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Mullite Formation by Reaction Sintering of Quartz and α-Al_2O_3—A TEM Study

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Abstract

Early stages of mullitization during reaction sintering of quartz and submicron α-Al_2O_3 *powders were investigated by means of analytical transmission electron microscopy. The reaction sequence starts by formation of a transient melt layer on the surface of the quartz grains. The viscous silica melt incorporates some alumina by dissolution of* α-Al_2O_3. *If the* Al_2O_3 *content of the liquid phase exceeds ≈4 mol% mullite formation occurs mainly at* α-Al_2O_3 *grain junctions. Less frequently, mullite formation inside the bulk of the liquid phase has been detected.*

Die frühen Stadien der Mullitbildung beim Reaktionssintern von Quarz und α-Al_2O_3 *wurden mittels analytischer Transmissionselektronenmikroskopie untersucht. Die Reaktionsfolge beginnt mit der Bildung einer intermediären Schmelzphase im Randbereich der Quarzkörner. Nachdem etwa 4 mol%* Al_2O_3 *in der Schmelze gelöst ist, entsteht Mullit. Der Mullit bildet sich im allgemeinen an der Grenzfläche* α-Al_2O_3*/Schmelzphase, vereinzelt jedoch auch im Inneren des Schmelzsaums.*

On a étudié les premiers stades de la mullitisation lors du frittage réactionnel de quartz et de poudres d'α-Al_2O_3 *submicroniques, ceci par microscopie à transmission analytique. La réaction commence par la formation d'un liquide transitoire à la surface des grains de quartz. La silice visqueuse absorbe de l'alumine* α-Al_2O_3 *par dissolution. Si la phase liquide contient plus de 4 mol% environ, de la mullite se forme alors aux joints de grains d'*α-Al_2O_3. *Moins fréquemment, il arrive que de la mullite se forme au coeur de la phase liquide.*

1 Introduction

Due to its excellent thermal shock and creep resistance, its high-temperature strength and chemical stability mullite has become increasingly important as a structural high-temperature material. Many investigations have been carried out during the last 30 years concerning mullite formation from naturally occurring aluminosilicates and from colloidally and molecularly prepared precursors.[1] Comparatively few works exist about mullite formation by reaction sintering of SiO_2 and α-Al_2O_3. This process, however, offers some advantages: the use of low-priced starting materials of relatively high purity and with good densification behaviour.

Wahl *et al.* were the first group to investigate reaction sintering of mullite from different alumina and silica sources systematically by means of high-temperature X-ray diffraction.[2] The microstructural development of mullite ceramics formed by reaction sintering of SiO_2 varieties and α-Al_2O_3 was examined by Nurishi & Pask[3] and Rana *et al.*[4] using scanning electron microscopy. Liquid-phase formation prior to mullitization was observed in the temperature range between 1300°C and 1500°C. In the case of cristobalite/α-Al_2O_3 mixtures liquid-phase formation was explained by the metastable eutectic of the alumina–silica system,[5] while in quartz-containing mixtures liquid phase may be formed during the transformation process quartz → cristobalite (e.g. Ref. 6). Johnson & Pask showed that the locus of mullitization is the interface between liquid (glassy) phase and corundum;[7] growth of the mullite layer occurs by Al^{3+} and Si^{4+} interdiffusion.

Processing parameters of reaction sintering (raw materials, firing conditions, particle size, Al_2O_3/SiO_2 ratio, influence of additives) leading to high-quality mullite ceramics were optimized by Rodrigo & Boch.[8] Recently Albers investigated sintering mechanisms of mullite from SiO_2 and α-Al_2O_3 by means of dilatometry, X-ray diffraction and scanning electron microscopy.[9]

In the present study the early stage of mullitization starting from a quartz/α-Al_2O_3-powder

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compact mixture is investigated by means of analytical transmission electron microscopy. The nature of a possibly occurring metastable liquid phase, its origin, chemical composition and influence on mullite nucleation was of particular interest.

