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Importance of Starting Materials on Reactions and Phase Equilibria in the Al_2O_3–SiO_2 System

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Abstract

Disagreements in the high Al_2O_3 side of the phase equilibrium diagram for the Al_2O_3–SiO_2 system have been reported consistently. Some of the disagreements are significantly different and have been reported many times. It is thus necessary to eliminate experimental errors as being primarily responsible. An examination and analysis of the starting materials and the development of a fundamental understanding of the chemical reactions that take place provide an explanation for the reported differences. The objective of this report is to briefly review the disagreements and correlate them with the starting materials and the associated solid-state reactions that occur in reaching stable or metastable equilibrium.

1 Literature Review

A review of a chronological assemblage of selected papers brings out the disagreements. In 1909 Shepherd et al.[1] published the first phase equilibrium diagram which indicated that sillimanite (Al_2O_3·SiO_2, 62·92 wt% Al_2O_3) was the only binary compound in the Al_2O_3–SiO_2 system; this compound was subsequently shown to be metastable at standard conditions of temperature and pressure and stable only at high pressures. In 1924, Bowen and Greig[2,3] published the first phase equilibrium at standard conditions which showed that mullite ($3Al_2O_3$·$2SiO_2$, 71·80 wt% Al_2O_3) was the only compound and that it melted incongruently at 1828°C with no solid solution range determined (Fig. 1). In 1950 and 1951, Bauer et al.[4,5] grew a single crystal of mullite containing about 83 wt% Al_2O_3 ($3Al_2O_3$–SiO_2) by the flame fusion process. These experiments raised doubts as to the reported incongruent melting of mullite.

In 1951, Toropov and Galakhov[6] heated mixtures of alumina gel and quartz; the mullite that formed melted congruently at about 1900°C. In

1954, Shears and Archibald[7] reported mullite with a solid solution range from $3Al_2O_3$·$2SiO_2$ to $2Al_2O_3$·SiO_2 (77·24 wt% Al_2O_3) which melted congruently at approximately 1810°C. In 1960, Welch[8] supported the proposed solid solution range and incongruent melting. In 1958, Trömel et al.[9] showed some data mostly in support of congruent melting behaviour. However, they also showed data generally indicating that in short time runs no corundum was obtained when it should have been found with incongruent melting, but that increasing the time caused the corundum to appear.

In 1962, Aramaki and Roy[10] showed mullite with a solid solution range of 71·8–74·3 wt% Al_2O_3 and a congruent melting point that was supported by the position of the α-Al_2O_3 liquidus (Fig. 1). They also determined that the solid solution range was extended to 77·3 wt% Al_2O_3 under metastable conditions which is not shown in the figure. They employed samples prepared from dry mixtures of reagent grade α-Al_2O_3 and powdered fused SiO_2 glass. The samples were held at temperature and quenched in mercury or water.

In 1972, Davis and Pask,[11] using semi-infinite diffusion couples of sapphire (α-Al_2O_3) and fused SiO_2 at temperatures up to 1750°C, determined the solid solution range of mullite as 71·0–74·0 wt% Al_2O_3. In 1975, Aksay and Pask[12] extended these experiments to higher temperatures and reported an α-Al_2O_3 liquidus profile (Fig. 2) that was similar to that of Bowen and Greig[2,3] with a peritectic at ~55 wt% Al_2O_3 which supported mullite as having an incongruent melting point. Single crystals of mullite were grown by the Czochralski technique in 1974 by Guse[13] and Guse and Mateika[14] of the 2:1 type instead of the 3:1 type obtained by the flame fusion process. In 1980, Shindo[15] also grew single crystals of the 2:1 type by the 'slow cooling float zone method' but showed incongruent melting.

