J Mater Sci (2010) 45:6841–6844
DOI 10.1007/s10853-010-4939-9

LETTER

Effect of alkaline earth metal oxide addition on flexural strength of porous mullite-bonded silicon carbide ceramics

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Received: 21 July 2010 / Accepted: 18 September 2010 / Published online: 2 October 2010

Silicon carbide ceramics containing a bonding phase and some porosity have a unique set of characteristics, such as high thermal shock resistance, chemical stability, high specific strength, controlled permeability, and cost-effectiveness. These materials have attracted considerable interest for use in the field of refractories, kiln furnitures, hot-gas filters, and high-temperature structural applications [1–6]. Silica, silicon nitride, and mullite phases were examined as bonding phases for ceramics. Among the bonding phases, mullite was reported to be most effective in improving the mechanical properties and oxidation resistance of porous SiC ceramics [7–12].

Porous mullite-bonded SiC (MBSC) ceramics are fabricated from SiC, Al_2O_3, and templates using an in situ bonding technique [10, 13–15]. During heating, the oxidation of SiC produces a SiO_2 phase, which reacts with Al_2O_3 to form a mullite bonding phase at 1400–1550 °C in air. Meanwhile, the templates are decomposed or burned out, leaving pores inside the materials. Previous studies suggested that the mullitization temperature was dependent on the SiC particle size [16] and additive addition [10, 17]. The smaller SiC particle size resulted in earlier mullitization due to the rapid oxidation of SiC particles [16]. A small amount of Y_2O_3 addition decreased the mullitization temperature from 1550 to 1450 °C, due to the formation of a lower viscosity Y–Al–Si–O amorphous phase that accelerates the oxidation of SiC and the formation of mullite [10]. A small amount of Sc_2O_3 addition accelerates the rate of solid state diffusion to form a ternary Sc-rich aluminosilicate, resulting in enhanced mullite formation at temperatures between 1350 and 1550 °C [17]. The addition of alkaline earth metal oxides to the starting composition should be more effective in lowering the mullitization temperature than Y_2O_3 and Sc_2O_3 because alkaline earth metal oxides with Al_2O_3–SiO_2 generally have lower eutectic temperatures than the Y_2O_3–Al_2O_3–SiO_2 (>1360 °C) [18] and Sc_2O_3–Al_2O_3–SiO_2 (>1450 °C) [17] systems. The eutectic temperatures of MgO–Al_2O_3–SiO_2 and CaO–Al_2O_3–SiO_2 systems are 1355 °C [19] and 1170 °C [20], respectively. The eutectic temperature of SrO–SiO_2 system is 1358 °C [21]. When Al_2O_3 exists, SrO–Al_2O_3–SiO_2 can form eutectic liquid at lower temperature than 1358 °C.

This article reports the effect of alkaline earth metal oxide addition (MgO, CaO, and SrO) on the mullitization temperature and flexural strength of porous mullite-bonded SiC ceramics. Since the addition of submicron SiC powder increases the strength of reaction bonded mullite-SiC composites significantly [11], 30 wt% of submicron SiC powder was added to coarse(~90 μm) SiC powder. Most studies on MBSC ceramics used smaller SiC particles (0.5–20 μm) as a starting material [2, 6, 10, 13, 16, 22], whereas one study used 65 μm-SiC as the starting material [11]. Therefore, the use of 90 μm-SiC powder to produce porous MBSC ceramics is more cost-effective.

Commercially available refractory-grade SiC (~90 μm, Chemgrit Co. Ltd., Zhengzhou, Henan, China), sub-micron SiC (~0.5 μm, Norton AS, Lillesand, Norway), Al_2O_3 (~0.4 μm, AKP30, Sumitomo Chemical Co., Tokyo, Japan), sintering additives (MgO, CaO, and SrO; High Purity Chemicals, Osaka, Japan), and poly(methyl methacrylate-co-ethylene glycol dimethacrylate) microbeads

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(~20 μm), Sigma-Aldrich Inc., St. Louis, MO, USA) were used as starting materials. CaO was added as $CaCO_3$. Four batches of the powder mixtures were prepared as shown in Table 1. All batches were milled separately in a polypropylene jar for 24 h using distilled water and SiC grinding balls. Polyethylene glycol and polyvinyl alcohol were added as binders. The milled slurry was dried at 100 °C for 24 h and pressed uniaxially under a pressure of 50 MPa. The compacts were then sintered at 350–1450 °C for 2 h in air.

