THE AMERICAN MINERALOGIST, VOL. 48, JANUARY-FEBRUARY, 1963

PHASE TRANSFORMATIONS IN SILICA-ALUMINA-MAGNESIA MIXTURES AS EXAMINED BY CONTINUOUS *X*-RAY DIFFRACTION: II. SPINEL-SILICA COMPOSITIONS

R. B. GRAF,[1] F. M. WAHL AND R. E. GRIM, *Department of Geology, University of Illinois, Urbana, Illinois.*

ABSTRACT

This paper is Part II of a series relating the investigation of phase transformations in silica-alumina-magnesia mixtures. Spinel-silica compositions were examined in detail and the variable reactivities of natural and synthetic components are discussed. In the synthesis of spinel the reactivity of corundum on initial firing is greater than that of the same material after preheating. The MgO (periclase) used in this reaction also contributed to a slower rate of spinel synthesis after preheating because of an increase in particle size and better crystallization of this component after initial firing.

With the addition of excess silica to a mix of spinel, periclase, and corundum, there is rapid formation of additional spinel at temperatures lower than those indicated on the phase-diagram of this system. It is considered that a liquid phase is important in this reaction.

In the presence of excess silica, there is a combination with periclase and corundum to form cordierite at 1300° C. This is followed at 1350° C. by a reaction between spinel and silica to form additional cordierite.

INTRODUCTION

The literature which concerns the mechanism of solid state reactions has been reviewed by Eitel (1954). Such reactions have been considered to proceed by means of a glassy transitional phase, which constitutes only a very small portion of the entire system. Several aspects of this type of reaction have been the subject of a recent symposium (Kingery, 1959). Chaklader and Roberts (1961) have indicated the probable presence of a glassy phase in the transformation of quartz to cristobalite.

Reaction temperatures between solids have been shown to be affected by the nature of the starting materials. Thus, materials which have the same chemical composition but different crystal structures may exhibit different reaction rates. This has been shown in the transformations of the various silica minerals to cristobalite in an investigation by Wahl *et al.* (1961a) using a continuous high-temperature *x*-ray diffraction technique. This technique has also been used to investigate the effects of the starting materials upon the synthesis of mullite (Wahl *et al.* 1961b). The effects of the starting materials have also been discussed by Fyfe (1960) and Alderman (1959).

In the present investigations, reaction rates between minerals in the system MgO-Al_2O_3-SiO_2 were examined by continuous high-temperature *x*-ray diffraction. The reaction between MgO and $Al(OH)_3$ to form

---

[1] Present Address: Research Laboratories, United Aircraft Corp., East Hartford, Conn.

spinel was studied, and the reactivities with silica of MgO and Al_2O_3 (corundum) were compared with that of spinel (MgO:Al_2O_3). Two forms of silica, quartz and cristobalite, were used to determine if the form of the silica influenced its reactivity with the MgO and Al_2O_3 compounds.

The furnace, all other equipment, and the experimental technique used in the work reported herein, were the same as described in the paper covering Part I of the present investigation (Graf *et al.*, 1962).

The following were used as starting materials: MgO, light powder, Allied Dye and Chemical Corporation; quartz, Hot Springs, Arkansas; $Al(OH)_3$ (synthetic gibbsite), Merck and Company; and silicic acid, A. R. grade, Mallinckrodt Chemical Works. In addition to these, synthetic cristobalite was obtained by firing the silicic acid at 1350° C. for 48 hours. The MgO gave an *x*-ray diffraction pattern corresponding to that of poorly crystallized periclase.

