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Subhash H. Risbud and Joseph A. Pask

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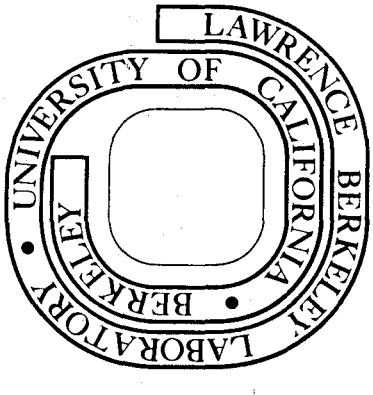

DISCLAIMER

MULLITE CRYSTALLIZATION FROM SiO_2-Al_2O_3 MELTS

Subhash H. Risbud* and Joseph A. Pask

Materials and Molecular Research Division, Lawrence Berkeley Laboratory
and Department of Materials Science and Mineral Engineering,
University of California, Berkeley, California 94720

ABSTRACT

SiO_2-Al_2O_3 melts containing 42 and 60 wt% Al_2O_3 were homogenized at 2090°C (±10°C) and crystallized by various heat treatment schedules in sealed molybdenum crucibles. Mullite containing ≈78 wt% Al_2O_3 precipitated from the 60 wt% Al_2O_3 melts at ≈1325±20°C which is the boundary of a previously calculated liquid miscibility gap. When the homogenized melts were heat treated within the above gap, the Al_2O_3 in the mullite decreased with a corresponding increase in the Al_2O_3 content of the glass. A similar decrease of Al_2O_3 in mullite was observed on reheating crystallized melts at 1725°±10°C; the lowest Al_2O_3 content (≈73.5 wt%) was in melts that were reheated for 110 hours. All melts indicated that the composition of the precipitating mullite was sensitive to the heat treatment of the melts.

*Now an Assistant Professor in the Mechanical Engineering Department, Metallurgy Option, University of Nebraska, Lincoln, NE.

I. INTRODUCTION

The SiO_2-Al_2O_3 system[1] is the basis of a large number of industrial materials in ceramic and glass technology. Microstructure evolution in glass-ceramic materials often involves intermediate metastable stages as the melt approaches its stable crystalline assemblage. Subliquidus immiscibility in the SiO_2-Al_2O_3 system has been suggested by several previous studies,[2-4] but the relationship to melt crystallization is not clear. In the present work, crystallization studies were conducted on selected melt compositions at temperatures chosen in relation to the phase boundary of a previously calculated miscibility gap.[4] Analyses of the two phase microstructures by electron beam microprobe (EM) made possible an estimate of the temperature at which crystallization commences on cooling a melt.

II. EXPERIMENTAL PROCEDURE

A. Materials Preparation

Mixtures containing 42 and 60 wt% Al_2O_3 were prepared from fused silica* and reactive α-Al_2O_3 powders.** After heating in air at ~600°C for ~12 h, the mixtures were loaded into molybdenum crucibles (≈11 mm diameter x 15 mm height) which were sealed around the lid by electron beam welding and helium leak checked. Sealing was necessary to prevent loss of silica by evaporation during the high temperature melting. The sealed crucibles were heat treated in a tantalum resistance furnace under a vacuum of 10^{-6} torr.

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*-325 mesh powder, Corning 7940, Corning Glass Works, NY; no measurable cation impurities, but contains ~1000ppm of OH and ~100ppm of C .

**Alcoa XA-16, Aluminum Co. of America, Pittsburgh, PA; chemical analysis (wt%): 0.08 Na_2O, 0.05 SiO_2, 0.03 CaO, 0.05 MgO, 0.01 Fe_2O_3, 0.0015 MnO 0.0002 Cr_2O_3, less than 0.001 B_2O_3.

The temperature of the furnace chamber was electronically controlled through the use of a W5Re-W26Re thermocouple (accuracy ±7° at 1800°C). In addition, the temperature of the samples in the furnace was monitored by optical pyrometers (±10°C accuracy at 2000°C) utilizing black body conditions. The pyrometers were calibrated against a NBS secondary standard pyrometer at the melting point of platinum (1772°C) and Al_2O_3 (2054°C).[5] All temperatures reported are based on the 1968 International Practical Temperature Scale (IPTS-68).[6]

All melts were homogenized at a temperature of 2090°C (±10°C) for ≈55 minutes prior to subsequent heat treatments. Two heating schedules were used. In the first schedule, the homogenized melts were rapidly cooled to a predetermined subliquidus temperature, held at the undercooled temperature for a fixed time, and quenched to room temperature by turning off the power and introducing helium (about 1 to 3 mins). In the second schedule, homogenized melts were heat treated by cooling to some subliquidus temperature and reheating at 1725°±10°C for various times before quenching to room temperature. The crucibles were then cut on a diamond saw, and the cross-sections were polished for ceramographic examination and phase composition analysis by EM.

