Journal of the European Ceramic Society **16** (1996) 1075–1081

PII: S0955-2219(96)00023-4
0955-2219/96/$15.00

Reaction and Sintering Mechanisms of Mullite in the Systems Cristobalite/α-Al_2O_3 and Amorphous SiO_2/α-Al_2O_3

B. Saruhan, W. Albers, H. Schneider & W. A. Kaysser

German Aerospace Research Establishment (DLR-Cologne),
Institute for Materials Research, D-51140 Köln, Germany

(Received 3 November 1995; revised version received 3 January 1996; accepted 8 January 1996)

Abstract

Powder mixtures of SiO_2 glass and cristobalite with fine α-Al_2O_3 were heat-treated at different temperatures up to 1700°C. Green samples consisting of SiO_2 glass plus α-Al_2O_3 (RSS) generally were sintered to higher densities than those consisting of cristobalite plus α-Al_2O_3 (RSC). In both powder compacts (RSS and RSC) two different sintering mechanisms were active before and after the onset of mullitization, respectively. Before mullite formation begins, densification occurs in the RSS sample through viscous flow sintering and in the RSC sample by solid-state sintering. After the formation of mullite crystals, transient liquid-phase sintering is assumed for both samples (RSS and RSC). The amount of SiO_2-rich liquid phase, which controls degree and rate of the second-stage sintering mechanism, depends on the amount of residual SiO_2 left unreacted after initial mullitization.

The temperature-dependent mullite formation process was complex. At 1700°C sample RSS formed ≈ 80% mullite, while the degree of mullitization of sample RSC at the same temperature was ≈ 90%. However, this tendency did not hold at higher temperatures, since both samples displayed near-total mullitization at 1750°C. Four different temperature-dependent steps of mullite formation could be distinguished: a temperature field where mullite nucleation was observed (<1500°C), a temperature range of high mullitization degree (1500–1550°C), followed by a low mullitization region (1550–1625°C). At higher temperatures (>1625°C) high mullitization rates were observed again. © 1996 Elsevier Science Limited.

Introduction

Reaction sintering of Al_2O_3 and SiO_2 powders is a low-cost processing route to achieve mullite ceramics with high quality.[1,2] The temperature and rates of mullite formation depend on different factors, the most important of which are the species used and their chemical purity and particle size distribution.[3–6] Most investigations on the reaction sintering of mullite were carried out by using diaspore (AlOOH), gibbsite ($Al(OH)_3$) or corundum (α-Al_2O_3) as Al-sources and silica glass powder, quartz or cristobalite as the Si-sources.[1–12] Mullitization mechanisms in mixtures of various polymorphs of Al_2O_3 and SiO_2 are greatly influenced by the properties of the reactants and less by the bulk chemical composition.[8] Therefore the processing parameters during reaction sintering have to be exactly tailored to produce complete mullitization and high densification of the mullite ceramics. It has been shown that, by using submicrometre-sized powders with high surface energies and choosing fast heating rates during sintering, almost the theoretical densities and very high mullite contents can be obtained at relatively low temperatures (>1600°C).[5–7]

Due to the wide variety of reaction parameters reported in previous studies, it is difficult to determine the sintering and mullitization mechanisms. The aim of this study was to clarify matters by a systematic investigation of the role of two SiO_2 reactants (amorphous glass and crystalline cristobalite) in mullitization and densification as well as the interactions between densification and mullitization during sintering, while the same α-Al_2O_3 powder was used in each case. Together with earlier studies on quartz/α-Al_2O_3,[9] it may develop a new understanding of the role of the SiO_2 source on the mullitization process.

Materials and Methods

Materials

The α-Al_2O_3 powder AKP-50 (corundum), provided by Sumitomo (Tokyo, Japan), is a highly

pure (>99·995 wt% Al_2O_3) and submicrometre-sized alumina powder was derived from aluminium alkoxide.

The SiO_2 glass powder, provided by Heraeus Quarzglas (Hanau, Germany), was achieved by melting quartz. The as-received powder has coarse particle sizes ranging from 63 to 125 μm and contains 99·9 wt% SiO_2 and a very low amount of Na_2O (119 ppm), K_2O (80 ppm) and CaO (80 ppm). In order to increase the sintering activity, the SiO_2 glass powder was previously ball-milled to a particle size of 2 to 3 μm. The particles after milling were irregularly shaped and had a smooth surface.

The cristobalite powder was achieved by heat-treating a quartz powder (Vp 795-10/1, Quarzwerke Frechen, Germany) at 1550°C for 10 h. The starting quartz powder has submicrometre size and consists of 98·5 wt% SiO_2, 1 wt% Al_2O_3, and 0·05 wt% Fe_2O_3, 0·1 wt% Na_2O + K_2O and 0·1 wt% CaO + MgO. After conversion of quartz to cristobalite, the concentrations of the impurities did not change. The cristobalite powder consists of spherical particles with smooth surfaces and particle sizes between 1 and 10 μm.

