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Publication Date
1982-05-01

LBL-12457
Preprint c.2

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Molecular
Research Division

Submitted to Ceramurgia International

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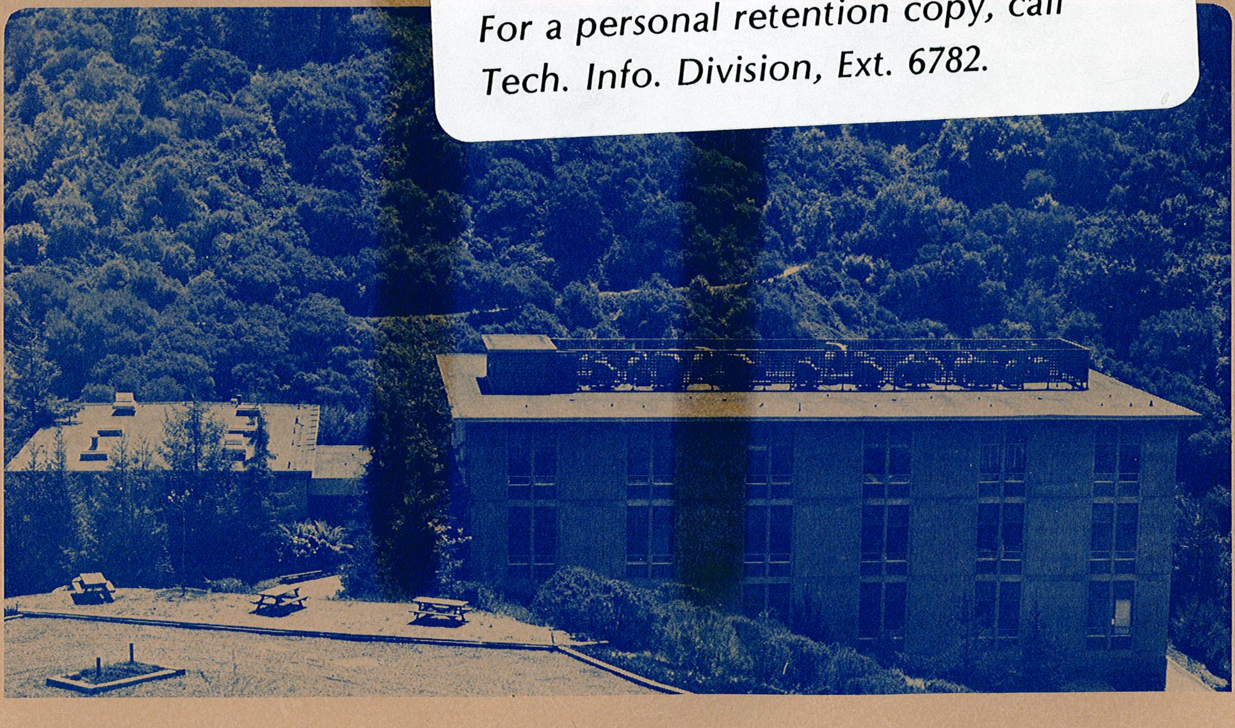
May 1982



Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

SINTERING OF α-Al_2O_3 - AMORPHOUS SILICA COMPACTS

by

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ABSTRACT

Sintering of α-Al_2O_3 - amorphous SiO_2 compacts at temperatures of 1350-1500°C indicate shrinkage maxima at about 15 mole % which approximately correspond to the eutectic of the metastable phase equilibrium diagram for SiO_2-Al_2O_3 without mullite. The retardation of densification of α-Al_2O_3 compacts with additions of SiO_2 up to about 50 mole % at temperatures above about 1370°C is associated with the appearance of mullite.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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1. INTRODUCTION

Metastable reactions between silica and alumina have been observed below the eutectic temperature in the Al_2O_3-SiO_2 stable phase equilibrium diagram (Fig. 1). Wahl et al[1] reported a reaction in powder mixtures of cristobalite and corundum as low as 1200°C which showed no mullite. Staley and Brindley[2] observed the formation of mullite at the sub-solidus temperatures of 1500° and 1550°C using pressed pellets of cristobalite in contact with pressed pellets of Al_2O_3 as well as mixed powders, but concluded that the formation of an amorphous phase was an essential feature of the reaction. No mullite was observed when the polycrystalline pellet was replaced by sapphire. Davis and Pask[3] in reaction studies in the Al_2O_3-SiO_2 system at subsolidus temperatures postulated the existence of a metastable phase equilibrium diagram with no mullite which caused the initial formation of a liquid that acted as a precursor for the formation of mullite. Aksay and Pask[4] supported the existence of such a metastable diagram by performing melt experiments under conditions that should have formed mullite but only α-Al_2O_3 and glassy phase were present. As shown in Fig. 1, the diagram was obtained by extension of the SiO_2 (cristobalite) and α-Al_2O_3 liquidi curves of the stable phase equilibrium diagram until intersection at approximately 1265°C and 16 wt % Al_2O_3 (12 mole %). Risbud and Pask[5] verified this metastable equilibrium diagram thermodynamically and by controlled heating of selected powder mixtures of cristobalite and α-Al_2O_3.

