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Low-temperature sintering of SiC reticulated porous ceramics with $MgO–Al_2O_3–SiO_2$ additives as sintering aids

Xiumin Yao · Shouhong Tan · Xiangyu Zhang ·
Zhengren Huang · Dongliang Jiang

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Abstract SiC reticulated porous ceramics (SiC RPCs) was fabricated with polymer replicas method by using $MgO–Al_2O_3–SiO_2$ additives as sintering aids at 1,000~1,450 °C. The $MgO–Al_2O_3–SiO_2$ additives were from alumina, kaolin and Talc powders. By employing various experimental techniques, zeta potential, viscosity and rheological measurements, the dispersion of mixed powders (SiC, Al_2O_3, talc and kaolin) in aqueous media using silica sol as a binder was studied. The pH value of the optimum dispersion was found to be around pH 10 for the mixtures. The optimum condition of the slurry suitable for impregnating the polymeric sponge was obtained. At the same time, the influence of the sintering temperature and holding time on the properties of SiC RPCs was investigated. According to the properties of SiC RPCs, the optimal sintering temperature was chosen at 1,300 °C, which was lower than that with $Al_2O_3–SiO_2$ additives as sintering aids.

Introduction

Ceramic foams have many potential advantages such as high temperature strength, high resistance to chemical attack, high refractoriness, and good insulating characteristics, and so on. These properties make ceramic foams suitable for many applications such as filters, membranes for separation, catalyst supports, gas burners, sensors and thermistors, and so on [1–4].

SiC RPCs is considered one of the optimal materials for high temperature molten metal filter due to its lower thermal expansion coefficient, high thermal conductivity and high strength [5, 6]. SiC RPCs has been prepared by adding the $A1_2O_3–SiO_2$ additive as sintering aids. SiC RPCs with the additives can be sintered at lower temperature. With alumina and silica from silica sol, Azumi and Shingo [7] fabricated SiC RPCs with 20–50 wt% SiC at 1,200~1,300 °C. However, when the content of SiC powders (relative to total weight of solids) was higher than 50 wt%, the most suitable sintering temperature was higher than 1,400 °C[8–13]. The obtained SiC RPCs with refractoriness about 1,600°C was used for filtration of molten iron. Brockmeyer et al. [8–10] used alumina, colloidal silica and montrillonite as sintering aids, SiC RPCs with at least 50 wt% SiC cloud be sintered at 1,050 °C, nevertheless, the suitable temperature was up to 1,400 °C. Rojas et al. [11] prepared SiC foams with alumina and silica fume as sintering aids at 1,450 °C. With alumina, silica and bentonite as sintering additives, Zhu et al. [12, 13] sintered SiC RPCs at 1,400 °C. In the present work, $MgO–Al_2O_3–SiO_2$ additives from alumina, talc and kaolin particles was used as sintering aids in preparing SiC RPCs to decrease sintering temperature.

The most popular method of production RPCs is the ‘‘polymer sponge’’ method [14, 15], which was invented by Schwartzwalder and Somers [15]. In the method, green RPCs including very few filled cells were fabricated by coating a polyurethane sponge with a

X. Yao (✉) · S. Tan · X. Zhang · Z. Huang ·
D. Jiang
The State Key Laboratory of High Performance Ceramics
and Superfine Structure, Shanghai Institute of Ceramics,
Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai
200050, P.R. China
e-mail: xmyao@mail.sic.ac.cn

thixotropic slurry. In order to obtain SiC RPCs with good properties, the properties of the slurry used to prepare SiC RPCs should be investigated.

In this study, the dispersion of ceramics powders (SiC, Al_2O_3, talc and kaolin) in silica sol was investigated by zeta potential and rheological measurements. The optimum condition of the slurry suitable for impregnating the polymeric sponge was obtained. The influence of sintering temperature and holding time on the properties of SiC RPCs was also investigated.

