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PHASE TRANSFORMATIONS IN SILICA-ALUMINA MIXTURES AS EXAMINED BY CONTINUOUS *X*-RAY DIFFRACTION

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ABSTRACT

The formation of mullite from mixtures of different varieties of alumina and silica was studied by high-temperature continuous *x*-ray diffraction techniques and by diffraction after soaking at high temperatures for various lengths of time. It is shown that the initial form of the alumina and silica has a large influence and that mole per cent variations in mix composition have little effect on mullite development.

The structural stability of component materials largely controls mullite nucleation, and the relationship between the formation of this mineral and preceding transformations in the normal thermal sequence of component alumina and silica materials is emphasized.

The addition of mineralizing ions can promote mullitization.

INTRODUCTION

The equilibrium diagram for the system Al_2O_3–SiO_2 has been critically examined and re-evaluated by many persons since it was first determined by Bowen and Greig in 1924. The most recent revision is that of Aramaki and Roy (1960) and is based on data from more than 700 runs. The standard quenching technique has generally been used in studying silicate phase equilibria, and liquidus-solidus relationships at high temperatures have received primary consideration.

The information to be presented herein also deals with high-temperature mineral transformations within the alumina-silica system; however, special consideration is given to the 900°–1500° C. temperature range and to the formation of mullite as it develops from synthetic mixtures of different varieties of alumina and silica. Insley and Ewell in 1935, and more recently West and Gray (1958) in examining reactions in artificial alumina-silica mixtures, suggested the influence which internal structures of materials could have in controlling thermal reactions within this temperature range.

In the present study the development of mullite from various mixtures of alumina-silica materials has been investigated by both continuous heating *x*-ray diffraction and *x*-ray diffraction after prolonged heating at elevated temperatures, and it will be shown that temperature and the structural nature of component materials are more important than mole per cent variations in the composition of the mixes in controlling the development of this mineral at elevated temperatures.

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SAMPLES AND PROCEDURE

The following varieties of alumina and silica were selected for firing: diaspore from Missouri; synthetic gibbsite, Merck and Co., Rahway, New Jersey; and corundum from Zoutpansberg District, Transvaal, Africa; also synthetic cristobalite; silicic acid, 100 mesh, A. R. grade, Mallinckrodt Chemical Works; and Ottawa quartz sand from near Ottawa, Illinois.

The effect of mole per cent variations of both alumina and silica on mullite formation was investigated by *x*-raying continuously diaspore-cristobalite mixtures of $Al_2O_3 \cdot 4SiO_2$; $2Al_2O_3 \cdot 3SiO_2$; $3Al_2O_3 \cdot 2SiO_2$; and $4Al_2O_3 \cdot SiO_2$ as they were heated to 1450° C. The combined intensities of the 3.41 Å and 3.38 Å mullite reflections, when present, were measured at regular temperature intervals up to 1450° C.

The role of crystallinity and structure of the alumina-silica components in controlling mullitization was determined by examining, both by continuous heating diffraction and by diffraction after prolonged heating at 1375° C., alumina-silica mixtures of the approximate $3Al_2O_3 \cdot 2SiO_2$ mullite composition. Diffraction intensity measurements of the major mullite reflections as observed from all combinations of these six component materials after firing are plotted, as are the diffraction intensities for cristobalite and corundum.* Both peak height intensity and integrated peak area intensity measurements were recorded and found to be indicative of changes in the diffraction intensity characteristics of these minerals. Thus, the intensity of diffraction data plotted in the following illustrations represent those relative intensity changes that took place as the materials were fired.

Continuous *x*-ray data are based on the heating of the mixtures at a firing rate of 5.6° C. per minute. The prolonged heating data were obtained from the same mixes after they were held at 1375° C. for 24 and 72 hours respectively. All *x*-raying was performed using nickel-filtered copper radiation at 45 kv. and 18 ma.

