Stable and Metastable Equilibria in the System SiO₂-Al₂O₃

I. A. AKSAF* and J. A. PASK*

Inorganic Materials Research Division, Lawrence Berkeley Laboratory and Department of Materials Science and Engineering, College of Engineering, University of California, Berkeley, California 94720

Concentration profiles of Al₂O₃ in diffusion couples made from sapphire and fused silica were used to determine the stable equilibrium phase diagram of the system SiO₂-Al₂O₃. The intermediate compound mullite, 3Al₂O₃·2SiO₂, melts incongruently at 1828°C ± 10°C; its stable solid-solution range regions from 70.5 to 74.0 wt% Al₂O₃ below 1753°C and from 71.6 to 74.0 wt% at 1813°C. The microstructures of diffusion zones and heat-treated specimens also indicate the incongruence of mullite. Additional information is given for 3 metastable systems: SiO₂-Al₂O₃ in the absence of mullite, SiO₂-"ordered"-mullite in the absence of alumina, and SiO₂-"disordered"-mullite in the absence of alumina. Under metastable conditions, ordered mullite melts congruently at ~1800°C and its solid-solution range extends up to ~77 wt% Al₂O₃. The solid-solution range of disordered mullite extends to ~83 wt% Al₂O₃ with an estimated congruent melting temperature of ~1900°C. The existence of metastable systems is associated with superheating of mullite above the incongruent melting temperature and with nucleation of alumina and mullite in supercooled aluminum-silicate liquids.

I. Introduction

The first systematic phase equilibrium study in the SiO₂-Al₂O₃ system showed mullite (3Al₂O₃·2SiO₂) as the only stable compound of this system and reported that it melted incongruently at 1828°C. Since then, numerous conflicting investigations have been conducted. The findings of Trocmel et al. generally agree with those in Ref. 1; Aramaki and Roy, however, indicate a congruent melting point for mullite. Mullite phase equilibria have been the subject of several reviews.

The solid-solution range of mullite has been reported to extend from 71.8 to 74.3 wt% Al₂O₃. This range, however, is realized only when mullite is prepared by solid-state reactions in the presence of alumina. The composition of mullite solidified from a melt may extend up to 82.6 wt% Al₂O₃, thus raising the question of Al₂O₃ in the melts was below the microprobe detection limit.

Most phase-equilibrium studies on the system SiO₂-Al₂O₃ have been conducted by either the static method of quenching or by differential thermal analysis. These techniques, especially in silicate systems with an incongruent melting compound, can lead to misinterpretation because of nucleation and growth problems. In a diffusion study by Davis and Pask semi-infinite couples of SiO₂ and Al₂O₃ and the electron microprobe were used for determining composition profiles; this technique was effective for obtaining stable and metastable phase-equilibrium data. The objectives of the present study (which used the same technique) were to determine (1) the phase equilibria of mullite above 1800°C and, thus, its stable melting behavior, and (2) the solid-solution range of mullite. Experiments using the static method of quenching provided additional data on stable and metastable equilibrium conditions. Diffusion-kinetics data obtained in the present experiments will be presented elsewhere.

II. Experimental Procedure

Much of the present experimental technique has been described by Davis and Pask and, unless otherwise specified, the same materials and equipment were used.

1. Diffusion-Couple Experiments

Diffusion couples were prepared with sapphire and fused silica or sapphire and aluminum-silicate glasses of 10.9, 22.8, and 42.2 wt% Al₂O₃. These binary glasses are in equilibrium with mullite at 1678°C, 1753°C, and 1813°C. Thus, sapphire-glass diffusion couples of these compositions at the corresponding annealing temperatures could be used to study the growth kinetics of mullite as an intermediate phase without solution of mullite in the liquid phase.