The purpose of this project was to study the sintering behavior of non-prereacted powder mixtures of α-Al_2O_3 and fused SiO_2 and to understand the effect of crystallization of mullite on sintering.

2. EXPERIMENTAL

Corning 7940 fused SiO_2 (-325 mesh) and Alcoa XA-16 reactive α-Al_2O_3 were used as the starting materials. Mixtures at 5 mole % Al_2O_3 intervals up to 30 mole % and then at 10 mole % intervals were prepared. Each powder composition was mixed with isopropyl alcohol for 24 h in PVC (polyvinyl chloride) bottles using teflon balls. Each slurry was then magnetically stirred while drying on a hot plate at 60°C, followed by 24 h drying in an oven at 160°C. The resulting cakes were broken up with the use of an automated lucite mortar and pestle for 30 s.

Specimens were prepared by placing 0.5g of material in a die with an 0.88 cm diameter hole and pressing at 5000 kg/cm^2. The heights of the green or unfired specimens were then determined by the degree of packing of the powders. The resulting calculated bulk molar volumes (cm^3/mole) of the green compacts versus mole % Al_2O_3 are shown in Fig. 2. The figure also shows the theoretical molar volume of solids in each of the green compacts. The difference between these 2 curves represents the equivalent total pore volume per mole of material, the minimum or densest packing occurring at 30 mole % Al_2O_3 with a packing factor of 0.71 (for SiO_2-0.69 and for Al_2O_3-0.59). The nature of the curves further indicates that a range of particle sizes exists, that the average size of the Sio_2 particles is larger than that of the Al_2O_3 particles, and that the difference in the average particle size of the two powders is not large enough to obtain the densest packing.[6]

The compacts were fired in a bottom-loading Super-Kanthal furnace by being placed on a pedestal which was raised into the furnace. Schedule 1, used for firings up to 1500°C, consisted of inserting the pedestal directly into the furnace at 1100°C, heating to the desired temperature at an approximate rate of 150°C/h, cooling to 1100°C in the furnace by turning the power off, and then cooling in air. Schedule II, after 1100°C, consisted of inserting the pedestal into the furnace at 1500°C, holding for the desired time, and then cooling in air.

3. RESULTS

Curves for fired molar bulk volume vs composition on heating to a number of temperatures from 1350° to 1500°C according to Schedule 1 are shown in Fig. 2. This volume was obtained by dividing the mean molecular weight of the mixture by the bulk density, which was obtained by dividing the dry weight of a compact by its geometrically measured bulk volume. The figure also shows the curve for the apparent theoretical molar volume of the solid phases after heating to 1400°C (Calculated from apparent density determined by using the suspended saturated weight in water); a comparison with the curve for the theoretical molar volumes of the starting solids indicates that the change in solid volume due to changes in phase composition caused by heating are not large. The position of the fired bulk volume curves relative to the green bulk volume and apparent theoretical volume curves is an indication of the degree of volume shrinkage and the remaining volume of pores as affected by composition and temperature. Specific values for fractional volume shrinkage can be obtained by dividing ($\bar{V}_{green}$-$\bar{V}_{fired}$) by $\bar{V}_{green}$ and for fractional pore volume by dividing ($\bar{V}_{fired}$ - $\bar{V}_{solid}$) by $\bar{V}_{fired}$: as an example, values for a compact with 50 mole % Al_2O_3 at 1400°C (using data in Fig. 2) are (39.9-34.3)/39.9 = 0.14 and (34.3-26.2)/34.3 - 0.24, respectively. The linear firing shrinkage for the series is shown in Fig. 3. Maxima in shrinkage and minima in bulk volume occur in the range of 10 to 30 mole % of Al_2O_3 at all temperatures and in high Al_2O_3 mixtures above 1400°C.

Conversion of amorphous SiO_2 to cristobalite occurred readily during the firing of the compacts. The amounts formed as determined by X-ray diffraction (XRD) using Cu K_α radiation of fired specimens are shown in Fig. 4. Similarly, data for mullite are shown in Fig. 5. Mullite was first detected by XRD at 1480°C in the mixture with 70 mole % Al_2O_3. However, reactions start earlier as indicated by a differential thermal analysis curve for a mixture containing 15 mole % Al_2O_3 which showed an exothermic peak starting at $\sim$1425°C. The volume changes during firing due to these phase transformations plus the formation of any aluminosilicate liquids that are retained as glasses is approximately equivalent to the difference between the apparent theoretical molar volume after firing and the theoretical molar volume of the solid phases before firing assuming that the fused SiO_2 was present as cristobalite; these are shown in Fig. 6 for a number of heatings.

