研究

Effects of SiC Addition on Microstructure of Porous $\text{CaZrO}_3/\text{MgO}$ Composites

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Received January 12, 2001

SYNOPSIS

Microstructure and pore-size distribution of the porous $\text{CaZrO}_3/\text{MgO}$ *in situ* composites were modified by the addition of SiC. A porous composite with bimodal pore-size distribution (peaks at $\sim 1\ \mu\text{m}$ and $\sim 17\ \mu\text{m}$, porosity $V_p = 59\%$) was obtained by the pressureless reactive sintering of $\text{CaMg}(\text{CO}_3)_2$ (dolomite), ZrO_2 and SiC mixtures with a small amount of LiF in air. In an oxidative sintering atmosphere, SiC presumably acted as a "precursor" of SiO_2 at elevated temperatures, and contributed to the "partial" liquid phase sintering in the powder compact.

KEY WORDS

calcium zirconate, magnesia, dolomite, silicon carbide addition, pore size control

1 Introduction

There is a growing interest in porous ceramics for hot-gas filter applications, e.g., for the pressurized fluidized bed combustion (PFBC) and the integrated coal gasification combined cycle (IGCC)¹⁻⁴. Oxide-based porous materials are promising for such purposes because of their good phase stability, erosion/corrosion resistance, and cost-performance⁵⁻¹⁰.

Calcium zirconate, CaZrO_3 , is a perovskite-structured oxide with very high melting point ($\sim 2362^\circ\text{C}^{11}$) and is compatible with MgO (eutectic temperature: $2050^\circ\text{C}^{12,13}$). Thus, the CaZrO_3 -MgO quasi-binary system is a candidate for high-temperature structural composites^{14,15}.

The authors have recently developed uniformly open-porous $\text{CaZrO}_3/\text{MgO}$ *in situ* composites with three-dimensional (3-D) network structure, via pressureless reactive sintering of $\text{CaMg}(\text{CO}_3)_2$ (dolomite) and ZrO_2 with 0.5 wt% LiF additive (see Fig. 1)¹⁶⁻¹⁹. The pore-size distributions of the composites were very narrow and almost constant (with pore size: $\sim 1\ \mu\text{m}$) for sintering temperatures of 1100 – 1400°C . The porosity in the range of ~ 30 – 50% can be obtained by changing the sintering temperature. In order to expand the applicability of the porous composites, it is indispensable to control the pore-size distribution towards a larger or smaller part; for example, open pores of $\sim 10\ \mu\text{m}$ are required for a diesel particulate filter⁶.

In this study, we have attempted to modify the microstructure and pore-size distribution of the porous

$\text{CaZrO}_3/\text{MgO}$ *in situ* composites by the addition of a fine SiC powder. In an oxidative sintering atmosphere, it is anticipated that SiC is gradually oxidized at high temperatures, which affects the microstructural development during the *in situ* processing. Thermogravimetry and differential thermal analysis (TG-DTA) of mixed powders were conducted to verify the oxidation effect. This paper focuses not on complicated phase relationships but on microstructural development. The phase relationships in the CaO - MgO - ZrO_2 - SiO_2 quaternary system were reported in detail by De Aza et al¹².

Fig. 1 Typical microstructure of the porous $\text{CaZrO}_3/\text{MgO}$ *in situ* composite (porosity $\sim 40\%$)¹⁶⁻¹⁹. Grains with bright contrast are CaZrO_3 and those with dark contrast are MgO.

2 Experimental Procedure

2.1 Sample preparation

Fig. 2 schematically illustrates the experimental procedure. The sample preparation method is similar to that of the previous work¹⁶⁾. High-purity $\text{CaMg}(\text{CO}_3)_2$ (natural dolomite, purity: >99wt%, particle size: <75 $\mu\text{m}^{20)$), undoped ZrO_2 (Sumitomo Cement Co. Ltd., 99.9 wt%), β - SiC (Mitsui Toatsu Chemical Co., Ltd., particle size: 150 nm) and LiF (Wako Pure Chemical Ind. Ltd., 99.9 wt%) were used as the starting powders. $\text{CaMg}(\text{CO}_3)_2$ and ZrO_2 were weighed to 50:50 in mol%, and SiC was added to be 7.3 and 15 wt% of the sum of $\text{CaMg}(\text{CO}_3)_2$ and ZrO_2 . LiF was also added to form liquid phase during sintering to enhance the reactivity and neck-growth (0.5 wt% to total starting powders). Table 1 summarizes the compositions of powder mixtures.