Experimental procedure

Materials

Commercial polyurethane sponges (No. 6 Plastic Factory, Shanghai, China) with dimensions of $50 \times 50 \times 22$ mm^3 and cell size approximate 8 and 25 PPI (pores per inch) were selected as the template. A thermogravimetric-differential scanning calorimetry (TG-DSC) analysis (STA-429, Netzseh Corporation, Germany) of the sponge was preformed in Ar with a heating rate of 10 °C/min. The complete pyrolysis of the sponge was reached at temperature of 600 °C observed from Fig. 1.

Silicon carbide powders (ρ = 3.18 g/cm^3, D_{50} = 21.09, 3.26 μm) were used as the major material. Alumina powder (α-Al_2O_3, d_{50} = 0.45 μm), talc particle (d_{50} = 5.9 μm, D = 2.70 g/cm^3, 99.99% purity) and kaolin powder (d_{50} = 0.68 μm, Suzhou, China) were added as sintering aids. A commercial silica sol (26.2 wt%, pH = 9.5–10) was used as both dispersant media and binder. Sodium carboxymethyl-cellulose (CMC) and a surfactant (SAG 630, Witco Hongkong Limited Co. China) were added to the slurry acting as a thickening agent and an antifoaming agent, respectively.

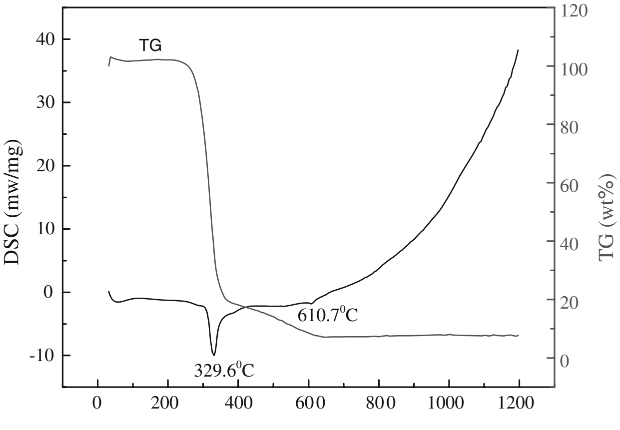


Fig. 1 TG-DSC curves of the polyurethane sponge

Slurry preparation

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. Then, CMC and the antifoaming agent were added to the resulting slurry and kept stirring for another 3 h.

Samples preparation

The polyurethane sponges were immersed in the above slurry. Then the sponges with slurry were passed by a preset roller to remove excess slurry, the distance of the two preset rollers was equal to 20% of the thickness of the sponge. After being dried, the coated sponge substrates were heated at 600 °C with a heating rate of 1 °C/min to burn out the sponge, and then fired at 1,000~1,450 °C for 0~6 h with a heating rate of 5 °C/min.

Measurements

Zeta potential of ceramics powders was measured by zeta potential analyzer (Zeta plus, Brookhaven, USA). 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) by the steady shear. The macrostructure of RPCs was characterized by digital camera (Olympus C-5050, Olympus optical CO., LTD, Japan) and the struts were observed by scanning electron microscopy (SEM) (model EPMA-8705Q, H((, Shimadzu, Japan). Bulk density of RPCs (ρ_b) was determined from the dimensions and mass of the sintered samples. The open porosity of the struts and the strut density (ρ_s) were measured using mercury porosimetry (Model Poresizer 9320, Micrometrics Instrument Group, Norcross, GA) on crushed materials consisted of broken cell walls and struts. Compressive strength (σ_c) of the samples with a dimension of $50 \times 50 \times 21$ mm^3, was measured in Instron 1195 universal testing machine using a crosshead speed 1.5 MPa/s with 50×50 mm^2 as compression face. The compressive strength of the samples was calculated by the following formula:

$$\sigma_c = P/WB \tag{1}$$

where P is the maximum load, W is the width of compression face, B is the length of compression face.