Powder processing and sintering

The starting oxide powders were mixed in the stoichiometric composition of 3/2 mullite (71·8 wt% α-Al_2O_3 and 28·2 wt% SiO_2). The mixed powders and 5 wt% of a combination of binders as pressing aids were dispersed in isopropanol and homogenized by ball-milling for 5 h in a polymer container with Si_3N_4 milling balls. After evaporation of isopropanol, the mixtures were dried, sieved in a sieving machine (500 μm) and finally granulated by a tumble-mixer. Granulation of the mixtures allowed homogeneous and reproducible filling of the die, thus minimizing density gradients in the uniaxially pressed bar samples which had dimensions of 5 × 6 × 55 mm. After uniaxially die-pressing, the waxes were carefully burned out at 600°C with a very slow heating rate. The samples were then pressureless sintered in air at temperatures ranging between 1100 and 1700°C.

Dilatometer measurements

Bar-shaped samples measuring 3·5 × 3·5 × 10 mm were heated up to 1700°C in air in a differential dilatometer (Bähr-Thermoanalyse GmbH, Hüllhorst, Germany). A constant heating rate of 400 K h^{-1} was applied. Dense α-Al_2O_3 was used as the reference material. The resulting data of length changes were differentiated using a computer program.

Microstructure and observation of the phase composition

Microstructural observations of fracture surfaces were carried out with a scanning electron microscope (Philips SEM 525 M). For further investigation, a transmission electron microscope (Philips EM 430) with an LaB_6 filament and an acceleration voltage of 300 kV was used. X-ray diffractometer studies were carried out with a computer-controlled powder diffractometer (Siemens D5000) using Ni-filtered Cu K_α radiation. Diffraction patterns were recorded in the 2θ range 10° to 80°, in step scan mode (3 s/0·02°, 2θ). Determination of the phase content was based on the comparison of X-ray diffraction intensities of samples with those of reference materials.

Results

Sintering behaviour

Dilatometer studies carried out on green samples display, for both Al_2O_3 plus SiO_2 combinations, similar sintering behaviours which can be divided into four stages, although the temperature limits of these stages and rates of densification are different for both samples [Fig. 1(a)].

During the first stage (up to 1100°C for RSS and 1200°C for RSC) no significant progress of the densification is observed, only a reversible low expansion effect at 270°C detected with the α-Al_2O_3 + cristobalite (RSC) sample by differenti-

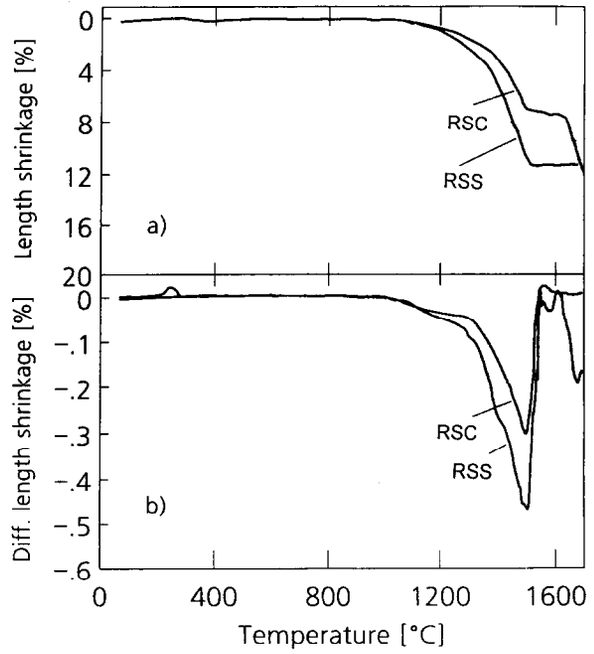

Fig. 1. Sintering behaviour of RSS and RSC samples during reaction sintering between room temperature and 1700°C, heated with a rate of 400 K h^{-1}, and illustrated as (a) length shrinkage (dl) and (b) differentiated length shrinkage (dl/dt) vs. temperature.

ating the shrinkage curves. This behaviour is related to the displacive low–high phase transition of cristobalite [Fig. 1(b)].

The second stage of densification starts with a relatively low rate above about 1200°C for the RSC sample and above about 1100°C for the RSS (α-Al_2O_3 plus SiO_2 glass) sample, and extends to the temperature at which mullitization starts (1500 and 1485°C, respectively). The rate and extent of densification depend on the SiO_2 reactant. Above 1200°C, the RSS and RSC samples densify with a higher rate. The extent of length shrinkage at the end of the second stage is 11·8% for RSS and 7·5% for RSC.

