

Phase Equilibrium Relationships in the System $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-SiO}_2$: an Update

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I. INTRODUCTION

For a number of reasons, mullite ($3\text{Al}_2\text{O}_3.2\text{SiO}_2$) has long been considered the silicate of the ceramists. Among its most attractive characteristics, from the point of view of advanced ceramics, are the low thermal expansion coefficient, low dielectric constant and high chemical stability. However, comparatively modest mechanical properties have hindered some of mullite's most promising applications. A lot of effort has been dedicated to improving its mechanical characteristics and during the past decade it has been shown how the addition of zirconia particles can, and does, enhance the mechanical properties of otherwise brittle matrices[1-2], which brought about new expectations for mullite-based ceramics.

An important contribution to the special appeal of mullite-zirconia composites came about when Claussen and Jahn[3] introduced the reaction-sintering concept, *i.e.* a seemingly straightforward mechanism by which zirconia-toughened mullite materials can be produced from the reaction between alumina and zircon (ZrSiO_4). The original version (Figure 1) of the phase diagram of the system $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-SiO}_2$, due to Budnikov and Litvakovskii[4], dates back to 1956. Since the 60's however, more accurate versions of the phase diagrams of the binary systems

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involved have been reported, namely the $\text{ZrO}_2\text{-SiO}_2$ system by W. C. Buttermann & W. R. Foster (1967)[4], the $\text{Al}_2\text{O}_3\text{-ZrO}_2$ system by G. Cevalles (1968)[4], and the $\text{Al}_2\text{O}_3\text{-SiO}_2$ system by A. Pask (1988)[5], and these clearly showed that the available ternary diagram needed to be updated.

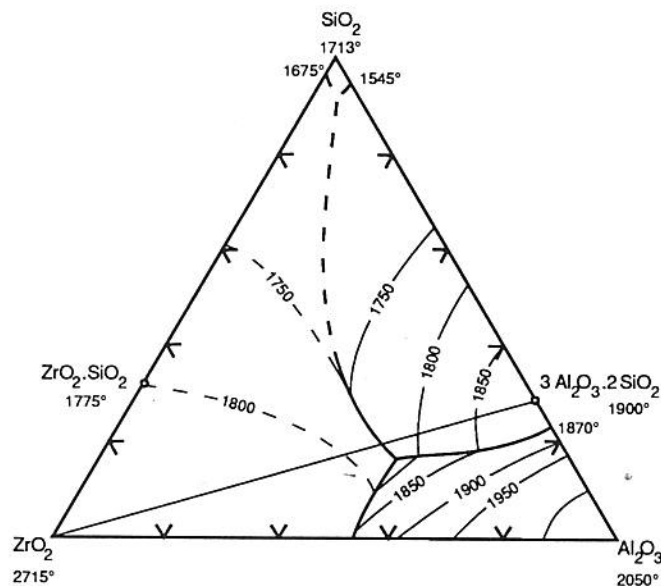


Figure 1. Phase diagram of the system $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-SiO}_2$, after P. P. Budnikov & A. A. Litvakovskii, 1956[4]

II. EXPERIMENTAL PROCEDURE

In the present work, selected compositions were prepared using alumina powder 90% below $2\mu\text{m}$, with purity better than 99.08% and BET specific surface area of $7.34\text{m}^2/\text{g}$, zircon powder with $32.9\text{SiO}_2+65.9\text{ZrO}_2$ (wt.%), with an average grain size of $1.35\mu\text{m}$ and a BET specific surface area of $6.0\text{m}^2/\text{g}$, and colloidal silica with a purity better than 99.00%.

The adequate amounts of the reactants were dry-mixed and uniaxially dry-pressed (100MPa) into 6mm cylindrical pellets. These were then wrapped in platinum foil, fired in a tube furnace at temperatures ranging from 1550 to 1750°C for 6 to 24h, and water-quenched. The resulting samples were then prepared for X-ray powder diffraction and SEM analysis (polished surface). The compositions of some of the phases so identified were evaluated semi-quantitatively by EPMA.

