THE SYSTEM MgO-FeO-Fe_2O_3 IN AIR AT ONE ATMOSPHERE.

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A comprehensive statement of equilibria in a system containing iron oxides would demand an investigation under a wide range of oxygen pressures as well as of temperatures. The present investigation is an attempt to determine the nature of the solid phases in one such system in equilibrium with air at atmospheric pressure and at temperatures above 1,000°. Consequently the single oxygen pressure is the partial pressure of oxygen in the atmosphere of the laboratory, approximately 150 mm., and the results represent an isobaric surface in the temperature-concentration diagram.

Parts of the binary system iron-oxygen have been the subject of several investigations.[1]

In the binary system MgO-Fe_2O_3 a number of investigators have noted the occurrence of magnesioferrite in magnesite refractories. The term "magnesioferrite" has been employed by mineralogists to designate a mineral isomorphous with magnetite and containing considerable MgO. In magnesite refractories it is presumably saturated with MgO and has a composition close to $MgO.Fe_2O_3$. The compound is described as occurring as inclusions in the grains of periclase (MgO), and the latter are colored brown or red, presumably by a ferric oxide compound in solid solution. K. A. Redlich[2] examined a sample of magnesite refractory that had been in use for a long time in the lining of a steel furnace. It was found to consist chiefly of a single black material which he thought was probably magnesioferrite.[3]

Nacker and Grünewald[4] in their investigation of the system MgO-Fe_2O_3 found that apparently $MgO.Fe_2O_3$ is the only compound formed by the interaction of these oxides. By heating a mixture of the two oxides with a flux of KCl Weyl[5] was able to form crystals large enough to be identified as a spinel.

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[1] See O. C. Ralston, U. S. Bureau of Mines Bulletin, No. 296, 1929, for a nearly complete summary and discussion.

[2] Doelter's Handbuch der Mineralchemie, 1, 255, 1912.

[3] McDowell and Howe, J. Am. Ceram. Soc., 3, 185-246, 1920, give an interesting account of magnesite refractories with a bibliography up to 1920.

[4] Zement, 15, 614, 1926.

[5] Tonind. Ztg., 53, 559, 1929.

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Forestier and Chaudron[6] in a study of the points of magnetic transformation in the system MgO-Fe_2O_3 located the compound and in addition found a slight solution, extending from the compound to 53 molecular per cent Fe_2O_3. Their preparations were made by precipitating a mixture of the two chlorides with soda, washing, and heating at 400° to equilibrium.

PREPARATION AND EXAMINATION OF MATERIALS.

Our preparations were made directly from the two oxides MgO and Fe_2O_3. The stock supply of MgO was made by igniting a basic magnesium carbonate between 1,500° and 1,600°. Qualitative tests[7] of the ignited material indicated the presence of less than 0.01 per cent CaO, less than 0.025 per cent Fe_2O_3 and of no material insoluble in HCl. Fe_2O_3 was taken from the lot of Kahlbaum's "Eisenoxyd zur Analyse mit Garantieschein" that had been used and analyzed by Sosman and Hostetter.[8] They found it to contain 99.70 percent Fe_2O_3 and 0.09 per cent FeO.

Most of the compositions in this system approach their final equilibrium very slowly; this is true not only of the combining of magnesia and iron oxide but of the ferrous-ferric ratio as well. The attainment of homogeneity by fusion was out of the question for lack of a container that would not react with the charge. After some experiments the following method was adopted; mixtures of MgO and Fe_2O_3 were thoroughly rubbed together in an agate mortar and the mixture heated in alundum thimbles, usually at about 1,250°. After a day or two a thin layer of the charge was found to be tightly adherent to the inside of the thimble, forming a coating that protected the rest of the charge from contamination. The charge thus protected was removed from the thimble, daily at first, and ground. This process was then continued in the same thimble with longer intervals between grindings until microscopic examination made it evident that a steady state had been reached.

At temperatures below 1,500°[9] determination of the phases present was made by microscopical examination of a few milli-

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[6] Compt. rend., **181**, 509, 1925.

[7] According to the methods given in Merck's Chemical reagents, their purity and tests, Merck and Co., New York, 1914.

[8] J. Am. Chem. Soc., **38**, 822, 1916.

