JOURNAL OF MATERIALS SCIENCE 13 (1978) 2449–2454

SiO_2-Al_2O_3 metastable phase equilibrium diagram without mullite

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A metastable binary phase diagram between SiO_2 (cristobalite) and α-Al_2O_3 (corundum) in the absence of any mullite phase is presented. A eutectic is indicated at a temperature of $\approx 1260^\circ$ C and a composition of ≈ 18 wt% (≈ 12 mol%) Al_2O_3. The liquidi of the proposed metastable system were positioned on the basis of the thermodynamic data calculated from the stable equilibrium diagram of Aksay and Pask [2]. Experimental evidence is also presented. A SiO_2–Al_2O_3 melt containing 80 wt% Al_2O_3 cooled at a slow rate in sealed molybdenum crucibles shows crystalline Al_2O_3 plus a glass phase whose composition followed the calculated extension of the stable Al_2O_3 liquidus to lower temperatures. Compacts of cristobalite–corundum mixtures were fired at subsolidus temperatures to estimate the eutectic temperature experimentally. The proposed metastable phase diagram effectively explains the formation of non-crystalline phases in subsolidus reactions, and microstructure obtained on solidification of high alumina melts.

1. Introduction

Phase diagrams indicate the location of stable equilibrium phase boundaries and do not, in general, include data on metastable equilibria. In many systems, especially those forming glasses, kinetic inaccessibility of stable phases makes metastability readily realizable under normal experimental conditions. Development of metastable diagrams for such systems is, therefore, of importance in understanding solid state reaction sequences as well as of practical utility.

In their studies on phase equilibria in the SiO_2–Al_2O_3 system, (Fig. 1) Davis and Pask [1] and Aksay and Pask [2] suggested the existence of a metastable SiO_2–Al_2O_3 phase diagram in the absence of any mullite phase. The occurrence of amorphous phases in solid state reactions between cristobalite and alumina has been reported by several authors. Wahl *et al.* [3] observed by high temperature X-ray diffraction reactions at temperatures as low as 1200° C with no mullite formation. Subsolidus formation of non-crystalline material was also reported by Staley and Brindley [4] in cristobalite–corundum reactions at 1500° C. Kennard *et al.* [5] observed microstructures containing only glass plus alumina during directional solidification of high alumina compositions.

The purpose of this study was to obtain by experimental and thermodynamic methods the metastable phase boundaries in the SiO_2–Al_2O_3 system that occur without precipitation of the mullite phase.

2. Procedures

2.1. Thermodynamic calculations

Using thermodynamic models [6–9] based on regular solution approximations, the activities of Al_2O_3 were calculated along the Al_2O_3 liquidus curve of the stable phase diagram (Fig. 1). The equation for calculating the activities takes the form:

$$\log_{10} a^{L} = \frac{\Delta H_M}{4.575}\left[\frac{1}{T_M} - \frac{1}{T_L}\right] = \log_{10} a^{S} \qquad (1)$$

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where a^L = activity of the liquid in the liquidus composition referred to pure liquid standard state, a^S = activity of solid at the liquidus temperature referred to pure liquid standard state, ΔH_M = heat of melting in cal mol^{-1}, T_M = melting temperature in K, and T_L = liquidus temperature in K.

The main assumptions in the calculation procedure were the constancy of the heat of fusion with temperature, and ideality in the solution mixing of high temperatures. Further, assuming that the partial molal heat of solution of Al_2O_3, $\overline{\Delta H}_{Al_2O_3}$, is independent of temperature [9] over the temperature range of interest, the activity data obtained from Equation 1 were used to calculate isothermal activity coefficients of Al_2O_3 at any chosen temperature T. Thus,

$$\Delta H_{Al_2O_3} = RT_L \log_{10}\gamma_L = RT \log_{10}\gamma_T \quad (2)$$

where T_L and γ_L are liquidus temperature and activity coefficients at the liquidus, respectively, T and γ_T are the temperature and activity coefficients at the chosen temperature T, and R is the gas constant (1.98 cal mol^{-1} K^{-1}); and