EXPERIMENTAL DATA

Effect of Alumina-Silica Mix Composition on Mullite Formation

Continuous *x*-ray diffraction data from different mole per cents of Al_2O_3 and SiO_2 in mixtures of diaspore-cristobalite while being heated to 1400° C. are shown in Fig. 1. The intensities of the (101) line of corun-

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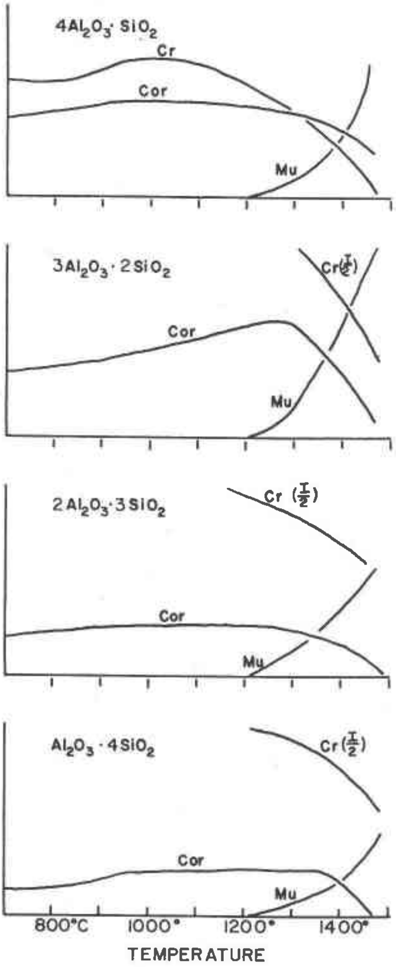
* Three major diffraction lines attributable to the alumina component after firing have *d*-values of 3.48 Å, 2.55 Å, and 2.38 Å and are representative of αAl_2O_3. To avoid confusion with the Al_2O_3 content of prepared mixes before firing, the mineral name for α-Al_2O_3, corundum, will hereafter be used when referring to the alumina component after firing.



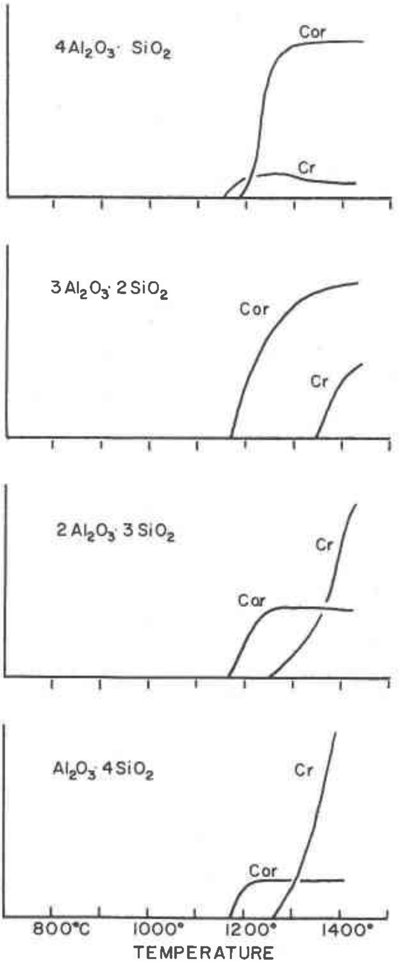


FIG. 1. (*Left*) Intensity of diffraction by high-temperature phases in heated alumina-silica mixtures prepared from diaspore-cristobalite. Cr—Cristobalite; Cor—Corundum; Mu—Mullite.

FIG. 2. (*Right*) Intensity of diffraction by high-temperature phases in heated alumina-silica mixtures prepared from gibbsite-silicic acid.

dum, the (111) line of beta-cristobalite, and the combined intensities of the 3.38 Å and 3.41 Å mullite reflections are plotted against temperature. Mullite diffraction lines first appeared at 1200° C. from all mixes regardless of their alumina to silica ratios. Just prior to the mullite nucleation temperature there was a slight but gradual increase in the intensities of the major corundum and cristobalite peaks in all mixes, but especially in that with composition $3Al_2O_3 \cdot 2SiO_2$. As the temperature was raised above 1200° C., the intensity of mullite diffraction continually increased with the development of this mineral; also, there was a gradual decrease in the diffraction intensities of corundum and cristobalite. This reduction coincided with, and was inversely proportional to, mullite development.

