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Effect of recoating slurry viscosity on the properties of reticulated porous silicon carbide ceramics

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Abstract

Reticulated porous silicon carbide ceramics (SiC RPCs) were fabricated by polymeric sponge replication using preset roller method, then recoating by centrifuging technique. Preparation and properties of the SiC RPCs prepared by roller method are presented in this communication. The loading content and pore diameter of the RPCs body greatly depends on the slurry viscosity. At the same time, the strut diameter and cell size of SiC RPCs are modulated by the recoating slurry.

Keywords: B. Porosity; C. Strength; D. Silicon carbide; Recoating

1. Introduction

Reticulated porous ceramics (RPCs) are highly porous ceramics (70–95%) with an open, three-dimensional network structure. The most common applications of the RPCs are molten metal and diesel engine exhaust filters, catalyst supports due to their high permeability, resistance to chemical attack and structural uniformity [1–4].

The most popular method of production of RPCs is the "polymeric sponge" process [5], invented by Schwartzwalder and Somers [6]. In the method, green RPCs consisting of a few filled cells were fabricated by coating a polyurethane sponge with a thixotropic slurry. In order to remove excess slurry from sponge, centrifuging or passing through preset rollers is the commonly used technique. RPCs produced by this process are of low strength and fracture toughness, because very thin struts of ceramic structure may remain and triangular pores exist after the organic sponge is burned out, making them sensitive to structural stresses and limiting their structural applications [7–8]. Several techniques have been tried to improve the slurry coverage [9–13]. A second coating of slurry may be applied to fill in any flaws or thin areas in the first coating. As suggested by Schwartzwalder and Somers [6] and Brown and Green [14], the second coat may be directly applied on the dried original coating. The dried body including the sponge substrate is difficult to recoat by dipping, because dipping can wash away some of the previously deposited ceramic coating and weaken the structure. At the same time, the recoat slurry floated by gravity will lead to filled cells, especially near the bottom portion of the part. Zhu et al. [15] developed a new recoating method. First, the green body prepared by preset roller method is preheated to produce a reticulated preform with enough handling strength after the sponge is burnt out. Then, the preform was recoated by a thinner slurry using centrifugal method. This technique greatly improved the mechanical properties of RPCs. Not much work has been reported on the influence of recoating on the structure and properties of reticulated porous silicon carbide ceramics.

In the present study, SiC RPCs ceramics were produced by a recoating technique. The loading content of the preform and the properties of recoated RPCs SiC were observed to be strongly dependent on the rheological behavior of recoating slurry. The main objective of this work was to study the

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influence of recoating slurry rheology on the microstructure and properties of SiC RPCs ceramics, and to compare it with those obtained by the single preset rollers technique.

2. Experimental procedure

Commercial polyurethane sponges (No. 6 Plastic Factory, Shanghai, China) with cell size from approximate 8 pores per inch were chosen in this study. Two kinds of commercially available silicon carbide powders (d_{50} = 21.09 μm, 3.26 μm, respectively, Qingzhou Micropowder Factory, Shandong, China) were used in the investigation. Alumina powder (α-Al_2O_3, d_{50} = 0.45 μm, Aluminum Corporation, Shandong, China), talc particle ($(Mg_3(Si_4O_{10})(OH)_2$, d_{50} = 5.9 μm, D = 2.70 g/cm^3, 99.99% purity, PR China) and kaolin ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, d_{50} = 0.68 μm, Suzhou, China) were added as sintering aids. A commercial silica sol (26.2 wt.%, pH = 9.5–10, Shanghai Second Reagent Plant, China) was used as a binder. Sodium carboxymethyl-cellulose (CMC) and a surfactant (SAG 630, Witco Hongkong Limited Co. China) were added to the slurry as a thickening agent and an antifoaming agent, respectively.

The slurry was prepared by the following procedure. Deionized water was first mixed with silica sol by stirring for about 10 min in an attritor (Szegvari Attritor System 01HD, Union process Inc., USA) using alumina balls as grinding media. Ceramic powders were subsequently added to the solution and stirred for 3 h. CMC and the antifoaming agent were added to the resulting slurry while continuing stirring for another 3 h.

