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Chemical Stability of Cordierite–ZrO_2 Composites

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Abstract

Cordierite–ZrO_2 composites containing unstabilized and Y_2O_3-stabilized ZrO_2 were sintered at temperatures between 1200 and 1400°C for up to 48 h. In most cases both types of composites reacted to form zircon and spinel when sintered for more than 24 h. Only when Y_2O_3-doped ZrO_2 composites were annealed for up to 48 h, hardly any compositional changes took place due to the formation of an Al_2O_3–SiO_2–Y_2O_3 reaction barrier between ZrO_2 and the matrix.

Cordierit–ZrO_2-Keramiken mit unstabilisiertem und Y_2O_3-stabilisiertem ZrO_2 wurden bei Temperaturen zwischen 1200 und 1400°C bis zu 48 h gesintert. In beiden Komposit-Typen reagierten die Ausgangsphasen zu Spinell und Zirkon, wenn länger als 24 h geglüht wurde. Nur in Kompositen mit stabilisiertem ZrO_2, die bei 1400°C bis zu 48 h geglüht wurden, trat fast keine Phasenänderung auf, da sich zwischen dem ZrO_2 und Matrix eine Reaktionsbarriere aus Al_2O_3–SiO_2–Y_2O_3 bildete.

Des composites cordiérite–ZrO_2 contenant de la zircone non stabilisée ou stabilisée par Y_2O_3 ont été frittés jusqu'à 48 h à des températures comprises entre 1200 et 1400°C. Dans la plupart des cas, lors d'un frittage de plus de 24 h, les deux types de composites réagissent pour former de la zircone et du spinelle. Dans le seul cas de la zircone stabilisée frittée jusqu'à 48 h à 1400°C, on n'observe pratiquement pas de changement de phase, en raison de la barrière de réaction en Al_2O_3–SiO_2–Y_2O_3 qui se forme entre ZrO_2 et la matrice.

1 Introduction

Cordierite ($2MgO.2Al_2O_3.5SiO_2$) and cordierite-based ceramics are utilized in various electronic and mechanical applications due to their relatively low thermal expansion, low thermal conductivity and low dielectric constant. Their wider use, however, is limited by relatively poor mechanical properties.

Recently, it has been demonstrated that dispersing unstabilized ZrO_2 or stabilized Y_2O_3-doped ZrO_2 particles in cordierite can considerably improve the mechanical properties.[1–4] Both zircon and spinel were detected in all sintered cordierite–ZrO_2 composites[1,2] which formed according to the reaction

$$5ZrO_2 + Mg_2Al_4Si_5O_{18} = 2MgAl_2O_4 + 5ZrSiO_4$$

becoming more intensive at temperatures >1280°C.[1,5] However, no consistent analyses of this reaction have been reported to date. The intention of the present work is to study the kinetics of microstructural changes in cordierite–ZrO_2 composites when annealed at temperatures >1200°C.

2 Experimental

Powders of cordierite (Cordierite ($2MgO.2Al_2O_3.5SiO_2$), 'Experimental', Schott Glaswerke), unstabilized (m)-ZrO_2 (Monoclinic ZrO_2, Dynazircon F, Dynamit Nobel), and 2 mole% Y_2O_3-stabilized (t)-ZrO_2 (ZrO_2 (2 mole% Y_2O_3), TZP-2Y, Tosoh, Japan) were used in this study. Mixtures with 30 vol.% m-ZrO_2 or t-ZrO_2 were attrition milled in a polyethylene-lined vessel for 6 h in isopropanol using Y-TZP balls (diameter 2–3 mm). Further processing included rotary evaporator drying, sieving through 63 μm mesh, cold isostatic pressing at 800 MPa into test bars and sintering in air at 1200, 1300 and 1400°C for up to 48 h.

The microstructures of the composites and the progress of chemical reaction between cordierite and ZrO_2 were studied by SEM, semi-automatic image and XRD analyses.