B. Materials Characterization

The polished samples were observed in reflected light by interference-contrast micrography.† In most cases a light etch in 10% HF aqueous solution for ~30 sec at room temperature was necessary to observe the microstructure. Specimens for scanning electron microscopy

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†Nomarski differential interference-contrast microscope, Zeiss Ultraphot II metallograph, Carl Zeiss, W. Germany.

(SEM) consisted of fracture surfaces of the heat treated melts etched in dilute HF. A thin film of gold was evaporated onto the samples prior to examination. Some polished sections were also examined in the SEM after etching in 10% HF for ~2 min.

Samples for phase identification by X-ray diffraction were crushed in a mortar with a pestle to pass a -325 mesh sieve. Approximately 10wt% silicon was added as an internal standard.

The chemical composition of the phases present in the microstructures was determined with an electron beam microprobe.[††] Standards of Al_2O_3 and SiO_2 were used. Mo contamination from the crucible was found to be negligible. The AlKα and SiKα intensities were simultaneously recorded on two spectrometers. Intensity counts in 1 μm steps starting with one phase and transversing 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, absorptions and fluorescence were made through a computer program adapted from Frazier et al.[7] for use with the CDC-7600 computer system of this laboratory.

III. RESULTS AND DISCUSSION

The 42 and 60 wt% Al_2O_3 compositions were selected for the crystallization study because the former lies near the center and the latter at the Al_2O_3-rich phase boundary of the calculated miscibility gap under the mullite liquidus (Fig. 1).[4]

[††]Materials Analysis Co., Model 400, Palo Alto, CA.

1. Compositions with 60 wt% Al_2O_3

Microstructures obtained after homogenized melts were held for 1-1/2 hours at undercooling temperatures of 1862, 1725, 1500 and 600°C and quenched were similar. The ones for the specimens held at 1862 and 600°C, shown in Figs. 2a and 2d, are typical; the upper part of the latter figures shows an end-on orientation of the elongated mullite crystals. In all cases mullite needles (~200 to 250 μm long) are surrounded by a siliceous glass matrix, and X-ray diffraction indicated mullite as the only crystalline phase. An analysis of the mullite needles and the glass matrix by point beam EM showed an Al_2O_3 content of ~78 wt% in the mullite and ~18.5 wt% in the glass (Table 1).

Figure 2b shows a typical microstructure for melts held for 1-1/2 hours at undercooling temperatures of 1325, 1220, and 1025°C and quenched. No significant microstructural changes were observed on comparison with the above group although the mullite crystals were slightly finer. The chemical composition of the crystals, however, was ≈76 wt% Al_2O_3 and the glass composition was ≈20.5 wt% Al_2O_3. Similar heat treatments at undercooling temperatures of 925 and 730°C indicated the mullite composition to be ≈74.5 and 75 wt% Al_2O_3 and the glass, ≈21 wt%; the microstructure of the former is shown in Fig. 2c.

The specimen undercooled to 600°C was similar to an as-quenched specimen since it was equivalent to quenching because this temperature lies below the estimated glass transformation temperature ($\eta = 10^{14.6}$ poise) for the 60 wt% Al_2O_3 composition (Fig. 1). All of the above data suggest that the liquid is supercooled without any crystallization down to 1500°C and that crystallization is initiated at some temperature

between 1500 and 1325°C. This interpretation is supported by the fact that a specimen supercooled to 1500°C for 15 mins, reheated at 1725°C for 1-1/2 hours, and quenched was similar to the specimens supercooled to 1862, 1725°C, and 1500°C and quenched, (Fig. 2a). Thus, no nucleation or crystallization occurred as long as the temperature of the initial melt was kept above the boundary of the miscibility gap after homogenizing above the liquidus temperature. This temperature closely corresponds to the calculated miscibility gap boundary value of ~1310°C at 60 wt% Al_2O_3.[4]

Also, the composition of mullite obtained by holding the homogenized melt at 925°C, within the miscibility gap, prior to quenching depended on the time of holding. As shown in Table 1, after a holding time of 15 minutes, mullite had a composition of ~77.6 wt% Al_2O_3 composition. When the undercooled melt was held for longer times, the mullite composition decreased and reached a value of ~73.2 wt% Al_2O_3 after 24 hours. This data suggest that the initially formed mullite on cooling into the immiscibility region has ~78.5 wt% Al_2O_3, and that the viscosity of the liquid is sufficiently low at 950°C to allow the occurrence of exsolution of Al_2O_3. The Al_2O_3 rejected by the mullite crystals during this reaction enriches the neighboring glass as indicated in the table.

