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Corrosion behaviors of porous reaction-bonded silicon carbide ceramics incorporated with CaO

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ABSTRACT

Reaction-bonded SiC (RBSC) porous ceramics were fabricated at 1450 °C in air by incorporating CaO using ZrO_2 as sintering aids, activated carbon as pore-forming agent, and mullite fibers as reinforcing agent. The effects of CaO content on the properties of the porous RBSC ceramics were studied. Corrosion behaviors of the prepared RBSC porous ceramics in different environments were also investigated. The optimal open porosity, bending strength, average pore size and gas permeability of the ceramics with 0.5% CaO were 40%, 22.5 MPa, 42.9 μm, and 2100 m^3/m^2 h kPa, respectively. A well-developed neck reaction-bonded by calcium zirconium silicate ($Ca_3ZrSi_2O_9$) was identified. The porous RBSC ceramics exhibited excellent corrosion resistance in acid and basic solutions. The anti-oxidation temperature of the porous RBSC ceramics could reach 1200 °C in air. The RBSC ceramics maintained the bending strength of 17.5 MPa after 60 cold-hot cycles in air (0–800 °C). The porous RBSC ceramics also exhibited relatively good corrosion resistance in molten salts (NaCl, Na_2SO_4 and $CaCl_2$). Melten NaOH can aggravate the reaction by breaking the SiO_2 layers on the SiC surface. Overall, these findings offer significant insights into expanding the applications porous RBSC ceramics incorporated with CaO.

1. Introduction

Silicon carbide porous ceramics are widely used in applications including water treatment, gas purification, gas separation and as catalyst carrier [1–6]. Among various silicon carbide porous ceramics, reaction-bonded silicon carbide (RBSC) porous ceramics have obvious advantages from an economic viewpoint because of the low cost of raw materials and the low energy consumption required for sintering, as compared to the other products [7–10]. In the fabrication process of RBSC, the surface of the SiC particles is first oxidized to form SiO_2 with high activity, and the oxidation-derived SiO_2 easily reacts with the sintering agents to form new phases among the SiC particles [11]. Therefore, the RBSC technique can overcome the requirement of extremely high-temperature in the fabrication of the SiC porous ceramics [12–14]. With the current technologies, the sintering temperature of RBSC porous ceramics can be reduced to below 1500 °C [15].

Recently, researchers have prepared RBSC porous ceramics with high bending strength by incorporating metal oxides to form mullite and cordierite [9,14,16,17]. However, few studies have been conducted on the corrosion resistance of these materials in acid or alkali, or on their stability in hot gas [18,19]. It is commonly known that high-purity SiC ceramics have very good chemical stability [20]. RBSC porous ceramics also have some good properties, such as high mechanical strength, a low thermal expansion coefficient and high thermal conductivity [16,21,22]; however, for application in liquid and in hot gas, the chemical stability of RBSC porous ceramics still needs to be improved. Most of the reaction-bonded phases are silicate and silica, which suffer from acid-base erosion and have a different thermal expansion coefficient than pure SiC ceramics. Baitalik et al. [23] prepared cordierite-silica bonded SiC porous ceramics and found that the residual bending strength of the SiC porous ceramics in acid and alkali decreased from 38.2 MPa to 28.4 MPa and 16.9 MPa, respectively after 240 h. Liu et al. [24] found that RBSC porous ceramics had poorer HF solution resistance than solid state sintered SiC porous ceramics. Further, in hot gas, the researchers revealed that the hot gas involved in the coal chemistry contained many acidic and basic ashes, which formed a silicate melt or glassy phase at the corrosion temperatures and caused cracks to occur due to the high thermal expansion mismatch [25,26]. The SiC grains were inclined to cause oxidation behavior in air and reacted with SiC to form silica at high temperatures (1100–1500 °C)

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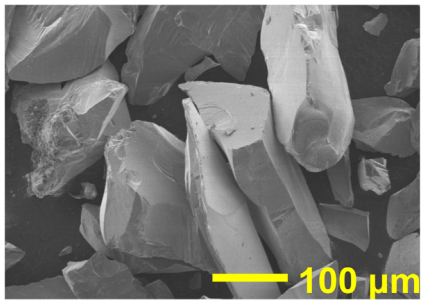

Fig. 1. The SEM image of SiC particles.

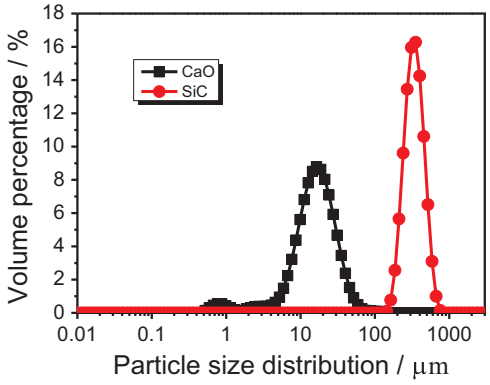

Fig. 2. The particle size distribution of both CaO and SiC.

Table 1
Mixing ratio and sample designation of starting mixtures.