3 Results and Discussion

3.1 Cordierite/m-ZrO_2 composites

Sintering of cordierite/m-ZrO_2 composites ('m'-composites) at 1200, 1300 and 1400°C leads to considerable changes in phase composition depending on sintering time. Cordierite and m-ZrO_2 are the dominant phases when sintered for >24 h. Sintering of 'm'-composites for >24 h results in composites containing mainly zircon and spinel. Traces of both zircon and spinel are already detected in 'm'-composites sintered for 30 min at 1200°C and for 15 min at 1300 and 1400°C.

The SEM micrographs (Figs 1, 2 and 3) show the effect of sintering time on the microstructure changes of 'm'-composites. Homogeneous microstructures with grain sizes between 1 and 3 μm are obtained for 'm'-composites sintered at 1400°C for 15 min, and full density is obtained after sintering for 30 min. The ZrO_2 grains are polygonal and located in intragranular positions (Fig. 3, 15 min). With progress of the reaction between cordierite and ZrO_2, it is possible to distinguish two kinds of residual ZrO_2 particles: (a) small intragranular rounded predominantly m-ZrO_2 particles inside large zircon and spinel grains and (b) intergranular m-ZrO_2 particles located between zircon, spinel and cordierite grains (Fig. 3, 8 h).

The kinetics of the reaction between cordierite and m-ZrO_2 can also be traced by semi-automatic image analyses. Figure 4 displays the decrease of

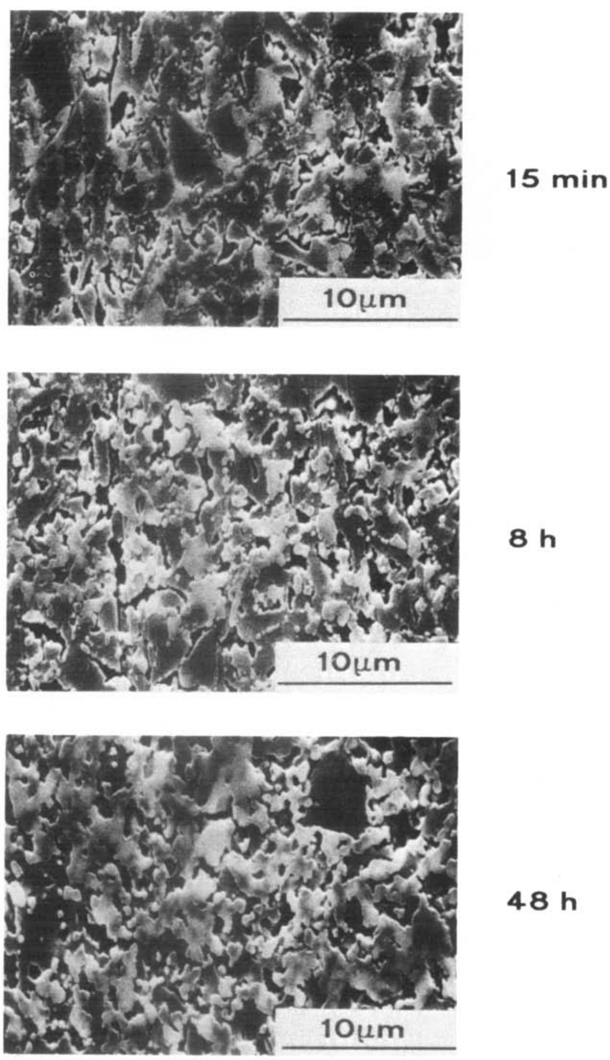

Fig. 1. SEM micrographs of 'm'-composites sintered at 1200°C for 15 min, 8 h and 48 h.

