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PHASE EQUILIBRIA AND TRANSFORMATIONS IN THE

ALUMINA-SILICA SYSTEM

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ABSTRACT

Concentration profiles of Al in diffusion couples made from sapphire and fused silica were used to determine the stable equilibrium phase diagram of the system SiO_2-Al_2O_3. Stable or ordered mullite of the $3Al_2O_3 \cdot 2SiO_2$ type melts incongruently at $1828° \pm 10°C$; its solid-solution region ranges from 70.5 to 74.0 wt% Al_2O_3 below $1753°C$ and from 71.6 to 74.0 wt% at $1813°C$; and under metastable conditions it melts congruently at $\approx 1880°C$ and its solid-solution range extends up to ≈ 77 wt% Al_2O_3. Metastable or disordered mullite of the $2Al_2O_3 \cdot SiO_2$ type is formed by precipitation from the melt on cooling; its solid-solution range extends to ≈ 83 wt% Al_2O_3 with an estimated congruent melting temperature of $\approx 1900°C$. Information is given for 3 metastable systems: SiO_2-3:2 mullite in the absence of α-Al_2O_3, SiO_2-2:1 mullite in the absence of α-Al_2O_3, and SiO_2-Al_2O_3 in the absence of mullite. The existence of metastable systems is associated with superheating mullite and supercooling aluminum-silicate liquids because of difficulties of α-Al_2O_3 nucleation, and with nucleation of 3:2 mullite.

I. Introduction

Since the SiO_2-Al_2O_3 phase equilibrium system is one of the most important systems in ceramics, primarily in the more traditional fields of refractories and whitewares, it would be expected that its relationships would be completely known and agreed upon. Such agreement existed on the presence of one stable compound (mullite with the stoichiometric composition of $3Al_2O_3 \cdot 2SiO_2$) under normal pressure conditions. Disagreements, however, were reported in regard to three questions: a) whether mullite has a congruent or incongruent melting point, b) the extent of its solid solution range, and c) whether two types of mullite occurred under certain conditions which would at least partially account for the observed variability of the mullite solid solution range.

The first systematic phase equilibrium study[1] which showed that mullite was the only stable compound with composition of $3Al_2O_3 \cdot 2SiO_2$ also showed that it melted incongruently at 1828°C (Fig. 1.). Since then numerous conflicting investigations have been reported and have been the subject of several reviews.[2] Figure 1 also shows the diagram that has been most widely accepted, presented by Aramaki and Roy[3], which indicates that mullite has a congruent melting point and a solid solution range of 71.8 to ≈74.3 wt% Al_2O_3. They also reported that mullite solidified from a melt had a higher alumina content which raised the question of metastability and the possible existence of a disordered form of mullite with the nominal composition of $2Al_2O_3 \cdot SiO_2$, sometimes referred to as the 2:1 type in contrast to the ordered or 3:2 type.

Most phase-equilibrium studies on the SiO_2-Al_2O_3 system have been conducted by either the static method of quenching[4] or by differential

thermal analysis. These techniques, especially in silicate systems with an incongruently melting compound, can lead to misinterpretation because of nucleation and growth problems.[5,6]

The objective of this paper is to show that the conflicting results in the literature have resulted primarily because of the unrecognized difficulty of the nucleation of α-Al_2O_3 from alumino-silicate melts containing up to $\approx$83 wt% Al_2O_3 on cooling and from mullite on heating, i.e. the melts could be easily supercooled and the mullite could be easily superheated. The significance of the supercooling and superheating phenomena is that the resulting phase transformations lead to metastable phase transformation relationships or metastable phase equilibrium diagrams, features of which have been confused with stable phase relationships. Taking these factors into account in the interpretation of currently obtained results, stable and metastable phase equilibrium diagrams within the SiO_2-Al_2O_3 system are presented.

II. Experimental Procedure

A diffusion couple technique has been the principle method for studying the stable phase equilibria in our laboratory. This technique was first described by Davis as part of his Ph.D. studies.[7] It was then used by Aksay in his Ph.D. studies which led to the principal features[8] to be presented and discussed in this paper. The studies which have been continued by Risbud[9] who is completing his Ph.D. research have contributed details to the metastable phase relationships and to the position of the metastable liquid immiscibility gap. Other features are being pursued by Draper[10] who is completing his M.S. studies. Quenching experiments were also used to obtain specific data on metastability.