In the preset roller method, the polyurethane sponges were immersed in the slurry. Then the sponges with slurry were passed by a preset roller to remove excess slurry. After being dried, the coated sponge substrates were heated at a heating rate of 1 °C/min to burn out the sponge at 600 °C, and subsequently heated at 1300 °C during 3 h with a hating rate of 5 °C/min.

In the recoating method, the green body was prepared by the preset roller method. After drying, the coated sponge substrates, were first heated to burn out the sponge at 600 °C at a heating rate of 1 °C/min. Subsequently, the samples were heated at 900 °C during 3 h at a heating rate of 5 °C/min in order to produce reticulated preforms with adequate handling strength. In the second coating stage, the preforms were coated repeatedly by centrifugal process with a thinner slurry, which had the same composition as the slurry used to coat the sponge. After drying, the final preforms were sintered in air at 1300 °C for 3 h at a heating rate of 5 °C/min.

The rheological behavior of slurries was measured using a stress-controlled rheometer (Model SR5, Rheological Scientific Inc., USA) with a parallel plate (25 mm diameter) under steady shear. The macrostructure of RPCs was characterized by a digital camera (Olympus C-5050, Olympus Optical Co., Ltd., Japan) and the struts were observed by scanning electron microscopy (SEM) (model EPMA-8705Q, Hii, Shimadzu, Japan). Bulk density of RPCs, ρ_b, was determined from the dimensions and mass of the sintered samples. The density (ρ_s) and open porosity of the struts, were measured using mercury porosimetry (Model Poresizer 9320, Micromertrics Instrument Group, Norcross, USA) on crushed materials consisted of broken cell walls and struts. The relative density, ρ_b/ρ_s, was the ratio of the bulk density of RPCs (ρ_b) and the density of the solid making up the struts (ρ_s). Compressive strength, σ_c, was measured in Instron 1195 universal testing machine using a crosshead speed 1.5 MPa/s. The cell size distributions were analyzed by Image-Pro Plus software (Media Cybernetics, Inc., Netherlands).

3. Results and discussions

In the preset rollers method, the polyurethane sponges were immersed in the slurry. The slurry must have the proper rheological characteristics. The slurry must be fluid enough to enter, fill and uniformly coat the sponge network and subsequently regain enough viscosity under static conditions to remain in the sponge. It is suggested that the slurry must have the proper thixotropic or shear-thinning behavior [16]. Fig. 1 shows the flow curve of the slurry (80 wt.%) used in this procedure. The curve exhibits a distinct thixotropy loop and a characteristic shear-thinning behavior that is required for the present application. The microstructure of SiC RPCs is shown in Fig. 4(a). There were many cracks observed on the struts. The cracks would greatly decrease the strength of the SiC RPCs. According to the Brown's work [14], the cracking was beginning to occur around or slightly below the sponge's melting point due to expansion of the sponge. A solution to the problem is to produce a thicker ceramic coating, which will allow a greater internal pressure (due to the volumetric increase) to be withstood. In our work, the method to produce a thicker ceramic coating was to recoat the strut by the centrifugal method.

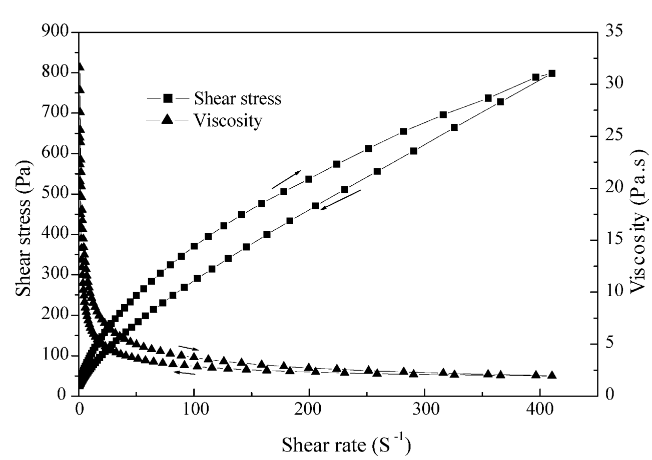

Fig. 1. Flow curve of the slurry (80 wt.%) used in the first coating stage.