[9] Temperatures are here expressed in terms of the scale in use in the Geophysical Laboratory. On this scale the melting points of gold, palladium and platinum are 1,062.6°, 1,549.5° and 1,755° respectively.

grams of the prepared material that had been wrapped in thin platinum foil and heated in a platinum wound furnace. The charges were cooled by dropping them through the bottom of the furnace into water. This rapid cooling was essential in most cases because some of the crystalline phases were found to break up or oxidize when cooled slowly, making it difficult to be certain whether or not other or different phases had been present at the high temperature.

The ferrous iron content of preparations lying between $MgO.Fe_2O_3$ and the Fe_3O_4-Fe_2O_3 solid solutions was obtained from the loss of weight after heating to constant weight. After oxidizing the preparation for two weeks at about 750° they were placed in small platinum crucibles tightly covered with platinum foil to prevent the access of oxygen on cooling, and heated at constant temperature until lowering the temperature 10° resulted in a small gain in weight.

In the case of the Fe_3O_4-Fe_2O_3 solid solutions of $MgO.$-Fe_2O_3, and of compositions in the MgO solid solution field, the ferrous iron was obtained by analysis of the individual charges.

At temperatures above 1,600° we used a furnace consisting of a strip of an alloy of 60% platinum and 40% rhodium. The strip was 8 mm. wide and 0.01 mm. thick and was bent into the form of the letter U, 10 mm. deep and about 1.2 mm. wide. It was entirely uninsulated and was heated by an alternating current of from 20 to 30 amperes.[10] Temperatures were measured with an optical pyrometer standardized at the melting points of anorthite; 1,550°,[11] and of a mixture containing 15% MgO and 85% SiO_2, 1,695°.[12] The readings of the pyrometer at either of these melting points could be duplicated within 10°.

For phase determination a few milligrams of each preparation was heated on the strip, at a temperature close to that to be investigated, for 10 to 20 minutes. It was then ground very fine and about a milligram of it heated again for another ten minutes at constant temperature. On turning off the current the strip cools almost instantaneously so that there was no need for a special quenching.

For determination of melting temperatures the temperature

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[10] The furnace is described in detail by Roberts and Morey, Rev. Sci. Instr., **1**, 576-580, 1930.

[11] Rankin and Wright, this Journal, **39**, 26, 1915.

[12] Greig, this Journal, **13**, 14, 1927.

of the strip was raised in steps of about 10°, cooling and taking the strip to a binocular microscope each time to determine whether or not a liquid phase had been definitely present. These compositions are particularly favorable for this type of furnace, for crystals grow rapidly during heating but before melting, presumably from a vapor phase, and the crystals adhere tightly to the strip, making their temperature more uniform than would be the case with a loose powder. The chief uncertainty lies in the possibility that some of the iron is removed by solution in the strip.[13]

No attempt was made to determine the ferrous iron content of preparations heated at these higher temperatures.

THE BINARY SYSTEM Fe_3O_4-Fe_2O_3.

The published data indicate that for any given oxygen pressure there is a temperature, or less probably a narrow temperature interval, below which the stable oxide contains less oxygen than Fe_2O_3 and above which it contains more oxygen than Fe_3O_4.

The corresponding point (or interval), where the gas phase is air at one atmosphere, marks the iron oxide end of Curve VI in Fig. 1, since this curve represents the temperatures at which hematite disappears. It was located by heating small quantities of hematite or of magnetite wrapped in platinum foil. The temperature was maintained within ±0.5° for two hours and the charge quenched in water. The data are given in Table I. They indicate that below 1,386° ± 5° the solid phase is hematite and that above this temperature it is magnetite.

TABLE I.

Original composition wt.% FeO	Temperature[9] ± 5°	Phases
0.09	1,378.0	All hematite
0.09	1,390.6	Nearly all magnetite
0.09	1,385.5	A few isolated grains magnetite
26.	1,386.3*	About half hematite

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* The charge of "magnetite" was held for 30 minutes at about 1,450° to drive off any oxygen that may have combined with it before it reached the dissociation temperature. The temperature was then lowered to 1,386.3° and held for 2 hours.

[13] Sosman and Hostetter, The reduction of iron oxides by platinum, J. Wash. Acad. Sci., 5, 293-303, 1915.

A sample of hematite heated for 4 hours in air at 1,405° was found on analysis to contain 76% Fe_3O_4. Examination under the microscope revealed the presence of about 5% undissociated hematite, indicating that the dissociated portion contained at least 80% magnetite. Another sample heated 6 hours at 1,345° was found on analysis to contain 0.6% Fe_3O_4.