On the other hand, undercooling to 925°C in the spinodal region for 15 minutes followed by heating at 1725°C for 1-1/2 hours resulted in a change in morphology and composition. A finer crystal size is evident in Fig. 3 in comparison with Fig. 2a. It also shows lower Al_2O_3 contents in the mullite, ≈75 wt%, and in the glass, ≈16 wt%, in comparison with only undercooling to 1725°C. In accordance with previously described

observations it is expected that, on cooling, mullite with high Al_2O_3 (≈78.5 wt%) precipitated and began to exsolve Al_2O_3 with all subsequent heating schedules.

In order to evaluate the rate at which the precipitated mullite changed in composition and the changes in morphology, melts quenched to room temperature were heated at 1725°C for 1-1/2, 5-1/2 and 70 hours. The data shown in Table 2 indicates that the Al_2O_3 content of the mullite decreased from ≈78.4 to ≈74.5 wt% and that of the glass increased from ≈18.5 to ≈23.5 wt%. The original rod-like mullite crystals (≈20 x 250 μm) in the as-quenched specimens (Figs. 2 and 3) recrystallized and then grew in cross-section size as seen in Fig. 4. The rod-like structure was still retained as shown by an SEM photograph of a fractured surface of the specimen held at 1725°C for 1-1/2 hours (Fig. 4d).

A change in liquid structure with increased holding time at a temperature above the miscibility gap, which subsequently affects the mullite composition, is suggested by the following experiments. A homogenized melt undercooled to 1725°C for 1-1/2 hours, quenched to room temperature, reheated to 1725°C for 1-1/2 hours, and quenched showed ≈75.5 wt% Al_2O_3 in the mullite and 16 wt% in the glass. This mullite value compares with ≈78.4 wt% in the specimen undercooled to 1725°C and quenched, and with ≈76.5 wt% on quenching and then reheating to 1725°C. A comparison of specimens 60-15R and 60-17 also indicates this phenomenon.

2. Compositions with 42 wt% Al_2O_3

Compositions with 42 wt% Al_2O_3 were also homogenized at 2090°C, quenched to room temperature and then heated to 1725°C for 1-1/2, 5-1/2,

18 and 110 hours. Figure 5 shows SEM photomicrographs of a quenched specimen after light HF etching and specimens heated for 1-1/2 and 5-1/2 hours. The crystals in the quenched specimen were ≈0.02 μm thick, showed a mullite X-ray diffraction pattern, but were too small for point EM analysis. The interconnectivity apparent in the as-quenched specimen (42-Q) as seen in Fig. 5a may be attributed to structure evolution by the spinodal mechanism of liquid immiscibility although this is not a necessary conclusion. On reheating, recrystallization and coarsening of the crystals occurred with time while the Al_2O_3 content in the mullite remained at ≈73.5 wt% and in the glass at ≈16 wt%. An optical photomicrograph of the 1-1/2 hour specimen (Fig. 5d) shows an overall structure. The randomness of the mullite needles in comparison with the 60 wt% Al_2O_3 specimens (Fig. 4) is due to the smaller amount of mullite. A close examination of the 5-1/2 hour specimen in Figs. 5b to 5d indicates a skeletal growth process.

The two additional experiments in Table 3 based on preliminary undercooling treatments prior to holding at 1725°C for 1-1/2 hours and quenching indicated, just as in the case of the 60 wt% Al_2O_3 composition, the sensitivity of the mullite composition to the history of the heat treatment of the melt. This behavior also suggests that the liquid structure must be sensitive to the homogenizing and undercooling treatment imposed on the melt.

3. Relationship Between Crystallization and Liquid Immiscibility

Since experiments with 60 wt% Al_2O_3 melt indicate that mullite crystallization commences at a temperature between about 1325°C and 1550°C and since the phase boundary of the calculated metastable liquid

immiscibility[4] (Fig. 1) is at about 1310°, a correlative analysis is suggested.