Due to the mullite formation, the third stage of the densification process starts at the temperature at which the densification decreases for both samples (RSS and RSC). For the RSS sample, this stage extends until the maximum temperature (1700°C, after 4 h) is reached.

For the RSC sample, after the third stage, a fourth stage above 1600°C has been observed. During this last stage, sample RSC exhibits a further length shrinkage of 4·7%. Counting the small amount of shrinkage which occurs during mullitization (0·6%), the total length shrinkage in the RSC sample amounts to 12·8% at about 1700°C. Sample RSS shows no length change during this stage.

Development of phase compositions

Before the beginning of the mullitization process by the reaction of Al_2O_3 and SiO_2, the amorphous SiO_2 particles of sample RSS transform partly to cristobalite. According to the literature data provided by Nurishi and Pask[3] on samples sintered using amorphous SiO_2 and α-Al_2O_3, amorphous SiO_2 transforms to cristobalite and the successive reaction of cristobalite with corundum results in the formation of a metastable eutectic liquid phase. In this study, it was also observed that amorphous SiO_2 transforms to cristobalite prior to mullitization. In the RSS sample, cristobalite appears in the temperature range extending from 1450 to 1650°C. Above about 1550°C, an amorphous SiO_2-rich liquid phase forms which is in agreement with the observations of Nurishi and Pask[3] (Fig. 2). Mullite formation in RSS sample occurs above about 1500°C and continues rapidly up to 1550°C. Between 1550 and 1600°C, the rate of mullitization slows down but takes up again above 1600°C with a relatively fast rate (Fig. 3). In agreement with previous observations,[7] it is determined that during reaction sintering of various Al_2O_3 and SiO_2 sources, mullitization is correlated to the presence of cristobalite.

Sample RSC begins to mullitize above about 1525°C. This temperature is somewhat higher than that of sample RSS, which starts at about 1500°C. Formation of amorphous SiO_2-rich liquid phase occurs in sample RSC above about 1500°C, being 50°C lower than that in sample RSS; the amount of this glass phase is significantly higher in sample RSC (Fig. 2).

Figure 3 shows that for both samples (RSS and RSC) mullite formation is a multiple-step process, extending over four temperature regions: nucleation (region I), a temperature range of high mullitization rates (region II), a temperature field of low mullitization rates (region III) and, finally, at high temperatures another high mullitization field (region IV).

Development of microstructure

By interrupting the heat treatment at definite temperatures in the range between 1000 and 1700°C and cooling the samples to room temperature, the development of grain morphology and the porosity have been observed for each sample by means of scanning electron microscopy (SEM). The first microstructural investigation was carried out on samples heat-treated at the temperature at which

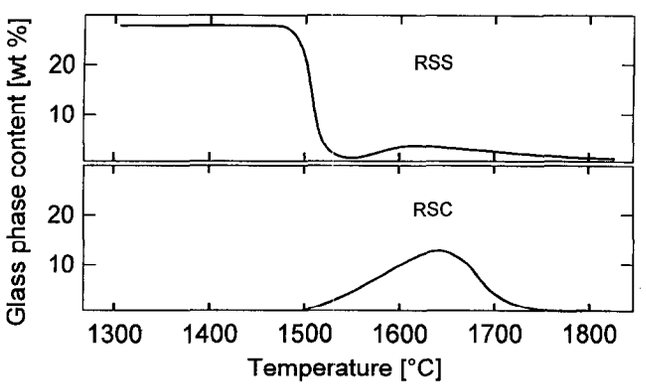

Fig. 2. Glass-phase formation in RSS and RSC samples during reaction sintering between room temperature and 1800°C with a constant heating rate of 400 K h^{-1}.

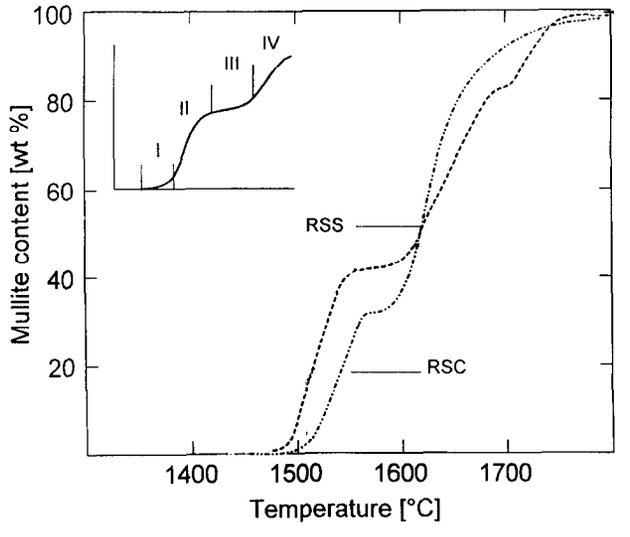

Fig. 3. Mullite formation in RSS and RSC samples during reaction sintering between room temperature and 1800°C with a constant heating rate of 400 K h^{-1}.

the initial shrinkage occurs (approximately 1200°C). The second check referred to the temperature of first appearance of mullite (approx. 1500°C). Finally, a third group of samples heat-treated at the temperature beyond the cristobalite stability field (>1600°C) were investigated microstructurally.