A considerable melting interval, indicating solid solution, was found for magnetite in an atmosphere of oxygen. A quantity of Fe_2O_3 was heated for some time at 1,420° and a portion of it was placed on the platinrhodium strip and melted in air. At 1,575° there was no evidence of melting, while at 1,585° it had partly melted. Sosman and Hostetter heated a platinum crucible containing 6.6 g. of Fe_2O_3 in air; they state[14] that "The charge melted down at about 1,582°, yielding black crystalline 'magnetite' on cooling." They evidently did not determine Fe_2O_3 in the melt.

COMPOUNDS IN THE BINARY SYSTEM MgO-Fe_2O_3.

The only intermediate compound encountered in our investigation, the well-known $MgO.Fe_2O_3$, was prepared by heating 79.84% Fe_2O_3 with 20.16% MgO at about 1,050°. Heating and fine grinding were alternated until after 11 days all of the Fe_2O_3 and MgO had combined to form a finely divided red material whose index of refraction varied from 2.38+ to 2.43 for sodium light. After 21 days' further heating the range of refractive index was found to be much narrower, the mean value being 2.39. Another preparation, containing 76.8% Fe_2O_3, was found to consist of a homogeneous red phase having an index of 2.38+ with considerable MgO, so finely divided, however, that its amount could not be estimated. It is evident, then, that the compound $MgO.Fe_2O_3$ at 1,050° lies in the middle of a short series of solid solutions extending toward MgO on the one hand and toward iron oxide—almost wholly Fe_2O_3—on the other. The compound $MgO.Fe_2O_3$ dissociates somewhat on heating, and the resulting ternary solid solution begins to melt in air at 1,750° ± 25°.

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[14] J. Wash. Acad. Sci., 5, 296, 1915.

THE TERNARY SYSTEM.

The phase relations in the ternary system are shown in Fig. 1. The upper portion of the figure is the conventional triangular diagram with compositions in weight per cent; in the lower diagram abscissae represent the compositions by weight that would be obtained after oxidizing all of the iron to the ferric condition. Some such treatment of the data is necessary because the FeO coördinates of the melting curves

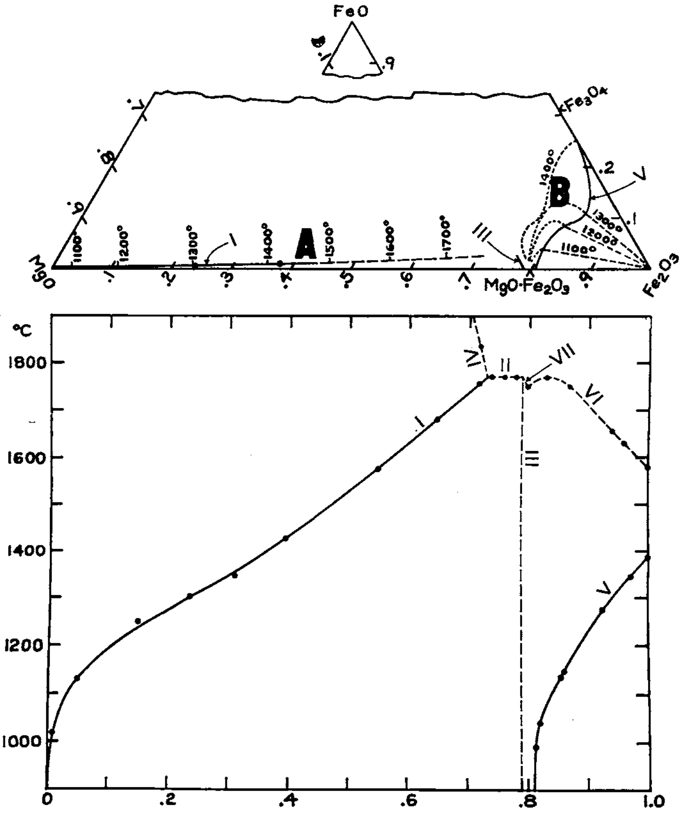

Fig. 1. Phase relations in the ternary system. In the upper diagram compositions are expressed in weight per cent of the three components. In the lower diagram abscissae represent the compositions that would be obtained by analysis after oxidizing all of the iron to the ferric condition.

were not obtained and it is therefore necessary to present these curves in terms of total iron. This particular plan was chosen, rather than the more obvious expedient of plotting the Mg-Fe ratio, because it seemed that it would be more easily presented.

