Reports

The Silica-Alumina System: Stable and Metastable Equilibria at 1.0 Atmosphere

Abstract. *Diffusion couples, consisting of sapphire and fused silica, which were annealed in the temperature range from 1678° to 2003°C and analyzed by electron beam microprobe, have provided data on the stable phase equilibrium of the silica-alumina system. Under stable equilibrium conditions, the intermediate compound of this system, mullite* ($3Al_2O_3 \cdot 2SiO_2$)*, melts incongruently at 1828° ± 10°C and its solid solution field extends from 70.5 to 74.0 percent (by weight) alumina. The stable phase diagram is a composite of the two binary eutectic diagrams: silica-mullite in the absence of alumina and silica-alumina in the absence of mullite. Under metastable conditions, mullite melts congruently at* $\approx$ *1890° ± 10°C and its solid solution field extends to* $\approx$ *83.2 percent (by weight) alumina.*

Phase equilibrium in the SiO_2-Al_2O_3 system has been studied extensively for almost a century. At high pressures, the equilibrium of the polymorphs of $Al_2O_3 \cdot SiO_2$, sillimanite, andalusite, and kyanite, is of significance in petrology in the understanding of metamorphic conditions. Under atmospheric conditions, with mullite ($3Al_2O_3 \cdot 2SiO_2$) as the only compound, the system is important in ceramics since the clay-rich sediments provide the primary source of raw materials in ceramics technology. The study of phase equilibrium in the SiO_2-Al_2O_3 system both under atmospheric conditions and at high pressures has not been conclusive. In this report we present data on the phase equilibria of the SiO_2-Al_2O_3 system at 1.0 atm that support the incongruent melting of mullite at 1828°C and show that under metastable equilibrium conditions congruency could be realized at $\approx$ 1890°C.

The first systematic study of the SiO_2-Al_2O_3 system, under atmospheric conditions, was conducted by Bowen and Greig (*1*) who showed that mullite but not sillimanite was the only stable compound of this system at 1.0 atm. Furthermore, they showed that mullite melted incongruently at 1828°C [International Practical Temperature Scale, 1968 (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. 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, 5*) supported the incongruency as originally determined by Bowen and Greig and some of which (*6, 7*) supported the congruency of mullite decomposition. Among these, the studies by Trömel *et al.* (*5*) and Aramaki and Roy (*7*) are 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 is the generally accepted one.

In addition to the melting behavior of mullite, a second outstanding problem of the SiO_2-Al_2O_3 system has been the determination of the stable solid solution range of mullite. Mullite corresponds to a nominal composition of $3Al_2O_3 \cdot 2SiO_2$, and its solid solution range, according to Aramaki and Roy (*7*), extends from 71.8 to $\approx$ 74.3 percent (by weight) Al_2O_3. This range, however, is realized only when mullite is prepared by solid-state reactions in the presence of Al_2O_3. When solidified from a melt, the composition of mullite may extend up to 77.3 percent Al_2O_3 ($2Al_2O_3 \cdot SiO_2$), a fact which raises the question of metastability. No satisfactory explanation for the fact that mullite with a high content of Al_2O_3 is formed only from a melt has yet been presented.

Most phase equilibrium studies on the SiO_2-Al_2O_3 system have been conducted either by the static method of quenching or by differential thermal analysis. These techniques, especially in silicate systems (*8*) with an incongruently melting compound, can lead to misinterpretation because of nucleation and growth problems. In a recent diffusion study, Davis and Pask (*9*), utilizing semi-infinite couples of SiO_2 and Al_2O_3 and the electron microprobe for determining composition profiles, demonstrated the power of the diffusion couple technique for obtaining accurate stable phase equilibrium data in the absence of convective flow. They provided new data on the mullite liquidus and also suggested the existence of a metastable SiO_2-Al_2O_3 binary system without any mullite phase.

In this report we provide additional data, obtained by the diffusion couple technique, on (i) the Al_2O_3 liquidus and thus the stable melting behavior of mullite and (ii) the stable solid solution range of mullite. Experiments by the static method of quenching were also carried out which provided data on the metastable equilibrium conditions.

The diffusion cell arrangement consisted of sealed molybdenum crucibles containing a fused SiO_2 disk on a sapphire substrate. The diffusion anneals, in a tantalum resistance-heating furnace, ranged from 15 minutes to 1 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, ± 10° at 2000°C) utilizing blackbody conditions and also with a W5Re-W26Re thermocouple [95 percent (by weight) tungsten and 5 per-