The diffusion cells consisted of fused-silica or alumino-silicate glass disks on a sapphire substrate, both having a dia. of ~0.9 mm, which were placed in a Mo crucible and heated in a Ta resistance furnace. The Mo crucibles had a Mo lid that was sealed on by electron-beam welding and He leak-checked in order to eliminate SiO_2 losses by evaporation during heating. 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 temperature and on the length desired for the diffusion zone. On cooling the couples were sectioned in halves parallel to the direction of diffusion, mounted in polyester resin, and polished for microscopic examination and electron microprobe analysis. All the microprobe measurements were made with an accelerating voltage of 15 kV and a specimen current of $0.03\mu A$. The diameter of the electron beam was $1\mu m$,

although the volume affected by it was probably in the order of 5 to

$10\mu m^3$.[11]   Concentration profiles were obtained by traversing the electron

beam along a desired path perpendicular to the diffusion-couple inter-

faces. 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 technique[7] provided

average compositions at any distance from an interface over an area con-

taining localized crystallization.

   Quench experiments were performed to supplement diffusion

experiments. Mixtures of fused-silica and $\alpha-Al_2O_3$ powders were sealed

in Mo crucibles as before. After heat treatment and cooling, the

crucibles were cut in half and polished for microscopic examination and

electron microprobe analysis. Sections were ground for X-ray diffrac-

tion analysis.

III. Results and Discussion

(1) Stable Phase Equilibria

(A) Diffusion Couples

Diffusion anneals at a number of temperatures in the range of 1550° to 2003°C provided information for the stable equilibrium phase diagram. Mullite growth at the diffusion couple interfaces was observed in specimens annealed at 1813°C and lower but not at 1853°C and higher. The diffusion-zone microstructures of couples annealed at 1803° and 1853°C shown in Fig. 2 are typical. The extensive crystallization of prismatic mullite seen 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% Al_2O_3 with the higher values in the grains closer to the interface; these values, however, were higher than that of the mullite grown at the interface at 1803°C which shows a gradient from 71.1 wt% Al_2O_3 at the mullite-liquid interface to 74.0 wt% Al_2O_3 at the mullite-alumina interface. The mullite observed at the interface of the 1853°C couple, on the other hand, has a constant composition throughout which is identical to the precipitates in the adjoining diffusion zone. Furthermore, the prismatic morphology of the mullite at the interface is similar to that of the precipitates in the diffusion zone and differs from that of the layer grown at 1803°C. Thus, all the mullite observed in the diffusion zone at 1853°C formed during cooling, with nucleation occurring at the sapphire interface.

Concentration diffusion profiles were obtained by the scanning technique because of the crystallization that occurs in the diffusion zone during cooling which involves short-range diffusion. An average

composition at a certain distance from the interface of the couple was obtained by rapidly scanning the electron beam parallel to the interface over a range from 40 to 150µm depending on the size of the crystals in the diffusion zone. When the standards are also analyzed by the same method, inaccuracies introduced by the decreased X-ray intensity as the beam deviates from the center of the cross hairs are eliminated. The profiles were then obtained by traversing the electron beam at fixed intervals (0.5 to 10µm) along a desired path perpendicular to the diffusion couple interface. Typical computer plotted diffusion profiles for several temperatures and times expressed as concentration of Al ions vs. distance are shown in Fig. 3. 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. Thus the average liquid interfacial composition at a given temperature corresponds to the mullite or alumina liquidus composition for that temperature depending on whether a mullite layer was present at the interface or not.

Normally, in a semi-infinite diffusion couple the growth of the mullite layer is retarded because of the competing process of dissolution of the mullite by the liquid. When the fused-silica portions of the couples were replaced by melts with compositions corresponding to the mullite liquidus for several temperatures, intermediate mullite

layers were grown to a thickness (>10µm) suitable for electron microprobe analysis. Cross-sections of runs made at 1678°, 1753° and 1813°C are shown in Fig. 4. The thickness of the mullite layers 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 stable mullite solid solution region.

