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MULLITIZATION OF KAOLINITE AND Al_2O_3-SiO_2 MIXTURES

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(M. S. thesis)

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MULLITIZATION OF KAOLINITE

AND Al_2O_3-SiO_2 MIXTURES

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ABSTRACT

Mullite formation from Al_2O_3-SiO_2 mixtures and kaolinite was studied. The effect of impurities present in kaolinite - TiO_2, Fe_2O_3, Na_2O, K_2O - as well as CaO, on crystal size and morphology were compared. The most pronounced effects were observed when Fe_2O_3 and CaO were added to Al_2O_3-SiO_2 mixtures and to kaolinite. Calcium oxide additions increased the mullite crystal size while iron oxide additions to the Al_2O_3-SiO_2 mixture not only increased the crystal size but also changed the crystal morphology from rectangular to acicular crystals reminiscent of kaolinite. Scanning electron microscopy was used to study the specimens. Four kaolinites were also examined by differential thermal analysis. The appearance of an exothermic peak at ~1400°C was tentatively linked to the state of order of the kaolinites.

I. INTRODUCTION

Mullite has many desirable properties - refractoriness, good thermal shock resistance, high strength at high temperatures, and spalling resistance, amongst others, and has consequently been extensively studied. Nevertheless, an aspect which appeared to be inadequately studied was the comparison of the formation of mullite from kaolinite and alumina-silica mixtures and the effect of additives on the microstructure. Microstructural changes and acceleration of growth of mullite could be useful in strength improvement. Kaolinite invariably contains impurities owing to its formation by weathering.

A relatively pure Georgia kaolinite was chosen for this study. The main impurities were TiO_2, Fe_2O_3, Na_2O and K_2O. Each was added to an Al_2O_3-SiO_2 mixture in proportions similar to those in the kaolinite. Calcium oxide and iron oxide, in equivalent molar amounts were also added to the Al_2O_3-SiO_2 mixtures and the kaolinite. Scanning electron microscopy was used to study the microstructures of samples subjected to different heating schedules in the temperature range of 1650°-1700°C. The additives increased the crystal size of the mullite formed from the Al_2O_3-SiO_2 mixture with CaO and Fe_2O_3 having the largest effect. Fe_2O_3 changed the morphology resulting in acicular crystals similar to those

of mullite formed from kaolinite.

Differential thermal analysis was used to study the Georgia kaolin and three other kaolins. The exothermic peak at ~1400°C attributed to the crystallization of cristobalite was of interest. The appearance of the peak is tentatively linked to the state of order of the original kaolinite with disordered kaolinite exhibiting the peak in contrast with ordered kaolinite which did not.

II. LITERATURE SURVEY

1. Kaolinite-Mullite Reaction Series

A. Structure of Kaolinite

The basic unit in the crystal structure of kaolinite, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, consists of a layer of SiO_4 tetrahedra and a layer of alumina octahedra. The oxygen ions in the O - (OH) plane of the $[AlO(OH)_2]_n^-$ layer are common to the $(Si_2O_3)_n$ layer. Kaolinite consists of layers of this basic unit which are held together by a type of van der Waals bonding.[1]

B. Thermal Decomposition of Kaolinite

There is much debate concerning the phases formed when kaolinite is heated.

a) Endothermic Reaction

An endothermic reaction occurs in the temperature range 450°C-600°C. Variations in the reported temperature are the result of different heating rates,[2] as well as being dependent on the crystallinity of the kaolinite.[3] The reaction involved is dehydroxylation,[1,4] i.e. $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow Al_2O_3 \cdot 2SiO_2 + 2H_2O$. This is not a normal equilibrium reaction and is irreversible.[5] The structure of the product is thought to be either an intimate

mixture of amorphous alumina and silica[3,5] or an amorphous compound of alumina and silica known as metakaolinite.[3] Brindley and Nakahira[6(b)] and Comeforo, Fischer and Bradley[5] report that metakaolinite does have a structure in the 'a' and 'c' directions but is disordered in the 'c' direction.

b) The First Exothermic Reaction

The first exothermic reaction occurs at ~980°C and involves the exsolution of silica:[4]

$$2(Al_2O_3 \cdot 2SiO_2) \rightarrow 2Al_2O_3 \cdot 3SiO_2 + SiO_2$$

There are two main schools of thought concerning the product. Brindley and Nakahira,[6(c)] Chakroborty and Ghosh,[2,8,9] and Duncan and Mackenzie[4] concur that the product is an Al-Si spinel while Glass,[3] Percival and Duncan,[10] Bulens, Leonard and Delmon[11] and Leonard[12] hold the opinion that it is a γ-Al_2O_3 phase.

c) The Second Exothermic Reaction

A second exothermic reaction, less pronounced than the first, occurs between 1200°C and 1250°C, the exact temperature depending upon the purity.[3] This peak is associated with the formation of mullite[1,3] although mullite has been reported as occurring after the first exothermic peak[3,10] and as a function of impurities.[3,11] Kingery[1] and Brindley and Nakahira[13] report that as the temperature increases from 980°C, a 'mullite type' phase forms which transforms to crystalline mullite above 1200°C. The formation of mullite requires further exsolution of silica.

d) Higher Temperature Reactions

Glass[3] reports that impure clays have an exothermic cristobalite peak at ~1300°C. Pure clays do not show this peak even

when heated to 1350°C, the highest test temperature reported.

C. Structure of Mullite

Mullite has the ideal stoichiometric formula $3Al_2O_3 \cdot 2SiO_2$, although solid solution has been reported as resulting in a range of formulae.[14]

The structure of mullite is similar to that of sillimanite.[15] Mullite appears to consist of octahedral chains of AlO_6 running parallel to the 'c' axis.[5,14] Al^{3+} and Si^{4+} ions are distributed in the tetrahedral positions which link the octahedral chains.[14] Mullite crystals are asymetric, and it has been suggested[5] that the alumina octahedral chains are carried over from the kaolinite structure.

Lattice parameters have been measured in an effort to determine the composition of mullite.[16,17,18]

2. Effect of Additives on Mullite Formation

Numerous researchers have investigated the effect of additives on mullite formation in kaolinite and alumina-silica mixtures. Those oxides most commonly studied are Fe_2O_3,[3,14,19,20,21,22,23,24,25,28] TiO_2,[3,14,20,23,24,25,28] CaO,[24,25,26] Cr_2O_3,[14,20] MgO,[20,21,24,25,26] and alkali oxides.[20,24,25] The amount of mullite formed, physical properties[28] and microstructure[29] have all been investigated.

Mullite formation has been determined by x-ray diffraction,[2,20,24,25,30] and by chemical analysis.[2] Physical properties such as porosity, thermal expansion and shrinkage have also been measured.[28] X-ray diffraction,[23,29] electron microscopy,[23,29] and polarizing microscopes[29] have all been used to determine average sizes and size distributions of mullite crystals.

Impurities have been introduced into kaolinite by two methods — mechanical mixing[2,24,28,30] and cation exchange.[20,25] In order to achieve the same degree of mullitization, more oxide is needed when mechanical mixing is used than when the cation exchange method is used.[25]

In general, it has been found that there is an optimum amount of an oxide which, when added to either alumina-silica mixtures or kaolinite, produces a maximum amount of mullite. Amounts in excess of this quantity tend to retard mullite formation. It has also been found that the relative effects of different oxides are not constant with temperature and that the order of effectiveness of the oxides depends on the temperature.[2]

A. Effect of Fe_2O_3

Iron oxide is one of the most commonly found impurities in kaolinite[19] and its effect on kaolinite,[2,20,29,31] alumina-silica mixtures,[22,28] and mullite [19] has been widely studied. Usually, however, the effect of iron oxide has been studied only at temperatures up to 1400°C in air as the iron oxide - Al_2O_3 spinel phase changes to other structures in the temperature range 1380°C to 1410°C.[22] There is a volume expansion involved which causes bloating and cracking.

Fe_2O_3 will form a solid solution with mullite.[19,31,32] Brownell[19] found that 7.7% Fe_2O_3 will enter into solid solution with mullite at 1300°C, Muan[22] observed that 10% Fe_2O_3 will substitute for Al_2O_3 in mullite formed from kaolinite at 1370°C while Gelsdorf et al[33] found that 6% would enter into the mullite structure at 1300°C and 8-9% at 1400°C. Murthy and Hummel[14] concluded that the limit was 10-12% at 1300°C, agreeing with the evidence of Agrell and Smith[16] and McGee and Wirkus [23] who

concluded that 12% was the limit at 1300°C for alumina-silica mixtures.

When Fe_2O_3 enters into solid solution with mullite, the lattice parameters change. Brownell[19] found an average linear increase of the mullite lattice dimensions of 0.3% for 7.7 wt% of Fe_2O_3. Gelsdorf, et al,[33] determined that there was a 0-81% increase in cell size at the maximum Fe_2O_3 solubility in mullite from AlO_3-SiO_2 mixtures. Agrell and Smith[16] found that the 'c' dimension increases most with increasing Fe^{3+} substitution followed by the 'a' and 'b' dimensions. The relative increase in ratios of lattice parameter increase found by Agrell and Smith[16] agrees with the results of Murthy and Hummel,[14] both for mullite as the starting material and McGee and Wirkus[23] for an alumina-silica mixture.

Fe^{3+} substitutes for Al^{3+} in mullite as a result of its size and ionic charge.[20,24,32] Although Fe^{3+} ions are larger than Al^{3+} ions, they have the same charge and will substitute for Al^{3+} ions in the main Al-O octahedral chains.[14] Fe_2O_3 also enters into the glassy phase[29,32] formed from kaolinite. Chaudhuri,[29] reports that the viscosity of the glass formed from Al_2O_3-SiO_2 is increased which hinders formation of large mullite needles and that those present are small and well separated. However, the presence of Fe_2O_3 up to a concentration of 4% tends to stabilize the mullite crystals formed from kaolinite.[32] Budnikov[34] has reported the formation of needles of mullite when mullite is in contact with glass containing iron oxide. McGee and Wirkus[23] reported that the mullite crystals originating from Al_2O_3-SiO_2 were well formed when Fe_2O_3 was present and Chaudhuri[31] found that Fe_2O_3 enhanced growth of mullite formed from kaolinite.

The efficiency of Fe_2O_3 in increasing the yield of mullite from kaolinite increases with temperature,[2,31] although the acceleration of mullitization decreases with temperature.[31] Maximum mullite yield from all starting materials occurs at a certain percentage of Fe_2O_3, after which it decreases.[2,23,24,28,31]

B. Effect of TiO_2

Titania is another commonly occurring impurity in kaolinite. The amount which enters into solid solution with mullite is much less than that of Fe_2O_3.[2,14,23,31] Gelsdorf, et al.[33] report that 2-2.5% TiO_2 is included in mullite formed from Al_2O_3-SiO_2 mixtures after firing at 1700°C for eight hours while McGee and Wirkus[23] report that the limit is 3%. Murthy and Hummel[14] have found that the amount of TiO_2 entering into the mullite structure is 2-4% which is in agreement with the results of Agrell and Smith.[16] At low temperatures, TiO_2 is a poor mineralizer. The optimum amount for kaolinite was found to be 0.75% in the range 1400-1600°C and larger additions tended to decrease the amount of mullite formed, particularly as the temperature increased.[2,31] In general, TiO_2 is less efficient as a mineralizer for kaolinite than Fe_2O_3 although mullite formation is accelerated more at high temperatures than at low.[2]

Murthy and Hummel[14] found that the 'b' and 'c' lattice parameters increased and that there was lattice distortion as well as expansion. Gelsdorf, et al.[33] observed an overall increase in cell size at 0.40%. McGee and Wirkus[23] also measured an increase in cell size for additions of 0-3 wt% TiO_2 to alumina-silica mixtures.

Ti^{4+} does not substitute as readily as Fe^{3+} because of its ionic charge. It concentrates in the glass giving it a high viscosity which hinders crystal growth.[29] McGee and Wirkus[23] claim that the low activation energy for TiO_2 prevents grain growth and that the crystals are not well formed. Parmelee and Rodriguez[2] found that TiO_2-bearing kaolinite did not have well-defined grains. However, the crystals are not very soluble in the glass and are therefore more stable.[29] Chaudhuri[29] also found that the microstructure of alumina-silica samples containing TiO_2 was very uniform and consisted of very fine interlocking needles.

C. Effect of CaO

Calcium is most commonly present in clay as calcium oxide,[31] and it has been found to be a moderate accelerator of mullite formation[2] from kaolinite, although Prabhakaram[35] reports that it has no effect. Chaudhuri[30] found that 1% CaO gave the maximum yield of mullite from kaolinite upon firing for 1 hour at 1300°C. The yield decreased with an addition of 2% but increased again with 4% CaO. At 1400°C the optimum amount is 2% CaO and at 1500°C, 1% when added to kaolinite.[31] Moore and Prasad[24] found that at 1400 and 1500°C the optimum for kaolinite-alumina mixtures was 1.0% and that at 1600°C it was slightly less.