The RSS sample shows a particle rearrangement process during heating >1100°C [Fig. 4(a)]. Owing to the production route of the cristobalite powder, sample RSC contains a coexisting relatively alkali-rich glass phase which was formed during the transformation of mother quartz to cristobalite [Fig. 5(a)]. This coexisting glass phase is transient and disappears above about 1200°C [Fig. 5(b)].

Above the mullite formation at about 1500°C, both samples (RSC and RSS) generally show formation of contact points and strong adhesion of Al_2O_3 particles to the surfaces of SiO_2 particles. In the RSS sample, adhesion of the Al_2O_3 particles is so strong that the surfaces of the SiO_2 particles become round [Fig. 4(b)]. In the RSC sample, the Al_2O_3 particles attach themselves onto the cristobalite particle surfaces by neck formation [Fig.

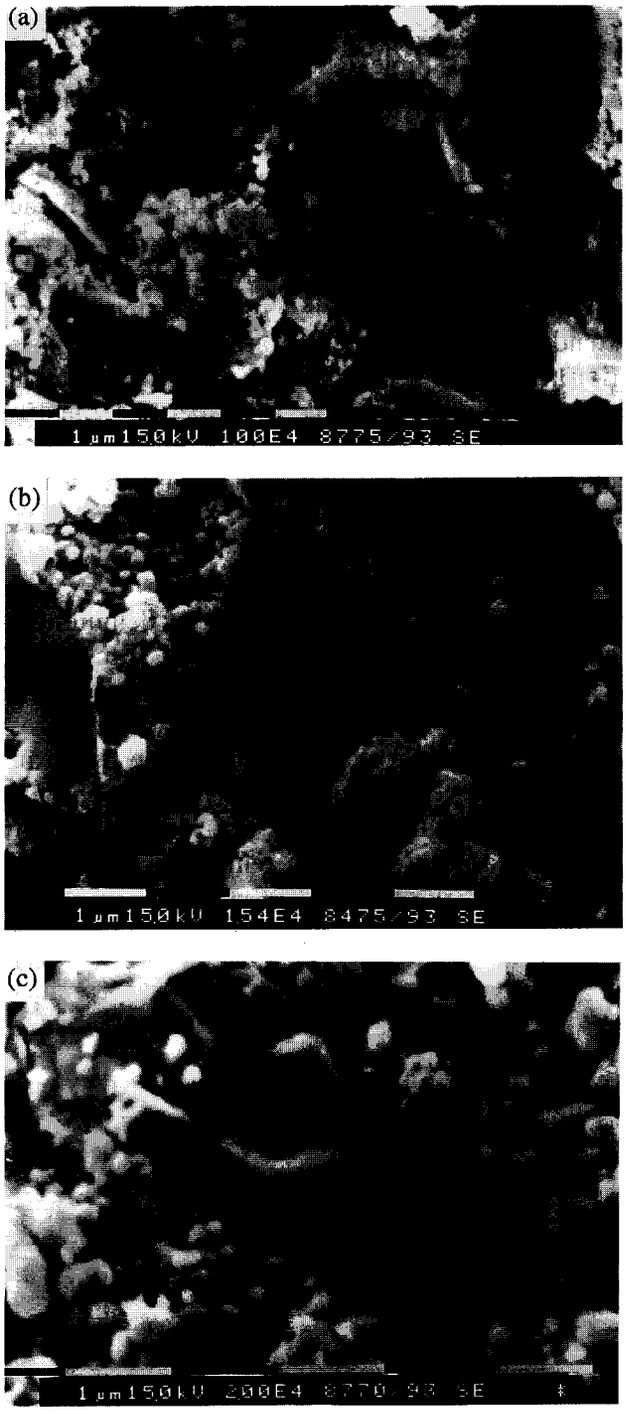

Fig. 4. SEM micrographs of RSS sample showing morphology changes during reaction sintering. Samples were heated to 1200°C (a), 1450°C (b) and 1600°C (c) with a rate of 400 K h^{-1}. No holding time was allowed at the temperature.

