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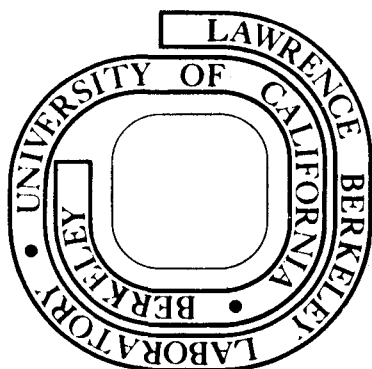
Ilhan A. Aksay and Joseph A. Pask

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THE $\text{SiO}_2\text{-Al}_2\text{O}_3$ SYSTEM:
STABLE AND METASTABLE EQUILIBRIA AT 1.0 atm

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ABSTRACT

Sapphire-fused silica diffusion couples, which were annealed in the temperature range of 1678° to 2003°C and analyzed by electron beam microprobe, provided data on the stable phase equilibrium of the $\text{SiO}_2\text{-Al}_2\text{O}_3$ system. Under stable equilibrium conditions, the intermediate compound of this system, mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), melts incongruently at $1828 \pm 10^\circ\text{C}$, and its solid solution field extends from 70.5 to 74.0 wt% Al_2O_3 . The stable phase diagram is a composite of two metastable binary eutectic diagrams: silica-mullite and silica-alumina. Under metastable conditions, mullite melts congruently at $\approx 1890 \pm 10^\circ\text{C}$, and its solid solution field extends to ≈ 83.2 wt% Al_2O_3 .

Phase equilibrium in the $\text{SiO}_2\text{-Al}_2\text{O}_3$ system has been studied extensively for almost a century. At high pressures, the equilibrium of the polymorphs of $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$, sillimanite, andalustite and kyanite, is most significant in petrology in the understanding of metamorphic conditions. Under atmospheric conditions, the system is most significant in ceramics since the clay-rich sediments provide the primary source of raw materials in ceramics technology. The study of phase equilibrium in the $\text{SiO}_2\text{-Al}_2\text{O}_3$ system both under atmospheric conditions and at high pressures has not been conclusive.

The first systematic study of the $\text{SiO}_2\text{-Al}_2\text{O}_3$ system, under atmospheric conditions, was conducted by Bowen and Greig⁽¹⁾ who showed that mullite ($3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$) but not sillimanite ($\text{Al}_2\text{O}_3\cdot\text{SiO}_2$) was the only stable compound of this system at 1.0 atm. Furthermore, they showed that mullite melted incongruently at 1828°C (IPTS-68). The findings of Bowen and Greig were generally accepted without any serious questions until 1950, when Bauer et al.⁽²⁾ were successful in growing mullite single crystals by the Verneuil method. Since single crystals of incongruently melting compounds are not ordinarily produced by this method, the incongruency of mullite was questioned. Subsequently, in 1951, Toropov and Galakhov⁽³⁾ provided additional evidence that mullite melted congruently. Since then, numerous conflicting investigations have been conducted, some of which⁽⁴⁾ supported the incongruency as originally determined by Bowen and Greig and some of which⁽⁵⁾ supported the congruency of mullite decomposition. Among these, the studies by Trömel et al.⁽⁴⁾ and Aramaki and Roy⁽⁵⁾ should be mentioned as the most extensive ones. The findings of Trömel et al., in general, are in agreement

with those of Bowen and Greig. Aramaki and Roy's diagram, however, supports the congruent melting of mullite; and, at the present, their study stands out as the generally accepted one.

In addition to the melting behavior of mullite, a second outstanding problem of the $\text{SiO}_2\text{-Al}_2\text{O}_3$ system has been the determination of the stable solid solution range of mullite. Mullite, nominally, corresponds to a composition of $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, and its solid solution range, according to Aramaki and Roy,⁽⁵⁾ extends from 71.8 wt% to ≈ 74.3 wt% Al_2O_3 . 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 77.3 wt% Al_2O_3 ($2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$), a fact which raises the question of metastability. No satisfactory explanation for the fact that high-alumina mullite is formed only from a melt has yet been presented.