Chaudhuri[31] found that CaO added to kaolinite produced much larger crystals than other additives. Moore and Prasad[24] observed no bloating with CaO additions up to 5% in kaolinite-alumina mixtures.

D. Effect of Na_2O and K_2O

Parmelee and Rodriguez[2] found that Na_2O and K_2O were poor catalyzers for kaolinite while Moore and Prasad[24] observed that the optimal amount of Na_2O was 2% at 1300°C and 1% at 1400-1600°C in kaolinite-

alumina mixtures. When K_2CO_3 is added, the optimal equivalent amount of K_2O is 1%. Chaudhuri[30] found that the optimal amount of Na_2O in kolinite at 1300°C was 1% and that of K_2O was 0.5%. With increasing amounts the yield decreases. Na_2O is similar to CaO in that it exhibits a minimum yield at a concentration greater than the optimum. The yield is very sensitive to slight changes in concentration.

If sodium and potassium are added as different salts the optimal amount in kaolinite is affected.[24,30] It has also been found that Na_2O and K_2O hindered the growth of crystals of mullite[31] formed from kaolinite.

E. Comparison of Oxides

Fe_2O_3 enters into solid solution with mullite in greater amounts than the other oxides discussed and it also has a greater mineralizing effect.

Ti^{4+} will enter into mullite by substituting for Al^{3+}, and TiO_2 is regarded as having a poor to fair catalytic effect.

Ca^{2+} does not enter into the lattice, and amounts necessary for optimum mullitization are lower than those for Fe_2O_3 and TiO_2.

Na_2O and K_2O tend to retard crystal growth. Small amounts and slight variations have a large effect on the amount of mullite formed. They are, in general, regarded as being poor mineralizers.

The relative effects of these oxides vary depending upon the temperature.

III. MATERIALS AND PROCEDURE

1. Materials

The alumina and silica used were Alcoa A-14* (α-alumina) and Ottawa silica flour** (α-quartz). A relatively pure Georgia kaolin*** was chosen for mullite crystallization studies. Chemical analyses of these materials are given in Table 1.

The oxides and sodium carbonate used were all of analytical reagent grade. Alcoa A-16* alumina was also used in one set of samples. Kaolinites used for the DTA study were Ione clay, Georgia Kaolinite++, K Ga-1 and K Ga-2.+++

2. Equipment

A. DTA Furnace

The DTA furnaces were wound with Pt-40% Rh wire and had a temperature capability of 1550°C with a controlled heating rate of 10°C/min. Pt-Pt 10% Rh thermocouples were used.

B. Quench Furnace

The quench furnace used was electrically heated with $MoSi_2$ elements and was capable of reaching a maximum temperature of 1725°C. Quenching was achieved by lowering the pedestal.

3. Experimental Procedure

Compositions of the mixtures that were prepared are given in Table 2. The basis of mixtures I-VI, VIII is the composition of the

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*Alcoa Aluminum Corporation of America.
**Ottawa Silica Co.
***Georgia Kaolin Co.
++Provided by the Georgia Kaolin Co., Sandersville, GA.
+++Provided by the Clay Minerals Society.

Table 1. Chemical Analysis of Materials

Constituent	Wt%		
	Georgia Kaolinite*	A-14	Silica Flour
Al_2O_3	50.60	99.6	0.06
SiO_2	47.22	0.12	99.80
Fe_2O_3	0.38	0.03	0.02
Na_2O	0.19	0.04	-
K_2O	0.19	-	-
TiO_2	1.40	-	0.013
CaO	<0.01	-	0.01
MgO	0.02	-	0.01
MnO	<0.01	-	-
P_2O_5	<0.002	-	-
LOI	-	0.2	0.09

*Chemical analysis performed by Anamet Laboratories, Inc.

Table 2. Composition of Mixtures.

	%							
Mix #	Al_2O_3	SiO_2	TiO_2	Fe_2O_3	Na_2O	K_2O	CaO	Kaolinite
I	51.73	48.27	-	-	-	-	-	-
II	51.00	47.59	1.41	-	-	-	-	-
III	51.53	48.09	-	0.39	-	-	-	-
IV	51.53	48.09	-	-	0.19	0.19	-	-
V	50.60	47.22	1.40	0.38	0.19	0.19	-	-
VI	-	-	-	-	-	-	-	100
VII	50.70	47.30	-	-	-	-	2	-
VIII	51.73	48.27	-	-	-	-	-	-
IX	48.78	45.57	-	5.68	-	-	-	-
X	-	-	-	-	-	-	2	98
XI	-	-	-	5.68	-	-	-	94.32

kaolinite. Mixtures VII, IX-XI contain more CaO and Fe_2O_3; the molar amount of oxide added in each of these cases was the same. Mixture VIII contained A-16 alumina as opposed to A-14 alumina in order to determine the effect of any remaining agglomerates in the A-14.

The oxides were weighed and placed in a vibrating mill* with alumina grinding media and isopropyl alcohol. The powders were ground for approximately sixteen hours in order to break up the agglomerates of A-14 alumina and to mix the components thoroughly. The slurry was dried and crushed with a mortar and pestle.

In order to press pellets it was necessary to spray the powders lightly with water and mix on a roller mill for a few minutes to form a free flowing, granular powder. The powders were compacted in a 9 mm diameter steel die under a uniaxial pressure of ~50 MPa. The pellets were prefired to 1000°C in a Heviduty furnace** to improve the strength.

The kaolinite was prefired to 1200°C, crushed and made into pellets. This was necessary to enable compacts to be made.

After prefiring, the samples were fired on a platinum disc in a quench furnace according to the schedules in Table 3. The samples were taken up to temperature as quickly as possible as was reduction in temperature from 1700°C to 1650°C. The temperature fluctuation at temperature was ±5°C. At the end of the run, the samples were quenched by lowering the pedestal.

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*Sweco Inc., Los Angeles, CA.

**Lindberg, Watertown, WI.

Table 3. Firing Schedules

Run #	Time	Temperature	Time	Temperature
1	8 hrs	1650°C	-	-
2	8 hrs	1700°C	8 hrs	1650°C
3	8 hrs	1700°C	16 hrs	1650°C
4	8 hrs	1700°C	-	-
5	8 hrs	1700°C	16 hrs	1650°C
6	24 hrs	1700°C	-	-
7	24 hrs	1650°C	-	-

Pellets were cut on an isomet saw and mounted in bakelite. Polishing was on 30μm, 15μm and 6μm diamond wheels followed by 6μm, 1μm and 0.25μm syntrons.

After polishing, the samples were examined in a metallograph at magnifications of 160 and 400X. Scanning electron microscopy was then employed to obtain photographs at higher magnifications, 1000X and 2000X. The samples were etched in 40% HF for ~30 seconds prior to SEM examination.

4. Determination of Volume Fraction and Size

Photographs at 1000X from the SEM were used for a line counting method of determining volume and size fractions. Five 10cm lines were taken at random across the photograph and the length of line contained in the crystals measured. This is equivalent to the volume fraction, i.e., volume fraction = area fraction = line fraction.

$$\text{Line fraction } \% = \frac{\text{Length of line in crystal} \times 100}{\text{Total length}}$$

The number of crystals per line was determined by counting the number of grain boundaries (two for each particle) per line and dividing by two. The size was calculated as follows,

$$\text{Size, } \% = \frac{\text{Vol. Fraction, } \%}{\text{Number of Particles}} .$$

The sizes are reported as the volume percentage per crystal. Some crystals were too small and indistinct to be measured. Only one photograph area was available for each measurement, leading to appreciable errors, particularly in those samples with very large crystals.

5. Differential Thermal Analysis

Four kaolinites were tested by DTA. (See 'Materials' Section). An Al_2O_3 reference was used in a covered platinum crucible. One gram of kaolinite was packed carefully and reproducibly into the holder. A hole was made for the thermocouple which was inserted so that the sheathing did not come into contact with the sample. A heating rate of 10°C/minute was maintained. An offset in the final temperature due to the controller means that the results for the last ~30°C are in doubt as a constant heating rate was not maintained. The lag in the system also means that the heating rate for the first 100-150°C was not constant.

6. X-Ray Diffraction

Samples of the ordered kaolinite, K-Ga-1, and the disordered kaolinite, K-Ga-2, at room temperature and fired in the DTA furnace to 1100°C, ~1300°C and ~1475°C (i.e. after the exothermic peaks) were ground to -325 mesh and analysed by x-ray diffraction using a Cu tube. The scanning conditions were 40kV and 20 mA, 1° 2θ/min. scanning rate, 1/2 in. min. recording rate, 1°/4°/1° collimation slits and a time constant, τ, of 3. The charts were analyzed for the presence of kaolinite, quartz (free silica), alumina, mullite and cristobalite.

IV. RESULTS AND DISCUSSION

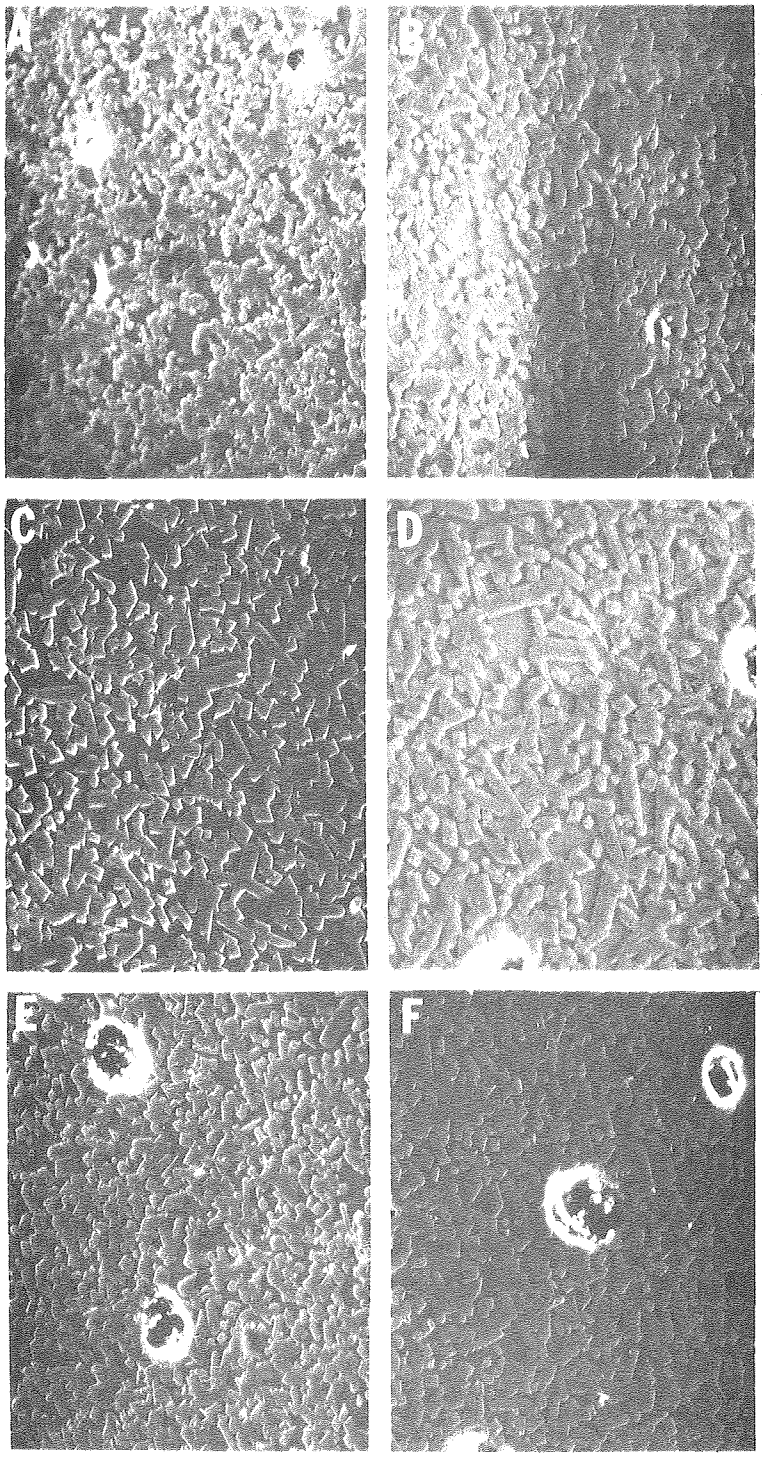
1. Crystallization of Mullite

The effects of differences in firing time and temperature and additives on the alumina-silica mixtures and kaolinite are discussed in this section.