4. DISCUSSION

The reactions that occur during firing affect the densification of the mixtures. If metastable equilibrium were achieved in the SiO_2-Al_2O_3 system in the absence of mullite in the test temperature range, the equilibrium phases would be an aluminum silicate liquid and cristobalite or α-Al_2O_3 depending on the composition (Fig. 1). On the other hand, if stable equilibrium were achieved, the equilibrium phases would be mullite and cristobalite or α-Al_2O_3. An additional complication existed in this study since the starting SiO_2 was amorphous instead of crystalline. The results indicate that the compact under the experimental conditions first underwent metastable reactions which were associated with changes in the theoretical molar volume of the solid phases, followed by a transition to the stable phase equilibrium state which was not completely reached.

The fused SiO_2 crystallized to form cristobalite, even metastably below 1470°C, the stable range for tridymite (Fig. 4). This crystallization is probably responsible for the SiO_2 compacts not reaching complete densification. With additions of α-Al_2O_3 the crystallizing cristobalite reacts to form the metastable eutectic with subsequent solution by the unsaturated fused SiO_2, which causes an increase of the amount of liquid with a lower viscosity and a higher apparent molar volume resulting in faster densification, particularly in the metastable eutectic range of compositions (Figs. 2 and 3). Up to 1400°C this reaction is slow enough so that the denser packing in the region of 30 mole % contributes to the shape of the shrinkage/composition curve. At higher temperatures the eutectic and solution reactions are fast enough to mask the effect of the greater unfired density in the region of maximum packing resulting in maximum shrinkage at about the metastable eutectic composition.

Other factors play a role in the high alumina range of the composition series. The sintering data for α-Al_2O_3 heated according to Schedule I indicate an overall expansion beyond 1450°C, and at 1500°C the shrinkage is less than that for a number of mixtures with additions of SiO_2. It is postulated that this effect is due to microcracking since a number of larger cracks were actually visible optically; these were introduced because of the high shrinkage of fine alumina powder combined with the severity of the cooling step. Also, of significance is the fact that the Al_2O_3

shrinkage is retarded above 1380° with silica contents at about 30 to 60 mole %. In this range the liquid that forms at Al_2O_3/SiO_2 contacts immediately wets the Al_2O_3 surfaces and reacts to form mullite (Fig. 5) which tends to add regidity to the existing α-Al_2O_3 framework. However, at temperatures up to $\sim$1400°C before any mullite forms the metastable eutectic liquid that forms increases the densification as expected. The microcracking experienced by the α-Al_2O_3 compacts at about 1500°C is apparently minimized in the presence of some liquid phase introduced by the SiO_2 additions.

The higher shrinkages shown by the entire series fired with Schedule II at 1500°C are postulated to be due to the slower transformation of fused SiO_2 to cristobalite and longer soaking time.

ACKNOWLEDGMENT

Thanks are extended to Amar P. S. Rana and Osamu Aiko for discussions and assistance in performing experiments. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U. S. Department of Energy under Contract Number DE-AC03-76SF00098.

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Figure Captions

Fig. 1 The extension of the SiO_2 (cristobalite) and α-Al_2O_3 (corundum) liquidi to form the metastable phase equilibrium diagram without mullite superimposed on the stable SiO_2-Al_2O_3 phase equilibrium diagram reported by Aksay and Pask.[4]

Fig. 2. Molar bulk volume and molar apparent theoretical volume for green (unfired) SiO_2-Al_2O_3 compacts. Molar bulk volume for compacts fired at a number of temperatures. Apparent theoretical volume for compacts fired at 1400°C.

Fig. 3. Linear shrinkage curves for compacts fired up to 1350 to 1500°C according to Schedule I, and at 1500°C for 6 to 24 h according to Schedule II.

Fig. 4. Relative amount of cristobalite formed after heating compacts up to a number of temperatures with Schedule I and at 1500°C for 6 hrs (Schedule II).

Fig. 5. Relative amounts of mullite formed after heating compacts at several temperatures with Schedule I (open points) and for several times at 1500°C with Schedule II (closed points).

Fig. 6. Changes in apparent theoretical molar volume of compacts after firing to 1350 to 1500°C according to Schedule I relative to calculated theoretical molar volume of unfired solid phases assuming that the fused SiO_2 was present as cristobalite.

