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STABLE AND METASTABLE EQUILIBRIA IN THE SiO_2-Al_2O_3 SYSTEM

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ABSTRACT

The concentration profiles of semi-infinite diffusion couples between sapphire and fused silica were used to determine the stable equilibrium phase diagram of the SiO_2-Al_2O_3 system. The intermediate compound mullite, $3Al_2O_3 \cdot 2SiO_2$, was shown to melt incongruently at 1828° ±10°C, and its stable solid solution region ranged from 70.5 to 74.0 wt% Al_2O_3 below 1753°C and from 71.8 to 74.0 wt% at 1813°C. The microstructures of the diffusion zones and of specimens heat treated by the static method of quenching supported the incongruency of mullite. These microstructural studies, combined with electron beam microprobe analysis, also provided additional information on the existence of metastable systems: (i) SiO_2-Al_2O_3 in the absence of mullite, (ii) SiO_2-ordered mullite in the absence of alumina, and (iii) SiO_2-disordered mullite in

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in the absence of alumina. Mullite, under metastable conditions, was shown to melt congruently at ≈1880° ±10°C with its solid solution range extending up to 75.8 wt% Al_2O_3. The solid solution range of disordered mullite extended to 83.2 wt% Al_2O_3 with a proposed melting temperature of ≈1900°C. The existence of metastable systems is associated with the superheating of mullite above the incongruent melting temperature and with problems related to nucleation of alumina and mullite in supercooled aluminum silicate liquids.

I. INTRODUCTION

The first systematic phase equilibrium study in the SiO_2-Al_2O_3 system was conducted in 1924 by Bowen and Greig[1] who showed that mullite ($3Al_2O_3 \cdot 2SiO_2$) was the only stable compound of this system and that it melted incongruently at 1828°C. Since then, numerous conflicting investigations[2-5] have been conducted. Among these, the studies by Trömel et al.[3] and Aramaki and Roy[5] were the most extensive and representative. The findings of Trömel et al., in general, are in agreement with those of Bowen and Greig. On the other hand, Aramaki and Roy indicate a congruent melting point for mullite. Mullite studies have been the subject matter of several reviews.[6]

Another problem of the SiO_2-Al_2O_3 system is the extent of the solid solution range of mullite. It has been reported to extend from 71.8 wt% to ∿74.3 wt% Al_2O_3.[5] This range, however, is only realized when mullite is prepared by solid state reactions in the presence of alumina. When solidified from a melt, the composition of mullite may extend up to 82.6 wt% Al_2O_3,[7] raising the question of metastability and the possible existence of a disordered form of mullite with a nominal composition of $2Al_2O_3 \cdot SiO_2$.[5]

Most phase equilibrium studies on the SiO_2-Al_2O_3 system have been conducted either by the static method of quenching[8] or by differential thermal analysis (DTA). These techniques, especially in silicate systems with an incongruently melting compound, can lead to misinterpretation due to nucleation and growth problems.[9,10]

In a recent diffusion study utilizing semi-infinite couples of silica and alumina and the electron microprobe for determining composition

profiles, Davis and Pask[11] demonstrated the usefulness of this technique for obtaining stable and metastable phase equilibrium data. These studies, however, were made in the temperature range of 1552° to 1803°C, which is below the melting point of mullite.

The objectives of the present study were to utilize the diffusion couple technique to determine (1) the phase equilibria above 1800°C and thus the nature of the stable melting behavior of mullite and (2) the solid solution range of mullite. Experiments by the static method of quenching were also carried out which provided additional data on stable and metastable equilibrium conditions. The data on the diffusion kinetics obtained by the same experiments will be presented elsewhere.[12,13]

II. EXPERIMENTAL WORK

A. Diffusion Couple Experiments

(1) Sapphire-Fused Silica Couples

Sapphire-fused silica couples were used to determine the Al_2O_3 and mullite liquidi. The couples were prepared from single crystals (8.7 mm in diameter by 1.6 mm) of Al_2O_3 (sapphire)* and fused silica† disks (9 mm in diameter by ∿7 mm). The sapphire single crystals were cut with the c-axis oriented ∿30° from the vertical and had an as-received surface finish of ∿0.27 μm. The fused silica disks were subjected to a standard

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*Union Carbide Corp., Torrance, Calif., Spectrographic analysis by American Spectrographic Labs., San Francisco, Calif.: as oxides (wt%) Si 0.210, Na 0.050, Sn 0.005, B 0.005, Fe 0.004, Ba 0.001, Ca 0.001, Ti 0.001, Mg 0.0005, Cu 0.0005.

†Amersil, Division of Engelhard Industries, Inc., Hillside, N.J. Spectrographic analysis by American Spectrographic Labs., San Francisco, Calif.: as oxides (wt%) Al 0.045, Fe 0.015, Mg 0.0007, Ca 0.0005, Cu 0.0005.

ceramographic polishing on one surface.

(2) Sapphire-Mullite-Liquid Couples

Aluminum-silicate glasses of 10.9, 22.8, and 42.2 wt% Al_2O_3 were prepared using powders of Alcoa XA-16* reactive α-Al_2O_3 and -325 mesh Corning 7940 fused silica.† The powders were mixed in isopropyl alcohol, calcined at 1000°C for 10 h, vacuum melted in open molybdenum crucibles at 1900°C for 30 to 60 min and quenched in He to room temperature in less than 5 min. Rods, 9 mm in diameter, were core-drilled, cut into 7 mm thick sections and polished on one side. A representative section of each glass was analyzed by electron microprobe, and the compositions were found to be within 1 wt% of the starting value.

These glasses are in equilibrium with mullite at 1678°, 1753°, and 1813°C according to the mullite liquidus of Davis and Pask.[11] Thus, the alumina-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 dissolution by the end phases.[13]

(3) Diffusion Cell

The diffusion cell arrangement consisted of molybdenum (Mo) crucibles containing a fused silica or aluminum-silicate glass disk on a sapphire substrate (Fig. 1). The runs at 1678°C were done in air with covered

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* Aluminum Co. of America, Pittsburgh, Pa. Chemical analysis (wt%) Na_2O 0.08, SiO_2 0.05, CaO 0.03, MgO 0.05, Fe_2O_3 0.01, MnO 0.0015, B_2O_3 <0.001, Cr_2O_3 0.0002.

†Corning Glass Works, Corning, N.Y. Produced by hydrolyzation of $SiCl_4$ when spraying into an oxygen-hydrogen flame. Practically free from metallic impurities, but contains a high amount of OH (∿1000 ppm) and Cl (∿100 ppm).

alumina crucibles.* The amount of molybdenum in the melts was below the detection limit of the electron beam microprobe. The crucibles and the diffusion couple parts were cleaned ultrasonically in ethyl alcohol. The Mo crucibles were sealed around the lid by electron beam welding (Fig. 1) and He leak-checked. This sealing was necessary to eliminate silica losses by evaporation during annealing.

(4) Diffusion Anneals

The tantalum resistance heating furnace† was used for all the anneals above 1700°C. The diffusion cell assembly as shown in Fig. 1 was placed on a Mo support stand and heated to 1200°C at 10^{-6} mm Hg. The chamber was then filled with helium slightly below atmospheric pressure, and the temperature was rapidly raised (2-3 min) to the annealing point.

The diffusion anneals ranged from 15 min to a month, depending on the diffusion zone length desired. The pricipal temperature range was from 1753° to 2003°C. The temperature of the tantalum chamber was monitored and electronically controlled (precision ±1°C) through a W5Re-W26Re thermocouple (accuracy ±7° at 1800°C). The specimen temperature, however, was measured separately with two optical pyrometers≠ (accuracy ±10° at 2000°C) utilizing black body conditions. The pyrometers were frequently calibrated against an NBS secondary standard pyrometer and at the melting point of platinum∥ (1772°C)[14] and Al_2O_3 (2054°C).[15] The

*Coors Porcelain Co., Golden, Colo. Crucible CN-2, AD998 (99.8 wt% Al_2O_3).

†Richard D. Brew and Co., Inc., Concord, N.H.; Model 466S.
≠Leeds & Northrup Co., Philadelphia, Pa.
∥NBS standard platinum was provided by K. S. Mazdiyasni, Air Force Materials Lab., Wright-Patterson Air Force Base, Ohio.

melting temperature of Al_2O_3 was verified within 2° utilizing black body conditions with a hole core-drilled directly into a sapphire crystal. Furthermore, the pyrometers themselves were frequently checked against each other to detect any malfunction. All the temperatures reported here are based on the 1968 International Practical Temperature Scale (IPTS-68).[14]

A Kanthal Super 33* resistance heating furnace was used for the air runs at 1678°C. The furance was loaded at 1200°C and raised to the annealing temperature in ∿45 min. The furnace temperature was monitored and electronically controlled (precision ±1°C) through a Pt6Rh-Pt30Rh thermocouple (accuracy ±5° at 1650°C). The specimen temperature was separately measured and recorded through a Pt6Rh-Pt30Rh thermocouple.

The diffusion anneals were completed by rapidly cooling the furnaces down to 1500°C (∿1 min) to prevent excessive crystallization in the diffusion zone. Continued cooling to room temperature, however, was very slow (up to 4 days) to avoid loss of integrity at the interface as a result of the difference in thermal expansion. Some crystal growth must have occurred in the diffusion zones below 1500°C (Section IIIB). The couples were subsequently sectioned in half parallel to the direction of diffusion, mounted in polyester resin and polished.