A. Al_2O_3-SiO_2 Mixture

Time and temperature effects with regard to the Al_2O_3-SiO_2 mixture are shown in Fig. 1. Al_2O_3 grains react with SiO_2 at 1650-1700°C to form mullite crystals and a SiO_2-rich liquid. The mullite forms on the surfaces and grows into the Al_2O_3 grains. During the reaction the particle size is dictated by the rate of reaction to form mullite and the rate of dissolution of mullite in the liquid. The shape of the original mullite crystals is determined by the Al_2O_3 particles and is essentially as seen in Fig. 1A which shows the appearance after firing at 1650°C for 8 hours. The crystals are small, rounded and tend to be agglomerated,which reflects the original aggregation of the starting alumina powder. Upon completion of the mullite reaction and saturation of the liquid with mullite, equilibrium compositions as indicated by the Al_2O_3-SiO_2 phase diagram, Fig. 2, should be reached.

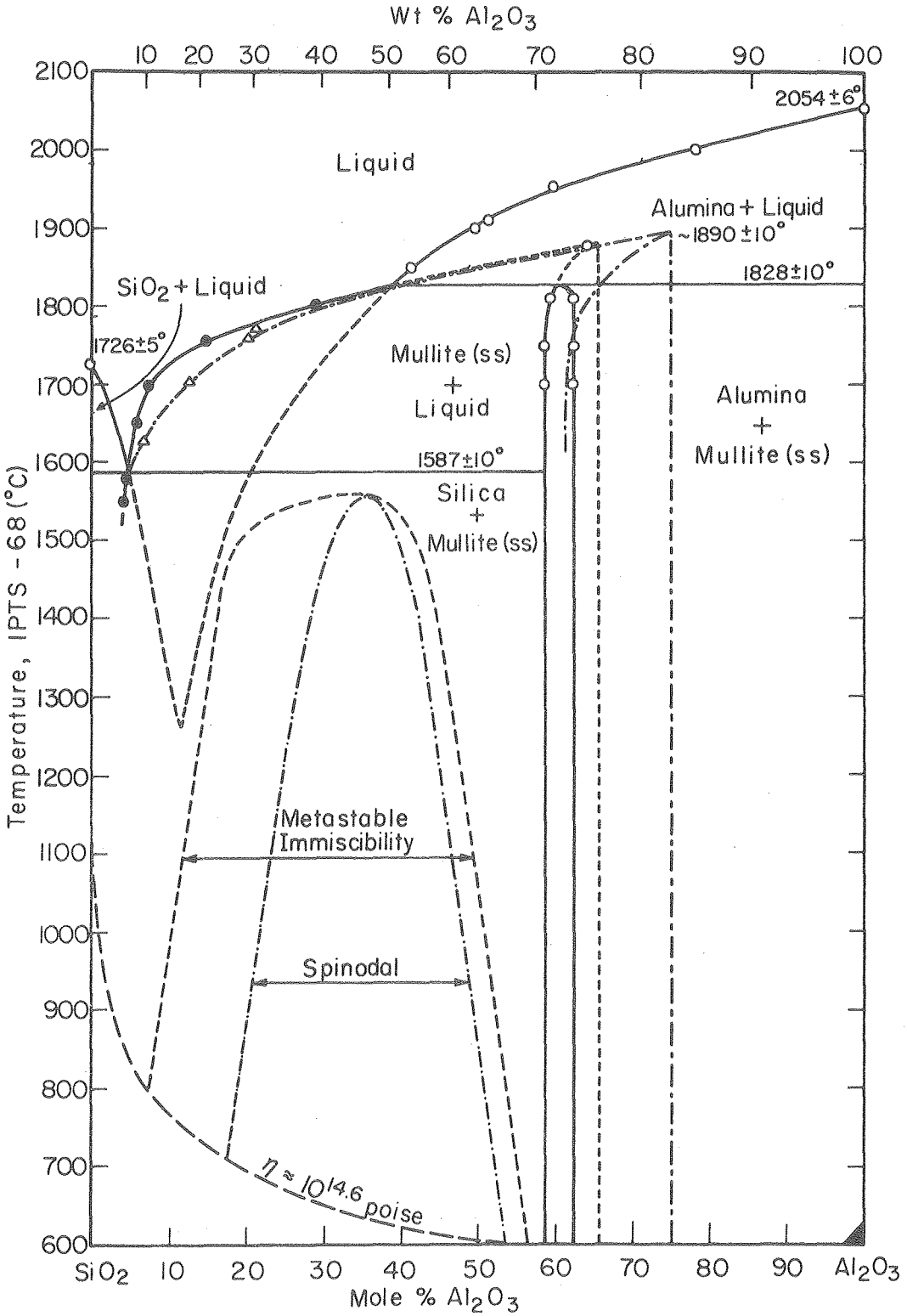
Calculations, assuming $\rho_{mullite} = 3.2$ g/cm^3 and $\rho_{glass} = 2.4$ g/cm^3, show that at 1650°C, the equilibrium amount of mullite present by volume should be 54.5% and at 1700°C, 52.6%. Line scan results from the microstructure (see Table 4) indicated that the volume of mullite present at 1650°C is 64.1% after 8 hours and 63.6% after 24 hours, and at 1700°C it is 54.4% after 8 hours and 58.1% after 24 hours. Statistical analysis reveals that these figures are the same within the error inherent in the procedure and that therefore equilibrium is achieved at a time less than 8 hours at these temperatures. The main source of error in the volume percentage determination was that only one area of each specimen was photographed and was therefore available for analysis. Although the photographed areas were chosen to be representative, it is possible that



XBB793-3126

20 μm

Fig. 1. Effect of Heat Treatment on Al_2O_3-SiO_2.
A. 1650°C/8 hours
B. 1650°C/24 hours
C. 1700°C/8 hours
D. 1700°C/24 hours
E. 1700°C/8 hours then 1650°C/8 hours
F. 1700°C/8 hours then 1650°C/16 hours



XBL 766-7008

Fig. 2. Al_2O_3-SiO_2 Phase Diagram.

Table 4. Volume Fraction, % mullite

	1 1650/8	7 1650-24	4 1700/8	6 1700/24	2 1700/8 1650/8	3/5 1700/8 1650/16
I A/S	64.1±10.6	63.6±8.8	54.4±7.2	58.1±9.9	59.3±5.3	57.0±9.7
II A/S/TiO_2	NE	61.4±5.8	53.8±8.3	54.4±8.2	54.9±8.2	63.0±3.0
IV A/S/Na_2O/K_2O	NE	-	NE	-	NE	60.3±7.1
V A/S/Al1	NE	-	NE	-	NE	58.7±4.0
III A/S/Fe_2O_3	NE	-	NE	-	NE	61.2±5.8
IX A/S/5.7%Fe_2O_3	-	66.0±3.2	-	58.8±8.8	-	58.7±4.0
VII A/S/CaO	56.5±10.9	57.8±11.4	54.6±7.2	55.1±8.9	46.6±4.0	53.5±9.8
VI K	NE	46.0±3.8	39.3±8.3	53.7±6.0	48.9±7.7	49.5±3.6
X K/CaO	-	47.0±6.3	-	39.5±10.7	-	40.5±5.9
XI K/Fe_2O_3	-	52.9±5.2	-	30.1*±7.5	—	42.5±5.5

NE - Not examined
- - No sample
* - 3rd phase present

the samples were not completely homogeneous with the result that a biased subsample may have been drawn. There might thus have been pronounced sampling error in the estimated percentages. The estimates serve only to corroborate the visual observations.

After phase equilibrium is reached, mullite crystal growth continues by Ostwald ripening, a process of solution of small particles and precipitation onto larger crystals. This process is thermodynamically favorable because of the resulting decrease in surface area and therefore total surface energy. The specific driving force is the higher energy and solubility (according to Kelvin's equation) of the smaller particles resulting in supersaturation of the liquid relative to the larger particles. Rate of growth is affected by the rate at which the ions or molecules diffuse in the liquid, this in turn being affected by temperature, viscosity and liquid composition (i.e. the presence of impurities).

Figure 1B shows a sample heated at 1650°C for 24 hours; the crystals appear larger and more separated in comparison with those heated for 8 hours (Fig. 1A). The shape has also changed and the crystals have elongated and formed flat faces although the ends still tend to be rounded. Elongation or change in shape is the result of differences in surface energies of the different crystal planes. A low value of γ_{sl}, the interfacial solid-liquid energy for a particular crystallographic face, causes the growth of that face with the development of flattening.

Comparison of Figs. 1C and 1D with Figs. 1A and 1B shows the effect of a 50°C rise in temperature. The crystals are much larger, more

distinct and well formed. Diffusivities are greater at higher temperatures which explains the size increases. Equilibrium with respect to the percentages of phases present is achieved well before 8 hours at 1700°C. The relative size increase between 8 and 24 hours, however, is not as large at 1700°C as it is at 1650°C. It is difficult to specify the size of crystals that are not equidimensional, especially with developing elongation. A number representing the size can be obtained by dividing the volume % of mullite in a sample found by a line scan by the number of crystals per same length of line. The two measurements must be performed on the same area to obtain meaningful results. This method is only useful as a means of comparison. One of the problems is related to being able to distinguish individual grains and obtain a valid count since grain boundaries are generally difficult to identify in these specimens. Error in the method is large for very small, agglomerated crystals. The units of the size are volume % crystal and are quoted as percentage figures. The average size of the crystals in the 8 hours/1700°C sample is 3.3% and in the 24 hours/1700°C sample is 3.6% (Table 5), indicating crystal growth as observed visually. The crystals in Figs. 1A and 1B were too small for this analysis.

The faster relative growth rate at the lower temperature can be explained if the size vs. time curve is non-linear and approaches a steady state value after a certain time. A curve of the form of Fig. 3 with a different time scale for each temperature is such an example. At 1700°C the most rapid growth occurs before 8 hours and is approaching the steady state value at 8 hours. Therefore, the change in size between 8 and 24 hours corresponds only to the distance AB on the y axis. At

Table 5. Crystal size, % crystal

	1 1650/8	7 1650/24	4 1700/8	6 1700/24	2 1700/8 1650/8	3/5 1700/8 1650/16
I A/S	S	S	3.3	3.6	2.3	2.9
II A/S/TiO_2	S	3.6	3.1	3.5	3.5	3.3
IV A/S/Na_2O/K_2O	NE	-	NE	-	NE	2.8
V A/S/Al1	NE	-	NE	-	NE	4.6
III A/S/FeO_3	NE	-	NE	-	NE	3.6
IX A/S/5.7%Fe_2O_3	-	5.3	-	5.3	-	4.7
VII A/S/CaO	3.8	5.0	5.5	7.2	4.3	4.7
VII K	NE	1.9	1.7	3.5	2.4	2.9
X K/CaO	-	2.3	-	3.8	-	2.4
XI K/Fe_2O_3	-	3.4	-	4.0	-	4.9

NE - Not examined
\- - No sample
S - Crystals too small to count

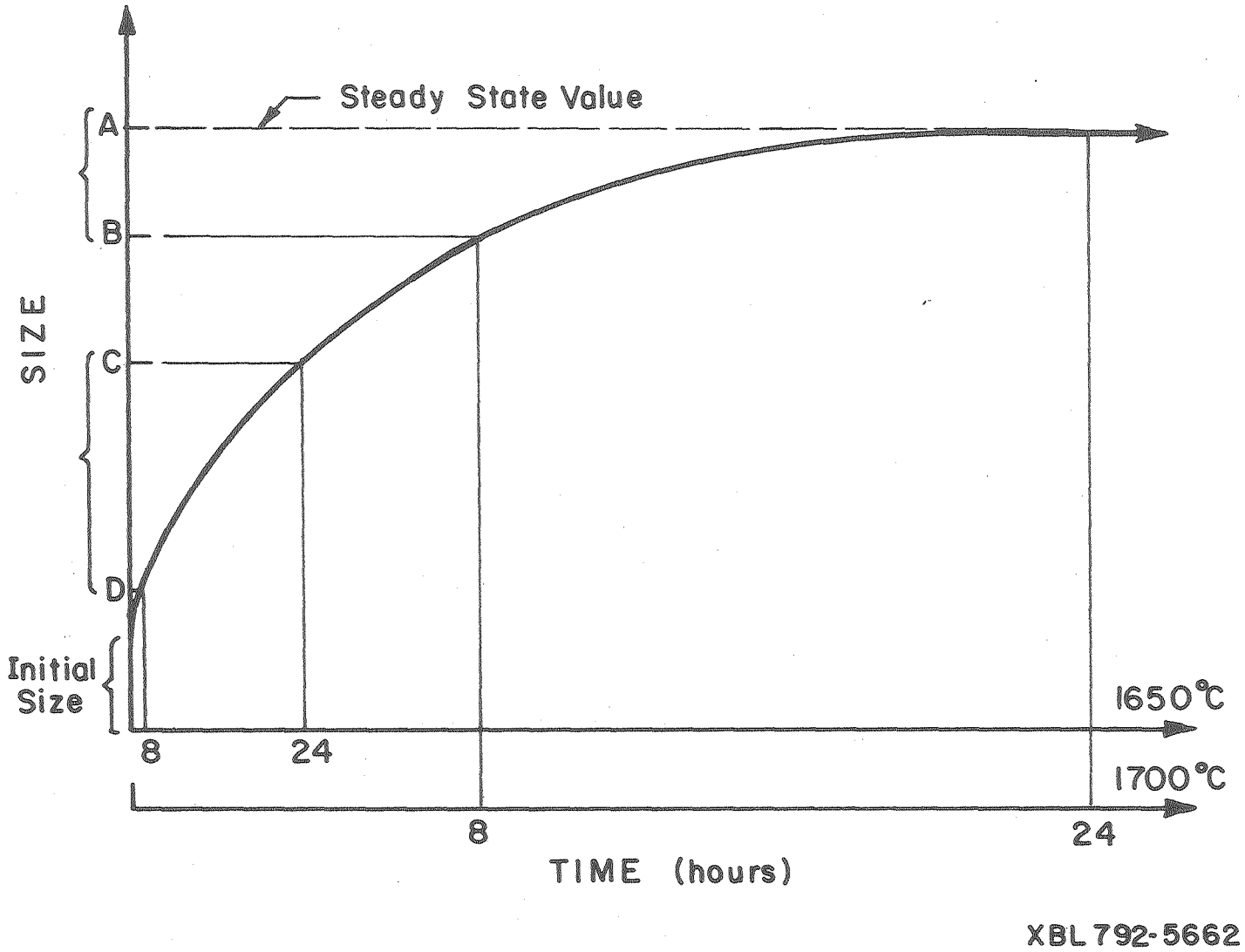


Fig. 3. Crystal Size vs. Time.