Most phase equilibrium studies on the $\text{SiO}_2\text{-Al}_2\text{O}_3$ system have been conducted either by the static method of quenching or by differential thermal analysis. Difficulties of obtaining accurate phase equilibrium data by these techniques, especially in a silicate system with an incongruently melting compound, have been discussed.⁽⁶⁾ In a recent diffusion study, Davis and Pask,⁽⁷⁾ utilizing semi-infinite couples of silica and alumina and the electron microprobe for determining composition profiles, demonstrated the power of the diffusion couple technique for obtaining accurate stable phase equilibrium data. They provided new data on the mullite liquidus and also suggested the existence of a metastable $\text{SiO}_2\text{-Al}_2\text{O}_3$ binary system without any mullite phase.

In this report, we provide additional data, obtained by the diffusion couple technique, (i) on the alumina liquidus and thus the stable melting behavior of mullite and (ii) on the stable solid solution range of mullite. Experiments by the static method of quenching were also performed which provided data on the metastable equilibrium conditions.

The diffusion cell arrangement consisted of sealed molybdenum crucibles containing a fused silica disk on a sapphire substrate. The diffusion anneals, in a tantalum resistance-heating furnace, ranged from 15 min to a month, depending on the desired diffusion zone length. The principal temperature range was from 1678° to 2003°C. The specimen temperature was measured with two optical pyrometers (accuracy $\pm 10^\circ$ at 2000°C) utilizing black body conditions and also with a W5Re-W26Re thermocouple (accuracy $\pm 7^\circ$ at 1800°C). The pyrometers were frequently calibrated against a NBS secondary standard pyrometer and at the melting point of platinum (1772°C) and $\alpha\text{-Al}_2\text{O}_3$ (2054°C).

When a diffusion couple is annealed at constant T and P, all the phase fields intersected by the corresponding isotherm and the isobar between the end phases form as layers in the diffusion zone (Fig. 1). The thickness of each layer is dependent upon the growth rate of the corresponding phase. At temperatures below the melting point of mullite, in order to eliminate the dissolution of the interfacial mullite layer into fused silica and thus maximize its growth rate, the fused silica portion of the diffusion couples was replaced with aluminum-silicate glasses of composition C_I (Fig. 1). These aluminum-silicate glasses were prepared using high purity powders of $\alpha\text{-Al}_2\text{O}_3$ and fused silica.

Extensive crystallization of alumina and/or mullite occurred in the liquid portion of the sapphire-fused silica diffusion couples when they were cooled rapidly in flowing He. Thus, the concentration profiles obtained by the point-beam electron microprobe analysis were extremely rough and did not represent the profiles at the annealing temperature. However, concentration profiles, smooth and representative of those at the annealing temperature, were determined by rapidly scanning the electron beam (up to 150 μm) parallel to the interface of the couple, at set intervals, in order to obtain an average composition over an area affected by localized crystallization. Interfacial compositions, obtained from these profiles at the discontinuities, remained constant with time at a given temperature, indicating that diffusion transport was the rate controlling mechanism. These interfacial compositions, then, corresponded to either a liquidus or a solidus composition⁽⁸⁾ and were used to construct the $\text{SiO}_2\text{-Al}_2\text{O}_3$ stable equilibrium phase diagram as outlined with solid lines in Fig. 1.

The most important feature of this diagram is that mullite melts incongruently to form a silica-rich liquid and solid alumina. Mullite growth at the sapphire-fused silica interface, at temperature, was observed at 1803°C but not at 1853°C, indicating that the stable mullite field lies below 1853°C. The incongruent melting temperature was then determined to be 1828 $\pm 10^\circ\text{C}$ from the intersection of the extrapolated liquidus lines of mullite and alumina. The mullite solid solution field at 1753°C ranged from 70.5 wt% to 74.0 wt% Al_2O_3 and was nominally $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$.

