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 (3Al₂O₃·2SiO₂), 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 ~1890° ± 10°C and its solid solution field extends to ~82 percent (by weight) alumina.

Phase equilibrium in the SiO₂-Al₂O₃ system has been studied extensively for almost a century. At high pressures, the equilibrium of the poly-
morphs of Al₂O₃·SiO₂, sillimanite, andalusite, and kyanite, is of signifi-
cance in petrology in the understanding of metamorphic conditions. Under atmospheric conditions, with mullite (3Al₂O₃·2SiO₂) as the only compound, the system is important in ce-
ramics since the clay-rich sediments provide the primary source of raw ma-
terials in ceramics technology. The study of phase equilibrium in the
SiO₂-Al₂O₃ system both under atmospheric conditions and at high pres-
sures has not been conclusive. In this report we present data on the phase equilibria of the SiO₂-Al₂O₃ system at 1.0 atm that support the incongruent melting of mullite at 1828°C and show that under metastable equilibrium condi-
tions congruency could be realized at ~1890°C.

The first systematic study of the SiO₂-Al₂O₃ 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 many 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 addi-
tional evidence that mullite melted con-
gruently. Since then, numerous con-
licting investigations have been con-
ducted, some of which (4, 5) supported the incongruency as originally deter-
mined by Bowen and Greig and some of which (6, 7) supported the con-
gruency 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 gen-
erally accepted one.

In addition to the melting behavior of mullite, a second outstanding prob-
lem of the SiO₂-Al₂O₃ system has been the determination of the stable solid solution range of mullite. Mullite corre-
sponds to a nominal composition of 3Al₂O₃·2SiO₂, and its solid solution range, according to Aramaki and Roy (7), extends from 71.8 to ~74.3 percent (by weight) Al₂O₃. This range, however, is realized only when mullite is prepared by solid-state reactions in the presence of Al₂O₃. When solidified from a melt, the composition of mullite may extend up to 77.3 percent Al₂O₃ (2Al₂O₃·SiO₂), a fact which raises the question of metastability. No satis-
factory explanation for the fact that mullite with a high content of Al₂O₃ is formed only from a melt has yet been presented.

Most phase equilibrium studies on the SiO₂-Al₂O₃ system have been con-
ducted either by the static method of quenching or by differential thermal analysis. These techniques, especially in silicate systems (8) with an in-
congruently 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 SiO₂ and Al₂O₃ and the electron micro-
probe for determining composition pro-
files, demonstrated the power of the diffusion couple technique for obtain-
ing accurate stable phase equilibrium data in the absence of convective flow. They provided new data on the mullite liquidus and also suggested the exis-
tence of a metastable SiO₂-Al₂O₃ binary system without any mullite phase.

In this report we provide additional data, obtained by the diffusion couple technique, on (i) the Al₂O₃ 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 SiO₂ disk on a sapphire substrate. The diffusion an-
neals, 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 per-
cent (by weight) tungsten and 5 per-
percent 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-Al₂O₃ (2054°C).

When a diffusion couple is annealed at constant temperature and pressure, all the phase fields intersected by the corresponding isotherm and the isoobar 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 SiO₂ and thus maximize its growth rate, the fused SiO₂ portion of the diffusion couples was replaced with aluminum silicate glasses of composition C₁ (Fig. 1). These aluminum silicate glasses were prepared from high-purity powders of α-Al₂O₃ and fused SiO₂.

Extensive crystallization of Al₂O₃ or mullite, or both, occurred in the liquid portion of the sapphire-fused SiO₂ 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 SiO₂-Al₂O₃ 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 SiO₂-rich liquid and solid Al₂O₃. Mullite was observed to grow at the sapphire-fused SiO₂ interface at 1803°C but not at 1835°C, an indication that the stable mullite field lies below 1835°C. The incongruent melting temperature was then determined to be 1829°C ±10°C from the intersection of the extrapolated liquidus lines of mullite and Al₂O₃. The mullite solid solution field at 1753°C ranged from 70.5 to 74.0 percent Al₂O₃ and corresponded to a nominal composition of 3Al₂O₃·2SiO₂.

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 Al₂O₃, were prepared from high-purity powders of α-Al₂O₃ and fused SiO₂. The mixtures were sealed in molybdenum crucibles and homogenized at temperatures above that of the Al₂O₃ liquidus shown in Fig. 1. Subsequent heat treatments, at varying temperatures, resulted in the formation of the liquids or solidus compositions corresponding to the stable (11) equilibrium phase diagram outlined with solid lines in Fig. 1.
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 Al₂O₃, the homogenized melts were supercooled through the Al₂O₃ + liquid field without any Al₂O₃ precipitation. However, when an identical or the same mixture was again homogenized and cooled slowly, the precipitation of Al₂O₃ as predicted by the stable Al₂O₃ liquidos was realized (Fig. 2). In fact, with slow cooling rates, it was possible to follow the extension of the Al₂O₃ liquids below the transition temperature and to maintain an Al₂O₃ + liquid (48 percent Al₂O₃) mixture at 1753°C for up to 1 month (Fig. 1).

Similarly, the extension of the mullite liquidos above the transition temperature was realized when an attempt was made to measure the melting temperature of a theorectically dense, poly-crystalline mullite specimen (12) with a composition of 71.8 percent Al₂O₃. The specimen started decomposing into a mixture of liquid and Al₂O₃-rich mullite above ~1816°C, and melting was completed congruently at ~ 1880 ± 10°C without the formation of Al₂O₃. The composition of mullite shifted along the extension of the solids up to 76 percent Al₂O₃ at 1880°C. In Fig. 1, we extended the mullite solids up to 83.2 percent Al₂O₃ since this composition was the highest Al₂O₃ 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 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 liquids and solids lines.

The stable phase diagram, outlined with solid lines in Fig. 1, is the composite of two binary eutectic diagrams: SiO₂-mullite in the absence of Al₂O₃ and SiO₂-Al₂O₃ in the absence of mullite. The metastable SiO₂-mullite equilibrium diagram, as presented here, thus effectively explains the controversial melting behavior of mullite and the formation of high-Al₂O₃ mullites only when they are precipitated from a melt. In the presence of Al₂O₃, the solid solution field is limited to a narrow range; thus the highest Al₂O₃ content that can be incorporated into mullite by solid-state reaction is 74.0 percent Al₂O₃. A detailed account of this work will be presented elsewhere (13).

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References and Notes

11. The possibility of the equilibrium of Al₂O₃ with a metastable liquid is overruled since it is unlikely to have more than one free energy of mixing-composition relationship for the liquid phase and thus there can be only one equilibrium state between Al₂O₃ and the liquid phase.
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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 dy-

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