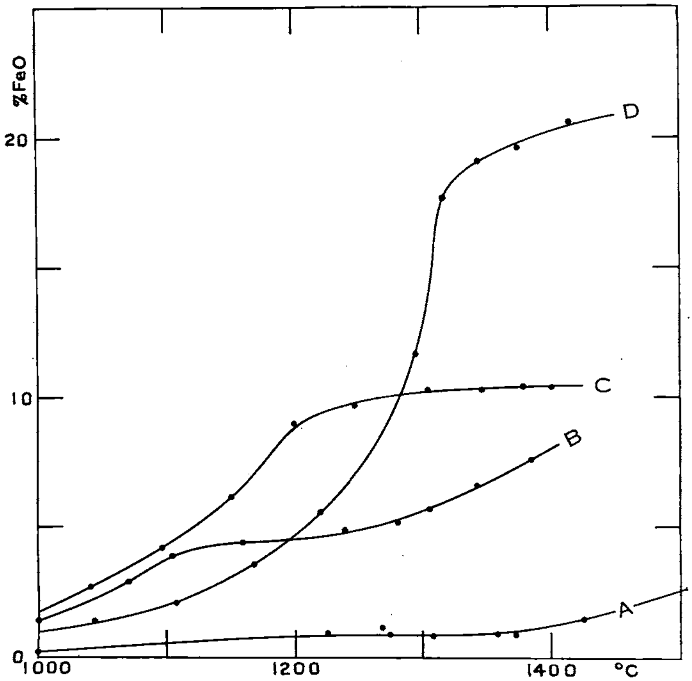

Fig. 2. FeO and temperature for four compositions in solid solution field B.

Curve A, initial composition 80.0% Fe_2O_3, 20.0% MgO
" B, " " 82.9% Fe_2O_3, 17.1% MgO
" C, " " 86.8% Fe_2O_3, 13.2% MgO
" D, " " 94.1% Fe_2O_3, 5.9% MgO

Fig. 2 shows the relation between ferrous iron and temperature for four preparations. Data taken from these curves formed the basis for the isotherms in Fig. 1. The experimental data for these two figures are given in Tables II, III and IV.

TABLE II.

Solid solution limits.

Initial composition, wt.%		Temperature ° C.	Time of heating	Second phase	Equilibrium	
Fe_2O_3	MgO				% iron oxide as Fe_2O_3	Temperature ± 10°[9]
Curve I. Excess magnesioferrite in MgO solid solutions.						
1	99	1,000	70 hrs.	trace		
same		1,040	16 “	none	1	1,020
5	95	1,112	20 “	2 phases		
same		1,152	16 “	none	5	1,132
14	86	1,250	140 “	none		
16	84	1,250	140 “	*ca.* 5%	15	7,250
25	75	1,302	700 “	trace	23.5	1,302
30	70	1,347	700 “	none		
35	65	1,347	700 “	*ca.* 5%	31	1,347
40	60	1,426	50 “	trace	39.5	1,426
55	45	1,550	10 min.	several %		
same		1,575	10 “	trace	55	1,575
65	35	1,660	10 “	small amount		
same		1,700	15 “	none	65	1,680
72	28	1,755	10 “	trace	72	1,755
Curve V. Excess hematite in magnesioferrite solid solutions.						
81.4	18.6	984	17 hrs.	trace		
same		1,040	16 “	none	81.4	990
82.9	17.1	1,040	16 “	*ca.* 5%		
same		1,085	17 “	none	82.0	1,040
86.9	13.1	1,134	16 “	*ca.* 10%	85.5	1,134
same		1,146	16 “	*ca.* 5%	86.2	1,146
94.1	5.9	1,275	16 “	*ca.* 20%	92.6	1,275
98.2	1.8	1,334	16 “	*ca.* 50%	96.4	1,334
same		1,346	16 “	*ca.* 25%	97.3	1,346

TABLE III.
Beginning of melting.

Initial composition, wt. %		Temperature[9] ± 25°	Initial composition, wt. %		Temperature[9] ± 25°
Fe_2O_3	MgO		Fe_2O_3	MgO	
	Curve IV			Curve VI	
72	28	1,835	83	17	1,770
			86.8	13.2	1,750
	Curve II		94	6	1,655
74	26	1,770	96	4	1,630
76	24	1,770			
78	22	1,770		Iron oxide	
			100	0	1,580
	($MgO.Fe_2O_3$)				
79.8	20.2	1,750			

TABLE IV.
FeO and temperature.