The diffusion cell consisted of Mo or Al₂O₃ crucibles containing a fused-silica or aluminum-silicate glass disk on a sapphire substrate. The runs at 1678°C were done in air with covered alumina crucibles. All anneals above 1700°C were done in a Ta resistance furnace with Mo crucibles which were sealed around the lid by electron-beam welding and He leak-checked in order to eliminate SiO₂ losses by evaporation during annealing. The amount of Mo in the melts was below the microprobe detection limit.

The diffusion anneals ranged from 15 min to one month, depending on the length desired for the diffusion zone. The temperature of the Ta chamber was monitored and electronically controlled using a W5Re—W26Re thermocouple (accuracy ±7°C at 1800°C). The specimen temperature, however, was measured separately using 2 optical pyrometers (accuracy ±10% at 2000°C) which were focused on a blackbody cavity placed atop the crucibles. The pyrometers were frequently calibrated against an NBS secondary standard pyrometer and at the melting point of Pt (1772°C) and Al₂O₃ (2054°C). The pyrometers themselves were frequently checked against each other to detect any malfunction. All temperatures reported herein are based on the 1968 International Practical Temperature Scale (IPTS-68).

The diffusion anneals were completed by rapidly cooling the furnaces down in 1500°C (~1 min) in order to "freeze-in" the diffusion profile by preventing long-range diffusion. Continued cooling to room temperature, however, was very slow (6 days) to avoid loss of integrity at the interface as a result of the difference in thermal expansion. Couples were subsequently sectioned in halves parallel to the direction of diffusion, mounted in polyester resin, and polished.

2. Phase Equilibrium Studies by Quenching

Quench experiments were performed to supplement diffusion experiments. Fused-SiO₂ and α-Al₂O₃ mixtures of 42.2, 60.0, 71.8, and 80.0 wt% Al₂O₃ were melted at 1953°C to 2003°C for 15 to 30 min. The composition of a representative section was analyzed by electron microprobe. Crucibles were then sealed and heat-treated in the Ta furnace in the range 1753°C to 1953°C after a homogenization treatment above the corresponding liquidus temperature. Specimens were cooled by turning off the furnace and allowing He to flow rapidly through it. Microscopic examination of a 78.3-wt% Al₂O₃ specimen showed that the mullite grains were surrounded by a continuous glassy phase.

3. Electron Microprobe Analysis

All the measurements were made with an accelerating voltage of 15 kV and a specimen current of 0.03 μA. The diameter of the electron beam was 1 μm, although the volume affected by it was probably in the order of 5 to 10 μm³. Two spectrometers recorded the intensities of the AlKa and SiKa peaks simultaneously. Concentration profiles were obtained by traversing the electron beam

*Member, the American Ceramic Society.

**Now with Department of Metallurgical Engineering, Middle East Technical University, Ankara, Turkey.

(1) Diffusion-Couple Experiments

Diffusion couples were prepared with sapphire and fused silica or sapphire and aluminum-silicate glasses of 10.9, 22.8, and 42.2 wt% Al₂O₃. These binary glasses are in equilibrium with mullite at

1678°C, 1753°C, and 1813°C. Thus, sapphire-glass diffusion couples of these compositions at the corresponding annealing temperatures could be used to study the growth kinetics of mullite as an intermediate phase without solution of mullite in the liquid phase.

The diffusion cell consisted of Mo or Al₂O₃ crucibles containing a fused-silica or aluminum-silicate glass disk on a sapphire substrate. The runs at 1678°C were done in air with covered alumina crucibles. All anneals above 1700°C were done in a Ta resistance furnace with Mo crucibles which were sealed around the lid by electron-beam welding and He leak-checked in order to eliminate SiO₂ losses by evaporation during annealing. The amount of Mo in the melts was below the microprobe detection limit.