1650°C, growth is rapid between 8 and 24 hours, resulting in an increase in size equivalent to CD. Since growth by Ostwald ripening starts after phase equilibrium is reached, another contributing factor to the differences in growth rate is that growth at 1650°C is comparatively more delayed. With a longer firing time at 1650°C it is expected that the crystal size would approach the steady state value and become similar to that in the 1700°C samples. Kinetic calculations based on a linear extrapolation of the values obtained for the size in this study would not be valid owing to the non-linearity of the growth curve and non-availability of data for all but two firing times.

Figures 1E and 1F are the results of a two stage firing process with a 1700°C hold for 8 hours, followed by 1650°C for 8 and 16 hours, respectively. The crystals have the same shape as those for the 1700°C fires but are intermediate in size between those fired at 1650°C and 1700°C for equivalent times, as observed on comparing, for example, Figs. 1E with Figs 1A and C for 8 hours. Line count values for the size (Table 5) are 2.3% for Fig. 1E and 3.3% for Fig. 1C. It could be expected that the crystals in Fig. 1E would be larger than those fired at 1700°C for 8 hours (Fig, 1C) as the sample was fired for an additional 8 hours at 1650°C and the equilibrium amount of mullite is greater at 1650°C than at 1700°C. This fact is supported experimentally by comparing the % volume fraction mullite values of 59.3 and 54.9% respectively from Table 4. However, there is a theoretical explanation for this phenomenon:

With phase equilibrium at 1700°C, the activity of alumina, $a_{Al_2O_3}$ is constant in mullite and in the liquid. When the temperature is

lowered to 1650°C, the value of $a_{Al_2O_3}$ at equilibrium is less and the liquid becomes supersaturated with mullite of lower $a_{Al_2O_3}$. Thus mullite does not precipitate onto the mullite with the high $a_{Al_2O_3}$ and nuclei form. The original mullite with a higher $a_{Al_2O_3}$ goes into solution as the new mullite grows until the equilibrium $a_{Al_2O_3}$ is reached throughout the system. The net result is a larger number of smaller crystals. The growth observed after an additional 8 hours (Fig. 1F, size = 2.9%, Table 5) can be attributed to Ostwald ripening.

B. Kaolinite

Kaolinite fired under different conditions and an alumina-silica mixture are compared in Fig. 4. The morphological difference in the mullite crystals between the Al_2O_3-SiO_2 mixture, Fig. 4A, and the kaolinite samples is noticeable. The mullite crystals in Fig. 4A are rectangular in shape with rounded ends while the mullite crystals formed from kaolinite are acicular with pointed ends.

The mechanisms for mullite formation are different. In mixtures of Al_2O_3 and SiO_2 mullite forms on the Al_2O_3 particles at 1650°C and 1700°C by interdiffusion of Al^{3+} and Si^{4+} ions through the mullite with some solution of mullite in the excess SiO_2; the growth and morphological development of the mullite crystals then occurs by Ostwald ripening. Kaolinite, however, undergoes a more complex series of reactions initiated by a dehydroxylation reaction. At this point it is a molecular mixture with some structure inherited from the kaolinite crystal structure. On heating, with progressive resolution of SiO_2, according to Brindley,[6] mullite forms at ~1250°C. With further heating a liquid phase forms at the eutectic temperature and continuing growth of mullite crystals should

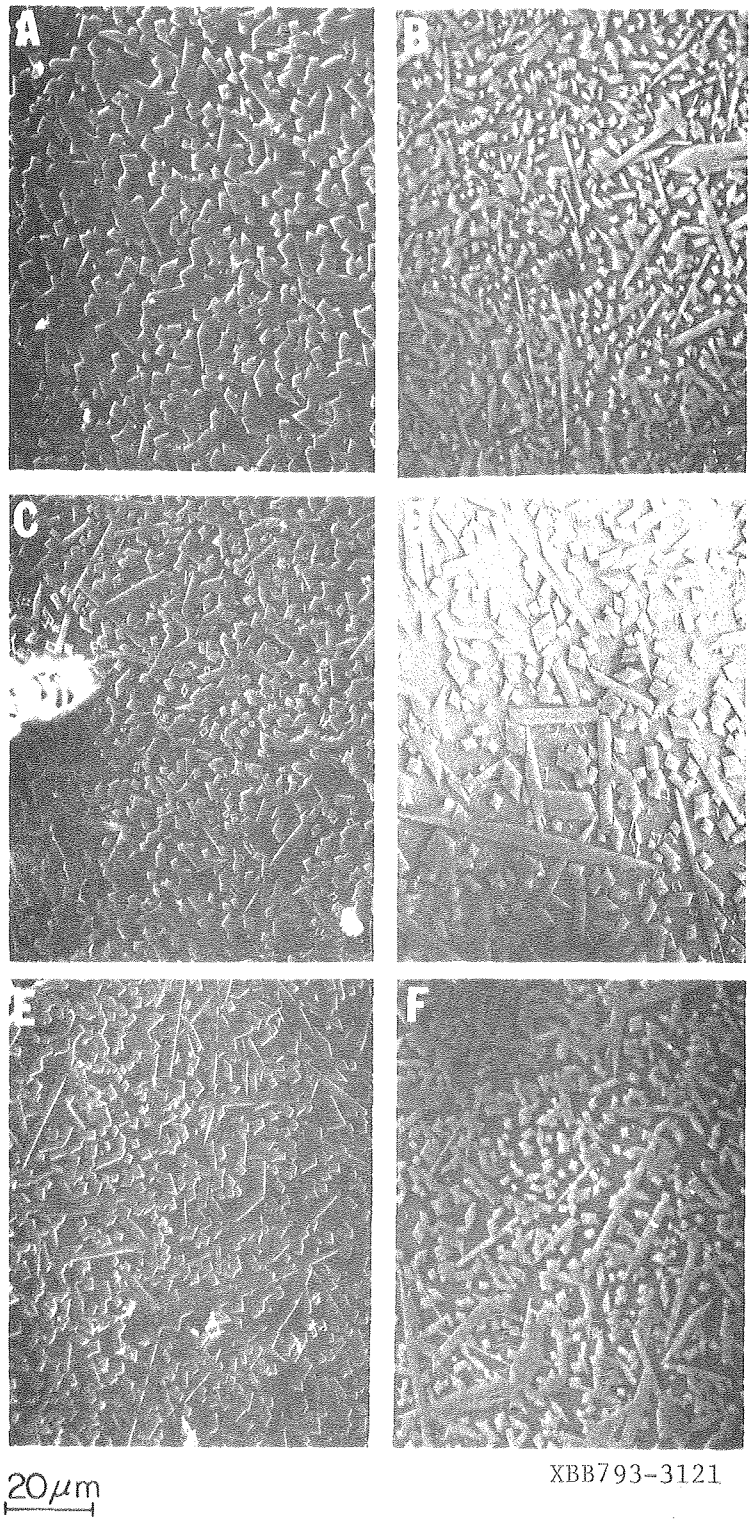


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Fig. 4. Effect of Heat Treatment on Kaolinite.
A. Al_2O_3-SiO_2, 1700°C/8 hours
B. Kaolinite, 1650°C/24 hours
C. 1700°C/8 hours
D. 1700°C/24 hours
E. 1700°C/8 hours then 1650°C/8 hours
F. 1700°C/8 hours then 1650°C/16 hours

occur by the Ostwald ripening process. A direct comparison with Al_2O_3-SiO_2 mixtures, however, may be questioned as kaolinite always contains larger amounts of impurities whose effect on the reaction series is not known. Nevertheless, comparisons will be made.

Examination of the photographs in Fig. 4, (excluding 4A), indicates that the mullite crystals formed from kaolinite are long and acicular with diamond shaped cross-sections. A comparison of Figs. 4C and 4D indicates that the principal growth of the crystals is lengthwise in the 'c'-direction. It can be assumed that this morphological development is due to the fact that the crystal faces parallel to the c-axis have lower interfacial energies. When kaolinite dehydroxylates, the layer structure collapses. The mullite that forms consists of octahedral chains of alumina and tetrahedral chains of silica parallel to the c-axis which result from the original structure. Growth can be viewed as forming extensions to the existing chains which is more likely to occur than formation of new chains.

The effect of firing at 1650°C and 1700°C for 24 hours can be seen by comparing Figs. 4B and 4D, the respective sizes being 1.9% and 3.5% (Table 5). Growth at 1700°C for 8 and 24 hours can be observed in Figs. 4C and 4D. The crystal size increased from 1.7% to 3.5%. Relics of small crystals can be seen in both of these photographs, indicating that the small crystals are being dissolved and that growth is by Ostwald ripening.

The growth rate at 1650°C is slow as can be observed from Figs. 4E and 4F for samples heated at 1700°C for 8 hours and then held at 1650°C for 8 and 16 hours, respectively. The crystal size only increases from

2.4% to 2.9%. The fact that the mullite crystals were slightly larger in Fig. 4E than in Fig. 4C, in comparison with Figs. 1E and 1C, indicates that phase equilibrium is achieved rapidly enough on lowering the temperature to 1650°C to allow some growth. This can also be attributed to the higher impurity content of the kaolinite.
the kaolinite.

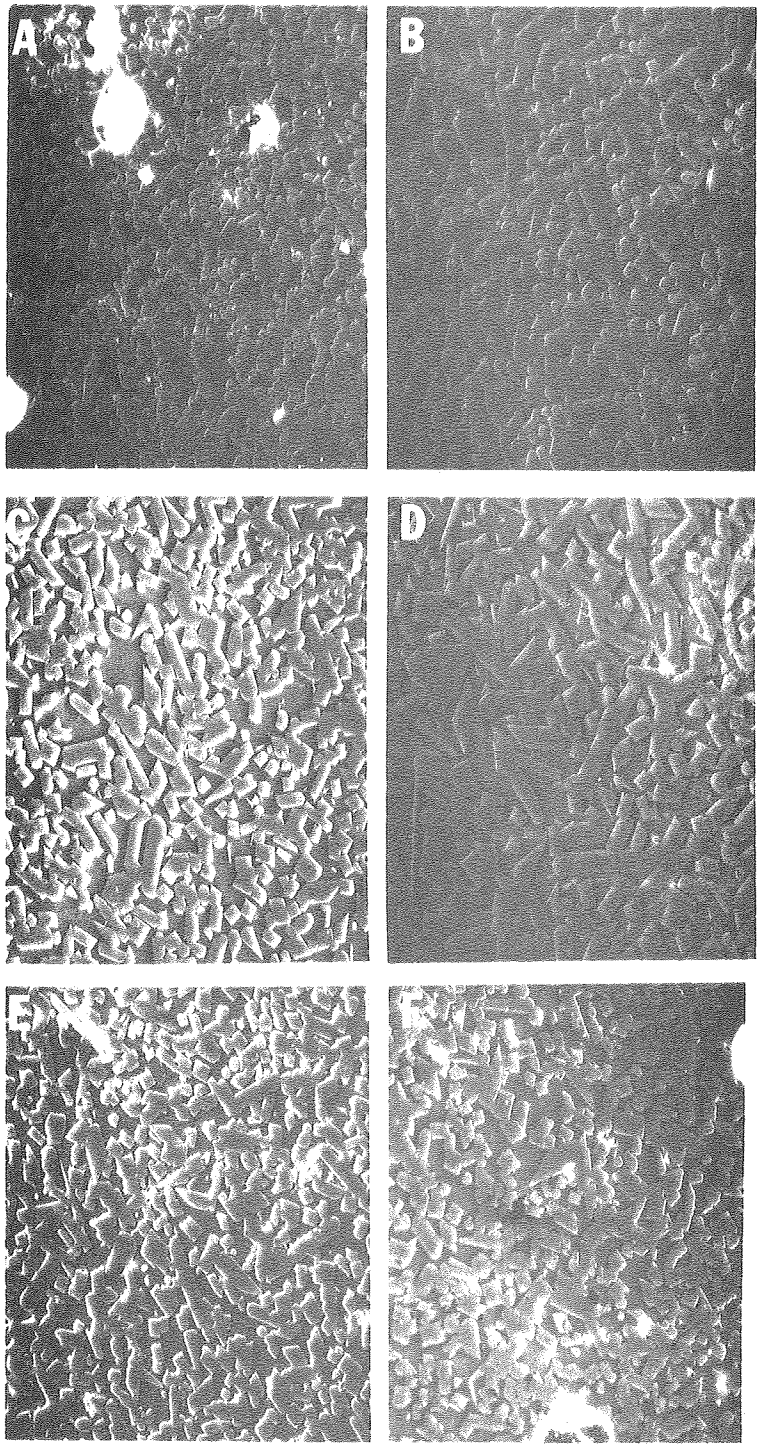
C. Al_2O_3-SiO_2 with TiO_2

The microstructures of Al_2O_3-SiO_2 samples containing 1.4 wt% TiO_2 can be seen in Fig. 5. A visual comparison of these specimens with those of Al_2O_3-SiO_2 mixtures without additions for comparable firing conditions in Fig. 1 indicates that no change in morphology occurred but that there was a small but noticeable increase in crystal size in all cases. The data in Tables 4 and 5 have too much experimental scatter to substantiate this observation precisely.

