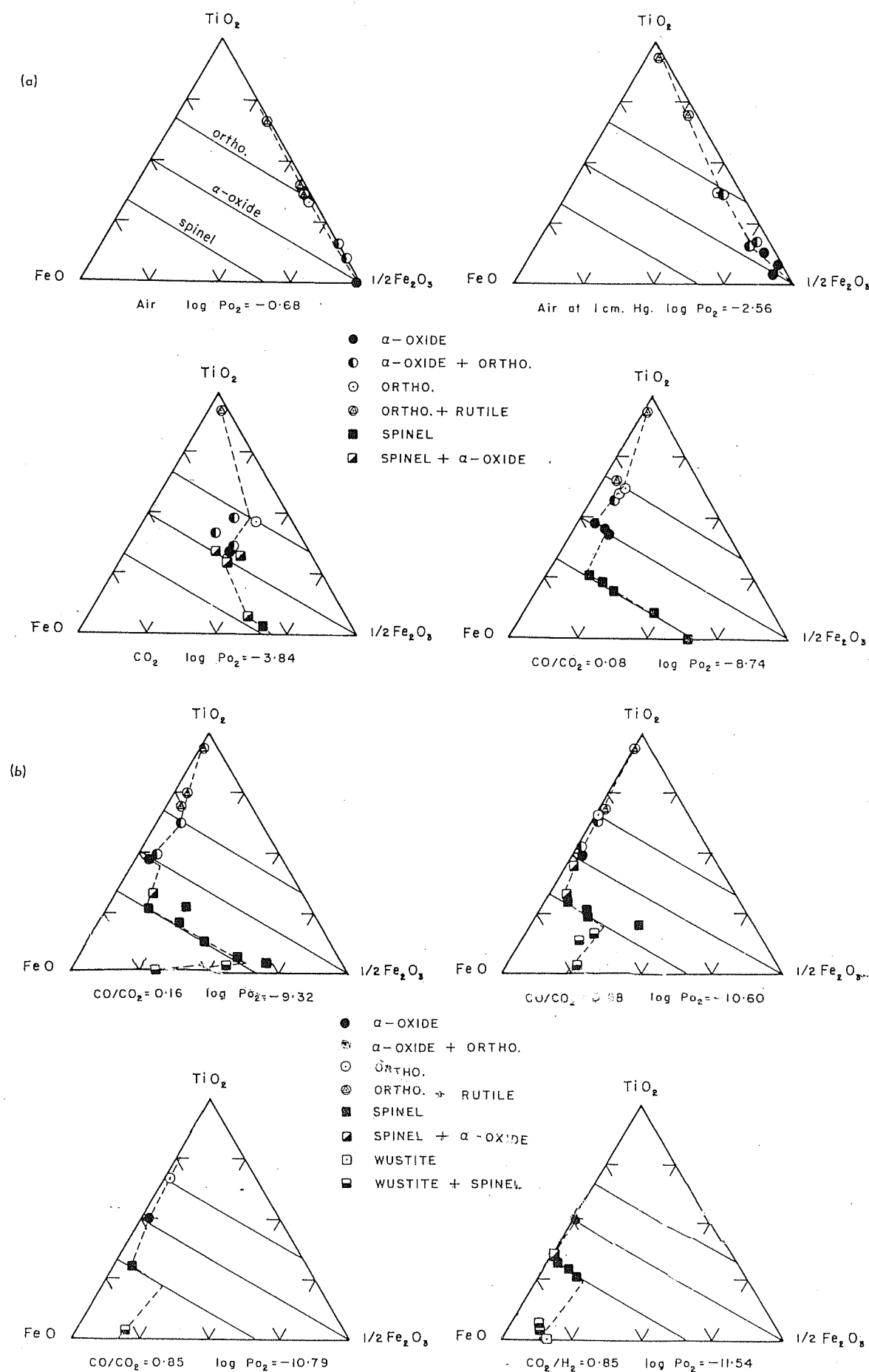


Fig. 4. The system  $FeO-Fe_2O_3-TiO_2$  at  $1200^\circ C$ . under eight different oxygen partial pressures. Compositions are expressed in mole %. [Ortho. = orthorhombic oxide.]