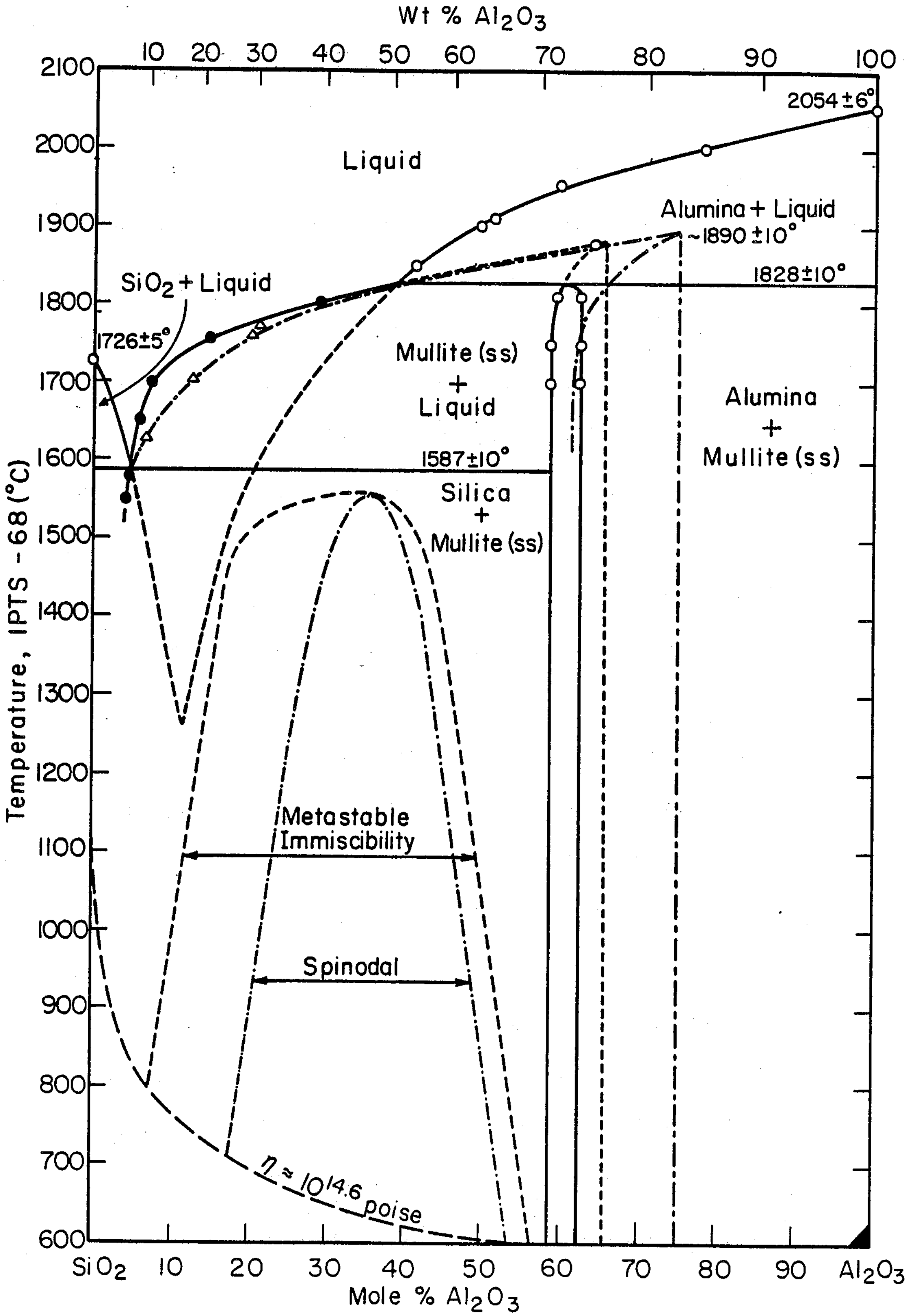

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Fig. 1

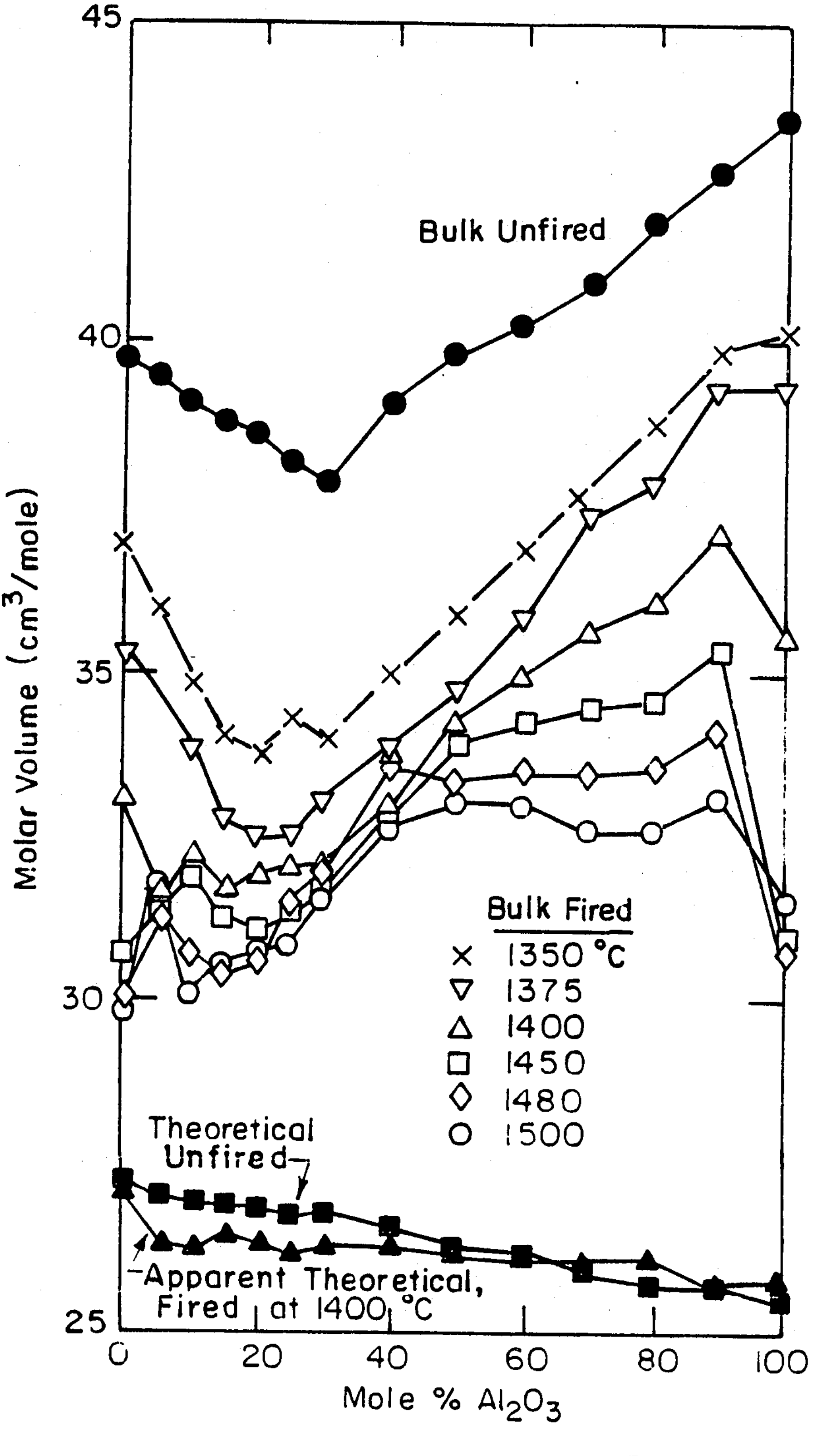
45
40
35
30
25
Molar Volume (cm^3/mole)
0
20
40
60
80
100
Mole % Al_2O_3
Bulk Unfired
Bulk Fired
× 1350 °C
▽ 1375
△ 1400
□ 1450
◇ 1480
○ 1500
Theoretical Unfired
Apparent Theoretical, Fired at 1400 °C
XBL808-5780