The diffusion anneals ranged from 15 min to one month, depending on the length desired for the diffusion zone. The temperature of the Ta chamber was monitored and electronically controlled using a W5Re—W26Re thermocouple (accuracy ±7°C at 1800°C). The specimen temperature, however, was measured separately using 2 optical pyrometers (accuracy ±10% at 2000°C) which were focused on a blackbody cavity placed atop the crucibles. The pyrometers were frequently calibrated against an NBS secondary standard pyrometer and at the melting point of Pt (1772°C) and Al₂O₃ (2054°C). The pyrometers themselves were frequently checked against each other to detect any malfunction. All temperatures reported herein are based on the 1968 International Practical Temperature Scale (IPTS-68).

The diffusion anneals were completed by rapidly cooling the furnaces down in 1500°C (~1 min) in order to "freeze-in" the diffusion profile by preventing long-range diffusion. Continued cooling to room temperature, however, was very slow (~6 days) to avoid loss of integrity at the interface as a result of the difference in thermal expansion. Couples were subsequently sectioned in halves parallel to the direction of diffusion, mounted in polyester resin, and polished.

(2) Phase Equilibrium Studies by Quenching

Quench experiments were performed to supplement diffusion experiments. Fused-SiO₂ and α-Al₂O₃ mixtures of 42.2, 60.0, 71.8, and 80.0 wt% Al₂O₃ were melted at 1953°C to 2003°C for 15 to 30 min. The composition of a representative section was analyzed by electron microprobe. Crucibles were then sealed and heat-treated in the Ta furnace in the range 1753°C to 1953°C after a homogenization treatment above the corresponding liquidus temperature. Specimens were cooled by turning off the furnace and allowing He to flow rapidly through it. Microscopic examination of a 78.3-wt% Al₂O₃ specimen showed that the mullite grains were surrounded by a continuous glassy phase.

(3) Electron Microprobe Analysis

All the measurements were made with an accelerating voltage of 15 kV and a specimen current of 0.03 μA. The diameter of the electron beam was 1 μm, although the volume affected by it was probably in the order of 5 to 10 μm³. Two spectrometers recorded the intensities of the AlKa and SiKa peaks simultaneously. Concentration profiles were obtained by traversing the electron beam

Presented at the 75th Annual Meeting, The American Ceramic Society, Cincinnati, OH, May 1, 1973 (Basic Science Division, No. 45-B-73). Received July 20, 1974; revised copy received July 14, 1975.


*Member, the American Ceramic Society.

**Now with Department of Metallurgical Engineering, Middle East Technical University, Ankara, Turkey.

(1) Commercial-grade fused cast aluminum-silicate, Carbonadorum Corp., Niagara Falls, NY. Wet chemical analysis performed by Coors Spectro Chemical Laboratory, Golden, CO. Spectrographic analysis (American Spectrographic Laboratory, San Francisco, CA) showed (in wt% as oxides) 0.12 Na, 0.02 Fe, 0.01 Mg, 0.01 Zr, 0.006 Ca, 0.005 Ti, 0.003 Cr, <0.005 Cu, and <0.001 Mn.
along a desired path perpendicular to the diffusion-couple interfaces. Because alumina and/or mullite generally crystallize in the liquid portion of the sapphire-fused-silica diffusion couples during cooling, concentration profiles obtained by the point-beam technique were extremely difficult to analyze. A scanning electron microprobe. Because alumina and/or mullite generally crystallize in the liquid portion of the sapphire-fused-silica diffusion couples during cooling, concentration profiles obtained by the point-beam technique were extremely difficult to analyze. A scanning electron microprobe. Because alumina and/or mullite generally crystallize in the liquid portion of the sapphire-fused-silica diffusion couples during cooling, concentration profiles obtained by the point-beam technique were extremely difficult to analyze. A scanning electron microprobe. Because alumina and/or mullite generally crystallize in the liquid portion of the sapphire-fused-silica diffusion couples during cooling, concentration profiles obtained by the point-beam technique were extremely difficult to analyze. A scanning electron microprobe.