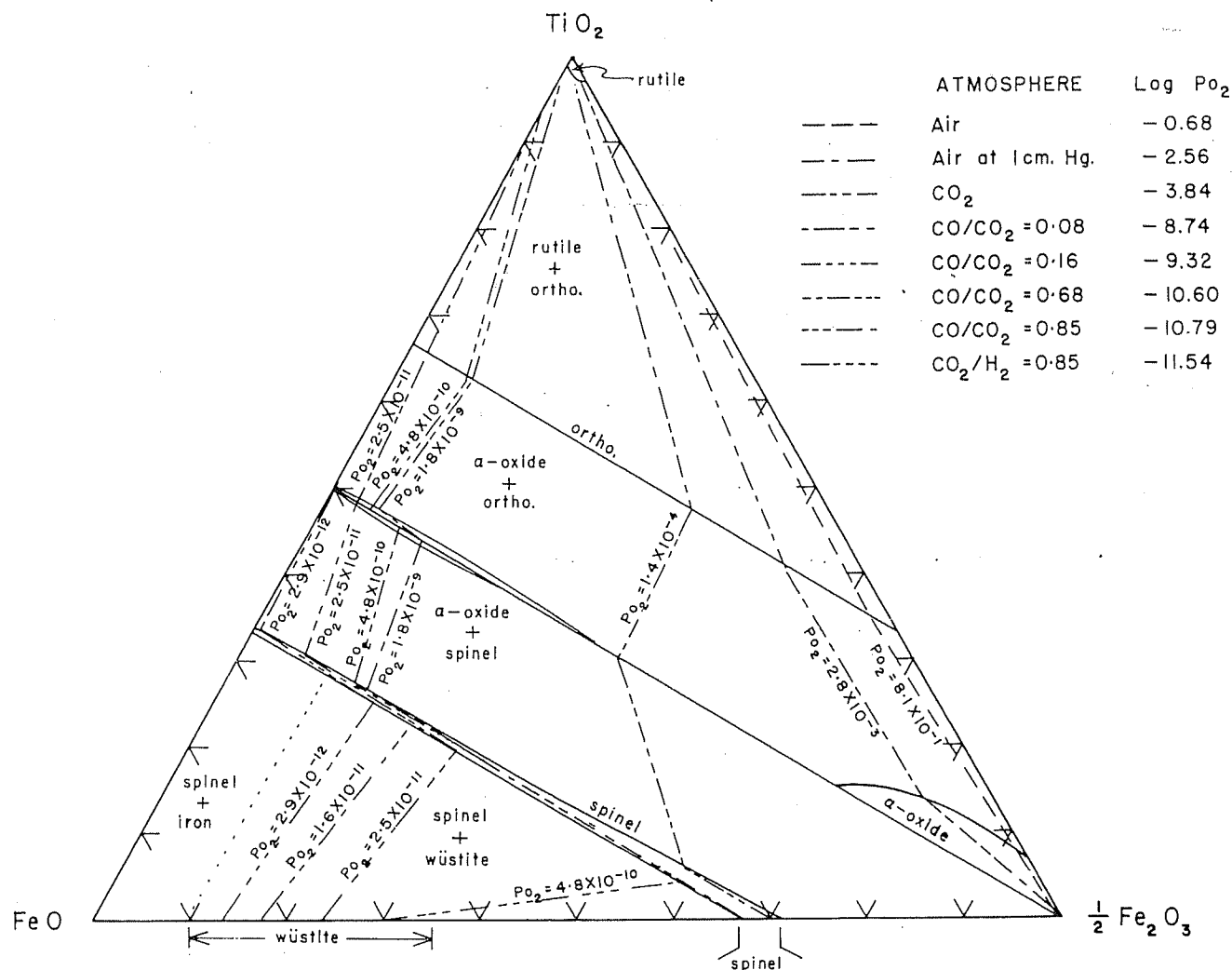


Fig. 5. The system  $\text{FeO}-\text{Fe}_2\text{O}_3-\text{TiO}_2$  at  $1200^\circ\text{C}$ ., showing oxygen isobars. Compositions are expressed in mole %. The  $1.6 \times 10^{-11}$  atm. isobar is shown in the (wüstite + spinel) field only, since it is almost coincident with the  $2.5 \times 10^{-11}$  atm. isobar in other fields. The  $4.8 \times 10^{-10}$  and  $1.8 \times 10^{-9}$  atm. isobars are similarly almost coincident within the spinel field and are represented by one line only, the experimental points in this field not being resolvable into two discrete lines. (Ortho. = orthorhombic oxide.)

The composite diagram combining the results of all these atmospheres is shown in Fig. 5. The areas in the composition plot corresponding to nonstoichiometric spinel and  $\alpha$ -oxide will be noted. The boundary between the (iron + spinel) region and the (wüstite + spinel) region was determined, using the Fe/(Fe + Ti) ratio of the spinel stable at the decomposition pressure of wüstite as read from Fig. 1. The wüstite and spinel compositions plotted on the FeO-Fe<sub>2</sub>O<sub>3</sub> axis were taken from the results of Darken and Gurry.<sup>2</sup>

This diagram indicates once again the marked stability of the spinel phase with respect to oxidation to  $\alpha$ -oxide and reduction to wüstite.

#### IV. Discussion

The results presented indicate that, at 1200°C., ilmenite ( $\text{FeTiO}_3$ ) can be reduced to an orthorhombic phase with partial reduction of the iron to the metallic state. In previous investigations conducted at lower temperatures, rutile was observed together with metallic iron as the reduction products of ilmenite. Extrapolation of the results of Shomate, Naylor, and Boericke<sup>5</sup> gives  $p_{\text{O}_2} = 6.0 \times 10^{-14}$  atm. as the oxygen partial pressure below which ilmenite decomposes at 1200°C., as compared with the figure of  $p_{\text{O}_2} = 9.3 \times 10^{-14}$  atm. found in the present investigation. This difference can be attributed to the difference in the products of reduc-

tion. In this connection, it is of interest to note that Walsh and co-workers,<sup>1</sup> in studying the reduction of ilmenite ores, observed rutile at low temperatures (generally below 1000°C.) but the orthorhombic phase at higher temperatures.