Fig. 2

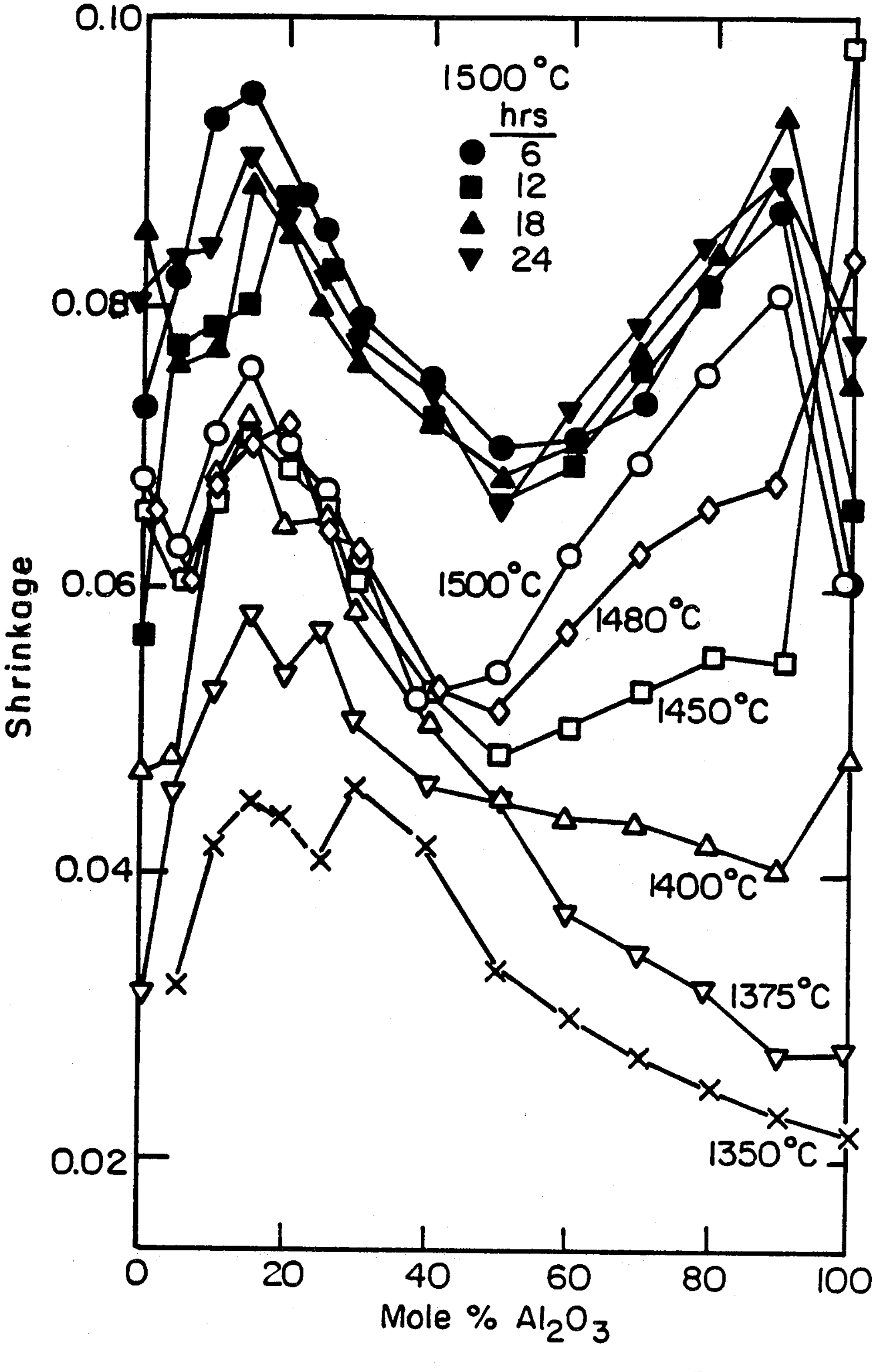
0.10
0.08
0.06
0.04
0.02
Shrinkage
0
20
40
60
80
100
Mole % Al_2O_3
1500°C
hrs
● 6
■ 12
▲ 18
▼ 24
1500°C
1480°C
1450°C
1400°C
1375°C
1350°C
XBL808-5779