Table I. Experimental Conditions and Data for Sapphire-Fused-Silica Runs

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Time (min)</th>
<th>C*</th>
<th>Al2O3 content (wt%)</th>
<th>Mullite thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1803</td>
<td>60, 240, 360, 480, 10,035</td>
<td>29.0</td>
<td>40.9</td>
<td></td>
</tr>
<tr>
<td>1903</td>
<td>15, 30, 60, 120, 1095, 1525</td>
<td>40.9</td>
<td>54.0</td>
<td></td>
</tr>
<tr>
<td>1913</td>
<td>15, 30</td>
<td>49.6</td>
<td>62.5</td>
<td></td>
</tr>
<tr>
<td>1953</td>
<td>15</td>
<td>51.2</td>
<td>64.0</td>
<td></td>
</tr>
<tr>
<td>2003</td>
<td>15</td>
<td>59.6</td>
<td>71.5</td>
<td></td>
</tr>
</tbody>
</table>

*Interfacial composition of the melt; see Fig. 1. †From Ref. 11.

III. Results and Discussion

(A) Diffusion Profiles and Phase Equilibria

The experimental conditions of the diffusion couples annealed in the range 1803° to 2003°C are outlined in Table I. At least 2 or 3 specimen runs were made at each set of annealing conditions. The interfacial compositions remained constant with time at a given temperature, indicating that diffusion in the liquid phase was slower than the intrinsic dissolution rate of sapphire. This fact was further verified by ascertaining that, at a given temperature, the distance from the original (Boltzmann-Matano) interface for a given concentration is directly proportional to the square root of time. Although no time studies were performed at 1953° and 2003°C, it was assumed that diffusion in the liquid phase was still the rate-controlling step at these temperatures. Thus the average interfacial compositions listed in Table I correspond to liquidus compositions. No Si was detected in the sapphire substrate by electron microprobe.

When the fused-silica portions of the couples described in Section II(1) were replaced by melts with compositions corresponding to the mullite liquidus, an intermediate mullite layer could be grown to a thickness (>10 µm) suitable for electron microprobe analysis. The results of these runs in the temperature range of 1678° to 1813°C are outlined in Table II. The thickness of the mullite layer increased linearly with the square root of time, indicating that the growth mechanism is diffusion-controlled. The interfacial compositions of the mullite layer obtained from these profiles, then, correspond to the equilibrium limits of the mullite solid solution range.

Mullite growth at the diffusion couple interfaces was observed in specimens annealed at 1803° and 1813°C but not at 1853°C (Section III(2)), indicating that mullite became stable at some temperature below 1853°C. Thus, C* values in Tables I and II correspond to the liquidus of Al2O3 at 1853°C whereas those at and above 1813°C correspond to the liquidus of mullite.

Table II. Experimental Conditions and Data for Sapphire-Equilibrium-Melt Runs

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Time (min)</th>
<th>C*</th>
<th>Al2O3 content (wt%)</th>
<th>Mullite thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1678</td>
<td>12,182</td>
<td>10.9</td>
<td>70.5–74.0</td>
<td>10</td>
</tr>
<tr>
<td>1678</td>
<td>47,380</td>
<td>10.9</td>
<td>70.5–74.0</td>
<td>18</td>
</tr>
<tr>
<td>1753</td>
<td>6,608</td>
<td>22.8</td>
<td>70.5–74.0</td>
<td>13</td>
</tr>
<tr>
<td>1813</td>
<td>10,025</td>
<td>42.2</td>
<td>71.6–74.0</td>
<td>36</td>
</tr>
</tbody>
</table>

*Interfacial compositions; see Fig. 1.

(B) Stable Phase Equilibria: The interfacial compositions listed in Tables I and II, data reported on the mullite liquidus, the melting temperatures of cristobalite, and corundum, and the cristobalite-mullite eutectic temperature were used to construct the SiO2-Al2O3 stable phase diagram in Fig. 1. The most important feature of this diagram is that, under stable equilibrium conditions, mullite melts incongruently, the liquid compositions in equilibrium with sapphire at 1853°C to 2003°C being the critical supporting evidence. The incongruent melting temperature (determined as 1828 ± 10°C from the intersection of the extrapolated liquidus lines of mullite and alumina) and the position of these liquidus are essentially identical to the results of Bowen and Greig.