In general, a metastable glass phase forms because the more stable crystalline phase is kinetically unfavorable. Also, if the system exhibits metastable liquid immiscibility, the metastable glass phase will separate into two glasses unless the more thermodynamically stable crystallization intervenes. However, a possibility exists that the precipitation of the crystalline phase is forbidden energetically until after the precursor metastable immiscibility reaction is complete, as suggested by Cahn.[8] Let us consider the free energy of mixing versus composition curves for the metastable liquid L and solid M_M at a temperature corresponding to about 1300°C, as shown schematically in Fig. 6 since thermodynamic data are not available; schematics of the stable solids S, M_s and A are also included. If metastable mullite of 78 wt% Al_2O_3 were to precipitate from the homogeneous metastable liquid of 60 wt% Al_2O_3, i.e. before separation occurs, the equilibrium free energy of the liquid would be represented by G_L; if the free energy of the solid is actually G_{M_s}, however, there is an overall increase of free energy of $G_L - G_{M_s}$, which prevents its crystallization. On the other hand, after the liquid immiscibility step is complete, the free energy of the phase separated liquids would correspond to G_{Sp}. Transformation to the solid phase would now involve a decrease in free energy from S_{Sp} to G_{M_s}. The actual composition of the solid precipitating from the high Al_2O_3 liquid and its change in composition with time depends on the shape, change in shape, and the relative position of the free energy curves. The absence of the stable M_s and S phases indicates that their precipitation is

kinetically unfavorable.

In contrast to the view of liquid immiscibility as a precursor to crystallization, it is also possible to consider the direct crystallization of a melt in terms of fluctuation theories.[9] According to these theories the melt, although macroscopically homogeneous, contains regions of fluctuational heterogeneities varying in size from 200 to 5000Å. These heterogeneous compositional and structural fluctuations do not have sharp interfaces but resemble the "future" precipitating phase (stable or metastable).

It becomes difficult to identify the actual process especially if the high Al_2O_3 liquid phase readily crystallizes to a mullite, since a fluctuation mechanism is also used to explain the occurrence of liquid immiscibility. The separation and crystallization occur rapidly (1 to 3 minutes) as observed experimentally in this study because no long range atomic diffusion is involved.

The close association of these experimental data on the 60 wt% Al_2O_3 melts with the position of the calculated miscibility gap[4] supports the occurrence of liquid immiscibility as a precursor to metastable mullite crystallization from melts. MacDowell and Beall[3] were able to quench melts more rapidly and observed liquid immiscibility in glasses in this range of compositions prior to mullite crystallization, which also supports this concept.

IV. SUMMARY AND CONCLUSIONS

The quenching or cooling time of ≈1 to 3 mins to room temperature was slow enough for metastable mullite to crystallize from the melts in all of the experiments. The composition of the mullite, however, was

dependent on the composition of the melts and the heat treatment imposed on them.

Melts with 60 wt% Al_2O_3 were undercooled to ≈1325°C before precipitation of metastable mullite occurred. Experimentally, it appears that the initial mullite composition has ≈78 wt% Al_2O_3. With continued heating at temperatures below 1325°C or subsequent heating at 1725°C, exsolution of Al_2O_3 occurs; the lowest Al_2O_3 content obtained was ≈73.2 wt%. This value is close to the mullite solidus composition for the metastable phase equilibrium diagram for SiO_2-2:1 type or metastable mullite proposed by Aksay and Pask[1] (Fig. 1). In contrast, stable 3:2 type mullite grown slowly at these temperatures by solid state reaction in a semi-infinite diffusion couple contains 70.5 wt% Al_2O_3 in equilibrium with excess liquid.[1]

The number of melts with 42 wt% Al_2O_3 were insufficient to present general conclusions. The highest Al_2O_3 content in precipitated mullite was ≈75 wt% and dropped to ≈73.5 wt% by exsolution of Al_2O_3 on heating at 1725°C which compares favorably with the value for the 60 wt% Al_2O_3 melts.