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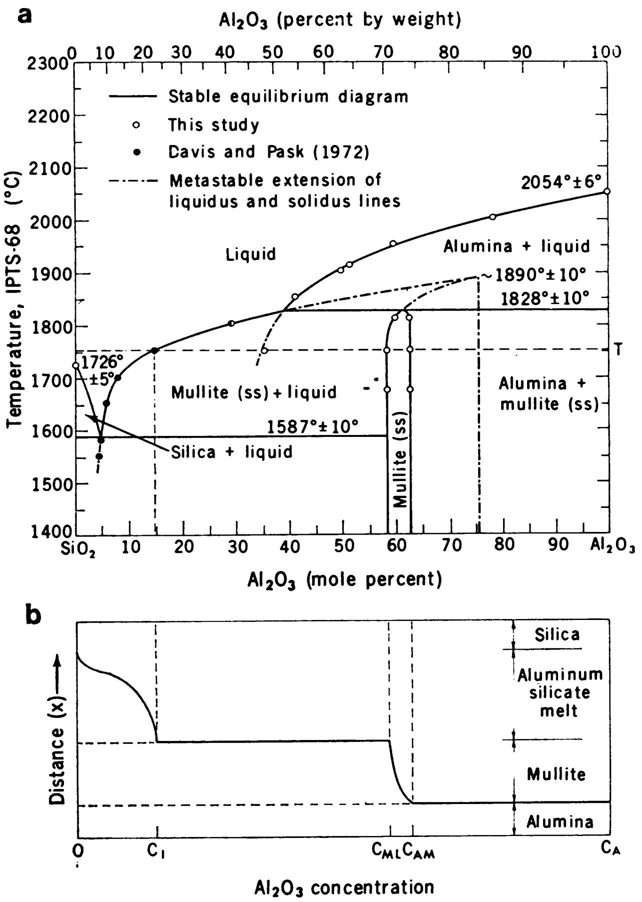

Fig. 1. The relationship between (a) the stable equilibrium phase diagram and (b) the concentration profile of a semi-infinite SiO_2-Al_2O_3 diffusion couple is shown at temperature T below the melting point of mullite. Metastable extensions of the SiO_2-mullite system and the Al_2O_3 liquidus are superimposed on the stable SiO_2-Al_2O_3 diagram; C_A, 100 percent Al_2O_3; C_{ML}, concentration of Al_2O_3 in mullite at the mullite-liquid interface; C_{AM}, concentration of Al_2O_3 in mullite at the Al_2O_3 mullite interface; and *ss*, solid solution.

cent rhenium coupled with 74 percent tungsten and 26 percent rhenium] (accuracy, ± 7° at 1800°C). The pyrometers were frequently calibrated against a National Bureau of Standards secondary pyrometer and at the melting points of platinum (1772°C) and α-Al_2O_3 (2054°C).

When a diffusion couple is annealed at constant temperature and pressure, 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 SiO_2 and thus maximize its growth rate, the fused SiO_2 portion of the diffusion couples was replaced with aluminum silicate glasses of composition C_I (Fig. 1). These aluminum silicate glasses were prepared from high-purity powders of α-Al_2O_3 and fused SiO_2.

Extensive crystallization of Al_2O_3 or mullite, or both, occurred in the liquid portion of the sapphire–fused SiO_2 diffusion couples when they were cooled rapidly in flowing helium. 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, an indication that diffusion transport was the rate-controlling mechanism. These interfacial compositions, then, corresponded to either a liquidus or a solidus composition (*10*) and were used to construct the SiO_2-Al_2O_3 stable (*11*) 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 SiO_2-rich liquid and solid Al_2O_3. Mullite was observed to grow at the sapphire–fused SiO_2 interface at 1803°C but not at 1853°C, an indication that the stable mullite field lies below 1853°C. The incongruent melting temperature was then determined to be 1828° ± 10°C from the intersection of the extrapolated liquidus lines of mullite and Al_2O_3. The mullite solid solution field at 1753°C ranged from 70.5 to 74.0 percent Al_2O_3 and corresponded to a nominal composition of $3Al_2O_3 \cdot 2SiO_2$.

Normally the data obtained from diffusion couple experiments are sufficient to complete a phase diagram. However, because of 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 to 80.0 percent Al_2O_3, were prepared from high-purity powders of α-Al_2O_3 and fused SiO_2. The mixtures were sealed in molybdenum crucibles and homogenized at temperatures above that of the Al_2O_3 liquidus shown in Fig. 1. Subsequent heat treatments, at varying

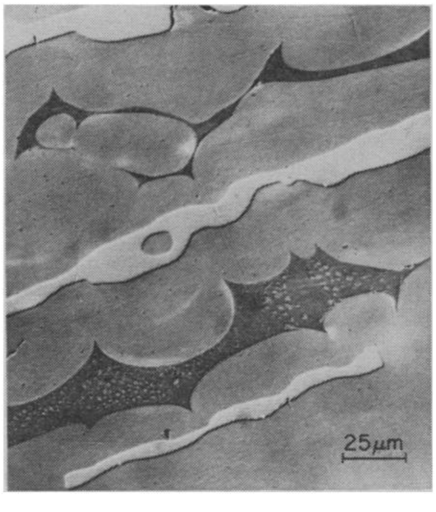

Fig. 2. The microstructure of a 71.8 percent Al_2O_3 + 28.2 percent SiO_2 mixture melted in a sealed molybdenum crucible at 1953°C for 460 minutes, cooled to 1753°C in 30 minutes, annealed at 1753°C for 42,392 minutes (29.4 days), and quenched from 1753°C (see Fig. 1). The light gray areas are Al_2O_3 precipitates that are completely enveloped with a layer of mullite (gray). The glassy inclusions (dark gray) between the mullite layers also contain fine precipitates of mullite formed during cooling. The overall specimen composition corresponds to that of the stoichiometric mullite; the formation of Al_2O_3 within a melt of this composition can only be explained by the incongruent growth of mullite. However, when this same specimen is heat treated again within the above-mentioned temperature intervals but with rapid cooling from 1953° to 1753°C, the microstructure shows no Al_2O_3 precipitates and could easily be misinterpreted as being indicative of the congruency of mullite.