The largest increase in size was seen in the specimens exposed to the two stage firing process as can be observed by comparing Figs. 5C and 5E with Figs. 1C and 1E. The TiO_2 had the effect of increasing the phase equilibration rate on dropping the specimen from 1700°C to 1650°C. The effect of TiO_2 on increasing the growth rate of mullite in kaolinite in the temperature range 1400 to 1600°C has been reported.[2,3]

D. Al_2O_3-SiO_2 with CaO

The series of Al_2O_3-SiO_2 mixtures with 2 wt% CaO samples are shown in Fig. 6. The mullite crystals are much larger than in either the pure mixture or with a TiO_2 addition. The growth rate from 8 to 24 hours is greater in the 1650°C samples (Figs. 6A and 6B) than in the 1700°C samples (Figs. 6C and 6D). The crystal size after 24 hours at 1650°C



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20 μm

Fig. 5. Effect of Heat Treatment on Al_2O_3-SiO_2 with TiO_2.
A. 1650°C/8 hours
B. 1650°C/24 hours
C. 1700°C/8 hours
D. 1700°C/24 hours
E. 1700°C/8 hours then 1650°C/8 hours
F. 1700°C/8 hours then 1650°C/16 hours

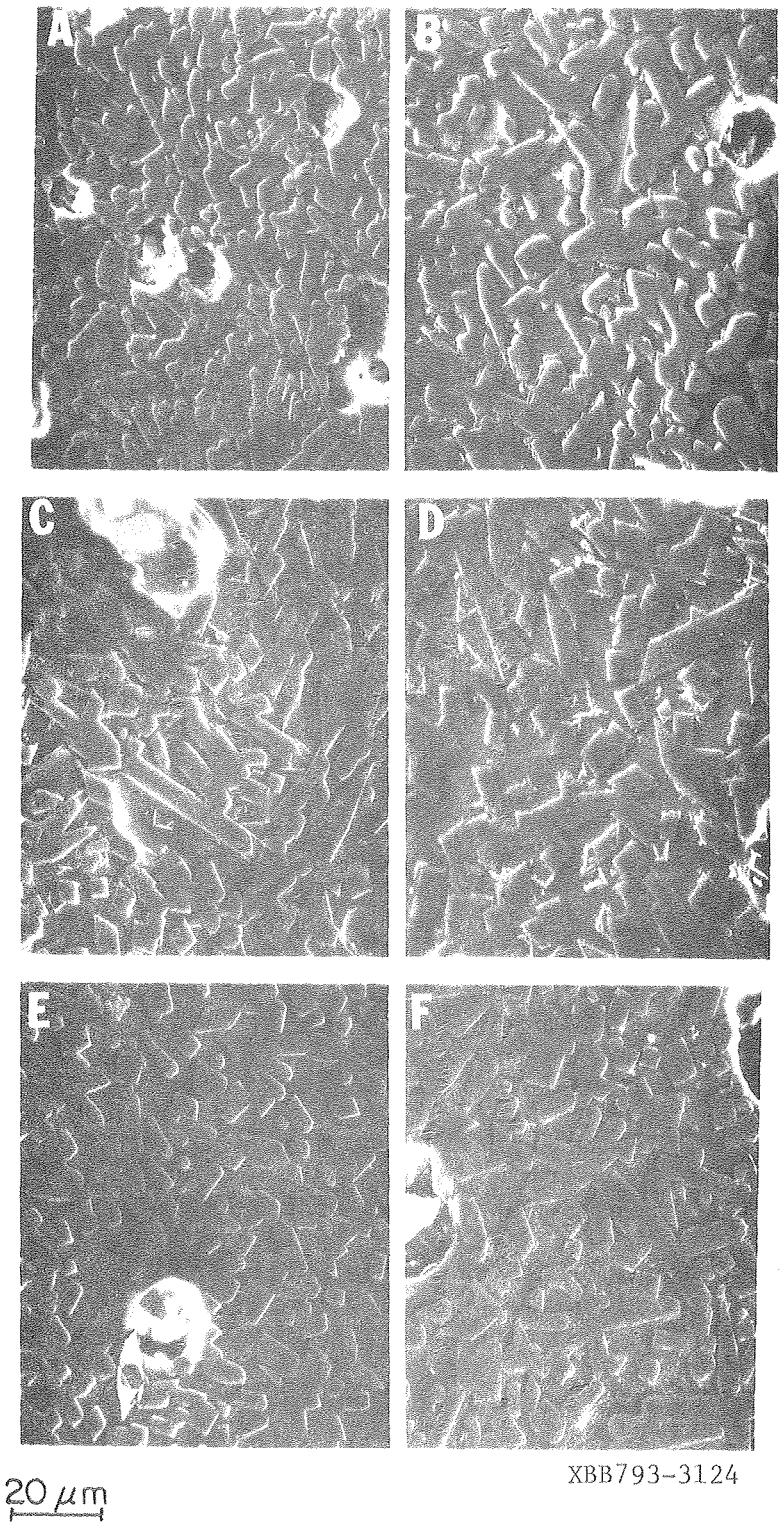


Fig. 6. Effect of Heat Treatment on Al_2O_3-SiO_2 with CaO.

A. 1650°C/8 hours
B. 1650°C/24 hours
C. 1700°C/8 hours
D. 1700°C/24 hours
E. 1700°C/8 hours then 1650°C/8 hours
F. 1700°C/8 hours then 1650°C/16 hours

(Fig. 6B, 5.0%), however, approaches that after 8 hours at 1700°C (Fig. 6C, 5.5%), indicating that the growth rate up to 8 hours is faster at 1700°C. The growth rate behavior can be discussed as before with the aid of Fig. 3. CaO apparently decreases the time to reach the equilibrium composition as well as accelerating the growth of mullite. However, it has no significant effect on the grain morphology.

The observation of Rodriguez and Parmelee[2] that CaO is a moderate accelerator of mullite formation is reinforced by these experiments. Chaudhuri[31] also reported large crystals in CaO-containing samples. The optimum amount of CaO is less than 1% at 1650°C[24] and excess tends to decrease the amount of mullite formed.[30] The line count results (Table 4) indicate that, in accordance with this statement, less mullite forms in the specimens with CaO than in those without.

The growth of mullite with time is by Ostwald ripening. Relics of dissolving crystals can be seen in Fig. 6D. It is also interesting to note that the vertices of the smaller dissolving crystals tend to dissolve first, leaving rounded particles. These pictures show the change in morphology from small rounded crystals to the rectangular and diamond shaped slightly elongated crystals which grow by precipitation. Line count results indicate that more mullite is formed at lower temperatures as was the case with both the titania and pure samples. The total amount of mullite formed is less than that in the Al_2O_3-SiO_2 samples without additives.

The two stage firing samples are shown in Figs. 6E and 6F which were held for 8 hours at 1700°C followed by 8 and 16 hours at 1650°C, respectively. The crystal size changes from 4.3% to 4.7%. The crystals

in Fig. 6E are more rounded and smaller than those in Fig. 6C: 4.3% vs. 5.5%. Additions of CaO thus appear to reduce the rate at which phase equilibrium is attained after dropping to 1650°C from 1700°C.

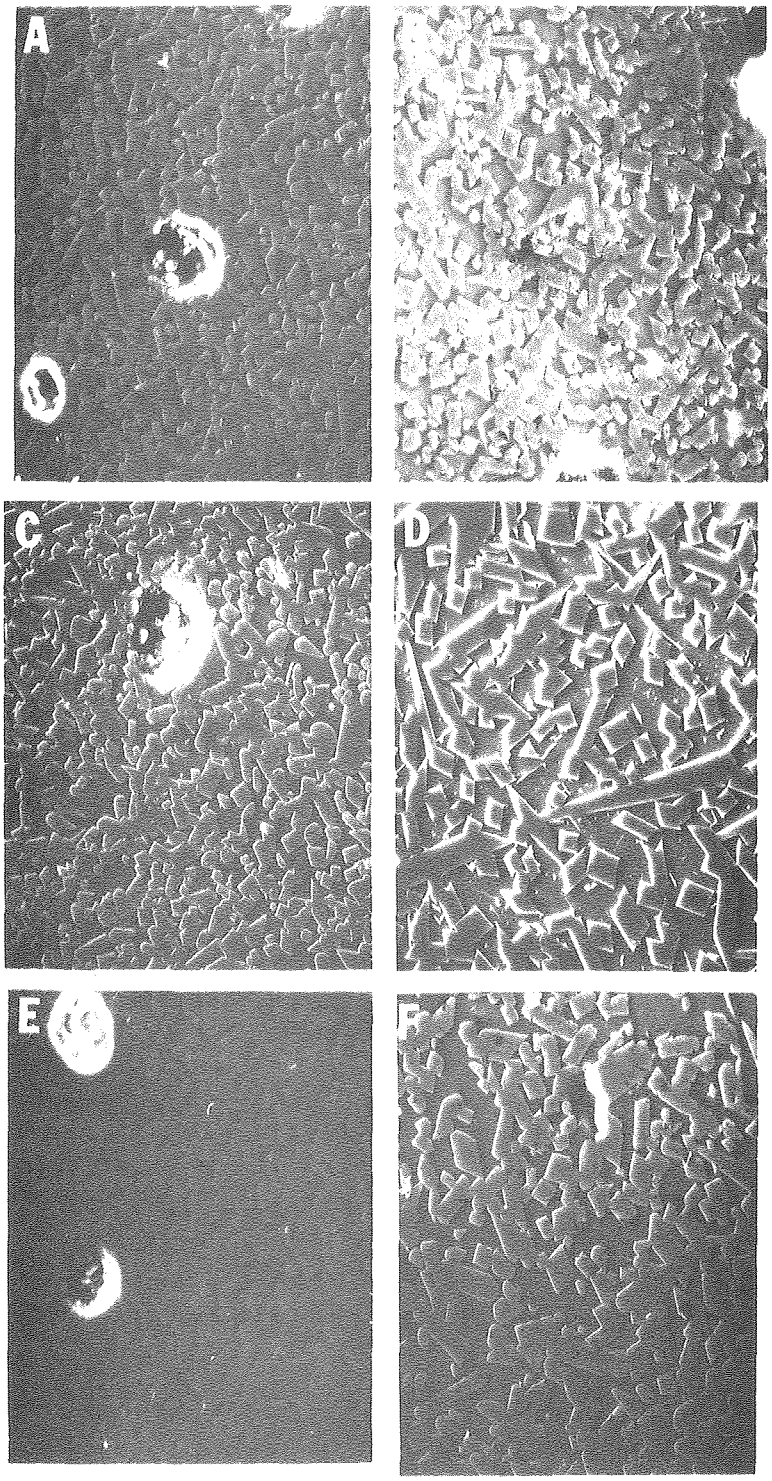
Bloating was observed in all the CaO samples, making them very porous. This behavior occurred only with CaO additions. Studies to determine the cause were not pursued.

E. Al_2O_3-SiO_2 Mixtures with Oxides Equivalent to Kaolinite

All samples shown in Fig. 7 were fired at 1700°C for 8 hours followed by 1650°C for 16 hours. The oxides were present in the Al_2O_3-SiO_2 mixtures in the same proportions as in the kaolinite as determined by chemical analysis with the exception of Fig. 7D which had 5.7 wt% Fe_2O_3 added.

