

EFFECT OF OTHER OXIDES ON THE MICROSTRUCTURE
OF PERICLASE (MgO) ABOVE STEEL MELTING TEMPERATURES

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ABSTRACT: The microstructures developed by periclase (MgO) in the presence of calcium-silicate, calcium-aluminate, and calcium-iron-aluminate liquids were examined after firing at temperatures up to 1800°C (3270°F). This study led to the following results pertaining to growth of the individual crystalline grains, liquid phase distribution, and second-solid-phase bonding in these microstructures.

The rate of periclase crystalline grain growth is controlled by the energy of the solid/liquid interface, and increases with the square root of time and temperature. It is also influenced by the composition of both the liquid and the solid.

The distribution of the liquid phase among the individual crystalline grains is controlled by the composition of the liquid. Solid-to-solid bonding is more effective in the presence of a liquid when there are two solid phases present rather than one. This last finding may lead to useful generalizations in formulating refractory compositions with improved high-temperature strength.

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I. INTRODUCTION

This report presents the results of a study of the effect of other oxide liquids on the microstructure of periclase (MgO) at temperatures up to 1800°C (3270°F). The purpose of the study was to learn more about the effects of such service factors as (1) time, (2) temperature, (3) liquid composition, and (4) liquid content upon the crystalline grain* growth, liquid-phase distribution, and solid-phase bonding.

This study was prompted by the fact that present-day service conditions for basic refractories demand higher temperatures than those previously reported.^{1,2} These reports indicated that balanced compositions might lead to more solid-to-solid contact in periclase (MgO) microstructures. A summary of previous work on microstructures and equilibrium phase relationships is presented in Appendix A.

Details of the experimental procedures used in the present study are presented in Appendix B. In brief, these include heat treatments of prescribed compositions which contain the solid periclase (MgO) and a liquid composed of various oxides. After heat treatment the compositions were subjected to quenching and microscopic examination.

The results of the study are discussed in Section II in terms of (A) the crystalline grain growth of the solid oxide, (B) the effect of liquid composition upon microstructural geometry, which includes the distribution of the liquid among the solid oxide grains, and (C) the effectiveness of the presence of a second solid phase in providing more solid-to-solid contact. The second consideration, (B), is illustrated in Fig. 1, which shows the effect of lime (CaO) additions in promoting solid-to-solid contact between magnesiowüstite grains. The effectiveness of a second solid phase in providing more solid-to-solid contact is illustrated in Fig. 2.

II. RESULTS AND DISCUSSION

The microstructure of periclase was examined after it had been exposed to calcium-silicate, calcium-aluminate, and calcium-iron-aluminate liquids, over the temperature interval 1400°C (2550°F) to 1800°C (3270°F). In addition to

*Because "grain" as used in the steel industry bears two connotations, in this report a separate term will be used for each. "Grog grain" denotes the refractory raw material particle, and "crystalline grain" denotes the conventional grain of a microstructure.

temperature and composition of the liquid, the variables included time and the amount of liquid. A limited number of magnesiowüstite compositions with an MgO/FeO ratio of 80/20 were examined to establish the relationship between magnesiowüstite and periclase microstructures. The complete data are presented in Table IV.

A. Growth of Individual Crystalline Grains

1. Time.—The crystalline grain size of periclase was found to increase with the square root of time for all of the conditions of temperature and time studied. A typical set of data for periclase in the presence of a calcium-silicate liquid is shown in Figs. 3 and 4. A similar correlation between crystalline grain size and time has previously been reported for both magnesiowüstite and magnesiomagnetite.^{1,2} This correlation indicates that the rate of growth at constant temperature is controlled by the energy of the interface between the solid and the liquid.

2. Temperature.—The periclase crystalline grain size was found to increase markedly with temperature at constant composition over the interval 1400°C (2550°F) to 1800°C (3270°F). Examples of this growth are shown in Figs. 5 and 6. The increased growth rates at higher temperatures may be attributed to two factors. First, the mobilities of the diffusing magnesium and oxygen ions are expected to be higher, which would allow for faster transport from small crystalline grains through the liquid and onto growing crystalline grains. Second, at higher temperatures the solubility of MgO is higher in the $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ liquids, as shown in Fig. 13. This would contribute to a higher diffusion rate. However, this second effect may be partially offset by an increase in liquid content, which is shown to retard grain growth.

3. Amount of Liquid.—As was previously reported for the magnesiowüstites and magnesiomagnetites,^{1,2} the amount of liquid has an effect upon the rate of crystalline grain growth. Although this effect is to be considered secondary to those of time and temperature, it is a measurable one. The rate of crystalline grain growth has been found to decrease as the liquid content is increased, with typical results for periclase and several oxide liquids as shown in Fig. 7. In this and earlier studies the amount of liquid was controlled through the amount of fluxing oxide added to it, and actual liquid contents were measured on the microstructures. A definite explanation for the decreased growth rate cannot be given at this time, but possible explanations have already been offered.¹

4. Liquid Composition.—The composition of the liquid was found to have an effect upon the growth rate of periclase crystalline grains. It was found that in general, the growth rate was highest in calcium-iron-aluminate liquids,

intermediate in calcium-aluminate liquids, and lowest in calcium-silicate liquids. Specific comparisons can be made for samples which have comparable liquid contents and have been fired at 1600°C for 64 hours. Several examples of this comparison (other factors constant) are presented in Table I.

TABLE I
CRYSTALLINE GRAIN SIZE VS. LIQUID COMPOSITION

Liquid Composition	Mean Diameter (mm)	Liquid Content (%)
C ₄ AF*	.091	14
CaO/Al ₂ O ₃ -56/44	.075	13
CaO/Al ₂ O ₃ -42/58	.076	19
CaO/SiO ₂ -53/47	.058	13
CaO/SiO ₂ -39/61	.076	13

*C₄AF = 4CaO·Al₂O₃·Fe₂O₃

The higher growth rate for the CaO/SiO₂-39/61 liquid as compared with the CaO/SiO₂-53/47 liquid may be explained in terms of the known phase relationships, which are reproduced in Fig. 12. As the CaO/SiO₂ ratio decreases along the 1600°C isotherm, the solubility of MgO in the liquid increases quite markedly. This would allow for a faster diffusion rate of MgO through the liquid.

Changing the CaO/Al₂O₃ ratio from 56/44 to 42/58 does not produce a change in the growth rate in the CaO-MgO-Al₂O₃ system. From the known phase relationships, which are reproduced in Fig. 11, it can be seen that changing the CaO/Al₂O₃ ratio in the liquid along the 1600°C isotherm does not change the solubility of MgO; therefore the growth rate would be expected to remain constant. The increase in growth rate with the addition of iron oxide to calcium-aluminate liquids cannot be definitely explained at this time. It should be noted, however, that there might be some solid solution of iron in the periclase, and that this would lead to a higher rate of crystalline grain growth.

5. Solid Composition.—The addition of FeO to the periclase solid to produce an over-all MgO/FeO ratio of 80/20 was found to increase the crystalline grain growth rate. After sintering for 4 hours at 1700°C (3190°F) the comparison shown in Table II were made (other factors constant).