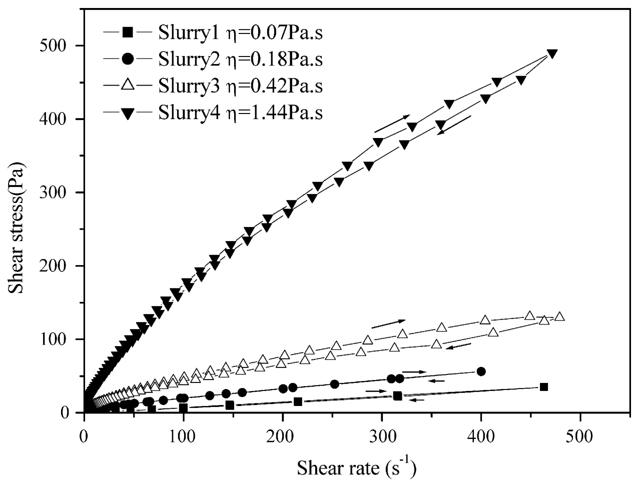

Fig. 2. Flow curve of the recoating slurry with different viscosity.

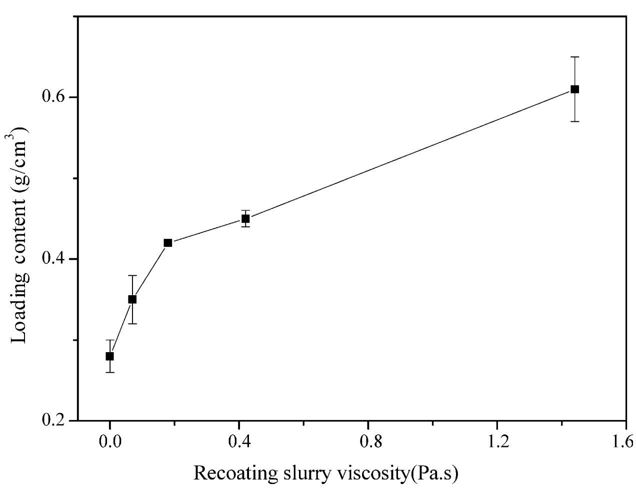

Fig. 3. Loading content of the slurry on the sponge and preformed samples, as a function of the slurry viscosity.

Fig. 2 shows flow curves of recoating slurries. The viscosity of the slurry was measured at 200 s^{-1} shear rate. The slurries showed a shear-thinning behavior. When the viscosity was above 0.18 Pa·s, the slurry exhibited a distinct thixotropic behavior indicating a flocculated state of the slurry. This kind of state was beneficial to the coating of the slurry on the reticulated preform. With decrease in viscosity to 0.07 Pa·s, the slurry exhabited Newtonian behavior. The kind of slurry was too floating to coat on the reticulated preform very well. At the same time, if the recoating slurry was too thin, the dipping slurry would partly dissolve the previously deposited ceramic coating and weaken the structure of the reticulated preform. Increasing viscosity of the recoating slurry, that is, increasing thixotropy, was beneficial in coating of the slurry on the strut. However, too high a viscosity made it difficult to let the slurry dip into the preform, and it was difficult to remove the excess slurry from the cells by centrifugal force, resulting in a large amount of filled cells.

Fig. 3 shows the loading content of the slurry on the sponge and preforms as a function of recoating slurry viscosity (where, the viscosity equal to zero, means the RPCs without recoating). After recoating, the loading content obviously increased and the consistency between the preform and the slurry greatly improved. At the same time, the loading content greatly increased with increasing viscosity of recoating slurry. The loading content of RPCs recoated by the slurry with 1.5 Pa·s viscosity is near twice as that of RPCs recoated by the slurry with 0.07 Pa·s viscosity essentially due to the increased thixotropy of recoating slurry.