Gibbsite-silicic acid mixtures of varying composition were also examined while being heated to 1400° C. Corundum and cristobalite de-

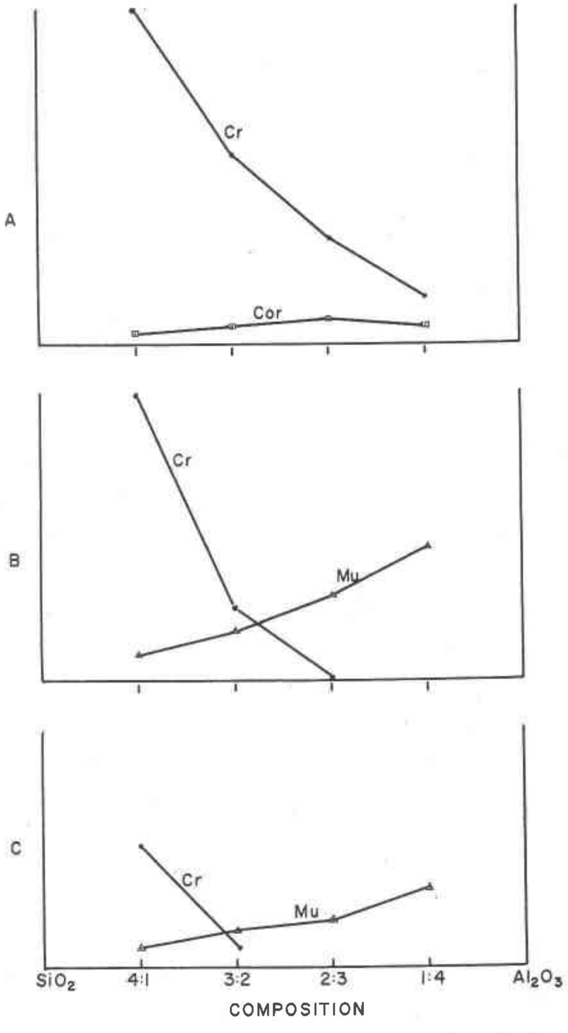


FIG. 3. Intensity of diffraction by high-temperature phases in heated diaspore-cristobalite mixtures after: A) 1 hour at 540° C.; B) 24 hours at 1375° C.; C) 72 hours at 1375° C.

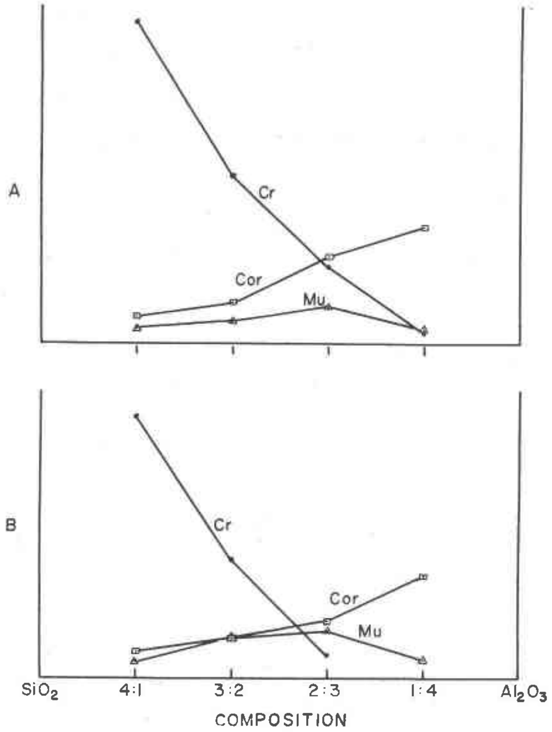


FIG. 4. Intensity of diffraction by high-temperature phases in heated gibbsite-silicic acid mixtures after A) 24 hours at 1375° C.; B) 72 hours at 1375° C.

veloped from each mixture, regardless of mole per cent variations in the mix composition (Fig. 2). In all cases corundum was first observed at 1170° C., but the formation temperature of beta-cristobalite ranged from 1150° to 1350° C. At no time were mullite diffraction lines detected from these components, even when heated to 1425° C.

