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DEPENDENCE OF PHASE COMPOSITION OF NUCLEI
AVAILABILITY IN $\text{SiO}_2\text{-Al}_2\text{O}_3$ MIXTURES

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Phase equilibria in the $\text{SiO}_2\text{-Al}_2\text{O}_3$ system have been studied extensively.¹⁻⁵ In general, data obtained by conventional static quenching and phase analysis are difficult to interpret due to persistent metastability in silicate systems. Aksay and Pask⁵, using a diffusion couple technique to determine stable phase equilibria, proposed the stable and metastable phase equilibria boundaries shown in Fig. 1 to explain experimentally observed behavior. The major areas of difference between Fig. 1 and previous phase equilibria studies⁴ is concerned with the nature of the stable equilibria in the high alumina portion of the diagram, i.e., the melting behavior of mullite and the extent of the $\alpha\text{-Al}_2\text{O}_3$ primary phase field. An experiment designed to seek improved resolution in these areas and to clarify the phase behavior in the $\text{SiO}_2\text{-Al}_2\text{O}_3$ system is reported in this study.

Mixtures of composition 60 w/o Al_2O_3 were prepared from fused silica* and $\alpha\text{-Al}_2\text{O}_3$ of three different average particle sizes: Linde $\sim 0.03\mu\text{m}$ ** , A-16*** $\sim 8\mu$ (ultimate median crystal size of $\sim 1\mu\text{m}$), and A-14*** $\sim 45\mu\text{m}$ (ultimate median crystal size of $\sim 6\mu\text{m}$). Well

* -325 mesh powder, Corning 7940, Corning Glass Work, NY.

** Linde Al_2O_3 , Union Carbide.

*** Alcoa XA-16, reactive alumina, and Alcoa A-14, Aluminum Co. of America, Pittsburgh, PA.

blended and dried mixtures were sealed in three molybdenum crucibles by electron beam welding around the rim⁵ and simultaneously heat treated according to the following schedule: Heating to 1725°C in 1 hour, holding at 1725°C for 96 hours, raising the temperature to 1855°C in <2 minutes, holding at 1855°C for 36 hours, and rapidly cooling to room temperature in flowing helium (<2 minutes).

The heat treated samples were prepared for characterization by cutting the crucibles with a diamond saw. Materials from the two halves of the crucibles were used for x-ray and microscopic examinations. X-ray patterns were obtained by crushing the heat treated samples to a size of -320 mesh. Silicon⁺ was used as an internal standard. Polished samples were prepared by ceramographic procedures and examined by interference contrast microscopy. The amount of Mo in the melts was below the microprobe detection limit.

The x-ray diffraction data are shown in Fig. 2. The data show that mullite is the only crystalline phase present in the mixtures prepared with Linde and A-16 Al₂O₃. The mixture formed with A-14 Al₂O₃, however, shows the presence of both mullite and α-Al₂O₃ as indicated in Fig. 2. Ceramographic examination of polished surfaces of all three samples showed mullite crystals in a glass matrix. The Al₂O₃ detected in the x-ray pattern of the A-14 Al₂O₃ mixture is presumably too small in size to be observed by light microscopy. Similar results were obtained for a second series with a heating schedule of 1755°C in 1 hour, raising to 1855°C in a few minutes, holding for 36 hours, and cooling.

⁺Silicon Standard #640, NBS, Washington, DC.