2 Experimental

2.1 Sample materials

Starting materials were Novacite L337 quartz powder (99·1 wt% SiO_2, 0·61 wt% Al_2O_3, 0·04 wt% Fe_2O_3, 0·015 wt% TiO_2; Chemag AG, Frankfurt/Main, Germany) with a grain size of 1–10 μm and submicron AKP 50 α-Al_2O_3 (99·995 wt% Al_2O_3 with traces of SiO_2, Fe_2O_3, Na_2O, MgO; Sumitomo Chemical Co., Ltd, Tokyo, Japan).

The powders were admixed in alcohol, dried, sieved, granulated and subsequently compacted into bars by dry-pressing. The overall Al_2O_3/SiO_2 ratio of the sample was 3/2 (60 mol% Al_2O_3, 40 mol% SiO_2) in each case.

2.2 Sintering experiments

Sintering runs were performed in a computer-controlled $MoSi_2$-heated laboratory furnace in air with a heating rate of 400 K/h up to 1450, 1475, 1500 and 1600°C, respectively. As maximum temperatures were reached sintering runs were terminated by switching off the heating power.

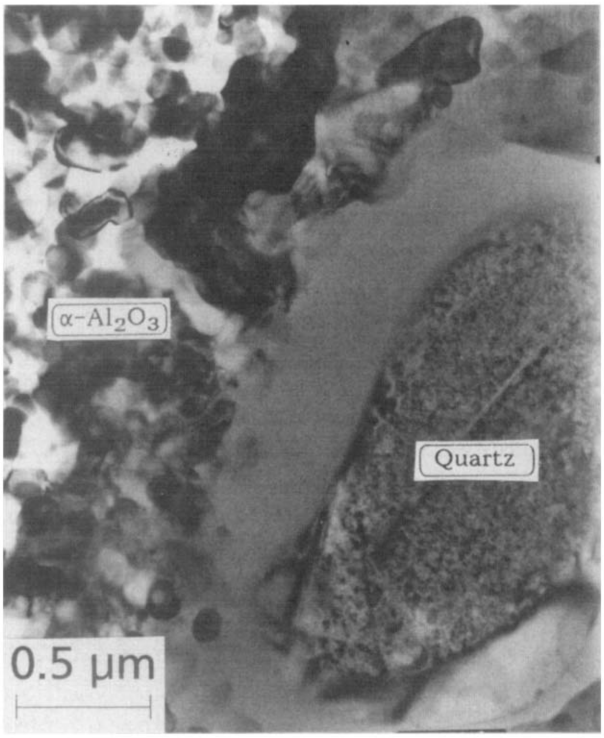

Fig. 1. Peripherally molten quartz grain heat treated at 1475°C. The viscous silica-rich melt has penetrated into the α-Al_2O_3 agglomerates.

2.3 Transmission electron microscopic characterization

Transmission electron microscopic (TEM) studies were performed with a Philips EM 430 microscope (LaB_6 filament, 300 kV accelerating voltage) equipped with a TRACOR system for energy dispersive X-ray analysis (EDX). Thin foils of specimens for the TEM observations were prepared by dimple grinding and argon ion thinning. The foils were coated with carbon films to avoid charging effects.

3 Results

3.1 Microstructural observations

Figure 1 shows the typical microstructure of samples sintered at 1475°C. Silica-rich amorphous phase occurring at the rims of quartz grains provides evidence for metastable peripherical melting of quartz. According to microscopic observation the melt does penetrate into the α-Al_2O_3 agglomerates. Cristobalite or mullite formation was not detected.