TABLE II

CRYSTALLINE GRAIN SIZE VS. SOLID COMPOSITION

Solid Composition	Liquid Composition	Mean Diameter (mm)	Liquid Content (%)
80/20 MgO/FeO	50/50 CaO/SiO ₂	.085	5.7
80/20 MgO/FeO	50/50 CaO/SiO ₂	.074	10
MgO	15/85 CaO/SiO ₂	.057	5
MgO	65/35 CaO/SiO ₂	.035	8

For comparable liquid contents it is seen that the crystalline grain growth rate for the 80/20 MgO/FeO solid solution is appreciably faster than that for pure periclase (MgO). This observation agrees with the results reported for magnesiowüstite, where it was found that the growth rate decreased with increasing MgO contents in the solid.¹

B. Liquid Phase Distribution

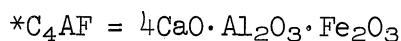
The effect of lime (CaO) additions to silicate liquids in promoting solid-to-solid contact in magnesiowüstite microstructures is illustrated in Fig. 1. Silicate liquids completely penetrate the solid grain boundaries. However, lime (CaO) additions to these liquids modify the solid/liquid interface energy so that the penetration is restricted to definite angular shapes, thus providing for increased solid-to-solid contact

Microstructures similar to those for magnesiowüstite in the presence of calcium-silicate liquids were found for periclase in the presence of various liquids. Three typical microstructures for periclase in the presence of calcium-silicate, calcium-aluminate, and calcium-iron-aluminate liquids are shown in Fig. 8. The liquid phase distribution in these microstructures can be characterized by the dihedral angle, which is the angle of penetration of the liquid along the solid grain boundaries. The median of a number of randomly measured angles provides a convenient index for comparing microstructures.³ A summary of dihedral angle measurements for periclase microstructures is presented in Table III.

TABLE III

DIHEDRAL ANGLES IN PERICLASE MICROSTRUCTURES
AFTER 64 HOURS AT 1600°C (2910°F)

Liquid Composition	Dihedral Angle (Degrees)
CaO/SiO ₂ -39/61	22
CaO/SiO ₂ -53/47	24
CaO/Al ₂ O ₃ -42/58	31
CaO/Al ₂ O ₃ -56/44	29
C ₄ AF*	30



Within a given system there is essentially no change in microstructure with the composition of the liquid. In the CaO-MgO-SiO₂ system this behavior can be explained in terms of the structure of the liquid. The 1600°C isotherm closely parallels and lies almost directly above the orthosilicate join. The structure of liquids in this region of the diagram is controlled by the SiO₄ = tetrahedra concentration, which is essentially constant in this case.

The amount of solid-to-solid contact is higher for calcium-aluminate liquids than for calcium-silicate liquids, as indicated by the larger dihedral angle. The most probable explanation for this behavior would note that calcium-aluminate liquids dissolve very little of the solid periclase, which may be in part responsible for the greater dihedral angle. This situation differs from that of silicate liquids in contact with magnesiowüstites, where the solubility of the solid is much higher. The addition of iron oxide to calcium-aluminate liquids has very little effect on the dihedral angle.

C. Solid Phase Bonding

As previously reported,^{1,2} the presence of a second solid phase is beneficial in promoting solid-to-solid contact. It was found that such contact is also promoted in periclase base refractories when forsterite (Mg₂SiO₄) and spinel (MgAl₂O₄) are present as the second solid phase. The compositions studied were chosen as illustrations of the surface energy relationships in a system containing two solids and a liquid, and do not reflect possible direct applications in formulating refractory compositions.

If the CaO/SiO_2 ratio is decreased below 39/61 in the CaO-MgO-SiO_2 system at 1600°C , a second solid—forsterite (Mg_2SiO_4)—will form as an equilibrium microconstituent. The distribution of this phase can be controlled through heat treatment. If the forsterite is formed on cooling from a higher temperature where only periclase and liquid are present, it will be precipitated in the liquid which is present as a film between the periclase grains. When formed under these conditions, the second solid phase is most effective in promoting solid-to-solid contact. An example of bonding with forsterite is shown in Fig. 9. With a 15/85 ratio of CaO/SiO_2 , only periclase and liquid will be present at 1800°C (3270°F). On cooling to 1600°C (2910°F), forsterite will be precipitated to form an intergranular bridge in the liquid between periclase grains. This treatment is effective in producing extensive solid-to-solid contact.

Spinel (MgAlO_4) can provide another example of second-solid-phase bonding in the $\text{CaO-MgO-Al}_2\text{O}_3$ system. With a $\text{CaO}/\text{Al}_2\text{O}_3$ ratio of 30/70 in this system, only periclase and liquid will be present at 1800°C (3270°F). On cooling to 1600°C (2910°F), spinel will be precipitated in the intergranular liquid and thus provide solid-to-solid contact. Figure 10 shows the microstructure produced under these conditions.

These two examples provide supporting evidence for a conclusion drawn earlier:^{1,2} the energy of the boundary between two unlike solid phases is lower than the energy of the boundary between like solids. This conclusion is reached by noting that the liquids present in the two examples cited above do not penetrate periclase-forsterite or periclase-spinel boundaries as extensively as they do periclase-periclase boundaries. This result could prove to be useful in formulating refractory structures with high-temperature properties.

III. CONCLUSIONS

The microstructures which are developed by periclase (MgO) in the presence of calcium-silicate, calcium-aluminate, and calcium-iron-aluminate liquids have been described. The major conclusions which can be drawn from this study are:

1. Growth of Individual Crystalline Grains.—The rate of crystalline grain growth of periclase was found to be controlled by the relative solid/liquid interface energy. It was found to increase with the square root of time and with temperature, but to decrease where liquid contents were increased. The growth rate was also found to be influenced by the composition of the liquid and, when solid solution occurred, by the composition of the solid.

2. Liquid Phase Distribution.—The degree of liquid penetration along boundaries between adjacent crystalline grains was found to be slightly sensitive to the composition of the liquid. Calcium-silicate liquids were found to penetrate the boundaries most deeply, whereas calcium-aluminate and calcium-iron-aluminate liquids provided for the most solid-to-solid contact.

3. Solid Phase Bonding.—Solid-to-solid bonding is more effective in the presence of a liquid when two solid phases are present rather than one.

TABLE IV

Sample No.	Figure No.	Composition		Temperature (°C)	Time (Hours)	Mean Diameter (mm)	Liquid Content (%)	Dihedral Angle* (Degrees)
		Solid	Liquid					
239		MgO	CaO/Al ₂ O ₃ -50/50	1400	60	.0570	7	
240		MgO	CaO/Al ₂ O ₃ -50/50	1400	60	.0410	16	
241		MgO	CaO/Al ₂ O ₃ -50/50	1400	60	.0377	30	
253		MgO	CaO/Al ₂ O ₃ -56/44	1500	4	.0259		
254		MgO	CaO/Al ₂ O ₃ -56/44	1500	4	.0273		
265		MgO	CaO/Al ₂ O ₃ -56/44	1500	16	.0428		
266		MgO	CaO/Al ₂ O ₃ -56/44	1500	16	.0381		
279		MgO	C ₄ AF**	1400	16	.0473		
281		MgO	C ₄ AF**	1400	4	.0353		
282		MgO	C ₄ AF**	1400	4	.0287		
283		MgO	C ₄ AF**	1400	36	.0636		
284		MgO	C ₄ AF**	1400	36	.0689		
285		MgO	C ₄ AF**	1400	36	.0677		
286		MgO	C ₄ AF**	1400	64	.0816		
287		MgO	C ₄ AF**	1400	64	.0715		
288		MgO	C ₄ AF**	1400	64	.0663		
361		MgO	CaO/Al ₂ O ₃ -56/44	1500	64	.0567	12	
362		MgO	CaO/Al ₂ O ₃ -56/44	1500	64	.0568	19	
363		MgO	CaO/Al ₂ O ₃ -56/44	1500	64	.0560	25	
364		MgO	CaO/Al ₂ O ₃ -42/58	1500	64	.0672	12	
365		MgO	CaO/Al ₂ O ₃ -42/58	1500	64	.0510	18	
366		MgO	CaO/Al ₂ O ₃ -42/58	1500	64	.0449	23	
392		MgO	CaO/SiO ₂ -39/61	1600	4	.0341	7	
393		MgO	CaO/SiO ₂ -39/61	1600	4	.0392	12	
394		MgO	CaO/SiO ₂ -53/47	1600	4	.0322	13	
395		MgO	CaO/SiO ₂ -53/47	1600	4	.0282	17	
396		MgO	CaO/SiO ₂ -39/61	1600	16	.0524	5	
397		MgO	CaO/SiO ₂ -39/61	1600	16	.0511	12	
398		MgO	CaO/SiO ₂ -53/47	1600	16	.0395	7	
399		MgO	CaO/SiO ₂ -53/47	1600	16	.0383	12	
402		MgO	C ₄ AF**	1600	4	.0524		
430		MgO	CaO/SiO ₂ -39/61	1600	64	.0795	6	23
431		MgO	CaO/SiO ₂ -39/61	1600	64	.0761	13	21