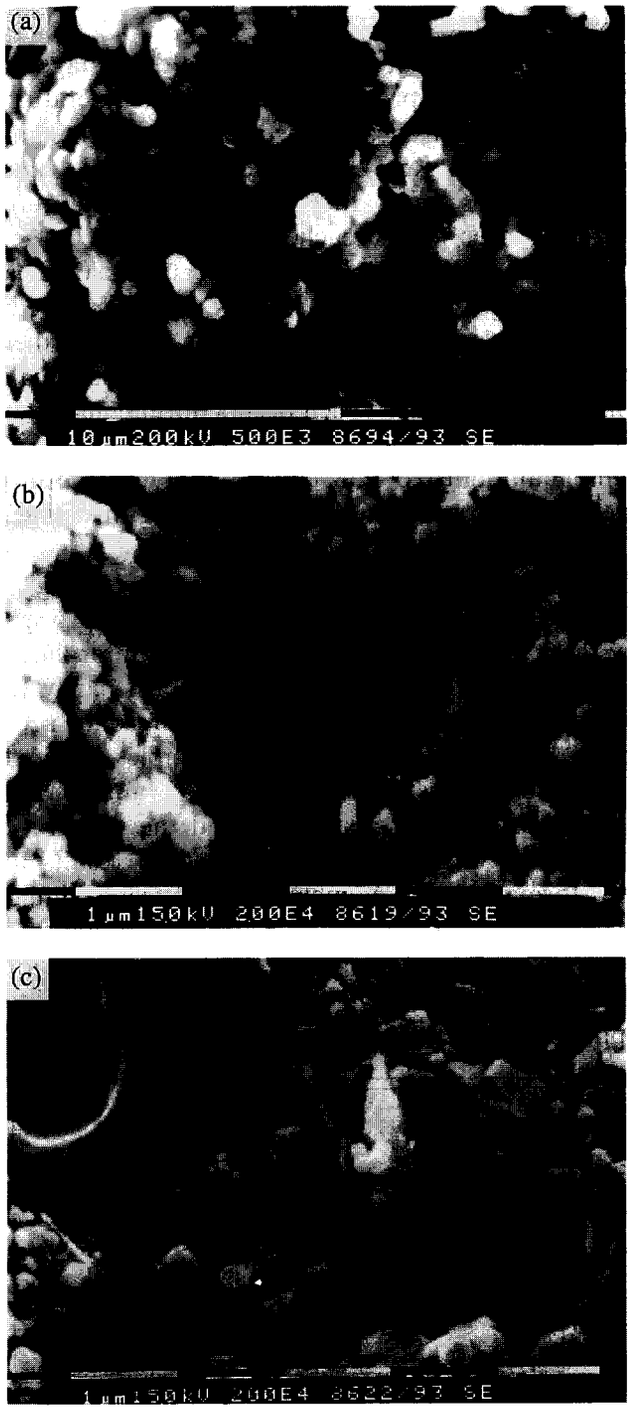

Fig. 5. SEM micrographs of RSC sample showing morphology changes during reaction sintering. Samples were heated to 1150°C (a), 1550°C (b) and 1625°C (c) with a rate of 400 K h^{-1}. No holding time was allowed at the temperature.

5(b)]. Therefore, the degree of shrinkage in sample RSC (7·5%) is not as high as in sample RSS (11·8%).

At temperatures higher than 1600°C cristobalite either melts or evaporates due to local reducing atmospheres, and, as a consequence, pores develop. These pores are surrounded by relatively coarse but well developed mullite grains and occur in previous contact areas of the Al_2O_3 and SiO_2 particles [Figs 4(c) and 5(c)].

Discussion

A schematic illustration of the microstructural development of reaction-sintered silica glass/α-Al_2O_3 phase assemblage (RSS) is given in Fig. 6. Impurity-free silica glass does not form a viscous liquid phase at temperatures lower than 1400°C but shows viscous softening only. Due to the superficial softening of the SiO_2 glass particles (>99·9 wt% SiO_2), the fine Al_2O_3 particles penetrate into the viscous particle surfaces, leading to a high degree of shrinkage. Especially above 1250°C, the densification rate becomes very high. We believe that sintering takes place by a semi-viscous flow mechanism of the solid Al_2O_3 particles in viscous SiO_2 (Fig. 6). At higher sintering temperatures up to 1450°C, the viscosity of the silica glass decreases, though the original grain shapes are preserved. Then, Al^{3+} ions may diffuse further within the SiO_2 particles until the stochiometrical mullite composition is achieved, although no mullite formation was observed [(Fig. 7(a)]. Above 1450°C, the SiO_2 glass starts to transform to crystalline cristobalite [Fig. 7(b)] and above 1500°C, mullite formation occurs by reaction of cristobalite and corundum (region I, Fig. 3). Due to the short diffusion distances achieved by viscous-flow-assisted sintering, the rate of mullitization is high [Figs 3 and 7(a)]. The newly formed mullite grains grow, successively replacing the SiO_2 particles (region II, Fig. 2). According to microstructural observations [Figs 4(c) and 7(c)] a ring-like formation of mullite grains develops around the former SiO_2 glass particles. Such mullite layers act as barriers for diffusing species and thus reduce the rate of mullitization (region III). Further increase in the sintering temperature above 1650°C causes melting of cristobalite and consequently promotion of mullitization (region IV, Fig. 2).