Figure 3-A shows that the diaspore in heating to 540° C. for one hour changes to corundum, and that under these conditions there is no reaction between the alumina and silica phases. In mixtures of all compositions, corundum diffraction lines were not discernible after heating to 1375° C. (Fig. 3-B). Mullite was present in all diaspore-cristobalite mixes after heating at 1375° C. for 24 hours (Fig. 3-B) and the amount formed was directly proportional to the original alumina content of the mixture. Mixtures rich in silica retained less beta-cristobalite after 72 hours than after 24 hours (Fig. 3-C) indicating more complete mullite development with prolonged heating.

All gibbsite-silicic acid mixtures developed mullite after 24 hours at 1375° C., but maximum mullitization was observed from the $3Al_2O_3$

$\cdot 2SiO_2$ mix (Fig. 4-A). This same development trend was maintained after 72 hours at 1375° C. (Fig. 4-B). Again, less beta-cristobalite was retained after 72 hours. Corundum development paralleled closely the amount of alumina present in the original mixes and the same was true for cristobalite development and the SiO_2 content.

Influence of Alumina Component on Mullitization

Several mixes equivalent to the mullite composition ($3Al_2O_3 \cdot 2SiO_2$) were fired to determine the role of alumina structure on consequent mullite formation. Continuous diffraction data for diaspore-cristobalite, gibbsite-cristobalite, and corundum-cristobalite mixtures are shown in Fig. 5. Mullite began forming from diaspore-cristobalite at 1200° C. and

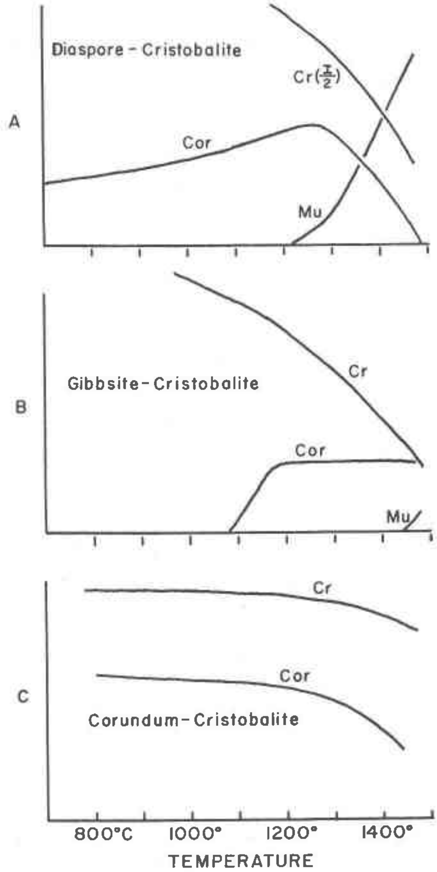


FIG. 5. Intensity of diffraction by high-temperature phases in heated $3Al_2O_3 \cdot 2SiO_2$ mixtures.

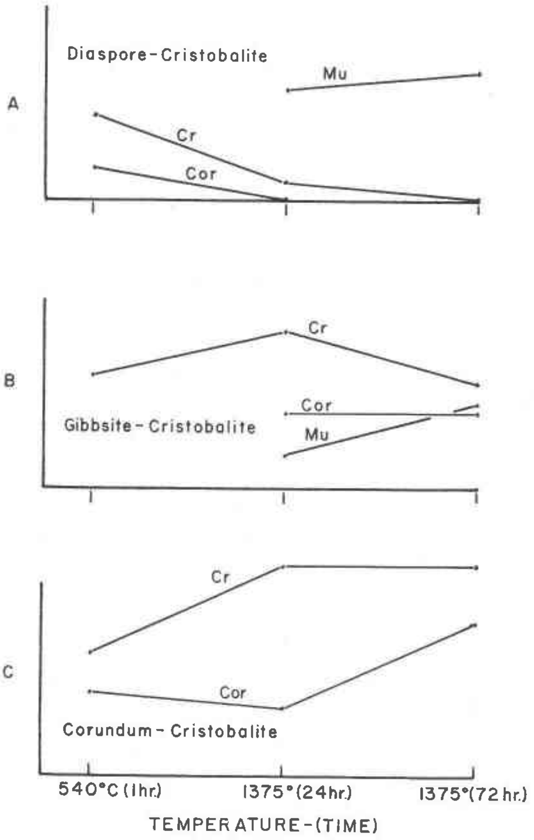


FIG. 6. Intensity of diffraction by high-temperature phases in $3Al_2O_3 \cdot 2SiO_2$ mixtures after prolonged heating.