In 1983, Prochazka and Klug[16] showed a solid solution range that shifted to higher Al_2O_3 contents with increase in temperature from 1600°C up
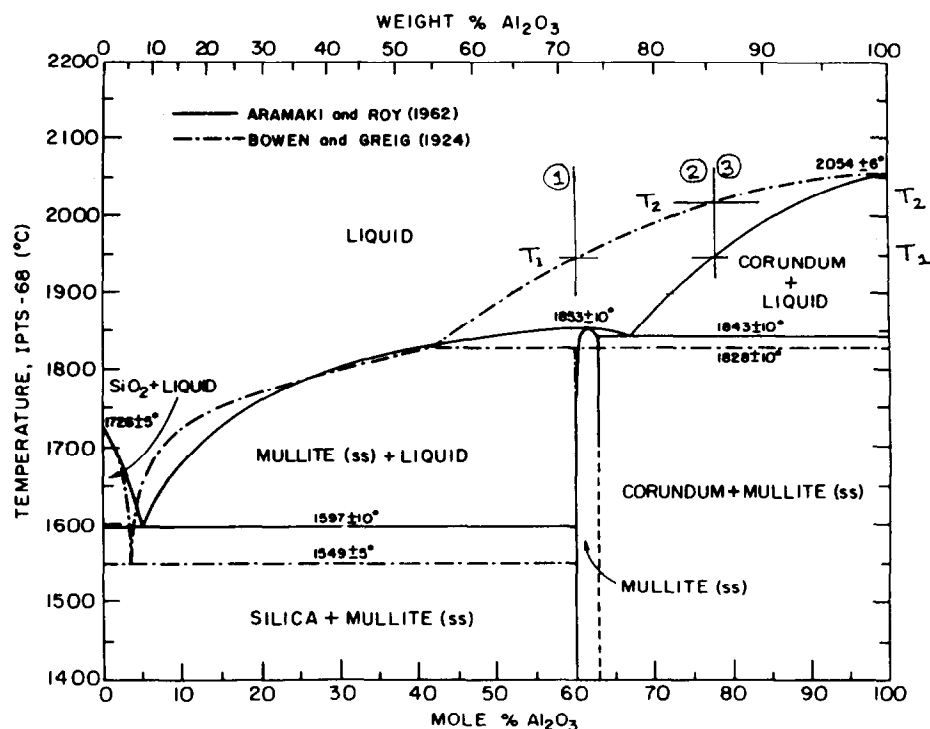
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Fig. 1. Superimposed SiO_2–Al_2O_3 phase equilibrium diagrams as determined by Bowen and Greig[2,3] and Aramaki and Roy.[10]

to about 1890°C, where the mullite reached the 2:1 composition (77·2 wt% Al_2O_3) and melted congruently since the peritectic composition had a slightly higher Al_2O_3 content. In 1987, Klug et al.[17] modified the diagram wherein the α-Al_2O_3 liquidus peritectic composition shifted to a slightly lower Al_2O_3 content than 77·2 wt% Al_2O_3 which technically indicated that the mullite melted incongruently. The latter diagram is included in Fig. 2. In both papers, homogeneous aluminosilicate powders produced by sol–gel processing from AlO(OH) and tetraethyl orthosilicate (TEOS) were used.
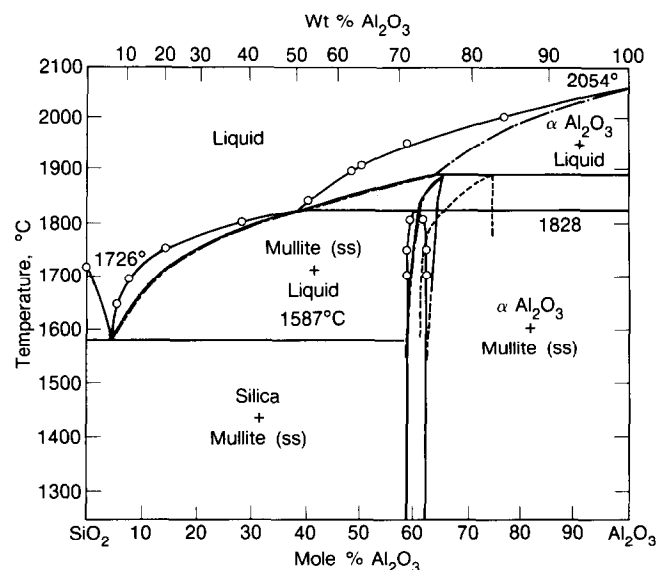

Fig. 2. Phase equilibrium diagrams by Klug et al.[17] (dot–dash line) and Aksay and Pask[12] (light solid line) superimposed. Nature of reported solid solution regions for mullite illustrated.