The interfacial compositions at the liquid-mullite, liquid-alumina and mullite-alumina interfaces, the melting temperatures of cristobalite[12] and corundum,[13] and the critobalite-mullite eutectic temperature[14] were used to construct the $SiO_2-Al_2O_3$ stable phase equilibrium diagram shown in solid lines in Fig. 5. The most important feature of this diagram is provided by the liquid compositions in equilibrium with sapphire at 1853° to 2003°C; these indicate that under stable equilibrium conditions mullite must melt incongruently. 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 liquidi are essentially identical to the results of Bowen and Greig[1] as seen in Fig. 1.

(B) Reaction Experiments

The lack of alumina in the diffusion zone adjacent to the sapphire at 1853°C (Fig. 2) indicates that supercooling of the liquid has occurred. It can be seen from Fig. 5 that this liquid has 54 wt% Al_2O_3 and becomes oversaturated with alumina just below 1853° which should precipitate under equilibrium conditions. Below 1828°C precipitated alumina would then be completely resorbed by reacting with the liquid to

form mullite. 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,[5] i.e. a mullite layer forms around the alumina, and continued reaction is dependent upon slow chemical interdiffusion through the mullite layer. However, a metastable mullite could also form if the liquid is sufficiently supercooled and no Al_2O_3 precipitation occurs. The absence of Al_2O_3 in the rapidly cooled diffusion zone and presence of mullite with the higher alumina content 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 of the furnace during quenching. Their microstructures differed drastically (Fig. 6) although the average diffusion profile in each case was identical, with 62.5 wt% Al_2O_3 at the interface. The precipitated crystalline phase, as determined by electron microprobe and X-ray diffraction, was only mullite in the couple cooled the most rapidly (Fig. 6A), only alumina in the couple cooled relatively slowly (Fig 6C), and alumina and mullite in the couple cooled at an intermediate rate (Fig. 6B). Equilibrium precipitation of alumina occurred in Fig. 6C which was cooled at a sufficiently slow rate; couple in Fig. 6A was cooled sufficiently rapidly to result in supercooling and precipitation of metastable mullite as in Fig. 2; and in Fig. 6B, after some equilibrium precipitation of alumina, the remaining liquid did not maintain equilibrium with alumina and behaved independently with the precipitation

of mullite.

Direct evidence for the difficulty of nucleating alumina out of a melt was provided by heating 3 mixtures of alumina and fused silica powders, each of which contained 60 wt% Al_2O_3.[9] The difference was in the size of the alumina particles: fine, medium and coarse. The mixtures were sealed in Mo crucibles, heated at 1725°C for 20 h, and then at 1855°C for 4 h. After quenching, X-ray diffraction showed mullite in the 3 specimens and alumina only in the one prepared with coarse alumina powder. The time at 1855°C was sufficiently long to dissolve all the alumina particles[7] which would be unstable if mullite had a congruent melting point as seen in Fig. 1. The presence of alumina indicated that the reaction to form mullite was not complete at 1750°C and that the alumina was stable at 1855°C according to the phase diagram with an incongruent melting point for mullite (Fig. 5). The absence of alumina in the first two mixtures indicated that the reaction to form mullite and liquid at 1725°C was complete and that mullite was superheated to melting without the nucleation of alumina, resulting in a metastable condition. Lack of awareness of the difficulty of nucleating alumina out of superheated liquid and mullite could lead to the incorrect interpretation of the indicated experiment as evidence in support of an equilibrium phase diagram with mullite having a stable congruent melting point.

Alumina, mullite, and glass were found in a mixture containing 71.8 wt% Al_2O_3 (corresponding to $3Al_2O_3 \cdot 2SiO_2$) which had been annealed at 1950°C(just below the liquidus), cooled slowly (≈30 min) to 1753°C, annealed further for ≈29 days, and quenched (Fig. 7). 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% Al_2O_3 at the alumina interfaces to 70.5 wt% Al_2O_3 at the glass interfaces (Fig. 5). 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 again easily be misinterpreted as being indicative of the congruency of mullite.

The reaction experiments described in this section support the stable equilibrium phase diagram shown as solid lines in Fig. 5.