TABLE IV (Concluded)

Sample No.	Figure No.	Composition		Temperature (°C)	Time (Hours)	Mean Diameter (mm)	Liquid Content (%)	Dihedral Angle* (Degrees)
		Solid	Liquid					
432		MgO	CaO/SiO ₂ -53/47	1600	64	.0588	10	22
433	3(c)	MgO	CaO/SiO ₂ -53/47	1600	64	.0575	13	25
437		MgO	CaO/Al ₂ O ₃ -42/58	1600	64	.0902	5	30
438	8(a)	MgO	CaO/Al ₂ O ₃ -42/58	1600	64	.0759	19	31
439		MgO	CaO/Al ₂ O ₃ -56/44	1600	64	.0860	6	
440	8(b)	MgO	CaO/Al ₂ O ₃ -56/44	1600	64	.0748	13	
441		MgO	C ₄ AF**	1600	64	.0814	4.6	28
442		MgO	C ₄ AF**	1600	64	.0970	9.5	31
443	8(c)	MgO	C ₄ AF**	1600	64	.0909	14	31
456		MgO	C ₄ AF**	1700	1	.0462		
458		MgO	CaO/Al ₂ O ₃ -50/50	1700	1	.0499		
462		MgO	CaO/Al ₂ O ₃ -65/35	1700	1	.0382		
464		MgO	CaO/SiO ₂ -15/85	1700	1	.0374		
466		MgO	CaO/SiO ₂ -65/35	1700	1	.0258		
476		MgO	C ₄ AF**	1700	4	.0724	5	
478		MgO	CaO/Al ₂ O ₃ -50/50	1700	4	.0562	9	
480		MgO	CaO/Al ₂ O ₃ -30/70	1700	4	.0614	13	
482		MgO	CaO/Al ₂ O ₃ -65/35	1700	4	.0512	11	
484		MgO	CaO/SiO ₂ -15/85	1700	4	.0568	5	
486		MgO	CaO/SiO ₂ -65/35	1700	4	.0346	8	
518	5(c)	MgO	C ₄ AF**	1800	4	.0879		
520		MgO	CaO/Al ₂ O ₃ -50/50	1800	4	.0660		
522		MgO	CaO/Al ₂ O ₃ -30/70	1800	4	.0684		
524		MgO	CaO/Al ₂ O ₃ -65/35	1800	4	.0784		
526		MgO	CaO/SiO ₂ -15/85	1800	4	.0711		
528		MgO	CaO/SiO ₂ -65/35	1800	4	.0659		
530***	10	MgO	CaO/Al ₂ O ₃ -30/70	1800	4			
534***	2(b), 9	MgO	CaO/SiO ₂ -65/35	1800	4			
558		MgO/FeO 80/20	CaO/SiO ₂ -50/50	1700	4	.0852	6	
559	1(b)	MgO	CaO/SiO ₂ -50/50	1700	4	.0741	10	
560		MgO	CaO/SiO ₂ -50/50	1700	4	.0608	15	

*The angle of penetration of the liquid phase between two grains of the solid phase.

**C₄AF = 4CaO·Al₂O₃·Fe₂O₃

***The two samples were refired at 1600°C for 16 hours.

ACKNOWLEDGMENTS

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APPENDIX A. REVIEW OF LITERATURE

Since a review of the pertinent literature concerning ceramic microstructures was included in an earlier report on magnesiowüstites [(Mg, Fe)O], this appendix includes only a summary of that report, a summary of a subsequent report on the microstructures of magnesiomagnetite ($Mg_xFe_{3-x}O_4$),² and a discussion of the phase relationships studied in the present investigation.

(a) Microstructures of Magnesiowüstite [(Mg,Fe)O] in the Presence of SiO_2

An investigation of the effect of time, temperature, amount of liquid, and ratio of MgO to FeO was carried out on periclase-type oxides. Results indicated that the magnesiowüstite crystalline grain size increases as the time and temperature of firing are increased. The crystalline grain size was found to decrease slightly as the amount of liquid was increased for a given firing time and temperature. The growth rate was found to decrease as the MgO/FeO ratio was increased and also to decrease in the presence of a second solid phase.

The location of the liquid phase was also an important consideration in this investigation. The liquid phase was found to penetrate as a film between the individual magnesiowüstite grains under all the conditions studied. When spinel-type phases were present, however, they were found to provide a solid-to-solid "bridge" between magnesiowüstite grains.

(b) Microstructures of Magnesiomagnetite ($Mg_xFe_{3-x}O_4$) in the Presence of SiO_2

An investigation similar to that described above was carried out on magnesiomagnetite, with results indicating the same effects on crystalline grain growth as were found for magnesiowüstite.

With respect to the location of the liquid phase, it was found that silicate liquids do not penetrate magnesiomagnetite grain boundaries as fully as in magnesiowüstites. However, the amount of solid-to-solid contact is limited. Over the range studied, the degree of liquid penetration was not found to be sensitive to the composition of the solid, but the presence of olivine as a second solid phase was found to provide a means of bridging magnesiomagnetite grains and of providing for more solid-to-solid contact

(c) Phase Relationships

In the CaO-MgO- Al_2O_3 ternary shown in Fig. 11 there is very little change

in the solubility of MgO with composition or with temperature along either the 1500 or 1600°C isotherm.

This situation is changed considerably in the CaO-MgO-SiO₂ ternary system shown in Fig. 12. The solubility of MgO in the liquid changes significantly with liquid content along the 1600°C isotherm. However, this isotherm is parallel to and almost directly above the join from forsterite (2MgO·SiO₂) to di-calcium silicate (2CaO·SiO₂) with the compounds monticellite (CaO·MgO·SiO₂) and merwinite (3CaO·MgO·2SiO₂) between, which would indicate that the structure of the liquids along the 1600°C isotherm are very similar.

The pseudo-binary C₄AF-MgO is shown in Fig. 13. The solubility of MgO is limited in the liquid phase in this system.

APPENDIX B. EXPERIMENTAL PROCEDURE

Samples were obtained by sintering reagent-grade raw materials at selected temperatures for various times. This heat treatment was followed by subsequent preparation of the samples for microscopic examination by reflected light.

(a) Sample Preparation

Reagent grades of Fe_2O_3 , MgO , CaO , SiO_2 and Al_2O_3 powders were weighed and mixed in the desired amounts. The respective mixtures were then pressed into pellet-size samples. Presintering and regrinding were not necessary for structures which contained a liquid phase during heat treating.

(b) Heat Treatments

For the sintering temperatures up to and including 1600°C (2910°F), a tube furnace heated by SiC heating elements was used. The furnace temperature was controlled by means of a thermocouple placed near the heating elements. Sample temperatures were determined by a separate Pt-PtRh thermocouple placed in the tube close to the sample. The tube was open at both ends to allow the sample composition to come to equilibrium with an atmosphere of air. The samples were water-quenched after being fired at these temperatures.