subliquidus 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, caused by difficulty in the nucleation of Al_2O_3, the homogenized melts were supercooled through the Al_2O_3 + liquid field without any Al_2O_3 precipitation. However, when an identical or the same mixture was again homogenized and cooled slowly, the precipitation of Al_2O_3 as predicted by the stable Al_2O_3 liquidus was realized (Fig. 2). In fact, with slow cooling rates, it was possible to follow the extension of the Al_2O_3 liquidus below the transition temperature and to maintain an Al_2O_3 + liquid (48 percent Al_2O_3) mixture at 1753°C for up to 1 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 (*12*) with a composition of 71.8 percent Al_2O_3. The specimen started decomposing into a mixture of liquid and Al_2O_3-rich mullite above ≈ 1816°C, and melting was completed congruently at ≈ 1880° ± 10°C without the formation of Al_2O_3. The composition of mullite shifted along the extension of the solidus up to 76 percent Al_2O_3 at 1880°C. In Fig. 1, we extended the mullite solidus up to 83.2 percent Al_2O_3 since this composition was the highest Al_2O_3 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 percent Al_2O_3) (*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 binary eutectic diagrams: SiO_2-mullite in the absence of Al_2O_3 and SiO_2-Al_2O_3 in the absence of mullite. The metastable SiO_2-mullite equilibrium diagram, as presented here, thus effectively explains the controversial melting behavior of mullite and the formation of high-Al_2O_3 mullites only when they are precipitated from a melt. In the presence of Al_2O_3, the solid solution field is limited to a narrow range; thus the highest Al_2O_3 content that can be incorporated into mullite by solid-state reaction is 74.0 percent Al_2O_3. A detailed account of this work will be presented elsewhere (*13*).

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12. Provided by K. S. Mazdiyasni, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio.
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Mesoscale Ocean Eddies in the North Pacific: Westward Propagation

Abstract. *A set of subsurface temperature measurements in the trade wind region northeast of Hawaii reveals large perturbations about the mean state, with zonal wavelengths of 480 kilometers. The perturbations are identified as mesoscale baroclinic eddies, and they appear to drift westward at a rate of 4.7 ± 2.0 centimeters per second. The large-scale (> 1000 kilometers) baroclinic flow at a depth of 200 meters is 1.5 ± 0.7 centimeters per second, also toward the west, and comparable in magnitude with the eddy drift velocity; this finding suggests that the eddy drift is strongly influenced by the large-scale flow. Mesoscale eddies have been discovered in the tropical and subtropical Atlantic Ocean. Their existence in the Pacific Ocean is now confirmed.*

Large perturbations have been observed in the general circulation of the Atlantic Ocean (*1*) with time and horizontal space scales of 100 days and 500 km, respectively. These features are frequently referred to as mesoscale eddies. Eddies with similar characteristics have now been discovered in the North Pacific, from the data of the "Trade Wind Zone Oceanographic Pilot Study" (*2*). To collect these data, the R.V. *Townsend Cromwell* repeatedly oc-

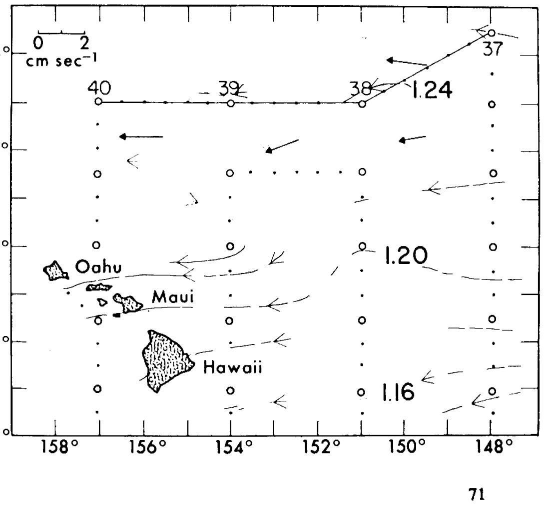

Fig. 1. R.V. *Townsend Cromwell* hydrographic (open circles) and bathythermographic (closed circles) stations. Contours of the dynamic height anomalies (boldface numerals) of the 200-dbar surface relative to the 1200-dbar surface (dashed lines) are based on a 16-month average at each hydrographic station; contour interval, 0.02 dynamic meter. Heavy arrows indicate the mean flow velocity according to the scale in the upper-left corner.