Many other studies on this system have been published. Sufficient experimental support is available for either opinion. It is thus not necessary to review them in detail. More extensive discussions of the phase equilibria are presented in several other review papers.[18–21] The diagrams shown in Figs 1 and 2 will suffice for further discussions.

2 Starting Materials

Various starting materials have been used to provide the Al_2O_3 and SiO_2 molecules for a desired composition. In the earlier studies Al_2O_3 was introduced primarily as α-Al_2O_3 powders of controlled particle size. It was mixed with fine ground fused SiO_2, quartz or cristobalite. A given mixture was normally heated above the liquidus temperature until it formed a homogeneous liquid phase, lowered to and held at the test temperature, and quenched. The homogenization step is critical since α-Al_2O_3 does not react rapidly because of the sluggishness of the liquid due to some covalency and high bond strength of α-Al_2O_3. On the other hand, if α-Al_2O_3 is melted completely, then nucleation and precipitation also may not occur easily on cooling especially when the aluminosilicate liquid does not become saturated with Al_2O_3 molecules. Kinetic problems then arise.

More recent studies utilized starting materials prepared chemically from alkoxides and sol–gels so that single-phase and diphasic gels were attained, i.e. no Al_2O_3 is introduced as α-Al_2O_3. Any segre-

gation or clustering of like atoms in single-phase gels could be critical since they can lead to nucleation and formation of colloidal particles, i.e. diphasic gel mixtures. Single-phase gels have also been called polymeric gels.[22,23] The basic objective of this approach is to attain or approach homogeneous mixing on an atomic or molecular basis. Sacks *et al.*[24] have reviewed the literature on the preparation of starting materials.
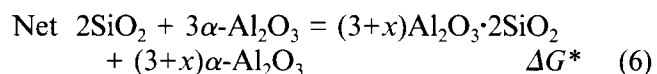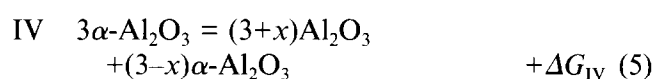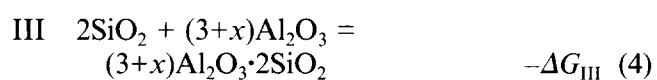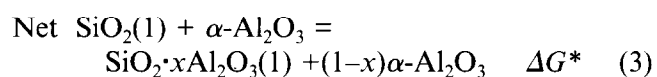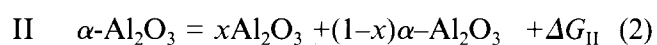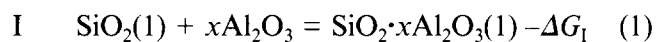
3 Mechanisms of Reactions

The critical factor in determining the nature of the solid-state reactions that occur in reaching equilibrium compositions at elevated temperatures in this system is the presence or absence of α-Al₂O₃ in the starting materials as a source of Al₂O₃ molecules. The α-Al₂O₃ particles react with SiO₂ at their interfaces to form mullite at temperatures below about 1828°C by interdiffusion of the cations through the forming mullite, which is a slow process. This kinetic effect could be counteracted in powder mixtures by reducing the particle size of α-Al₂O₃ and thereby increasing the overall rate by increasing the interfacial area. At temperatures above 1828°C mullite does not form, and α-Al₂O₃ is dissolved in the SiO₂ liquid to form aluminosilicate liquids. The most reactive precursors are those chemically prepared, wherein homogeneous atomic mixtures are formed in the absence of α-Al₂O₃ as a constituent. In this case the reaction rates are considerably faster.

