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THE SYSTEM IRON OXIDE-MANGANESE OXIDE IN AIR*

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ABSTRACT. Phase relations in the system iron oxide–manganese oxide in air have been determined by the quenching technique. The system is not binary because of varying oxidation states of iron as well as manganese. The following crystalline phases occur in the temperature interval studied in the present investigation (800 to 1585°C): Spinel solid solution (approximately Fe_3O_4–Mn_3O_4); hematite solid solution (Fe_2O_3 with some manganese oxide dissolved in its structure); Mn_2O_3 solid solution (α-Mn_2O_3 with some iron oxide dissolved in its structure); tetragonal Mn_3O_4 solid solution (Mn_3O_4 with some iron oxide dissolved in its structure).

There are two isobaric invariant situations in the system. At 932 ± 5°C Mn_2O_3 solid solution, spinel solid solution and tetragonal Mn_3O_4 solid solution are in equilibrium with gas ($pO_2 = 0.21$ atm). At 997 ± 5°C hematite solid solution, Mn_2O_3 solid solution and spinel solid solution coexist in equilibrium with gas ($pO_2 = 0.21$ atm).

Melting relations of mixtures in this system are characterized by liquidus and solidus curves going through a temperature minimum of 1565 ± 5°C.

A plot of d-spacing versus composition for the spinel solid solution series (Fe_3O_4–Mn_3O_4) shows a pronounced change in slope of the curve at approximately 32 wt % manganese oxide. In the hematite and Mn_2O_3 solid solution phases the d-spacings change relatively little with composition, and X-ray methods are not practical as tools for determining compositions of these phases.

INTRODUCTION

Very few phase equilibrium studies have been reported for systems containing oxides of more than one transition element. The present investigation deals with one important such system, the combination iron oxide–manganese oxide. The study was carried out at the constant oxygen potential provided by air, $pO_2 = 0.21$ atm.

Of the two bounding binary systems Fe–O and Mn–O, the former has been studied in great detail, the latter only sparingly.

Stability relations existing among the various oxides of iron have been determined by Greig, Posnjak, Merwin, and Sosman (1935) and later by Darken and Gurry (1945, 1946) and by Phillips and Muan (1960). Particularly pertinent to our study are the phase relations prevailing as iron oxide is heated under equilibrium conditions in air. Hematite (Fe_2O_3) is the stable phase under these conditions up to approximately 1390°C, and magnetite (Fe_3O_4) is stable from 1390°C to the melting temperature, 1591°C.

Some of the high temperature equilibrium relations of manganese oxides have been established recently by Muan and Hahn (1959) and by Hahn and Muan (1960). The oxide Mn_2O_3 is stable in air only up to 877°C. At this temperature it decomposes, under equilibrium conditions, to the tetragonal ("low") form of hausmannite (Mn_3O_4), which is stable to approximately 1160°C (Van Hook and Keith, 1958). The tetragonal form inverts to the cubic form of hausmannite at this temperature, and the latter exists as a stable phase up to the melting temperature in air, 1567°C.

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Phase relations existing in mixtures of iron oxide and manganese oxide have been investigated only sporadically. Mason (1943) was interested in the conditions prevailing during formation of natural hausmannites and conducted laboratory experiments to delineate stability relations existing in parts of the system Fe–Mn–O. The diagram reproduced in figure 1 shows his conception of phase relations in air from approximately 600 to 1000°C. Mason sketched an "approximate dissociation curve" (dashed in fig. 1) with a continuously changing tangent slope. This curve in reality must have discontinuities in its slope corresponding to various phase changes, as will be shown later in the present paper.

Bergstein, Rozsival, and Mikulaš (1959) reported chemical compositions and phases present in two iron oxide-manganese oxide mixtures cooled to room temperature following heating for three and one-half hours in air at temperatures ranging from 400 to 1350°C.

Shafer (1958) studied melting relations of iron oxide-manganese oxide mixtures in various atmospheres.