The photographs showing microstructure of SiC RPCs are presented in Fig. 4. Without recoating, some large flaws, such as large lateral cracks within the strut (denoted by the arrow in Fig. 4(a)), appear in the struts of SiC RPCs. These flaws contributed significantly to the

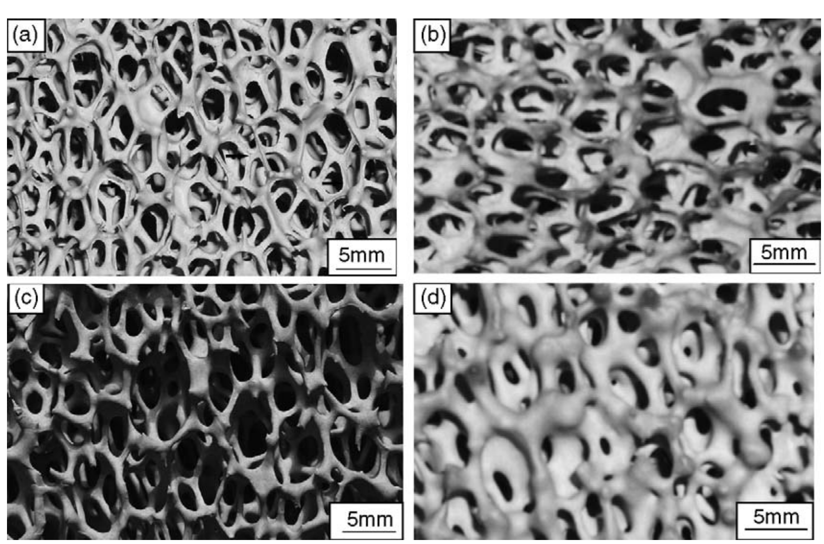

Fig. 4. Microstructure of SiC RPCs: (a) without recoating; (b) recoated by slurry with viscosity of 0.07 Pa·s; (c) recoated by slurry with viscosity of 0.42 Pa·s; (d) recoated by slurry with viscosity of 1.44 Pa·s.

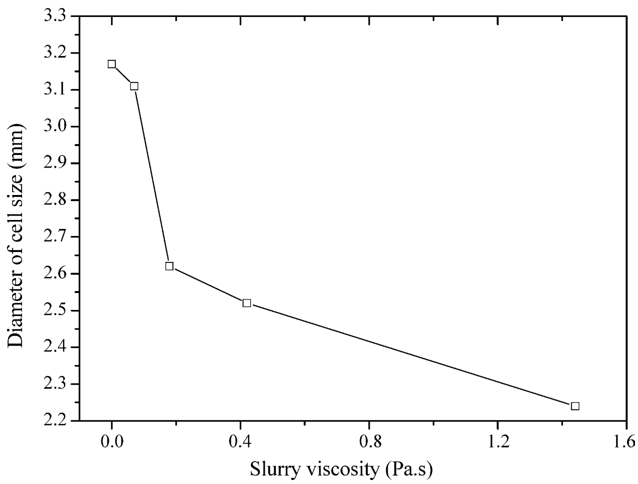

Fig. 5. Cell size of the prepared RPCs, as a function of the recoating slurry viscosity.

deterioration in mechanical properties of SiC RPCs. At the same time, several thin struts remained, also causing deterioration in mechanical properties of SiC RPCs. It is clearly observed that the microstructure of the SiC RPCs was more uniform after recoating. Very thin struts still existed in the samples recoated with slurry of 0.07 Pa·s slurry (Fig. 4(b)). When the viscosity of recoating slurry was above 0.07 Pa·s, the strut diameter increased and the strut thickness became more uniform. This is also seen in Fig. 5. The cell sizes of SiC RPCs are also shown in Fig. 5. It is noted that, without recoating, the cell size was about 3.2 mm. After recoating, the cell size decreased to very small diameters.

The strut microstructure photographs of SiC RPCs are shown in Fig. 6. There were two kinds of pores observed in the strut of SiC RPCs, large pores and small pores. A large amount of small pores with diameter about 1 μm were caused by sintering process. There were fewer large pores in SiC RPCs made without recoating. After recoating, fraction of large pores in the struts of SiC RPCs increased. These large pores resulted from the entrapped air bubbles. In the preset rollers method, the roller pressing to remove excess slurry could also remove a part of air bubbles. In case of recoating done by centrifugal force, the bubbles in the slurry could not be gotten rid of during the process. Therefore, after recoating, the porosity of the strut was observed to increase (Fig. 7).

