



# MICROSTRUCTURES OF MAGNESIOWUSTITE $[(\text{Mg},\text{Fe})\text{O}]$ IN THE PRESENCE OF $\text{SiO}_2$

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ABSTRACT: Periclase-type oxides were examined microscopically after they were exposed to siliceous liquids. The variables included: (1) time, (2) temperature, (3) amount of liquid, and (4) the ratio of  $\text{MgO}$  to  $\text{FeO}$ .

The results are discussed in terms of (A) the grain size (Fig. 1), and (B) the location of the liquid (Fig. 2). The conclusions include:

## A. Grain growth.

(1) The average magnesiowustite grain size increases with the square root of time.

(2) Grain growth occurs more rapidly at higher temperatures if the liquid content is maintained constant.

(3) The grain growth decreases slightly if the liquid content is increased.

(4) Magnesiowustites with higher  $\text{MgO}$  contents grow less rapidly than those with higher  $\text{FeO}$  contents.

(5) The growth rate is reduced by the presence of a second solid phase.

## B. Liquid location.

(6) The silica-containing liquid penetrates as a film between the individual magnesiowustite grains. This is independent of time, temperature, amount of liquid, or the  $\text{MgO}/\text{FeO}$  ratio, and is in contrast to microstructures encountered in silica refractories.

(7) When present, spinel-type phases provide a solid-to-solid "bridge" between magnesiowustite grains.

The last conclusion may be the most important of the seven. It suggests a means for increasing the high-temperature service strength of periclase brick.

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## I. INTRODUCTION

This report presents the results of a study of the microstructures of periclase type oxides in the presence of a silicate liquid. The purpose was to learn more about the effect of service factors such as (1) time, (2) temperature, and (3) liquid content upon (A) grain growth, and (B) liquid location among the solid grains.

This study was prompted by the fact that periclase refractories are known to have very little solid-to-solid contact when the phases which are present are limited to periclase and liquid. Such a microstructure gains industrial significance because it permits fracture during service when stresses are applied at high temperatures. Additional background factors will be discussed in Appendix A.

Details of experimental procedures are presented in Appendix B. In brief, these include heat treatments of prescribed compositions which contain an (Mg,Fe)O solid and a silica-containing liquid. Heat treatments were followed by quenching and microscopic examinations.

The results will be discussed in the next section in terms of (A) the grain size of the solid oxide and (B) the microstructural geometry which includes the location of the liquid among the solid oxide grains. These two considerations are illustrated by Fig. 1 where examples show the change in grain size with high temperatures, and in Fig. 2 where a liquid film is shown penetrating along the boundaries between adjacent solid grains.

## II. RESULTS AND DISCUSSION

Initial attention was given to wustite/liquid structures because they were more amenable to heat treatments as a consequence of their lower solidus temperatures. Effects of treatment times, treatment temperatures, and liquid quantities were examined. This was followed by increases in the MgO/FeO ratio. Finally, the microstructures were examined when small amounts of CaO and Al<sub>2</sub>O<sub>3</sub> were added to a wustite-base composition. Data are presented in Table I.

### A. Grain Size

1. Time. Grain size is a function of several factors. The change in grain size with time is shown in Figs. 3 and 4 for wustite plus liquid. To a first approximation the grain growth proceeds according to the relationship cited in the Appendix A Eq. (1) by Burke.<sup>1</sup> This relationship may be rewritten for these particular conditions as:

$$D_2 - D_1 = 0.009t$$

Here t is the time in hours, and  $D_1$  and  $D_2$  are the initial and final grain

size in mm. This implies that the grain growth is controlled by the energies of the boundary between the two phases (solid wustite and liquid).

2. Temperature (constant liquid). Grain growth proceeds more rapidly at the higher temperatures if other factors such as liquid content, time, and composition are constant (Figs. 5 and 6). It may be assumed that this is partially a consequence of higher mobilities of the diffusing iron and oxygen ions from the smaller grains, through the liquid, and onto the growing grains. In addition, the higher temperatures produce a liquid with increased FeO contents, as shown in Figs. 21 and 22. This will also contribute to more growth of the average grain size.

3. Amount of liquid. Grain growth depends less on the amount of liquid than on time or temperature. However, an effect is present. It is inverted, i.e., the growth rate is faster with less liquid present. The results are shown in Figs. 7 and 8; the samples contained MgO/FeO weight ratios of 10/90 and 20/80. The liquid content was varied through the silica additions. Actual liquid contents were measured from the microstructures. This effect is not noticeable until the sintering is established. For example, zero percent SiO<sub>2</sub> and therefore zero liquid, reveals negligible grain growth. However, this is probably a consequence of little or no contact between the grains for diffusion. A definite explanation cannot be given for the decreased grain growth rate with higher liquid contents. The source of this correlation is not clear. It can be suggested that higher liquid contents for any particular composition and temperature arrest growth when a liquid-solid balance is achieved. Thus, the larger size in Fig. 7(a) would be simply a result of growth to fill the volume. A second possibility can also be suggested. With higher liquid contents, the solid grains have more uniform surface curvatures (cf. Fig. 7(b) with 7c). Thus, the driving force for grain growth (between small surface radii and large surface radii) is not as pronounced as when less liquid is present.

4. Temperature (constant composition). If the temperature is increased and the composition is maintained constant so that the liquid content increases, the grain size is affected. This is shown in Figs. 9 and 10 and is in contrast to the condition shown in Figs. 5 and 6 where microstructures with comparable liquid contents show increased growth rates at higher temperatures. Figures 9 and 10 reveal the same phenomenon as is shown in Figs. 7 and 8.

5. Magnesiowustite compositions. It is impossible to measure the independent effect of the MgO/FeO ratio on the grain size or growth rate because a change in this ratio produces a change in the liquid content unless a simultaneous change is made in the treatment temperature, and/or in the liquid composition. However, it is still possible to make comparisons between different MgO/FeO ratios if the temperatures and compositions are chosen so as to have comparable solid/liquid ratios. Such comparisons are shown in Figs. 11-14 for four different sets of samples. In general there is a slight decrease in the growth rate as the MgO/FeO ratio is increased. The present results do not permit extrapolation to high MgO/FeO ratios. However, it may be noted that the slow growth rate within low FeO periclase refractories (Fig. 15) is consistent with this observation.

6. Impurities. A limited amount of attention was given to the effect of impurity oxides such as CaO and Al<sub>2</sub>O<sub>3</sub> upon grain growth. In general, higher liquid contents reduced grain growth. One such example is shown in Fig. 16

7. Second solid phase. The presence of a second solid phase limits the grain growth of the wustite structure. This is shown in Fig. 17, where sufficient alumina was added to produce hercynite (FeAl<sub>2</sub>O<sub>4</sub>). Although the alumina was not uniformly distributed, its effect on grain growth is evident. A second example is shown in Fig. 18(b). Here, the MgO/FeO ratio was increased until olivine [(Mg,Fe)<sub>2</sub>SiO<sub>4</sub>] was also present as a solid phase at 1600°C (2912°F). The growth of the oxide grain size was limited to 0.03-0.05 mm. This is in contrast to larger growth in adjacent olivine free areas (0.06-0.08 mm) and in lower MgO/FeO compositions (Fig. 18a). This inhibition effect of a second solid phase is closely associated with the energies of the interfaces between the several phases. This will be discussed in the next section.

## B. Microstructural Geometry

There was a consistent pattern among all the samples which contained the (Mg,Fe)O solid and a liquid (Figs. 1-18). (1) The solid grains are essentially equidimensional. They are anhedral. (2) The liquid film penetrated deeply along the grain boundaries.

1. Shape. The isotropic dimensions may be related to the cubic NaCl structure of the (Mg,Fe)O solid. As such it corresponds directly to cubic cristobalite when it is treated in contact with liquid.<sup>2</sup> It contrasts with the plate-like structure of hexagonal tridymite or corundum when they grow within a liquid.