Van Hook and Keith (1958) investigated phase relations in the system Fe_3O_4–Mn_3O_4. They contained mixtures of the two stoichiometric oxides in sealed platinum tubes in order to prevent oxidation at low temperatures. Their results were in essential agreement with those previously reported (McMurdie and Golovato, 1948; McMurdie, Sullivan, and Maur, 1950). The two cubic structures form a complete solid solution series (spinel) above 1160°C. The

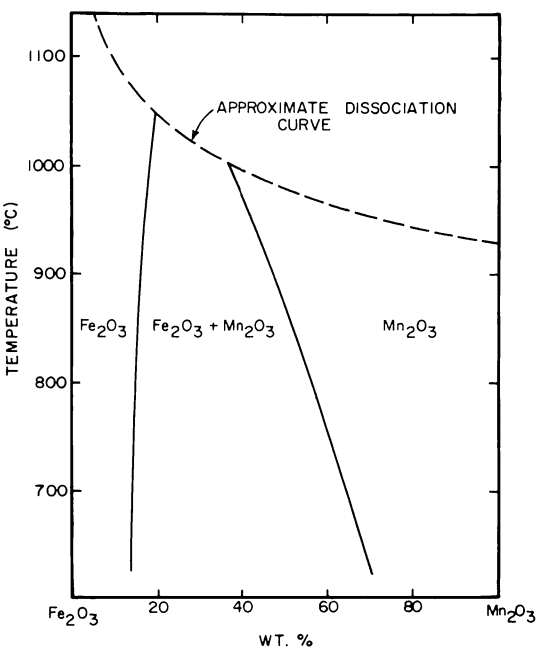

Fig. 1. Diagram showing phase relations in the system Fe_2O_3–Mn_2O_3 in air after Mason (1943).

inversion at 1160°C from tetragonal to cubic hausmannite was found to be lowered drastically as Fe_3O_4 was added to manganese oxide, giving rise to a two-phase region where tetragonal hausmannite and a spinel solid solution phase coexist in equilibrium at lower temperatures. Van Hook and Keith also obtained data for the liquidus temperature region, and reported the existence of a minimum at approximately 67 wt % Mn_3O_4 and 1543°C in the system Fe_3O_4–Mn_3O_4 (stoichiometric oxides).

EXPERIMENTAL METHODS

General procedure.—Phase relations were determined by the quenching technique. Oxide samples made up from pure chemicals were heated in air until equilibrium was established among condensed phases and gas. The samples were then quenched rapidly to room temperature and the phases present determined by X-ray and occasionally by microscopic examination.

Starting materials.—Analytical grade chemicals served as starting materials. "Baker Analyzed" Fe_2O_3 was the source of iron oxide and "Baker Analyzed" MnO_2 was the source of manganese oxide. These materials were weighed and mixed in desired proportions and heated slowly to sintering temperatures in order to decompose MnO_2 in successive steps to Mn_3O_4. The final heating was carried out at approximately 1000°C for 24 hours. These mixtures were used as starting materials in most of the equilibration runs. Other samples, obtained by heating the mixtures at lower temperatures, were occasionally used as starting materials in order to check that true equilibrium was reached in the subsequent quench runs.

Furnaces and temperature control.—Equilibration runs were made in a conventional vertical-tube quench furnace with resistance winding of an 80 percent platinum 20 percent rhodium alloy.

Temperatures were kept constant by a commercial electronic controller connected to a thermocouple inserted close to the hot spot of the furnace. In this way constancy of temperature could be maintained to approximately ± 2°C.

Actual temperatures in the furnace were measured with a platinum—90 percent platinum 10 percent rhodium thermocouple calibrated at melting points defined as follows: Gold (Au), 1063°C; diopside ($CaMgSi_2O_6$), 1391.5°C; pseudowollastonite ($CaSiO_3$), 1544°C. Temperatures thus defined are in accordance with the Geophysical Laboratory Scale, which is almost identical to the 1948 International Scale in this region. Temperatures above 1550°C have been converted to the 1948 International Scale.

Examination of quenched samples.—The phases present in quenched samples were determined mainly by X-ray methods, using a Norelco spectrometer unit with iron radiation. Accurate d-spacing measurements for quantitative determination of compositions of solid solution crystals were carried out on a GE-XRD-3 spectrometer unit, using NaCl as internal standard in all samples.

Boundary curves in the liquidus temperature region were determined by reflected light examination of polished samples under an ore microscope. Although the very fluid liquids occurring in this system gave rise to extensive

formation of dendritic quench crystals even upon most rapid quenching. these crystals could be distinguished by shape and size from those grown under equilibrium conditions in contact with liquids at the high temperatures of the quench runs.