Melts of both compositions were quenched to room temperature after homogenization and then heated with increasing time at 1725°C. The quenched microstructure of the 42 wt% Al_2O_3 composition shows interconnectivity and suggests a precursor spinodal separation; the 60 wt% Al_2O_3 specimens show large mullite crystals. On reheating to 1725°C, recrystallization and growth of crystals occurs, and the Al_2O_3 content decreases and approaches a composition of ≈73.5 wt%. This exsolution occurs more slowly for the higher Al_2O_3 content melt probably because

of the larger amount of mullite phase. It is diffucult to obtain accurate mullite growth rates because of their irregular shapes although an approximate analysis of the growth rates from both melts indicated linear relationships between thickness and square root of time consistent with a diffusion process.

ACKNOWLEDGEMENT

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Table I. Phase Compositions in Undercooled 60 wt% Al_2O_3 Melts.*

Sample #	Undercooling, °C	Composition	
		Mullite, wt% Al_2O_3	Glass, wt% Al_2O_3
60-Q	Quench	78.4	18.5
60-18	1862(1-1/2 hrs)	77.8	18.5
60-17	1725(1 1/2 hrs)	78.4	17.8
60-15	1500(1 1/2 hrs)	78.0	18.0
60-13	1325(1 1/2 hrs)	76.1	20.7
60-12	1220(1 1/2 hrs)	76.0	19.5
60-10	1025(1 1/2 hrs)	75.9	20.0
60-9	925(15 mins)	77.6	18.0
60-9	925(1 1/2 hrs)	74.5	20.8
60-9	925(5 1/2 hrs)	73.7	22.5
60-9	925(24 hrs)	73.2	23.0
60-7	730(1 1/2 hrs)	74.9	20.9
60-6	600(1 1/2 hrs)	78.8	17.9

*All melts homogenized at 2090°C for ~55 mins, and quenched after undercooling treatment.

Table II. Phase Compositions in Undercooled and Reheated 60 wt% Al_2O_3 Melts.*

Sample #	Undercooling, °C	Time at 1725±10°C	Composition	
			Mullite, wt% Al_2O_3	Glass, wt% Al_2O_3
60-925	925(15 mins)	1 1/2 hrs	76.0	16.0
60-17RR	1725(1 1/2 hrs) + Room Temp.	1 1/2 hrs	75.5	16.0
60-15R	1500(15 mins)	1 1/2 hrs	77.9	19.0
60QR	Room Temp.	none	78.4	18.5
60QR-1	Room Temp.	1 1/2 hrs	76.5	18.9
60QR-5	Room Temp.	5 1/2 hrs	76.0	19.8
60QR-7	Room Temp.	70 hrs	74.5	23.5

*All melts homogenized at 2090°C for ~55 mins, and quenched after 1725±10°C treatment.

Table III. Phase Compositions in Undercooled and Reheated 42 wt% Al_2O_3 Melts.*

Sample #	Undercooling °C	Time at 1725±10°C	Composition	
			Mullite, wt% Al_2O_3	Glass, wt% Al_2O_3
42-15R	1500(15 min)	1 1/2 hrs	75.0	16.9
42-17RR	1725(1 1/2 hrs) + Room Temp.	1 1/2 hrs	74.5	19.6
42QR-1	Room Temp.	1 1/2 hrs	73.5	16.0
42QR-5	Room Temp.	5 1/2 hrs.	73.2	15.6
42QR-18	Room Temp.	18 hrs	73.8	16.2
42QR-110	Room Temp.	110 hrs	73.5	16.4

*All melts homogenized at 2090°C for ~55 mins, and quenched after 1725±10°C treatment.

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(b) E. A. Porai-Koshits, ibid., p. 1.

FIGURES

1. Calculated liquid miscibility gap with spinodal (corresponding to heat of fusion of mullite ~27,000 cals/mole)[4] superimposed on the stable phase diagram.[1]
2. Microstructures of 60 wt% Al_2O_3 melts homogenized at 2090°C and prior to quenching undercooled to (a)-1862°C, (b)-1220°C, (c)-925°C, and (d)-600°C.
3. Microstructure of 60 wt% Al_2O_3 melt homogenized at 2090°C, undercooled to 925°C for 15 mins, heated at 1725°C for 1-1/2 hrs, and quenched.
4. Microstructure of 60 wt% Al_2O_3 melt homogenized at 2090°C, quenched to room temperature, and reheated at 1725°C for (a)-1-1/2 hrs, (b)-5-1/2 hrs, and (c)-70 hrs followed by quenching. (d) shows SEM fractography of specimen (b).
5. SEM microstructures of 42 wt% Al_2O_3 melt homogenized at 2090°C, quenched to room temperature: (a) after etching in 10% HF solution for ~2 mins, (b) after reheating at 1725°C for 1-1/2 hrs, and (c) after reheating for 5-1/2 hrs. (d) shows another part of specimen (b) by reflected optical microscopy.
6. Schematic of free energy vs. composition diagram at ~1300°C illustrating conditions under which a liquid immiscibility reaction acts as a precursor to the precipitation of metastable mullite.