(2) Diffusion-Zone Microstructures

Typical diffusion-zone microstructures of the sapphire-fused-silica couples annealed at 1803° and 1853°C are shown in Fig. 2. Extensive crystallization of prismatic mullite in the melt portion of these and other couples occurred during cooling. The alumina content of these grains (determined by electron microprobe analysis) varied between 73 and 79 wt% Al2O3. In contrast, the stable mullite solid-solution range (determined from mullite grown at sapphire interfaces) varied from 70.5 to 74.0 wt% Al2O3 below 175°C and from 71.6 to 74.0 wt% Al2O3 at 1813°C (Fig. 1).

Based on the kinetic data of mullite growth, if the stable mullite solid-solution field extended up to 1853°C, a growth layer 5.3 µm thick with a composition gradient across it would have been observed at the sapphire interface of the couple shown in Fig. 2(B). The essentially continuous mullite layer observed at the interface of
this couple, however, has a constant composition throughout which is identical to the precipitates in the adjoining diffusion zone. Furthermore, the prismatic morphology of the mullite layer is similar to that of the precipitates and differs from that of the layer grown at 1803°C (Fig. 2(A)), whose composition differs distinctly from that of the precipitates. The composition of the 1803°C layer varies from 71.1 wt% Al₂O₃ at the mullite-liquid interface to 74.0 wt% Al₂O₃ at the mullite-alumina interface. In addition, the appearance of the alumina interfaces in both couples is different. Thus, all the mullite observed in the diffusion zone at 1853°C formed during cooling, with nucleation occurring at the sapphire interface.

Since the liquid composition in the diffusion zone adjacent to the sapphire at 1853°C has 54.0 wt% Al₂O₃ (Fig. 1) and becomes oversaturated with alumina just below 1853°C, alumina should precipitate under equilibrium conditions. Below 1828°C precipitated alumina would then be completely resorbed by reacting with the liquid to form a mixture of mullite and liquid. The realization of such an equilibrium is rare, especially in silicates, since the crystal phase to be resorbed becomes unavailable for a direct reaction because of incrustation, i.e., a mullite layer forms around the alumina. However, a metastable mullite could also form if the liquid is sufficiently supercooled and no Al₂O₃ precipitation occurs. The absence of Al₂O₃ in the rapidly cooled diffusion zone thus indicates that such supercooling occurred.

Direct evidence for the importance of the rate of supercooling in the diffusion zone was established in 3 diffusion couples which were annealed together at 1903°C for 15 min but cooled at relatively different rates as a result of the directional flow of He into the hot zone during quenching. Their microstructures differed drastically (Fig. 3) although the average diffusion profile in each case was identical, with a range of 0 to 62.5 wt% Al₂O₃. The precipitated crystalline phase, as determined by electron microprobe and X-ray diffraction, was only mullite when the couple was quenched (Fig. 3(A)), only alumina when the couple was cooled relatively slowly (Fig. 3(C)), and alumina and mullite when cooled at a moderate rate (Fig. 3(B)). In all cases, the matrix was a high-silica glass. Since the liquidus composition at the peritectic temperature is 52.3 wt% Al₂O₃, the diffusion zone adjacent to the sapphire would have experienced some alumina precipitation under equilibrium cooling. The absence of alumina in this portion of the diffusion zone of a quenched couple (Fig. 3(A)) and the presence of alumina in a slowly cooled couple (Fig. 3(C)) can be explained only by considering nucleation and supercooling phenomena in the liquid. The coexistence of alumina, mullite, and liquid (glass) in the diffusion zone of the couple cooled at a moderate rate (Fig. 3(B)) is in violation of the phase rule. In this case, after some equilibrium precipitation of alumina, the remaining liquid did not maintain equilibrium with alumina and behaved independently with the precipitation of mullite.