from gibbsite-cristobalite at 1440° C. but none developed from the corundum-cristobalite mix at this rate of firing up to 1450° C. The intensity decrease of both the cristobalite and corundum peaks (Fig. 5-C) as higher temperatures are attained indicates that a possible structural readjustment to mullite is beginning to take place but is still too slight to be detected.*

X-ray diffraction analyses of these same cristobalite mixtures after prolonged heating at 1375° C. showed the same trend of mullite development (Fig. 6).

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* Firing of this same mixture after extensive grinding to an extremely small particle size gave mullite at 1340° C.

Influence of Silica Component on Mullitization

Continuous diffraction data from $3Al_2O_3 \cdot 2SiO_2$ mixtures of diaspore-cristobalite, diaspore-silicic acid, and diaspore-quartz while being fired to 1425° C. are listed in Fig. 7. Cristobalite and silicic acid promote mullite nucleation at 1200° and 1300° C. respectively; whereas, the quartz-diaspore mix developed mullite only after heating to 1320° C. at this rate of firing. The same reactivity trend was observed for these silica components when gibbsite was substituted for diaspore in the mixtures. The batch containing cristobalite was still the first to form mullite (Fig. 5-B), however, none was observed from either the gibbsite-silicic acid mix (Fig. 2) or the gibbsite-quartz mix when heated to 1400° C. at this same firing rate.

All three varieties of silica formed mullite with either diaspore or

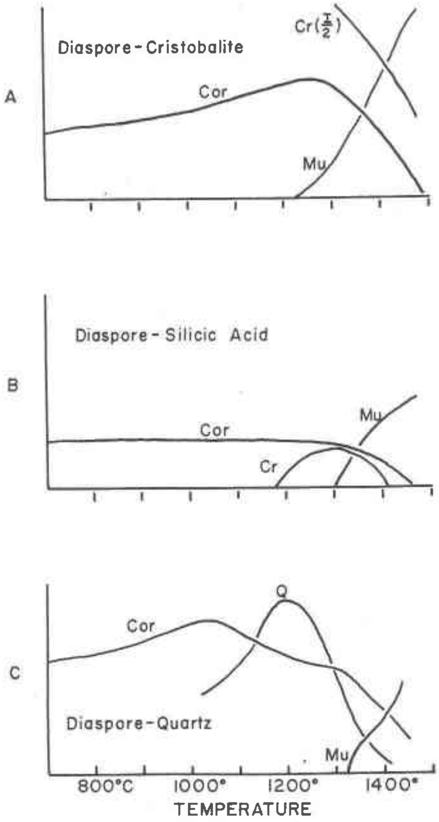

FIG. 7. Intensity of diffraction by high-temperature phases in heated $3Al_2O_3 \cdot 2SiO_2$ mixtures.