Different microstructures were observed in samples heated up to 1500°C, indicating competitive processes. Most quartz grains were found to be surrounded by the silica-rich amorphous phase. In some cases a dense ≈300 nm mullite layer was formed in the liquid silica–alumina contact zone (Fig. 2). In addition, small mullite crystals (15–50 nm in size) were detected in the bulk of the silica-rich liquid phase (Figs 3 and 4). Some minor

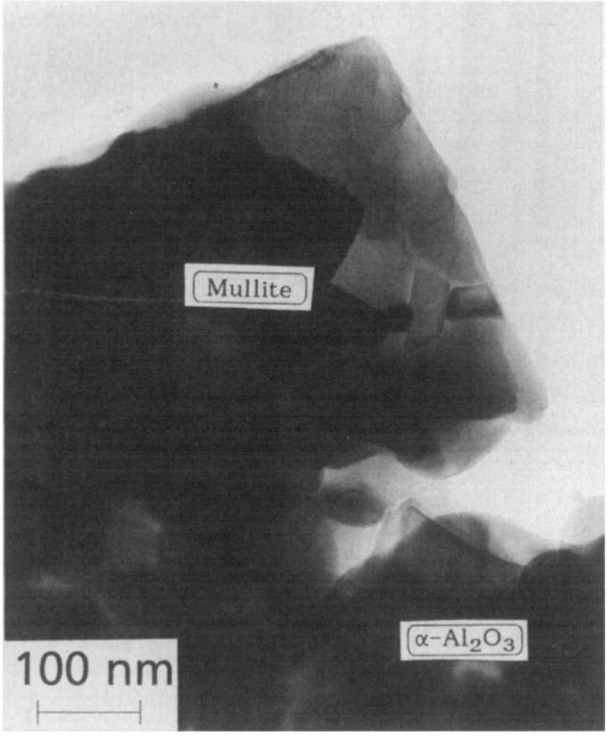

Fig. 2. Mullite layer formed at the α-Al_2O_3/silica-rich melt contact zone (T = 1500°C).

Fig. 3. Mullite crystals formed in the bulk of the silica-rich melt (T = 1500°C)

amount of the silica melt was transformed into cristobalite (Fig.5).

At 1600°C quartz was transformed to cristobalite entirely and a ≈0.5 μm thick mullite layer was formed at the cristobalite/α-Al_2O_3 interfaces (Fig.6).

3.2 Composition of the amorphous phase

The chemical composition as measured by EDX analyses of the amorphous phase surrounding the quartz crystals is plotted in Fig. 7. The glassy silica phase of samples sintered at 1450 and 1475°C contains approximately 4 mol% Al_2O_3. After sintering at 1500°C the frequency distribution of Al_2O_3 content exhibits two maxima near 2.5 mol% and 4 mol%, respectively. No systematic Al_2O_3 concentration gradient was found in any of the amorphous layers.

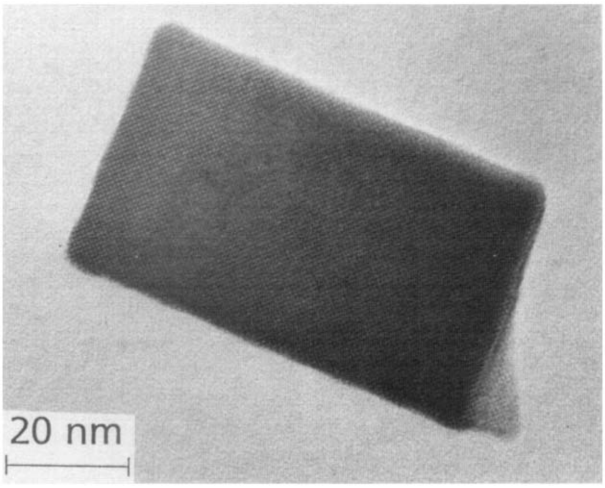

Fig. 4. High-resolution micrograph of a mullite crystal formed in the bulk of the melt. The crystallite is idiomorphous with boundaries parallel {110} to crystallographic planes.

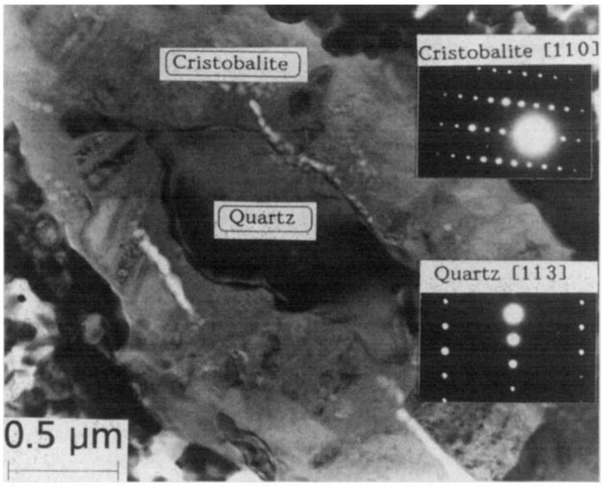

Fig. 5. Quartz grain partially transformed to cristobalite; diffraction patterns: quartz [113], cristobalite [110] (T = 1500°C).