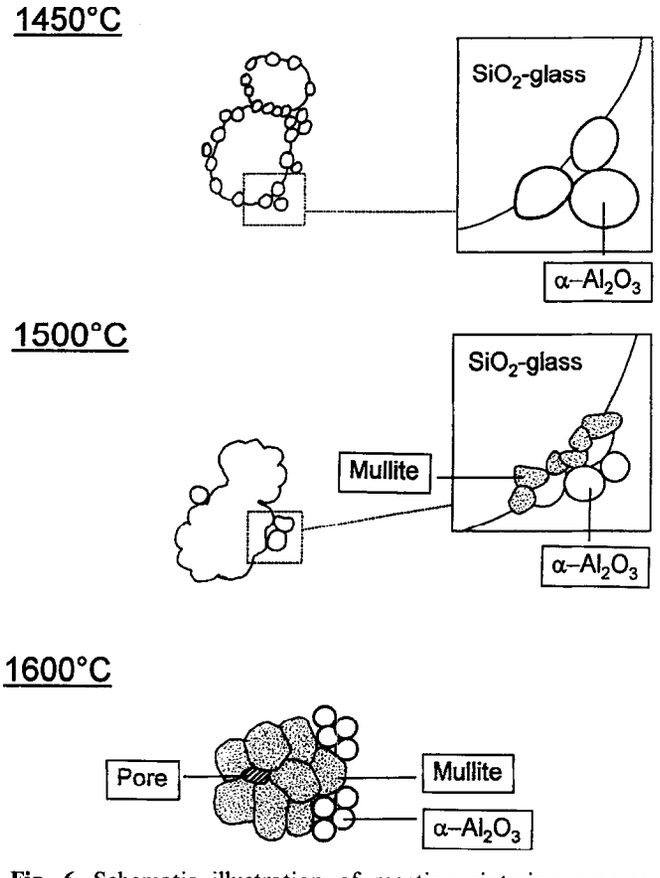

Fig. 6. Schematic illustration of reaction sintering process in RSS (amorphous SiO_2 + α-Al_2O_3) sample demonstrating sintering and mullitization mechanisms.

A schematic illustration of the microstructural development of reaction-sintered cristobalite/α-Al_2O_3 phase assemblage (RSC) is given in Fig. 8. The microstructural investigation carried out on the reaction couple cristobalite/α-Al_2O_3 (RSC) heat-treated at 1150°C indicates the formation of a metastable eutectic liquid phase [Fig. 5(a)]. This is in agreement with the observation of Rana *et al.*[4] and Risbud and Pask.[12] The occurrence of a metastable liquid phase, in our case, is attributed to the presence of some small amount of alkali and iron impurities, introduced into the system by the cristobalite raw material (see Materials section). Densification is promoted by the rearrangement of cristobalite and corundum particles at temperatures lower than 1300°C in the presence of coexisting viscous glass phase. The liquid phase is transient and disappears above 1300°C. As is shown in SEM micrographs [Fig. 5(b)], the particles of cristobalite and corundum form contact points allowing species transport and giving rise to the formation of neck areas, which is typical of a solid-state sintering.[13] The slow mullitization rate may be attributed to the low diffusion rates and to the large diffusion distances which have to be considered from the bulk to the neck areas. Formation of mullite at the neck areas leads to the build-up of a stiff skeleton which cannot shrink further. This may explain the formation of a porous structure which is associated with a low degree of densification for RSC. The increase of the surface area of cristobalite particles by a prolonged milling time does not increase the sinterability of the RSC sample but results in an increase in mullitization. This behaviour may be

attributed to the fact that the increase of particle contact areas promotes neck formation and mullitization but reduces the densification.

As the mullite grains around the former large cristobalite particles grow, diffusion barriers form between the reaction partners and therefore further reaction to mullite is hindered [Figs 5(c) and 8]. As a result, large residual SiO_2 regions are observed which are normally surrounded by layers of mullite. Above about 1620°C, cristobalite is converted to SiO_2-rich liquid which enhances densification by liquid-phase-assisted sintering but does not close all pores. This secondary densification, after mullitization, has been observed in cristobalite/α-Al_2O_3 (RSC) system but not in silica glass/α-Al_2O_3 (RSS) system (Fig. 1).