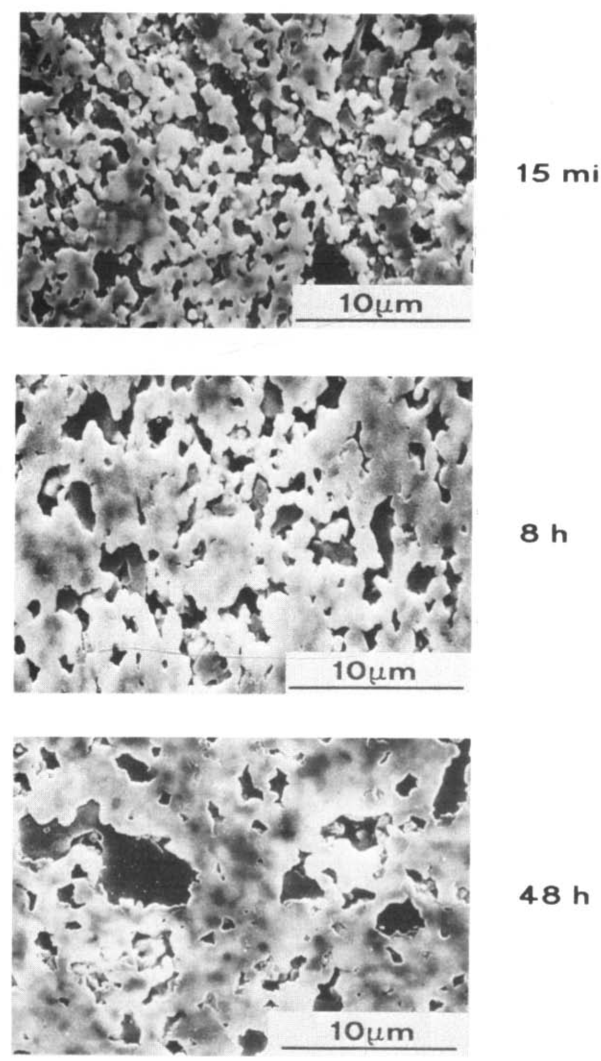

Fig. 2. SEM micrographs of 'm'-composites sintered at 1300°C for 15 min, 8 h and 48 h.

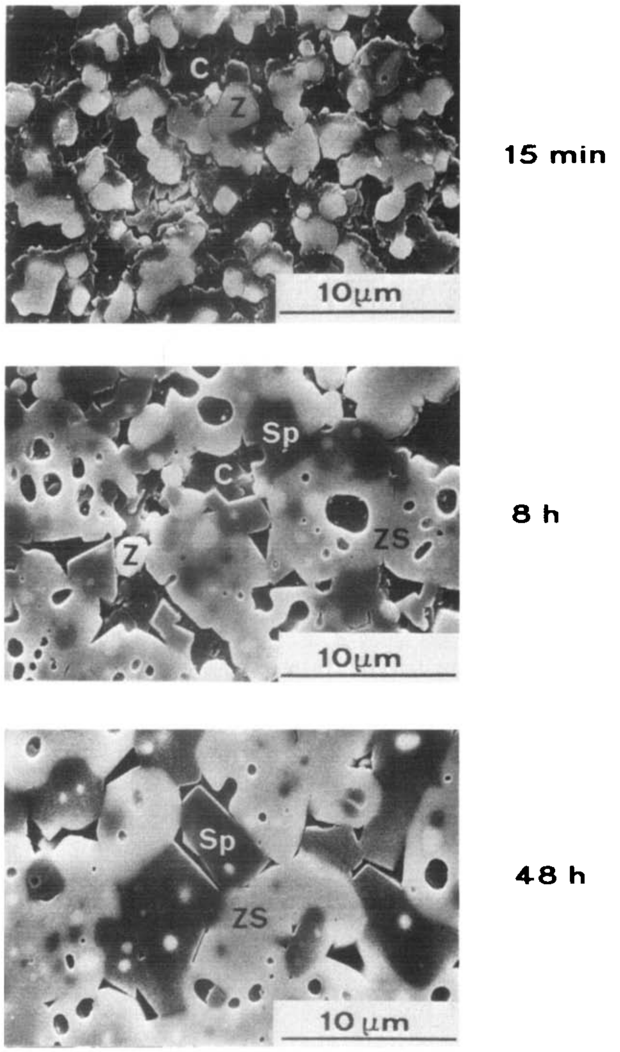

Fig. 3. SEM micrographs of 'm'-composites sintered at 1400°C for 15 min, 8 h and 48 h (C, cordierite; Z, zirconia; Sp, spinel; ZS, zircon; arrows show intra- and inter-granular zirconia particles).

volume fraction of m-ZrO_2 and the increase of volume fraction of $ZrSiO_4$ with sintering time.