RESULTS

Results obtained in the present investigation are listed in table 1 and shown graphically in figure 2. The system iron oxide–manganese oxide in air is not binary because both iron and manganese are present in varying degrees

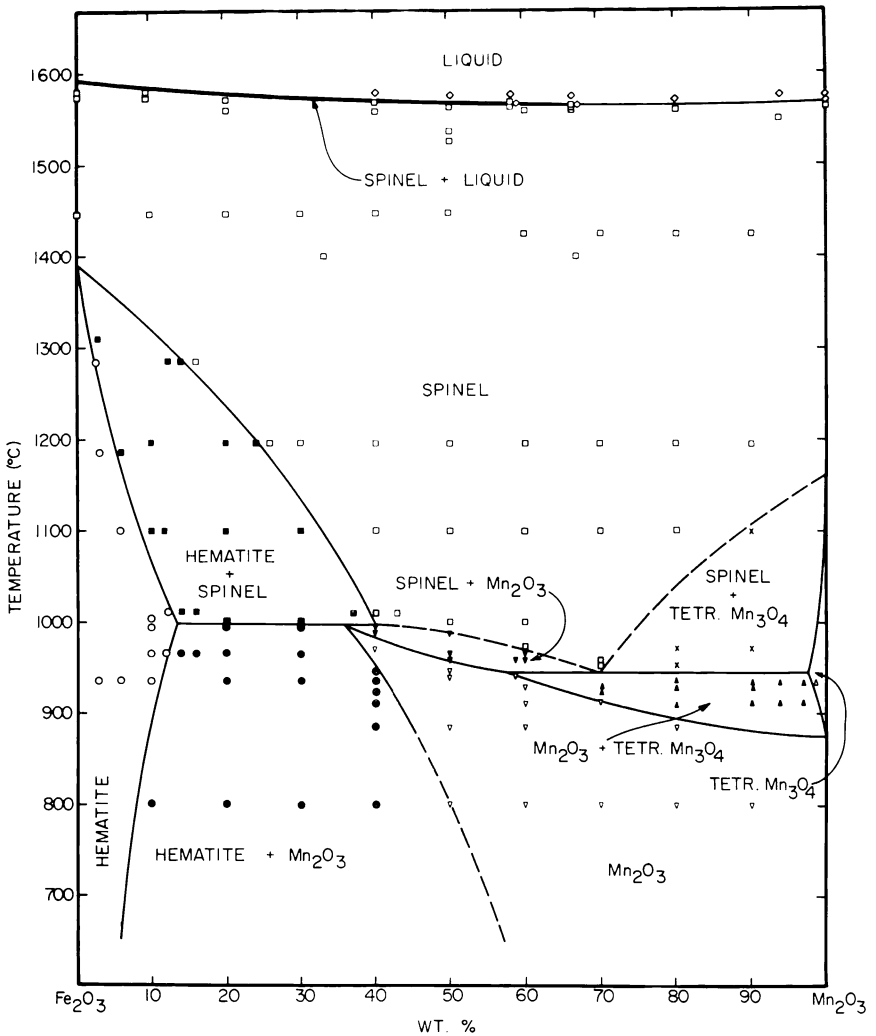

Fig. 2. Diagram showing phase relations in the system iron oxide–manganese oxide in air, as determined in the present investigation. A different symbol is used to designate each phase assemblage, as seen from the diagram.