Conclusion

Silica glass/α-Al_2O_3 (RSS) and cristobalite/α-Al_2O_3 (RSC) samples display two different sintering mechanisms at low temperatures (<1500°C). RSS sample densifies through semi-viscous-flow sintering, whereas RSC sample is characterized by a solid-state sintering. Solid-state sintering in RSC

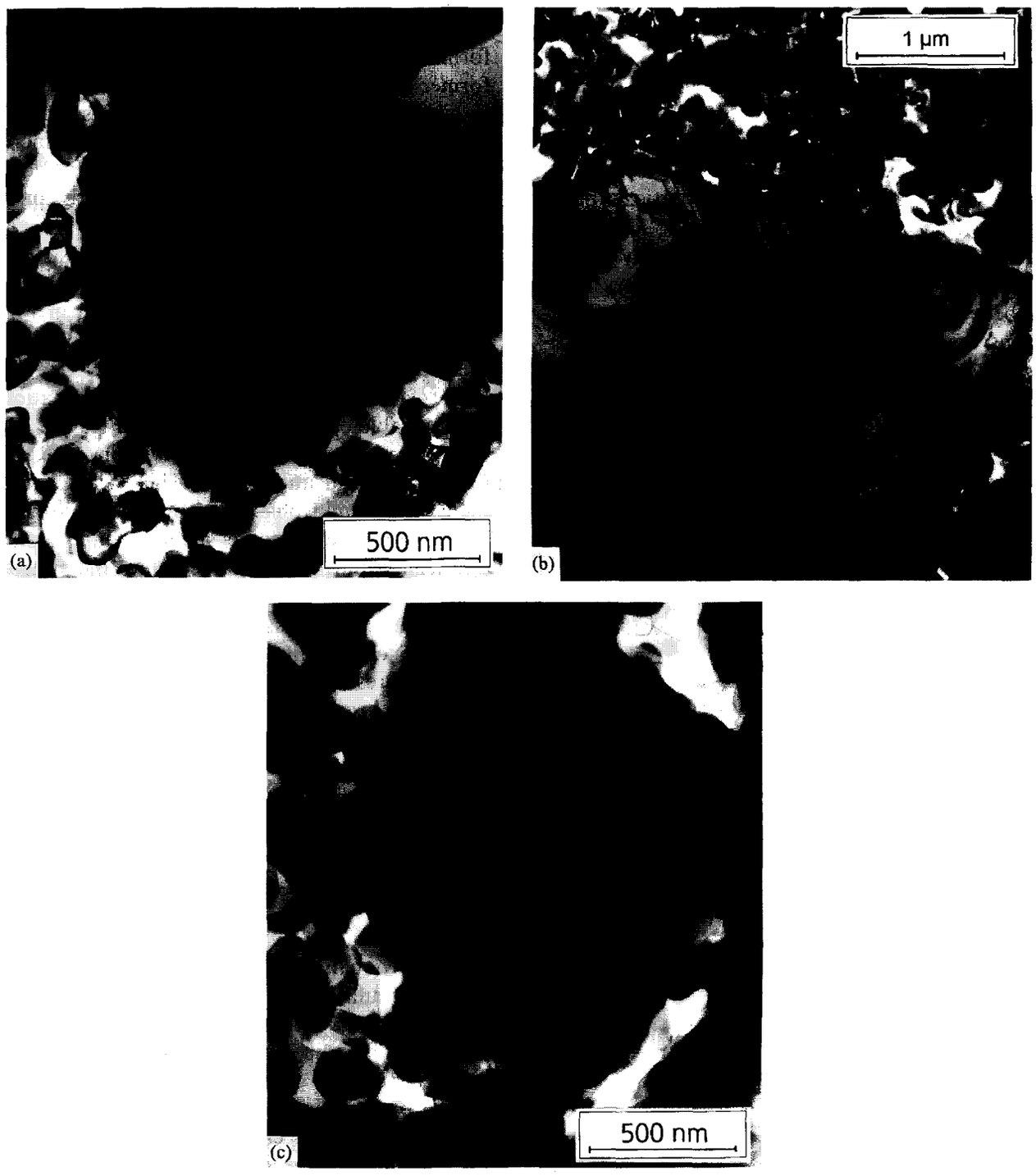

Fig. 7. TEM micrographs of reaction-sintered RSS sample at 1450°C (a), at 1625°C (b) and RSC sample at 1450°C (c). Samples were heated up with a rate of 400 K h^{-1} to the given temperature and no holding time was allowed.