B. Phase Equilibrium Studies by Static Method of Quenching

Quench experiments were also performed to supplement the diffusion experiments. Aluminum-silicate mixtures of 42.2, 60.0, 71.8 and 80.0 wt% Al_2O_3 were prepared as before, but they were melted at 1953° or

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*The Kanthal Corp., Bethel, Conn.

2003°C for 15 to 30 min. The composition of a representative section was analyzed by electron microprobe. Crucibles were then sealed in argon and heat treated in the tantalum furnace in the temperature range of 1753° to 1953°C. The specimens were cooled by turning off the power to the furnace and allowing He to flow rapidly through the furnace.

A 78.3 wt% Al_2O_3 specimen was a commercial grade fused cast aluminum-silicate* prepared by the arc fusion process. Microscopic examination showed that the mullite grains were surrounded by a continuous glassy phase.[16] Specimens 9 mm in diameter by 10 mm thick were core-drilled from a pore-free portion of a fused cast ingot.

C. Electron Microprobe Analysis

The aluminum and silicon concentration profiles of the diffusion couples and the compositions of the microstructure specimens of the quenching experiments were determined using an electron microprobe analyzer.† 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 5-10 cu μm.[17] Two spectrometers were used to record the intensities of the AlK_α and SiK_α peaks simultaneously.

The concentration profiles were obtained by traversing the electron beam along a desired path perpendicular to the diffusion couple inter-

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*Carborundum Corp., Niagara Falls, N.Y. Sold as fused cast mullite. Wet chemical analysis was performed by Coors Spectro Chemical Lab., Golden, Colo. Spectrographic analysis by American Spectrographic Lab., San Francisco, Calif.: as oxides (wt%) Na 0.12, Fe 0.02, Mg 0.01, Zr 0.01, Ca 0.006, Ti 0.005, Cr 0.003, Cu <0.005, Mn <0.001.

†Model 400, Materials Analysis Co., Palo Alto, Calif.

faces. Because crystallization of alumina and/or mullite generally occurred 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 described by Davis and Pask[11] provided average compositions at any distance from an interface over an area affected by localized crystallization. It was thus possible to obtain diffusion profiles in the liquid adjoining the interface at temperature.

A computer program written by Frazer, et al.[18] was used to correct the electron microprobe data for dead time, drift, background, absorption, and fluorescence. Atomic number correction was not necessary since the difference between the atomic number of Al and Si is small. The output of this electron microprobe program given in wt% of the elements or their oxides in the melt was converted to gm/cm^3 of the elements and their oxides with an additional program utilizing density data.[19] The density vs wt% relationship used in this second program was

$$\rho_{1900} = 2.106 + 0.0085\ (\text{wt\% } Al_2O_3) \qquad (1)$$

where ρ_{1900} is the density of the melt at 1900°C. This single relationship rather than a separate equation for each temperature anneal was used since the differences in the densities were too small (±0.003 gm/cm^3 at 1800°-2000°C) to introduce any significant change in the diffusivity values.

III. RESULTS AND DISCUSSION

A. Diffusion Profiles and Phase Equilibria

(1) Sapphire-Fused Silica Couples

The experimental conditions of the diffusion anneals in the temperature range of 1803° to 2003°C are outlined in Table I. The annealing times were at least 15 min in order to ensure that the annealing time was considerably longer than the time needed to attain thermal stability in the furnace (∿30-60 sec). Above 1913°C, however, a 15 min anneal was the maximum since at longer times the diffusion profiles were too long (>2000 m) for convenient electron microprobe analysis.

At least two or three specimen runs were made at each set of annealing conditions. The interfacial compositions remained constant with time at a given temperature, indicating that the diffusion in the liquid phase was slower than the intrinsic dissolution rate of sapphire.[12] Although no time studies could be performed at 1953° and 2003°C, it was assumed that the diffusion in the liquid phase was still the rate controlling step at these temperatures. The average interfacial compositions listed in the table, then, correspond to liquidus compositions.[12] No silicon was detected in the sapphire subtrate by the electron microprobe.

Mullite growth at the sapphire-fused silica interface was observed in specimens annealed at 1803°C but not at 1853°C (Section IIIB), indicating that mullite became stable at some temperature below 1853°C. Thus, the interfacial compositions of Table I correspond to the liquidus of alumina at 1853° to 2003°C while the one at 1803°C corresponds to that of mullite.

Typical computer plotted diffusion profiles used in the determination of the interfacial compositions are shown in Fig. 2. The Boltzmann-Matano,[20] or the original interface, is located at x = o. The basic requirement of the Boltzmann-Matano analysis, i.e., that diffusion is the rate controlling process, was further verified by ascertaining that at a given temperature the distance from x = o for a given concentration is directly proportional to the square root of time.[12]

(2) Sapphire-Mullite-Liquid Couples

When the fused silica portions of the couples of the previous section were replaced by melts with compositions corresponding to the mullite liquidus,[11] the intermediate mullite layer could be grown to a thickness (>10 μm) suitable for electron microprobe analysis (Fig. 3).* The results of these runs in the temperature range of 1678° to 1813°C are tabulated in Table II. The thickness of the mullite layer increased linearly with the square root of time,[13] indicating that the growth mechanism is diffusion controlled. The interfacial compositions of the mullite layer obtained from these profiles, then, correspond to equilibrium solidus compositions.

(3) Stable Phase Equilibria

The interfacial compositions listed in Table I and II are incorporated with the data on the mullite liquidus by Davis and Pask,[11] the melting temperatures of cristobalite[21] and corundum,[15] and the eutectic temperature of cristobalite-mullite[22] are used to construct the stable SiO_2-Al_2O_3 phase diagram, as shown by the solid lines in Fig. 4.

*All the micrographs are by reflected light, Nomarski differential interference-contrast microscopy utilizing a Zeiss Ultraphot II metallograph.

The most important feature of this diagram is that mullite melts incongruently. The temperature, which was determined as 1828 ±10°C from the intersection of the extrapolated liquidus lines of mullite and alumina, is essentially identical to the one measured by Bowen and Grieg.[1]

B. Diffusion Zone Microstructures

Typical diffusion zone microstructures of the sapphire-fused silica couples annealed at 1803° and 1853°C are shown in Fig. 5. The extensive crystallization of mullite in the melt (top portion of the micrographs) occurred even though the couples were cooled to 1500°C in less than a minute, suggesting that some crystal growth occurred below 1500°C. The alumina content of such prismatic mullite grains, as determined by electron microprobe analysis, varied between 73-79 wt% Al_2O_3 in contrast to the stable equilibrium values of 71.1 wt% Al_2O_3 at the melt interface to 74.0 wt% Al_2O_3 at the sapphire interface in mullite grown at 1803°C by solid state reactions (Fig. 4). Similarly, mullite that precipitated in the diffusion zone of the sapphire-mullite-liquid couples annealed at 1678°C, 1753°C and 1813°C (Fig. 3) also was always richer in alumina (73-79 wt% Al_2O_3). In all cases, however, the liquidus compositions as determined by the technique mentioned in Section IIC corresponded to the values shown in Fig. 4.

The essentially continuous mullite layer at the interface of the couple annealed at 1853°C (Fig. 5B) has a constant composition throughout and identical to that of the precipitates in the adjoining diffusion zone. Furthermore, its prismatic morphology is similar to that of the precipitates and differs from that of the layer grown at 1803°C (Fig. 5a). Therefore, the precipitates in the diffusion zone of the specimen

annealed at 1853°C formed on cooling with nucleation starting at the sapphire interface.

The composition of the liquid in the diffusion zone at 1853°C varies from 0 to 54.0 wt% Al_2O_3 (Figs. 2 and 4). On cooling, the diffusion zone adjacent to the sapphire becomes oversaturated with respect to alumina just below 1853°C. Under equilibrium conditions, alumina would then precipitate in the liquid and below 1828°C would be completely resorbed by reacting with the liquid to form a mixture of mullite and liquid. The realization of an equilibrium of this nature, especially in silicates, is rare since the crystal phase to be resorbed becomes unavailable for a direct reaction through incrustation,[9] i.e., in this case formation of a mullite layer zone around alumina. A mixture of mullite and liquid, however, could also form metastably if the liquid were sufficiently supercooled without any precipitation of alumina. The absence of alumina in the rapidly cooled diffusion zone, then, indicates that such supercooling occurred.

The direct evidences for supercooling of the liquid in the diffusion zone were clearly brought out in three diffusion couples, each of which was annealed at 1903° for 15 min but cooled at relatively different rates due to directional flow of the He into the hot zone during quenching. The microstructures differed drastically as shown in Fig. 6 although the average diffusion profiles were identical to the one shown in Fig. 2 with a range of 0 to 62.5 wt% Al_2O_3. The precipitated crystalline phase as determined by electron microprobe and X-ray diffraction was only mullite when the couple was quenched (Fig. 6a), only

alumina when the couple was cooled relatively slowly (Fig. 6c), and alumina and mullite when cooled at a moderate rate (Fig. 6b). Since the liquidus composition at the peritectic temperature is 52.3 wt% Al_2O_3, ∿350 μm of the diffusion zone adjacent to the sapphire would experience some alumina precipitation during equilibrium cooling. The absence of alumina in this portion of the diffusion zone of a quenched couple (Fig. 6a) and presence of alumina in a slowly cooled couple (Fig. 6c) can only be explained on the basis of nucleation and supercooling phenomena of the liquid.

The coexistence of alumina, mullite and liquid (glass) in the diffusion zone of the moderately cooled couple (Fig. 6b) is in violation of the phase rule. With this intermediate cooling rate the residual liquid, which does not maintain equilibrium and does not react extensively with alumina, behaves independently and upon supercooling precipitates mullite. Therefore, the phase rule is only observed locally, while the entire mixture itself is unstable.