Sample	SiC (wt%)	Mullite fiber (wt%)	ZrO_2 (wt%)	CaO (wt%)	C (wt%)
S0	82.5	2	0.5	0	15
S1	82.25	2	0.5	0.25	15
S2	82	2	0.5	0.5	15
S3	81.5	2	0.5	1	15
S4	80.5	2	0.5	2	15

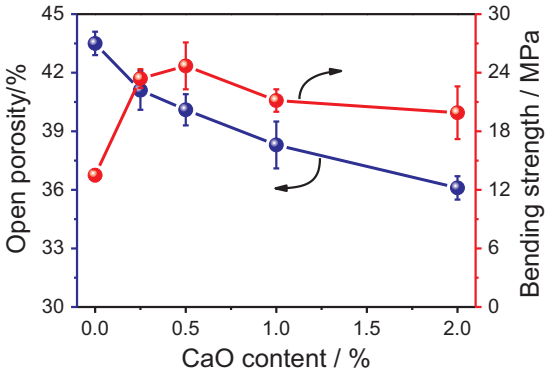

Fig. 3. The open porosity and bending strength of RBSC porous ceramics changed with CaO content.

[27].

In order to improve the corrosion behavior of RBSC porous ceramics hot gas filtration, in our previous works, we prepared new zircon-bonded SiC porous ceramics by using a in situ reaction-bonded technique to ensure similar thermal expansion coefficients with SiC [28]. The prepared RBSC porous ceramics showed good bending strength and excellent thermal shock resistance. On the basis of this, non-oxide SiC membranes were prepared for PM2.5 interceptions [29]. In addition, high gas permeable SiC porous ceramics were successfully prepared by using mullite fiber reinforcement, according to the principle of zircon-bonded SiC porous ceramics and using an in situ reaction-bonded technique [30]. However, we found that a small amount of silica remained in the RBSC porous ceramics. Moreover, the zircon phase was unstable when sintered at temperatures above 1450 °C. Calcium oxide (CaO) is a common sintering aid material, which can promote sintering and reduce the calcination temperature [31]. The content of silica in the system can be reduced by reacting with calcium oxide. Furthermore, zirconia can be stabilized by doping CaO. Due to the similar ion radii of Ca^{2+} and Zr^{2+}, it can promote the sintering of zircon [32,33].

In this work, we prepared RBSC porous ceramics by incorporating mullite fibers, CaO, ZrO_2 and C powders. These were used as reinforcing materials, sintering agents and pore-forming agents, respectively. The RBSC porous ceramics were prepared in air at 1450 °C for 4 h. On the basis of our previous research, the effect of CaO content on the open porosity, bending strength, pore size distribution, gas permeability, microstructure and composition were investigated. In particular, the property of corrosion resistance in liquid and the stability of the RBSC porous ceramics in hot gas, were comprehensively studied and analyzed.

2. Experimental

2.1. Material preparation

Commercial α-SiC powder (~ 300 μm, ≥ 99%, Haian Corundum Co., Jiangsu, China) was used as the raw material. The carbon powder (~ 20 μm, Hainuo Carbon Industry Co., Shanghai, China) was used as a pore-forming agent. High purity zirconia (~ 5 μm, Sansai Ultrafine Co., Jiangsu, China) and calcium oxide (~ 5 μm, Xilong Chemical Co., Shanxi, China) were used as sintering aids. Mullite fibers (99% purity, with an average diameter of 11.0 μm and length = ~ 60 μm, from Jiahe Crystal Fiber Co., Deqing, China) were added as a reinforcing agent. Fig. 1 shows the SiC microstructure morphology and Fig. 2 shows the particle size distribution of SiC and CaO. The compositions of the samples are presented in Table 1. After mixing, polyvinyl alcohol (PVA) and liquid paraffin were added to the powder mixture for further grinding for an hour. The milled slurry was pressed into a circular sheet (Φ30 mm × 3 mm) and strip (50 mm × 6 mm × 6 mm) of green body at 8 MPa. The green bodies were dried for 4 h in a 70 °C oven and sintered in air at 1450 °C for 4 h. The heating rate was 2 °C/min from room temperature to 500 °C and the temperature was held at 500 °C for 2 h. The temperature was then raised to 1450 °C at a rate of 1 °C/min and hold for another 4 h before natural cooling to room temperature.

2.2. Characterization and test

2.2.1. Materials characterization

The identification of crystalline phases was carried out with an X-ray diffractometer (XRD; D8-Advance, Bruker, Germany) with Cu Kα radiation (at a wavelength of 0.154 nm), operated at 15 mA, 40 kV, and at a step width of 0.02° with a scanning range of 10–80 °. The microstructure was observed using a field emission scanning electron microscope (FESEM, HitachiS-4800, Japan). The bending strength was detected using the three-point bending test with a 40 mm span and a crosshead speed of 0.5 mm/min. The bending strength was calculated using Eq. (1)

$$\sigma = 3FL/2bh^2 \quad (1)$$

where the F is the force at which the fracture occurs (N), L is the length of the span (40 mm), b is the width of the specimens (mm), h is the height of the specimens (mm) and σ is the bending strength (MPa). The gas flow rate of the SCPCs was measured using PSDA-20 (Gaoqian function Co., Nanjing, China). The gas permeability was calculated using Eq. (2)