Spinel was synthesized by firing MgO and $Al(OH)_3$ in proportions corresponding to the spinel composition. This mix contained MgO and

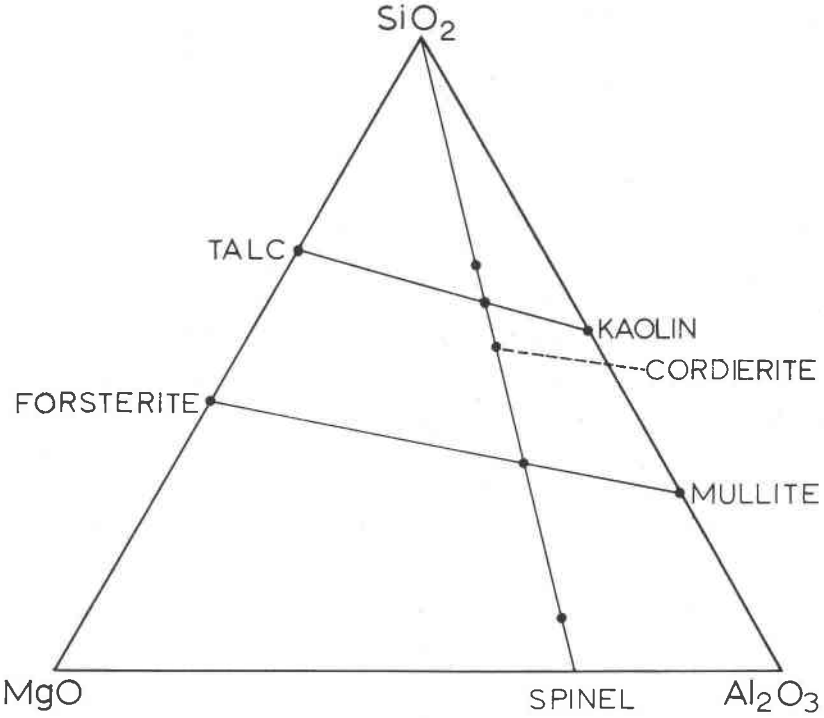

FIG. 1. The system MgO-Al_2O_3-SiO_2 with selected compositions plotted on the SiO_2—Spinel join.

corundum in addition to spinel after firing. This mix was combined with quartz in one series of mixtures, and with cristobalite in another series. The compositions of the two series were the same, so that any differences in the reactivities of quartz and cristobalite could be determined. One of the compositions was calculated so as to fall on a join between forsterite and mullite, one to fall on a talc-kaolinite join, one to have the composition of cordierite, one to be 81.25% spinel mix-18.75% silica, and one to be 18.75% spinel mix-81.25% silica (Fig. 1). The latter two (hereafter designated 4:1 and 1:4 mixes) were prepared so as to have compositions which could be equally spaced on a mole per cent diagram.

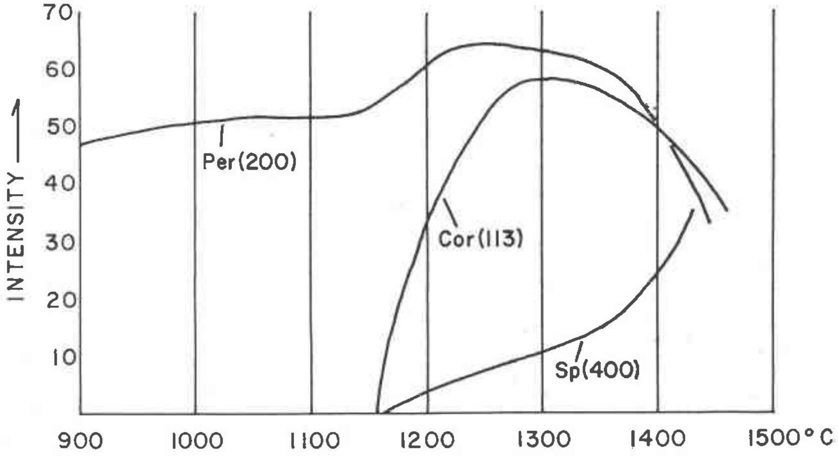

FIG. 2. Intensity of diffraction by high-temperature phases in a heated mixture of MgO and $Al(OH)_3$ in the ratio of 1:2.