Excluding Fig. 7D all the samples have similarly shaped grains which tend to be rectangular with varying degrees of roundness at the ends. Figure 7D, on the other hand, shows large, sharply pointed elongated crystals. All of the corners on all of the crystals are sharp. The Al_2O_3-SiO_2 sample, Fig. 7A, and that with Na_2O and K_2O, Fig. 7E, have the smallest crystals followed by the sample with TiO_2, Fig. 7B, with 0.34% Fe_2O_3, Fig. 7C, and with all of these oxides, Fig. 7F, in accordance with the data in Table 5. Table 4 indicates that the amount of mullite formed in this series does not vary significantly.

It has been suggested[29] that titania concentrates in the glass raising its viscosity, which impedes crystal growth resulting in the small crystals observed. The relatively small number of well formed grains in the TiO_2 sample, Fig. 7B, is in accordance with prior observations.[23] Apparently, Ti^{4+} does not substitute in the mullite



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20 μm

Fig. 7. Comparison of Al_2O_3-SiO_2 Mixtures with Additives. Heat treatment: 1700°C/8 hours then 1650°C/16 hours.

A. Without Additives
B. TiO_2
C. 0.34 wt% Fe_2O_3
D. 5.7 wt% Fe_2O_3
E. Na_2O and K_2O
F. TiO_2, Fe_2O_3, Na_2O, K_2O and MgO

structure or adsorb on the surfaces of the grains.

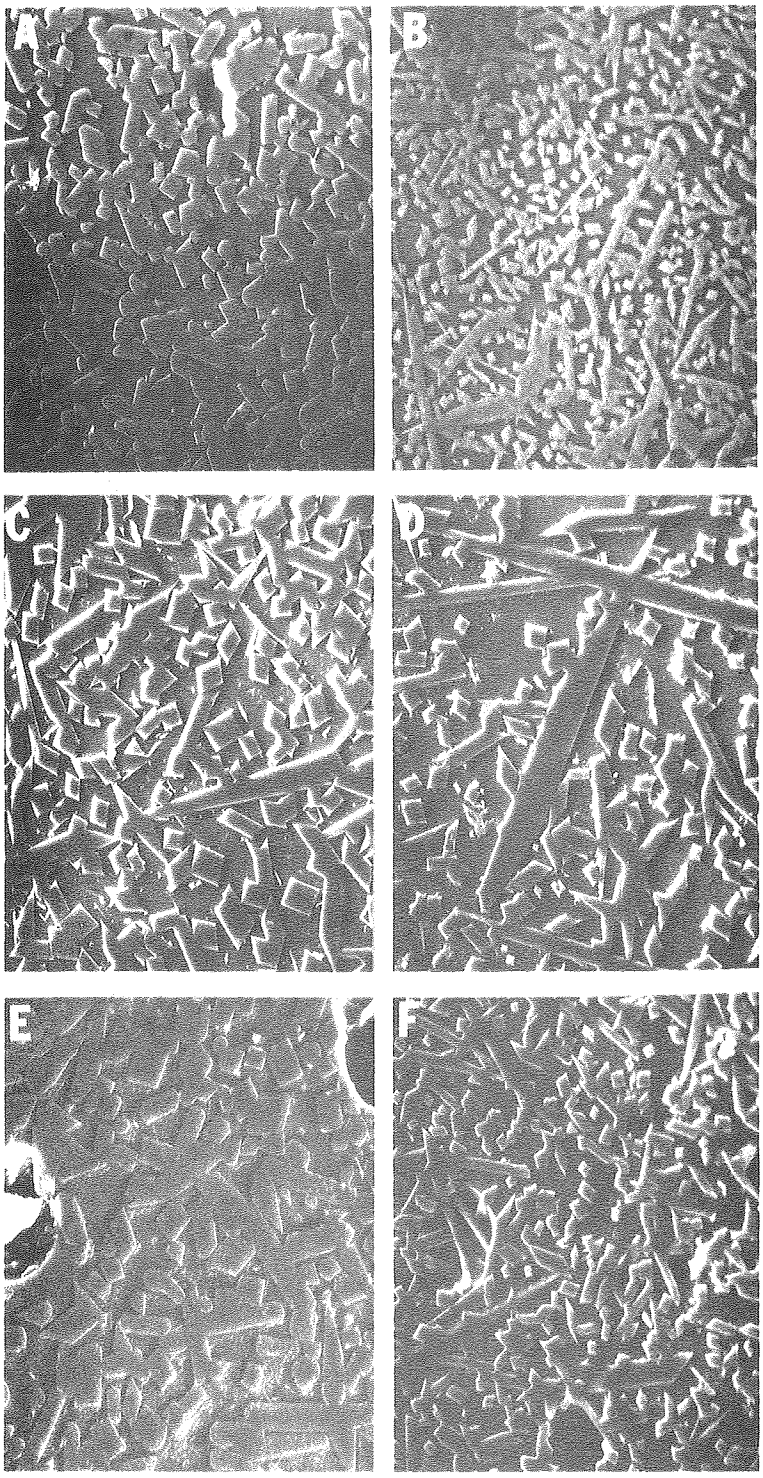
The sample containing alkalis has the smallest grain size in this series which is consistent with Na_2O and K_2O being poor catalyzers for mullite crystallization.[2] Previous results[31] have also indicated that Na_2O and K_2O hinder crystal growth.

The effect of Fe_2O_3 additions is significantly different. Small amounts, Fig. 7C, produce crystals of the same shape as in the Al_2O_3-SiO_2 sample but slightly larger while a larger addition produced the elongated crystals with sharp corners observed in Fig. 7D. Some crystals are up to 50μm long. The shape of the crystals is similar to that observed in the kaolinite, Figs. 4B-F.

Iron oxide can enter into solid solution with mullite in amounts up to 10-12% while other oxides have limited solubilities. All the oxides, however, take part in liquid formation and affect the viscosity. Crystal growth is enhanced by low liquid viscosity which generally is associated with an increase in the diffusivity of the ions. The larger amount of Fe_2O_3, in addition to apparently lowering the viscosity of the liquid, has also promoted the preferential growth in the c-direction. Its solution in the mullite structure must result in greater anisotropy of the surface energies of the crystal faces with the energies of the faces parallel to the c-axis being the lowest.

F. Comparison of Additions of Fe_2O_3 and CaO

The effects of additions of 5.7 wt% Fe_2O_3 and 2.0 wt% CaO are compared in Fig. 8 for the two-stage heat treatment, 8 hours at 1700°C followed by 16 hours at 1650°C. The molar amounts of CaO and Fe_2O_3 added were the same.



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20 μm

Fig. 8. Comparison of effects of Fe_2O_3 and CaO. Heat treatment: 1700°C/8 hours, 1650°C/16 hours.

A. Al_2O_3-SiO_2 with all additives
B. Kaolinite
C. Al_2O_3-SiO_2 with 5.7 wt% Fe_2O_3
D. Kaolinite with 5.7 wt% Fe_2O_3
E. Al_2O_3-SiO_2 with CaO
F. Kaolinite with CaO

An Al_2O_3-SiO_2 mixture with additives to form essentially the same chemical composition as the kaolinite is compared with kaolinite in Figs. 8A and 8B. The crystals in the former are larger, 4.0% vs. 2.9%. Actually, the crystals in the mixture with no additives and the same heat treatment, Fig. 1F, were similar in size to those of kaolinite, 2.9%. The morphology, however, was significantly different. Kaolinite has acicular crystals with sharp corners and the Al_2O_3-SiO_2 mixture has more rectangular crystals with rounded ends and corners. On the other hand, Al_2O_3-SiO_2 and kaolinite samples containing Fe_2O_3, Figs. 8C and 8D, have very similar appearances. The crystals are acicular in both cases and have grown to similar sizes 4.7% vs. 4.9%. A visual comparison of the microstructures with the CaO addition, Figs. 8E and 8F, indicate a similarity in appearance to Figs. 8A and 8B, respectively, except for a small increase in size.

The persistence of the acicular shape of the mullite crystals formed from all kaolinite-based mixtures and only in the Al_2O_3-SiO_2 mixture containing Fe_2O_3 is of great interest. An explanation of this phenomenon must be related to the mechanism of the respective mullite forming reactions discussed earlier. The exsolution of SiO_2 from kaolinite to form mullite leaves a residual structure that results in growth in the c-direction and acicular crystals, and is associated with an anisotropy of interfacial energy that persists during heat treatments. Impurities associated with the kaolinite may be incorporated in the mullite structure during its formation and play a contributory role in this morphology. The impurities, other than Fe_2O_3, when added to Al_2O_3-SiO mixtures, do not cause the formation

of acicular crystals and apparently do not enter the mullite structure being formed by chemical interdiffusion. The oxide Fe_2O_3, which is the only one of those tested that can form an appreciable solid solution with mullite, caused structural changes that led to the formation of acicular crystals. Both Fe_2O_3 and CaO, on the other hand, when added to Al_2O_3-SiO_2 mixtures, affect the liquid and permit increased mass transport rates and thus increased mullite growth rates in comparison with relatively small amounts of Fe_2O_3, TiO_2 and alkalis.

The effects of 5.7 wt% Fe_2O_3 on Al_2O_3-SiO_2 mixtures and kaolinite are seen in Fig. 9. The difference in crystal size of the mullite formed from the Al_2O_3-SiO_2 mixtures with Fe_2O_3 fired at 1650°C for 24 hours, Fig. 9A, and at 1700°C for 24 hours, Fig. 9C is minimal and the figures in Table 5, 5.3% for both, also indicate this fact. The size increase over the Al_2O_3-SiO_2 sample fired at 1700°C for 24 hours, Fig. 9E, is large (5.3% vs. 3.6%). When iron oxide is added to kaolinite, the particle size does not increase as much as can be seen by comparing Figs. 9D (4.0%) and 9F (3.5%), both fired at 1700°C for 24 hours. The increase is greater at 1650°C, Fig. 9B being kaolinite with Fe_2O_3 and Fig. 13B being for kaolinite. This comparison also applies to the Al_2O_3-SiO_2 samples with and without Fe_2O_3 at 1650°C, Figs. 9A and 13A. The implication is that Fe_2O_3 accelerates crystal growth, and consequently the steady state value depicted in Fig. 3 is not only higher but is also reached in shorter times at both 1650°C and 1700°C.

The crystal shape remained acicular in the kaolinite crystals. Crystals in the Al_2O_3-SiO_2 samples containing iron were similar to those in kaolinite.

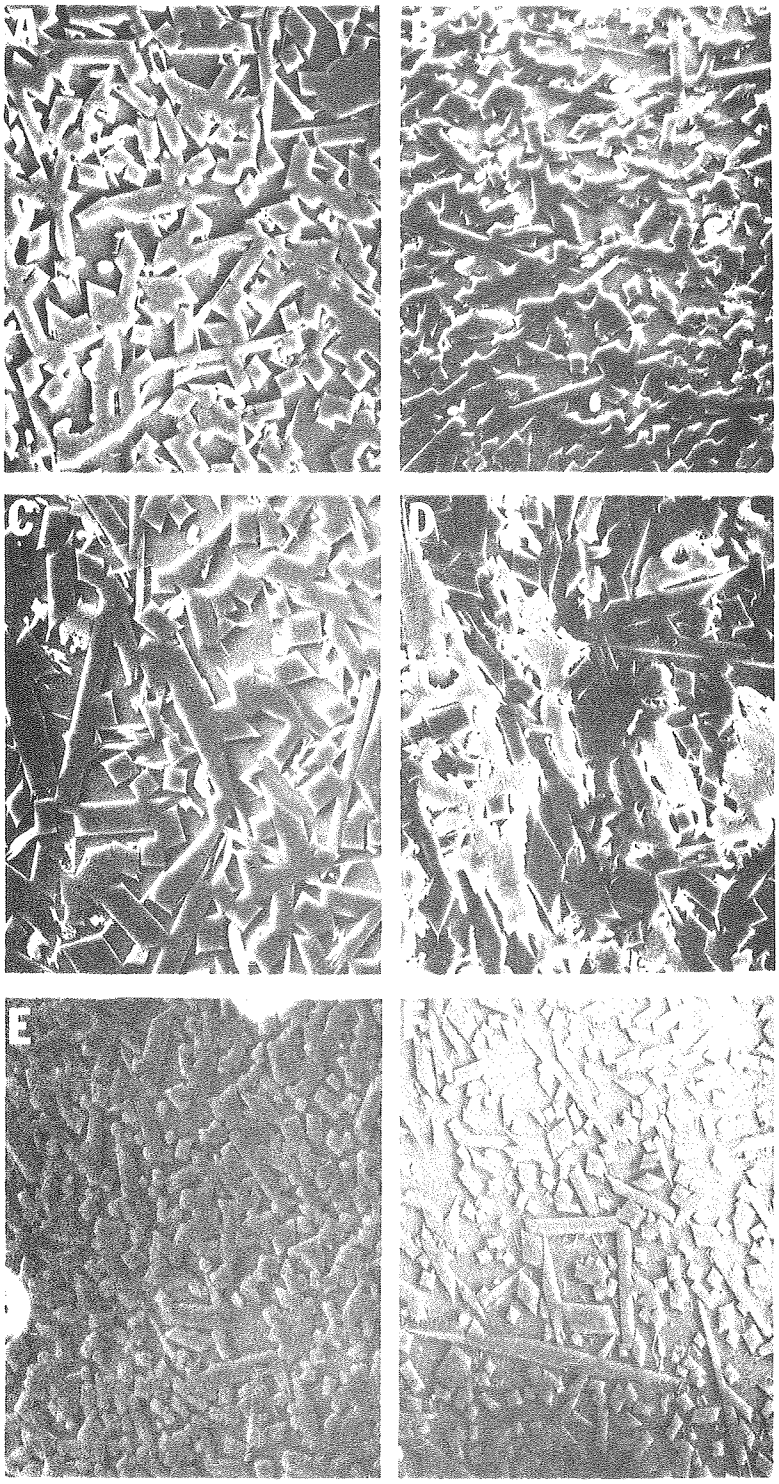

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Fig. 9. Effect of Heat Treatment on Kaolinite with CaO and Fe_2O_3.
A. With CaO, 1650°C/24 hours
B. With Fe_2O_3, 1650°C/24 hours
C. With CaO, 1700°C/24 hours
D. With Fe_2O_3, 1700°C/24 hours
E. Al_2O_3-SiO_2, 1700°C/24 hours
F. Kaolinite, 1700°C/24 hours