3.2 Cordierite/t-ZrO_2 composites

Considerable changes in phase composition are detected by XRD in cordierite/t-ZrO_2 composites ('t'-composites) sintered at 1200 and 1300°C for up to 48 h, e.g., after 24 h at 1300°C, the microstructure contains mainly zircon and spinel. The time-dependence of phase content for 't'-composites sintered at 1300°C is similar to that obtained for 'm'-composites. Figures 5 and 6 show the microstructure changes observed by SEM in 't'-composites sintered for up to 48 h at 1200 and 1300°C, respectively.

In contrast to all results described so far, chemical reaction between cordierite and ZrO_2 is not detectable by XRD in 't'-composites sintered at 1400°C for up to 48 h. Also, by semi-automatic

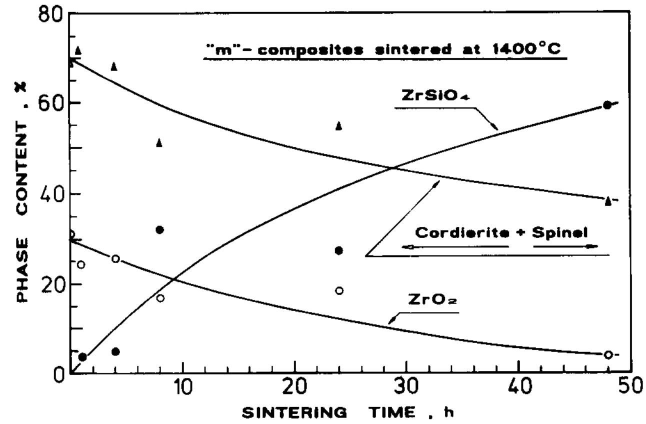

Fig. 4. Phase changes in 'm'-composites sintered at 1400°C.

image analysis, no changes in the contents of cordierite and ZrO_2 are found.

With increasing sintering time, however, an increasing amount of m-ZrO_2 appears at the expense of t-ZrO_2, i.e. 't'-composites sintered at 1400°C for >15 min contain mainly m-ZrO_2. Only small

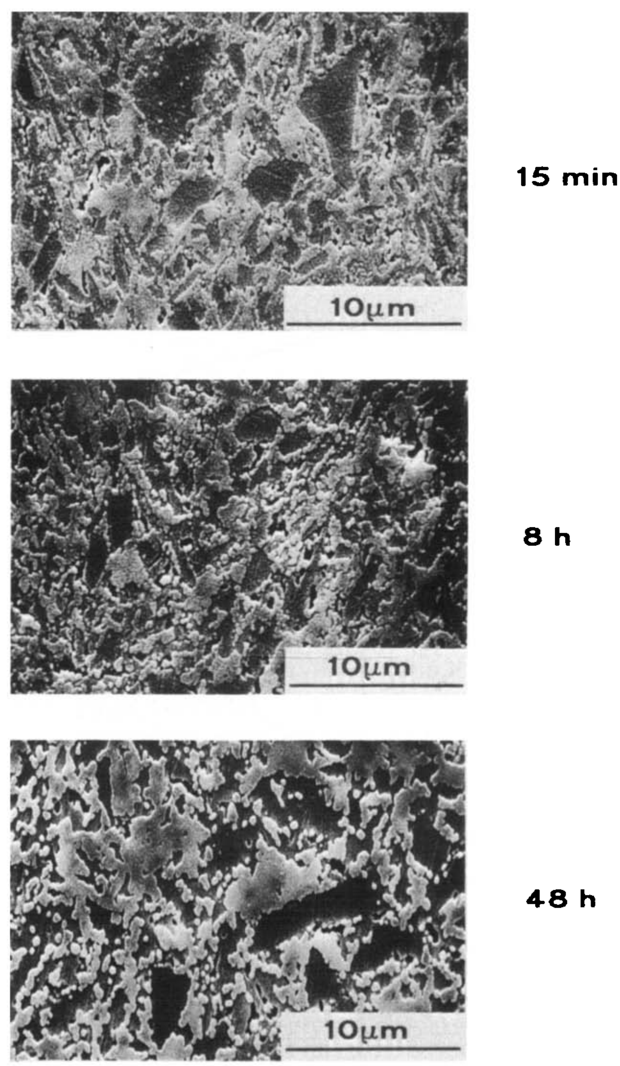

Fig. 5. SEM micrographs of 't'-composites sintered at 1200°C for 15 min, 8 h and 48 h.