TABLE 1

Results of equilibration experiments

Composition of Mixture (Wt %) Fe_2O_3	Mn_2O_3	Temp. (°C)	Time (hrs)	Phases Present* and Observed d-Spacings (A)
100	0	1447	48	Magn. (1.4849)
97	3	1309	48	Hem. + Spin.
		1285	48	Hem.
		1185	48	Hem.
		936	84	Hem. (1.6947)
94	6	1185	48	Hem. + Spin.
		1100	47	Hem.
		936	84	Hem. (1.6945)
90	10	1585	24	Spin. + trace Liq.
		1580	24	Spin.
		1575	24	Spin.
		1447	58	Spin. (1.4903)
		1196	47	Hem. (1.6947) + Spin. (1.4998)
		1101	84	Hem. (1.6943) + Spin. (1.5037)
		1003	59	Hem.
		994	171	Hem.
		965	68	Hem. (1.6945)
		936	82	Hem. (1.6945)
		800	72	Hem. (1.6943) + Mn_2O_3
88	12	1285	48	Hem. + Spin.
		1010	68	Hem.
		965	72	Hem.
86	14	1285	48	Hem. + Spin.
		1010	68	Hem. + Spin.
		965	72	Hem.
84	16	1285	48	Spin.
		1010	68	Hem. + Spin.
		965	72	Hem. + Mn_2O_3
80	20	1570	11	Spin.
		1559	12	Spin.
		1447	58	Spin. (1.4978)
		1196	47	Hem. (1.6947) + Spin. (1.5013)
		1101	84	Hem. (1.6941) + Spin. (1.5040)
		1001	93	Hem. + Spin. + Mn_2O_3
		994	171	Hem. + Mn_2O_3
		965	68	Hem. (1.6939) + Mn_2O_3 (1.6638)
		936	82	Hem. (1.6939) + Mn_2O_3 (1.6634)
		800	72	Hem. (1.6945) + Mn_2O_3 (1.6640)
70	30	1447	58	Spin. (1.5038)
		1195	78	Spin. (1.5032)
		1101	84	Hem. (1.6947) + Spin. (1.5052)
		1001	93	Hem. + Spin. + Mn_2O_3
		994	171	Hem. + Mn_2O_3
		965	68	Hem. (1.6939) + Mn_2O_3 (1.6634)
		936	82	Hem. (1.6939) + Mn_2O_3 (1.6634)
		800	72	Hem. (1.6943) + Mn_2O_3 (1.6638)

TABLE 1 (Continued)

Composition of Mixture (Wt %) Fe_2O_3	Mn_2O_3	Temp. (°C)	Time (hrs)	Phases Present* and Observed d-Spacings (A)
66.9	33.1	1400	45	Spin. (1.5055)
60	40	1579	24	Liq.
		1570	11	Spin.
		1559	12	Spin.
		1447	58	Spin. (1.5057)
		1195	78	Spin. (1.5056)
		1101	84	Spin.
		1010	59	Spin.
		994	171	Mn_2O_3 + Spin. (1.5063)
		987	48	Mn_2O_3 (1.6636) + Spin. (1.5064)
		970	68	Mn_2O_3
		945	72	Hem. + Mn_2O_3
		936	82	Hem. + Mn_2O_3
		923	48	Hem. + Mn_2O_3
		911	55	Hem. + Mn_2O_3
		884	62	Hem. + Mn_2O_3 (1.6636)
		800	72	Hem. (1.6945) + Mn_2O_3 (1.6636)
50	50	1575	24	Liq.
		1562	24	Spin.
		1537	20	Spin.
		1527	24	Spin.
		1447	58	Spin. (1.5066)
		1195	78	Spin. (1.5066)
		1101	84	Spin. (1.5064)
		1001	93	Spin.
		987	48	Mn_2O_3 + Spin.
		965	68	Mn_2O_3 + Spin.
		958	120	Mn_2O_3 + Spin.
		945	72	Mn_2O_3
		940	58	Mn_2O_3 (1.6636)
		884	62	Mn_2O_3 (1.6640)
		800	72	Mn_2O_3 (1.6638)
40	60	1559	12	Spin.
		1424	48	Spin. (1.5071)
		1195	78	Spin. (1.5072)
		1100	48	Spin.
		999	171	Spin. (1.5074)
		973	93	Spin.
		965	68	Mn_2O_3 + Spin.
40	60	958	123	Mn_2O_3 + Spin.
		928	85	Mn_2O_3 (1.6642)
		911	55	Mn_2O_3
		884	62	Mn_2O_3 (1.6642)
		800	72	Mn_2O_3 (1.6642)
39	61	1575	24	Liq.
		1566	24	Spin. + Liq.
		1562	24	Spin.
		960	72	Mn_2O_3 + Spin.
		940	72	Mn_2O_3

TABLE 1 (Continued)