Davis and Pask,¹¹ who observed the formation of an interfacial nonequilibrium liquid in cristobalite-sapphire couples at subsolidus temperatures, suggested the existence of an SiO₂-Al₂O₃ metastable phase diagram with a eutectic and no mullite, which was represented by extensions of the SiO₂ and Al₂O₃ liquidus curves. The diffusion-zone microstructure shown in Fig. 3(C) further supports their observations since the absence of mullite indicates a cooling rate sufficiently slow to maintain equilibrium between the liquid and alumina, resulting in the metastable extension of the alumina liquidus below the peritectic temperature.

Diffusion-zone microstructures of 1953°C and 2003°C couples showed only alumina precipitates in a high-silica glassy matrix within the high-alumina (> 50 wt% Al₂O₃) portion of the diffusion zones even when they were quenched at the fastest rate experimentally possible. The sapphire substrate acted as a site for heterogeneous nucleation of alumina. Mullite precipitates, however, were always present at the low-alumina end of the zones.
(3) Microstructures of Quenched Mixtures

At the outset of a quenching experiment, the mixtures of \( \alpha \)-\( \text{Al}_2\text{O}_3 \) and fused \( \text{SiO}_2 \) were, unless otherwise stated, homogenized above the corresponding alumina liquidus temperature. Within the present homogenization periods, the fact that the crystalline phases completely dissolved in the melt was established by an X-radiographic technique.\(^2\) When a mixture containing 60.0 wt% \( \text{Al}_2\text{O}_3 \) was homogenized at 1953°C and cooled slowly (~60 min) below the peritectic temperature before quenching, its microstructure showed mullite and glass. In comparison, a melt of similar composition (62.5 wt% \( \text{Al}_2\text{O}_3 \)) in the diffusion zone adjacent to the sapphire (Fig. 3) had only precipitates of mullite when quenched; slower cooling rates resulted in precipitates of alumina. This difference in behavior can be attributed to the presence of sapphire in the diffusion couple, which acted as a site for heterogeneous nucleation of alumina for the more slowly cooled specimens.

Alumina, mullite, and glass were found in a mixture containing 71.8 wt% \( \text{Al}_2\text{O}_3 \) (corresponding to 3\( \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \)) which had been annealed at 1953°C, cooled slowly (~30 min) to 1753°C, annealed further for ~29 days, and quenched (Fig. 4). The presence of alumina clearly indicates the incongruency of mullite; alumina could not be present under any circumstances if mullite solidified congruently from a melt. The presence of mullite around the alumina also indicates that the peritectic reaction was incomplete because diffusion through the mullite layer was slow. The diffusion mechanism is indicated by the presence of concentration profiles through the mullite layers ranging from 74 wt% \( \text{Al}_2\text{O}_3 \) at the alumina interfaces to 70.5 wt% \( \text{Al}_2\text{O}_3 \) at the glass interfaces (Fig. 1). However, when this mixture was homogenized at 2003°C and rapidly cooled to 1753°C, the fact that, in the absence of sapphire nucleation sites, the microstructure showed no alumina precipitates could easily be misinterpreted as being indicative of the congruency of mullite.