$$\log_{10}a_L = \log_{10}\gamma_{10}X \quad (3)$$

where X is the Al_2O_3 mole fraction between 0.4 and 1.0 (liquidus compositions). The isothermal activity coefficients of Al_2O_3 were fitted by the method of least squares to yield an expression of the form:

$$\log_{10}\gamma_T = A + BX + CX^2 + DX^3 \quad (4)$$

where X is the mole fraction of Al_2O_3 and A, B, C and D are constants. Assuming that the fit represented by Equation 4 is valid for Al_2O_3 mole fractions, X, less than 0.4 (Fig. 1) $\log_{10}\gamma_T$ values at chosen mole fractions X, (between 0.15 and 0.34) were obtained. The activity coefficients at the liquidus temperature were then calculated from Equation 2. Using these calculated values of $\log_{10}\gamma_2$ in Equations 1 and 3, the liquidus temperature at each Al_2O_3 mole fraction, X, ($0.15 < X < 0.35$) was calculated. Similar calculations were performed for extension of the SiO_2 liquidus (Fig. 1) to lower temperatures.

2.2. SiO_2–Al_2O_3 melts

High purity fused silica* and reactive α-Al_2O_3† powders were blended in isopropyl alcohol, dried at ≈110° C, and calcined in a platinum crucible at ≈600° C for 12 h. Calcined mixtures containing 80 wt% Al_2O_3 were pressed into molybdenum crucibles (≈11 mm diameter by 15 mm height) which were then sealed around the lid by electron beam welding and helium leak-checked [10]. The sealing and leak-checking procedures were necessary to prevent loss of silica by vaporization during the high temperature melting. The sealed crucibles were heat treated in a tantalum resistance furnace‡ at a temperature of ≈1985° C under a vacuum of ≈10^{-6} Torr. The furnace temperature was electronically controlled through the use of a W5Re–W26Re thermocouple (accuracy ± 7° C at 1800° C). In addition, the crucible temperature was monitored by an optical pyrometer (accuracy ± 10° C at 2000° C) utilizing black body conditions [2]. The pyrometers were calibrated against a NBS secondary standard pyrometer at the melting points of platinum (1772° C) and Al_2O_3 (2054° C). All temperatures reported are based on the 1968 International Practical Temperature Scale (IPTS-68).

2.3. Cristobalite–alumina mixtures

The same high-purity fused silica powder that was used for preparation of the melts was heated in platinum crucibles in air at ≈1420° C for 7 days to obtain the cristobalite phase. Cristobalite–alumina batches were dry-milled and cold-pressed into pellets. The pressed compacts were fired in platinum crucibles in air at temperatures ranging from 1100 to 1280° C for various times. The diameters of the pellets before and after firing were accurately measured to obtain shrinkage data.

2.4. Materials characterization

Crystalline phases obtained after heat treating the SiO_2–Al_2O_3 melts and the cristobalite–corundum pellets were identified by X-ray diffraction using silicon§ as an internal standard after crushing specimens to a powder.

*– 325 mesh Corning 7940 silica, Corning Glass Works, NY (free from metallic impurities).

†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.

‡Richard D. Brew and Co., Concord, NH. Model 14665-4.

§Standard No. 640, NBS, Washington, DC, USA.