4 Discussion

It is obvious from these studies that mullite formation by reaction sintering of silica and alumina is strongly influenced by the existence of a metastable liquid phase. The partial melting of quartz may be explained in accordance with the metastable reaction processes in the system SiO_2–Al_2O_3 or with the formation of a transient liquid during the quartz–cristobalite transformation.

Annealing experiments on pure Novacite quartz powder at 1450°C yielded similar behaviour as in the system Al_2O_3–SiO_2: Regardless of the presence of α-Al_2O_3, quartz particles were found to be molten peripherally (Fig. 8). In many cases small amounts of impurity elements (Ti, Fe, K, Na) were detected

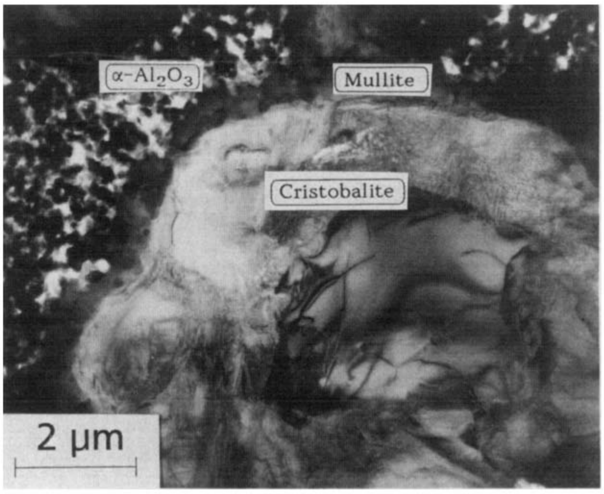

Fig. 6. Mullite layer at cristobalite/α-Al_2O_3 interface (T = 1600°C).

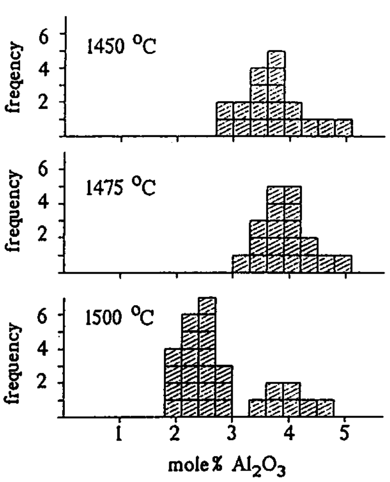

Fig. 7. Al_2O_3 content of the silica-rich glass zone depending on temperature.

in the amorphous phase. This observation leads to the assumption that quartz powders containing some minor amount of impurities which are usually enriched at grain peripheries[10] form transient melts, later crystallizing to cristobalite. However, this does not mean that the quartz–cristobalite transformation in virtually pure SiO_2 has to occur via a non-crystalline phase, as postulated by Ref. 6.

The viscous silica phase, once formed, acts as a sink for Al_2O_3, thus leading to dissolution of corundum. As the Al_2O_3 concentration in the liquid phase surmounts ≈4 mol% mullite is formed. Mullite crystallization mainly occurs at α-Al_2O_3/liquid interfaces; however, some minor amount also nucleates within the bulk of the liquid phase (Figs 3 and 4). In the vicinity of these newly formed mullites the Al_2O_3 content of the amorphous phase is reduced to ≈2.5 mole%. This composition will correspond to that of the (metastable) equilibrium composition of amorphous Al silicate coexisting with mullite at 1500°C, as illustrated in Fig. 9. A similar composition was estimated by Sundaresan & Aksay (4 mol% at 1300°C).[11]