Results and discussions

TG-DSC of the polyurethane sponge

Polymeric sponge was selected on the basis of porosity, pore size, resiliency and volatility. After the sponge was chosen, the volatility of it should be discussed. Figure 1 shows TG-DSC curve of polyurethane sponge with a heating rate of 10 °C/min. It is observed that there are two exothermic peaks in the DSC curve of the sponge. The first peak (250~400 °C) is caused by decomposition of the sponge. The decomposition is basically completed through oxidation and generates much gas, resulting in a dramatic loss in weight. The second peak (about 610 °C) is attributed to the oxidation of a minute amount of carbon produced in the decomposition of sponge, resulting in a little loss in weight. At temperature >650 °C, there is no significant change in weight. In order to decrease microcracks on the struts of SiC RPCs and let complete decomposition of the sponge, the heating rate should be very slow from 0 to 600 °C.

Rheology of slurries

Zeta potential

The zeta potential arising from net effective surface charge on the particles in the suspension, directly reflects the dispersability levels of the particles in aqueous solution. The zeta potentials measured as a function of pH for SiC, Al_2O_3, talc and kaolin powders are shown in Fig. 2. Zeta potential of all powders in silica sol shows a great change in comparison with that of them in water. This is attributed to the absorption of silica colloidal particles with negative change on the surface of the ceramics particles. Zeta potential curves show that silica sol can improve greatly the dispersion of all particles in aqueous medium. All powders dispersed in silica sol have highest zeta potential values in the pH range around 10, which indicated that the pH of optimizing the co-dispersion of SiC, alumina, talc and kaolin powders should be around pH 10 in the presence of silica sol.

Rheological behavior

The viscosity values of the composite slurry dispersed in 5 wt% silica sol as a function of pH is shown in Fig. 3. In the pH range 2~6, the viscosity of the slurry increases as pH value increases. Higher viscosities are observed in the pH range 5~6. High viscosity around