EXPERIMENTAL RESULTS

Spinel was synthesized from MgO and $Al(OH)_3$ by firing a 1:2 mixture to 1300° C. A continuous high-temperature run was first made of this mix in order to select this firing temperature of 1300° C. The diagram of this first run (Fig. 2) indicates that corundum and spinel began to form simultaneously at approximately 1150° C., and that the corundum and MgO then reacted to form additional spinel at a higher temperature. This is indicated by a rise in the spinel curve which corresponds to a comparable decrease in the corundum curve. Some spinel forms from the alumina prior to its crystallization as corundum. The periclase slightly increases in crystallinity up to about 1250° C. where it begins to disappear with the formation of spinel. Another high-temperature run was then made, with this spinel mix (spinel:unreacted

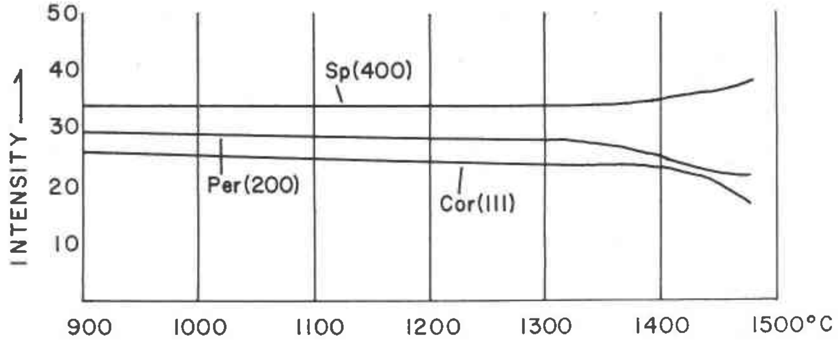

FIG. 3. Intensity of diffraction by high temperature phases in a heated mixture of spinel: unreacted MgO and corundum.

MgO and corundum) which had been fired to 1300° C. as a starting material (Fig. 3). When this pre-fired mix was again heated after cooling, the unreacted periclase and corundum were much less reactive. These materials were heated to 1480° C., and the result was only a slight increase in the amount of spinel as compared to the amount originally formed in the MgO-Al$(OH)_3$ run (Fig. 2). When the sample was cooled and *x*-rayed again, there was no significant change in the diffraction intensity of spinel between the cold sample and the sample as observed at 1480° C. The non-reactivity of the periclase and corundum might have been due to some annealing effect (such as a change in particle size) caused by previous firing. Hedvall (1938) has shown experimentally that MgO formed by the decomposition of $MgCO_3$ is apparently more reactive than MgO which was formed at some previous time. In the present case, however, the nature of the alumina phase might have been

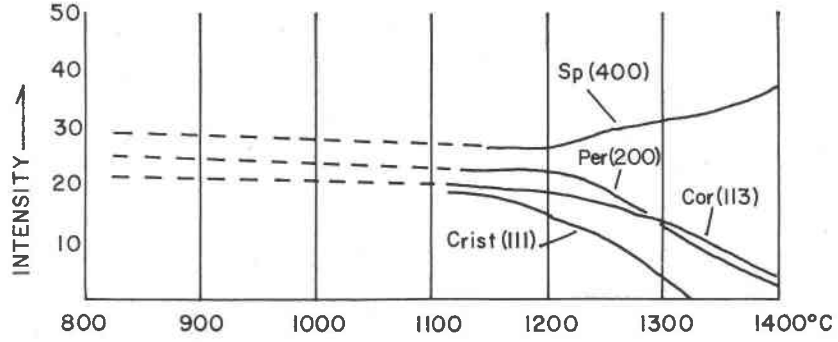

FIG. 4. Intensity of diffraction by high-temperature phases in a heated spinel mix (spinel: unreacted MgO and corundum) combined with silica in the ratio of 4:1.

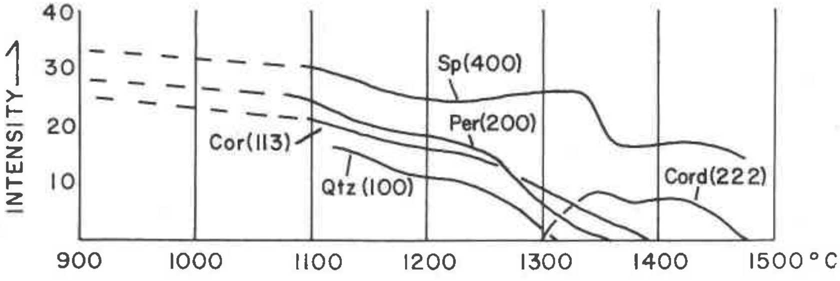

FIG. 5. Intensity of diffraction by high-temperature phases in a heated spinel-silica mixture with composition on the forsterite-mullite join.

the controlling factor. Wahl *et al.* (1961b) have shown gibbsite to be more reactive than naturally occurring corundum in the reaction with silica to form mullite, and possibly the synthetic corundum is also comparatively non-reactive in the mixes studied.