Davis and Pask,[11] who observed the formation of an interfacial non-equilibrium liquid in the cristobalite-sapphire couples at subsolidus temperatures, suggested the existence of a metastable SiO_2-Al_2O_3 phase diagram with a eutectic and no mullite phase formed by extensions of the SiO_2 and Al_2O_3 liquidus curves. The diffusion zone microstructure shown in Fig. 6c, then, is in further support of their observations since the total absence of mullite indicates a sufficiently slow cooling rate to maintain equilibrium between the liquid and alumina and thus necessitates the metastable extension of the alumina liquidus below the peritectic temperature.

Diffusion zone microstructures of 1953° and 2003°C couples showed only alumina precipitates in a glassy matrix even when they were quenched at the fastest rate possible. The sapphire substrate acted as a site for heterogeneous nucleation of alumina.

C. Microstructures of Quenched Specimens

The interpretation of microstructures obtained by the static method of quenching mixtures of a given composition is assisted by the facts that have been established in the previous sections: (1) mullite melts incongruently under equilibrium conditions, (2) a metastable SiO_2-Al_2O_3 phase diagram can exist without the mullite phase, and (3) liquid phases can be supercooled through the alumina-liquid field under certain conditions. Numerous quenching experiments were conducted. Only some of the more critical microstructures are discussed below.

The microstructure of a mixture containing 60.0 wt% Al_2O_3 that was homogenized above the alumina liquidus at 1953°C and cooled slowly (~60 min) below the transition temperature before quenching showed mullite and glass. The absence of alumina again suggests the supercooling of the melt below the alumina liquidus. For comparison, on slow cooling of a melt of similar composition (~60.0 wt% Al_2O_3) that was formed in the diffusion zone adjacent to the sapphire in the 1903°C diffusion couples (Figs. 2 and 4), alumina readily precipitated (Figs. 6b and c); supercooling with precipitation of mullite in the diffusion zone was only achieved by quenching (Fig. 6a). The difference in behavior can be attributed to the presence of the 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 present in a mixture of 71.8 wt% Al_2O_3 ($3Al_2O_3 \cdot 2SiO_2$) that was annealed at 1953°C, cooled slowly (∿30 min) to 1753°C and further annealed for approximately 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 still incomplete due to the slow diffusion through the mullite layer. The diffusion mechanism is supported 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. 4).

Typical microstructures of the silicate mixtures of 78.3 and 80.0 wt% Al_2O_3 that were homogenized at 2003°C, above the alumina liquidus, are shown in Fig. 8; the degree of mullite and/or alumina precipitation in these melts was highly dependent on the cooling rate followed. A quench by turning off the power and a rapid introduction of helium into the furnace always resulted in the precipitation of only mullite with compositions varying up to 83.2 wt% Al_2O_3 and some residual high-silica glass between the mullite grains (Fig. 8a). Occasional precipitation of alumina was observed around the sharp edges of the crucibles that must have acted as nucleation sites for alumina. When the melts cooled moderately by just turning off the power to the furnace, alumina precipitated readily (Fig. 8b). 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 surrounded by a glassy matrix were present (Fig. 8c). The needles embedded in the glassy matrix were in general 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-Al_2O_3 as the only crystalline phase. These needles were thus identified as secondary alumina that precipitated out during quenching from 1753°C. The overall composition of the matrix surrounding the primary alumina precipitates, as determined by scanning-beam electron microprobe analysis, was ∿48 wt% Al_2O_3. This composition is identical to that of the alumina liquidus at 1753°C when it is extended below the peritectic temperature (Fig. 4), and provides additional evidence for the existence of a metastable SiO_2-Al_2O_3 binary diagram without any mullite phase.

D. Melting Behavior of Mullite

The melting behavior of mullite was studied using polycrystalline stoichiometric 3:2 mullite (71.8 wt% Al_2O_3) specimens* synthesized by vacuum hot pressing coprecipitated high-purity, submicron oxide powders.[23] The specimens (5 mm x 5 mm x 8 mm), placed in Mo crucibles, were melted in vacuum in the tantalum heating element furnace. The specimen temperature was measured utilizing black body conditions with a hole drilled directly into the specimen. The heating rate to 1800°C was fast (5-10 min) followed by a 5°C/min heating rate from thereon in order to maintain thermal equilibrium. The melting temperature was assumed to be

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*The specimens were provided by K. S. Mazdiyasni, Air Force Materials Lab., Wright-Patterson AFB, Ohio.

that at the first instant of the specimen slumping. Some specimens were only partially melted and quenched by turning off the power to the furnace and allowing He to flow rapidly through the furnace.

The melting temperature of stoichiometric mullite was consistently determined to be 1880°C. The same melting temperature was determined independently by Mazdiyasni and Brown[23] 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. 4). Furthermore, the microstructure of a partially melted specimen (Fig. 9) showed no alumina formation in the molten portion but only recrystallized mullite and some glass. Thus, stoichiometric mullite melted congruently at 1880°C.

According to the stable phase diagram presented in Fig. 4, a mullite of 71.8 wt% Al_2O_3 composition becomes unstable at 1816°C and dissociates to a mixture of a silica rich liquid phase and a higher alumina mullite as temperature is increased above 1816°C. The test specimens had submicron size grains and contained no liquid phase.[23] The non-slumped portion of such a specimen after heating to a black body temperature of 1880°C (Fig. 9) shows a mixture of ∿5-10 μm size mullite grains and a glassy phase indicating that in addition to the formation of a liquid phase, considerable amount of grain growth also took place above 1816°C. The composition of these mullite grains as determined by point-beam microprobe analysis was consistently 75.8 wt% Al_2O_3.

Eitel[10] has pointed out that incongruently melting silicates can be superheated above the peritectic temperature with the metastable prolongation of the corresponding liquidus. The result of this prolongation

then, is the metastable congruent melting of that compound at a higher temperature than the peritectic temperature. It is interesting to note that the mullite liquidus of Fig. 4 when extended beyond the peritectic temperature intersects the 71.8 wt% Al_2O_3 composition line at ∿1880°C which corresponds to the congruent melting temperature measured in this study. Such metastable congruent melting of mullite would also necessitate the extension of the mullite solidus above the transition temperature to higher alumina contents and thus provides the explanation for the shift in alumina content of mullite to 75.8 wt% Al_2O_3.

E. Metastable Phase Equilibria

The results of the last two sections on metastable equilibria can be represented by metastable binary eutectic diagrams between silica-mullite in the absence of alumina and silica-alumina in the absence of mullite superimposed on the stable silica-alumina diagram, shown as dotted lines in Fig. 4. The silica-mullite diagram as drawn represents a composite of all the analyzed data experienced in the study. The upper limit of the mullite solid solution range is uncertain but has been set at 83.2 wt% Al_2O_3 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% Al_2O_3) and Neuhaus and Richartz[24] (77.5 wt% Al_2O_3) although mullite precipitated from a melt with a higher alumina contents has recently been reported.[25] The maximum melting temperature for mullite in this composite diagram is set at ∿1890°C as obtained from the extrapolation of the mullite liquidus to 83.2 wt% Al_2O_3. The metastable silica-mullite equilibrium diagram, as presented in Fig. 4 thus includes the

high-alumina mullites formed by solidification from a melt in the absence of alumina. Mullite grown by solid state reactions with alumina is limited to 74.0 wt% Al_2O_3.

The diagram, however, does not provide an explanation for the precipitation of alumina-rich mullite (∿73-79 wt% Al_2O_3) in the diffusion zones of the couples annealed at 1678°C to 1813°C (Section IIIB), in which the melts at the interfaces ranged from 10.9 to 42.2 wt% Al_2O_3. Mullite precipitated from these melts, under stable equilibrium conditons, could not be richer than 71.5 wt% Al_2O_3 at 1813°C and 70.5 wt% Al_2O_3 below 1753°C. A possible explanation could be the existence of a disordered mullite phase with a broader and higher alumina solid solution range as illustrated by the free energy of mixing vs composition curves in Fig. 10.

Aramaki and Roy[5] by X-ray studies, observed that heat treatment of mullite caused nearly as much change in its lattice parameters as variation in composition and suggested Al-Si order-disorder as a possible explanation. Later, similar observations were made by Majumdar and Welch[26] and Mazdiyasni and Brown.[23] On the basis of the available information, the possibility of the existence of disordered mullite necessitates two overlapping mullite solid solution fields as shown in Fig. 10 instead of the single field shown in Fig. 4. The ordered mullite has a field that extends up to about 75.8 wt% Al_2O_3 and melts at 1880°C as determined in this study, and the disordered mullite formed by precipitation from a liquid phase extends from ∿73 to 83.2 wt% Al_2O_3 or possibly higher alumina content.[25] A study of the literature[6] strongly supports the existence of such a metastable mullite phase,

frequently referred to as 2:1 or melt-mullite. Temperatures as high as 1913°C have been associated with the melting behavior of 2:1 mullite;[4,24] an average of the reported values of 1900°C is used in Fig. 10. The values that were used for the disordered mullite liquidus were taken from the diagram of Aramaki and Roy[5] who obtained their data by the quenching technique.

The immiscibility region shown in Fig. 10 was determined by MacDowell and Beall.[27] Recently, Takamori and Roy[28] questioned the accuracy of this immiscibility region based on their crystallization temperature measurements on flame-sprayed and/or splat-cooled glasses. The position of the alumina liquidus as determined in this study also raises questions on the position of the spinodal region since the extention of the alumina liquidus cuts through the center of this region. Below the critical temperature of the immiscibility region, the ΔG mixing curve of the liquid will require two minima, and alumina will be at equilibrium with liquid compositions in the immediate vicinity of one of these minima. Thus, any proposed spinodal region has to be either completely under or outside the extension of the alumina liquidus.