Composition of Mixture (Wt %) Fe_2O_3	Mn_2O_3	Temp. (°C)	Time (hrs)	Phases Present* and Observed d-Spacings (A)
33.6	66.4	1575	24	Liq.
		1565	24	Spin. + Liq.
		1563	24	Spin.
		1559	24	Spin.
		1400	45	Spin.
30	70	1424	48	Spin.
		1196	47	Spin.
		1100	48	Spin.
		958	123	Spin.
		952	72	Spin.
		928	85	Mn_2O_3 (1.6642) + Tetr. Mn_3O_4
		923	48	Mn_2O_3 + Tetr. Mn_3O_4
		911	55	Mn_2O_3
		800	72	Mn_2O_3 (1.6646)
20	80	1570	11	Liq.
		1559	12	Spin. **
		1424	48	Spin. **
		1196	47	Spin. **
		1100	48	Spin. **
		973	93	Spin. ** + Tetr. Mn_3O_4
		953	72	Spin. + Tetr. Mn_3O_4
		937	380	Mn_2O_3 + Tetr. Mn_3O_4
		928	85	Mn_2O_3 (1.6642) + Tetr. Mn_3O_4
		911	55	Mn_2O_3 (1.6642) + Tetr. Mn_3O_4
		800	72	Mn_2O_3 (1.6646)
10	90	1424	48	
		1196	47	Spin. **
		1100	48	Spin. + Tetr. Mn_3O_4
		973	93	Spin. + Tetr. Mn_3O_4
		936	380	Mn_2O_3 + Tetr. Mn_3O_4
		928	85	Mn_2O_3 (1.6640) + Tetr. Mn_3O_4
		913	68	Mn_2O_3 (1.6646)
		800	72	Mn_2O_3 (1.6644)
6	94	1570	24	Liq.
		1550	24	Spin. **
		936	82	Mn_2O_3 (1.6644) + Tetr. Mn_3O_4
		913	68	Mn_2O_3 (1.6644) + Tetr. Mn_3O_4
3	97	936	82	Mn_2O_3 + Tetr. Mn_3O_4
		913	68	Mn_2O_3 + Tetr. Mn_3O_4
1.5	98.5	937	380	Tetr. Mn_3O_4
0	100	1568	24	Liq.
		1565	24	Mn_3O_4

* Abbreviations used have the following meanings: Magn. = crystals of magnetite; Hem. = crystals of hematite with some manganese oxide in solid solution; Spin. = solid solution crystals (approximately Fe_3O_4–Mn_3O_4) with spinel structure; Liq. = liquid; Tetr. = tetragonal.

** This spinel transforms to a tetragonal phase during quenching.

of oxidation. The two components Fe_2O_3 and Mn_2O_3 have been chosen for purpose of easy illustration of the phase relations.

Designations used in labeling crystalline phases in the diagram are: Hematite (Fe_2O_3 with some Mn_2O_3 in solid solution), spinel (a solid solution between magnetite (Fe_3O_4) and high hausmannite (Mn_3O_4)), Mn_2O_3 (con-