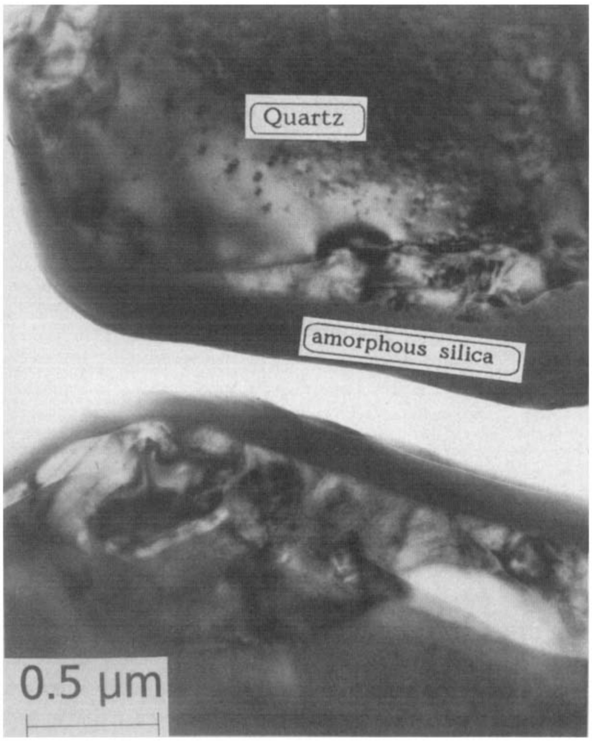

Fig. 8. Quartz-powder heat treated at 1450°C: quartz grains are surrounded by an amorphous layer.

The present experimental observation suggests that Al_2O_3 incorporation into the viscous silica-rich glass occurs by corundum dissolution, and, if a certain supersaturation is exceeded, mullite nucleation takes place. In contrast, Rana *et al.*[4] and Johnson & Pask[7] explained the Al_2O_3 incorporation into the silica melt by simultaneous growth and dissolution of mullite crystals just formed at α-Al_2O_3 interface. However, mullite formation prior to Al_2O_3 saturation of the liquid phase can be expected only if dissolution of corundum occurs faster than diffusion of the Al species inside the viscous melt, thus leading to an Al_2O_3 concentration gradient within the glassy phase. This has never been observed.

5 Conclusion

Mullite formation by reaction sintering of quartz and α-Al_2O_3 is controlled by the sequence of the following reaction steps:

—Metastable peripheral melting of quartz, presumably related to the presence of impurity elements.

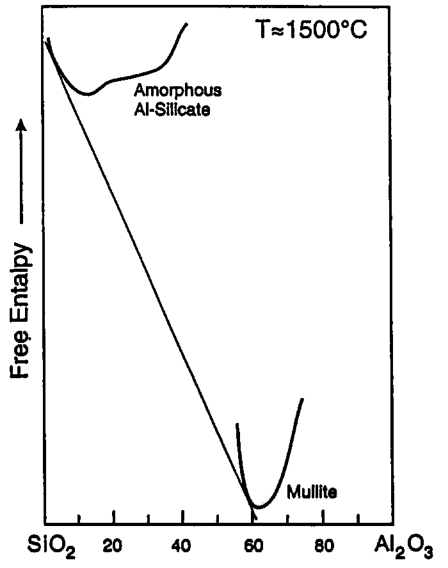

Fig. 9. Schematic plot of free enthalpy versus composition for amorphous Al silicate (after Risbud & Pask[12]) coexisting with mullite at 1500°C.

—Penetration of the viscous silica melt into α-Al_2O_3 aggregates.
—Incorporation of Al_2O_3 in the silica melt by dissolution of α-Al_2O_3.
—Nucleation of mullite from the alumina–silica melt mainly at α-Al_2O_3 contacts, and, in some minor amount, in the bulk of the melt.
—Crystallization of the residual silica-rich melt forming cristobalite.
—Growth of the mullite layer by interdiffusion of Al and Si diffusion species.

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