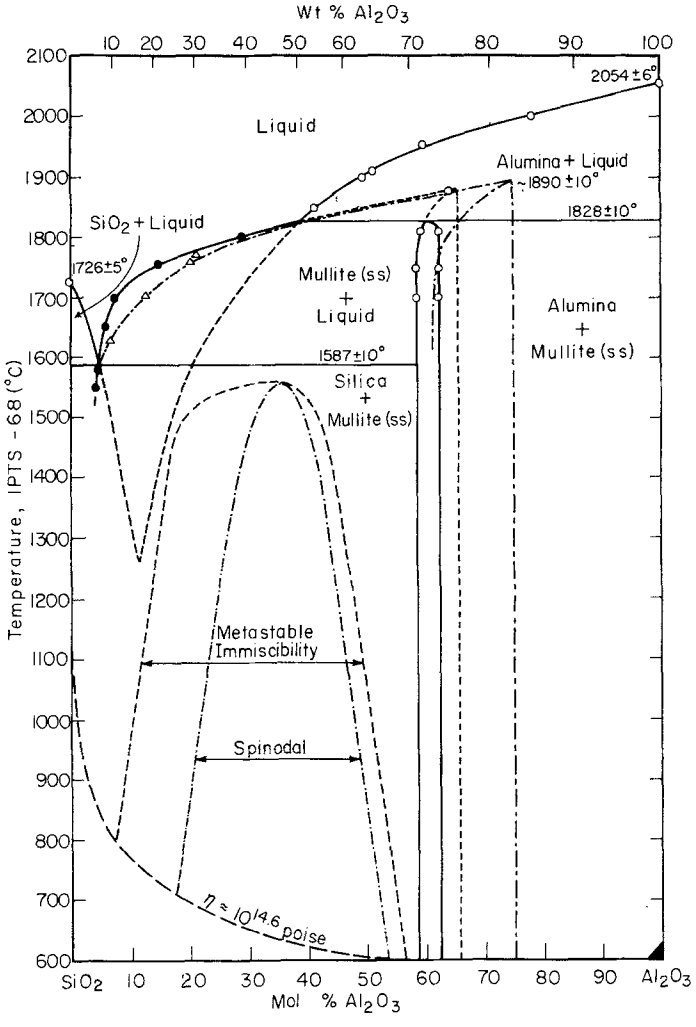

Figure 1 The extensions of the SiO_2 (cristobalite) and α-Al_2O_3 (corundum) liquidi to form the metastable phase equilibrium diagram without mullite superimposed on the SiO_2–Al_2O_3 phase equilibrium diagram reported by Aksay and Pask [2].

The molybdenum crucibles were cut on a diamond saw after the heat treatment and highly polished surfaces were prepared by ceramographic procedures. The polished sections were lightly etched in dilute HF and observed by interference constrast microscopy.*

Samples for chemical analysis of the phases present in the microstructure were prepared by depositing a conducting carbon film on the polished sections and by painting the edges of the mounting material with a carbon–ethanol slurry. The samples were loaded into the vacuum chamber of the electron beam microprobe† and the primary characteristic X-ray intensities emitted from a specific phase in the microstructure were compared with the emission from an identically coated standard of Al_2O_3 and SiO_2. All measurements were made with an accelerating voltage of 15 kV at an X-ray emergence angle of 41°. The AlKα and SiKα intensities were simultaneously recorded on two spectrometers. Intensity counts in 1 μm steps starting with one phase and traversing across the various phases in the microstructure were monitored by logic circuit counters and simultaneously punched on IBM cards for data correction. Corrections for dead time, drift, background, absorption and fluorescence were made through a computer program adapted from Frazer *et al.* for use with the CDC-7600 computer system of this laboratory. Since the difference in atomic

*Nomarski differential interference contrast Micrography, Zeiss Ultraphot II metallograph, Carl Zeiss, W. Germany.
†Materials Analysis Co., Palo Alto, Ca, USA.

numbers of Al and Si is small, no correction for atomic number was made.

3. Results and discussion

3.1. Calculated metastable liquidi

Calculated thermodynamic data for the Al_2O_3 liquidus (Fig. 1), assuming SiO_2 and Al_2O_3 as the mixing components, are listed in Table I. These data were obtained from Equations 1 and 2 using experimentally reported values of the heat of fusion (25 700 cal mol^{-1}) and melting point (2323 K) of Al_2O_3.

The activity coefficients $\log_{10}\gamma_{Al_2O_3}$ listed in Table I were used to calculate isothermal activity coefficients at a particular temperature T. For example, at a temperature of 1673 K the $\log_{10}\gamma^{L}_{Al_2O_3}$ values calculated from Equation 2 were fitted by the least squares method to the expression:

