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Preparation and characterization of cordierite–zirconia composites from co-precipitated powder

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Composite materials with 85 to 65 wt% cordierite and 15 to 35 wt% ZrO_2 were prepared from co-precipitated cordierite powder, and their densification behaviour, microstructure, mechanical strength, fracture toughness, thermal expansion and thermal shock resistance were studied. Addition of ZrO_2 to pure cordierite lowered the sintering temperature needed to obtain a dense sintered body. The fracture strength could be increased from 110 to 260 MPa and the thermal shock resistance from 350 to 500 °C by dispersing 15 wt% ZrO_2 particles in the cordierite matrix.

1. Introduction

Cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) and cordierite-based glass–ceramics are used as structural materials due to their low thermal expansion, the resulting thermal shock resistance, low density, and low thermal conductivity. Usually, cordierite ceramics are produced by calcination of a mixture of clays, talc and aluminium hydroxide, or by devitrification of cordierite glass with a suitable composition. However, sintering is also difficult without any sintering aid [1] because of the narrow sintering temperature range, and the mechanical properties are relatively poor. Recently, pure and crystalline cordierite powders were prepared by the sol–gel method [2–5]. These powders could be sintered without any sintering aid, but no improvement of mechanical properties was observed. It has been shown that a fine ZrO_2 dispersion in a ceramic matrix can affect the sinterability and increase the mechanical properties of the composites [6–8]. The enhancement of the mechanical properties of cordierite by dispersing ZrO_2 particles as a second phase has been reported [9, 10]. In these attempts, the starting material for cordierite was a powder of a cordierite-base glass or crystalline cordierite which had been obtained by devitrifying a cordierite-base glass.

In the present study, cordierite–zirconia composites containing 15 to 35 wt % ZrO_2 were prepared from co-precipitated cordierite powder. The preparation, sintering, mechanical strength, fracture toughness, thermal expansion, and thermal shock resistance of the composites were studied.

2. Experimental procedure

2.1. Sample preparation

Cordierite gel powder, having a BET surface area of 250 $m^2 g^{-1}$ and prepared by the co-precipitation method using aluminium sulphate, magnesium sulphate and sodium silicate solution, was calcined at 900–1400 °C in air and ball-milled for 48 h. The fine cordierite powder obtained was wet-mixed with amounts of 0, 15, 25, and 35 wt % unstabilized ZrO_2 powder (99.9% pure, EP, Daiich Kigenso Kagaku Kogyo Co. Ltd, Japan) by ball-milling with zirconia balls and dried in air. Cordierite–zirconia composite powders containing 15, 25 and 35 wt % of dispersed ZrO_2 were prepared; these powders will hereafter be referred to as C/Z15, C/Z25, and C/Z35, respectively. The mixed powders thus prepared were uniaxially pressed preliminarily at 19.6 MPa to form plates, and then isostatically cold-pressed at 196 MPa. The green compacts were sintered at 1325 to 1450 °C for 1 to 2 h in air.

2.2. Analytical procedure

The gel powders dried at 100 °C and calcined at each temperature for 2 h were analysed. Differential thermal analysis (DTA) and thermogravimetry (TG) were carried out in air up to 1300 °C. Specific surface areas of calcined cordierite powders were determined by the BET method. The bulk density of the sintered bodies was measured by water displacement. Fracture strength was measured in three-point bending on a universal testing machine using a span of 30 mm and a crosshead speed of 0.5 mm min^{-1}. The samples were 3 mm high, 4 mm wide and 40 mm long. Fracture toughness was measured by the indentation microfracture (IM) method using the formula of Lawn *et al.* [11]. Thermal shock resistance was examined by measuring the retained flexural strength of specimens after quenching from different temperatures into water at 100 °C. The coefficient of thermal expansion and thermal expansion curves were measured with specimens 17 mm long. The crystalline phases were identified by X-ray diffraction analysis. Microstructures of the surfaces were observed by SEM.