VI. CONCLUSIONS

Diffusion couple experiments in the SiO_2-Al_2O_3 system, in the temperature range of 1678° to 2003°C, yielded information on stable and several metastable phase equilibria diagrams. The dissolution of alumina in fused silica and the growth of interfacial mullite were diffusion-controlled. The interfacial compositions of the phase boundaries, thus, corresponded to the equilibrium liquidus and solidus compositions and were used to construct the stable equilibrium

SiO_2-Al_2O_3 phase diagram, in which mullite is shown to melt incongruently at 1828° ±10°C as originally determined by Bowen and Greig.[1] The stable solid solution range of mullite was at 70.5 to 74.0 wt% Al_2O_3 below 1753°C and at 71.8 to 74.0 wt% Al_2O_3 at 1813°C.

The examination of the diffusion zone microstructures and the microstructures of specimens heat treated by the static method of quenching supported the incongruency of mullite. They also produced information indicating the existence of metastable equilibria and indicated metastable mullite solid solutions up to at least 83.2 wt% of Al_2O_3. When aluminum-silicate melts with alumina contents up to the solid solution limit of mullite were cooled rapidly below the alumina liquidus, precipitation of only mullite was realized. When the specimens were cooled slowly or sites for heterogeneous nucleation of alumina were available, alumina did precipitate as predicted by the stable SiO_2-Al_2O_3 phase diagram. Direct evidence was also provided for the existence of a metastable SiO_2-Al_2O_3 binary phase diagram without any mullite phase formed by the extensions of the silica and alumina liquidus curves.

Stoichiometric or ordered mullite of 71.8 wt% Al_2O_3 composition melted congruently at 1880 ±10°C due to the superheating of mullite indicating the existence of a metastable silica-mullite phase diagram in the absence of alumina with compositions up to 75.8 wt% Al_2O_3. The possible presence of disordered mullite that occurs only on precipitation from the melt is indicated with the existence of a metastable silica-disordered mullite phase diagram with compositions up to at least 83.2 wt% Al_2O_3.

The conflicting investigations that have appeared in the literature appear to be associated with problems related to nucleation of alumina and ordered mullite, and supercooling of aluminum silicate liquids.

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Table I. Experimental conditions and data for sapphire-fused silica runs

Temp. IPTS-68 (°C)	Time (sec x 10^3)	Interfacial Composition in the Melt C_I		
		Al^{3+} (g/cm^3)	Al_2O_3 (mol%)	Al_2O_3 (wt%)
1803	3.6, 14.4, 21.6,* 28.8,* 602.1	0.547	29.0	40.9
1853	0.9, 1.8, 3.6, 7.2, 65.7, 91.5	0.752	40.9	54.0
1903	0.9, 1.8, 3.6	0.893	49.6	62.5
1913	0.9, 1.8	0.919	51.2	64.0
1953	0.9	1.048	59.6	71.5
2003	0.9	1.313	78.2	85.9

*Davis and Pask[11]

Table II. Experimental conditions and data for sapphire-mullite-liquid diffusion runs

Temp. IPTS-68 (°C)	Time (sec x 10^5)	Interfacial Composition (wt% Al_2O_3) in Melt $[C_I]$	in Mullite $[C_{ML}-C_{AM}]$	Mullite Thickness (μm)
1678	7.309	10.9	70.5-74.0	10.00
1678	28.428	10.9	70.5-74.0	18.00
1753	3.965	22.8	70.5-74.0	13.00
1813	6.015	42.2	71.6-74.0	36.00

The runs with a melt composition of 15.0 wt% Al_2O_3 were conducted by Davis and Pask.[11]

FIGURE CAPTIONS

Fig. 1. Diffusion cell assembly. All of the container parts are molybdenum. Crucibles had a 9.1 mm I.D.

Fig. 2. 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 interface.

Fig. 3. Interference-contrast micrographs of the diffusion zones in couples of sapphire (bottom) and (A) 10.9 wt% Al_2O_3 containing silicate at 1678°C for 7.309×10^5 sec, (B) 22.8 wt% Al_2O_3 containing silicate at 1753°C for 3.965×10^5 sec, and (C) 42.2 wt% Al_2O_3 containing silicate at 1813°C for 6.015×10^5 sec. Couples were cooled rapidly to 1500°C (~1 min) and then very slowly to room temperature. The intermediate layers are mullite formed by solid state reaction at the annealing temperatures. The prismatic precipitates in the top portion of the diffusion zone in the silicate are mullite that crystallized during cooling.

Fig. 4. The stable SiO_2-Al_2O_3 equilibrium phase diagram is shown by the solid lines. A composite metastable equilibrium SiO_2-mullite system is shown by the dotted lines; metastable extensions of the alumina liquidus and silica liquidus are also shown. The relationship between the concentration profile of a semi-infinite SiO_2-Al_2O_3 diffusion couple and the stable phase equilibrium diagram is drawn for temperature T; C_A corresponds to 100% Al_2O_3.

Fig. 5. Interference-contrast micrographs of the diffusion zones in couples of sapphire (bottom) and fused silica annealed at (A) 1803°C for 602.1 x 10^3 sec and (B) 1853°C for 7.2 x 10^3 sec. Couples were cooled rapidly to 1500°C (~1 min) and then very slowly to room temperature. The prismatic precipitates (light gray) in the top portion of the diffusion zone are mullite that crystallized during cooling; the mullite layer at the sapphire-melt interface of microstructure (A) grew at the interface at temperature.

Fig. 6. Interference-contrast micrographs of the diffusion zones in couples of sapphire (bottom) and fused silica annealed at 1903°C for 0.9 x 10^3 sec and (A) quenched, (B) cooled at a relatively moderate rate, and (C) cooled relatively slowly, to 1500°C (slowest overall time ~1 min) and then very slowly to room temperature. The precipitates in the diffusion zone are (A) mullite (light gray), (B) alumina (light gray needles) and mullite (fine precipitates between the alumina needles), and (C) alumina (light gray needles); the precipitates along the interface in (B) and (C) are also alumina.

Fig. 7. Microstructure of the 71.8 wt% Al_2O_3 containing silicate melted in a 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. The light gray precipitates are alumina that are completely surrounded with a layer of mullite (gray). The dark gray portions between the

mullite layers are glass containing fine precipitates of mullite formed on quenching.

Fig. 8. Microstructure (A) of a 78.3 wt% Al_2O_3 containing silicate melted in a sealed Mo crucible at 2003°C for 30 min and quenched in He (the matrix is mullite with glassy inclusions). Microstructure (B) of a 80.0 wt% Al_2O_3 melt cooled at a moderate rate in vacuum by turning off the power to the furnace (the light gray portions are alumina; the gray, mullite; and dark gray, glass). Microstructure (C) of a 80.0 wt% Al_2O_3 melted at 2003°C for 90 min, cooled to 1753°C in 60 min, and quenched in He to room temperature (the large and needle precipitates are all alumina in a glass matrix).

Fig. 9. Microstructure of stoichiometric mullite (71.8 wt% Al_2O_3) after partial melting at 1880°C and quenching in He. Recrystallization of mullite has occurred; the dark gray portions are glass and the black, pull-outs. The upper portion was in contact with the crucible and shows more melting.

Fig. 10. Superimposed on the stable SiO_2-Al_2O_3 phase equilibrium diagram are possible metastable phase diagrams for SiO_2-mullite and SiO_2-disordered mullite systems. The hypothetical free energy of mixing vs concentration curves for 1753°C represent phase relationships shown by the phase diagram. The immiscibility region is by MacDowell and Beall.[27]