The anhedral shapes of (Mg,Fe)O grains are to be contrasted with growing cristobalite grains. The latter develop euhedral outlines during their initial period of growth. However, with more extensive treatment times, the cristobalite will undergo anhedralization.<sup>2</sup> The (Mg,Fe)O grows directly as anhedral grains. This contrast in behavior between the two phases can be explained best on the basis of response to interfacial energies. In each case, the anhedral outlines are developed to minimize surface energies by the reducing surface (or interface) areas. It logically implies that the diffusion of the Fe<sup>+2</sup>, Mg<sup>+2</sup>, and O<sup>-2</sup> ions is greater than for the silicon and oxygen in SiO<sub>2</sub>. This same fact is observed when grain growth rates are compared for the two oxides.

2. Liquid location. The grain-boundary penetration of the liquid is also explicable in terms of surface energies of the interface between the liquid and solid phases. It is evident that less energy is required to form two liquid/solid surfaces than one solid/solid surface (Fig. 23c).\*

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\*Occasional departures may be obtained. (See the lower right corner of Fig. 12a.) It has been suggested that a limited number of grain pairs may not be separated by the liquid if they possess a twinned or similar low-energy boundary orientation.

This produces only a minor amount of solid-to-solid contact. This is in contrast to cristobalite/liquid or tridymite/liquid structures.

The consistency of the low-angle liquid penetration with variations in testing conditions requires some explanation. The solid compositions ranged from MgO (Fig. 15) to FeO (Fig. 5). The amount of liquid was varied from 1% to nearly 20%. Times ranged from 1 to 64 hr in laboratory tests. A similar distribution of liquid may be observed in periclase refractories after extended service periods in steel plant furnaces.<sup>3</sup> The one similarity in each case is that the liquid contains large quantities of (Mg + Fe)O and is therefore very similar in composition to the solid. With one exception among the samples studied, the equilibrium liquid contained 75% or more (Mg + Fe)O. This is in contrast to the previously compared cristobalite (and tridymite) structures where the liquid contained only about 50% SiO<sub>2</sub>.

The one exception was the microstructure containing wustite and a liquid of CaO and SiO<sub>2</sub> (Fig. 16). Here the liquid contains approximately 50% FeO.<sup>4</sup> It is evident that the relative energy of the liquid/solid interface is higher because there is more solid-to-solid contact.

The presence of the spinel-type phase, hercynite (FeAl<sub>2</sub>O<sub>4</sub>) makes a significant change in the microstructure (Fig. 19). The hercynite provides a solid-to-solid contact between the wustite grains. The liquid does not penetrate along the boundary between the two different solid phases. Preliminary evidence also suggests that magnetite (FeFe<sub>2</sub>O<sub>4</sub>) serves as a similar solid-to-solid bond for wustite (FeO). Finally, a similar relationship has been observed in used periclase brick where the magnesioferrite (MgFe<sub>2</sub>O<sub>4</sub>) provides contact between periclase (MgO) grains.

Compositions or temperatures which permit the presence of olivine provide situations for similar solid-to-solid contact between the (Mg,Fe)O grains. As yet this observation has not been matched by used refractories.

The observations in the previous two paragraphs suggest that the energies of the boundaries between unlike solid phases are less than the energy between two like grains. This implies that a greater coherency is developed when the adjacent grains are given the additional freedom of composition change. Further discussion must await further observations.

### III. SIGNIFICANCE AND CONCLUSIONS

Microstructures have been described which are comparable to microstructures encountered in periclase refractories before and after service. Some of the grain-growth characteristics are determined. The fact that the liquid distribution is rather consistently present as an intergranular film which provides little or no solid-to-solid contact is probably more important. Variations in time, temperature, or MgO/FeO ratios do not alter this microstructure. However, if the composition is changed so that a second solid phase is present, the intergranular liquid is bridged. This offers possibilities for refractory formulation. It also can explain why cracking occurs behind the hot face of a periclase brick in a steel plant furnace while the hot face which contains higher Fe<sub>2</sub>O<sub>3</sub> contents to provide magnesioferrite does not crack. Finally, it may be possible to rationalize further the role of chromite and oxidized steel plates in magnesia brick.

Itemized conclusions include:

#### A. Grain Growth

(1) Grain growth proceeds at a rate,  $dD/dt = k/D$ . This implies that the liquid/solid interface energy is the driving force.

(2) Grain growth is more rapid at higher temperatures if the liquid content is maintained constant. Observations indicate that a slightly slower growth rate occurs when more liquid is present. Possible explanations are cited.

(3) When the liquid content is maintained constant, an increase in the MgO/FeO ratio produces a slight decrease in the growth rate.

(4) The growth rate is reduced in the presence of a second solid phase.

#### Phase Distribution

(5) A wide range of solid compositions, liquid contents, and testing conditions show the same extensive penetration of liquid between the (Mg,Fe)O grains.

(6) This distribution can be related to relative interfacial energies.

(7) Spinel-type phases provide a means of bridging the grain boundary film.

#### C. Significances

(8) Certain refractory properties may be rationalized in terms of the microstructures.

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Table I. Test Data

Sample No.	Figure No.	MgO/FeO	Composition SiO <sub>2</sub> CaO Al <sub>2</sub> O <sub>3</sub>	Temp., °C	Time, Hours	Mean Diameter, mm.	Approx. Liquid Content, %
15	3(a)	/100	3	1200	4	.07	11
18	3(b)	/100	3	1200	16	.10	13
21	5(a)	/100	3	1185	16	.06	12
23	5(c)	/100	3	1300	16	.20	11
24	5(b)	/100	3	1250	16	.14	9
31	3(c)	/100	3	1200	64	.16	10
38		/100	3	1200	16	.09	17
134(a)	9(a) + 14(a)	10/90	3	1400	4	.13	4
138(a)	7(a) + 13(a)	10/90	0.5	1450	1	.13	1
138(b)	7(b) + 12(a)	10/90	1	1450	1	.08	6
139(a)	7(c)	10/90	3	1450	1	.07	16
139(b)	11(a)	10/90	5	1450	1	.06	18
141	2(a) + 9(b)	10/90	3	1450	4	.10	11
152	10(a)	20/80	3	1500	2	.09	5
156	14(b)	20/80	3	1500	4	.10	5
159	8(b) + 13(b)	20/80	0.5	1550	1	.09	1
160	8(b) + 12(b)	20/80	1	1550	1	.08	5
161	8(b)	20/80	3	1550	1	.07	10
162	8(b) + 11(b)	20/80	5	1550	1	.05	18
165	10(b)	20/80	3	1550	2	.07	10
167		20/80	1	1550	4	.11	8
169	14(c)	30/70	3	1550	4	.12	5
172		30/70	3	1550	9	.14	8
174		/100	3	1200	4	.08	13
175	16(b)	/100	3	1200	4	.04	15
176		/100	3	1200	4	.11	7
180		/100	3	1200	36	.18	8
181		/100	3	1200	36	.08	20
182		/100	3	1200	36	.22	8
187		/100	1	1200	16	.10	6
190	16(a)	/100	1	1200	4	.06	6

(continued)

Table I. Test Data (con't.)

Sample No.	Figure No.	MgO/FeO	Composition SiO <sub>2</sub> CaO Al <sub>2</sub> O <sub>3</sub>	Temp., °C	Time, Hours	Mean Diameter, mm.	Approx. Liquid Content, %
196	17	/100	2	1200	4	.02-.08	5
197		/100	1	1200	4	.03-.08	4
203		/100	1	1200	36	.2	3
204	19	/100	2	1200	36	.15	8
205		/100	1	1200	36	n.d.	n.d.
206		/100	2	1200	36	n.d.	n.d.
215		30/70	3	1600	1	.07	8
216	1(a) + 18(a)	30/70	5	1600	1	.06	15
217		30/70	1	1600	2	.09	4
218		30/70	3	1600	2	.08	9
219		30/70	5	1600	2	.07	15
222	18(b)	40/60	5	1600	1	.03-.06	5
224		40/60	3	1600	2	n.d.	n.d.
227	1(b) + 14(d)	40/60	3	1600	4	.11	6
228		40/60	3	1600	4	.10	6
229	2(b) + 15	100/	5	1600	5	.04	10

## APPENDIX A. REVIEW OF LITERATURE

The details of ceramic microstructures have not received extensive attention. This is in contrast to the extensive attention given to (a) the phase relationships pertaining to refractory compositions, and (b) the details of the microstructures of comparable metallic materials. A brief review will be made of the pertinent phase relationships and microstructural considerations in general, as well as of refractory compositions.