There is a third phase present in the kaolinite and Fe_2O_3 sample fired at 1700°C for 24 hours, Fig. 9D. Figure 10 shows this phase at higher magnifications. It has a very fine structure and is interspersed with the glass phase. It appears to form around the points of the mullite crystals and striations can be seen clearly on the crystals. The composition is unknown as the crystals were too small for EDAX analysis. The glass composition is SiO_2 with some Fe_2O_3 and Al_2O_3. A phase diagram at the $FeO \cdot Fe_2O_3$-SiO_2 system (Fig. 11) shows a two liquid region above 1700°C. The $FeO \cdot Fe_2O_3$-Al_2O_3-SiO_2 phase diagram (Fig. 12) shows the two phase region on the $FeO \cdot Fe_2O_3$-SiO_2 join extending slightly into the composition triangle. The composition of the glass is probably within this region and upon cooling, one liquid has crystallized to form the third phase. A small amount of this phase can be seen in the Al_2O_3-SiO_2-Fe_2O_3 sample (Fig. 9C), probably due to a local inhomogeneity, but it is not present in the 1650°C samples (some foreign material is present in the photograph). The amount of mullite present in the sample shown in Fig. 9D is low owing to the presence of the third phase.

A comparison of the effects of CaO on Al_2O_3-SiO_2 mixtures and kaolinite can be seen in Fig. 13. The increase in crystal size is greater for the Al_2O_3-SiO_2 samples (Figs. 13A, 13C and 13E) than it is for the kaolinite samples (Figs. 13B, 13D and 13F). At 1650°C the increase in crystal size when CaO is added to kaolinite (Fig. 13D vs. 13B) is slight (1.9% vs. 2.3%) when compared to that when CaO is added to Al_2O_3-SiO_2 (Fig 13C vs. 13A). At 1700°C, (Figs. 9F and 13F for kaolinite and Figs. 9E and 13E for Al_2O_3-SiO_2), the crystal size increase is more similar. The crystal size after 24 hours at 1650°C, Fig. 13B is

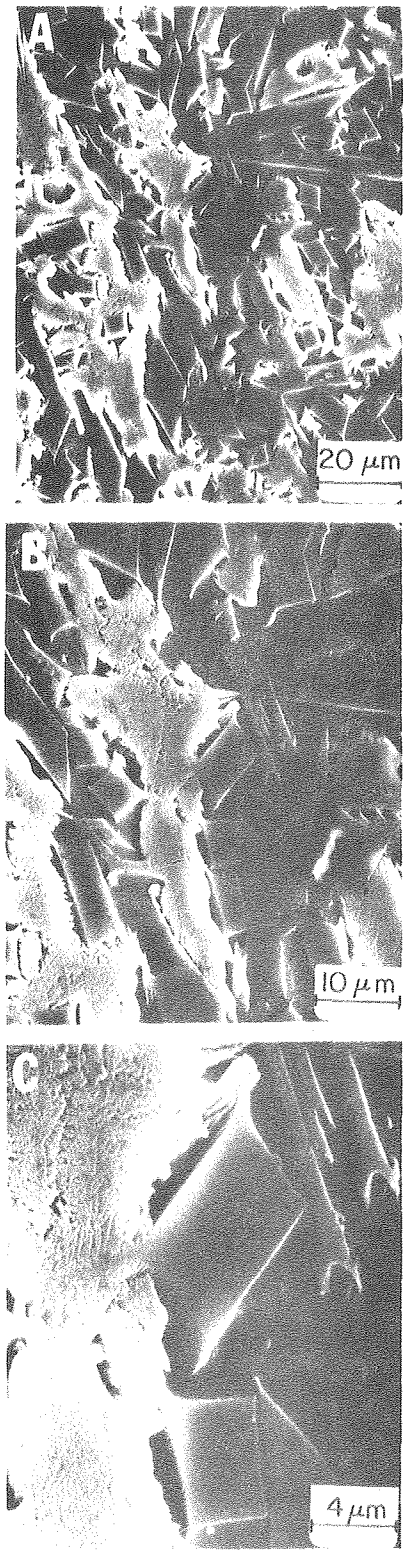

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Fig. 10. Al_2O_3-SiO_2 with 5.7 wt% Fe_2O_3.

Heat Treatment: 24 hours at 1700°C

A. 1000X
B. 2000X
C. 5000X

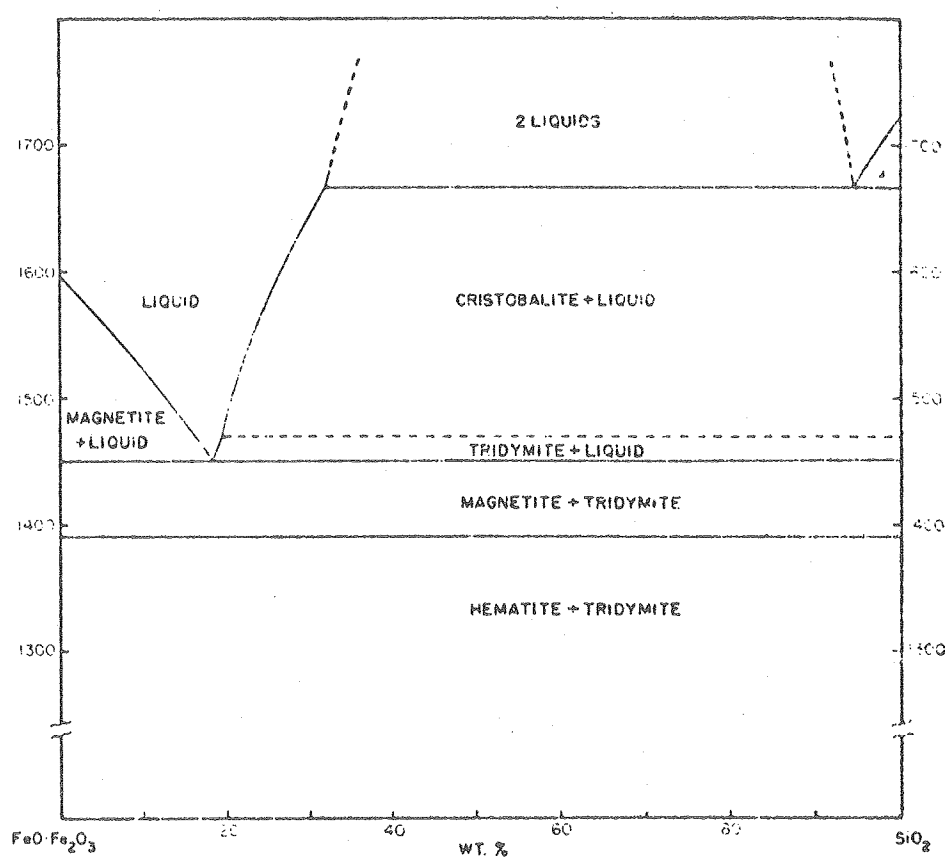

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Fig. 11. $FeO \cdot Fe_2O_3$ - SiO_2 Phase Diagram.[22]

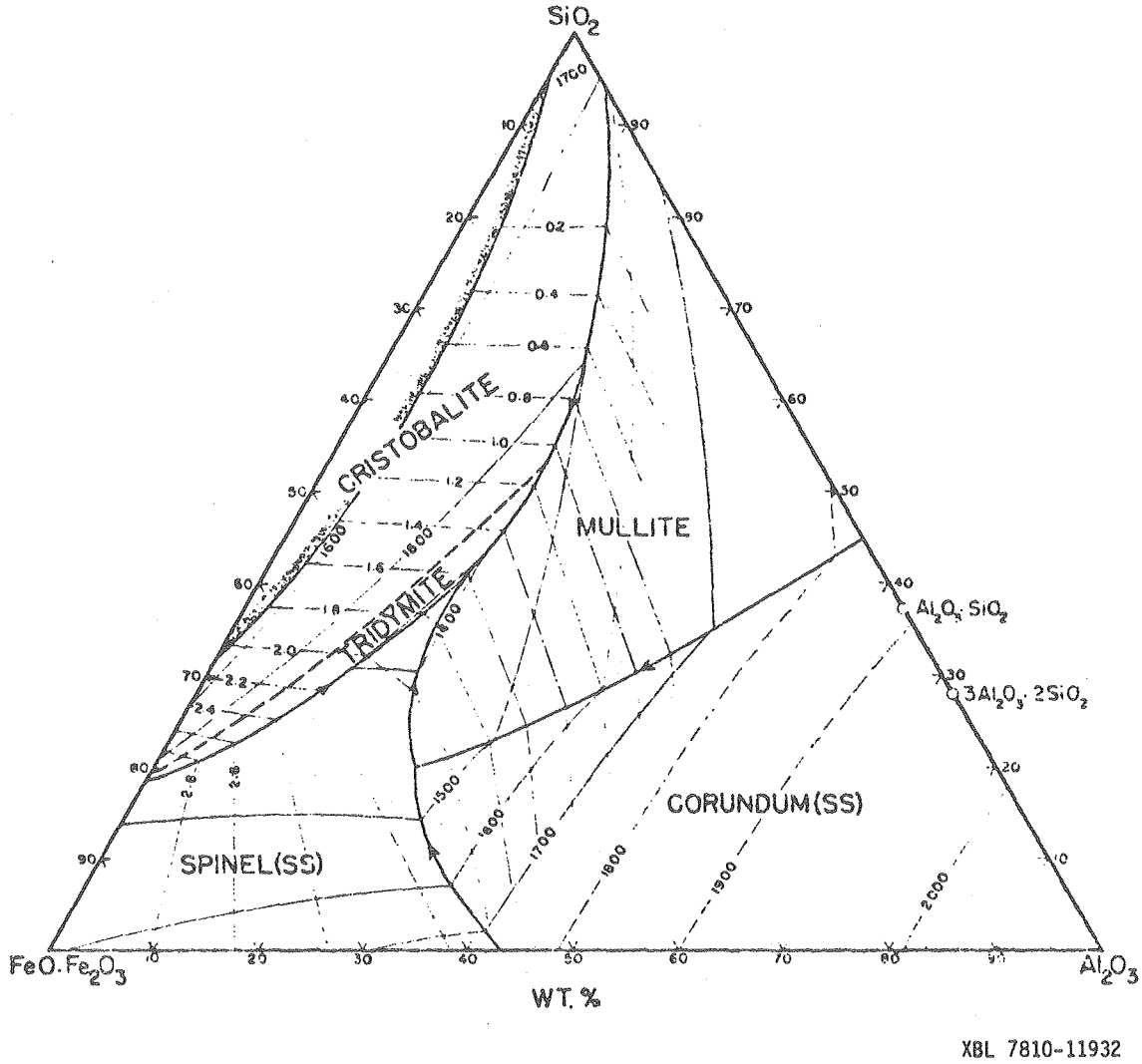
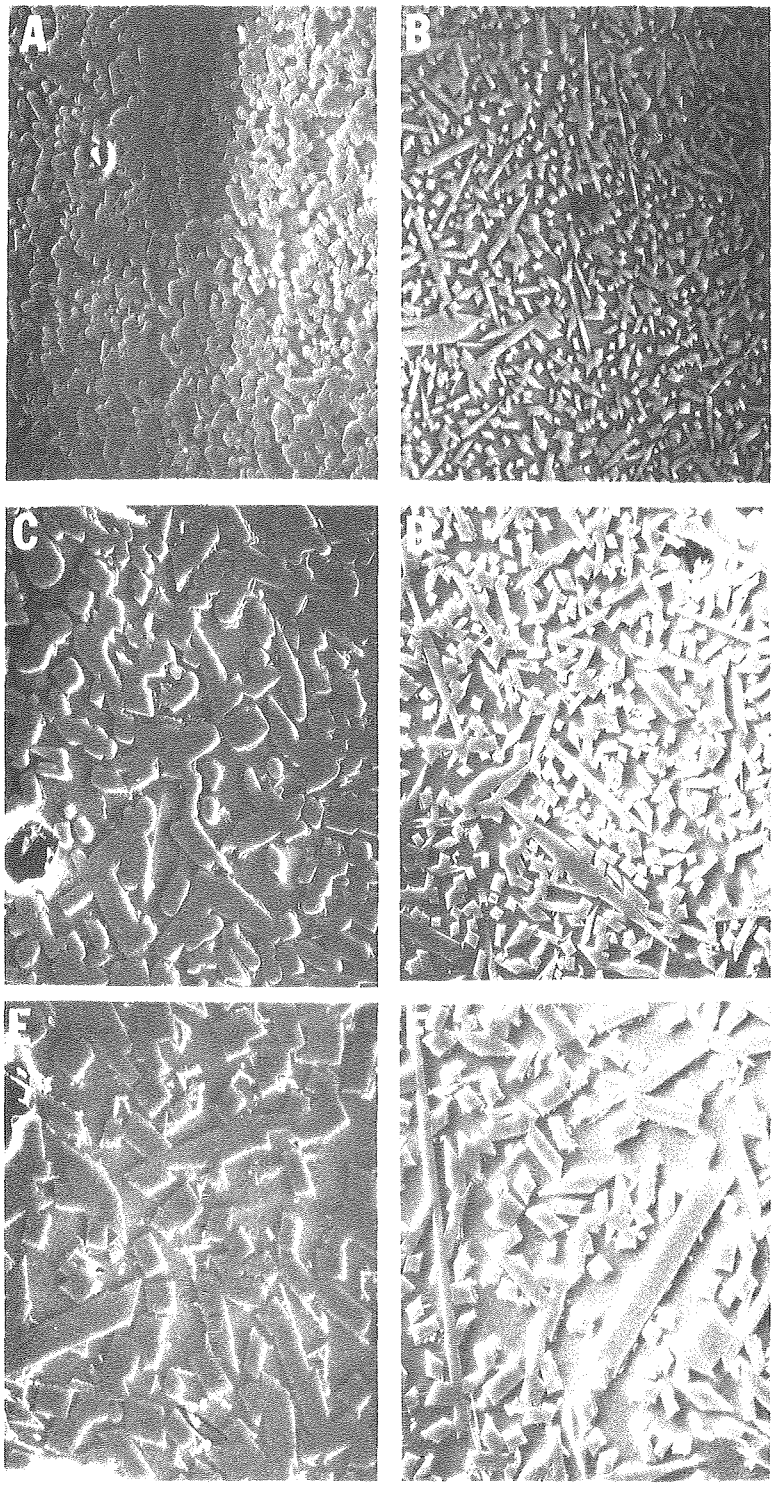