Davis and Pask[11] developed the technique of using diffusion couples of sapphire single crystals and fused SiO₂ up to 1750°C to obtain kinetic data on mullite formation as well as equilibrium compositions. Aksay and Pask[12] extended the technique to higher temperatures. Analysis of polished cross-sections at a number of temperatures for Al and Si with an electron microprobe provided data for calculating concentration profiles for Al₂O₃ and SiO₂ and determining equilibrium compositions at the interfaces. It was determined that the reaction rates at the interfaces are faster than the diffusion rates away from them. The composition at a given temperature thus remained constant at a given interface and maintained equilibrium. Below about 1828°C and down to about 1634°C mullite grew at the α-Al₂O₃/SiO₂ interface and the resulting compositions at the liquid/mullite and mullite/α-Al₂O₃ interfaces were also at equilibrium. The fact that the Al₂O₃ content of about 55 wt% at the peritectic at 1828°C remains constant and is less than that of mullite theoretically indicates incongruent decomposition of mullite in the presence of α-Al₂O₃.

It is now necessary to determine the nature of the driving forces for the solid-state reactions occurring at the interfaces of the α-Al₂O₃/SiO₂ diffusion couples since they determine the composition of the α-Al₂O₃ liquidus. Experimental temperatures above 1828°C will be considered first. SiO₂ dissolves Al₂O₃. The driving force is the reduction of the internal free energy of the fused SiO₂ as Al₂O₃ molecules are incorporated into the liquid's atomic structure according to step I (Eqn (1)). The Al₂O₃ molecules are obtained by surface dissociation of crystalline Al₂O₃ by breaking bonds for which energy is required according to step II (Eqn (2)). The required energy is provided by the release of internal free energy by the siliceous liquid as it incorporates Al₂O₃ molecules into its structure. Summation of these step reactions above 1828°C results in the observed net reaction (Eqn (3)).

At experimental temperatures below 1828°C mullite forms at the interface. Energetically it appears more favourable to form mullite than to continue dissolving α-Al₂O₃, i.e. $\Delta G_{III} > \Delta G_{I}$ (Eqn (4) > Eqn (1)). ΔG_{III} is greater than ΔG_{IV} (Eqn (5)) which results in the net reaction (Eqn (6)) being negative and the determining occurrence of the reaction. If $\Delta G_{IV} > \Delta G_{III}$, then the net ΔG^* is positive and the reaction will not take place.

I $SiO_2(l) + xAl_2O_3 = SiO_2 \cdot xAl_2O_3(l) -\Delta G_I$ (1)

II $\alpha\text{-}Al_2O_3 = xAl_2O_3 +(1-x)\alpha\text{-}Al_2O_3 +\Delta G_{II}$ (2)

Net $SiO_2(l) + \alpha\text{-}Al_2O_3 =$
$SiO_2 \cdot xAl_2O_3(l) +(1-x)\alpha\text{-}Al_2O_3 \quad \Delta G^*$ (3)

III $2SiO_2 + (3+x)Al_2O_3 =$
$(3+x)Al_2O_3 \cdot 2SiO_2 \quad -\Delta G_{III}$ (4)

IV $3\alpha\text{-}Al_2O_3 = (3+x)Al_2O_3$
$+(3-x)\alpha\text{-}Al_2O_3 \quad +\Delta G_{IV}$ (5)

Net $2SiO_2 + 3\alpha\text{-}Al_2O_3 = (3+x)Al_2O_3 \cdot 2SiO_2$
$+ (3+x)\alpha\text{-}Al_2O_3 \quad \Delta G^*$ (6)

With the formation of mullite two interfaces have to be considered: liquid/mullite and mullite/α-Al₂O₃. In this case the α-Al₂O₃ atomic structure does not change with temperature but the SiO₂ content of the mullite decreases slightly at temperatures approaching dissociation. The bulk structures and compositions along the interfaces at a given temperature are at equilibrium as represented in Eqns (4), (5) and (6), and provide data for the phase equilibrium diagram.

The relative values for the free energies for the step reactions (1) plus (2) and (4) plus (5) determine the amount of solution and compositions. As the solution proceeds, ΔG_I and ΔG_{III} become

less negative until ΔG^* becomes zero in both cases with the establishment of equilibrium for the test temperature. With continuation of the reaction, when large quantities of the reactants are present, the equilibrium compositions are maintained at the interfaces because the reaction rates are faster than the diffusion rates. In an experimental study, the constancy of the compositions at the interface were verified.[11,12] It is evident that these reactions do not continue when one of the reactants is consumed.