Fig. 3

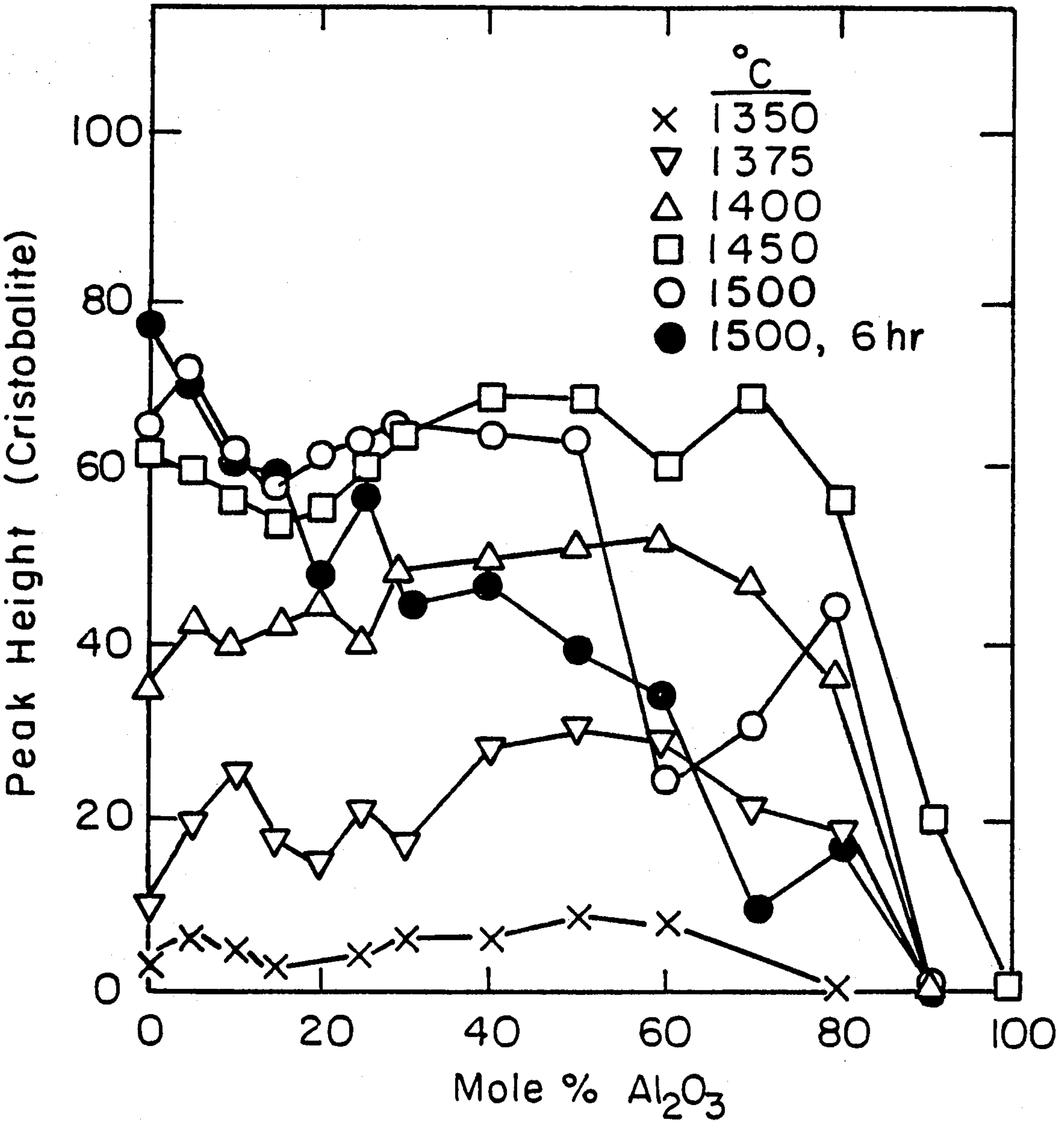

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Fig. 4

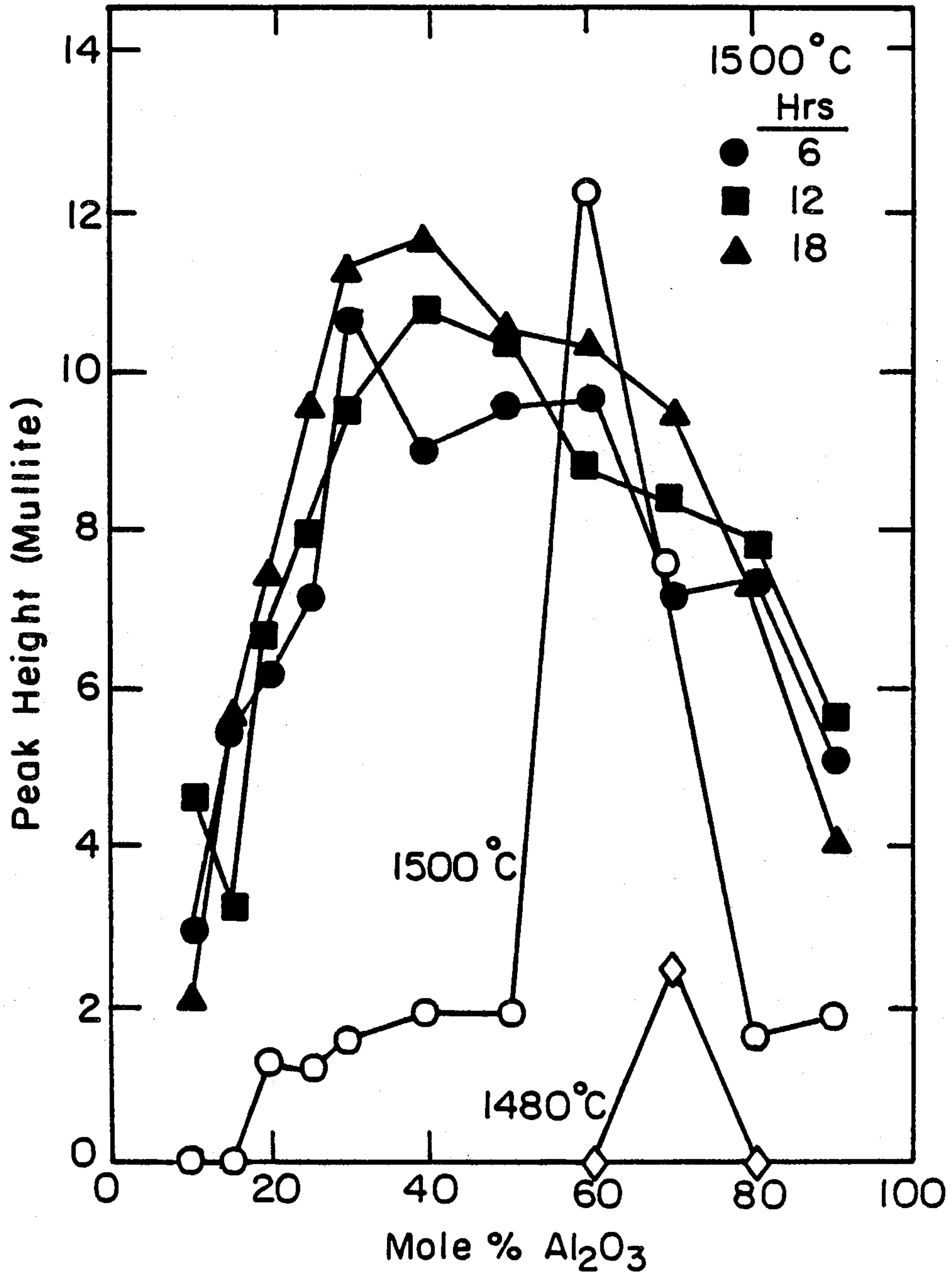