When the spinel mix (spinel: unreacted MgO and corundum) is combined with quartz or cristobalite in proportions of 4 spinel mix: 1 quartz or cristobalite and fired, the MgO and corundum react at 1200° C. to form additional spinel (Fig. 4). This reactivity may be due to the presence of a liquid phase, which is suggested by the fusion of cristobalite which begins at 1150° C. Furthermore, no cristobalite is formed from the quartz in the spinel-quartz (4:1) mix or from the spinel-quartz mix on the forsterite-mullite join. In fact, quartz is not present in these samples at temperatures above 1300° C. and possibly may have been converted directly to a liquid phase.

Additional spinel is also formed in the spinel-quartz and spinel

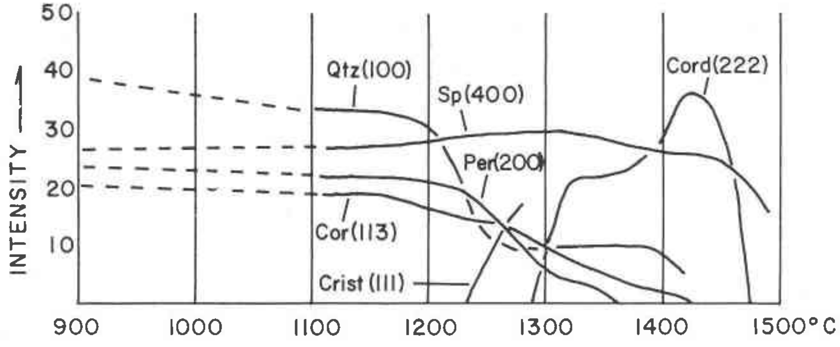

FIG. 6. Intensity of diffraction by high-temperature phases in a heated spinel-quartz mix of cordierite composition.

cristobalite mixtures which have compositions on the forsterite-mullite join (Fig. 5). In these mixtures, cordierite is formed at 1300° C., as it is in all of the other spinel-silica mixes (except the 4:1 mixes). The curve depicting the growth of spinel in the spinel-quartz mix which falls on the forsterite-mullite join (Fig. 5), has an abrupt decrease in slope at 1350° C. which corresponds to an increase in the cordierite curve. The spinel-silica mixes of cordierite composition exhibit approximately the same relationships (Figs. 6, 7). Periclase and corundum, however, show a decrease in intensity at lower temperatures, usually about 1200° C. to 1250° C. These factors suggest that the first formation of cordierite at 1300° C. is the result of the reaction of periclase and corundum with silica, and that the break in the cordierite curve is due to the reaction of spinel with silica at 1350° C. to 1375° C. to form additional cordierite. This two-stage reaction is not seen in the samples containing more silica than the cordierite composition.