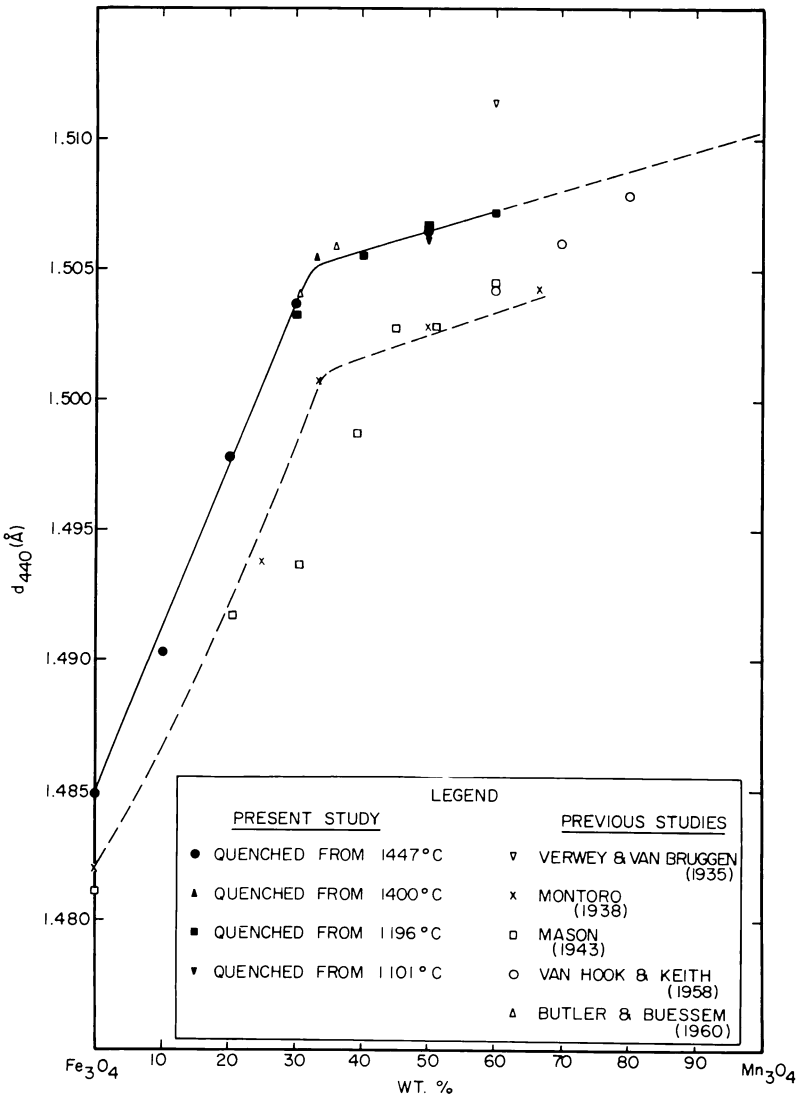

Fig. 3. Diagram showing variation in d-spacing with composition for (440)-reflection in spinel solid solutions, as determined in the present investigation and as reported in previous literature (Verwey and Von Bruggen, 1935; Montoro, 1938; Mason, 1943; Van Hook and Keith, 1958; Butler, 1960).

taining some Fe_2O_3 in solid solution), Mn_3O_4 (containing some Fe_3O_4 in solid solution).

The most prominent features of the diagram are as follows: The decomposition of hematite to magnetite, which in air takes place at 1390°C in the pure iron oxide system, decreases to a minimum of 997°C as manganese oxide is added. Decomposition of Mn_2O_3 to tetragonal Mn_3O_4, which takes place at 877°C in pure manganese oxide in air, increases to a maximum of 932°C as iron oxide is added. Inversion from the tetragonal to the cubic form of Mn_3O_4, which takes place at approximately 1160°C in the system Mn–O, decreases to a minimum of 932°C upon iron oxide addition. Phase assemblages and temperatures of two isobaric binary invariant situations in the system are as follows: At 997°C hematite with ~ 13 wt % Mn_2O_3 in solid solution, Mn_2O_3 with ~ 64 wt % Fe_2O_3 in solid solution, spinel (~ 60 wt % Fe_3O_4, 40 wt % Mn_3O_4) and gas (pO_2 = 0.21 atm) coexist in equilibrium. At 932°C spinel (~ 30 wt % Fe_3O_4, 70 wt % Mn_3O_4), Mn_2O_3 with ~ 42 wt % Fe_2O_3 in solid solution and tetragonal Mn_3O_4 with ~ 2 wt % Fe_3O_4 in solid solution are present together with gas (pO_2 = 0.21 atm) in stable equilibrium. Liquidus temperatures decrease very slightly from either end of the system, with solidus as well as liquidus curves having a minimum of approximately 1565°C.

DISCUSSION

The data obtained in the present investigation are in good agreement with those reported by Mason (1943) for the mutual solubilities of Fe_2O_3 and Mn_2O_3 at temperatures up to approximately 1000°C. The smooth curve representing temperatures of dissociation of the sesqui-oxide phase according to Mason is, however, only a rough approximation. The actual course of this curve can be traced in figure 2 as the boundary curve marking the lower temperature limit of the areas in which spinel or tetragonal Mn_3O_4 is present in the phase assemblage. Starting at the iron oxide end of the system, the curve descends from the 1390°C point corresponding to the hematite-magnetite