The bulk density of each sample was calculated from its weight-to-volume ratio. The porosity was determined from the bulk density to true density ratio. The true density was calculated using the method reported elsewhere [11]. The fracture surface morphology was observed by scanning electron microscopy (SEM, S4300, Hitachi Ltd., Japan). Bar-shaped samples were cut to a size of 3 × 4 × 30 mm. Bending tests were performed at room temperature on five to seven specimens under each condition using a four-point method (Instron 4465, Instron Co., Ltd., USA) with inner and outer spans of 10 and 20 mm, respectively. The specimens were loaded at a constant crosshead speed of 0.5 mm/min. The samples were then ground using a mortar. The powder was sieved (through 100 μm) and the phase was analyzed by X-ray diffraction (XRD, D8 Discover, Bruker AXS GmbH, Germany) with CuKα radiation.

The XRD of the MBSC samples showed peaks for α-SiC, mullite, SiO_2 (cristobalite), and Al_2O_3 after sintering at all temperatures. However, the intensity of the SiO_2 and Al_2O_3 phases were relatively weaker, i.e., the intensities of the mullite peaks were stronger in the samples containing additives, compared to the samples sintered with no additives. A mullite bonding phase was synthesized at temperatures as low as 1350 °C and was accelerated by adding alkaline earth metal oxides as a sintering additive.

Figure 1 shows the typical fracture surfaces of the MBSC samples. Spherical pores templated from the polymer microbeads were formed in the synthesized mullite and submicron SiC region, whereas irregular-shaped pores were formed near coarse SiC grains. The observation of a pore structure at higher magnification is shown in Fig. 2. Porous strut regions were observed when no additives were added (Fig. 2a), whereas dense strut regions were formed when alkaline earth metal oxides were added as a sintering additive (Fig. 2b, c, d). The strut porosity refers to the very fine intergranular porosity between the submicron SiC grains. The observation of a pore structure also shows that the MBSC–Sr specimen (Fig. 2d) had a denser strut than the other specimens.

The addition of alkaline earth metal oxides resulted in a denser strut and reduced porosity (Fig. 3). The porosities of the MBSC specimens with no additives and with the alkaline earth metal oxides ranged from 48.8 to 50.4% and 44.3 to 49.8%, respectively. The porosities generally decreased with increasing sintering temperature due to further densification at higher temperatures. The addition of CaO led to the lowest porosity of 44.3% when sintered at 1450 °C. Thus, the added alkaline earth metal oxides formed a lower viscosity liquid at the sintering temperatures and accelerated both the synthesis of mullite phase and densification of the strut.

Figure 4 shows the flexural strength of the MBSC specimens as a function of the porosity. The strength generally increased with increasing sintering temperature when the composition was the same due to larger amount of mullite formation and lower porosities at higher temperatures. The addition of alkaline earth metal oxides increased the strength dramatically, compared to the MBSC specimens with no additives. The MBSC–Sr specimens showed the highest average strength of 44 MPa at 46% porosity among the specimens investigated. In contrast, the flexural strength of the MBSC specimens with no additives was ~6 MPa at ~49% porosity. The flexural strengths of the MBSC–Mg and –Ca specimens were ~18 MPa at ~47% porosity and ~29 MPa at ~44% porosity, respectively. Strength of the ceramic depends on

Table 1 Batch composition of porous mullite-bonded SiC ceramics

Sample designation	Composition (wt%)				
	Coarse SiC[a]	Submicron SiC[b]	Al_2O_3[c]	Template[d]	Additive
MBSC	40.572	17.388	34.04	8	No additive
MBSC–Mg	38.808	16.632	32.56	8	4 wt% MgO[e]
MBSC–Ca	38.808	16.632	32.56	8	4 wt% CaO[e]
MBSC–Sr	38.808	16.632	32.56	8	4 wt% SrO[e]

[a] α-SiC, ~90 μm, Chemgrit Co. Ltd., Zhengzhou, Henan, China

[b] α-SiC, ~0.5 μm, Norton AS, Lillesand, Norway

[c] Al_2O_3, ~0.4 μm, 99.9% pure, Sumitomo Chemical Co., Tokyo, Japan

[d] ~20 μm, poly(methyl methacrylate-co-ethylene glycol dimethacrylate), Sigma-Aldrich Inc., St. Louis, MO, USA

