Fabrication and mechanical properties of cordierite/ZrO₂ composites by pressureless sintering

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Cordierite/ZrO₂ composites with 5 to 25 wt% ZrO₂ were fabricated by pressureless sintering, and their densification behavior, fracture strength, fracture toughness, microstructure and thermal expansion behavior were studied. The ZrO₂ addition into cordierite matrix affects the densification behavior and mechanical properties of the composites. By dispersing 25 wt% ZrO₂, densified cordierite/ZrO₂ composite with a relative density of 98.5% was obtained at optimum sintering condition of 1440°C/2h. Both fracture strength and toughness were enhanced with increasing ZrO₂ content. The fracture strength and toughness were increased from 140 to 290 MPa and from 1.6 to 3.5 MPa·m$^{1/2}$, respectively, by dispersing 25 wt% ZrO₂ into the cordierite matrix. ZrO₂ particles were homogenously dispersed into cordierite matrix, which intragranular particles were fine (< 100 nm) and intergranular particles were coarse. The toughening mechanisms in the present composites were mainly attributed to martensitic transformation toughening. Then, the addition of ZrO₂ is likely to have little deleterious effect upon thermal expansion coefficient of cordierite.

Key words: Cordierite, ZrO₂, Composite, Toughening, Pressureless Sintering.

Introduction

Cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) ceramics have a superior thermal shock resistance due to their intrinsic low coefficient of thermal expansion (CET), coupled with relatively high refractoriness and high chemical stability. Therefore, they are often used as industrial furnaces, heat exchangers for gas turbine engines; honeycomb-shaped catalyst carriers in automobile exhaust systems [1-2]. However, difficulties in sintering because of its narrow sintering temperature range [3], as well as relatively poor mechanical properties, have prevented their more widespread applications.

In the present study, ZrO₂ toughened cordierite was fabricated by dispersing 5 to 25 wt% ZrO₂ into cordierite matrix under presureless sintering. The densification behavior and microstructure were investigated, and the fracture strength, fracture toughness and thermal expansion behavior were evaluated.

Experimental Procedure

Cordierite was prepared from the component high-purity oxide powders. The oxides were mixed at the composition ratio of $MgO : Al_2O_3 : SiO_2 = 14 : 37.2 : 48.8$ (wt%), and calcined at 1400°C for 12h. Crystalline phase was identified by X-ray diffraction of this cal-

cined sample, and only α-cordierite phase was detected. M-ZrO₂ powder from 5 to 25 wt% was added to this obtained cordierite powder; these powders will hereafter be referred to as CorZr5 to CorZr25, respectively. The resultant granules were pressed uniaxially and then cold-isostatically-pressed (CIP) under a pressure of 196 MPa. Then, the green compacts were sintered under ambient pressure at various temperatures from 2h to 12h.

Sintered compacts were analyzed for phase identification using an X-ray diffractometer (XRD). The bulk densities were determined by the modified Archimedes displacement method. Fracture strength was measured in three-point bending on a universal testing machine. The fracture toughness values were determined using an indentation-fracture method. The critical stress intensity factor (K_{Ic}) was then estimated using the crack length and analysis method described by Niihara [4]. Microstructures of sintered compacts were observed by a scanning electron microscope (SEM) and transmission electron microscope (TEM). The coefficient of thermal expansion (CET) was measured by thermomechanical analysis (TMA) at a heating rate of 10°C/min from room temperature to 600°C. And the theoretical value of CET was calculated using the equation given by Kerner [5].

Results and Discussion

Table 1 shows the relative density of sintered bodies with ZrO₂ dispersed amount as a function of the

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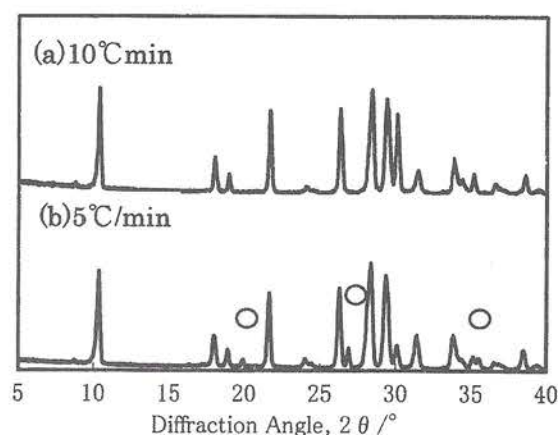Fax: +81-6-6879-8444
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Table 1. The relative density for the composites obtained under various sintering conditions