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Fig. 5

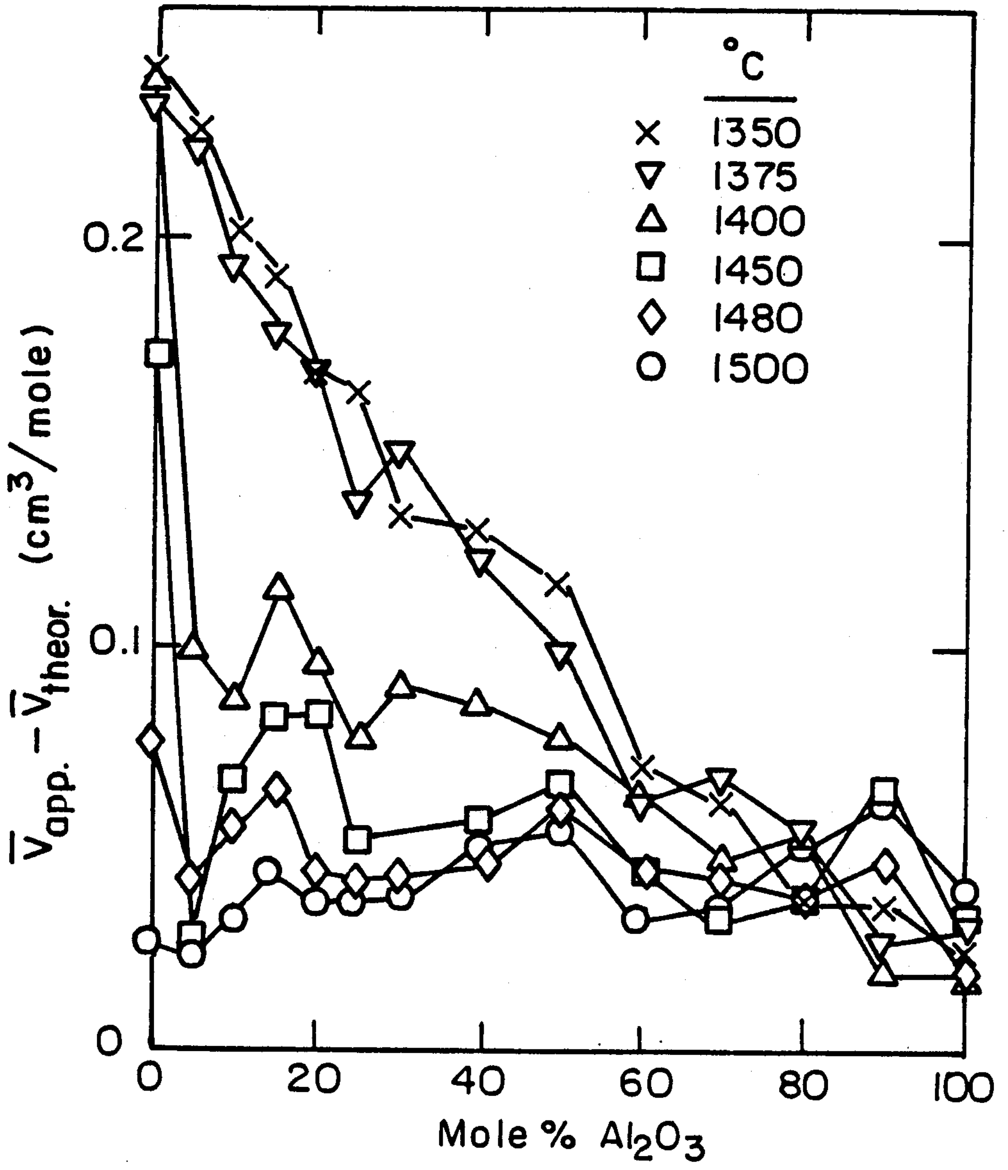

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Fig. 6