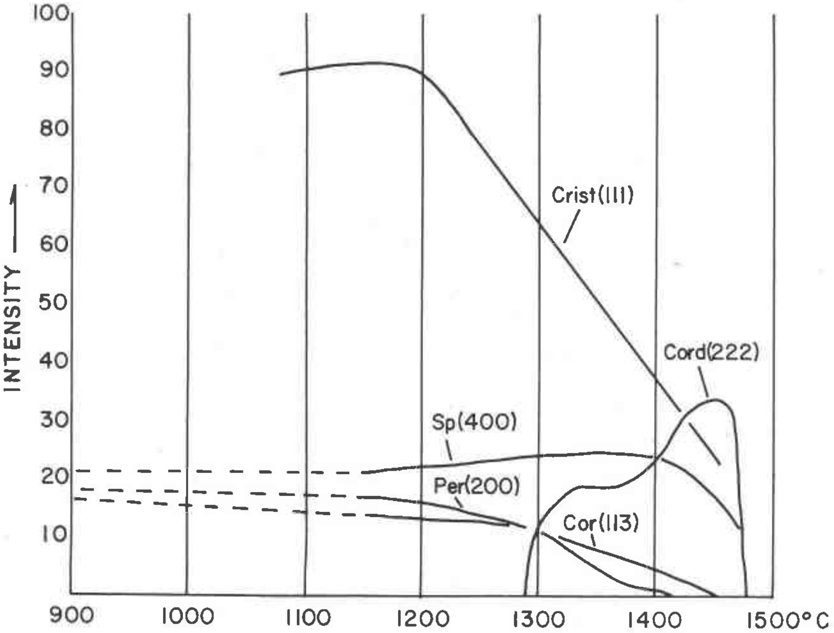

FIG. 7. Intensity of diffraction by high-temperature phases in a heated spinel-cristobalite mix of cordierite composition.

The nature of the silica phase has no apparent effect upon the formation of cordierite. The curves depicting the amounts of cordierite as grown from either quartz or cristobalite are strikingly similar (Figs. 6, 7). Cordierite forms at the same temperatue (about 1300° C.), and generally begins to fuse at approximately the same temperature (1425° C.). The lack of effect of the silica component upon the reaction may be explained by considering that the spinel, or the MgO and corundum, are reacting with fused silica to form cordierite. It should be emphasized that in the spinel-quartz mixes (Fig. 6), cristobalite is formed at approximately 1225° C., except in the mix with the composition of the forsterite-mullite join (Fig. 5) and in the 4:1 mix in which no cristobalite is observed, even though the quartz is gone at 1300° C. It seems probable that some liquid may be present in the temperature interval from 1225° to 1300° C., at which temperature cordierite is formed. It should also be noted that the cristobalite in the spinel-cristobalite mixes begins to fuse at about 1200° C. (Fig. 7) and that cordierite does not form in these mixes until a temperature of 1300° C. is attained, *i.e.*, above the fusion point of cristobalite.

Discussion of Results

When the spinel mix is used as a starting material, the MgO and corundum react only slightly to form additional spinel, even when heated to 1480° C. However, when the spinel mix is fired with silica in proportions of 4:1, additional spinel begins to form at 1200° C. and continues until the MgO and corundum are completely reacted (Fig. 4). This increase in the amount of spinel may also be seen in the spinel-quartz (forsterite-mullite join) mix (Fig. 5).

It seems probable that the silica phase and the MgO and Al_2O_3 phases may be reacting to form a liquid which has a composition in that area of the MgO-Al_2O_3-SiO_2 system which has the lower melting temperatures. Thus, it is considered that the adjacent grains of periclase, corundum and silica (quartz or cristobalite) react to form a liquid which has a composition in or near the stability field of cordierite, or the low temperature portion of the stability field of spinel. However, the lowest temperature at which spinel can crystallize from a liquid in this system is 1372° C., so the spinel was formed at temperatures considerably lower than would be predicted from the phase diagram.

The quartz in the mixes appears to be transformed directly to a liquid phase in the spinel-quartz (4:1) mix and the spinel-quartz (forsterite-mullite join) mix (Fig. 5). At the firing rate used, quartz is usually converted to cristobalite at about 1225° C. In these two mixes, no cristobalite was formed, which indicates that the silica may have been used up in the formation of the initial liquid. Cristobalite was formed in those mixes which had a higher silica content than that of the initial liquid. Because such an initial liquid should have a composition in or near the stability field of spinel, the mixes with higher contents of silica than those in the area of lowest melting temperatures in the stability field of spinel should form cristobalite upon being fired. This may be observed to occur in the mixes containing as much or more silica than cordierite. The presence of a liquid phase is supported by the results from the spinel-cristobalite mixes, in which cristobalite begins to decrease in intensity at about 1200° C., the same temperature at which the additional spinel is formed in the spinel-cristobalite mixes.