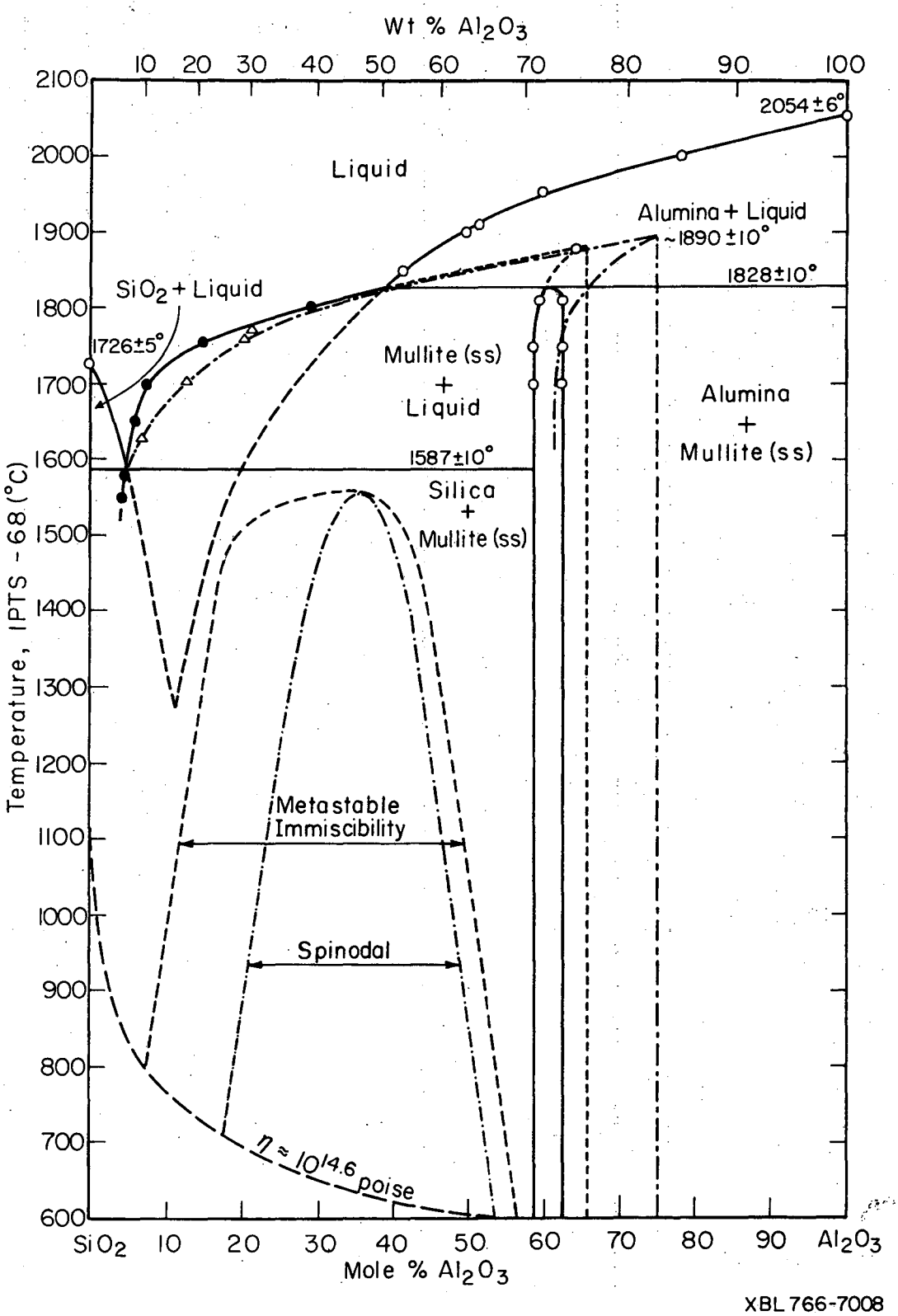

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Fig. 1

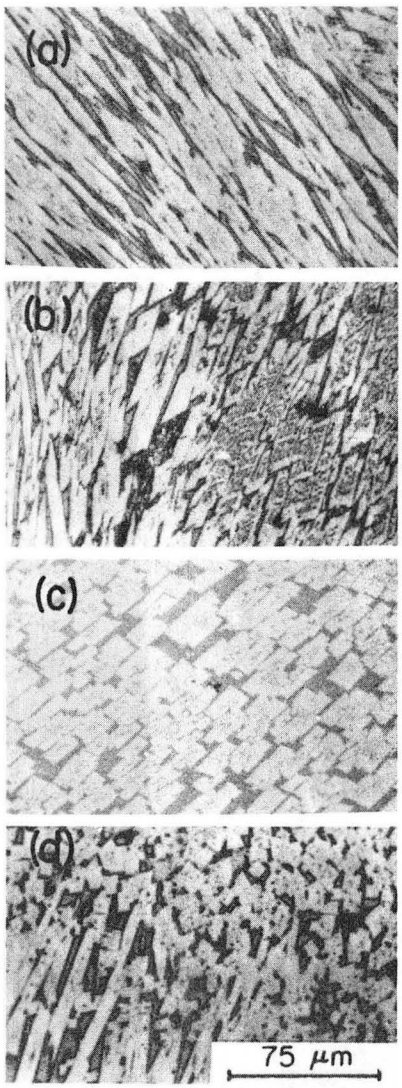

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Fig. 2