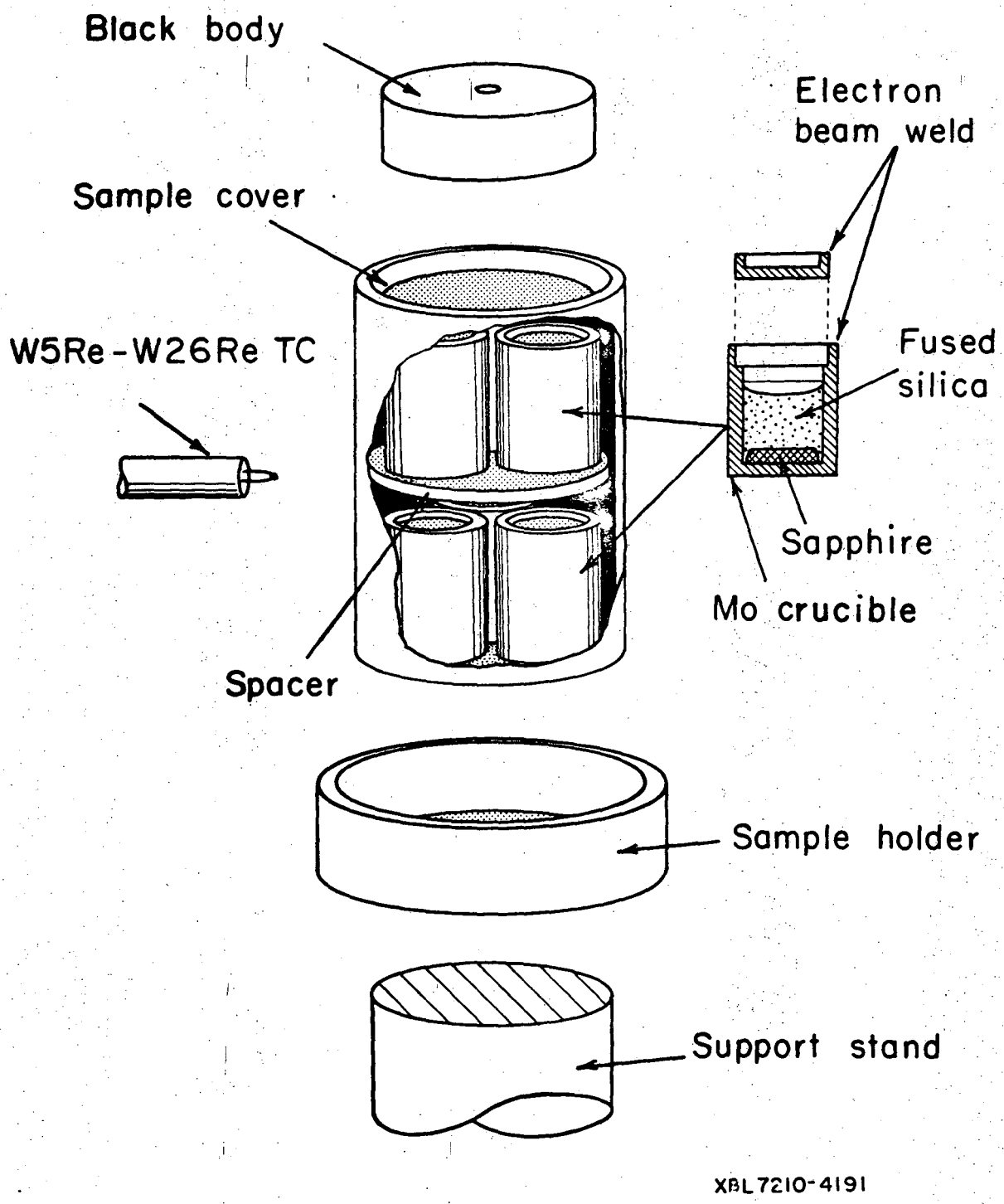
Black body
Electron beam weld
Sample cover
W5Re-W26Re TC
Fused silica
Sapphire
Mo crucible
Spacer
Sample holder
Support stand
XBL7210-4191

Fig. 1

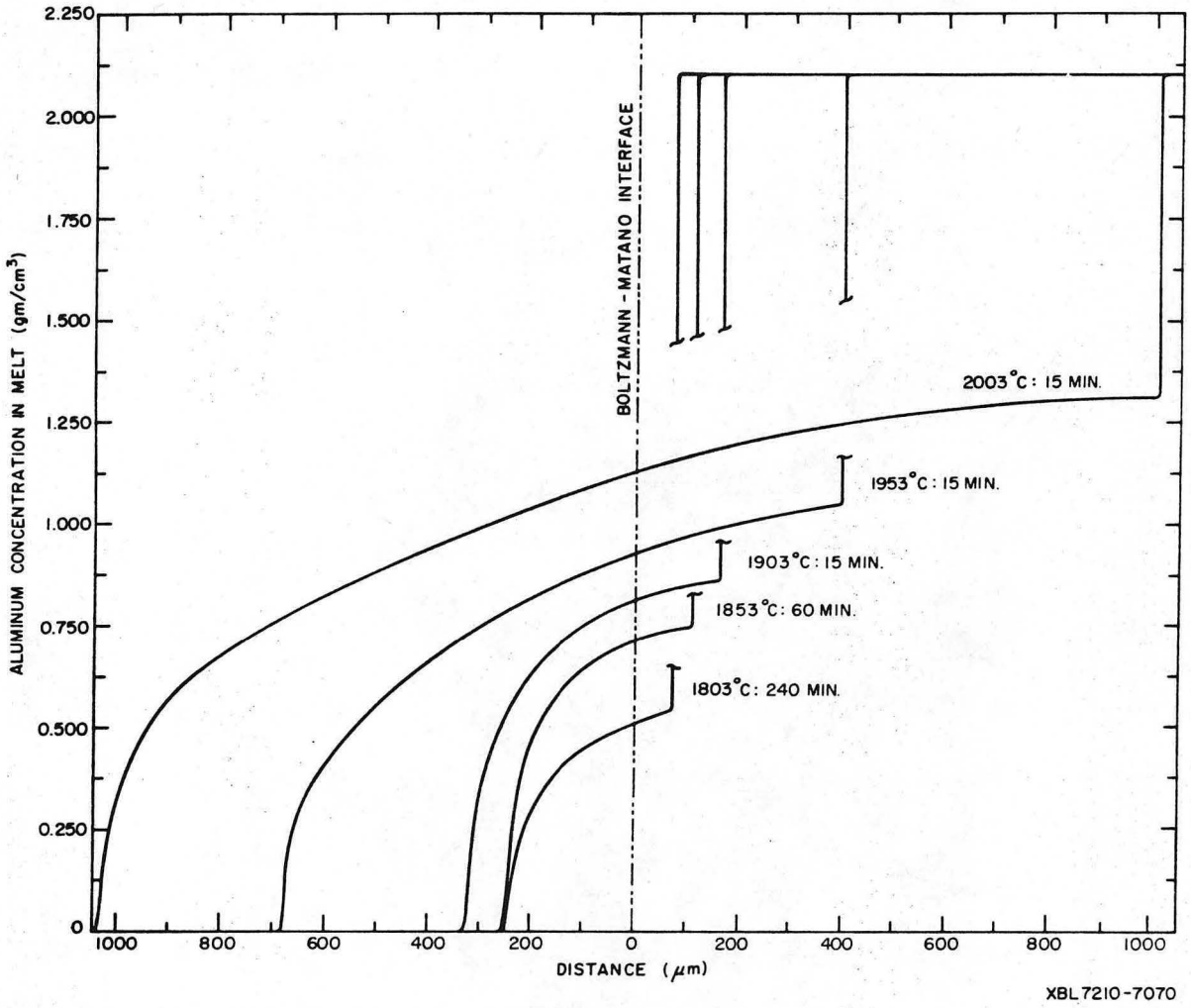
2.250
2.000
1.750
1.500
1.250
1.000
0.750
0.500
0.250
0
ALUMINUM CONCENTRATION IN MELT (gm/cm³)
BOLTZMANN - MATANO INTERFACE
2003°C : 15 MIN.
1953°C : 15 MIN.
1903°C : 15 MIN.
1853°C : 60 MIN.
1803°C : 240 MIN.
1000
800
600
400
200
0
200
400
600
800
1000
DISTANCE (μm)
XBL7210-7070