Fig.2 Schematic illustration of the experimental procedure.

The $\text{CaMg}(\text{CO}_3)_2$, ZrO_2 , SiC and LiF powders were wet-ball milled in ethanol for 6 h by using a planetary ball-mill process (acceleration: 6g). The mixed slurry was dried, subsequently dry-ball-milled for 24 h, and then, sieved through a 100-mesh screen. The mixed powders were cold isostatically pressed at 200 MPa after mold-pressing. The green compacts (15 mm in diameter and ~5 mm in thickness) were sintered in air at 1000–1300°C for 2 h.

2.2 Evaluation

The microstructure of the porous composites was characterized using a scanning electron microscope (SEM, Model 6330F, JEOL, Tokyo, Japan). The porosity and the pore-size distribution of the porous composites were determined by mercury porosimetry (Poresizer 9320, Micromeritics, Norcross, GA). Mercury intrusion was carried out at pressures between 0 to 207 MPa. A cylindrical pore model²¹⁾ was used for the calculation of the total pore volume (V_p), specific surface area (S_p), and porosity (P). The reaction behavior of mixed powders during heating in air was evaluated by TG-DTA (10°C/min) up to 1200°C.

3 Results and Discussion

3.1 Characterization of Bulk Porous Composites

For the porous $\text{CaZrO}_3/\text{MgO}$ composite without SiC addition¹⁶⁾, a very uniform 3-D network microstructure was obtained throughout the specimen (including surface). On the other hand, the surface and internal structures became different each other with the SiC addition. Fig. 3 shows the microstructure of the 15 wt% SiC added composite (15S) sintered at 1100°C. It is assumed from Fig. 3(a) and (b) that a liquid phase was extensively formed near the specimen's surface, probably due to the oxidation of SiC. Almost dense shell structure was observed around the specimen (Fig. 3(b)). Figs. 3(c) and (d) demonstrate the interior of the specimen. It remained porous, and there existed large pores of the order of ~10 μm . At higher

Table 1 Compositions of powder mixtures in wt%.

Designation	$\text{CaMg}(\text{CO}_3)_2$	ZrO_2	SiC	LiF
0S	59.6	39.9	-	0.5
7.3S	55.3	36.9	7.3	0.5
15S	50.6	33.8	15.1	0.5

The amounts of SiC nominally correspond to the compositions of $\text{CaZrO}_3\text{-MgO}:\text{SiC}=90:10$ and $80:20$ in wt% after sintering for the 7.3S and 15S powders, respectively. However, fine SiC particles actually tend to convert into oxide form (SiO_2 or SiO) under oxidative sintering conditions.

Fig.3 SEM micrographs of the 15 wt% SiC added composite sintered at 1100 °C.

sintering temperatures (1200 ° and 1300 °C), the whole composite tends to densify due to the more liquid formation; the densification proceeded toward the interior of specimens. At lower sintering temperature (1000 °C), the specimen remained porous without larger pore formation. The microstructure of 7.3 S composite was apparently similar to that of the 15 S composite.

The total pore volume and the pore size distribution of the porous composites (7.3 S) evaluated by mercury porosimetry are shown in Fig. 4. Note that the specimen was crush into ~5 mm in order to minimize the dense shell effect. The sample sintered at 1000 °C had very narrow pore size distribution with mean size of ~1 μm, similarly to the composite without SiC addition¹⁶⁾. The mechanism of the 1 μm-pore formation was probably the same as that of the 0 S composite¹⁶⁾, i.e., based on the CO₂ gas emission during the sintering. On the other hand, the SiC-added composite (7.3 S) sintered at 1100 °C possessed bimodal pore-size distribution (peaks at ~1 μm and ~17 μm, porosity V_p=59%). These results were in good agreement with the above SEM observation. Table 2 summarizes the pore

structure of the 7.3 S porous composites sintered at different sintering temperatures.