(2) Metastable Phase Equilibria

    (A) Silica-3:2 Mullite System

    The melting behavior of mullite was studied using polycrystalline stoichiometric 3:2 mullite[15] (71.8 wt% Al_2O_3) specimens.* They were placed in Mo crucibles and heated in vacuum. Temperature was measured using blackbody conditions with a hole drilled directly into the specimen. The melting temperature was consistently 1880°C. This value is considerably higher than the peritectic temperature of 1828°C, as determined from the diffusion studies (Fig. 5). Furthermore, the microstructure of the molten portions showed only recrystallized metastable mullite and some glass. No alumina formed because of nucleation difficulties. Thus, when superheated, stoichiometric mullite behaved as a

*Provided by K. S. Mazdiyasni, Air Force Materials Laboratory, Wright Patterson Air Force Base, Ohio.

congruently melting compound.

Incongruently melting silicates can be superheated above the peritectic temperature and are represented by the metastable prolongation of the corresponding liquidus and solidus.[6] A metastable equilibrium phase diagram for silica-3:2 mullite (referred to as ordered[3]) in the absence of crystalline alumina can then be indicated by an extension of the stable mullite liquidus and solidus, the indifferent point of the extensions being $\approx$77 wt% Al_2O_3 (Fig. 5), indicating a maximum solid solution range of $\approx$71 to $\approx$77 wt% Al_2O_3.

The upper limit agrees well with the compositions of mullite single crystals grown from the melt at a constant temperature by the Czochralski method by Neuhaus and Richartz[16] (77.5 wt % Al_2O_3) and by Guse and Mateika[17] (77.3 wt % Al_2O_3) in the absence of alumina nucleation.

(B) Silica-2:1 Mullite System

Aramaki and Roy[3] observed that heat treatment of mullite obtained by precipitation from a quenched melt caused almost as much variation in its lattice parameters as in its composition and suggested Al-Si order-disorder as a possible explanation. Previous studies[2] strongly support the existence of such a disordered or metastable mullite phase which is frequently referred to as 2:1 or melt-mullite. The upper limit of the 2:1 mullite solid-solution range has been set at $\approx$83 wt% Al_2O_3 since this was the highest alumina content detected in any mullite. Subsequently, Draper[10] verified this value by preparing a series of powder mixtures with the alumina content increasing up to 87 wt% Al_2O_3, sealed them in Mo crucibles, annealed them at 2050°C, and then quenched them. An examination by X-ray diffraction indicated α-Al_2O_3 only in

the specimens with more than 83 wt% Al_2O_3.

Mullite precipitating from a melt on quenching always shows a higher alumina content than $\approx$71wt% of the 3:2 type in equilibrium with the melt, including the mullite precipitating in the diffusion zones as indicated earlier. This mullite is then considered to be the metastable 2:1 type. On heat treatment such specimens tend to exsolve alumina and approach the composition of $\approx$73 wt% Al_2O_3 in the presence of liquid.

A metastable equilibrium phase diagram for silica-2:1 mullite in the absence of crystalline alumina can be indicated by a diagram similar to the one for the silica-3:2 mullite but using values for the disordered mullite liquidus taken from the diagram of Aramaki and Roy,[3] and the metastable mullite solid solution range of $\approx$73 to $\approx$83 wt% Al_2O_3.

The upper limit agrees well with the composition of mullite single crystals formed by solidification from a melted spray using the flame-fusion method as reported by Bauer et al.[18]

(C) Silica-Alumina System in the Absence of Mullite

Davis and Pask[7] observed the formation of an interfacial nonequilibrium liquid in cristobalite-sapphire couples at subsolidus temperatures as a precursor to the formation of mullite and suggested the existence of a silica-alumina metastable phase equilibrium diagram with a eutectic and no mullite, which was represented by extensions of the stable silica and alumina liquidus curves. Risbud[9] has determined the eutectic temperature to be 1270°C on the basis of sintering experiments. The diffusion-zone microstructure shown in Fig. 6(c) supports the extension of the alumina liquidus below the peritectic temperature; the absence of mullite indicates a cooling rate sufficiently slow to

maintain equilibrium between the liquid and alumina. This metastable equilibrium phase diagram is included in Fig. 5.

(D) Metastable Liquid Immiscibility

Risbud[9] has made thermodynamic calculations that outlined an immiscibility and a possible spinodal region as shown in Fig. 5. This spinodal region is similar to that proposed by MacDowell and Beall[19] but at a lower convolute temperature. The proposed region is compatible with the positions of the liquidi of the phase diagram.