Fig. 2

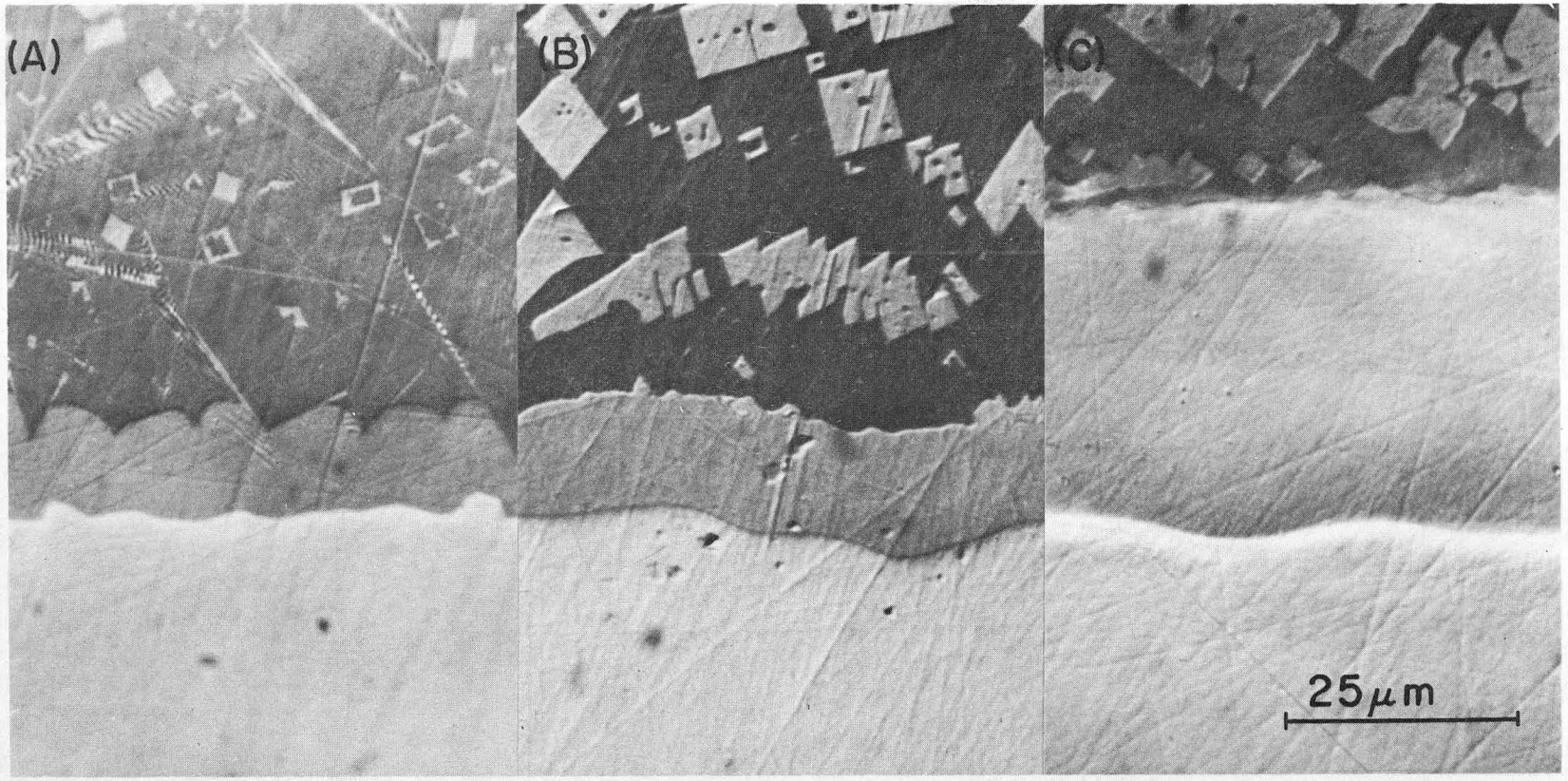

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Fig. 3

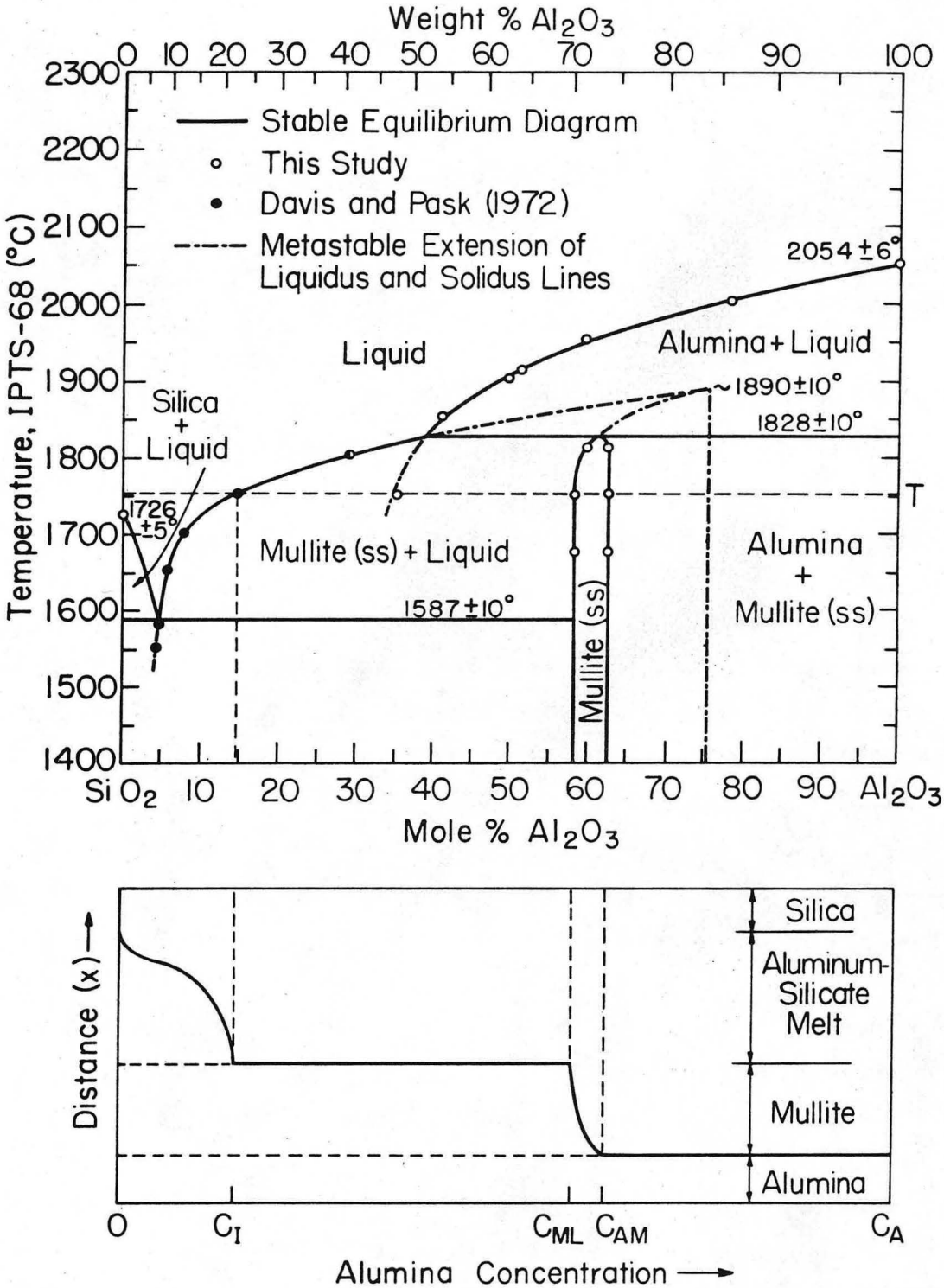
Weight % Al_2O_3
0 10 20 30 40 50 60 70 80 90 100
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
Temperature, IPTS-68 (°C)
Stable Equilibrium Diagram
This Study
Davis and Pask (1972)
Metastable Extension of Liquidus and Solidus Lines
2054 ±6°
Liquid
Alumina + Liquid
~1890±10°
1828±10°
Silica + Liquid
1726 ±5°
T
Mullite (ss) + Liquid
1587±10°
Mullite (ss)
Alumina + Mullite (ss)
SiO_2 10 20 30 40 50 60 70 80 90 Al_2O_3
Mole % Al_2O_3
Distance (x)
Silica
Aluminum-Silicate Melt
Mullite
Alumina
0
C_I
C_{ML}
C_{AM}
C_A
Alumina Concentration
XBL 736-6222