3.3 TG-DTA analysis of the mixed powders

Fig. 5 shows the TG-DTA diagrams for (a) the 0 S (without SiC) and (b) the 7.3 S mixed powders. In Fig. 5 (a), the decomposition of dolomite into CaCO₃ (half-decomposition) and the formation of CaZrO₃ were clearly observed below <800 °C, judged from the two -step weight loss and two endothermic peaks at 626 and 763 °C, which was described in previous works^{16,19)}.

and then,

For SiC-added powder, in Fig. 5 (b), complex endo- and exothermic peaks were observed at 600–900 °C. It is considered that these peaks are yielded as convolution of the endothermic peak by CO₂ emission (expressed in Eqs. (1) and (2)) and the exothermic peak by the oxidation of SiC particles (~650–900 °C). A slight increase in weight

at > 800 °C is attributable to the oxidation of SiC, which is not observed in Fig. 1(a).

3.4 Microstructure development

For the SiC-added system, the mechanism of larger pore formation (Fig. 3(c) and (d)) can be deduced as follows. During the sintering, SiC particles were gradually oxidized to form SiO₂. They are regarded as "SiO₂-precursor" at

elevated temperature (~650–900 °C, see in Fig. 5(b)) in an oxidative sintering atmosphere. At ~1100 °C, multiphase eutectic reactions including SiO₂ yielded liquid phase enough to wet and join the fine grains. In other words, "partial" liquid phase sintering took place in the porous

Fig. 4 Pore size distribution of the porous composites (7.3S) sintered at (a) 1000 °C and (b) 1100 °C in air.

Fig. 5 TG-DTA diagrams measured in a static air atmosphere at 10 °C/min: (a) the 0S mixed powder (CaMg(CO₃)₂ + ZrO₂ + 0.5 wt% LiF), and (b) the 7.3S mixed powder (CaMg(CO₃)₂ + ZrO₂ + SiC + 0.5 wt% LiF).

Table 2 Pore Structure of the 7.3 wt% SiC added porous composites.

Sintering Temperature (°C)	Total pore Volume V _p (cm ³ /g)	Specific surface area ^{a)} S _p (m ² /g)	Peak pore diameter ^{b)} D (μm)	Porosity ^{c)} p (%)
1000	0.208	0.74	1.2	46
1100	0.187	0.27	1.2 and 17	59
1200	0.025	0.16	0.45	8.6
1300	0.007	0.03	—	2.7

a) Determined by mercury porosimetry, b) $D = 4V_p/S_p$, c) $p = 100 \times V_p \times (\text{Sample mass})/(\text{Sample volume})$

Table 3 Microstructural classification for the *in situ* composites with/without SiC.

Source	Liquid quantity	Sintering condition	Microstructure	Reference
Without SiC	+ (LiF-base)	1100-1400°C	uniformly porous (~1μm)	Ref. 16-19
With SiC	++	1000°C	uniformly porous (~1μm)	Fig. 4(a)
	+++	1100°C (inner)	bimodal (~1μm, ~17μm)	Fig. 3 (c,d), Fig. 4(b)
	++++	1100°C (outer)	almost dense	Fig. 3 (b)
	++++	1200-1300°C	almost dense	Table 2

composite, leaving large pores (~17 μm) in the porous body. Thus, the silica formation at elevated temperature is responsible for the unique microstructural development (i.e. bimodal pore-size distribution) shown in Fig. 3(c) and (d). Microstructural classification is summarized in Table 3.

4 Conclusions

In this study, we have attempted to modify the microstructure and pore-size distribution of the porous CaZrO₃/MgO *in situ* composites by the addition of SiC.

- (1) A unique bimodal pore structure (~1 μm and ~17 μm) was obtained for the SiC-added porous composite sintered at 1100 °C, without losing the simplicity of the *in situ* processing. The microstructural development can be attributable to the formation of silica at elevated temperature. The porous composite had dense shell structure because of the further oxidation near the surface.
- (2) Although some problems remain in controlling microstructure, the SiC addition as "SiO₂-precursor" at elevated temperature can be a new strategy to modify the pore structure of oxide-based ceramics processed in air atmosphere. Larger open pores (~17 μm) obtained in this study may be suitable for the diesel particulate filtration.

Acknowledgement

This work has developed out of earlier work and useful discussions with Dr. Peter E. D. Morgan of Rockwell Science Center. The authors also thank Kawatetsu Mining Co. Ltd. for the kind provision of pure dolomite rock. This work has been supported by METI, Japan, as part of the Synergy Ceramics Project. The authors are members of the Joint Research Consortium of Synergy Ceramics.

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