MacChesney and Muan<sup>6</sup> showed that the  $\alpha$ -oxide (hematite), orthorhombic oxide (pseudobrookite), and rutile all exist as single phases in air over a range of Fe/(Fe + Ti) ratios. The absence of a single-phase region of significant width for the orthorhombic phase, and the small extent of the single-phase region for the rutile phase, as found in the present investigation, are attributable to the lower temperature at which this investigation was conducted. The absence of solid solution in these two phases in air was reported by Karkhanavala and Momin<sup>7</sup> for temperatures up to 1200°C. These workers, however, did not detect any solid solution of titanium oxide in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, in contrast to the results of the present investigation; no explanation for this discrepancy is apparent.

## V. Summary

(1) The system Fe-Ti-O has been studied at 1200°C. over a wide range of oxygen partial pressures.

(2) The oxygen partial pressures below which ulvöspinel and ilmenite can be reduced to yield free metallic iron were determined as  $2.1 \times 10^{-13}$  and  $9.3 \times 10^{-14}$  atm., respectively.



(3) The orthorhombic phase was stable over the full range of oxygen partial pressures investigated.

(4) The marked stability of the spinel phase was noted.

(5) Some nonstoichiometry was observed in the  $\alpha$ -oxide and spinel solid-solution series.

(6) An inflection in the  $\log p_{O_2}$  vs.  $Fe/(Fe + Ti)$  plot for the  $\alpha$ -oxide solid-solution series was attributed to the proximity of the miscibility gap in this series at lower tempera-

tures. Similar inflections in the orthorhombic oxide series may indicate discontinuities in this series at temperatures lower than 1200°C.

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# Mechanism of Solid-State Reaction Between Magnesium Oxide and Aluminum Oxide and Between Magnesium Oxide and Ferric Oxide

by R. E. CARTER

Research Laboratory, General Electric Company, Schenectady, New York

Inert marker experiments have shown that the solid-state reactions forming  $MgAl_2O_4$  and  $MgFe_2O_4$  occur by counterdiffusion of the  $Mg^{2+}$ ,  $Fe^{3+}$ , and  $Al^{3+}$  ions through the relatively rigid oxygen lattice of the spinel or ferrite. It is suggested that earlier claims that  $ZnAl_2O_4$  forms by diffusion of  $Zn^{2+}$  and  $O^{2-}$  ions were probably due to a splitting of the markers, leaving some marker on the specimen surface. Pores in one component of a reacting couple are shown to serve as inert markers. The formation of those materials, e.g., ferrites and stannates, which dissolve marker materials can now be studied.

## I. Introduction

ALMOST all ceramics are formed by solid-state reactions. Although most such reactions are recognized as being diffusion-controlled, the mechanism is not as well understood as that of analogous tarnishing reactions. Koch and Wagner<sup>1</sup> first indicated that such reactions could occur by counterdiffusion of the cations of the reactants through the anion lattice of the product. In 1936<sup>1</sup> this mechanism was demonstrated for the formation of  $Ag_2HgI_4$  from  $AgI$  and  $HgI_2$ , the iodide ions forming a relatively rigid lattice. At this time a similar mechanism was suggested for the formation of  $MgAl_2O_4$ .

In 1947, however, Bengtson and Jagitsch<sup>2</sup> by means of inert markers showed that  $Al_2O_3$  and  $ZnO$  react by diffusion of the  $ZnO$  through the  $ZnAl_2O_4$  to the  $ZnAl_2O_4$ - $Al_2O_3$  interface. In recent years the mechanism of solid-state reactions has been examined by Lindner and co-workers.<sup>3</sup> These investigators have usually compared the kinetics of compound formation with cation diffusion rates through the product layer and in a few cases have made marker studies. The comparison of the reaction and diffusion rates indicated that  $ZnFe_2O_4$ ,  $ZnCr_2O_4$ ,  $NiCr_2O_4$ , and  $Zn_2SnO_4$  form by the Wagner mechanism, although diffusion of  $O^{2-}$  ions is not excluded if the diffusion rate of  $O^{2-}$  ions were fortuitously near that of the cations. Earlier, Hopkins had indicated that  $Fe_2O_3$  diffused through  $ZnFe_2O_4$ , although the evidence was

only circumstantial.<sup>4</sup> From marker studies, however, Lindner *et al.* concluded that  $ZnAl_2O_4$  and  $NiAl_2O_4$  form by diffusion of  $Zn^{2+}$ ,  $Ni^{2+}$ , and  $O^{2-}$  ions through the aluminate.

The problem is therefore confused. Why should ferrites, chromites, and stannates form by one mechanism and the aluminates by another? The structures and lattice parameters are almost identical and as Lindner<sup>3(a)</sup> has discussed, no consistent hypothesis can be developed relating ion mobilities in terms of valence or coordination.

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The writer is ceramist, Ceramic Studies Section, Metallurgy and Ceramic Research Department, Research Laboratory, General Electric Company.

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