IV. Conclusions

Diffusion couple experiments in the SiO_2-Al_2O_3 system yielded information on stable and metastable phase equilibria. Stable, ordered or 3:2 mullite is formed by growth at temperature and melts incongruently at 1828°±10°C as originally determined by Bowen and Greig.[1] On heating, it can be easily superheated because of difficulties of nucleating α-Al_2O_3 and shows a metastable congruent melting temperature of ≈1880°C. 3:2 mullite can also be superheated in the presence of a liquid phase if Al_2O_3 nuclei are not present.

Melts with alumina contents up to ≈83 wt% Al_2O_3 can be easily supercooled and precipitate mullite and no alumina on cooling. This mullite is referred to as metastable, disordered or 2:1 type and is always higher in alumina content. In the presence of a liquid phase this mullite tends to exsolve alumina until it reaches an equilibrium content of ≈73 wt% Al_2O_3. Difficulties of distinguishing between the 3:2 and 2:1 types of mullite are increased because their solid solution ranges overlap.

The extensive metastability relationships in the system arise primarily because of the difficulty of nucleating α-Al_2O_3 both from the liquid phase and from mullite resulting in commonly occurring supercooling and superheating, respectively. However, under conditions of equilibrium cooling of a melt with α-Al_2O_3, mullite precipitation also may not occur in the absence of mullite nuclei.

ACKNOWLEDGMENTS

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Figure Captions

Fig. 1. SiO_2-Al_2O_3 phase equilibrium diagrams as determined by Bowen and Greig[1] and by Aramaki and Roy.[3]

Fig. 2.   The relationship between the concentration profile of a semi-infinite SiO_2-Al_2O_3 diffusion couple and the phase diagram, at temperature T above the melting point of mullite. Boltzmann-Matano interface corresponds to the phase boundary at t = o.[45-46]

Fig. 3.   Typical computer plotted concentration profiles of sapphire-fused silica couples in the temperature range of 1803° to 2003°C arranged with a common Boltzmann-Matano or original interface. The 1803°C profile has a mullite layer which is not evident in the profile because its thickness is only ≈10μm.

Fig. 4.   Interference-contrast micrographs of the diffusion zone between a couple of sapphire and (A) 10.9 wt% Al_2O_3 containing silicate at 1678°C for 12,182 min, (B) 22.8 wt% Al_2O_3 containing silicate at 1753°C for 6,608 min, and (C) 42.2 wt% Al_2O_3 containing silicate at 1813°C for 10,025 min. The prismatic precipitates in the top portion of the diffusion zone in the silicate are mullite that crystallized during cooling.