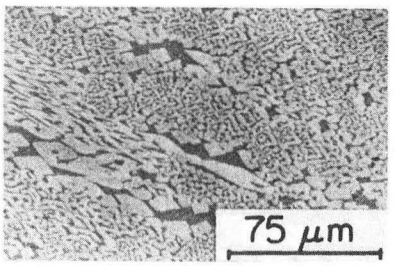

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Fig. 3

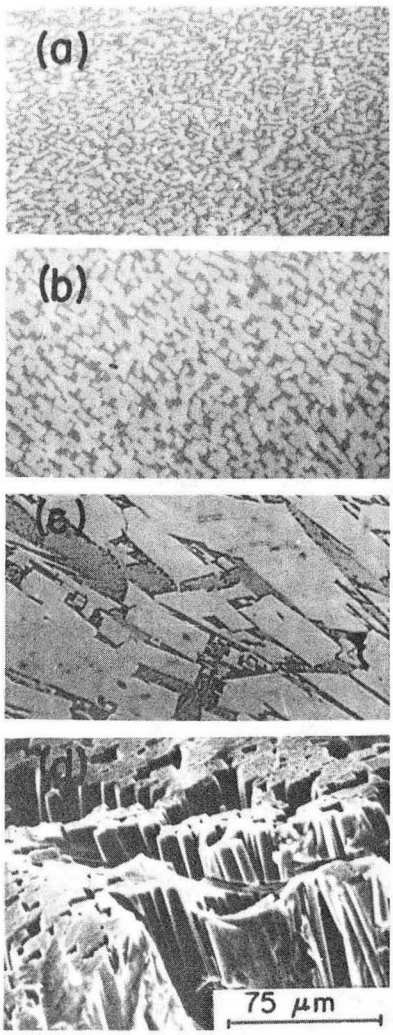

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Fig. 4