The samples run at 1700 and 1800°C were fired in an oxy-acetylene fusion test furnace. Sample temperatures were determined by sighting directly on the sample with an optical pyrometer. The desired temperature was maintained by manually adjusting the gas flow rate.

(c) Microscopic Examination

Standard reflected light metallographic procedures were used in preparing the samples for analysis. This included grinding, impregnation, mounting, and polishing.

Grain sizes were determined by measuring the mean diameter of a number of randomly selected grains 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 size of similar microstructures.³

Liquid contents were measured using a point counting technique on a number of randomly selected areas in a two-dimensional microsection.

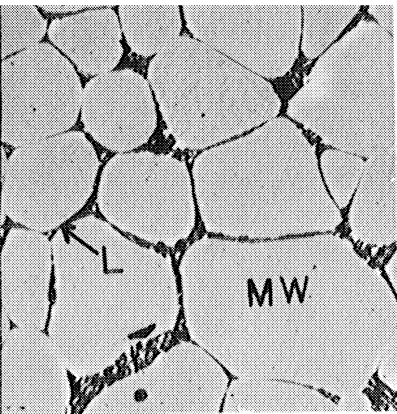
The dihedral angles were measured using an ocular rotating-stage combination on a two-dimensional cut of the sample.⁴

REFERENCES

1. L. H. Van Vlack and O. K. Riegger, Microstructure of Magnesiowüstite [(Mg,Fe)O] in the Presence of SiO₂, The University of Michigan, ORA Report O3683-5-T, Ann Arbor, April, 1961.
2. L. H. Van Vlack, O. K. Riegger, and G. I. Madden, Microstructure of Magnesiomagnetite [Mg_xFe_{3-x}O₄] in the Presence of SiO₂, The University of Michigan, ORA Report O3683-8-T, Ann Arbor, November, 1961.
3. L. H. Van Vlack, Physical Ceramics for Engineers, Ann Arbor, Malloy Printing, p. 49 (1960).
4. O. K. Riegger and L. H. Van Vlack, "Dihedral Angle Measurement," Trans. AIME, 218 (1960), 933.
5. R. B. Sosman and Olaf Andersen, Phase Equilibrium Diagrams of the Refractory Oxides, Research Laboratory, U.S. Steel Corp. (1946), Plate 4.
6. G. A. Rankin and H. E. Merwin, "Das Ternare System: Calciumoxyd-Aluminiumoxyd-Magnesiumoxyd," Z. anorg. u. allgem. Chem., 96 (1916), 309.
7. E. F. Osborn and A. Muan, Phase Equilibrium Diagrams of Oxide Systems, The American Ceramic Soc., Columbus (1960), Plate 2.
8. R. W. Ricker and E. F. Osborn, "Additional Phase Equilibrium Data for the System CaO-MgO-SiO₂," J. Am. Ceram. Soc., 37 (1954), 133.
9. J. R. Rait, "Basic Refractories," Iron and Steel, 23 (1950), 90.

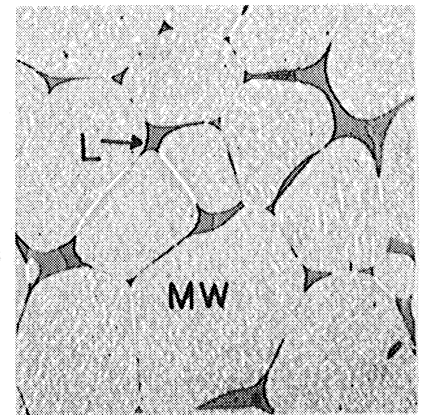
SYMBOLS USED IN ALL FIGURES

P - periclase MW - magnesiowustite
 S - spinel F - forsterite
 L - liquid



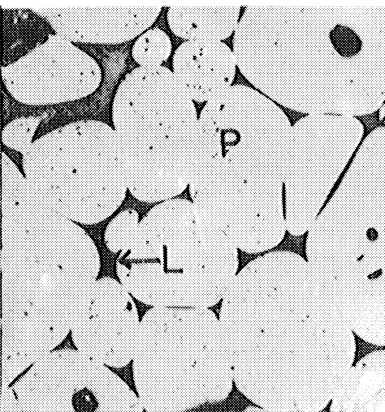
(a)
 4 hours
 1600°C
 3
 0
 40/60
 X250

Time
 Temperature
 Percent SiO₂
 Percent CaO
 MgO/FeO
 Magnification



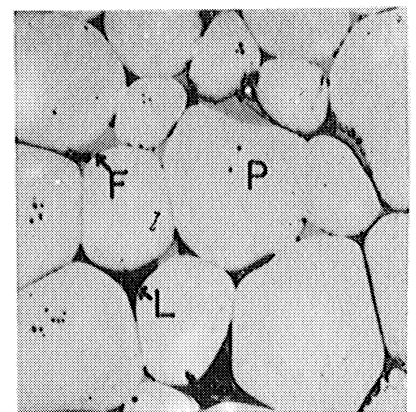
(b)
 4 hours
 1700°C
 2
 2
 80/20
 X150

Fig. 1. Lime (CaO) additions. There is less penetration of the silicate liquid between the crystal grains and more solid-to-solid contact.



(a)
 64 hours
 1600°C
 39/61

Time
 Temperature
 CaO/SiO₂ in liquid



(b)
 4 hours
 1800°C
 15/85

Fig. 2. Effect of a second solid phase in promoting solid-to-solid contact between periclase (MgO) grains. Sample (b) was refired at 1600°C for 16 hours. X250

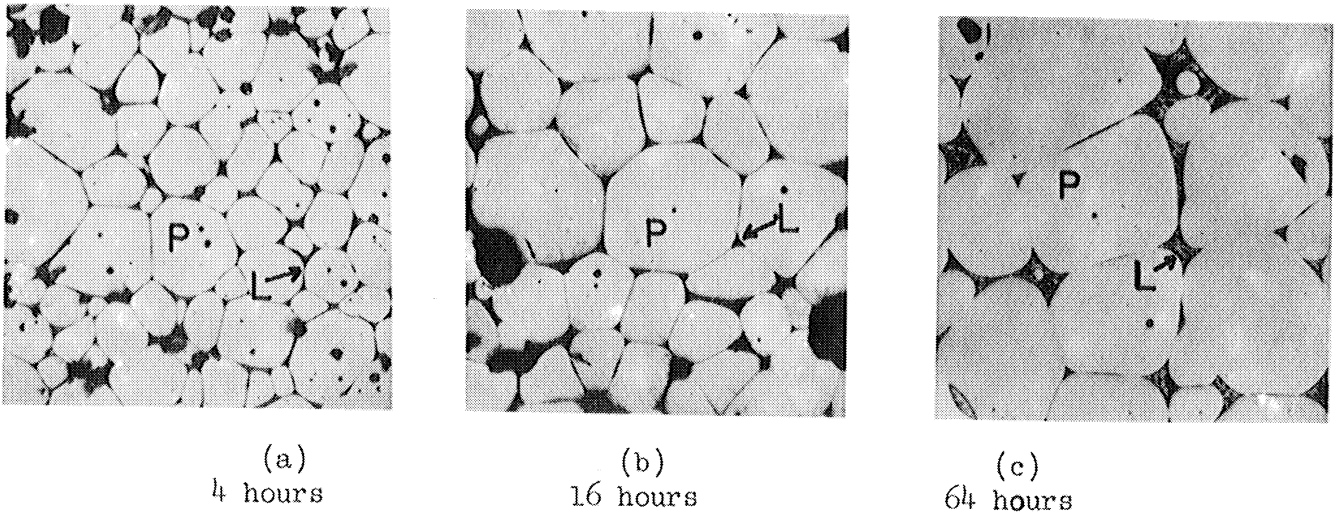


Fig. 3. Effect of time on Crystalline grain size. X250. Microstructures are periclasite in the presence of a liquid with a CaO/SiO_2 ratio of 53/47. Fired at 1600°C . Etched with 5% HF.