Fig. 5.   Stable SiO_2-Al_2O_3 equilibrium phase diagram is shown by <u>solid lines</u>. Superimposed on the stable equilibrium diagram are possible metastable phase diagrams for SiO_2- "ordered" or 3:2 type mullite and SiO_2- "disordered" or 2:1 type mullite systems in the absence of crystalline Al_2O_3. Data points for disordered mullite liquidus are from diagram of Ref. 3.
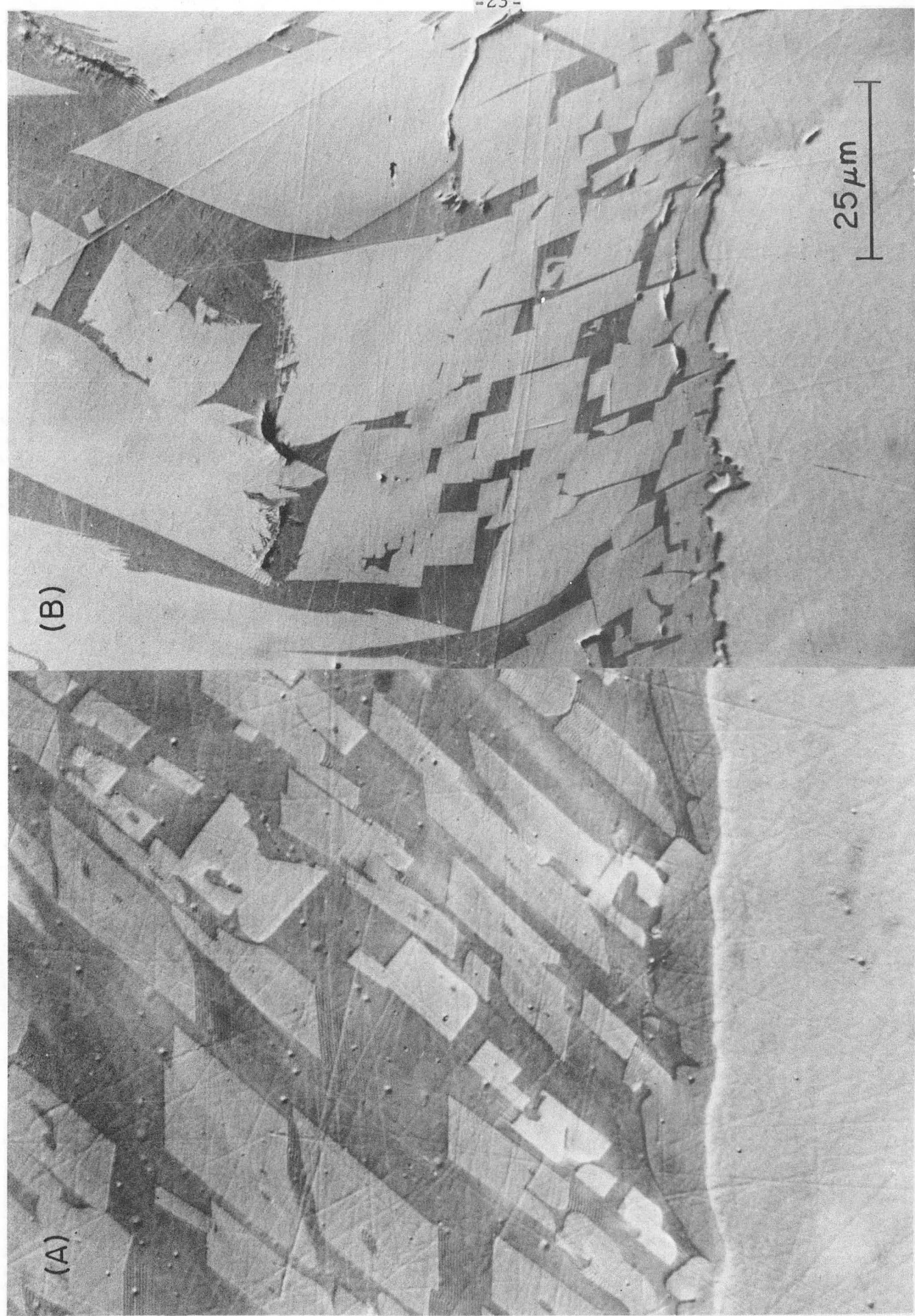
Metastable phase diagram for SiO_2-Al_2O_3 in the absence of mullite by extension of silica and alumina liquidus curves is also shown.[9] Immiscibility region was thermodynamically calculated.[9]

Fig. 6. Microstructures of diffusion zones in couples of sapphire (bottom) and fused silica annealed at 1903°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 gray), in (B) alumina (light gray needles) and mullite (fine precipitates between alumina needles), and in (C) alumina (light gray needles); precipitates along interface in (B) and (C) are also alumina.