[e] High Purity Chemicals, Osaka, Japan

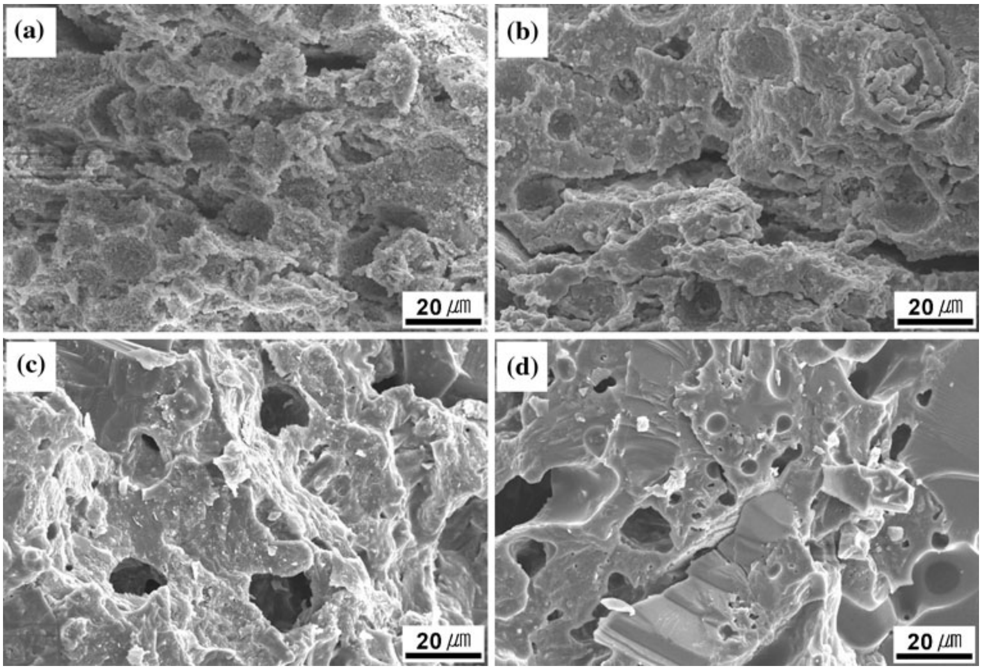

Fig. 1 Typical fracture surfaces of the porous MBSC ceramics sintered at 1400 °C for 2 h: **a** MBSC, **b** MBSC–Mg, **c** MBSC–Ca, and **d** MBSC–Sr (refer to Table 1)

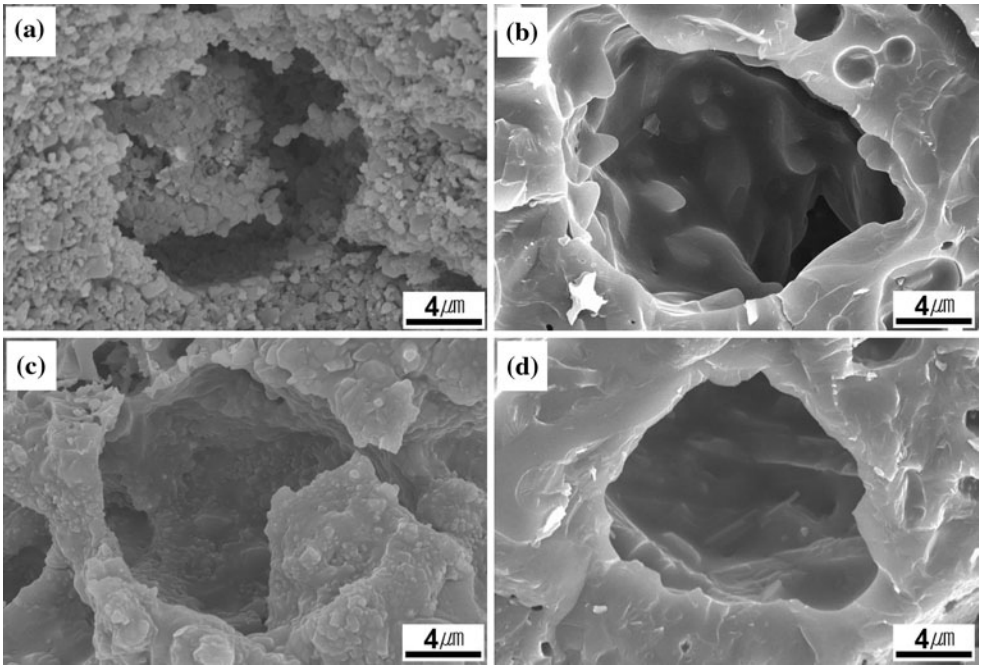

Fig. 2 Typical pore morphology and strut microstructure of porous mullite-bonded SiC ceramics sintered at 1450 °C for 2 h: **a** MBSC, **b** MBSC–Mg, **c** MBSC–Ca, and **d** MBSC–Sr (refer to Table 1)