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3. Results and discussion

3.1. Heat-treatment of gel powders

DTA–TG data of the co-precipitated gel powder are shown in Fig. 1. The endotherm at 69 °C is attributed to the desorption of physically absorbed water. The other endotherm at 188 °C is associated with the dehydration of γ-$Al_2O_3 \cdot 3H_2O$ to form γ-$Al_2O_3 \cdot H_2O$. The endotherm at 376 °C is associated with the dehydration of γ-$Al_2O_3 \cdot H_2O$ to form the γ-Al_2O_3 phase. The DTA curve in Fig. 1 shows a broad exothermic peak in the range from 1100 to 1250 °C, which was also analysed by X-ray diffraction. X-ray diffraction analysis of powders heated at various temperatures are shown in Fig. 2. X-ray diffraction patterns corresponding to the spinel phase, both α-cristobalite and spinel phase and α-cordierite alone were observed for specimens heated at 1100, 1200 and 1250 °C, respectively.

The specific surface areas of the co-precipitated cordierite gel powders calcined at different temperatures were measured and the results are shown in Fig. 3. The uncalcined powder had a specific surface area of 250 $m^2\,g^{-1}$. The specific surface area gradually decreased below 1000 °C and then drastically diminished above 1100 °C. The value of the specific surface area of the powder calcined above 1200 °C was less than 1 $m^2\,g^{-1}$. The composition of calcined powder is shown in Table I. The composition is almost equal to the stoichiometric value for cordierite.

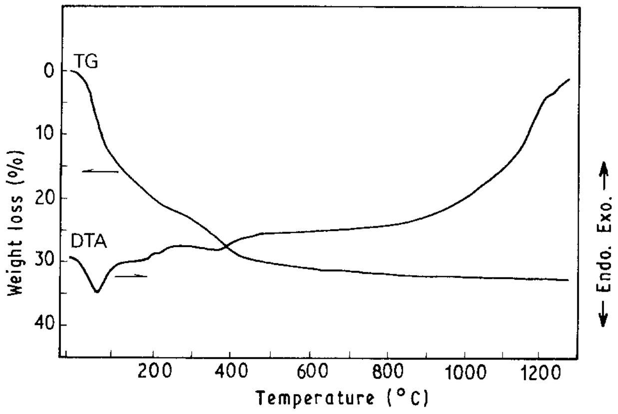

Figure 1 DTA–TG curves of cordierite gel powder prepared by a co-precipitation method.

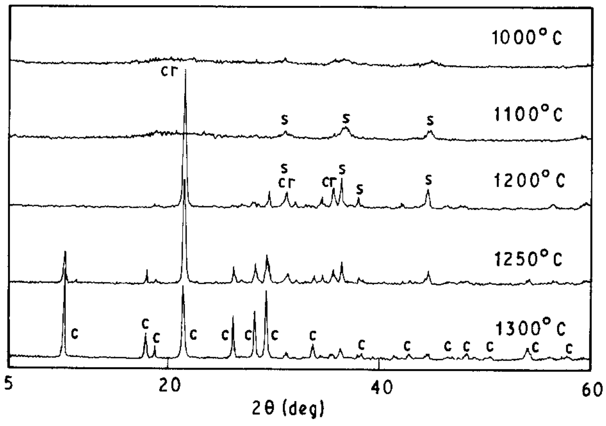

Figure 2 X-ray diffraction patterns of cordierite gel powders heated at various temperatures: (C) cordierite, (S) spinel, (Cr) cristobalite.