It should be further evident that at these points the chemical potentials for Al_2O_3 and SiO_2 are equal in the silicate liquid and the mullite but neither phase is necessarily saturated with Al_2O_3 molecules. The limiting factor in these cases is established by the bond strength of the α-Al_2O_3 atomic structure, which determines the amount of energy necessary to dissociate an Al_2O_3 molecule (Eqns (2) and (5)). Thus, if another source of Al_2O_3 is used whose atomic bond strength is weaker, i.e. ΔG_{II} and ΔG_{IV} are smaller, then the aluminosilicate liquid could dissolve more Al_2O_3 molecules before equilibrium is reached or until the liquid structure itself becomes saturated with Al_2O_3 molecules. In such cases, the liquid is supersaturated relative to α-Al_2O_3, but it tends to retain the dissolved Al_2O_3 molecules in the absence of saturation and α-Al_2O_3 nuclei or particles.

In the reported studies, the maximum availability of Al_2O_3 molecules is provided by single-phase sol–gel mixtures wherein essentially atomic homogeneity is present in the absence of any clusters or colloidal assemblages. Compounds can form by rearrangement of atoms and molecules or by short-range diffusion. In the absence of strong α-Al_2O_3 bonds, more Al_2O_3 molecules can become available for the mullite composition which can vary within the solid solution range with temperature.

The alumina–silica system is subject to significant indications of metastability based on equally verified equilibria experiments. At present, because of lack of adequate thermodynamic data, it is difficult to unequivocally claim that one of the experimentally determined phase equilibria diagrams is stable and others are metastable. It is thus more logical to differentiate them on the basis of the nature of the critical starting materials. In this system that material is alumina. It has been shown that the nature of the most controversial equilibria are dependent on the presence or absence of α-Al_2O_3 as the starting material for a source of Al_2O_3 molecules. Thus, the diagrams can be differentiated on this basis. The earliest reported diagrams were derived with the use of fine-ground α-Al_2O_3 or forms of alumina, e.g. γ-Al_2O_3, that

readily converted to α-Al_2O_3 before they were completely reacted. Silica was added as fine-ground, fused or crystalline SiO_2. Later diagrams were determined with sol–gel or alkoxide type of starting materials. In these cases the objective was to introduce the Al_2O_3 molecules on the basis of a homogeneous atomic mixture.

In summary, the significance of the types of starting materials used is that the bond strengths of the different types are dependent on their atomic and electronic structures. α-Al_2O_3 has strong bonds requiring a relatively large amount of energy for release of Al_2O_3 molecules in comparison with the energy requirement for dissociation from a sol–gel type of starting material. Silica has a high degree of covalency which makes restructuring more difficult. Both states lead to difficulties affecting the kinetics of nucleation and precipitation of α-Al_2O_3. Another factor that leads to slow kinetics is the nature of the structure and bonding of aluminosilicate liquids, which at present are not completely understood.

An illustration of the above discussions can be made by use of Fig. 1. When the α-Al_2O_3/SiO_2 diffusion couple is held at 1950°C, the equilibrium liquid composition (about 72 wt% Al_2O_3) at the interface is indicated by pt. 1 which provides a point on the α-Al_2O_3 liquidus of Bowen and Greig's[2,3] diagram. Aramaki and Roy,[10] on the other hand, used dried mixtures of reagent-grade activated α-Al_2O_3 and powdered SiO_2 glass, homogenized them at temperatures above the 'high temperature liquidus' so that all of the α-Al_2O_3 particles were dissolved to form an aluminosilicate liquid, and lowered the temperature to the test temperature. They found that a composition equivalent to pt. 2 (about 86 wt% Al_2O_3) was in equilibrium with α-Al_2O_3 at 1950°C.