the largest flaw and does not depend on additive composition [23–26]. However, the difference in strength was clearly dominated by the additive composition rather than the porosity because the difference in porosity was only 2–3%. Figure 4 also shows a comparison of the reported strengths and present data. As shown, the flexural strengths of MBSC with no additives in the literature were 9.8 MPa at 50% porosity [6], 24 MPa at 43% porosity [13] and 39 MPa at 36% porosity [2, 15]. The lower strength of the present MBSC specimens with no additives was attributed

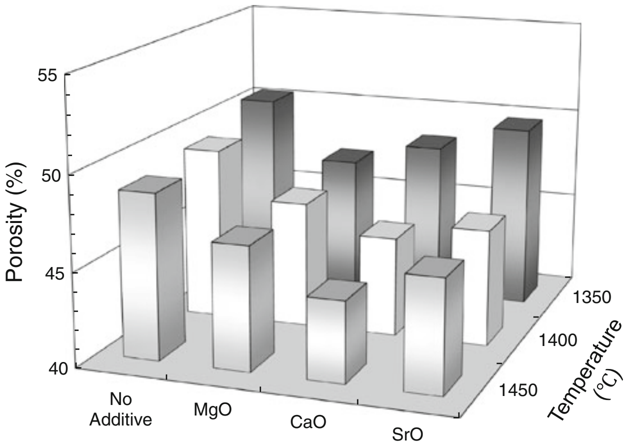

Fig. 3 Effect of the sintering additive composition on the porosity of the porous mullite-bonded SiC ceramics sintered at various temperatures for 2 h in air

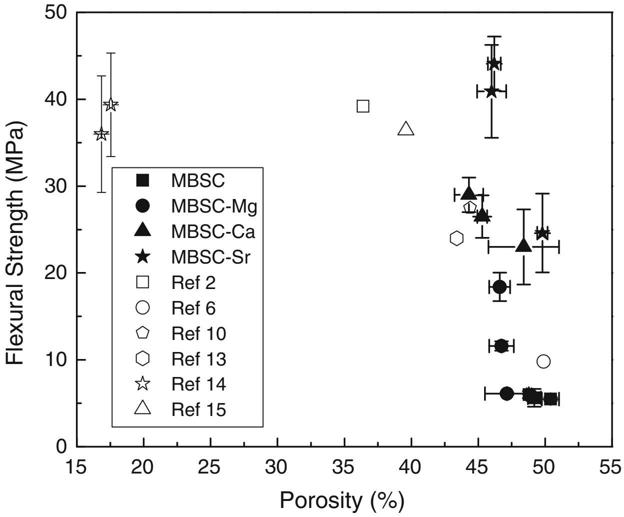

Fig. 4 Flexural strength of the porous mullite-bonded SiC ceramics sintered at 1350–1450 °C as a function of porosity. Flexural strength reported by other researchers was also plotted for comparison

to the use of a coarser starting SiC powder (~90 μm), whereas the particle size of SiC in the literature was 0.5–20 μm, which was much smaller than the present experiments. When 30% submicron SiC (~0.5 μm) was added to 65 μm-SiC, the strength increased to 36–39 MPa at 17–18% porosity [14]. Ding et al. [10] used 20 μm-SiC powder and added Y_2O_3 as a sintering additive to fabricate MBSC, and reported a flexural strength of 28 MPa at 44% porosity. Therefore, the flexural strength of 44 MPa at 46% porosity obtained in MBSC–Sr is superior to that reported by other researchers. Furthermore, the sintering temperature in this study was 1350–1450 °C, which is lower than that reported in the literature (1450–1550 °C) [2, 6, 10, 13–15]. Therefore, the addition of alkaline earth metal oxides is beneficial for lowering the sintering temperature and improving the flexural strength. In particular, SrO was quite effective in improving the flexural strength of MBSC ceramics because the addition of SrO formed a denser strut than the other alkaline earth metal oxides (Fig. 2). Therefore, SrO is a very efficient sintering additive for improving the flexural strength by reinforcing the strut, compared to the reported Y_2O_3 additive [10] and other alkaline earth metal oxides.

Acknowledgements This study was supported by the Energy Technology Innovation (ETI) Program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant (2007MCC12P1130102009) funded by the Korea government (Ministry of Knowledge Economy).

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