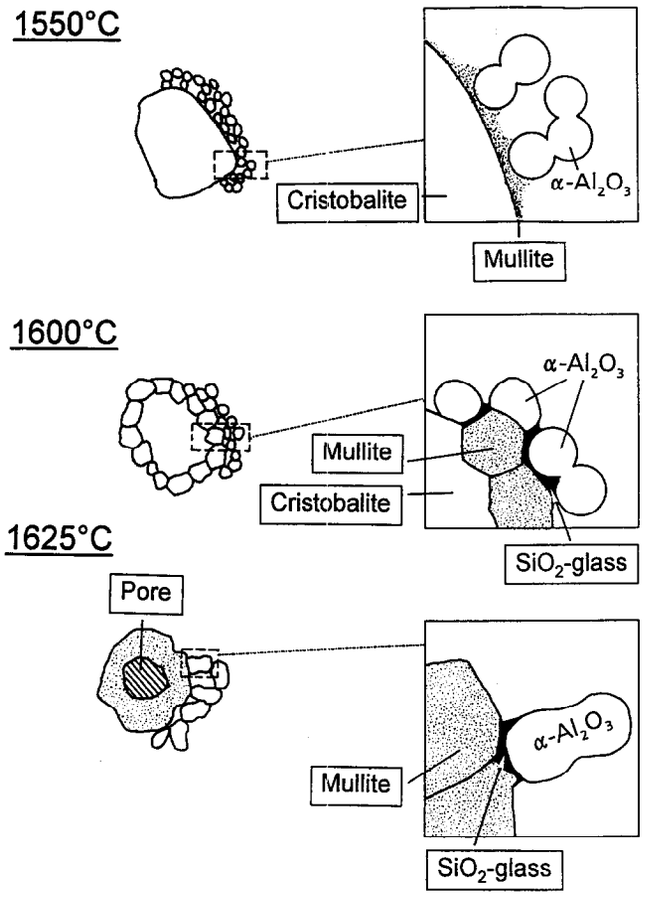

Fig. 8. Schematic illustration of reaction sintering process in RSC sample (cristobalite + α-Al_2O_3) demonstrating sintering and mullitization mechanisms.

samples causes a slower nucleation rate and a longer incubation period for mullite formation than does the viscous-flow sintering mechanism of RSS sample. This also can explain the higher mullitization temperatures in RSC sample than in RSS. At temperatures higher than 1600°C, further densification and mullitization are supported by a transient liquid-phase sintering in both RSS and RSC samples. Since a larger amount of unreacted SiO_2 remains in RSC sample during the solid-state sintering, due to the slower densification and mullitization rates at temperatures lower than 1500°C, formation of SiO_2 liquid phase at temperatures above 1600°C results in a higher mullitization rate and in an acceleration of densification compared with sample RSS [Fig. 1(a)]. The two-stage process leads to a bimodal grain morphology.

Acknowledgement

The TEM studies were performed by Dr M. Schmücker (DLR, Köln), who is gratefully acknowledged.

References

1. Aksay, I. A., Dabbs, D. M. & Sarikaya, M., Mullite for structural, electronic and optical applications. *J. Am. Ceram. Soc.*, **74** (1991) 2343–2358.
2. Hirata, Y., Matsushita, S., Ishihara, Y. & Katsuki H., Colloidal processing and mechanical properties of whisker-reinforced mullite matrix composites. *J. Am. Ceram. Soc.*, **74** (1991) 2438–2442.
3. Nurishi, Y. & Pask, J. A., Sintering of α-Al_2O_3/amorphous silica compacts. *Ceram. Int.*, **8** (1982) 57–59.
4. Rana, A. P. S., Aiko, O. & Pask, J. A., Sintering of α-Al_2O_3/quartz, and α-Al_2O_3/cristobalite related to mullite formation. *Ceram. Int.*, **8** (1982) 151–153.
5. Rodrigo. P. D. D. & Boch, P., High purity mullite ceramics by reaction sintering. *Int J. High Tech. Ceram.*, **1** (1985) 3–30.
6. Rodrigo, P. D. D., Reaction sintering of mullite base ceramics. PhD Thesis, University of Limoges, Limoges, 1986.
7. Boch, P., Chartier, T. & Rodrigo, P. D. D., High purity ceramics by reaction sintering. In *Ceramic Transactions 6: Mullite and Mullite Matrix Composites*, eds S. Somiya, R. F. Davis, & J. A. Pask. American Ceramic Society, Westerville, OH, 1990, pp. 353–374.
8. Wahl, F. M., Grim, R. E. & Graf, R. B., Phase transformations in silica–alumina mixtures as examined by continuous X-ray diffraction. *Am. Mineral*, **46** (1961) 1064–1076.
9. Schmücker, M., Albers, W. & Schneider, H., Mullite formation by reaction sintering of quartz and α-Al_2O_3 — A TEM study. *J. Eur. Ceram. Soc.*, **14** (1994) 511–515.
10. Pankratz, L. B., Weller, W. W. & Kelley, K. K., Low temperature heat content of mullite. US Bur. Mines Rep. Invest. No. 6287,7 (1963).
11. Johnson, S. M. & Pask, J. A., Role of impurities on formation of mullite from kaolinite and Al_2O_3–SiO_2 mixtures. *Am. Ceram. Soc. Bull.*, **61** (1982) 838–842.
12. Risbud, S. H. & Pask, J. A., Mullite, crystallization from SiO_2–Al_2O_3 melts. *J. Am. Ceram. Soc.*, **61** (1978) 63–67.
13. Kingery, W. D., Bowen, H. K. & Uhlmann D. R., *Introduction to Ceramics*, 2nd Edition. John Wiley, New York, 1976.