Typical microstructures of the silicate mixtures of 78.3 and 80.0 wt% \( \text{Al}_2\text{O}_3 \) were homogenized at 2003°C (Fig. 5); the degree of mullite and/or alumina precipitation in these melts was highly dependent on the cooling rate. A quench by turning off the power and rapid introduction of He into the furnace always resulted in mullite with compositions varying up to 83.2 wt% \( \text{Al}_2\text{O}_3 \) and some residual high-silica glass (Fig. 5(A)). Occasional precipitation of alumina was observed around the crucibles' sharp edges, which must have acted as nucleation sites. When the melts were moderately cooled by just turning off the power to the furnace, alumina precipitated readily (Fig. 5(B)). The intermediate liquid phase apparently did not maintain equilibrium with the precipitated alumina and cooled independently to form mullite and residual...
glass. When the melts were cooled slowly to 1753°C and quenched, only precipitates of alumina were present (Fig. 5(C)). The needles in the glassy matrix were only a few microns thick and thus were too small for electron microprobe analysis; X-ray diffraction analysis of such specimen surfaces, however, indicated α-Al₂O₃ as the only crystalline phase. The overall composition of the matrix surrounding the primary alumina precipitates, as determined by scanning-beam electron microprobe analysis, was ≈48 wt% Al₂O₃. This composition is identical to that of the alumina liquidus at 1753°C when it is extended below the peritectic temperature (Fig. 1) and provides additional evidence for the existence of a metastable SiO₂-Al₂O₃ binary without any mullite phase.

(4) Melting Behavior and Composition of Mullite

The melting behavior of mullite was studied using polycrystalline stoichiometric 3:2 mullite⁹ (71.8 wt% Al₂O₃) specimens.⁹ They were placed in Mo crucibles and heated in vacuum. Temperature was measured using blackbody conditions with a hole drilled directly into the specimen. Heating to 1800°C was rapid (5 to 10 min) followed by a 5°C/min heating rate to maintain thermal equilibrium. The temperature of complete liquidation was assumed to be that at the first instant of specimen slumping. Some specimens were only partially melted before quenching.

The melting temperature was consistently 1880°C. The same melting temperature was determined independently by Maddiyasni and Brown³ using an identical material and similar experimental conditions. This value is considerably higher than the peritectic melting temperature of 1828°C, as determined from the diffusion studies (Fig. 1). Furthermore, the microstructure of the completely molten portion showed only recrystallized mullite and some glass. No alumina formed because of nucleation difficulties. Thus, when superheated, stoichiometric mullite behaved as a congruently melting compound.

According to the stable phase diagram (Fig. 1), a mullite of 71.8 wt% Al₂O₃ becomes unstable at 1816°C and dissociates to a mixture of a silica-rich liquid phase and to a higher-alumina mullite above 1816°C. The nonslumped portion of the specimens after heating to a blackbody temperature of 1880°C showed a mixture of glass and mullite grains (≈5 to 10 µm) whose composition was consistently 75.8 wt% Al₂O₃, as determined by point-beam microprobe analysis.

Incongruently melting silicates can be superheated above the peritectic temperature and are represented by the metastable prolongation of the corresponding liquidus and solidus.⁸ The extension of the stable mullite liquidus of Fig. 1 intersects the 71.8 wt% Al₂O₃ line at ≈1875°C, which closely corresponds to the present complete liquidation temperature. Such metastable congruent melting of mullite necessitates higher alumina contents in the recrystallized mullite and thus provides an explanation for the measured shift to 75.8 wt% Al₂O₃. Also, since liquid is present, the indifferent point of the metastable extensions has to be higher than 75.8 wt%.

The phase relations developed thus far do not provide an explanation for the higher alumina contents in the mullite (≈73 to 79 wt% Al₂O₃) precipitated from the liquid phase. Under stable equilibrium conditions the mullite composition in contact with liquid should contain 70.5 to 72 wt% Al₂O₃ (Fig. 1). A possible explanation could be the formation, under these conditions, of a "disordered" mullite phase with a broader shifted alumina solid-solution range.

Aramaki and Roy⁹ observed that heat treatment of mullite prepared by quenching caused almost as much variation in its lattice parameters as in its composition and suggested Al-Si order-disorder as a possible explanation. Later, similar observations were made by Mazdiyasni and Brown³ and Majumdar and Welch.⁴ Previous studies⁵ strongly support the existence of such a disordered mullite phase, frequently referred to as 2:1 or melt-mullite. The upper limit of the disordered-mullite solid-solution range is uncertain but has been set at 83.2 wt% Al₂O₃ since this was the highest alumina content detected in any mullite. This limit agrees well with the compositions of mullite single crystals grown from a melt by Bauer et al.⁷ (82.57 wt% Al₂O₃), by Neuhaus and Richartz⁸ (77.5 wt% Al₂O₃), and by Guse and Mateika⁹ (77.3 wt% Al₂O₃). Temperatures as high as 1913°C have been associated with the melting behavior of 2:1 mullite⁴; an average of the reported values is ≈1900°C.