III. RESULTS AND DISCUSSION

(1) Initial melting temperature in the alumina-zirconia-mullite triangle

In the binaries that form two of the edges of this triangle, initial melting occurs at $1828\pm 10^\circ\text{C}$ in the $\text{Al}_2\text{O}_3\text{-SiO}_2$ system, and at $1710\pm 10^\circ\text{C}$ in the $\text{Al}_2\text{O}_3\text{-ZrO}_2$ system. If the ternary invariant point is of the eutectic type, it must occur at a temperature below $1710\pm 10^\circ\text{C}$. Simple observation of samples fired above 1700°C suggests

the presence of an abundant liquid phase: these samples show significant shrinkage, are shiny and have rounded contours.

Most of the SEM observed microstructures seem to present a continuous phase around the crystalline grains (the usual appearance of a liquid phase), even at temperatures below 1700°C. At these lower temperatures, however, this phase is not clearly defined and sometimes is detected by X-ray diffraction. EPMA showed that its chemical composition is close to mullite, ranging from 75.5 to 79.6 wt.% Al_2O_3 . Given that the samples were prepared with alumina and zircon (and silica when needed), the reaction-sintering mechanism should prevail, and it has been shown[6] that the development of crystalline mullite is always delayed relatively to the production of silica as a result of the decomposition of zircon. It might thus be concluded that this continuous phase is an amorphous mullite solid solution.

In the microstructures of samples fired at higher temperatures (1735 and 1750°C), the well developed liquid (glassy) phase usually contains great number of dendritic zirconia crystals (Figure 2), and in some cases also needle-like alumina and/or mullite crystals, presumed to have precipitated from the liquid phase during the quenching process.

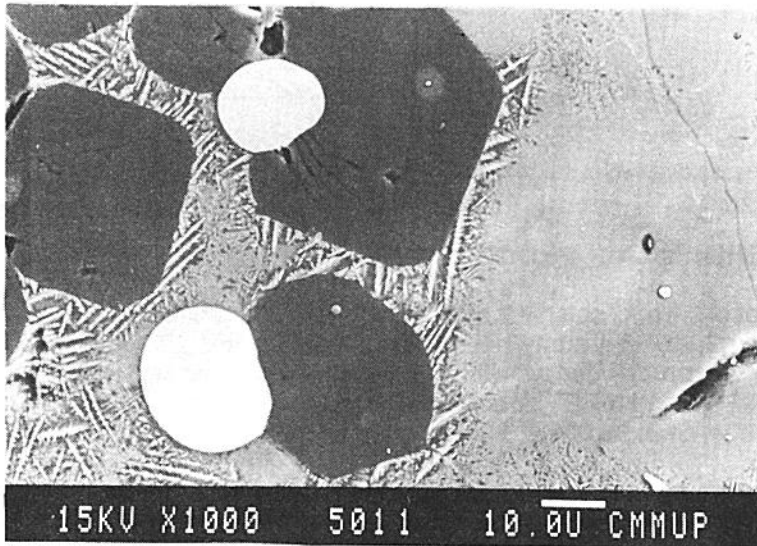


Figure 2. Microstructure of the sample with 55% Al_2O_3 +35% ZrO_2 +10% SiO_2 , fired at 1750°C for 24h, showing round white zirconia grains, polygonal dark alumina grains and zirconia dendrite crystals in the devitrified light grey liquid phase

In the microstructures of samples fired at 1700 and 1715°C, in which a liquid phase is not readily identified, the grain morphology of the crystalline phases suggests a growth mechanism in the presence of a liquid phase, namely zirconia grains appear as rounded crystals, mullite grains develop a lath-like, angular shape and alumina grains present polygonal contours. These morphologies are consistently observed in the microstructures of all samples fired above 1700°C (Figure 3).