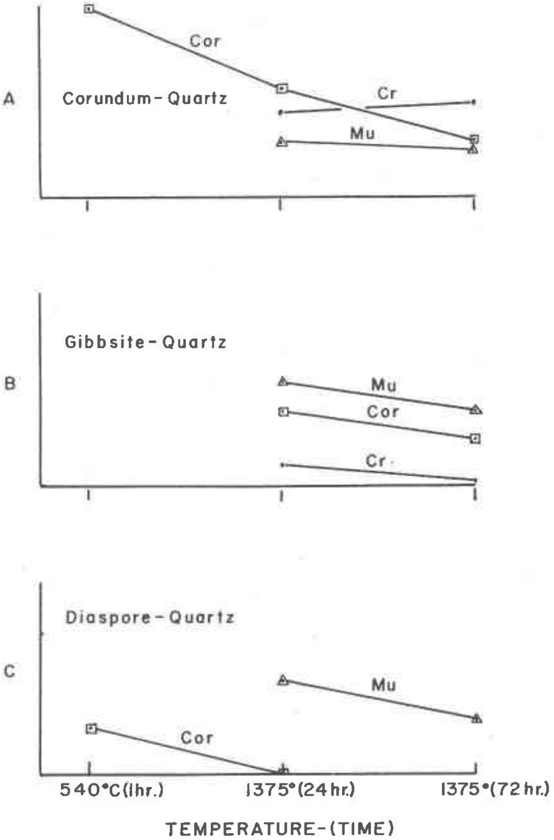

FIG. 8. Intensity of diffraction by high-temperature phases in $3Al_2O_3 \cdot 2SiO_2$ mixtures after prolonged heating.

gibbsite when heated to 1375° C. for 24 hours, Figures 6, 8, and 9; however, after 72 hours at this temperature, mullite diffraction intensity decreased in those batches which contained quartz as the silica component (Fig. 8). The mixtures prepared with cristobalite (Fig. 6) and with silicic acid (Fig. 9) showed the expected normal increase in mullite development after 72 hours.

The effects of chemical additives on mullite nucleation from $3Al_2O_3 \cdot 2SiO_2$ corundum-cristobalite mixes were examined briefly. This particular mixture produced no mullite when fired at 1375° C. for 72 hours; however, the addition of 5% by weight of $CaCl_2$ or $BiCl_3$ promoted mullite nucleation from these components at 1300° and 1400° C. respectively (Fig. 10).

Discussion and Conclusions

The data show that mullitization in synthetic mixtures of various forms of alumina and silica is influenced by the structure of the components used. Limitations imposed by structure may be more important in controlling the formation of this mineral than mole per cent variations in the compositions of the alumina-silica mixes. The temperatures at which these materials combine to give mullite are thus an indirect consequence of this structure stability.

The formation of mullite at 1200° C. from all diaspore-cristobalite mixes, even though they varied in composition from $Al_2O_3 \cdot 4SiO_2$ to $4Al_2O_3 \cdot SiO_2$ shows that component materials need not be present in correct molecular ratios before combination and mineral synthesis can oc-

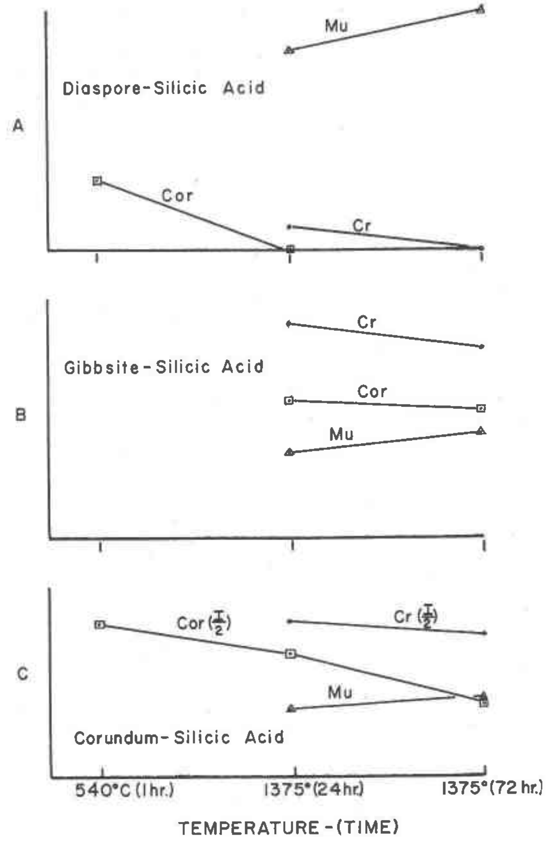

FIG. 9. Intensity of diffraction by high-temperature phases in $3Al_2O_3 \cdot 2SiO_2$ mixtures after prolonged heating.