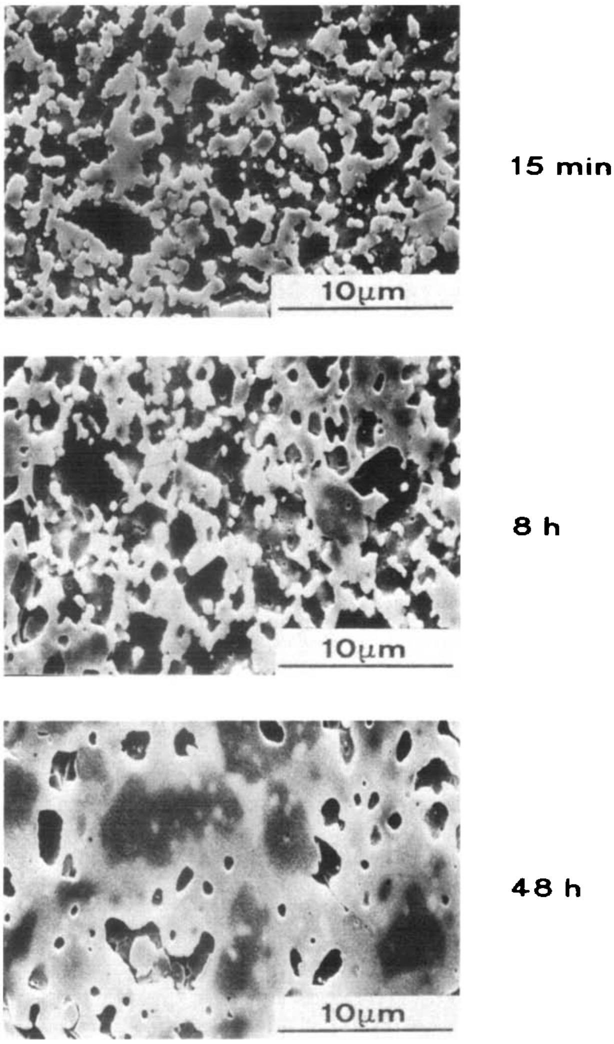

Fig. 6. SEM micrographs of 't'-composites sintered at 1300°C for 15 min, 8 h and 48 h.