### (a) Phase relationships

This investigation was limited to those compositions in which  $(\text{Mg,Fe})\text{O}$  was the solid phase.  $\text{MgO}$  and  $\text{FeO}$  form a complete series of solid solutions as shown in Fig. 20. Pure  $\text{MgO}$  has the name of periclase. The related  $\text{FeO}$  composition is called wustite. Both have the  $\text{NaCl}$ -type structure; however, wustite possesses a cation deficiency so that the true composition is  $\text{Fe}_{<1}\text{O}$  even in the presence of metallic iron.

The phase relationships involving solid  $(\text{Mg,Fe})\text{O}$  and a silicate liquid is shown in Fig. 21. In this case, the liquid is saturated with  $(\text{Mg,Fe})\text{O}$ . Therefore its  $\text{SiO}_2$  content is below that encountered in orthosilicate liquids. As a consequence the liquid phase species are primarily the following ions:  $\text{SiO}_4^{-4}$ ,  $\text{Mg}^{+2}$ ,  $\text{Fe}^{+2}$  and  $\text{O}^{-2}$  plus occasional  $\text{Fe}^{+3}$  ions. Two features are of importance: (a) the liquid contains relatively small species and (b) the liquid contains large quantities of the same species as the solid, viz.,  $\text{Fe}^{+2}$ ,  $\text{Mg}^{+2}$ , and  $\text{O}^{-2}$ .

Figure 22 shows the system,  $\text{FeO-SiO}_2$  which will be used in some of the discussions that follow. This diagram is the right side, vertical section of Fig. 21. Here, as previously, the  $\text{FeO}$  end of the diagram is nonstoichiometric, varying from  $\text{Fe}_{0.97}\text{O}$  when the liquid oxide is in contact with solid iron to about  $\text{Fe}_{0.90}\text{O}$  when the solid oxide is in equilibrium with an atmosphere of equal proportions of  $\text{CO}$  and  $\text{CO}_2$  at the solidus temperature.<sup>5,6</sup>

### (b) Microstructures

In general, published attention to refractory microstructures has been directed toward the phase analyses that accompany compositional variations. This is illustrated by Harvey<sup>7</sup> in his work on silica brick and by Wells<sup>3</sup> in his work on periclase brick. In each case, a series of altered zones are encountered which provides a sequence of phase associations. If due consideration is given to reaction kinetics, such an examination reveals phases that are compatible with equilibrium studies. Admittedly, however, it is often necessary to determine more complicated polycomponent systems to account for all the phases present.<sup>8</sup>

Relatively little attention has been given to microstructural geometry in ceramic materials. Certainly less attention has been given to this aspect of ceramic microstructures than to the size, shape, and

distribution of the constituent phases in metals. Burke<sup>1</sup> has pointed out that the grain size of oxides follows the same growth rules as for metals, viz., grain growth,  $dD/dt$ , is inversely proportional to the grain diameter,  $D$ .

$$dD/dt = k/D. \quad 1$$

Kingery<sup>9</sup> describes liquid phase sintering as a consequence of the natural tendency to minimize surface energies and thereby reduce the surface areas.

Although prime consideration was given by Kingery to external liquid/vapor surfaces, the same driving forces are encountered at interfaces between condensed phases. In particular, Smith<sup>10</sup> has shown rather conclusively that the relationship

$$\gamma_{S/S} = 2 \cos \frac{\Theta}{2} (\gamma_{L/S}) \quad 2$$

is applicable in a microstructure which contains a liquid and a solid. Within the above relationship,  $\gamma_{S/S}$  is the grain-boundary energy between two adjacent grains of the solid, while  $\gamma_{L/S}$  is the interface energy at the phase boundary between the liquid and the solid grains. Finally,  $\Theta$  is the dihedral angle of penetration which the liquid makes between the two solid grains. Three exemplary situations are presented in Fig. 21. It becomes apparent that the microstructures are influenced by the relative energies of the associated boundaries. Examples can be cited in work by Dodge and Hubble<sup>11</sup> for periclase refractories and by Van Vlack for silica-iron oxide compositions.<sup>2</sup> In the former of these two and in earlier work by Wells,<sup>3</sup> it was noted that periclase grains are essentially separated by a silicate film so that there is very limited solid-to-solid contact. In contrast, silica grains maintain considerable solid-to-solid contact even though there may be a large amount of liquid present. The chief difference is the relative interfacial energies as shown by the dihedral angles (Fig. 4).

### (c) Properties

It is suggested that the properties of refractory materials may be correlated with the microstructures.<sup>2</sup> The high strength of silica brick up to temperatures immediately below the monotectic depends upon the microstructural skeleton of cristobalite grains in actual contact. In contrast, considerable cracking is encountered in periclase brick in zones where a liquid film penetrates between the solid periclase grains.

## APPENDIX B. EXPERIMENTAL PROCEDURES

Samples were made from reagent grade raw materials by sintering. These were held at selected temperatures for appropriate periods of time to develop equilibrium microstructures. This heat treatment was followed by water quenching and preparation of reflected light microscopic specimens.

### (a) Sample preparation

Reagent grades of  $\text{Fe}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{MgO}$ ,  $\text{CaO}$ , and  $\text{Al}_2\text{O}_3$  were used. Desired amounts were ground and mixed prior to the pressing of sample pellets. Presintering and regrinding were not necessary for 2-phase structures when a liquid phase was developed during subsequent heat treatments.

### (b) Heat treatments

Two procedures were used for heat treatments. At  $1300^\circ\text{C}$  ( $2372^\circ\text{F}$ ) and below the pressed samples were sealed in small crucibles of "ferro-vac" iron. As such,  $\text{Fe}_2\text{O}_3$  was reduced to produce an equilibrium Fe/O ratio of about 0.97/1. Although presintering was not necessary for homogenization, a presinter was used for densification purposes so that a greater quantity could be introduced into the crucible.

At temperatures of  $1350^\circ\text{C}$  ( $2462^\circ\text{F}$ ) and above, the samples were treated in a  $\text{CO}_2/\text{CO}$  atmosphere containing equal premixed quantities of the two gases. It can be shown that this atmosphere produces a Fe/O ratio of approximately 0.9/1 in wustite. Thus,  $\text{Fe}_2\text{O}_3$  is reduced to approximately  $\text{Fe}_{0.9}\text{O}$ . (This ratio will be maintained in wustite in the presence of  $\text{SiO}_2$ . However, the  $\text{Fe}^{+++}/\text{Fe}^{++}$  ratio in the liquid will be lower because of the effect of the  $\text{SiO}_2$  on the activity of the FeO. With the addition of MgO to wustite, it is quite probable that a smaller fraction of the  $\text{Fe}^{+++}$  is reduced to  $\text{Fe}^{++}$ . However, in the over-all composition  $(\text{Mg,Fe})_x\text{O}$ , the value of  $x$  lies between 0.9 and 1.0 when the  $\text{CO}_2/\text{CO}$  ratio is 1.)

Although two different furnaces were used, they were similar in principle, each being heated by electrical resistance. The lower-temperature furnace ( $1300^\circ\text{C}$  and below) utilized thermocouple control; the higher-temperature furnace had a radiation head coupled in with a reactrol power supply. Sample temperatures were determined by separate Pt-PtRh thermocouples in each case.

### (c) Microscopic examination

Reflected light examination was utilized. This required established procedures for grinding, impregnation, mounting, and polishing.