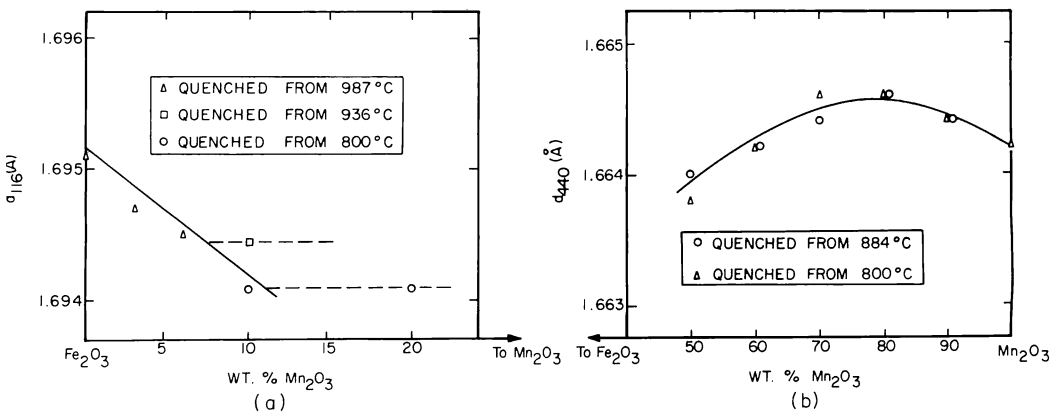

Fig. 4. Diagrams showing changes in d-spacing with composition for (116)-reflection in hematite and (440)-reflection in Mn_2O_3 crystals, as determined in the present investigation.

equilibrium in pure iron oxide, down to the 997°C point of the isobaric invariant situation where hematite, Mn_2O_3, spinel and gas coexist in equilibrium. The next part of the curve is a straight horizontal line connecting the points representing compositions of hematite and spinel at this invariant situation. From here on it follows the boundary curve between the phase fields of Mn_2O_3 and Mn_2O_3 plus spinel. The slope of the tangent to the curve changes discontinuously again at the isobaric invariant situation where Mn_2O_3, spinel, and tetragonal Mn_3O_4 coexist with gas, and from here on follows the smooth curve separating the area of Mn_2O_3 from that where Mn_2O_3 and tetragonal Mn_3O_4 are present together with gas.

The very small temperature decrease from the melting point of Mn_3O_4 to the minimum point on the liquidus and solidus curves is within the limit of error of the temperature measurements. Nevertheless, this minimum is thought to exist, as indicated by the following observations: A mixture containing 33.6 wt % Fe_2O_3, 66.4 wt % Mn_2O_3 was run in the quench furnace side by side with a sample of 100 percent Mn_3O_4. The former sample after quenching gave conclusive evidence of having contained liquid, the latter was completely powdery. Also, the courses of the fractionation curves determined by Muan and Somiya (1961) for the system iron oxide–manganese oxide–SiO_2 in air indicate strongly that a minimum exists on the liquidus and solidus curves in the system iron oxide–manganese oxide in air.

A plot of d-spacing for (440) reflections of the spinel phase versus composition shows a distinct change in the slope of the curve at approximately 32 wt % Mn_3O_4, as illustrated in figure 3. In this graph are plotted data obtained in the present investigation as well as those obtained by previous investigators: Verwey and Von Bruggen (1935), Montoro (1938), Mason (1943), Van Hook and Keith (1958), Butler (1960). Although the d-spacing values determined in the present study are slightly higher than those of Montoro (1938), the slopes of the curves are very similar, and the same characteristic break in slope is seen to be present in both curves. This is in contrast to the observations of Mason (1943), who stated:

> "Montoro's curve for the variation of lattice dimensions with composition also shows an irregularity at 33.3% Mn_3O_4, which he ascribed to the presence of a compound, $MnO.Fe_2O_3$, manganous ferrite. I believe that this irregularity is more imaginary than real, being within the possible limit of error in determining the lattice dimensions."

The data obtained in the present study refute Mason's objections to Montoro's work. The change in slope of the curve at approximately 32 wt % Mn_3O_4 probably results from a change in the manner of substitution of manganese for iron as this manganese concentration is reached.

Only very small changes in d-spacings with compositions of the hematite and Mn_2O_3 phases were observed (fig. 4), in agreement with the findings of Montoro (1938). X-ray methods were therefore not suitable for determining compositions, and hence boundary curves, where the solid solution crystals above were involved. It is interesting to note that d-spacing values of Mn_2O_3 first increase slightly with increasing iron oxide content (up to approximately 20 wt %) and subsequently decrease as more iron oxide is added.

ACKNOWLEDGMENTS

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