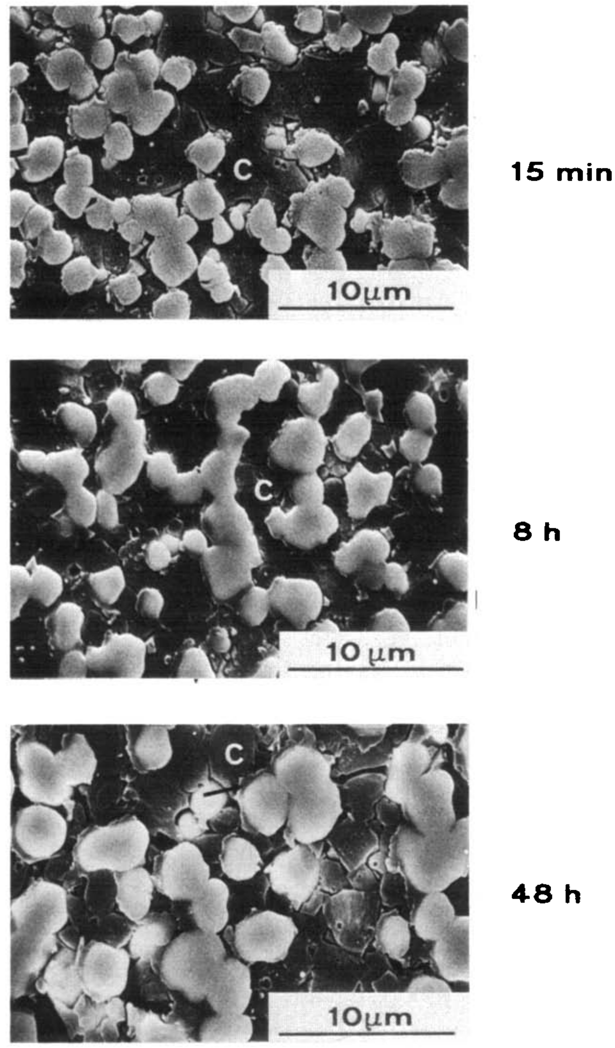

Fig. 7. SEM micrographs of 't'-composites sintered at 1400°C for 15 min, 8 h and 48 h (C, cordierite; Z, zirconia; arrow shows an intergranular glassy phase around ZrO_2 grains).

amounts of t-ZrO_2 are detected in 't' composites sintered at 1400°C for 48 h.

The SEM micrographs in Fig. 7 show the effect of sintering time on the microstructure of 't'-composites sintered at 1400°C. The existence of an intergranular phase around ZrO_2 grains is clearly visible. EDAX analysis of this phase yields Si, Al and Y, indicating a diffusion of Y from the Y_2O_3-doped ZrO_2 particles into liquid silicate. Appearance of Y is already detectable after 15 min. The presence of the glassy intergranular phase in cordierite–ZrO_2 composites has been reported previously.[2]

Diffusion of Y into the glassy phase leads to destabilization of t-ZrO_2 and to the formation of a eutectic phase which exists in the system Al_2O_3–SiO_2–Y_2O_3 between 1300 and 1400°C.[6] The formation of a Y-, Si- and Al-rich boundary phase was also reported for Y-TZP and mullite/Y-TZP ceramics.[7–9] The rapidly forming Al_2O_3–SiO_2–Y_2O_3 intergranular eutectic in 't'-composites at 1400°C is probably suppressing the chemical reaction between cordierite and ZrO_2 resulting in chemical stability.

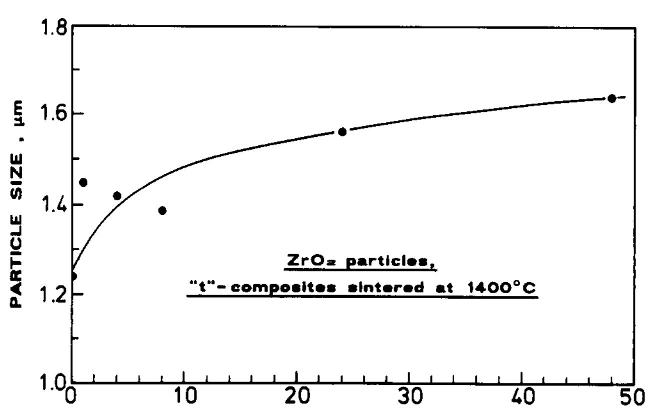

Fig. 8. ZrO_2 particle growth in 't'-composites sintered at 1400°C.

The effect of sintering time on ZrO_2 particle size in 't'-composites sintered at 1400°C is shown in Fig. 8. Many ZrO_2 particles are actually particle clusters (Fig. 7), indicating coarsening by coalescence.

4 Conclusions

In Cordierite/m-ZrO_2 composites sintered between 1200 and 1400°C for up to 48 h, ZrO_2 particles react in a cordierite matrix to form zircon and spinel. The same is true for cordierite/t-ZrO_2 composites sintered at 1200 and 1300°C. Sintering of 't'-composites at 1400°C, however, prevents the reaction of ZrO_2 particles with cordierite which is explained by the formation of an Al_2O_3–SiO_2–Y_2O_3 intergranular phase acting as chemical reaction barrier. Due to the loss of Y, though, ZrO_2 is increasingly destabilized leading to transformation to m symmetry.

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