Grain sizes were indexed as the mean diameter observed in a two-dimensional microsection. Although this dimension will be smaller than the true mean diameter by a factor of approximately 0.86, this index is a consistent means of comparing the grain sizes of similar microstructures.<sup>12</sup>

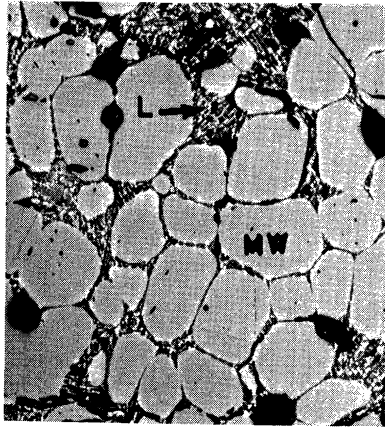
Liquid contents were measured from the same sample areas as the grain size. The point-counting procedure utilized grid intersections to avoid selectivity bias.

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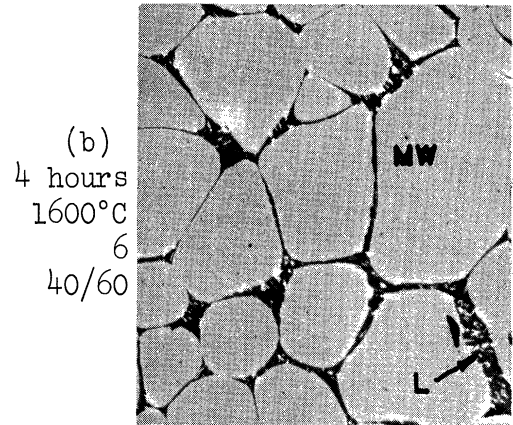
## SYMBOLS USED IN ALL FIGURES.

P - periclase  
 MW - magnesiowustite  
 CW - calciowustite  
 L - liquid  
 W - wustite  
 H - hercynite  
 O - olivine



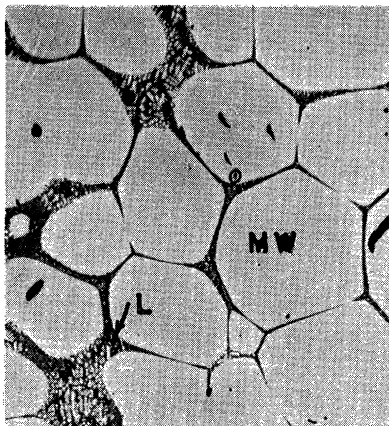
(a)  
 1 hour  
 1600°C  
 15  
 30/70

Time  
 Temperature  
 Percent Liquid  
 MgO/FeO



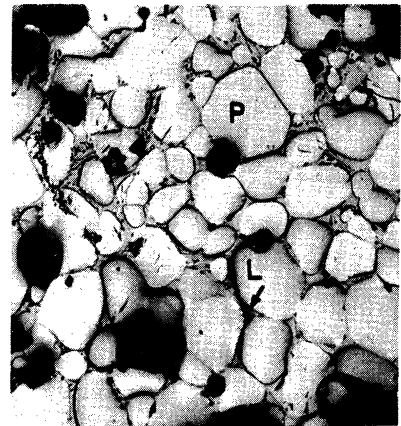
(b)  
 4 hours  
 1600°C  
 6  
 40/60

Fig. 1. Grain growth. X 150. The grains are individual crystals of (Mg,Fe)O located within a liquid matrix. The average grain size is affected by the following factors: time, temperature, liquid content, and the MgO/FeO ratio.



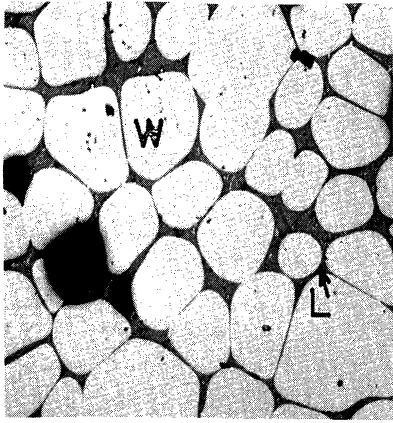
(a)  
 4 hours  
 1450°C  
 10  
 10/90

Time  
 Temperature  
 Percent Liquid  
 MgO/FeO

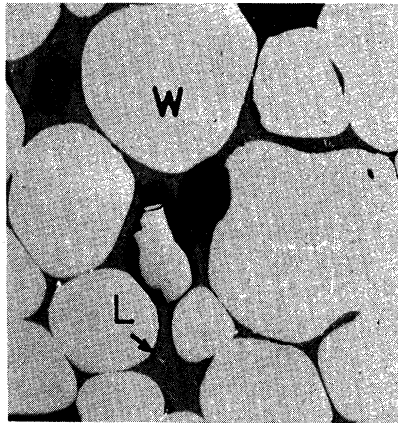


(b)  
 5 hours  
 1600°C  
 10  
 100/0

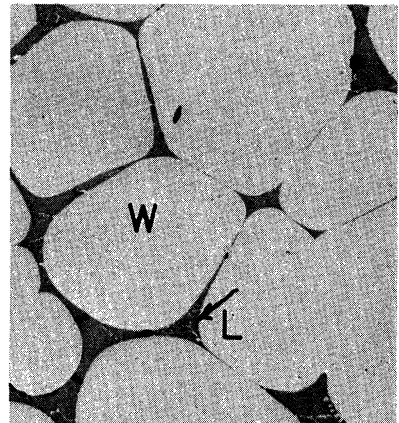
Fig. 2. Liquid location. X 150. The liquid phase is located between the grains of (Mg,Fe)O allowing negligible solid-to-solid contact. This is independent of time, temperature, amount of liquid or MgO/FeO ratio, but will be influenced by the presence of a second solid.



(a)  
4 hours



(b)  
16 hours



(c)  
64 hours

Fig. 3. Effect of time on grain size. X 150. Example: wustite (FeO) + silica-containing liquid. Treatment temperature: 1200°C (2192°F).

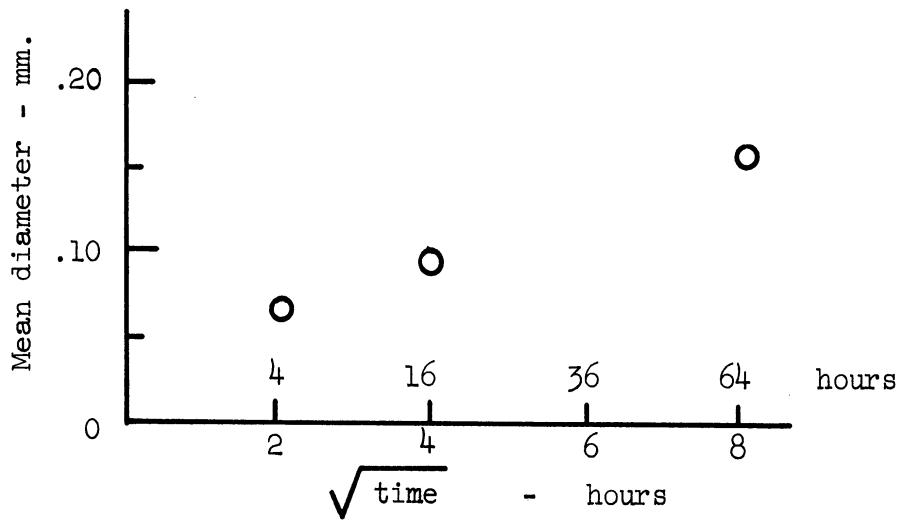
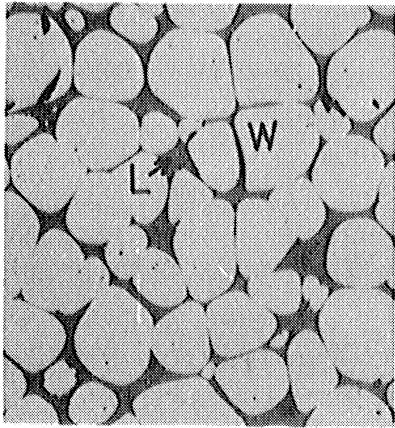
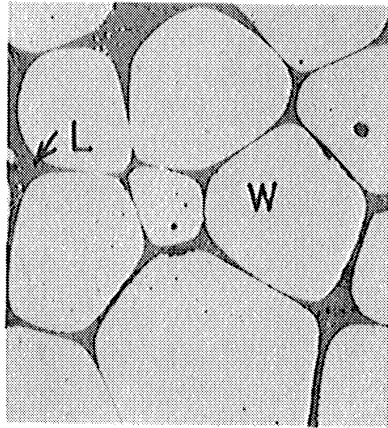


Fig. 4. Grain size vs. time. (Same examples as in Fig. 3.)