Although cordierite is not detected in the 4:1 spinel-silica mixes, it is formed at 1300° C. in all other mixes of these components. The intensity curves of cordierite in certain of the mixes have a pronounced upward change in slope at about 1350° C. This change in slope is due to the difference in reactivity of periclase and corundum as compared to spinel. The liquid phase from which cordierite is initially formed is apparently due to the reaction of periclase, corundum, and silica. These three materials appear to react to form cordierite at 1300° C. regardless of their relative abundance. The intensity curves of these three phases always begin to decrease at about 1200° C., which is 100° C. below the temperature of the formation of cordierite. The spinel curve, however, exhibits a decrease in intensity which corresponds to an upward change of slope of the cordierite curve (about 1350° to 1375° C.). This indicates that spinel is reacting with silica to form additional cordierite. All of the diagrams show this relationship to some degree, but it is probably best illustrated by the spinel-quartz mix with the composition of cordierite (Fig. 6).

Because the maximum temperatures attained in firing this series of components was about 1500° C., most of the mixes could not be completely melted. Thus, it was observed that the mixes with compositions containing the larger amounts of spinel had more spinel remaining after being heated to the maximum temperature. When certain of the samples were quickly cooled after being heated to the maximum temperature, considerable increases (approximately 50% to 75%) in the diffraction intensities of cordierite and spinel were observed.

SUMMARY

In the synthesis of spinel, the reactivity of freshly prepared corundum (formed from gibbsite) appears to be greater than that of the same corundum when it is refired. The MgO (periclase) used in this reaction also becomes better crystallized (or increases in particle size) and may contribute to the slower reaction rate which was observed.

When the spinel mix (spinel, periclase, corundum) is fired with silica, spinel is rapidly formed from the periclase and corundum. In some instances the spinel forms at temperatures considerably below those indicated on the phase diagram. It is considered that a liquid phase is important in this reaction. When amounts of silica in excess of 4 spinel: 1 silica are added to the mixes, cordierite is formed at 1300° C. The diffraction data indicate that periclase, corundum, and silica are involved in this first reaction to produce cordierite and that spinel and silica later react at 1350° C. to form additional cordierite. The nature of the reactants is considered to be more important than their relative abundance in so far as the formation temperature of cordierite is concerned. Diffraction intensity measurements made upon samples cooled to room temperature (from 1475° C.) indicate that large amounts of cordierite and spinel may be recrystallized from the liquid phase in some of the samples.

REFERENCES

ALDERMAN, A. R. (1959) Contemplation on certain types of metamorphic reactions. *Jour. Proc. Royal Soc. New South Wales*, **XCII,** 99–103.

CHAKLADER, A. C. D. AND A. L. ROBERTS (1961) Transformation of quartz to cristobalite. *Jour. Am. Ceram. Soc.* **44,** 35–41.

EITEL, W. (1954) *The Physical Chemistry of the Silicates.* Univ. Chicago Press, Chicago, Illinois.

FYFE, W. S. (1960) Hydrothermal synthesis and determination of equilibrium between minerals in the sub-liquidus region. *Jour. Geol.* **68,** 553–566.

GRAF, R. B., F. M. WAHL, AND R. E. GRIM, Phase transformations in silica-alumina-magnesia mixtures as examined by continuous *x*-ray diffraction: I. Talc-kaolinite compositions. *Am. Mineral.* (in press).

GRIM, R. E. AND G. KULBICKI (1957) Etude aux rayons x des reactions des minéraux argileux à haute temperature. *Bull. Soc. Franc. Ceram.* pp. 21–27.

HEDVALL, J. A. (1938) Reactions between substances in solid state. Symposium on the chemistry of cements, Stockholm, pp. 42–58.

KINGERY, W. D. (ed) (1959) *Kinetics of High Temperature Processes.* John Wiley & Sons, New York.

WAHL, F. M., R. E. GRIM, AND R. B. GRAF, (1961a) Phase transformations in silica as examined by continuous *x*-ray diffraction. *Am. Mineral.* **46,** 196–208.

——————, (1961b) Phase transformations in silica-alumina mixtures as examined by continuous *x*-ray diffraction. *Am. Mineral.* **46,** 1064–1076.

Manuscript received, July 5, 1962; accepted for publication, July 20, 1962.