At this point it is important to consider, on the basis of basic principles, the general behaviour of aluminosilicate liquids with changes in composition and temperature at standard pressures. Mixtures of various condensed phases equivalent to aluminosilicate liquid compositions undergo complete melting on raising the temperature above the liquidus temperatures. The atomic and molecular homogeneity of the liquid, if not present, would be expected to increase with increase in temperature and/or time. With decrease in temperature some clustering would be expected. On dropping below the liquidus with saturation, nuclei formation would be started. Their type and rate of actual formation would be controlled by kinetic factors and their composition. On cooling liquids with more than 55 wt% Al_2O_3 too rapidly, α-Al_2O_3 nuclei may not form easily because the liquid is not saturated with Al_2O_3 molecules.

Dropping below the melting temperature of mullite, the liquid structure and composition are such that it becomes saturated with mullite which precipitates.

This behaviour can be illustrated by experiments with a series of starting mixtures with an increasing amount of Al_2O_3 from about 55 wt%.[25] The mixtures are first homogenized above the liquidus temperature and then cooled rapidly or quenched. Mixtures with increasing amounts of Al_2O_3 up to about 84 wt% do not easily nucleate α-Al_2O_3 and mullite is precipitated whose Al_2O_3 content is higher than that of the starting mixture, with which it converges at about 83 wt%. With still higher amounts of Al_2O_3 in the starting mixture, liquid becomes saturated with Al_2O_3 and the first precipitates are spherulites of α-Al_2O_3 followed by mullite with a lower Al_2O_3 content. The coprecipitates of mullite have about 77 wt% Al_2O_3, which corresponds to $2Al_2O_3 \cdot SiO_2$ mullite. These results indicate that at 1950°C the aluminosilicate liquids become saturated with Al_2O_3 at a total content of about 83 wt% Al_2O_3.

X-ray diffraction analyses of mullites by Kriven and Pask[26] showed that mullite with increasing amounts of Al_2O_3 up to about 77 wt% Al_2O_3 saturated the Si sites with Al atoms. Further increase of Al_2O_3 up to about 83 wt% resulted in the formation of a crystallographic superstructure superimposed on the mullite structure. These Al_2O_3 values for mullite supported the Al_2O_3 content of about 83 wt% for the single crystal grown by the flame fusion process,[4,5] and about 77 wt% for the crystal grown at a constant temperature by the Czochralski technique.[13,14]

The experimental variations in the Al_2O_3 content of mullite indicate that structures and bond strengths of the mullite are critically dependent on the reaction environment. Competition for Al_2O_3 molecules between the aluminosilicate structures and Al_2O_3 when present as part of the reacting mixture, as pointed out above, determines the composition variabilities that have been reported in the literature. Use of chemically-prepared starting mixtures to give more homogeneous atomic structures also introduces some variability because the atomic structure of the amorphous mixtures are expected to change with increasing temperature and changing conditions. The development of better homogeneity could result in increasing availability of Al_2O_3 molecules from the liquid structure. This behaviour would account for the increasing Al_2O_3 content of the mullite with temperature as seen in the diagram of Klug *et al.*[17] shown in Fig. 2. It is thus supported experimentally that the maximum content of Al_2O_3 in the mullite structure is about 77 wt%. In the presence

of α-Al_2O_3 at the time of mullite growth, however, the maximum amount is about 74 wt% because of the lesser availability of Al_2O_3 molecules. The mullites with Al_2O_3 contents above 77 wt% up to about 84 wt% appear only on quenching melts from above the liquidus temperature. The Al_2O_3 molecules in excess of the total available Si/Al atomic sites are accommodated by a crystallographic superstructure as pointed out by Kriven and Pask.[26] At about 84 wt% Al_2O_3 the aluminosilicate structure becomes saturated with Al_2O_3 molecules. Further additions cause the primary precipitation of Al_2O_3 spherulites on cooling.

3.1 Effect of rate of cooling

There have been several definitive experiments indicating the importance of kinetics in determining the nature of the phase equilibria with different cooling rates.[12] Three diffusion couples of sapphire/fused SiO_2 were heated together at 1900°C for 15 min. They were cooled together by turning off the furnace and directing the flow of a stream of He gas onto the assembly of sealed crucibles so that small differences existed in their rate of cooling.