ZrO_2 content	0 wt%	5 wt%	10 wt%	15 wt%	20 wt%	25 wt%
1400°C/2h	68.0	72.6	74.9	78.3	79.1	82.9
1440°C/2h	70.4	89.8	95.6	97.8	97.8	98.5
1440°C/12h	79.0	90.0	96.6	99.0	99.2	99.0

Table 2. Fracture strength and toughness of cordierite/ZrO_2 composites at various ZrO_2 content sintered at 1440°C/2h and 1440°C/12h

	ZrO_2 (wt%)	Fracture Strength (MPa)	Fracture Toughness (MPa m$^{1/2}$)
1440°C/2h	0	140 ± 12	1.66 ± 0.02
	15	272 ± 28	3.23 ± 0.10
	25	289 ± 41	3.88 ± 0.17
1440°C/12h	0	155 ± 15	1.60 ± 0.02
	15	223 ± 19	3.09 ± 0.17
	25	251 ± 35	3.51 ± 0.14

sintering temperature. The density of the sintered samples is strongly dependent on sintering temperature and dispersed amount of ZrO_2. The relative densities of sintered bodies with the same ZrO_2 dispersed amount increased with sintering temperature, and at the same sintering temperature, it also increased gradually with an increase of ZrO_2 dispersed amount. It can be concluded that dispersing ZrO_2 decreased the densification temperature of cordierite.

Although the formation of zircon was predicted at temperature in excess of 1280°C [6], phase identification (Fig. 1(a)) of the sintered compacts did not revealed any presence of zircon phase. It was believed that at the processing temperature and the heating rate used, the reaction kinetics were insufficiently fast to produce any evidence of a reaction. To confirm this hypothesis, CorZr25 specimen was sintered at the heating rate of 5°C/min. The result of X-ray analysis is shown in Fig. 1(b). A small peak due to zircon formation is seen at 27°. This result agrees with that of Nieszery *et al.* [7, 8] who used rate-controlled sintering with the final stage involving a soaking at 1400°C for 1h to produce dense cordierite/ZrO_2 composites. Therefore, it can be concluded that the reaction between cordierite and zirconia is thermodynamically possible, but can be suppressed by employing a faster heating rate.

Table 2 shows the indentation toughness and fracture strength as a function of the weight percent of ZrO_2 in the cordierite matrix. It can be seen that the fracture toughness and strength increase gradually with increas-

ing ZrO_2 content. Several toughening mechanism may occur simultaneously in ZrO_2 toughened composites. Since the stress-induced transformation from tetragonal phase to monoclinic phase is known as the most effective toughening mechanism for ZrO_2-reinforced matrix composites, the extent of martensitic transformation was qualitatively estimated by examining the change in the relative phase distribution before and after the polishing. X-ray diffraction analysis was performed to determine the volume fraction of the monoclinic ZrO_2 phase (*Vm*). The *Vm* was increased from ~60% for the asñsintered surface to ~70% for the polished surface, demonstrating that the transformation toughening contributes to the increase in the fracture toughness of the present cordierite/ZrO_2 composites. The observation of indentation crack in the CorZr25 composite (Fig. 2) shows little crack deflection around the dispersed ZrO_2 particles, therefore a crack deflection mechanism seems to hardly contribute to the toughening in present work.

The SEM micrograph (Fig. 3(b)) of CorZr25 shows an essentially pore-free microstructure and a uniform spatial distribution of the dispersed ZrO_2 particles, with little agglomeration between them, and cordierite matrix grains size are smaller than that of CorZr0 (Fig. 3(a)) specimen. It is believed that ZrO_2 dispersions limit the cordierite grains growth by pinning and prohibiting the grain boundary movement. ZrO_2 parti-

Fig. 1. XRD patterns of CorZr15 composite specimen sintered at 1440°C for 2h, showing the effect of heating rate on the formation of zircon. ○ : zircon.