(5) Metastable Phase Equilibria

Based on the above information, the possibility of the existence of ordered and disordered mullites with metastable congruence necessitates two overlapping mullite solid-solution fields that exist in the absence of alumina. Metastable phase equilibrium diagrams are formed by each mullite with SiO₂, as shown in Fig. 1.

The phase diagram for SiO₂--ordered-mullite in the absence of alumina shows an extension of the stable mullite liquidus and solidus, the indifferent point of the extensions being ≈77 wt% Al₂O₃. The SiO₂--disordered-mullite diagram in the absence of alumina indicates a mullite solid-solution range of ≈73 to ≈83...
w1% Al2O3. (The values that were used to position the disordered mullite liquidus were taken from the diagram of Aramaki and Roy.) MacDowell and Beall22 observed evidence for metastable liquid immiscibility in the system SiO2-Al2O3 and outlined an immiscibility and a possible spinodal region as shown in Fig. 1. Takamori and Roy23 have questioned the existence and especially the location of this immiscibility region on the grounds that inadequate data existed to locate it. The present results similarly cast doubt on the location of the spinodal region as proposed by MacDowell and Beall since the extension of the alumina liquidus cuts through the center of this region. However, the extension of the alumina liquidus as shown in Fig. 1 directly intersects the center of the proposed immiscibility region, in violation of this rule. Any proposed spinodal region must then be either completely under or outside the extension of the alumina liquidus.

VI. Summary

Diffusion-couple experiments in the system SiO2-Al2O3 yielded information on stable and several metastable phase equilibria. Mullite, under stable equilibrium conditions, was shown to melt incongruently at 1828 ± 10°C, as originally determined by Bowen and Greig.1 The measured stable solid-solution range of mullite in the presence of alumina was 70.5 to 74.0 wt% Al2O3 below 1753°C and 71.6 to 74.0 wt% Al2O3 at 1813°C.

Diffusion-zone microstructures and microstructures of specimens heat-treated by the static method of quenching indicated the incongruity of mullite as well as the existence of metastable equilibria. The congruent melting of mullite during superheating in the absence of alumina indicates the existence of an SiO2-ordered-mullite metastable phase diagram. The precipitation of disordered mullite from melts indicates the existence of an SiO2-disordered-mullite metastable phase diagram in the absence of alumina, with a broader and shifted solid-solution range of mullite. Direct evidence was also provided for the existence of an SiO2-Al2O3 metastable binary without any mullite phase, as represented by the extensions of the silica and alumina liquidus curves to form a eutectic.

Metastable phase equilibria result from various difficulties associated with nucleation of phases. When a melt is supercooled into an alumina primary phase region, alumina nucleates less readily as the silica content of the melt increases (with the consequent precipitation of disordered mullite) and sapphire provides a heterogeneous nucleation site, allowing alumina to precipitate more readily. Mullite grown at temperature by a solid-state reaction appears to form a eutectic.

Acknowledgments: The writers thank George J. Georgakopoulous for assistance in electron beam microprobe analysis, Vicenf Daven and Thomas Gardner for technical assistance, and Robert F. Davis for valuable discussions.

References

14 I. A. Akasy and J. A. Pask, "Diffusion in Mullite (3Al2O3. 2SiO2)", for abstract see ibid.
19 Z. Frazier, R. W. Fitzgerald, and A. M. Reid, "Computer Programs EMX and EMM2 for Electron Microprobe Data Processing," Scripps Institute of Oceanography, University of California at San Diego, La Jolla, Calif.; unpublished work.