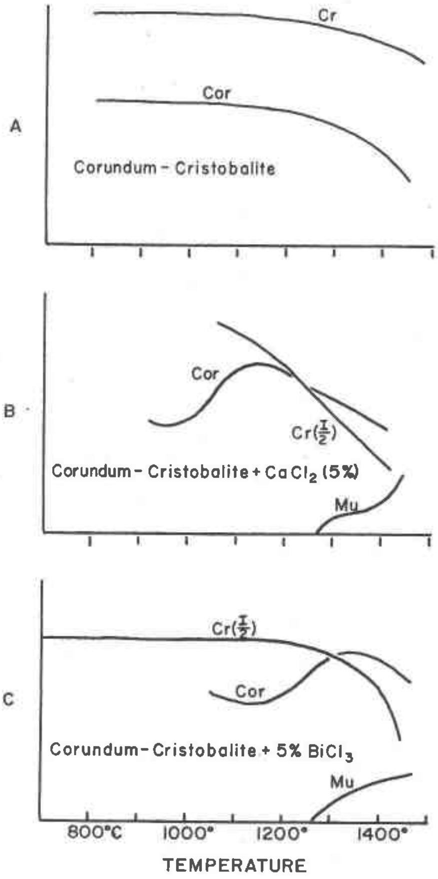

FIG. 10. Intensity of diffraction by high-temperature phases in heated $3Al_2O_3 \cdot 2SiO_2$ corundum-cristobalite mixtures treated with Ca^{++} and Bi^{+++}.

cur. As long as the proper components are present in the mix, regardless of their relative molecular amounts, they will combine to give mullite when heated to the proper temperature.

Of the varieties of alumina tested, diaspore with the composition of $HAlO_2$ combines more readily with SiO_2 to produce mullite than does gibbsite which is $Al(OH)_3$. On heating, each of these alumina materials ultimately converts to corundum, the diaspore at a low temperature, and gibbsite not until about 1100° C. Consequent development of mullite through combination with the silica that is present is related to this preliminary corundum development. Diaspore forms corundum at a relatively low temperature ($<500°$ C.), and contributes to mullite development at 1200° C; whereas gibbsite does not convert to corundum until

1100° C. and does not combine with silica to produce mullite until 1440° C. The reactivity of naturally occurring corundum follows this same pattern of thermal behavior. It does not react with silica to form mullite even when held at 1375° C. for 72 hours. This suggested association between structural stability of the aluminum component and consequent mullite development is in agreement with the findings of West and Gray (1958) who showed that the reactivity in forming mullite from silica-alumina mixtures was dependent on the crystalline modification of alumina that was used.

Analogous to the formation of corundum from alumina components is the transformation of the silica component to beta-cristobalite. Silicic acid, when mixed with diaspore, transforms to beta-cristobalite at 900° C. with consequent mullite nucleation at 1300° C. Quartz, however, does not form beta-cristobalite until 1200° C. and, when mixed with diaspore, does not form mullite until 1325° C. The development of mullite at 1200° C. from mixes prepared with synthetic cristobalite is as expected. The beta-cristobalite used had been prepared at approximately 900° C. from silicic acid. Above this temperature the material apparently becomes relatively unstable, more reactive, and can readily combine with the alumina component to give mullite.

Because the actual temperature of mullite nucleation as determined from a heated alumina-silica mix is related to the development temperatures of corundum and beta-cristobalite, it follows that the original structures of the alumina-silica component materials, which in turn control the transformations to corundum and beta-cristobalite, are fundamental factors in limiting the ultimate development of mullite.

Because mullitization generally precedes the formation of beta-cristobalite when natural alumino-silicate minerals such as kaolinite are heated, and follows beta-cristobalite development from synthetic alumina-silica oxide mixtures, it is emphasized that any material, on heating, will first tend to follow its normal transformation sequence which is determined by the structure of that material. Only after this has occurred is there a reaction to form mullite. The firing of alumina-silica components to form mullite can often be enhanced by the addition of mineralizing ions as when either Bi^{+++} or Ca^{++} were added to corundum-cristobalite mixtures. These same ions also promoted mullitization in kaolinite (Wahl, 1958).

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