Fig. 12. $FeO \cdot Fe_2O_3$-Al_2O_3-SiO_2 Phase Diagram.[22]



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20 μm

Fig. 13. Effect of CaO Additives on Al_2O_3-SiO_2 and Kaolinite.

A. Al_2O_3-SiO_2, 1650°C/24 hours
B. Kaolinite, 1650°C/24 hours
C. Al_2O_3-SiO_2 with CaO, 1650°C/24 hours
D. Kaolinite with CaO, 1650°C/24 hours
E. Al_2O_3-SiO_2 with CaO, 1700°C/24 hours
F. Kaolinite with CaO, 1700°C/24 hours

similar to that after 24 hours at 1700°C, Fig. 13E for the Al_2O_3-SiO_2 mixtures with CaO; the difference is that crystals in the 1650°C sample have rounded ends while those in the 1700°C sample have flat ends and sharp corners. CaO does not accelerate growth in the c-direction as does Fe_2O_3. The crystals in the kaolinite sample remain the same shape. CaO added to kaolinite accelerates the growth rate of mullite more than Fe_2O_3 does. CaO appears, therefore, to increase the diffusivity of Si^{4+} and Al^{3+} ions in the liquid in the kaolinite sample more than Fe_2O_3 does. Kaolinite contains other impurities and thus its liquid will be more impure than that arising from the Al_2O_3-SiO_2 samples meaning that the effects of further additions differ.

2. Differential Thermal Analyses of Kaolinites

Four clays were examined by DTA: the Georgia kaolin used in the additive experiments, Ione Clay, K-Ga-1 and K-Ga-2. K-Ga-1 and K-Ga-2 are known to be structurally ordered and disordered, respectively. The samples were heated to ~1500°C at a uniform rate. The thermograms can be seen in Fig. 14. The peak positions and type are given in Table 6.

The main point of interest in the DTA study was the appearance of a third exothermic peak at ~1400°C in two of the samples, K-Ga-2 and Georgia kaolin. The other three peaks of these kaolins occur at lower temperatures than the corresponding peaks of K-Ga-1, implying that both K-Ga-2 and Georgia kaolin are disordered. The peaks arising from the Ione clay occur closer to those of K-Ga-1, indicating a more ordered structure.

X-ray diffraction (XRD) was used to investigate the 1400°C reaction in the disordered kaolins. The two kaolinites known definitely to be

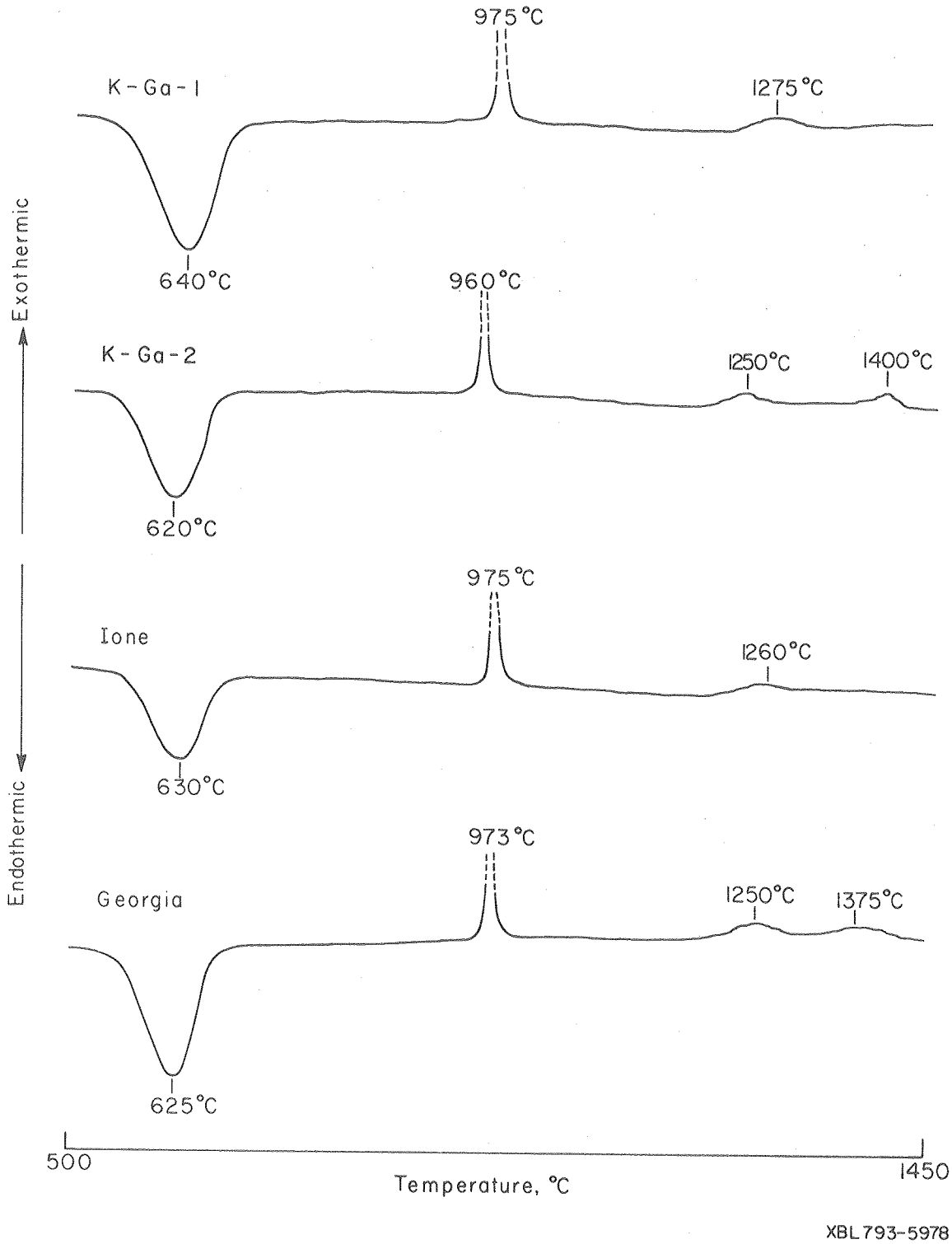

Fig. 14. DTA Thermograms.

Table 6. Differential Thermal Analysis of Kaolins

Peaks	Clay			
	K-Ga-1	K-Gl-2	Georgia	Ione
	Temperature, °C			
Endothermic	635	625	620	628
1st Exothermic	975	960	973	972
2nd Exothermic	1275	1250	1250	1260
3rd Exothermic	-	1400	1375	-

ordered and disordered were chosen for this study. X-ray analysis was performed at room temperature on samples heated to 1100°C (after the first exothermic peak), heated to ~1300°C (after the second exothermic peak) and to 1475°C (the upper limit). Table 7 lists the major crystalline compounds found in each sample.

The main kaolinite peak in the room temperature K-Ga-2 sample was displaced to 7.16Å and was smaller than that of K-Ga-1, indicating disorder. The only evidence of crystal structure in the 1100°C samples was a broad peak in the region of the main kaolinite peak, indicating some residual kaolinite structure. Only mullite was present after the 1250°C exothermic peak. Cristobalite and mullite were both present at 1475°C.

The main cristobalite peak at d = 4.09Å was larger and sharper in the disordered specimen. The 1400°C exothermic peak in the sample is a result of the crystallization of amorphous silicate cristobalite. Cristobalite also forms from the ordered kaolinite but more slowly and over a larger temperature range, which would account for the lack of a distinct exothermic peak at ~1400°C.

Free crystalline silica was not detected by either XRD or DTA. The cristobalite thus forms from the silica exsolved from the kaolinite during mullite formation. The rate and temperature range of crystallization appear to be functions of the orderliness of the kaolinite.

V. CONCLUSIONS

The formation of mullite from kaolinite and Al_2O_3-SiO_2 mixtures occurs by different mechanisms, each producing different crystal morphologies. The acicular crystals of mullite formed from kaolinite are a

Table 7. X-ray Diffraction Data

Temperature °C	K-Ga-1 Ordered Kaolinite	K-Ga-2 Disordered Kaolinite
Room Temperature	Main kaolinite peak d=7.13Å	Main kaolinite peak d=7.16Å
1100°C	Amorphous-broad peak in region of main kaolinite peak	Amorphous-broad peak in region of main kaolinite peak
1300°C	Mullite	Mullite
1475°C	Mullite cristobalite main peak d=4.09Å	Mullite cristobalite main peak larger and sharper, d=4.09Å

consequence of the residual structure of kaolinite. Crystals of mullite arising from Al_2O_3-SiO_2 mixtures are initially pseudomorphic after the Al_2O_3 grains. With subsequent growth by a solution-precipitation process (Ostwald ripening), they become rectangular with rounded ends, and elongate after long firing times, indicating that their eventual appearance would be similar to the crystals originating from kaolinite.

All the additives increase the growth rate of mullite formed from Al_2O_3-SiO_2 mixtures as the viscosity of the liquid is decreased and the diffusivities are increased. CaO and Fe_2O_3 have the most pronounced effect on crystal size. The effect is not as great on kaolinite, possibly because the liquid formed is less pure owing to the impurities present in the kaolin, which can modify the viscosity effects.

Iron oxide changes the mullite crystal morphology in the Al_2O_3-SiO_2 samples to that of the kaolinite samples. Iron oxide is the only additive which will enter into solid solution with mullite in significant amounts. It is postulated that the growth in the 'c' direction is caused by a relative lowering of the surface energy of the parallel faces. Fe_2O_3 appears to occupy atomic sites that affect the surface energies resulting in energies similar to those of the mullite formed from kaolinite.

Growth is by the process of Ostwald ripening which does not seem to start until after phase equilibrium is reached. The additives increase the rate of Ostwald ripening. The effect of CaO and Fe_2O_3 is the most pronounced but differs according to the heat treatment and starting material.

The results of the DTA study imply that the state of order of the kaolinite affects the crystallization of cristobalite from amorphous silica released during the phase transformations of kaolinite. D.T.A. thermograms of disordered kaolinites exhibit an exothermic peak at ~1400°C while those of ordered kaolinites do not. More investigation is needed in this area.

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