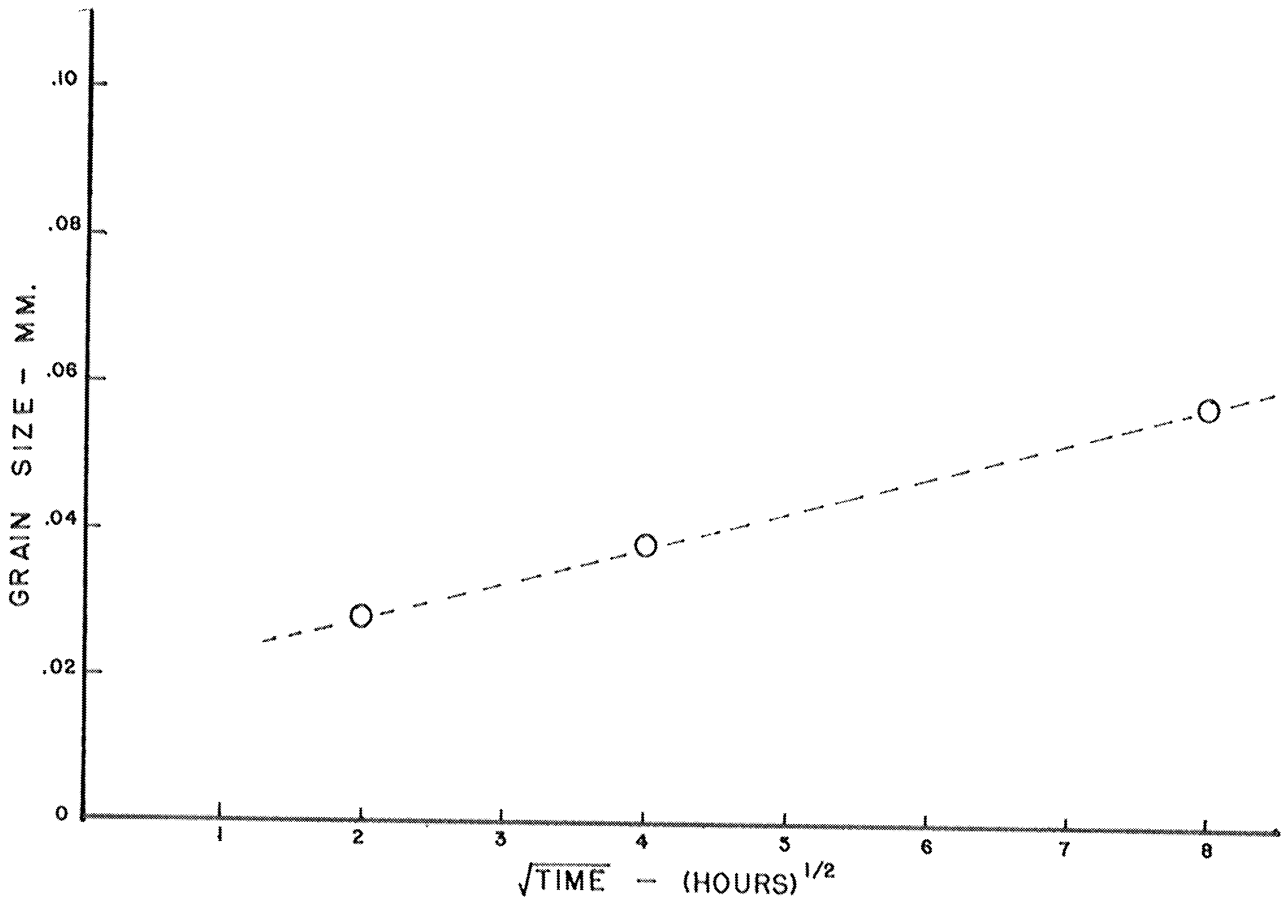


Fig. 4. Crystalline Grain Size vs. Time. (Same examples as in Fig. 3.)

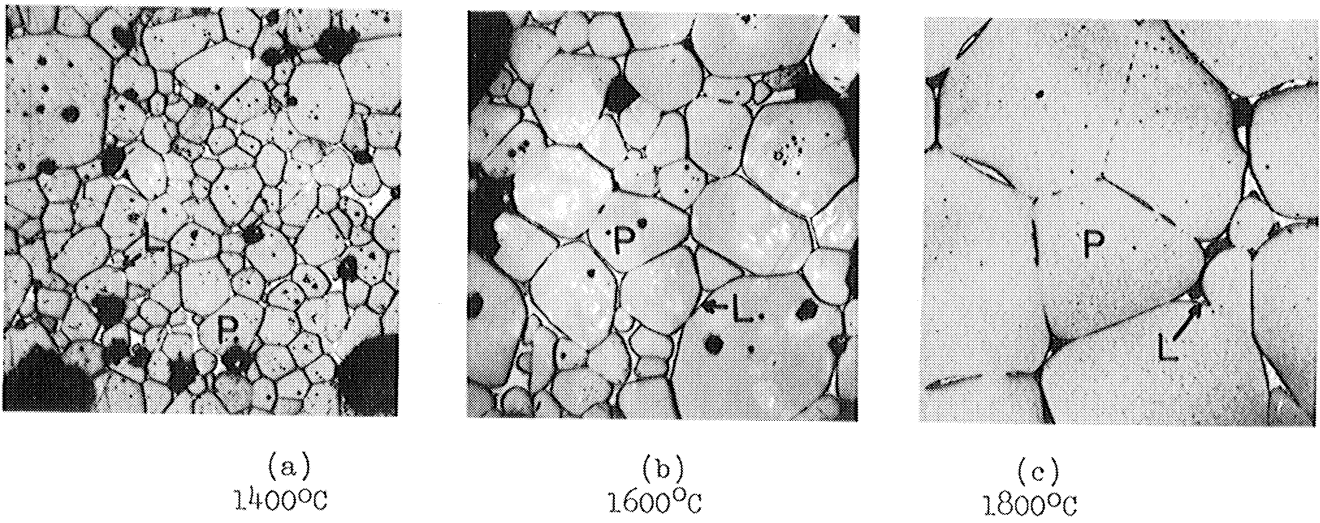


Fig. 5. Crystalline grain growth of periclase as a function of temperature after 4 hours in the presence of a $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ -rich liquid. Etched with 5% HF. 250X