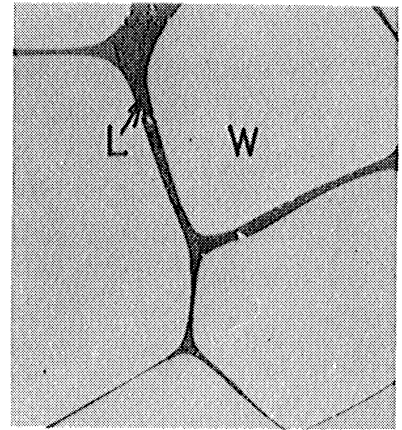




(a)  
1185°C  
(2165°F)



(b)  
1250°C  
(2282°F)



(c)  
1300°C  
(2372°F)

Fig. 5. Effect of temperature upon grain size at comparable liquid contents. X 150. Example: wustite (FeO) + silica-containing liquid. Treatment time: 16 hours. The liquid contains 78, 85, and 90% FeO at the three temperatures (cf. Fig. 22). The balance is SiO<sub>2</sub>. (Micrographs selected to show comparable wustite/liquid ratios.)

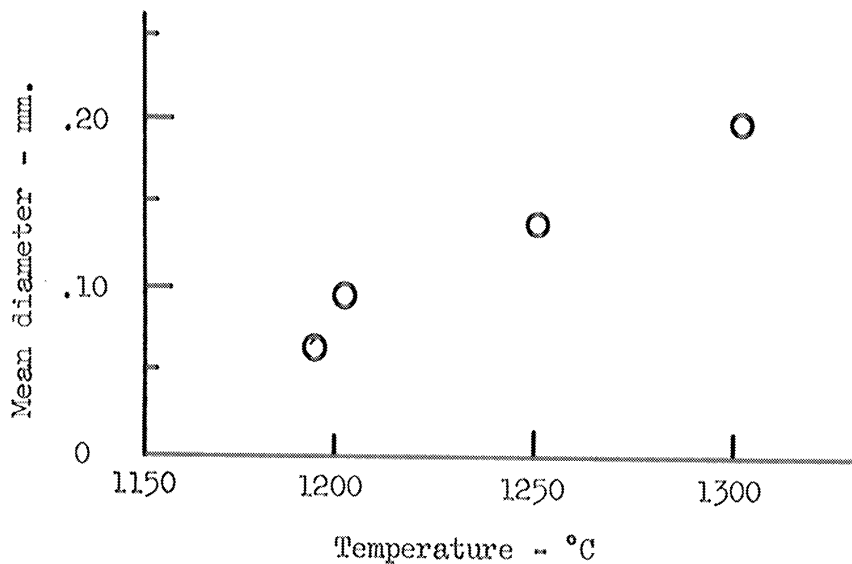
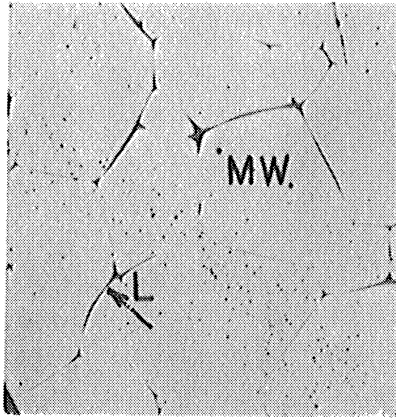
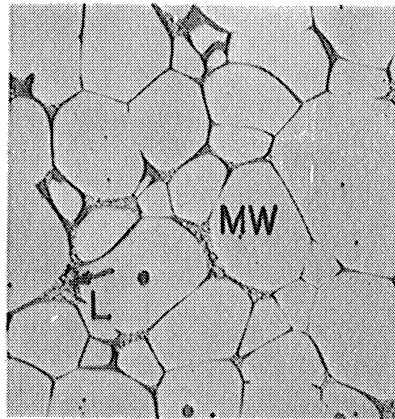


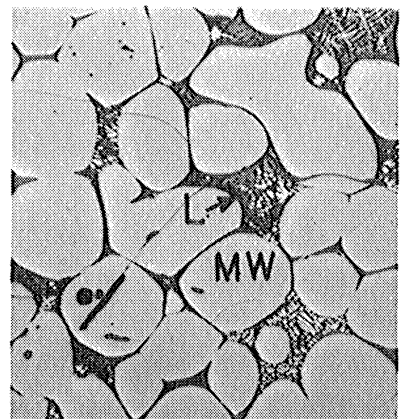
Fig. 6. Grain size vs. temperature. (Comparable liquid contents.) Same examples as in Fig. 5.



(a)  
Liquid - 1%

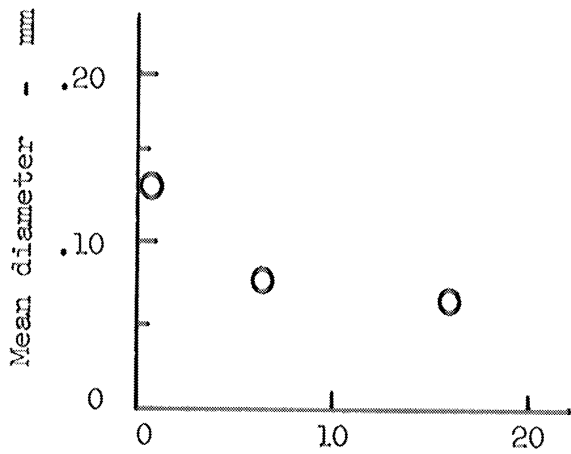


(b)  
Liquid - 6%

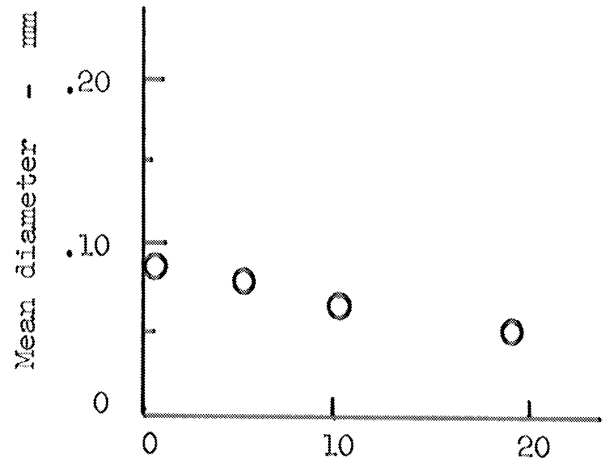


(c)  
Liquid - 16%

Fig. 7. Effect of liquid content upon grain growth.  
X 150. Example: magnesio-wustite (10MgO/90FeO) plus  
silicate liquid. Treatment time: 1 hour. Treatment  
temperature: 1450°C (2642°F).



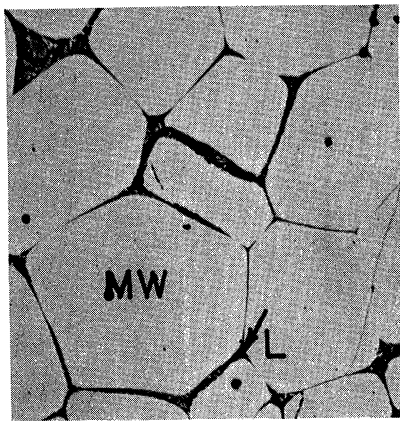
(a)



(b)

Percent Liquid (measured)

Fig. 8. Grain size vs. liquid content. (a) 10MgO/90FeO  
at 1450°C (2642°F) for 1 hour. (b) 20MgO/80FeO at  
1550°C (2822°F) for 1 hour.