This experimentally observed behavior can be interpreted in terms of the existing diffusion data in the $\text{SiO}_2\text{-Al}_2\text{O}_3$ system^{6,7}, and "nucleation and growth" phenomena. According to Fig. 1, the stable equilibrium phases for a 60 w/o Al_2O_3 composition at 1725-1755°C should be mullite and liquid, and 1855°C, $\alpha\text{-Al}_2\text{O}_3$ and liquid. Data for diffusion in mullite⁷ indicates a chemical diffusivity of $\approx 1.2 \times 10^{-11} \text{ cm}^2/\text{sec}$ at 1725°C. Since the mixtures were held at 1725°C for 96 hours, the thickness of $\alpha\text{-Al}_2\text{O}_3$ that can be expected to react to form mullite at an interface under these diffusion conditions is estimated to be $\approx 11.5\mu\text{m}$. Davis⁶ observed mullite thicknesses of up to $\approx 9.5\mu\text{m}$ in diffusion studies between fused silica-sapphire and glass-sapphire couples at 1750°C for 4 days (96 hours). The mullite thickness of $\approx 11.5\mu\text{m}$ estimated above indicates that, during the 1725°C heat treatment in the present study, the mixtures containing Linde Al_2O_3 and A-16 Al_2O_3 could have reacted completely to form mullite while the A-14 Al_2O_3 mixture would still contain some unreacted $\alpha\text{-Al}_2\text{O}_3$ after 96 hours if the agglomerates were not completely dispersed.

The effect of the subsequent heat treatment at 1855°C can now be interpreted keeping in mind that $\alpha\text{-Al}_2\text{O}_3$ nucleation heterogeneities would be available only in the mixture prepared with A-14 Al_2O_3 . The diffusion data⁷ for Al_2O_3 in the 60 wt% composition at $\approx 1855^\circ\text{C}$ indicates a diffusivity of $\approx 2 \times 10^{-6} \text{ cm}^2/\text{sec}$. According to this data, an $\alpha\text{-Al}_2\text{O}_3$ particle of $\approx 80\mu\text{m}$ should undergo complete dissolution in roughly 100 seconds. If mullite melted congruently under stable equilibrium conditions, then the heat treatment at 1855°C should have resulted in solution of all of the $\alpha\text{-Al}_2\text{O}_3$, and the presence of a single liquid phase; on cooling mullite would be the only phase to precipitate in all three specimens. The fact

that $\alpha\text{-Al}_2\text{O}_3$ was observed in the A-14 Al_2O_3 mixture, in which the starting agglomerate size was $\approx 45\mu\text{m}$, even after 36 hours of heat treatment implies that all of the Al_2O_3 did not react at 1725°C and subsequently did not go into solution since this composition at 1855°C is in the stable phase field of $\alpha\text{-Al}_2\text{O}_3$ plus liquid as shown in Fig. 1. On cooling, the $\alpha\text{-Al}_2\text{O}_3$ persisted because the peritectic reaction to form mullite is far too slow to reach completion⁵ and metastable mullite precipitated from the liquid phase resulting in the presence of $\alpha\text{-Al}_2\text{O}_3$, mullite and glass in this specimen.

On the other hand, the reaction to form mullite in the Linde and A-16 mixtures must have been complete at 1725°C . On heating to 1855°C the mullite under stable equilibrium conditions should melt incongruently to form $\alpha\text{-Al}_2\text{O}_3$ and liquid. Unavailability of Al_2O_3 nuclei due to nucleation difficulties prevented $\alpha\text{-Al}_2\text{O}_3$ precipitation and the occurrence of incongruent melting of mullite. As a result mullite is superheated and melts congruently under metastable equilibrium conditions (following the SiO_2 -mullite metastable phase equilibrium diagram in the absence of $\alpha\text{-Al}_2\text{O}_3$, Fig. 1) to form a single liquid phase. On cooling, mullite precipitates from the liquid phase resulting in the presence of mullite and glass in these specimens. Under all conditions the residue liquid freezes as a metastable glass on cooling.

Our results thus indicate that precipitation of $\alpha\text{-Al}_2\text{O}_3$, either from the liquid phase or on incongruent melting of mullite, is dependent on the availability or generation of nuclei which apparently do not form easily in this system. In the absence of such nuclei metastable phase relationships may appear that could lead to misinterpretation of the stable phase

relationships in the $\text{SiO}_2\text{-Al}_2\text{O}_3$ system.