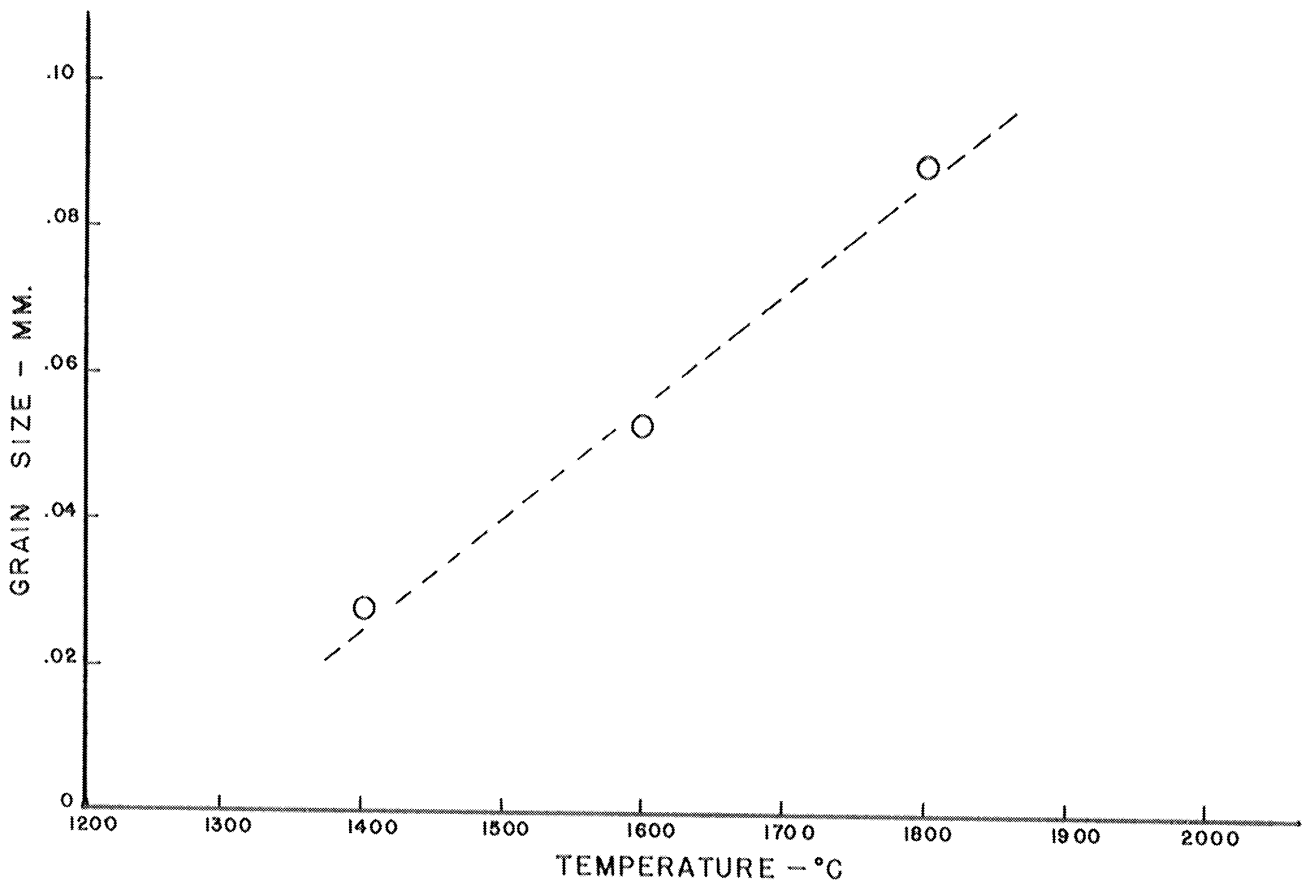


Fig. 6. Crystalline Grain Size vs. Temperature. (Same examples as in Fig. 5.)

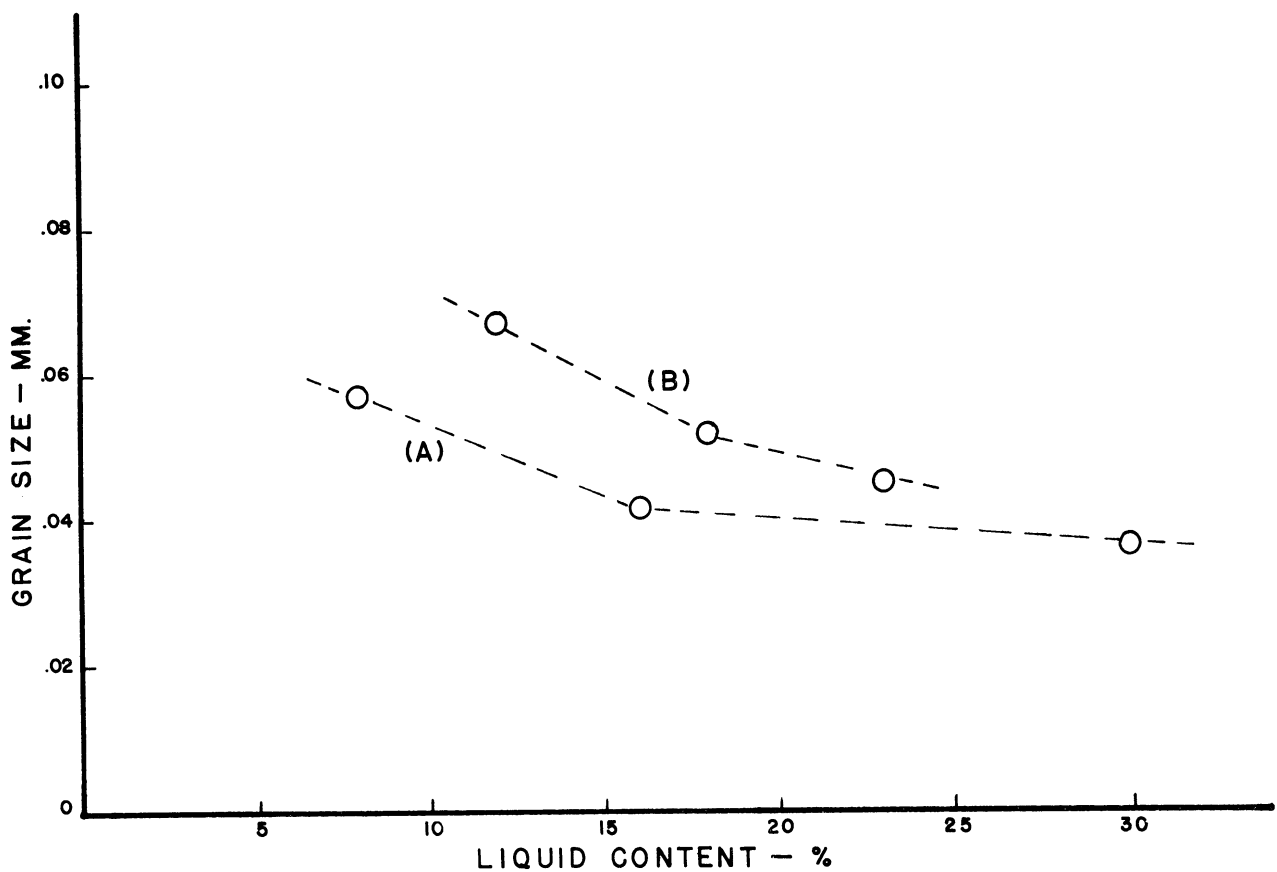
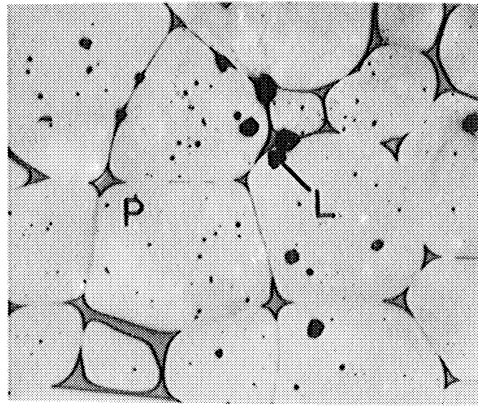
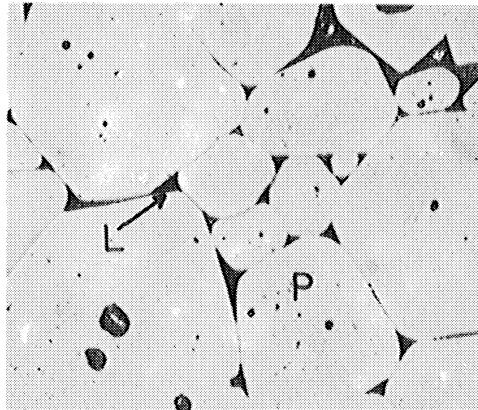