Table 1 gives the properties of SiC RPCs. The bulk density of SiC RPCs without recoating was lower than that of samples with recoating. The bulk density of SiC RPCs increased with increase in the viscosity of recoating slurry. After recoating procedure, the compressive strength of SiC RPCs increased significantly. The compressive strength of

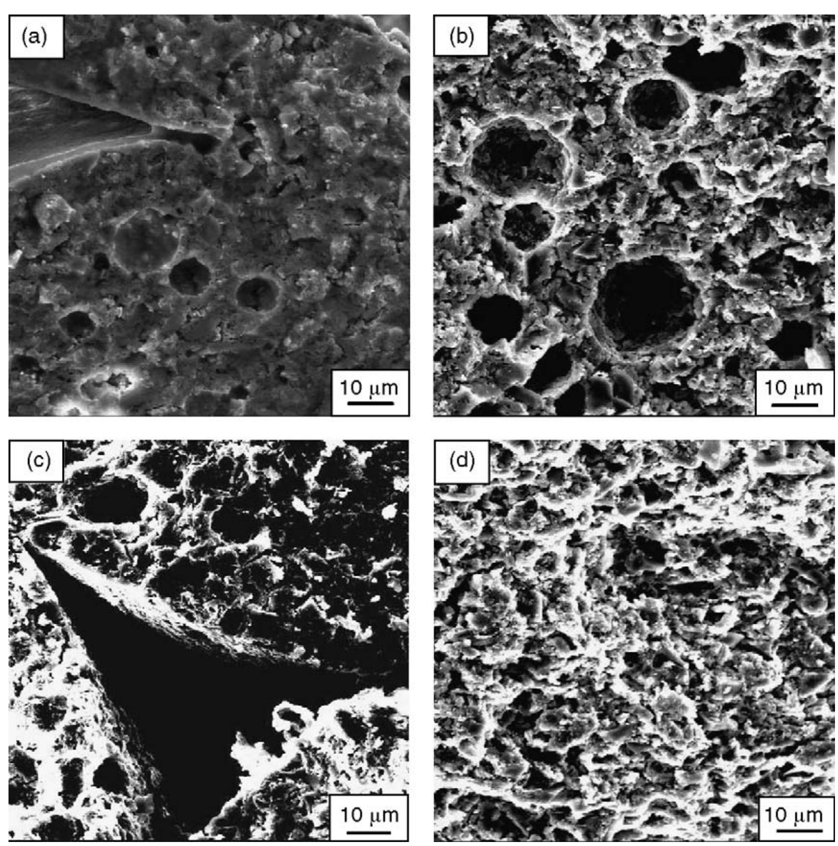

Fig. 6. Microstructure of SiC RPCs: (a) recoated by slurry with viscosity of 0.07 Pa·s; (b) recoated by slurry with viscosity of 0.42 Pa·s; (c) recoated by slurry with viscosity of 1.44 Pa·s; (d) without recoating.

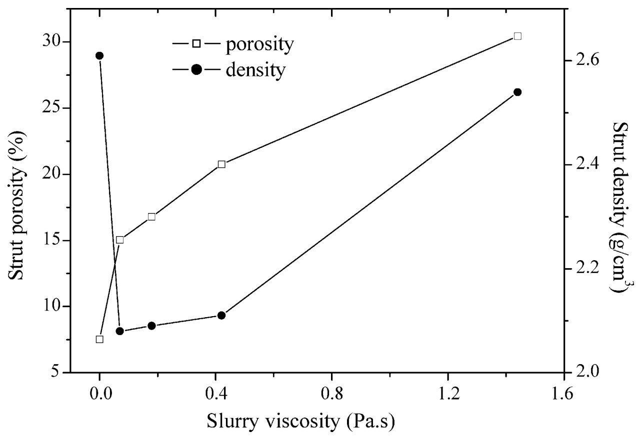

Fig. 7. Strut porosity and density of the prepared RPCs, as a function of the recoating slurry viscosity.