Fig. 4

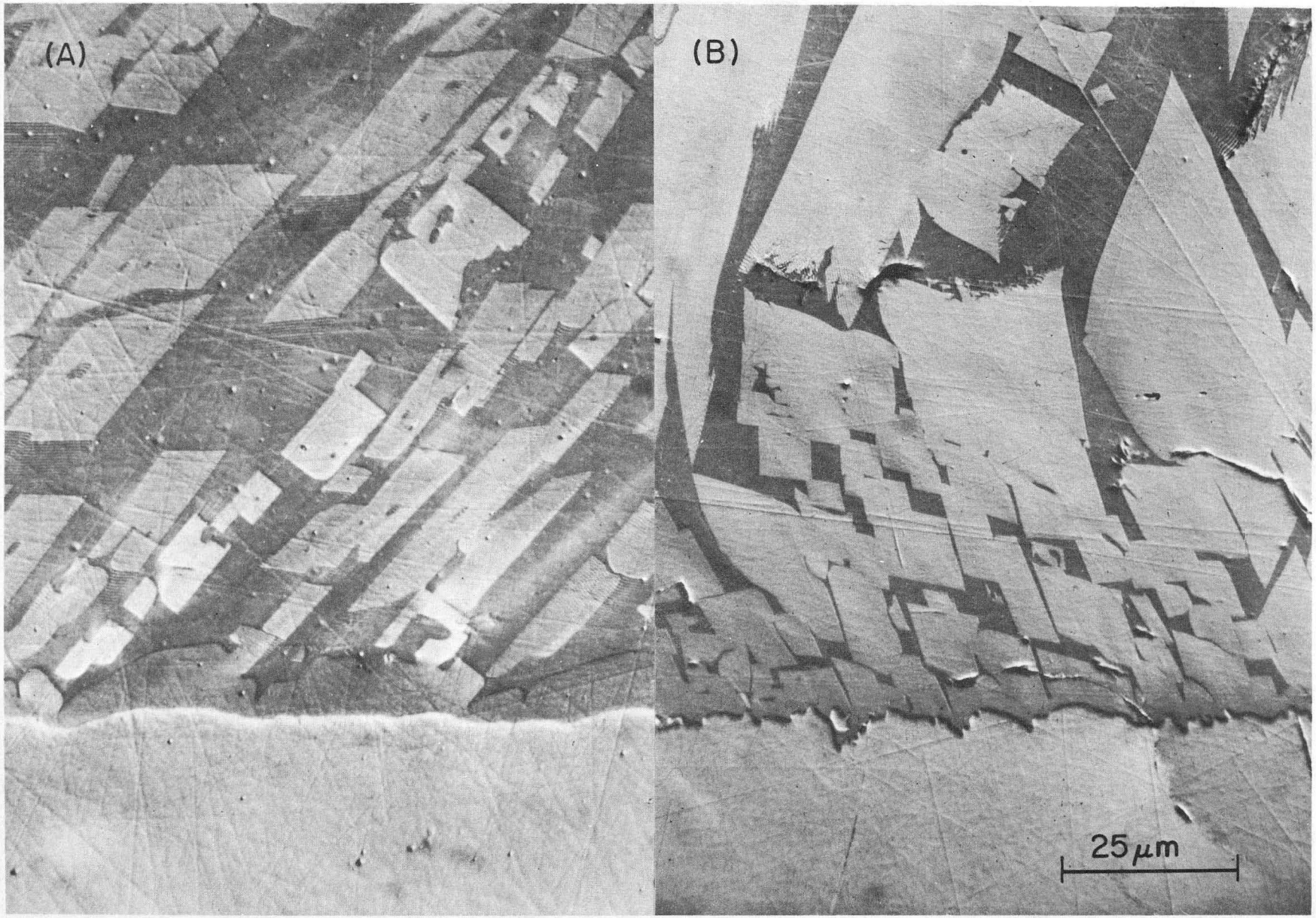

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Fig. 5

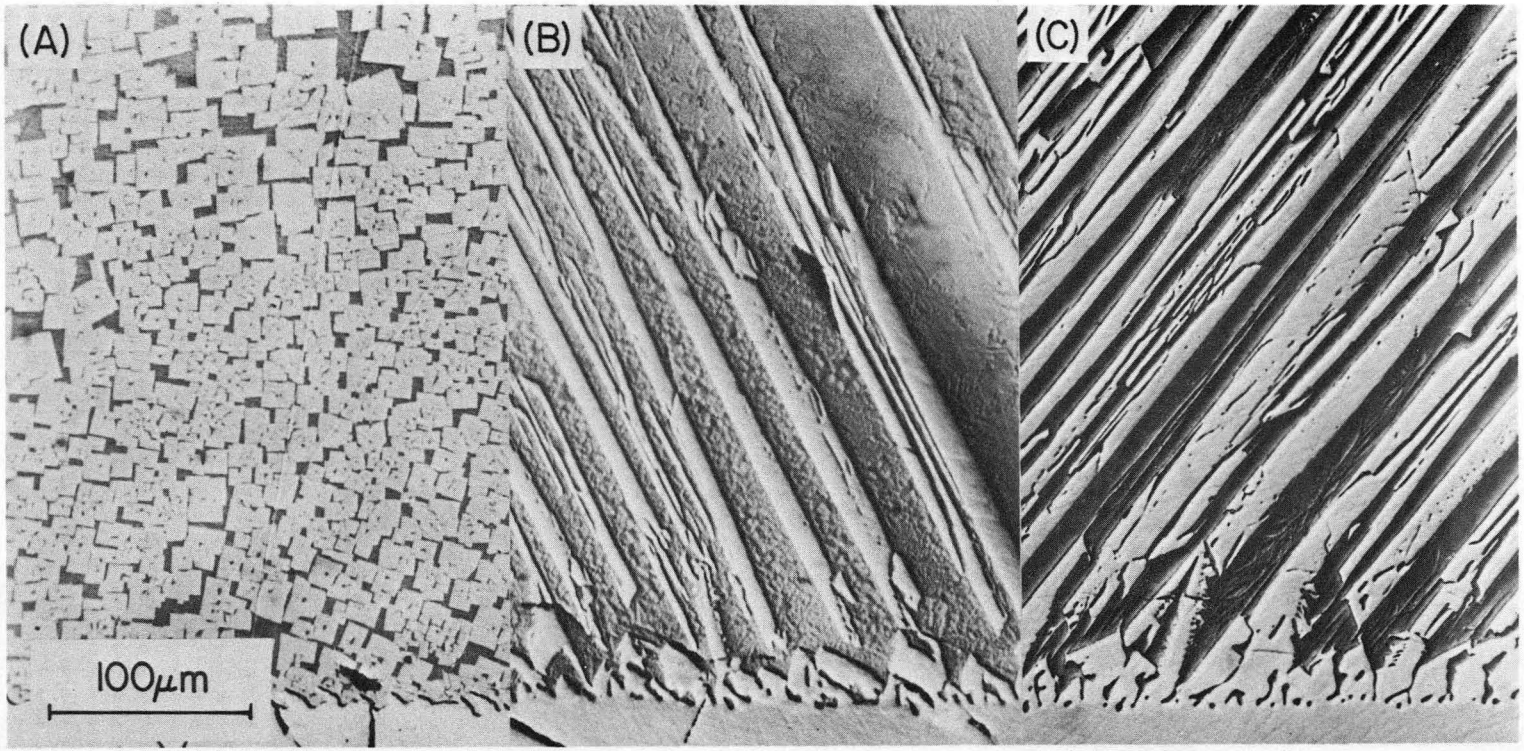

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Fig. 6

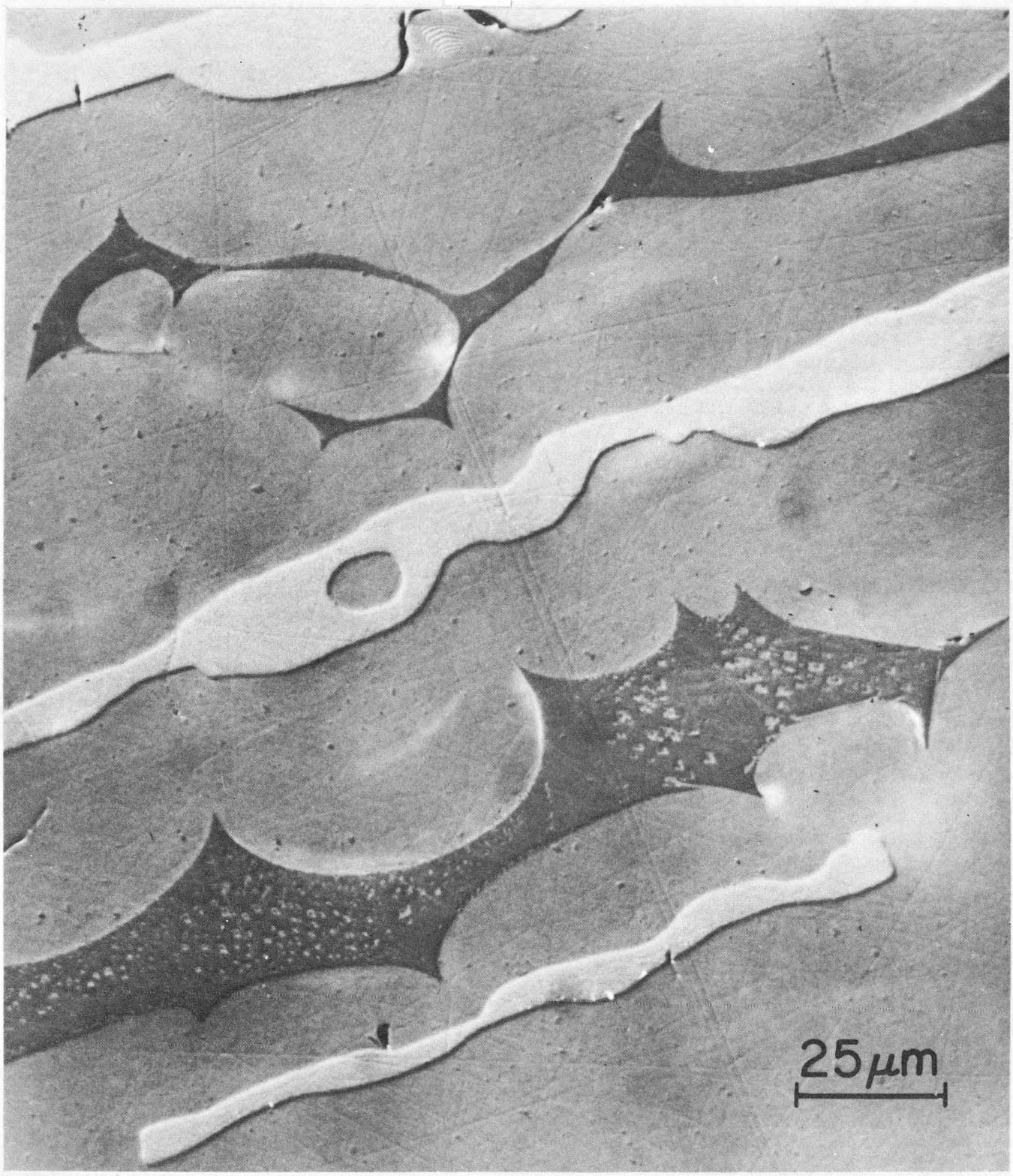

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Fig. 7

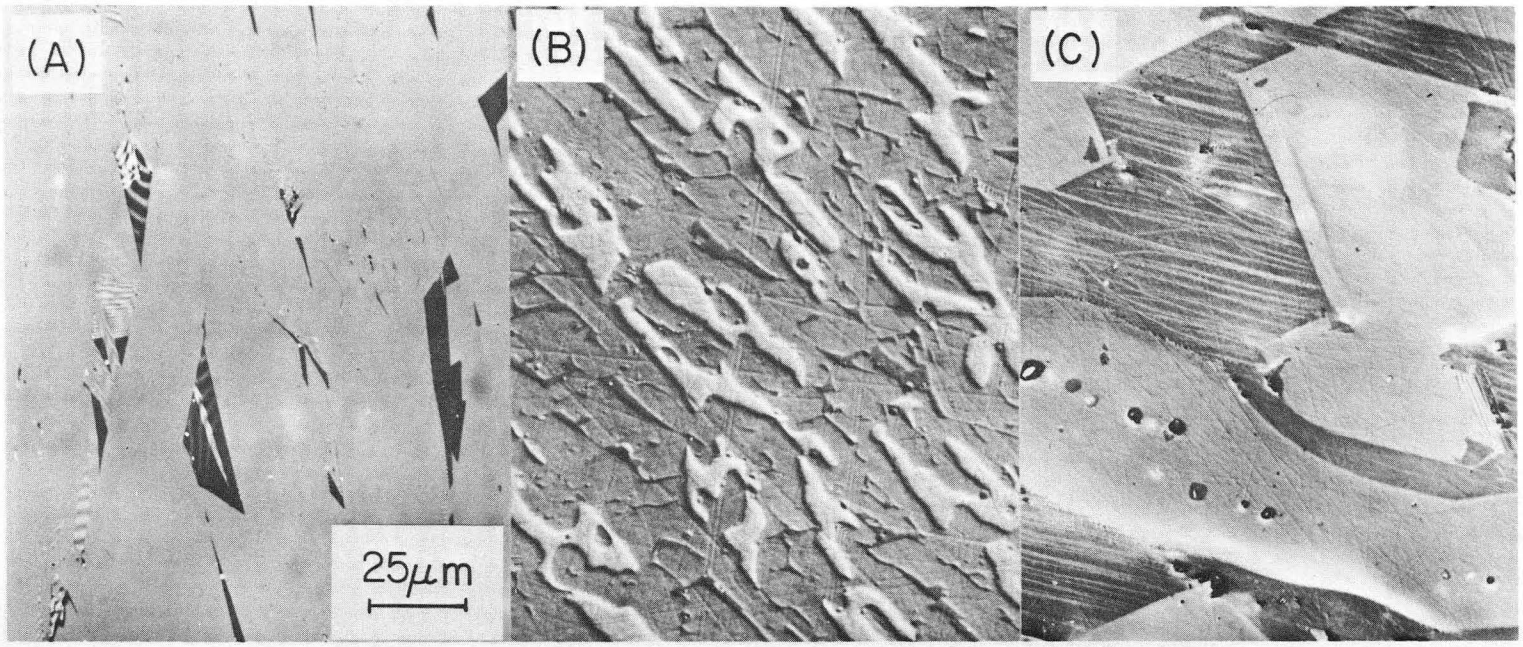

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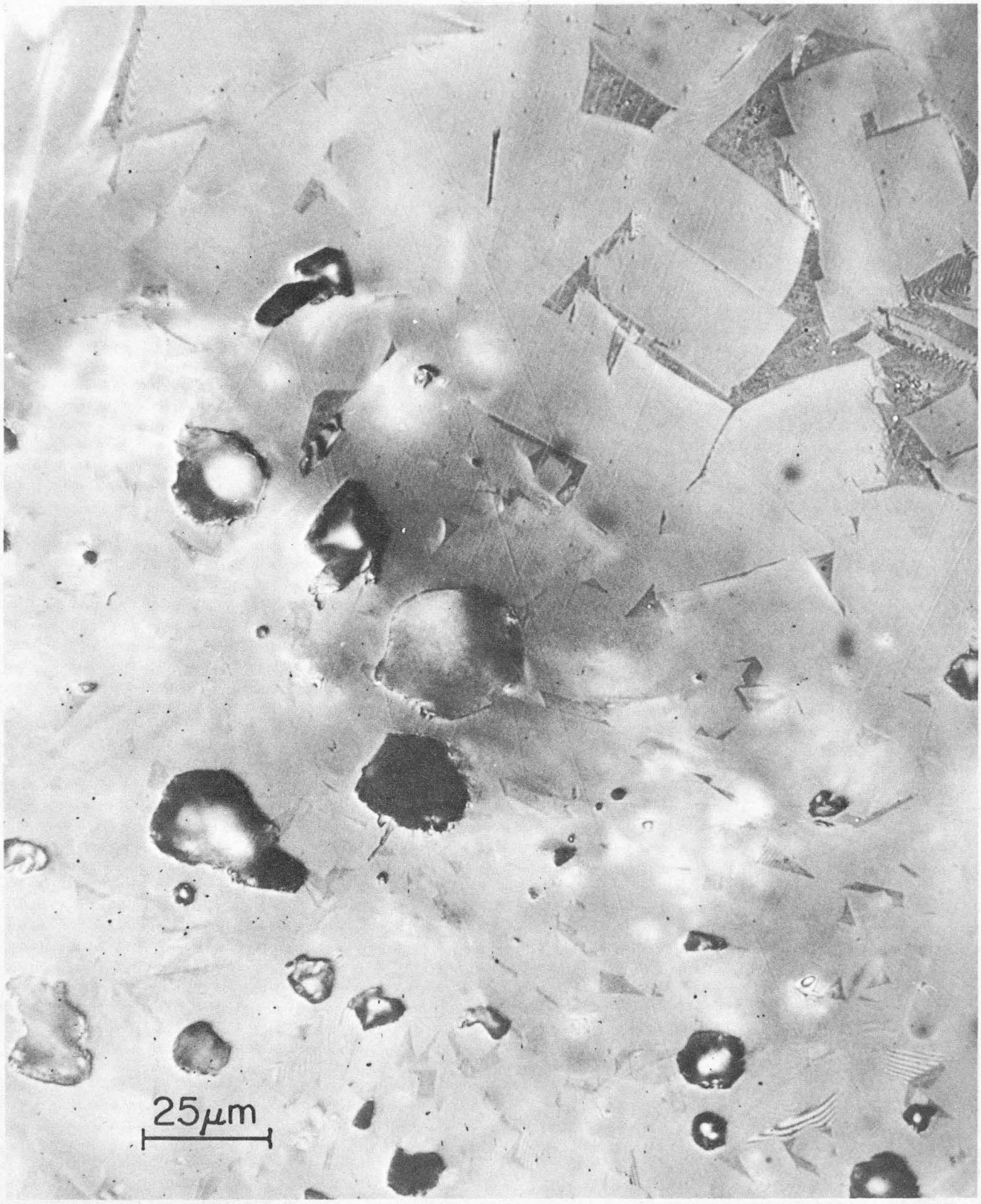
Fig. 8



XBB 7210-5320

Fig. 9

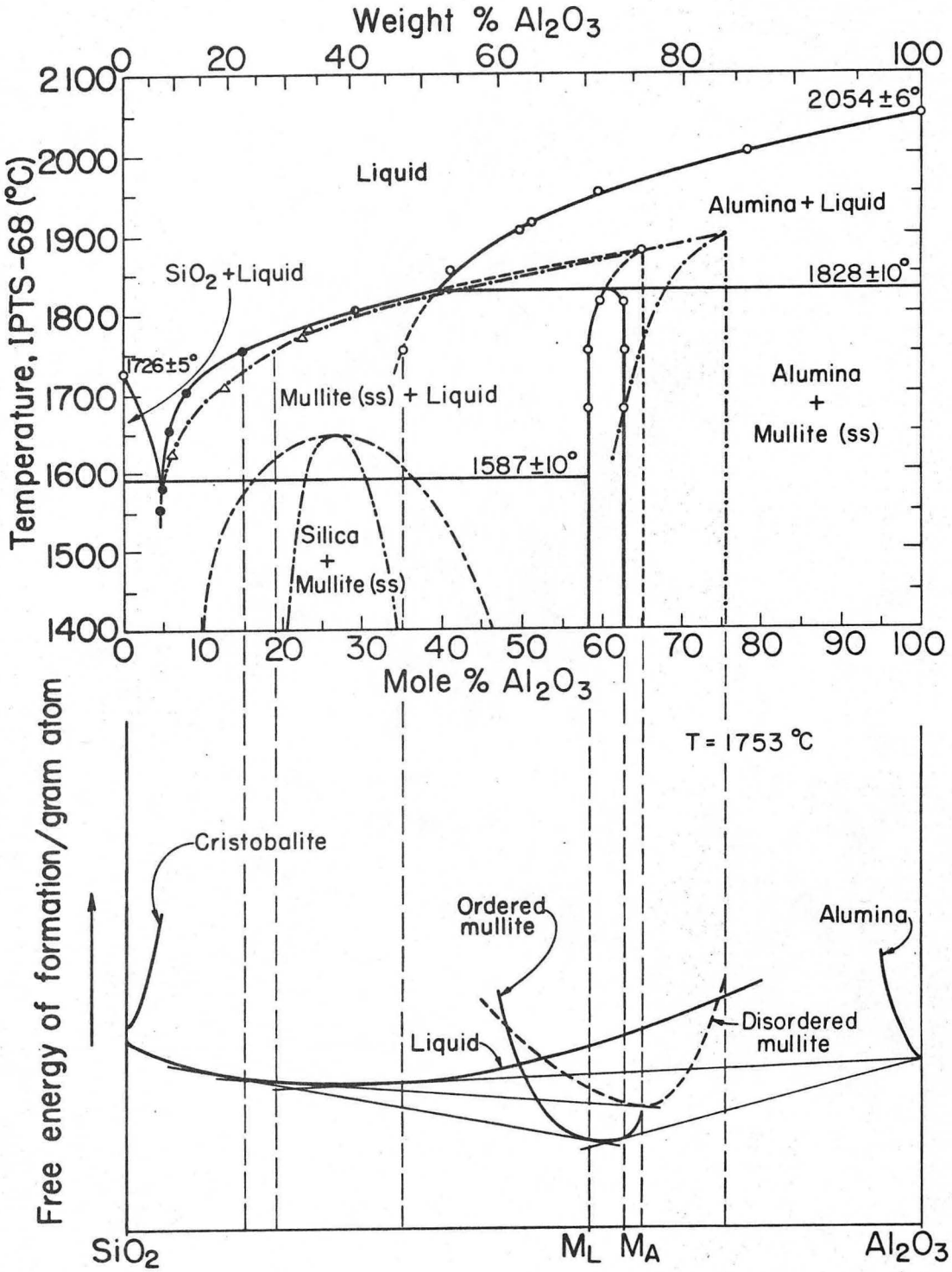

Weight % Al_2O_3
0 20 40 60 80 100
2100 2000 1900 1800 1700 1600 1500 1400
Temperature, IPTS-68 (°C)
2054±6°
Liquid
Alumina + Liquid
SiO_2 + Liquid
1828±10°
1726±5°
Mullite (ss) + Liquid
Alumina
+
Mullite (ss)
1587±10°
Silica
+
Mullite (ss)
0 10 20 30 40 50 60 70 80 90 100
Mole % Al_2O_3
T = 1753 °C
Cristobalite
Ordered mullite
Alumina
Liquid
Disordered mullite
Free energy of formation/gram atom
SiO_2
M_L M_A
Al_2O_3
XBL 745-6309

Fig. 10

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