$$\log_{10}\gamma^{1673}_{Al_2O_3} = (-0.187 + 2.05\,X - 3.37\,X^2 + 1.5\,X^3)$$

where X = mole fraction of Al_2O_3 ($0.4 < X < 1.0$). Assuming that this expression is valid for Al_2O_3 mole fractions less than 0.4, isothermal $\log_{10}\gamma_{Al_2O_3}$ values at 1673 K were obtained for Al_2O_3 mole fractions between 0.15 and 0.35. These $\log_{10}\gamma_{Al_2O_3}$ values, when used in Equations 1 and 2, yielded the temperatures of the metastable Al_2O_3 liquidus in the mole fraction range 0.15 to 0.35. Similar calculations were performed for the SiO_2 liquidus. The calculated extensions of the SiO_2 and Al_2O_3 liquidi are shown in Fig. 1 superimposed on the stable and metastable equilibria proposed by Aksay and Pask [2]; a metastable binary eutectic is indicated at a Al_2O_3 mole fraction of 0.12 (18 wt %) and 1260° C. The figure also shows the recently proposed miscibility gap [8].

TABLE I Thermodynamic data from Al_2O_3 liquidus with SiO_2 and Al_2O_3 as mixing components

Mole fraction Al_2O_3 (Liquidus Composition)	Liquidus Temperature (K)	$\log_{10}\gamma_{Al_2O_3}$
1.00	2327	0.0000
0.95	2310	0.0087
0.90	2301	0.0226
0.85	2288	0.0335
0.80	2280	0.0512
0.75	2266	0.0639
0.70	2254	0.0806
0.65	2243	0.1004
0.60	2226	0.1159
0.55	2205	0.1293
0.50	2195	0.1590
0.45	2148	0.1478
0.40	2105	0.1444
0.30	2004	0.1382
0.25	1937	0.1195
0.20	1856	0.0090
0.15	1759	0.0047

3.2. Subsolidus cristobalite–corundum reactions

The eutectic temperature of the metastable SiO_2–Al_2O_3 system was determined experimentally by firing cristobalite–corundum pellets and measuring the shrinkage. Table II summarizes the shrinkage data for a mixture containing ~27 wt % (~18 mol %) Al_2O_3. No mullite formation was detected after firing, as determined by X-ray diffraction. However, the shrinkage of the compacts was increased considerably at firing temperatures above 1250° C. At 1280° C a linear shrinkage of ~13% was observed. This sharp change in sintering characteristics from 1250 to 1280° C suggests the formation of some liquid phase which promotes sintering. Since liquid formation is to be expected at the eutectic temperature in the metastable SiO_2–Al_2O_3 system, the eutectic temperature from the above data is expected to be between 1250 and 1280° C. The correspondence of the calculated eutectic point with the experimental data of 1260° C is good. Furthermore, Staley and Brindley [4] reported an average composition of $Al_2O_3 \cdot 5\,SiO_2$ (≈17 mol % Al_2O_3) for the non-crystalline component formed in reactions between cristobalite and corundum

TABLE II Subsolidus reactions in cristobalite–corundum mixtures (~27 wt % Al_2O_3).

Temperature (° C ± 20)	Time (h)	Diameter of compacts (in.)		Linear shrinkage (%)
		Before firing	After firing	
1130	960	0.250	0.250	Pellet crumbled
1200	150	0.250	0.249	Pellet crumbled
1230	120	0.250	0.249	< 1
1250	120	0.250	0.248	1
1280	24	0.250	0.218	13

Crystalline phases after firing determined by X-ray diffraction: α-Al_2O_3, cristobalite.