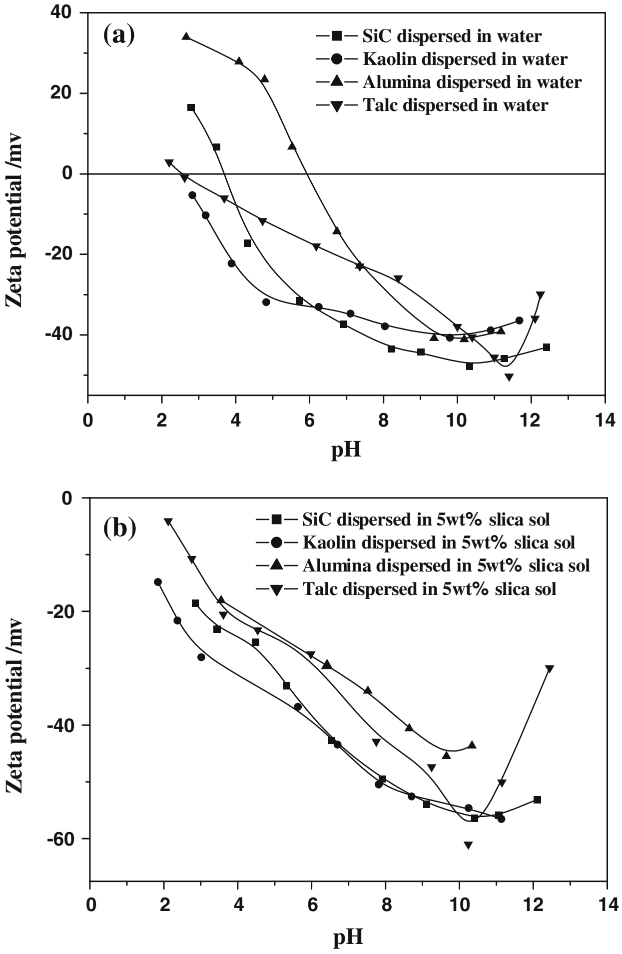


Fig. 2 Zeta potential as a function of pH for original particles

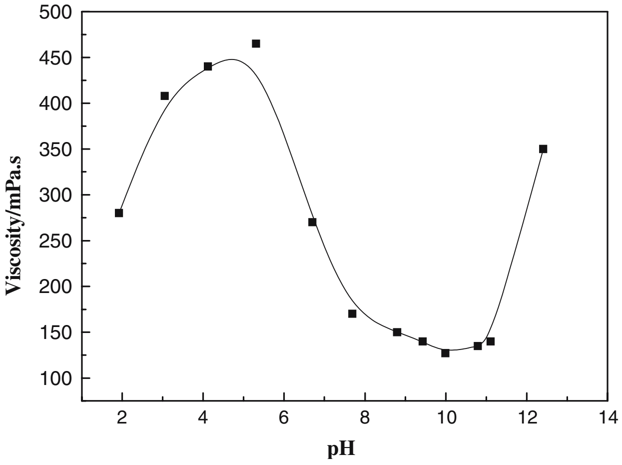


Fig. 3 Viscosity versus pH for 65 wt% the composite slurry in 5 wt% silica sol

pH 5~6 is associated with the condensation of silanol groups around pH 5~6 as follows [16]:

$$\equiv \mathrm{SiOH} + \mathrm{HOSi} \equiv \rightarrow \equiv \mathrm{SiOSi} \equiv - + \mathrm{H_2O} \qquad (2)$$

In the pH 5~6 range, the combination between the silica colloid particles absorbed on the surface of ceramics particles causes the aggregation, which results in a rapid increase of the viscosity. As pH increases further, the viscosity decreases and reaches a minimum value at about pH = 10. In this pH region, silica colloidal particles are dispersed and absorbed on the surface of ceramics particles. The absorbed colloidal particles are beneficial to dispersion of ceramics particles by electrostatic repulsion. This is in good agreement with the zeta potential results.

Viscosity versus silica sol concentration curve for the composite slurry (around pH 10) is shown in Fig. 4. Viscosity curves versus shear rate indicate that the slurries dispersed with 5~25 wt% silica sol display shear-thinning behavior. It can be observed that slurry viscosity decreases with increasing silica sol concentration and reaches a minimum value with silica sol concentration of 20 wt%. As the silica sol concentration increases further, the viscosity increases slowly. The results confirm that the silica sol concentration has an effect on the dispersion of ceramics powders in silica sol. And the silica sol concentration of optimum dispersion for ceramics powder is about 10~20 wt%.

When the polymeric sponge is impregnated with the ceramic slurry, the slurry must be fluid enough to enter, fill, and uniformly coat the sponge web and subsequently regain enough viscosity under static condition to remain in the sponge. It is suggested that the slurry must have the proper thixotropic behavior. In order to obtain proper thixotropic properties, a thickening agent, CMC, was introduced into the slurry. Flow curves versus CMC contents for the slurry (around pH 10) are shown in Fig. 5. It is observed that slurry viscosity increases with increasing CMC contents. From shear stress curves versus shear rate, the slurry exhibits complicated thixotropy with CMC contents of 0.05 and 0.1 wt%, which indicates that there were unstable network in the slurries. Whereas the slurry exhibits positive-thixotropy with CMC contents of 0.2 wt%. These results indicate that 0.2 wt% is the optimal CMC contents.