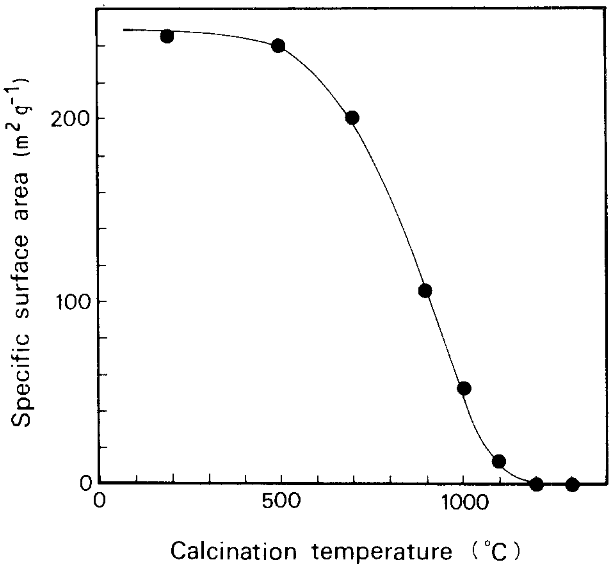

Figure 3 Variation of specific surface area of the cordierite gel powders with calcination temperature.

TABLE I Composition of powders by chemical analysis

	Al_2O_3 (wt %)	SiO_2 (wt %)	MgO (wt %)
Calcination at 1200 °C	34.13	52.52	13.35
Stoichiometry	34.86	51.36	13.78

3.2. Densification

The sintering of the powder compacts was carried out at temperatures between 1325 and 1450 °C. The densification curves of pure cordierite and cordierite–zirconia composites examined using the firing profile A (Table II) are shown in Fig. 4. The bulk density of the sintered specimens increased with temperature for pure cordierite up to 1425 °C, therefore it was considered that a temperature above 1425 °C was required for full densification. For cordierite–zirconia composites the optimal sintering temperature lies at 1400 °C. These results showed that the sintering temperature of cordierite needed to obtain a dense sintered body was lowered by the addition of ZrO_2.

The effect of sintering conditions, i.e. sintering time and heating rate, on the final density of the cordierite–zirconia composites was investigated using the firing schedules as given in Table II. Table III shows the bulk density of cordierite–zirconia composites sintered at 1400 °C by the firing profiles A and B. For the calculation of the theoretical density of the composite material, densities of 2.51 and 5.86 $g\,cm^{-3}$ have been used for cordierite and zirconia, respectively. The difference between the bulk density of the sintered body and the calculated theoretical density increased with increasing zirconia content in the composite. For

TABLE II Firing schedules

Profile	Heating rate (°C min^{-1})	Holding time (min)
A	10	60
B	1.6	120

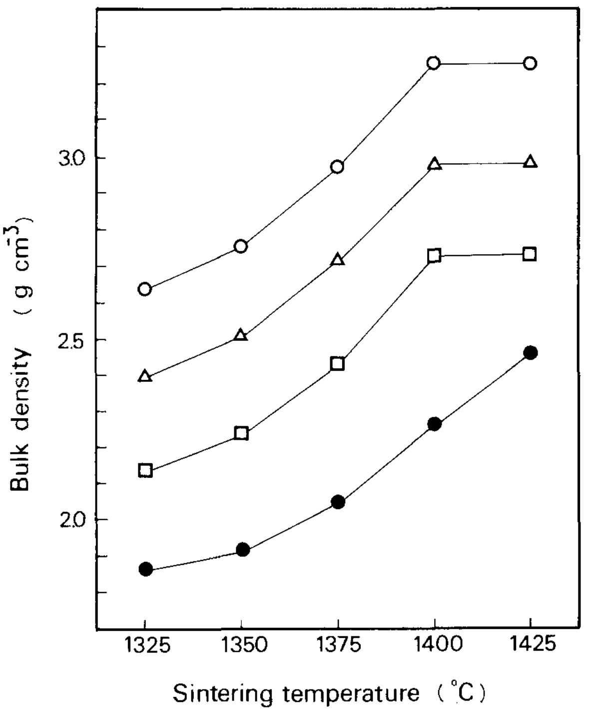

Figure 4 Densification curves for cordierite and cordierite-zirconia composites: (●) cordierite, (□) C/Z15, (△) C/Z25, (○) C/Z35.