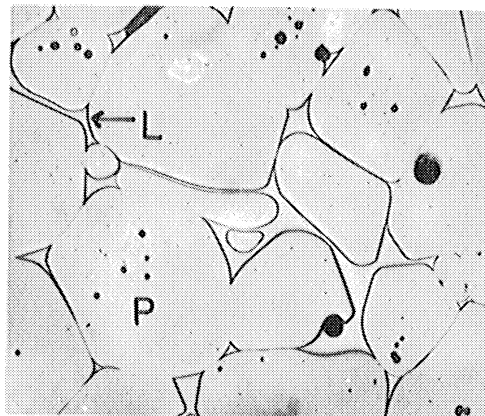
Fig. 7. Crystalline Grain Size vs. Liquid Content. Periclase (MgO) plus other oxide liquids. Curve (a): liquid composition 50/50 CaO/Al₂O₃, temperature 1400°C (2550°F), and time 60 hours. Curve (b): liquid composition 42/58 CaO/Al₂O₃, temperature 1500°C (2730°F), and time 64 hours.



a) Calcium-silicate liquid.



b) Calcium-aluminate liquid.



c) Calcium-iron-aluminate liquid.

Fig. 8. Periclase microstructures after 64 hours at 1600°C (2910°F) and water quenched. Etched with 5% HF. 250X

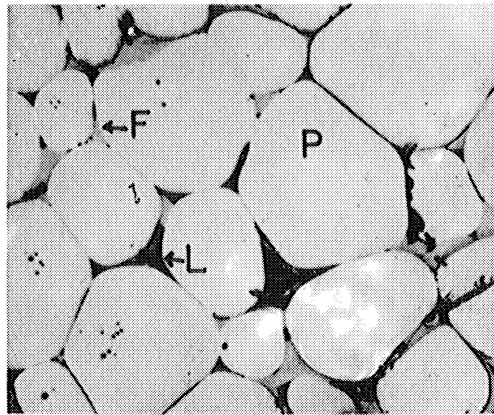


Fig. 9. Forsterite (Mg_2SiO_4) bonding. 250X. CaO/SiO_2 ratio 15/85. Sintered 4 hours at $1800^\circ C$ ($3270^\circ F$) followed by 16 hours at $1600^\circ C$ ($2910^\circ F$). This treatment produced extensive solid-to-solid contact. Etched with 5% HF.

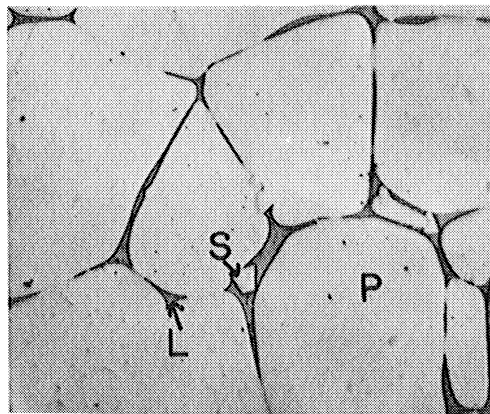


Fig. 10. Spinel ($MgAl_2O_4$) bonding. 250X. CaO/Al_2O_3 ratio 30/70. Sintered 4 hours at $1800^\circ C$ ($3270^\circ F$) followed by 16 hours at $1600^\circ C$ ($2910^\circ F$). Etched with 5% HF.

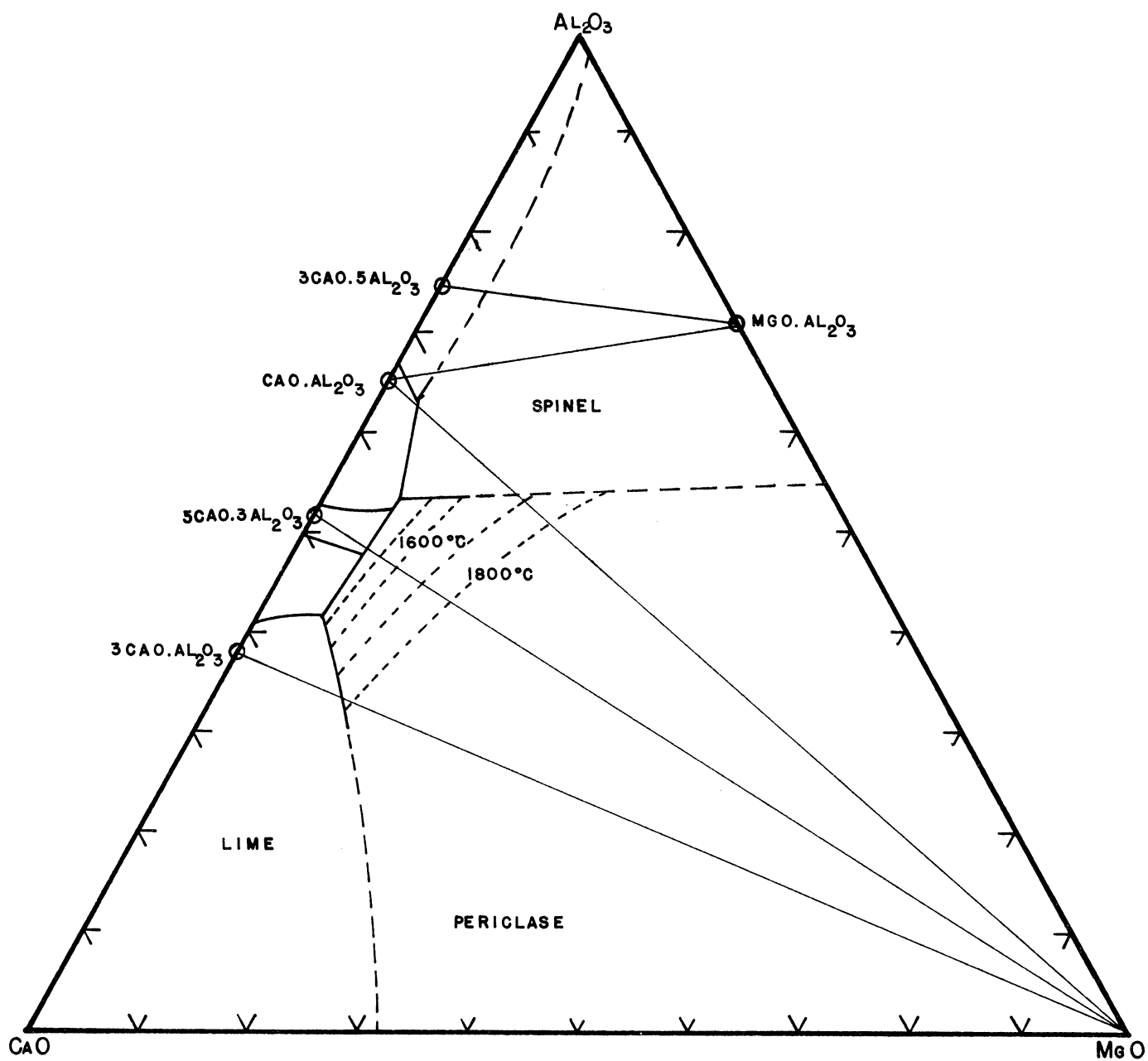


Fig. 11. System $\text{CaO-MgO-Al}_2\text{O}_3$. (After Sosman and Andersen⁽⁵⁾ and Rankin and Merwin⁽⁶⁷⁾).