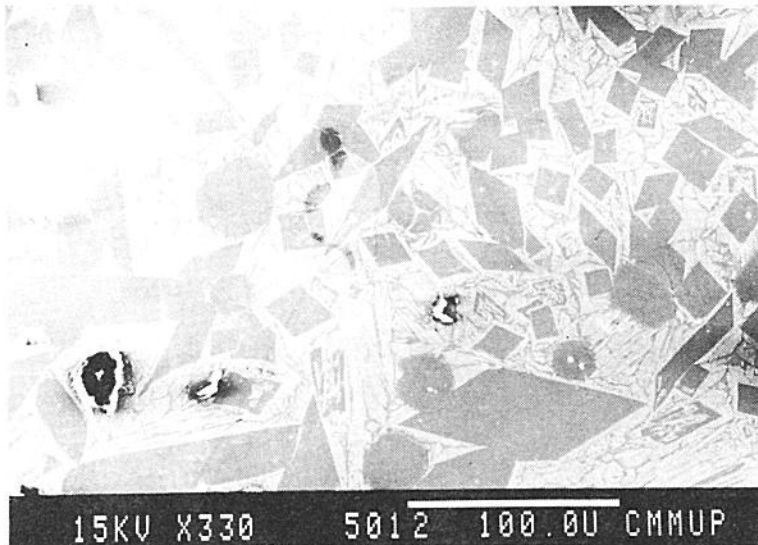


Figure 3. Microstructure of the sample with 55% Al_2O_3 +25% ZrO_2 +20% SiO_2 , fired at 1750°C for 24h, showing lath-like mullite crystals (dark grey) and interstitial zirconia (white)+mullite eutectic surrounded by light grey liquid phase

In view of the above reasoning, it should be concluded that the ternary invariant point relating alumina, zirconia and mullite must occur at a temperature between 1700 and 1715°C. Given that the binary eutectic in the Al_2O_3 - ZrO_2 system occurs at 1710°C, the ternary invariant point must occur below this temperature.

(2) Location of boundary curves between primary-phase fields

Some samples presented microstructures containing well developed grains of a primary phase surrounded by liquid, together with an interstitial phase formed by numerous small zirconia and mullite crystals, too coarse to be just the result of devitrification during quenching (Figure 3). This morphology suggests a eutectic (simultaneous) crystallization of these two phases and the composition of the liquid phase that accompanies them should thus be located on the boundary curve between the corresponding primary-phase fields. As shown in Figure 4, the liquid phases in some of such samples, fired at the same temperature, were found to have the same composition, within experimental accuracy, and were therefore used to locate temperature/composition points on that boundary curve (namely at 1700, 1735 and 1750°C).

Based on the above, and on the relevant information extracted from the binary systems, in special the position and temperature of the binary eutectics and the incongruent melting of mullite, the phase diagram presented on Figure 5 was produced. In this diagram, the features in the silica-rich region were kept essentially the same as in Budnikov's diagram[4].

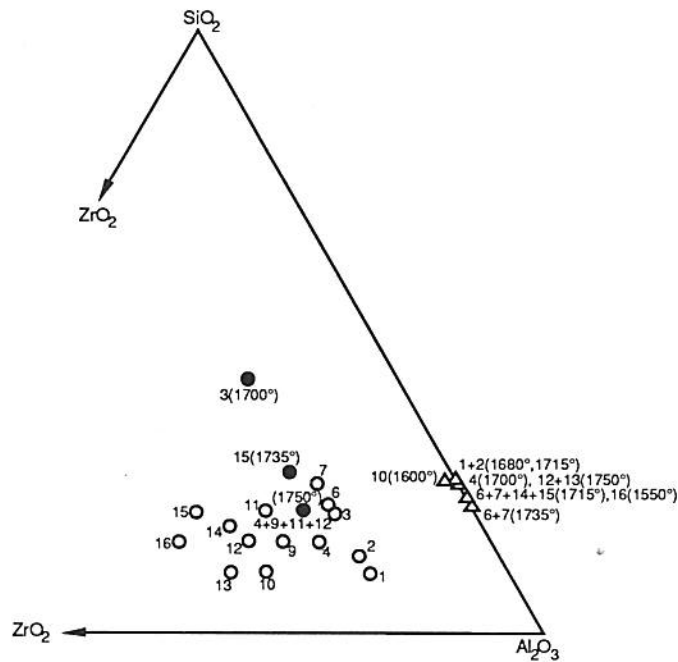


Figure 4. Relationships between the starting compositions of selected samples (open circles) and the corresponding liquid phase (filled circles) and mullite (triangles) in equilibrium at the temperatures shown