Normally, the data obtained from diffusion couple experiments are sufficient to complete a phase diagram. However, due to the great controversy about the melting behavior of mullite, experiments by the static method of quenching were also performed to supplement the diffusion couple experiments. Mixtures, ranging in composition from 42.2 wt% to 80.0 wt% Al_2O_3 , were prepared from high purity powders of $\alpha\text{-Al}_2\text{O}_3$ and fused SiO_2 . The mixtures were sealed in Mo crucibles and homogenized at temperatures above that of the alumina liquidus shown in Fig. 1. Subsequent heat treatments, at varying sub-liquidus temperatures and at varying cooling rates, did not always yield microstructures as predicted by the stable phase diagram of Fig. 1. With rapid cooling rates, the homogenized melts were supercooled through the alumina+liquid field without any alumina precipitation. However, when an identical or the same mixture was again homogenized and cooled slowly, the precipitation of alumina as predicted by the stable alumina liquidus was realized. In fact, with slow cooling rates, it was possible to follow the extension of the alumina liquidus below the transition temperature and maintain an alumina+liquid (48 wt% Al_2O_3) mixture at 1753°C up to a month (Fig. 1).

Similarly, the extension of the mullite liquidus above the transition temperature was realized when an attempt was made to measure the melting temperature of a theoretically dense, polycrystalline mullite specimen⁽⁹⁾ of 71.8 wt% Al_2O_3 composition. The specimen started decomposing into a mixture of liquid and alumina-rich mullite above $\approx 1816^\circ\text{C}$, and melting was completed congruently at $1880 \pm 10^\circ\text{C}$ without the formation of Al_2O_3 . The composition of mullite shifted along the extension of the solidus up

to 76 wt% Al₂O₃ at 1880°C. In Fig. 1, we extended the mullite solidus up to 83.2 wt% Al₂O₃ since this composition was the highest alumina content detected in any mullite precipitated from a melt during this study. This value agrees well with the compositions of mullite single crystals grown from a melt by Bauer et al. (82.57 wt% Al₂O₃).⁽²⁾ The maximum temperature for this composition is tentatively set at ≈1890°C. The solid solution limit and the maximum temperature, however, are subject to change as more data become available on the metastable extensions of the mullite liquidus and solidus lines. The stable phase diagram, outlined with solid lines in Fig. 1, is the composite of two metastable binary eutectic diagrams: silica-mullite and silica-alumina. The metastable silica-mullite equilibrium diagram, as presented here, then effectively explains the controversial melting behavior of mullite and the formation of high-alumina mullites only when they are precipitated from a melt. In the presence of alumina, the solid solution field is limited to a narrow range; thus, the highest alumina content that can be incorporated into mullite by solid state reactions is 74.0 wt% Al₂O₃. A detailed account of this work will be presented elsewhere.^(10,11)