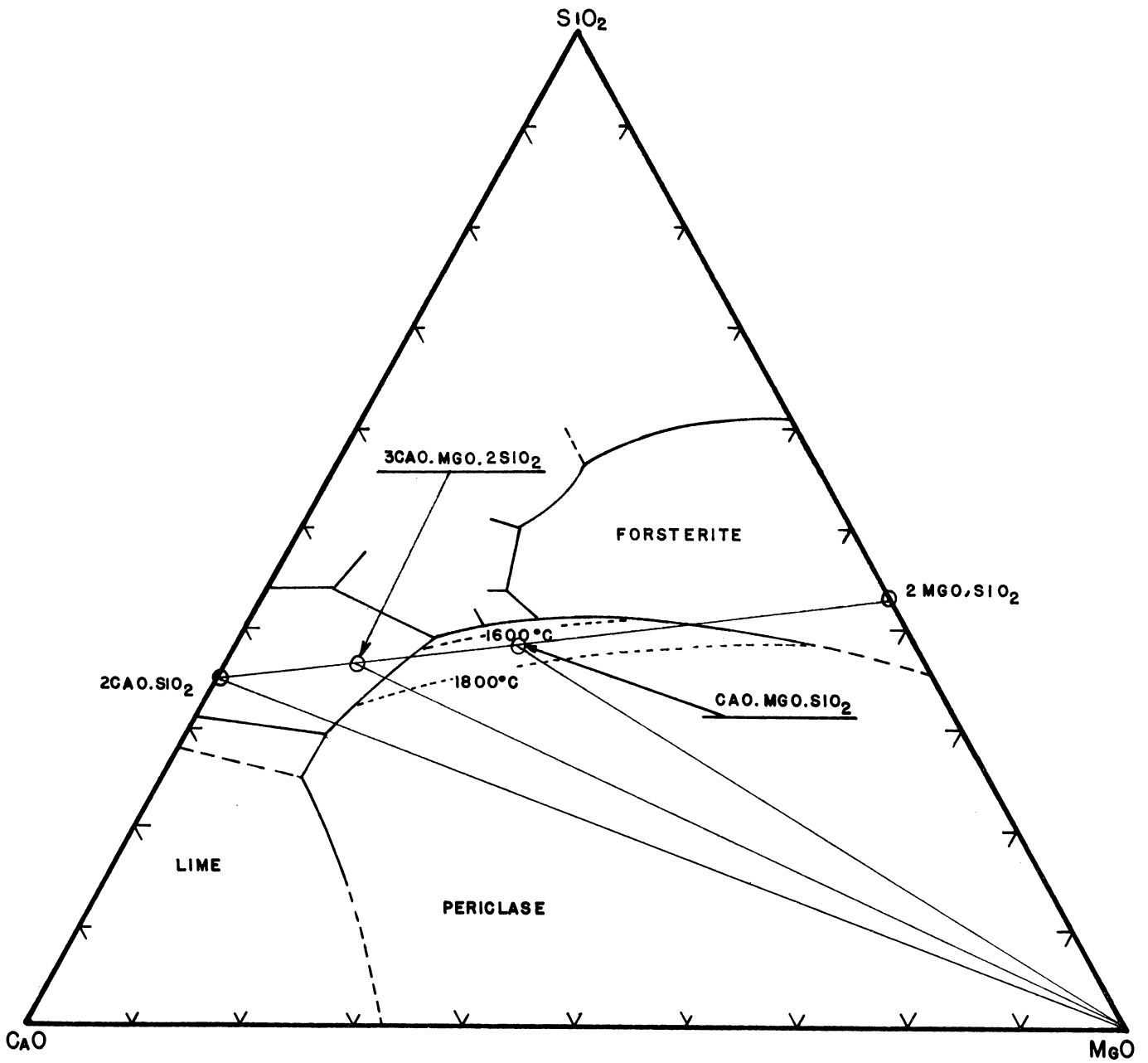


Fig. 12. System CaO-MgO-SiO_2 . (After Osborn and Muan⁽⁷⁾ and Ricker and Osborn⁽⁸⁾).

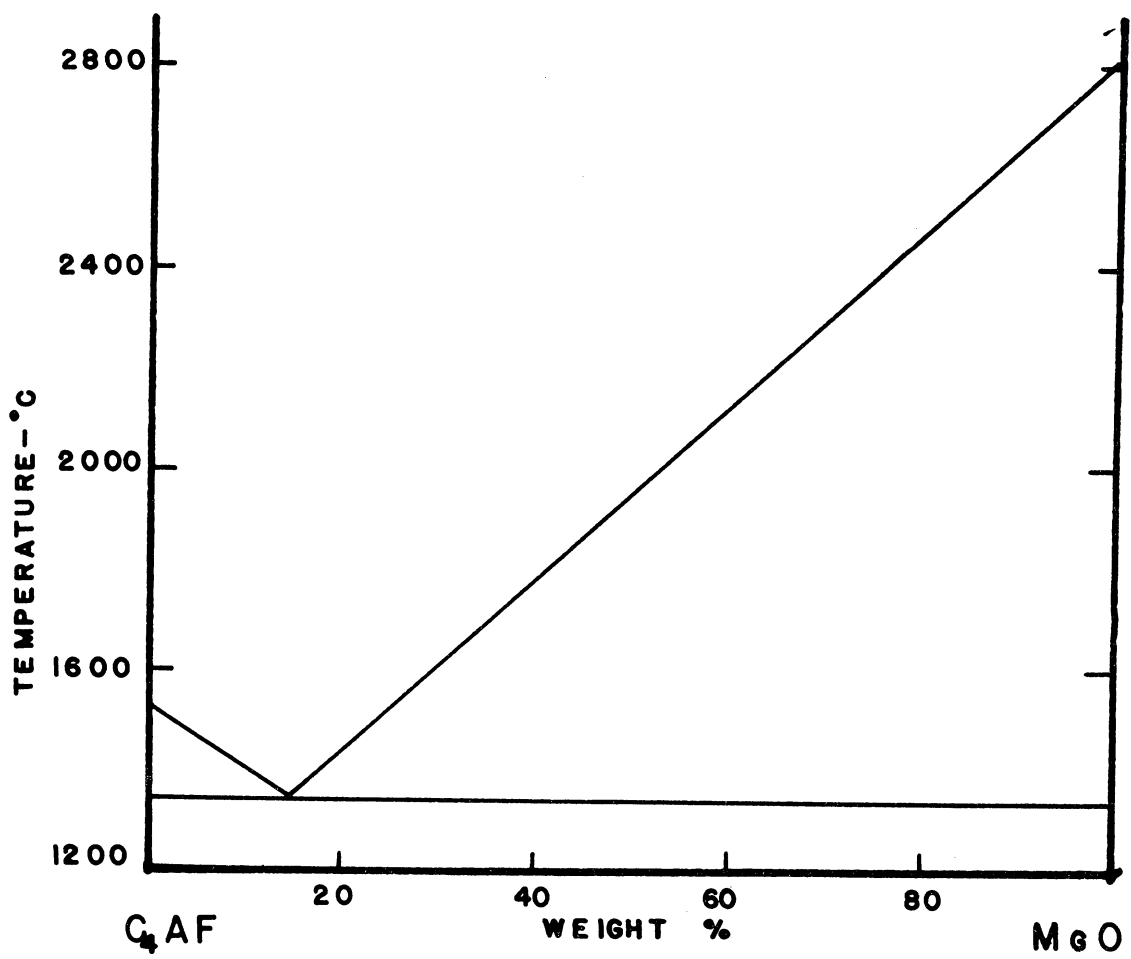


Fig. 13. System $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3\text{-MgO}$; C=CaO, A= Al_2O_3 , F= Fe_2O_3 .
(After Rait⁽⁹⁾).