Fig. 2. SEM micrograph of crack propagation in CorZr25 composite sintered at 1440°C/2h.

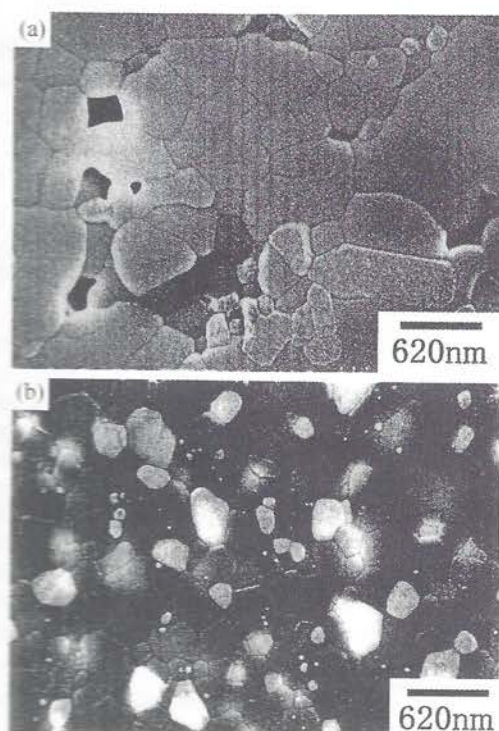**Fig. 3.** SEM micrographs of polished and thermal-etched surfaces of the CorZr0 (a) and CorZr25 (b) specimen sintered at 1440°C for 2h.

Table 3. CTE of cordierite/ZrO$_2$ composites at various ZrO$_2$ content under the sintering condition of 1440°C/2h

Samples	ZrO$_2$ content (wt%)		
	0	15	25
Measured CTE (× 10^6)	1.17	1.47	1.78
Calculated CTE (× 10^6)	1.5	1.55	1.59

cles were located inside and between the cordierite grains, which intragranular particles were fine (< 100 nm) and intergranular particles were coarse.

Although there is a large thermal expansion mismatch between cordierite (CTE, ~1.2 × 10^{-6}) and ZrO$_2$ (CTE, ~9.2 × 10^{-6}), TEM observation revealed that microcracking did not occur around the transformed m-ZrO$_2$ inclusions. It is reported that there are several morphologies of t-ZrO$_2$, such as dendritic, rod and spheroid. In present composite, the former two morphologies were not observed.

Measured and estimated CTE of CorZr0, CorZr15 and CorZr25 prepared at 1440°C/2h are shown in Table 3. There is little difference between the measured CTE

and estimated CTE. Between room temperature and 600°C, the average the CTE of pure cordierite (CorZr0) is 1.17×10^{-6}°C^{-1}, which is a litter lower than the value of the literature shown [9]. The little increase of CTE of CorZr15 and Corr25 is believed to be due to the dispersion of ZrO$_2$ in the cordierite matrix, because the CTE of zirconia is 10×10^{-6}°C^{-1}, higher than that of cordierite. But they are still at low value, 1.47×10^{-6}°C^{-1} and 1.78×10^{-6}°C^{-1} of CorZr15 and CorZr25, respectively. Therefore the addition of ZrO$_2$ is likely to have little deleterious effects upon thermal expansion coefficient of cordierite.

Conclusions

On the basis of the above study, the following conclusions can be drawn.

1. Densified cordierite/ZrO$_2$ composite with a relative density of 98.5% was prepared by dispersing 25 wt% ZrO$_2$ under pressureless sintering.

2. The fracture strength and toughness were increased from 140 to 290 MPa and from 1.6 to 3.5 MPa · m$^{1/2}$, respectively, by dispersing 25 wt% ZrO$_2$. This toughening was mainly attributed to martensitic transformation toughening.

3. The dispersion of ZrO$_2$ particles in cordierite matrix was homogenously. Intragranular particles were fine (< 100 nm) and intergranular particles were coarse.

4. The addition of ZrO$_2$ is likely to have little deleterious effects upon thermal expansion coefficient of cordierite.

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