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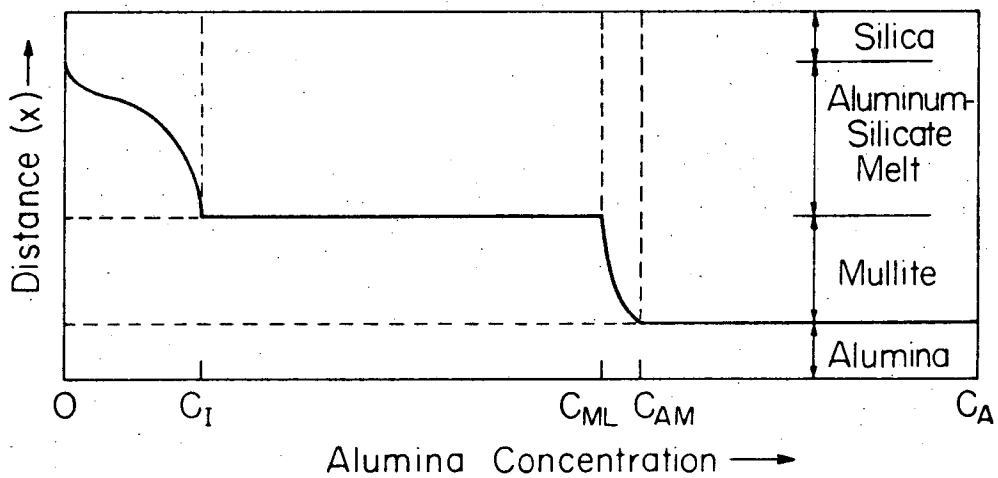
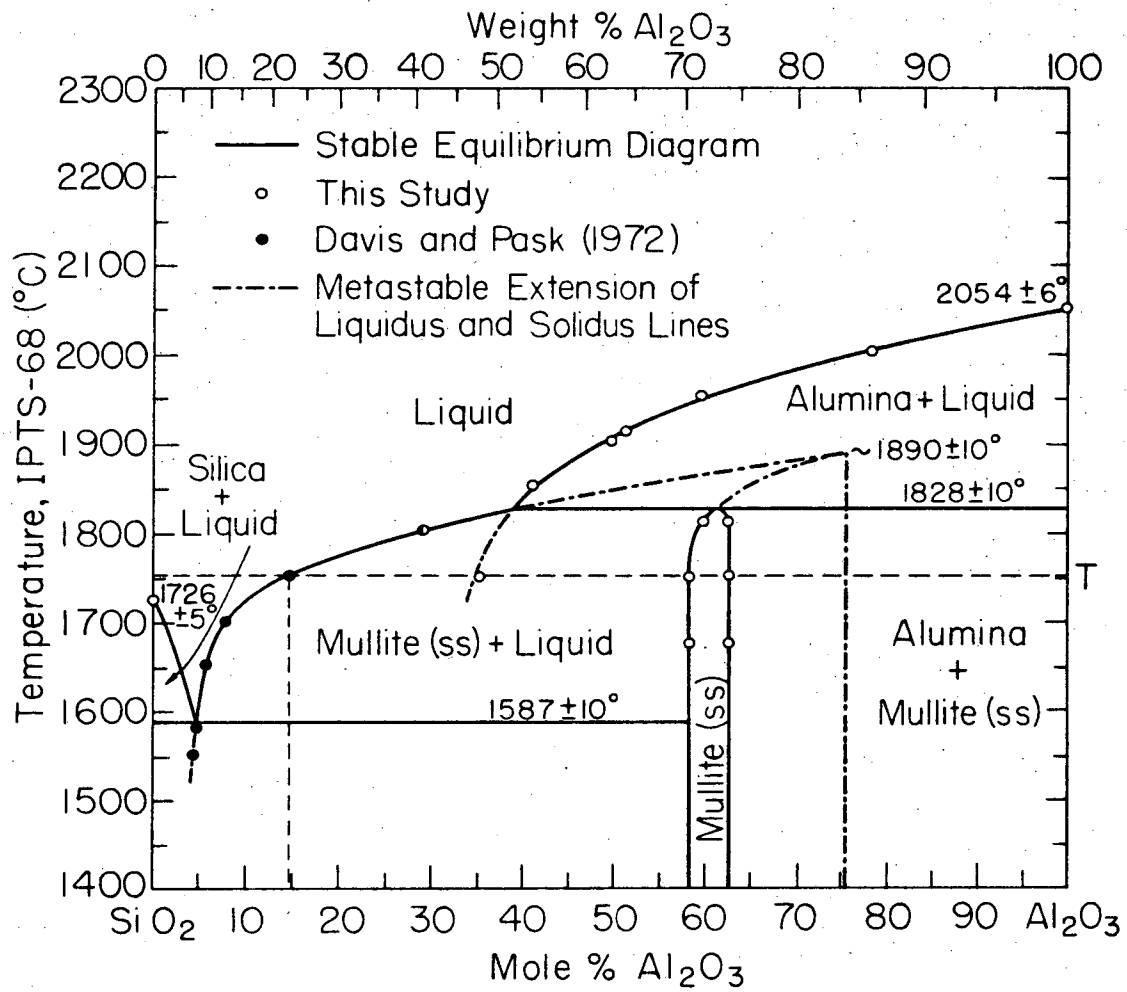
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FIGURE CAPTION

Fig. 1. The relationship between the concentration profile of a semi-infinite $\text{SiO}_2\text{-Al}_2\text{O}_3$ diffusion couple and the stable equilibrium phase diagram, at temperature T below the melting point of mullite. Metastable extensions of the silica-mullite system and the alumina liquidus are superimposed on the stable silica-alumina diagram.



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Fig. 1

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