TABLE III Bulk density of cordierite–zirconia composites sintered at 1400 °C

Specimen	Bulk density (g cm^{-3})		Calculated theoretical density
	Profile A	Profile B	(g cm^{-3})
C/Z15	2.73	2.74	2.75
C/Z25	2.98	3.08	2.93
C/Z35	3.25	3.40	3.14

the specimens sintered by firing profile B, noticeable discrepancies in the density were observed. Fig. 5 shows the relationships between the X-ray intensity of zircon formed by the following reaction and the sintering temperature for cordierite–zirconia composites containing 15 and 35 wt % ZrO_2 sintered by the firing profile A:

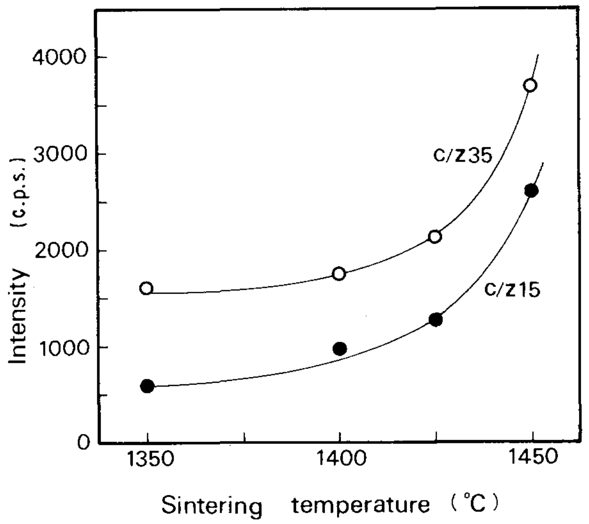

Figure 5 Relation between the X-ray diffraction intensity of zircon in samples and sintering temperature.

$$Mg_2Al_4Si_5O_{18} + 5ZrO_2 \rightarrow 2MgAl_2O_4 + 5ZrSiO_4 \quad (1)$$

During the sintering of the cordierite–zirconia composites, two processes are occurring: densification, and zircon and spinel formation. It is seen from Fig. 5 that the formation of zircon is promoted at higher sintering temperatures. It is obvious that the discrepancies in the densities of Table III result from the formation of zircon and spinel. It was observed that a slow heating rate, higher sintering temperature and prolonged holding time at the sintering temperature promote the reaction of formation of zircon and spinel.

3.3. Characteristics of sintered bodies

Fig. 6 presents SEM photographs of the cordierite–zirconia composites containing 15, 25, and 35 wt % ZrO_2 sintered at 1400 °C. The microstructural feature of the cordierite matrix were the same as those of pure cordierite. In Fig. 6, the ZrO_2 particle size and distribution can be seen. ZrO_2 particles are dispersed uniformly in the materials. For the samples in Fig. 6, the average particle size of zirconia was 1 to 2 μm. Since $ZrSiO_4$ particles give the same mass contrast as ZrO_2 no clear distinction of the particles was possible. In the SEM photograph of the cordierite–35 wt % ZrO_2 composite material (Fig. 6) some large features can be observed in addition to the otherwise homogeneous distribution of white particles. These features have not been analysed by microanalytical methods but it is considered that they indicate the formation of zircon.

The degree of thermal expansion of cordierite–zirconia composites up to 1000 °C is shown in Fig. 7 as a function of zirconia content. Thermal expansion curves of all samples were nearly linear. The average values of linear thermal expansion from room temperature to 1000 °C are 2.3×10^{-6}, 2.5×10^{-6}, and 3.5×10^{-6} for pure cordierite, cordierite–15 wt % ZrO_2 composite and cordierite–35 wt % zirconia composite sintered at 1400 °C, respectively.