ACKNOWLEDGMENT

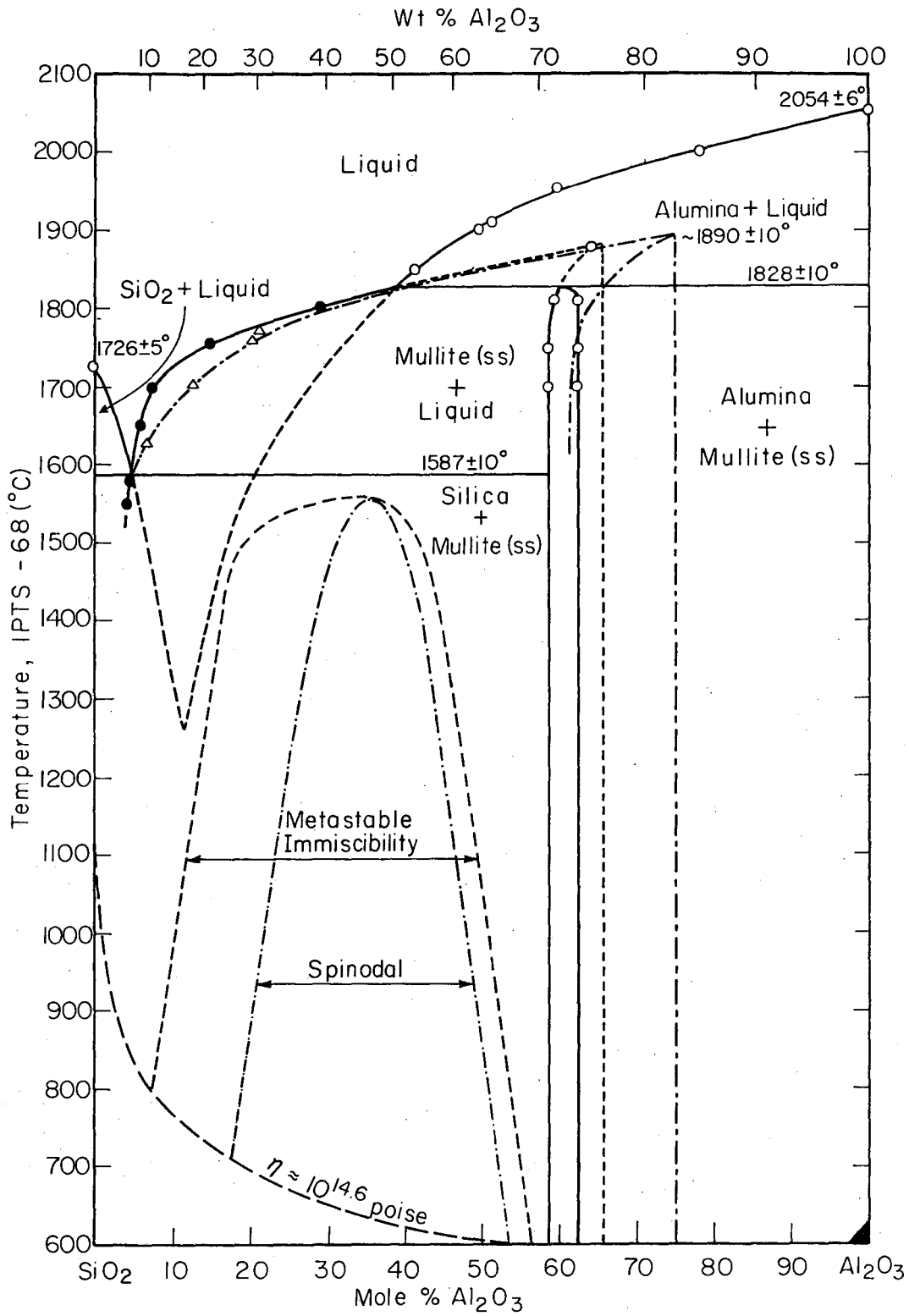
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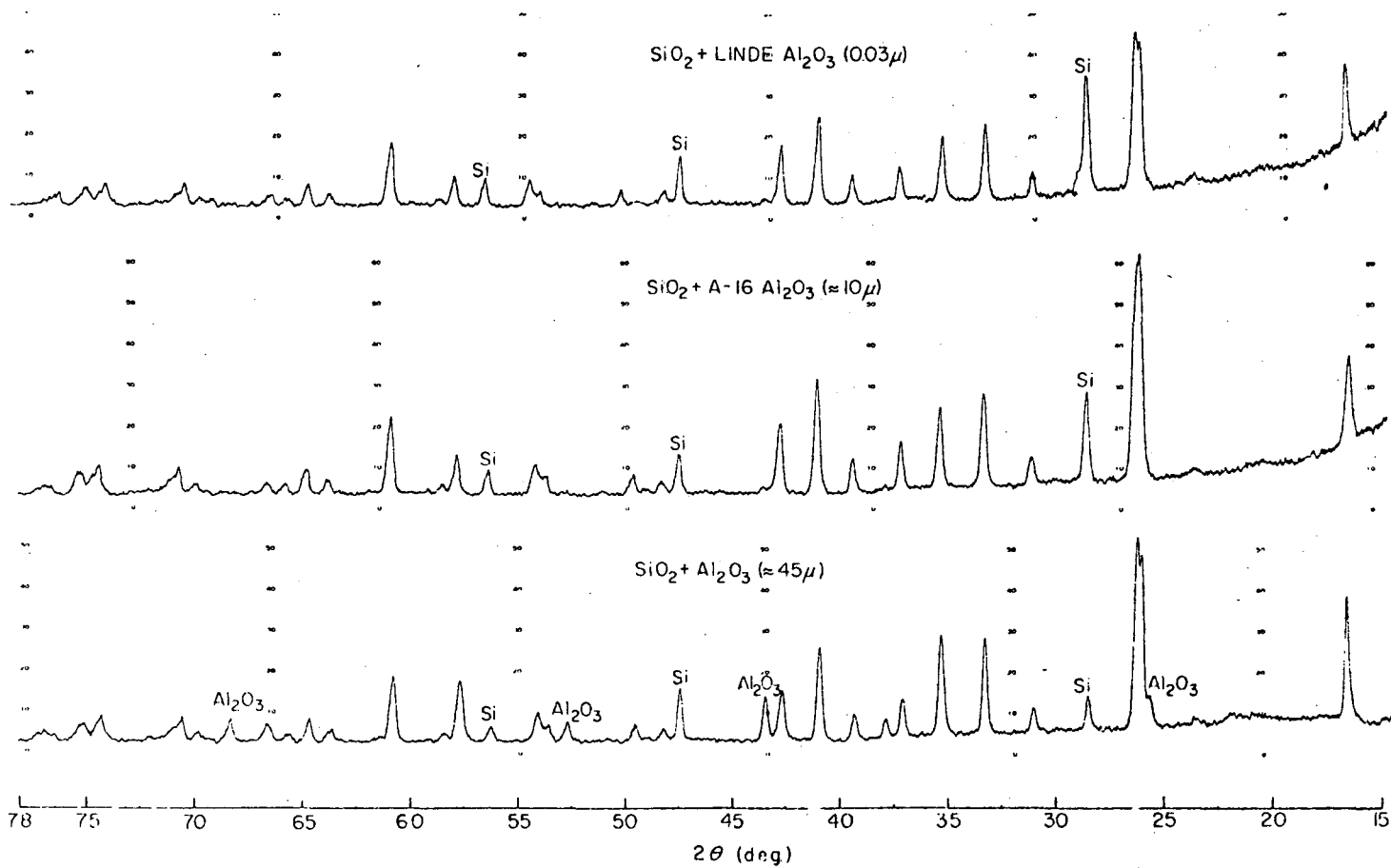
FIGURES

1. Stable and metastable phase equilibrium diagram for $\text{SiO}_2\text{-Al}_2\text{O}_3$ system. 5,8
2. X-ray diffraction data for phases obtained in three mixtures of 60 wt% Al_2O_3 composition containing Al_2O_3 particles of three different sizes.



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Fig. 1



XBL 766-7048

Fig. 2

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