(a)  
1400°C  
4  
4 hours

Temperature  
Percent Liquid  
Time

1450°C  
11  
4 hours

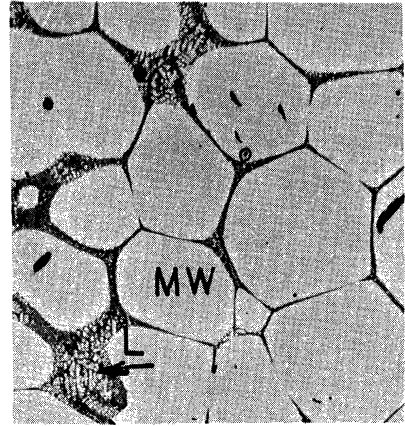
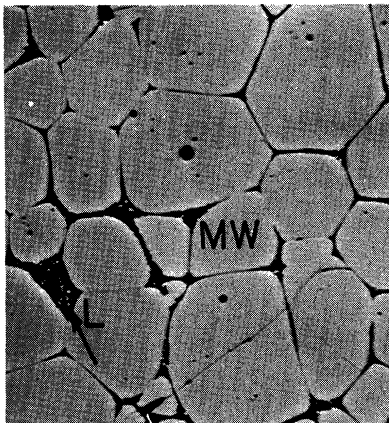


Fig. 9. Grain growth vs. temperature (increased liquid content). X 150. Example: 10MgO/90FeO plus 3% SiO<sub>2</sub>.



(a)  
1500°C  
5  
2 hours

Temperature  
Percent Liquid  
Time

(b)  
1550°C  
10  
2 hours

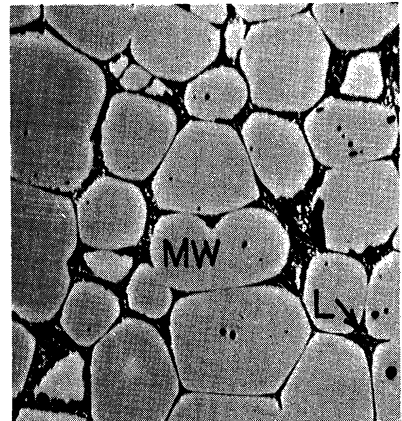
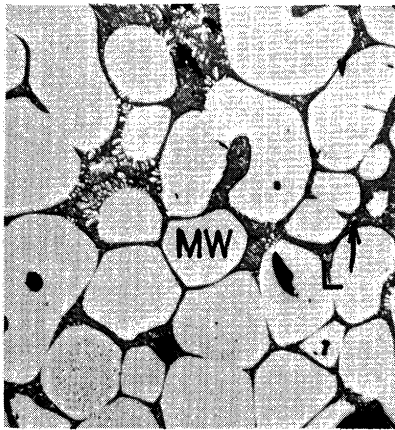
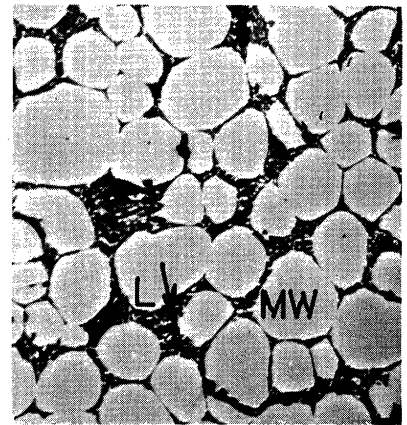


Fig. 10. Grain growth vs. temperature (increased liquid content). X 150. Example: 20MgO/80FeO plus 3% SiO<sub>2</sub>.



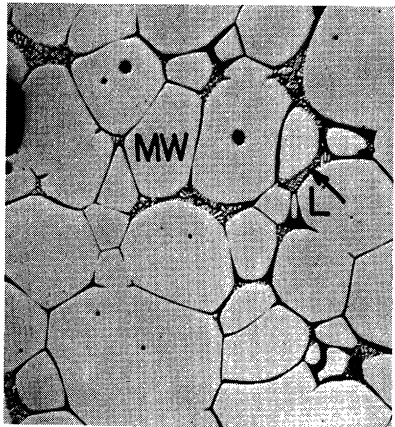
(a)  
10/90  
18  
5  
1450°C  
1 hour

MgO/FeO  
Percent Liquid  
Percent SiO<sub>2</sub>  
Temperature  
Time



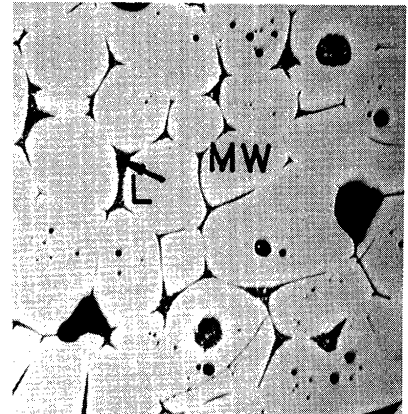
(b)  
20/80  
18  
5  
1550°C  
1 hour

Fig. 11. Grain growth vs. MgO/FeO ratio. X 150. Examples: high liquid content. (Comparable liquid contents maintained by temperature adjustments.)



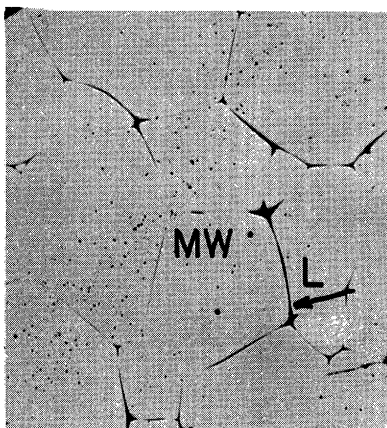
(a)  
10/90  
6  
1  
1450°C  
1 hour

MgO/FeO  
Percent Liquid  
Percent SiO<sub>2</sub>  
Temperature  
Time



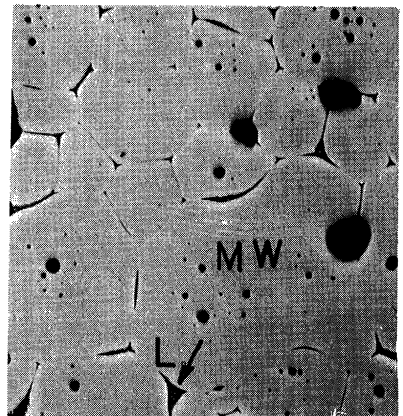
(b)  
20/80  
5  
1  
1550°C  
1 hour

Fig. 12. Grain growth vs. MgO/FeO ratio. X 150. Example: intermediate liquid content. (Comparable liquid contents maintained by temperature adjustments.)



(a)  
10/90  
1  
0.5  
1450°C  
1 hour

MgO/FeO  
Percent Liquid  
Percent SiO<sub>2</sub>  
Temperature  
Time



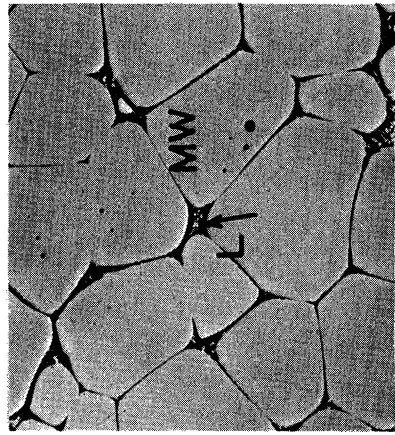
(b)  
20/80  
1  
0.5  
1550°C  
1 hour

Fig. 13. Grain growth vs. MgO/FeO ratio. X 150. Example: low liquid contents. (Comparable liquid contents maintained by temperature adjustments.)