Fig. 7. Microstructure of 71.8 wt%-Al_2O_3-containing silicate melted in sealed Mo crucible at 1953°C for 460 min, cooled to 1753°C in 30 min, annealed at 1753°C for 42,392 min (29.4 days), and quenched from 1753°C to room temperature. Light gray precipitates are alumina completely surrounded by layer of mullite (gray). Dark gray portions between mullite layers are glass containing fine precipitates of mullite formed on quenching.
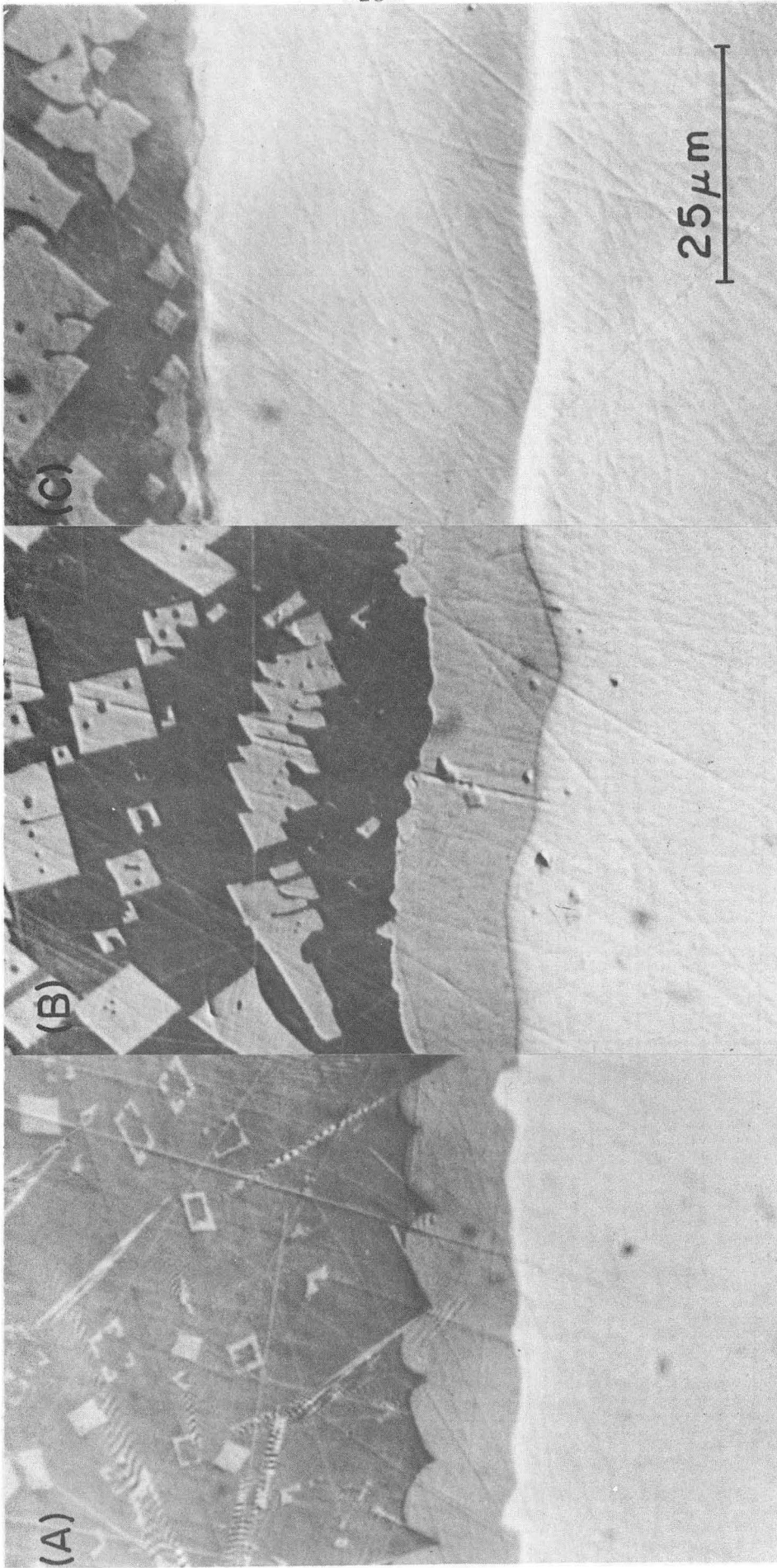
WEIGHT % Al_2O_3

MULLITE (ss) + LIQUID

ARAMAKI and ROY (1962)

BOWEN and GREIG (1924)

LIQUID

$2054 \pm 6°$

CORUNDUM
+
LIQUID

$1853 \pm 10°$

$1843 \pm 10°$

$1828 \pm 10°$

$SiO_2 + LIQUID$

$1726 \pm 5°$

MULLITE (ss) + LIQUID

CORUNDUM + MULLITE (ss)

$1597 \pm 10°$

$1549 \pm 5°$

MULLITE (ss)

SILICA + MULLITE (ss)

TEMPERATURE, IPTS-68 (°C)

MOLE % Al_2O_3

XBL 7210-7078 A
Fig. 1

-22-

(B)

(A)

25 μm

XBL 7210-7070

Fig. 3

25 μm

XBL 766-7008

Fig. 5

25μm

XBB7210-5188
Fig. 7