Figure 3 shows polished cross-sections perpendicular to the interfaces of the three specimens, with the sapphire on the bottom of the photographs. The specimen in photo A, which was cooled the fastest, shows precipitates of mullite; the specimen in photo C, which was cooled the slowest, shows precipitates of Al_2O_3; and the photo B specimen, which was cooled at an intermediate rate, shows large mullite precipitates with small precipitates of Al_2O_3 in the glass phase between. Average diffusion profiles into the fused SiO_2 established at 1900°C were identical for all three specimens with an overall composition of 63 wt% Al_2O_3 in the aluminosilicate at the interfaces. This composition liquid was in equilibrium with Al_2O_3 but its structure was not saturated with Al_2O_3 molecules as previously described. In photo C, the cooling rate was slow enough so that α-Al_2O_3 nuclei formed at the interface, leading to the formation of elongated α-Al_2O_3 crystals. In photo A, with a faster cooling rate, sufficient time for rearrangement and assembly to form α-Al_2O_3 nuclei and crystals was not available before the temperature was reached at which the liquid was saturated with mullite, leading to the nucleation and growth of the elongated mullite crystals. This behaviour supports the concept that α-Al_2O_3 does not nucleate easily unless the aluminosilicate atomic structure becomes saturated with Al_2O_3 molecules.

3.2 Mullite peritectic reaction

Another significant experiment is one that showed

Fig. 3. Microstructures of diffusion zones in couples of sapphire (bottom) and fused silica annealed at 1900°C for 15 min and (A) quenched, (B) cooled at a relatively moderate rate and (C) cooled relatively slowly. Precipitates in diffusion zone in (A) are mullite (light grey), in (B) alumina (light grey needles) and mullite (fine precipitates between alumina needles) and in (C) alumina (light grey needles; precipitates along interface in (B) and (C) are also alumina).

the formation of mullite by a peritectic reaction.[12] A mixture containing 71·8 wt% Al_2O_3 was homogenized in a sealed Mo crucible at 1950°C for 460 min, cooled to 1750°C in 30 min, annealed at 1750°C for 29·4 days, and quenched. A polished cross-section is shown in Fig. 4. The light grey crystals are α-Al_2O_3 surrounded by medium grey growths of mullite, with a dark grey aluminosilicate glass between the mullite growths. The concentration profiles across the mullite growths correspond to those obtained in α-Al_2O_3/SiO_2 diffusion couples at 1750°C. The reactions at the interface are fast and maintain equilibrium compositions for 1750°C at the interfaces. The overall reaction is slow because the rate-determining step is interdiffusion through the forming mullite, which is slow.

The formation of α-Al_2O_3 crystals which participate in the formation of mullite in a melt of this composition clearly indicates that mullite melts incongruently. If mullite had formed directly from the melt and thus melted congruently, then it would have been impossible to form as a stable phase under the above conditions. It could also be pointed out that if Bowen and Greig,[2,3] using α-Al_2O_3 particles as part of their starting materials, did not completely dissolve it into their starting mixture and performed experiments at about 70 wt% Al_2O_3 and temperatures of about 1900°C, α-Al_2O_3 could not have persisted under these conditions if mullite melted congruently. Concentration profile discontinuities across the phase

boundaries provide very accurate information about the stable composition range of the phase fields.

Fig. 4. Microstructure of specimen containing 71·8 wt.% Al_2O_3 held at 1950°C for 7·7 h, cooled to 1750°C in 30 min, annealed at 1750°C for 29·4 days, and quenched to room temperature. Light grey precipitates are alumina completely surrounded by layer of mullite. Dark grey portions between mullite layers are glass containing precipitates of mullite formed on quenching. The microstructure formed during the heating schedule indicates a peritectic reaction.

4 Summary and Conclusions

A critical study of the mechanisms and kinetics of the solid-state chemical reactions that take place with different starting materials provides an explanation for the differences that have been reported in the high alumina region of the phase equilibria diagrams for the Al_2O_3–SiO_2 system. Since the equilibria are formed by reactions, the bond strengths, atomic structures and free energies of the participating phases are critical. The nature of the reactions and their driving forces are the principal factors. Both the source of Al_2O_3 molecules and the nature of the aluminosilicate liquid structures are important in this system.