IV. CONCLUSIONS

The main implications of the proposed diagram are (1) the larger extent of the zirconia primary-phase field, down to significantly lower zirconia contents; (2) mullite is present as solid solution extending up to 79.6 wt.% Al_2O_3 , defining a mullite-zirconia compatibility zone, instead of a single Alkemade line; (3) the ternary invariant point relating zirconia, alumina and mullite is of the eutectic type, since temperatures on the zirconia-mullite boundary curve are higher than the invariant temperature determined, *i.e.* there will be a temperature maximum on this curve somewhere across the zirconia-mullite compatibility zone; and (4) the tentative composition of the ternary eutectic is *circa* 11 SiO_2 + 58 Al_2O_3 + 31 ZrO_2 (wt.%), as opposed to 15.6 SiO_2 + 53.2 Al_2O_3 + 31.2 ZrO_2 (wt.%) indicated by Budnikov *et al.*'s original diagram[4] and it occurs at $\sim 1710^\circ\text{C}$, a temperature significantly lower than previously reported.

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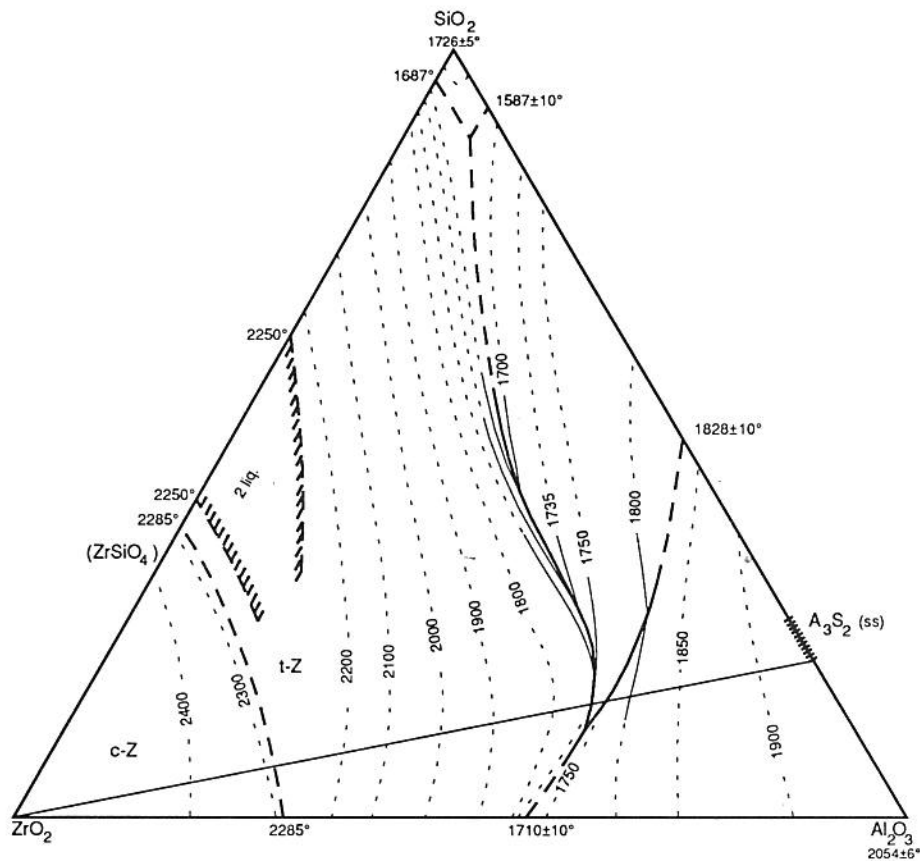


Figure 5. Proposed phase diagram of the system $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-SiO}_2$

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