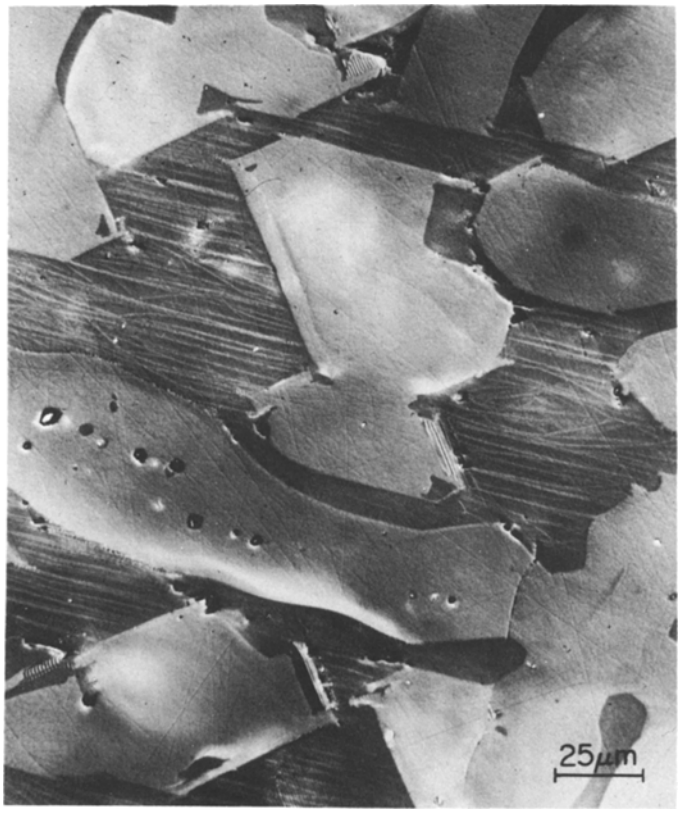

Figure 2 Microstructure of specimen containing 80 wt% Al_2O_3 melted in sealed Mo crucible at ~1985° C for 1.5 h cooled to 1750° C in 1 h, and quenched to room temperature [2]. Both large and needle-like precipitates are α-Al_2O_3 surrounded by a glassy matrix.

mixtures fired at 1500° C. This composition is very close to the Al_2O_3 liquidus at 1500° C shown in Fig. 1.

3.3. microtructures of slowly cooled melts

A SiO_2–Al_2O_3 melt containing 71 mol% (80 wt%) Al_2O_3 was cooled from the homogenization temperature of ~1985° C to 1750° C in 1 h to allow the precipitation and growth of Al_2O_3 [2]; a rapid quench from the homogenization temperature always resulted in crystallization of mullite plus residual glass [2, 10]. The microstructure of the slowly cooled specimen is shown in Fig. 2. X-ray diffraction indicated the presence of α-Al_2O_3 as the only crystalline phase. An average composition of ≈48 wt% Al_2O_3 (~36 mol% Al_2O_3) was reported for the matrix surrounding the primary Al_2O_3 precipitates. Since this average value was obtained by an electron microprobe scan of the matrix consisting of glass plus the fine Al_2O_3 needles, it is likely to indicate a slightly higher Al_2O_3 content than the actual glass composition. Consequently, the composition of the metastable Al_2O_3 liquidus at 1750° C may be expected to be slightly less than 48 wt% Al_2O_3 (~36 mol% Al_2O_3). The Al_2O_3 liquidus obtained in the present work (Fig. 1) shows a composition of ≈44 wt% Al_2O_3 (~32 mol% Al_2O_3) at 1750° C.

The observations of Kennard *et al.* [5] also provided indirect evidence for the existence of a metastable SiO_2–Al_2O_3 diagram. They solidified SiO_2–Al_2O_3 ingots by the Bridgman technique. A 78 wt% Al_2O_3 melt yielded a microstructure of glass plus crystalline Al_2O_3; the glass composition was reported to be ~23 wt% Al_2O_3 (~15 mol% Al_2O_3) on the basis of refractive index measurements. This composition lies at a temperature of ~1470° C on the Al_2O_3 liquidus shown in Fig. 1. The metastable Al_2O_3 plus glass assemblage observed by Kennard *et al.* can thus be explained on the basis of the presented metastable diagram.

4. Summary

A metastable phase diagram between SiO_2 (cristobalite) and α-Al_2O_3 (corundum) without mullite is proposed. The eutectic point of the diagram lies at a temperature of ≈1260° C at an Al_2O_3 composition of ≈18 wt% (≈12 mol%) Al_2O_3. The proposed diagram explains experimentally

observed reactions in cristabolite–corundum compacts and microstructures of slowly cooled $SiO_2-Al_2O_3$ melts with high Al_2O_3 contents.

Acknowledgement

This work was supported by the Division of Basic Energy Sciences, US Department of Energy.

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Received 31 January and accepted 3 March 1978.