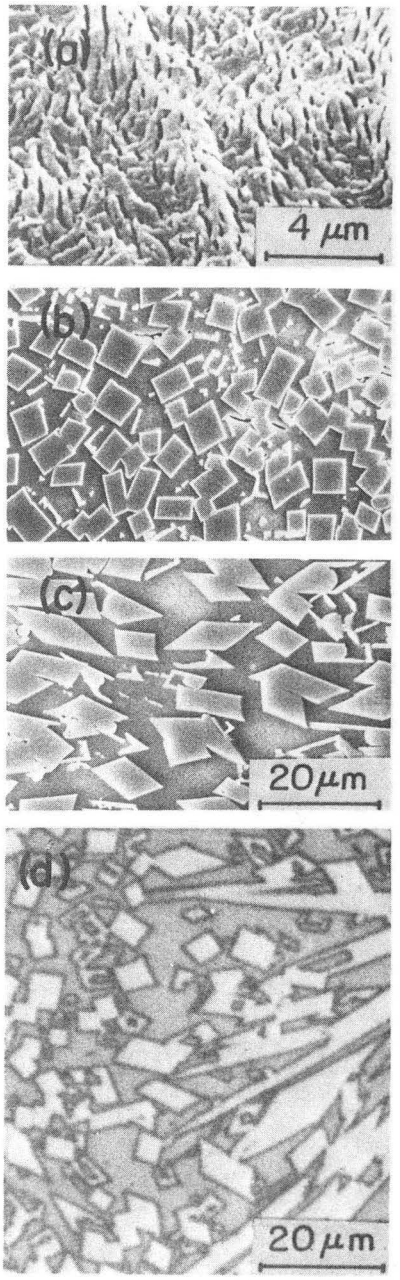

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Fig. 5

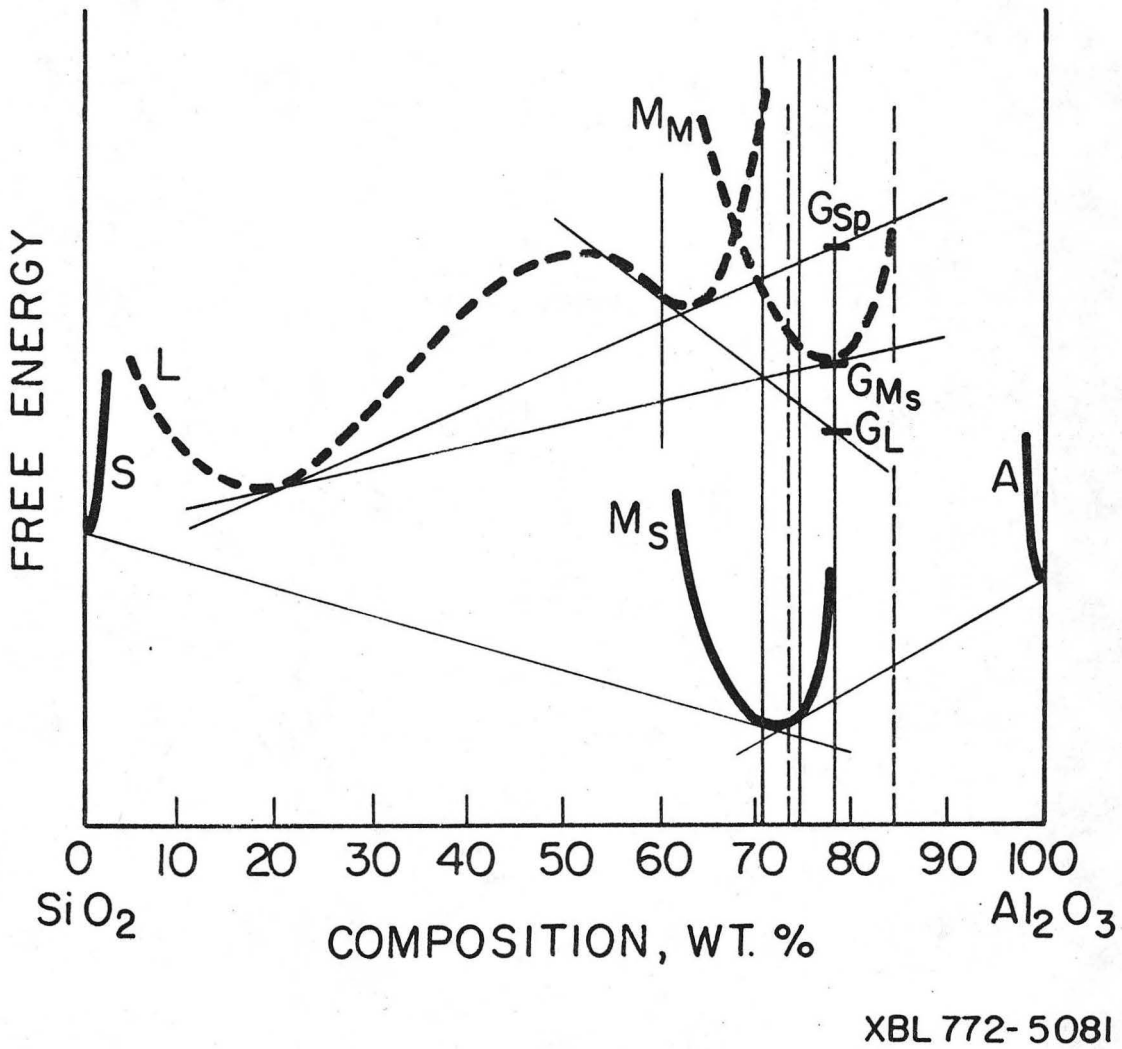

Fig. 6

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