Fig. 8 shows the dependence of the three-point bending strength on the amount of ZrO_2. The fracture strength of samples containing ZrO_2 increased from 110 MPa for pure cordierite to 260 MPa. Fracture toughness determined by the indentation method for sintered bodies containing the various concentrations of ZrO_2 are shown in Fig. 9. The fracture toughness increased from 2.1 MPa m$^{1/2}$ for pure cordierite to 3.2 MPa m$^{1/2}$ at a content of 35 wt % ZrO_2. The fracture strength and toughness were related to the microstructure and depend on the amount and the phase type of zirconia (tetragonal or monoclinic). The results of thermal shock tests of cordierite and cordierite–15 wt % ZrO_2 composite are shown in Fig. 10. The thermal shock resistance ΔT_c was increased from 350 °C for pure cordierite to 500 °C for cordierite–zirconia composite by dispersing 15 wt %

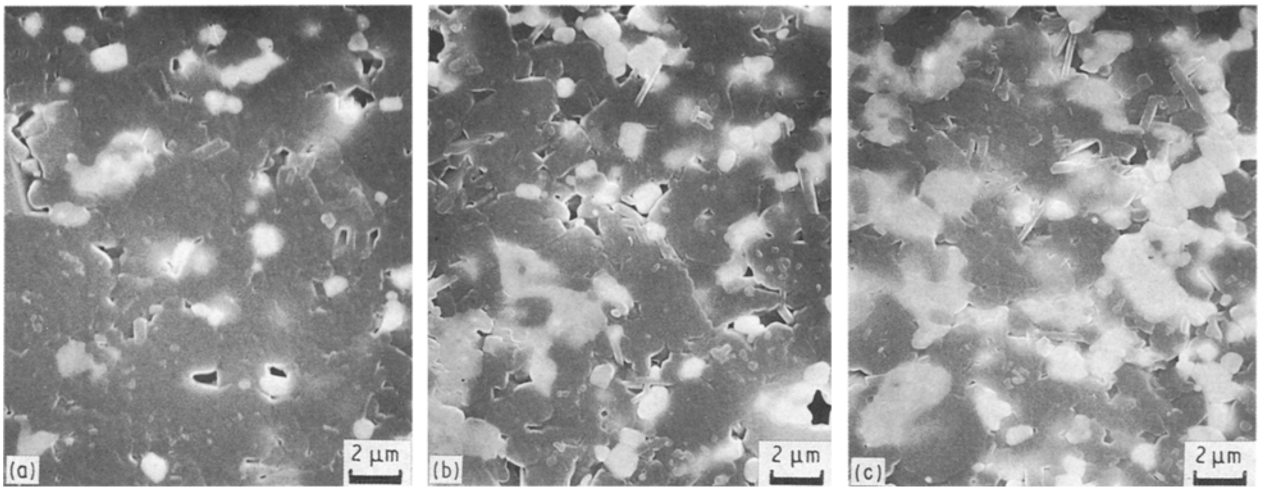

Figure 6 SEM photographs of the thermally etched surface of cordierite–zirconia composites sintered at 1400 °C: (a) C/Z15, (b) C/Z25, (c) C/Z35.

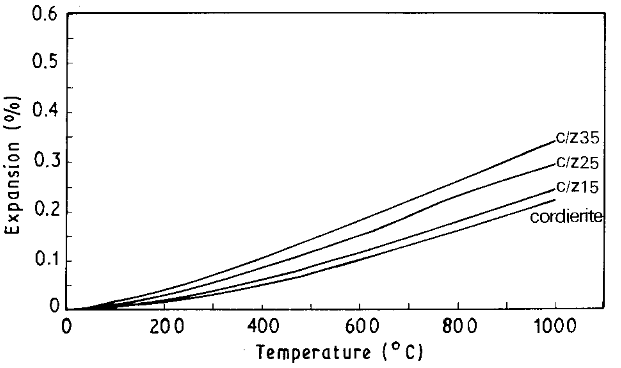

Figure 7 Thermal expansion curves.