Table 1
Properties of SiC RPCs

Viscosity of recoating slurry (Pa·s)	ρ_b (g/cm^3)	ρ_b/ρ_s	Compressive strength (MPa)
0	0.29 ± 0.02	0.11 ± 0.01	0.32 ± 0.06
0.07	0.37 ± 0.03	0.18 ± 0.02	0.78 ± 0.11
0.18	0.44 ± 0.01	0.21 ± 0.005	0.88 ± 0.23
0.42	0.49 ± 0.02	0.23 ± 0.01	1.20 ± 0.19
1.44	0.65 ± 0.04	0.26 ± 0.02	1.59 ± 0.13

open cell ceramics can be expressed by the following general form [17],

$$\sigma_{fc} = C\sigma_{fs}\left(\frac{\rho_b}{\rho_s}\right)^{3/2} \quad (1)$$

where ρ_b is the bulk density of foam ceramics, ρ_s is the density of solid struts, C is a geometric constant, σ_{fs} is the strength of the strut. From Eq. (1), it is clear that the strut strength is a key parameter. According to Rasto Breny's work [18], the strut strength was invariant with density (at constant cell size) but could be dependent on the cell size. The strength of the samples recoated with the slurry of 0.07 Pa·s viscosity was more than twice as that of samples without recoating. This was attributed to the elimination of the strut cracks. According to Eq. (1), the compressive strength is also dependent on relative density. With increase in recoating slurry viscosity, the relative density of the SiC RPCs increased and the cell size of SiC RPCs decreased (Fig. 5) leading to improved strength. Both of them led that the compressive strength of SiC RPCs increases from 0.78 MPa to 1.59 MPa as the recoating slurry viscosity increases from 0.07 Pa·s to 1.44 Pa·s. It is suggested that viscosity of recoating slurry was very important to improve the mechanical properties of SiC RPCs.

The compressive strength is plotted as a function of relative density for SiC RPCs in Fig. 8. The value of the exponent on the relative density term in Eq. (1) was given by the slope of the data. The linear fit of our data yielded a slope

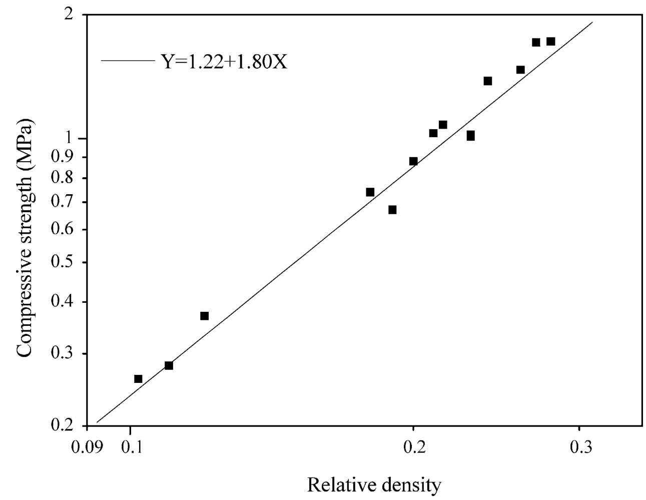

Fig. 8. Compressive strength of SiC RPCs, as a function of relative density.

of 1.82 not in agreement with a value of 1.5 in Eq. (1). Brezny and Green [8] had predicted that the deviation could be due to the presence of partially filled cell at higher density, causing the material to deviate from a truly open cell structure. From Fig. 4, it is seen that there are almost no filled cells in these samples. The disagreement was attributed to the discrepancy between the fracture mode characteristic of the materials and the one assume in the model [17].

4. Conclusions

SiC RPCs were fabricated by a recoating process with the polymeric sponge as the substrates. The slurry used for coating on the sponge had higher viscosity and a distincter thixotropy loop than those used in recoating procedure. This kind of slurry rheology behavior was required by the coating on the sponge. The recoating quality depended strongly on the viscosity of the recoating slurry. With increase in viscosity, the loading content of SiC RPCs increased, leading to a decrease in the cell size and an increase in the strut thickness of SiC RPCs. The microstructure and strength of SiC RPCs was improved by the recoating process.

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