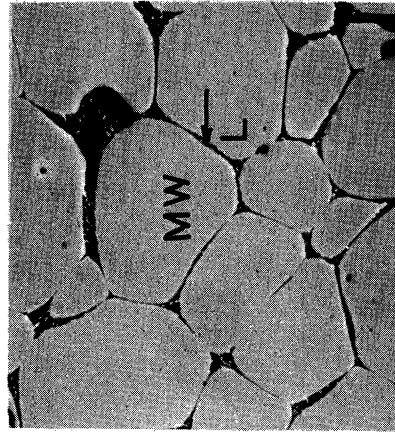
(a)

10/90  
4  
3  
1400°C  
4 hours



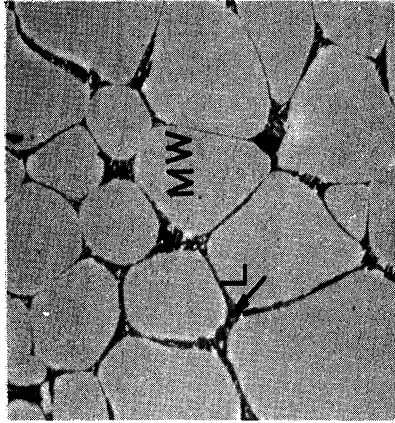
(b)

20/80  
5  
3  
1500°C  
4 hours



(c)

30/70  
5  
3  
1550°C  
4 hours



(d)

40/60  
6  
3  
1600°C  
4 hours

Fig. 14. Grain growth vs. MgO/FeO ratio. X 150. Example: intermediate liquid content. (Comparable liquid contents maintained by temperature adjustment.) Note: Both time and temperatures have been altered from the previous three figures.

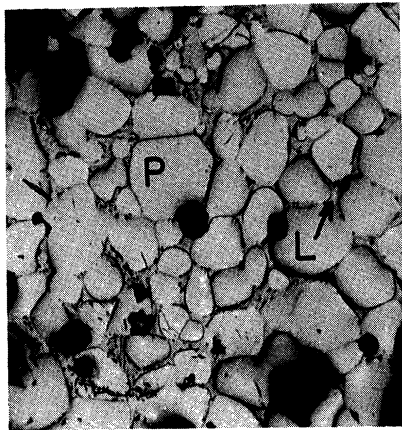
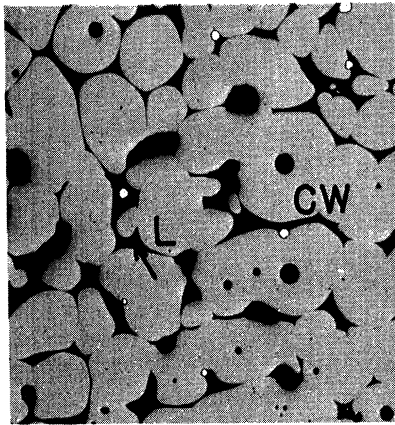
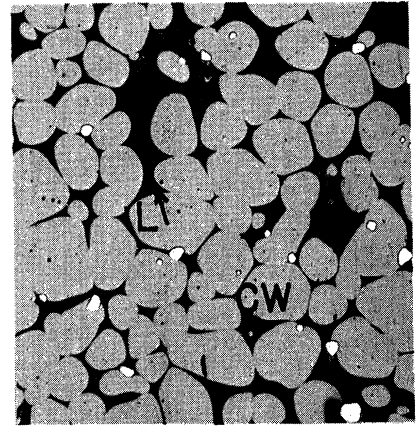


Fig. 15. Periclase refractories. X 150. Example: Unused periclase brick. The intergranular silicate was not altered significantly during 5 hours at 1600°C (2912°F).





(a)  
 1 Percent CaO  
 1 Percent SiO<sub>2</sub>  
 1200°C Temperature  
 4 hours Time



(b)  
 3  
 3  
 1200°C  
 4 hours

Fig. 16. CaO additions. X 150. Example: wustite (FeO) plus liquid containing CaO and SiO<sub>2</sub>.

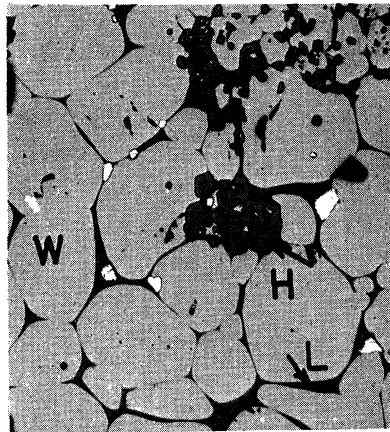
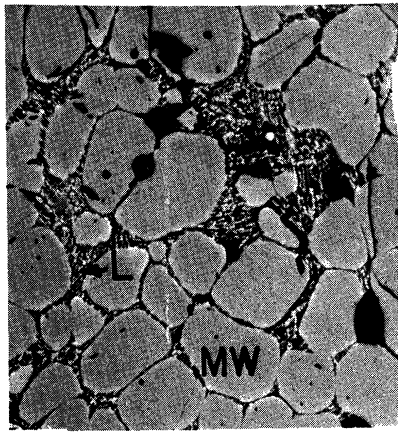
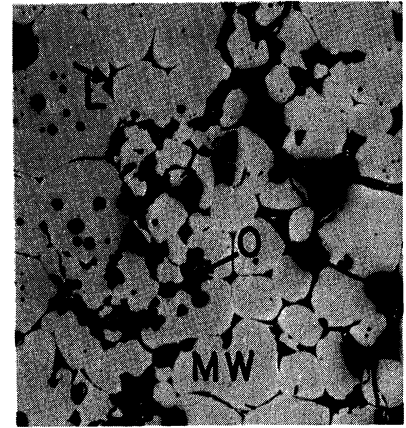


Fig. 17. Grain growth inhibition by hercynite (FeAl<sub>2</sub>O<sub>4</sub>). X 150. Example: wustite (FeO) + equal additions of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> to give an iron oxide saturated aluminosilicate liquid and hercynite. Treatment temperature: 1200°C (2192°F). Treatment time: 4 hours.



(a)  
30/70  
5  
1600°C  
1 hour

MgO/FeO  
Percent SiO<sub>2</sub>  
Temperature  
Time



(b)  
40/60  
5  
1600°C  
1 hour

Fig. 18. Grain growth inhibition by olivine  $[(\text{Mg,Fe})_2\text{SiO}_4]$ .  
X 150.

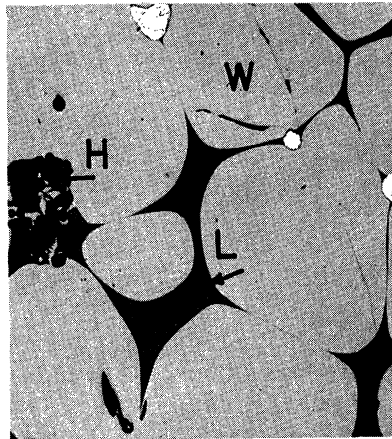


Fig. 19. Hercynite ( $\text{FeAl}_2\text{O}_4$ ) bonding. X 150. Example:  
wustite ( $\text{FeO}$ ) + equal additions of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  to  
give an iron oxide saturated aluminosilicate liquid and  
hercynite. The presence of hercynite provides a solid-  
to-solid bond through the intergranular liquid.