FeO by loss of weight

Temperature ± 5°[9]	Total days	Loss mg.	%FeO	Temperature ± 5°[9]	Total days	Loss mg.	%FeO
Initially 6.794 g 82.9% Fe_2O_3, 17.1% MgO							
995	2	10.5	1.4	1,281	12	39	5.2
1,071	3	21	2.8	1,306	16	43	5.7
1,105	5	29	3.8	1,343	21	50	6.6
1,160	7	33	4.4	1,385	27	57	7.6
1,239	9	37	4.9				
Initially 2.612 g 86.8% Fe_2O_3, 13.2% MgO							
1,041	8	9	2.7	1,248	20	32	9.7
1,097	10	14	4.2	1,305	22	34	10.3
1,151	14	21	6.3	1,347	23	34	10.3
1,200	17	30	9.0	1,401	32	34.5	10.4
Initially 7.756 g 94.1% Fe_2O_3, 5.9% MgO							
986	3	8	0.9	1,296	12	100	11.7
1,044	4	12	1.4	1,318	16	150	17.7
1,108	5	18	2.1	1,345	18	162	19.1
1,168	9	30	3.5	1,376	19	166	19.6
1,220	11	48	5.6	1,416	20	175	20.6

FeO by analysis
Initial composition $MgO.Fe_2O_3$

Temperature[9]	Total hours	%FeO	Temperature[9]	Total hours	%FeO
1,000	240	0.16	1,425	4	1.5
1,226	6	0.9	1,505	4	2.6
1,275	5	0.9	1,663	3	8.0
1,359	4	0.9			

The system is characterized by two solid solution fields, A and B in Fig. 1. Field A lies between boundary curve I and the MgO-FeO side of the triangular diagram; it is enclosed on the high temperature side by solidus curve IV and possibly by other curves at temperatures that were beyond our reach. Field B is enclosed by boundary curves III and V, solidus curves VI and VII, by part of the iron oxide side of the diagram and by the MgO-Fe_2O_3 side for, presumably, a short distance on either side of the compound $MgO.Fe_2O_3$. At temperatures below 1,386° hematite forms a distinct solid phase while above this temperature iron oxide appears as the magnetite solid solution forming a boundary of field B, or as a liquid.

Mixtures lying within the area bounded by curves I, II, III and the MgO-Fe_2O_3 side are found to consist of the two solid phases A and B. The composition of A starts with pure MgO below 1,000° and follows curve I with increasing temperature to a maximum of 73% iron oxide, calculated as Fe_2O_3, at 1,770° where a liquid phase appears. The composition of phase B in these mixtures follows curve III with little change in its Fe_2O_3 equivalent. This is indicated by the fact that the refractive index of a composition on the curve at 1,745° is the same, within the error of measurement, as that of one at 1,050° where we find a solid solution of about 1% MgO in $MgO.Fe_2O_3$. The transparency of the two phases indicates that little dissociation takes place in either; probably less than the equivalent of 10% FeO even at 1,770°.

Mixtures lying to the right of curve V, field B, are found to contain free hematite and the solid solution B whose composition follows curve V to pure iron oxide at 1,386° where the solid solution contains approximately 25% FeO.

The melting curves represent the lowest temperatures at which we found visible evidence of the formation of the liquid phase, and lie therefore above, rather than below, the true solidus curves. The liquidus curves seem to lie at considerably higher temperatures; for the compositions $MgO.Fe_2O_3$, 74% and 83% Fe_2O_3, heated to temperatures between 1,810° and 1,835° and quenched, showed the familiar matte surface of these solidified liquids surrounding a few large crystals which had presumably been present at the high temperature.

Points on curve II represent equilibria between two solid phases, liquid and air; since the equilibrium can not be affected by the relative amounts of the two solid phases the solidus must be horizontal. The temperature along curve II lies 20° above the point obtained for the compound $MgO.Fe_2O_3$ (dissociated); therefore the intersection of curves II and III must lie on the MgO side of the "compound" and be connected with its solidus by a short solidus corresponding to curve VII.