The Al_2O_3 sources have been either as α-Al_2O_3 particles or chemically-prepared sol–gel aluminosilicates or alkoxides. The α-Al_2O_3 has a high negative free energy of formation. Thus, the energy necessary to break its bonds to provide Al_2O_3 molecules is relatively high. This energy is provided by the aluminosilicate liquid since its free energy is lowered by incorporating Al_2O_3 molecules into its atomic structure. A thermodynamic balance is reached when the free energy change for the overall reaction becomes zero and the chemical potentials for each of the components are equal in both participants at the reacting interface. The source of the phase equilibria differences is the fact that, at this point, equilibria are reached because of insufficient energy to make more Al_2O_3 molecules available. The aluminosilicate liquid at this point, thus, does not become saturated with Al_2O_3 molecules.

In the case of the sol–gel source of Al_2O_3, the bond strengths are weaker and Al_2O_3 molecules are more readily available. Thus, the aluminosilicate liquid becomes saturated, or near-saturated, with Al_2O_3 molecules. The additional significance of this fact is that in intermediate Al_2O_3 compositions the liquid can be saturated with Al_2O_3 but supersaturated with respect to α-Al_2O_3. Because of this situation and the high covalency of its bonding, nucleation and growth of α-Al_2O_3 are sluggish in the aluminosilicate liquids.

Consequently, there are two phase equilibria diagrams for the Al_2O_3–SiO_2 system. The controlling factor is whether α-Al_2O_3 is present or absent throughout the reactions leading to the steady or equilibrium state. In the presence of α-Al_2O_3, the peritectic composition is 55 wt% Al_2O_3, mullite corresponds to the 3:2 type and melts incongruently at 1828°C. Its solid solution range remains essentially constant with temperature. In the absence of α-Al_2O_3, mullite corresponds to the 2:1 type and melts congruently at 1890°C; its solid solution range increases in Al_2O_3 up to 77 wt%

Al_2O_3 but would be expected to vary with the nature of the chemically-prepared source of Al_2O_3. The 3:1 type of mullite is only formed on quenching homogenized aluminosilicate liquids from above the high temperature α-Al_2O_3 liquidus. This behaviour is the basis of a third phase equilibrium diagram for the Al_2O_3–SiO_2 system which has not been extensively studied.

Aramaki and Roy[27] also performed experiments with ternary mixtures composed of additions of MgO or CaO to Al_2O_3 and SiO_2. These were used to support the arguments that mullite melted congruently on the basis of the position of the boundary between the primary fields of mullite and α-Al_2O_3 in the corresponding ternary phase equilibrium diagrams. However, since the starting materials were first completely homogenized above the liquidi temperatures, the equilibrium phase compositions were obtained in the absence of α-Al_2O_3 as a starting material.

In summary, the controlling factor in determining the nature of the phase equilibrium diagram for the Al_2O_3–SiO_2 system is the presence or absence of α-Al_2O_3 during the reactions leading to stable or metastable equilibrium. In the presence of α-Al_2O_3, the higher temperature α-Al_2O_3 liquidus represents an atomic structure thermodynamically in equilibrium with α-Al_2O_3 but not saturated with Al_2O_3 molecules. In the absence of α-Al_2O_3 as a source of Al_2O_3 molecules, the lower temperature α-Al_2O_3 liquidus represents an atomic structure that is saturated with Al_2O_3 molecules. On cooling, α-Al_2O_3 nucleates and precipitates from liquids when they become saturated with Al_2O_3 molecules. The region between the two liquidi represents liquid structures that are supersaturated with respect to α-Al_2O_3. In order to further differentiate the two conditions, the phase equilibrium diagram derived in the presence of α-Al_2O_3 as one of the starting materials could be identified as the α-Al_2O_3–SiO_2 system; and in the absence of α-Al_2O_3, the phase equilibrium diagram could be identified as the Al_2O_3–SiO_2 system.

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