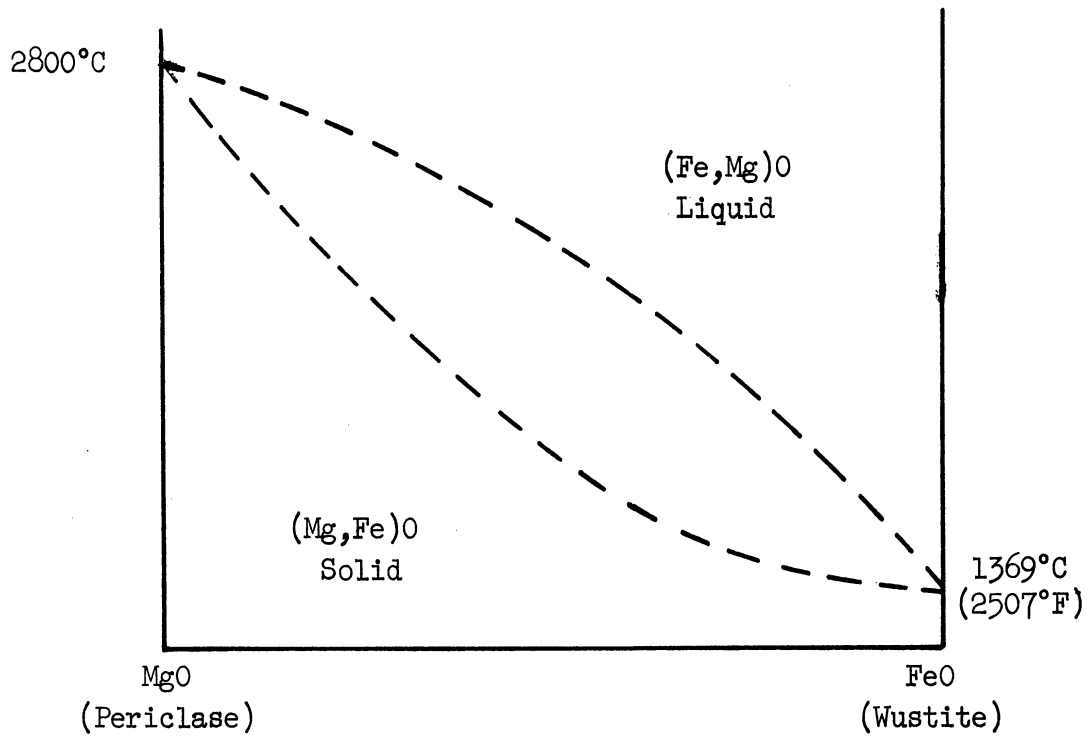


Fig. 20. MgO-FeO system. Based on Bowen and Schairer,<sup>13</sup> and Darken and Gurry.<sup>14</sup> This, and the following two diagrams ignore the nonstoichiometric composition of wustite.

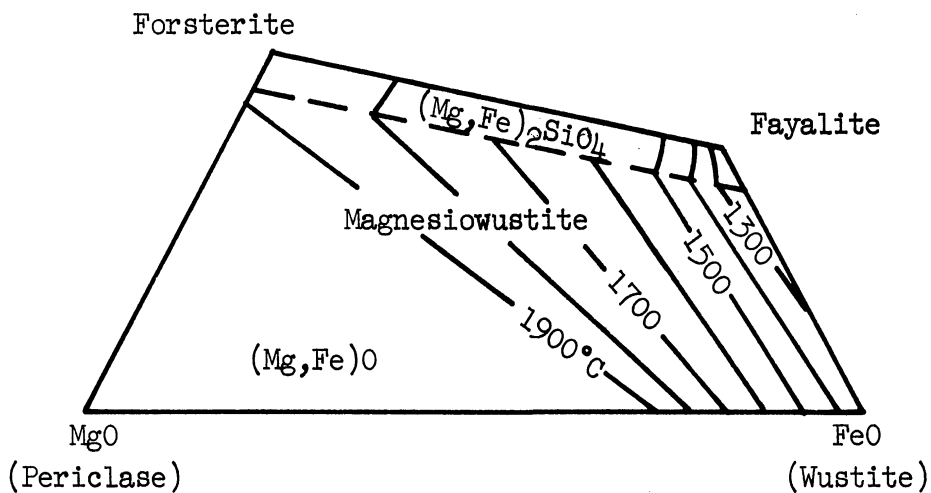


Fig. 21. MgO-FeO-SiO<sub>2</sub> system. Estimated liquidus temperatures are shown for compositions with primary (Mg,Fe)O. From E. F. Osborn and A. Muan.<sup>4</sup>

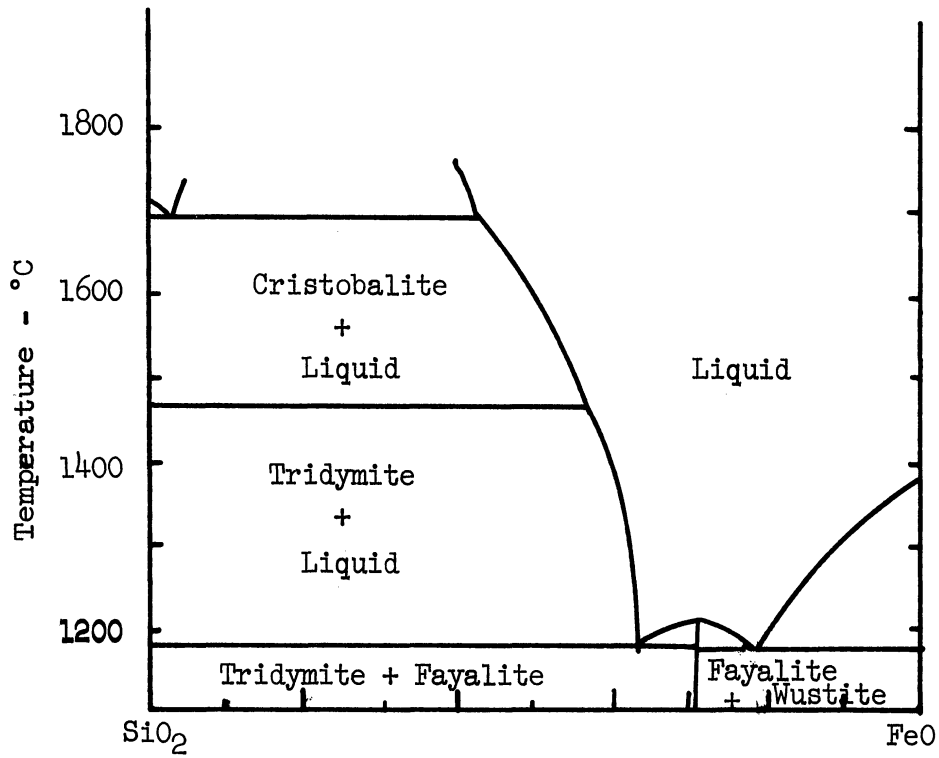


Fig. 22. FeO-SiO<sub>2</sub> system. From Bowen and Schairer.<sup>15</sup>

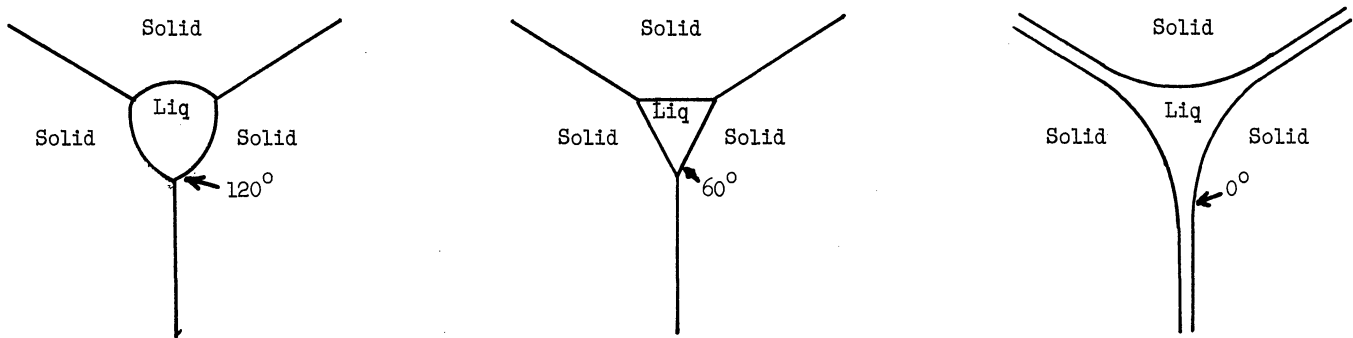


Fig. 23. Liquid/solid microstructures. (a)  $\gamma_{S/S} = \gamma_{S/L}$ : therefore,  $\theta = 120^\circ$ . (b)  $\theta = 60^\circ$ . (c)  $\gamma_{S/S} = 2\gamma_{S/L}$ ; therefore  $\theta = 0^\circ$ , and complete grain-boundary wetting occurs.