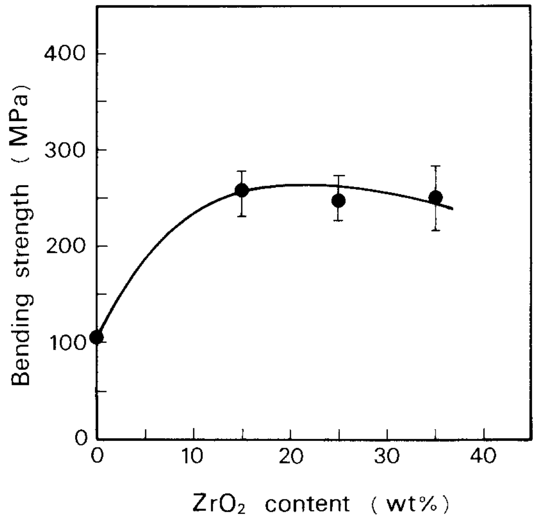

Figure 8 Effect of zirconia content on the bending strength of cordierite–zirconia composites sintered at 1400 °C.

ZrO_2 particles in the cordierite matrix. The experimental data have thus indicated that incorporating a zirconia dispersed phase in a cordierite matrix can lead to improvements in thermal stress resistance by increasing the fracture toughness and strength without noticeable change in the coefficient of thermal expansion.

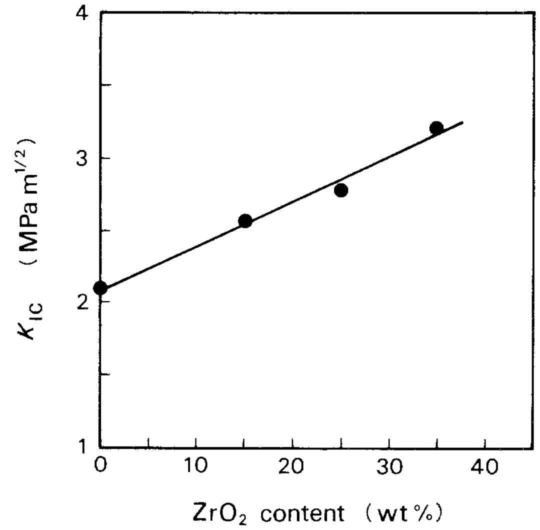

Figure 9 Effect of zirconia content on the fracture toughness of cordierite–zirconia composites sintered at 1400 °C.

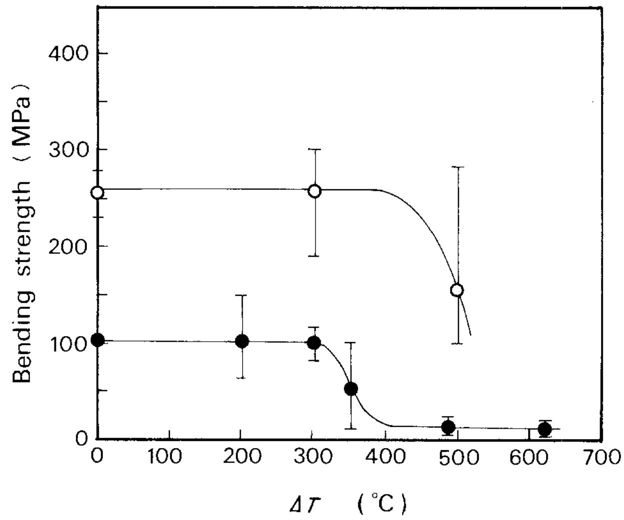

Figure 10 Thermal shock behaviour of (●) cordierite and (○) cordierite–zirconia composites containing 15 wt% ZrO_2, quenched into water at 100 °C.

4. Conclusions

1. Cordierite–zirconia composites containing 15 to 35 wt % ZrO_2 have been prepared from co-precipitated cordierite powder.

2. Dense cordierite–zirconia composite ceramics were obtained by sintering at 1400 °C.

3. The thermal expansion coefficient increased gradually with increasing ZrO_2 content.

4. The fracture strength and toughness increased respectively from 110 to 260 MPa and from 2.1 to 3.2 MPa $m^{1/2}$ on dispersing ZrO_2 particles in the cordierite matrix.

5. The thermal shock resistance was increased from 350 to 500 °C by dispersing 15 wt % of ZrO_2 in the cordierite matrix.

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