Curve IV, representing the solidus of the solid solution field A, rises so steeply that it could be followed only to 72% "Fe_2O_3" at 1,835°. Curve VI, however, could be followed throughout its whole course. It passes through a maximum at about 83% "Fe_2O_3" and 1,770°. In a binary system this maximum would be common to both liquidus and solidus; here, however, it apparently is not, for we find evidence of a solid phase persisting in two of the compositions at a much higher temperature.

UNMIXING IN THE TWO SOLID SOLUTION FIELDS.

As has been pointed out, compositions in field A, solid solutions of magnesioferrite in MgO, often unmix on cooling and particles of magnesioferrite appear distributed through a matrix richer in MgO. In certain cases we found preparations that appeared homogeneous and birefringent, and others with a thin film of apparently birefringent material on the surface of otherwise isotropic grains. As the work progressed it became evident that this phenomenon was not due to the appearance of a new, birefringent phase but to the fineness of the inclusions. These, particularly when they are too minute to be resolved by the microscope, act as diffracting and reflecting centers and the light scattered by them is partly polarized. Under these conditions the grains appear to be homogeneous and birefringent while, where the inclusions are large enough to be seen, it is evident that both matrix and inclusions are isotropic.

In field B we found no evidence of unmixing on cooling except in the case of material that had cooled so slowly that it became oxidized. There is strong evidence that at room temperature magnesium ferrite and magnetite have the same crystal structure and nearly the same lattice dimensions.[15] It

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[15] Posnjak, The crystal structure of magnesium, zinc and cadmium ferrites, this Journal, **19**, 67-70, 1930.

Wyckoff and Crittenden, An X-ray examination of some ammonia catalysts, J. Am. Chem. Soc., **47**, 2866-2876, 1925.

is therefore reasonable to suppose that they should be completely isomorphous.

X-ray powder photographs of the two compounds and of compositions within the field are so nearly identical that they can not be used confidently as evidence for or against isomorphism. Some evidence in favor of it was obtained, however, from differential heating curves for these preparations. This work was done in an atmosphere of nitrogen to prevent oxidation. A discontinuity or break appeared in the curve at a different temperature for each composition. These discontinuities are presumably close to the magnetic transformation temperatures for all of these compositions. The data are given in Table V.

TABLE V.

Magnesium ferrite—iron oxide solid solutions.
Thermal break and magnetic transformation.

Wt. % MgO	20.2	13.4	6.0	0
Wt. % FeO	0.1	10.4	20.1	31.1
Wt. % Fe_2O_3	79.7	76.2	73.9	68.9
Thermal break	369°	471°	535°	563°
Magnetic transformation	310°[a]			578°[b]

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[a] Forestier and Chaudron, op. cit., p. 510.

[b] Weiss and Foex, International Critical Tables, vol. 6, 413, 1929.

When compositions in field B become oxidized, however, lamellae of hematite appear within the grains of the solid solution and are arranged parallel to prominent crystallographic directions of the isotropic matrix. Here again unmixing often causes the grains to appear birefringent while still apparently homogeneous. If, however, they are embedded in sealing wax, polished and viewed by reflected light, some lamellae are seen as a pattern of fine lines standing out in relief from the surface of the softer matrix.

SUMMARY.

The system MgO-FeO-Fe_2O_3 has been investigated at temperatures above 1,000° on the isobar 1/5 atmosphere O_2. In the binary system MgO-Fe_2O_3 we find no compound other than $MgO.Fe_2O_3$ which dissociates slightly on heating and begins to melt at 1,750° ± 25°.[9] Solid solution extends from this compound for a short distance toward MgO. In the binary system $FeO-Fe_2O_3$ the stable phase at temperatures below 1,386° ± 5°[9] is a hematite solid solution containing less oxygen than Fe_2O_3; just above 1,386° ± 5° the stable phase is a magnetite solid solution containing considerably more oxygen than Fe_3O_4.

The ternary system contains two solid solution fields. The first begins at MgO below 1,000° and extends, with increasing temperature, toward $MgO.Fe_2O_3$ and FeO; a liquid phase appears at 1,770° ± 25°, where the solid contains iron oxide equivalent to 73% Fe_2O_3. The second solid solution extends, with increasing temperature, from $MgO.Fe_2O_3$ toward the iron oxide boundary which it reaches at 1,386° ± 5°; solid solutions of about 1% of MgO in $MgO.Fe_2O_3$ are possible from 1,750° to 1,000° or below.

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