The slurry used preparing SiC RPCs must have the proper rheological characteristic. Figure 6 (which has been published in Ref. [17]) shows the rheological behavior of the optimized slurry used for the preparation of RPCs. The thixotropic behavior is evident from an apparent thixotropic loop between the increasing

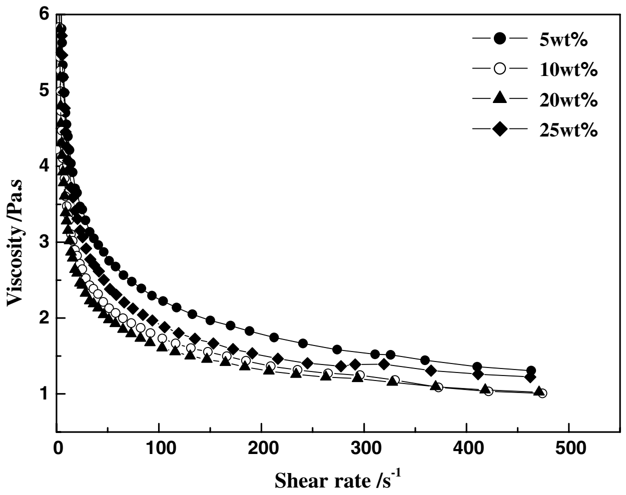


Fig. 4 Flow curves as a function of silica sol concentration for 75 wt% slurry at pH = 10

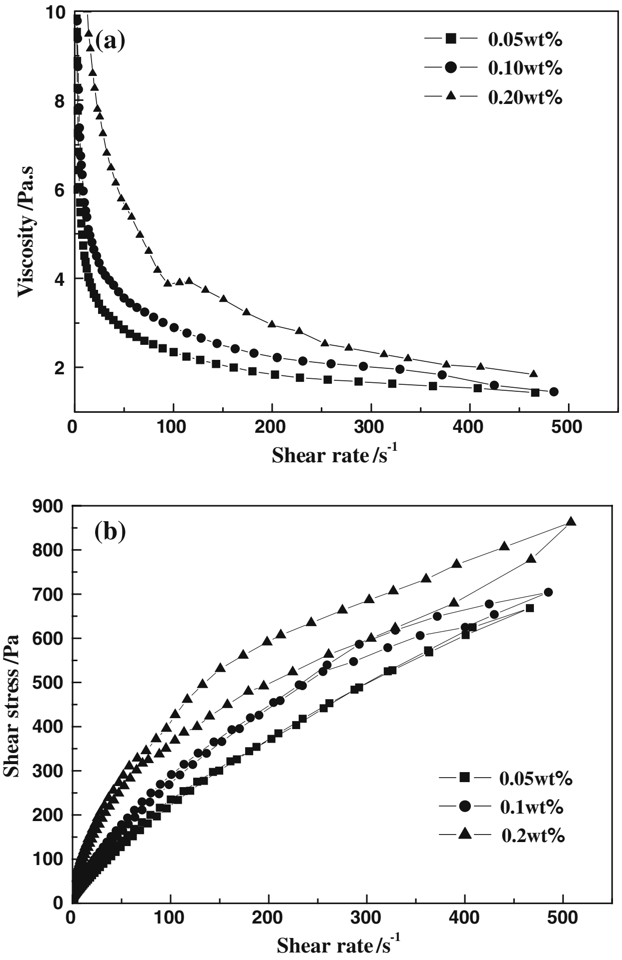


Fig. 5 Flow curves of 78 wt% slurries in silica sol with various CMC contents at pH = 10

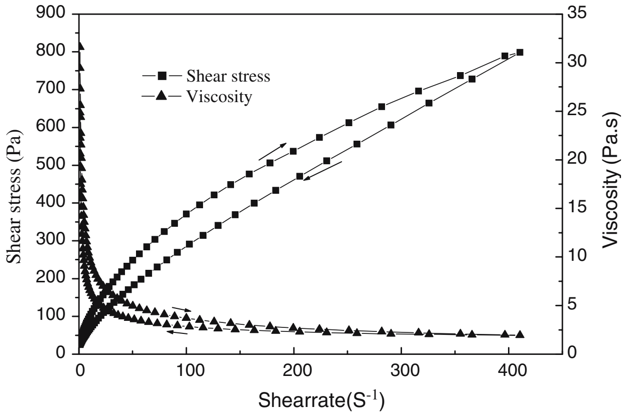


Fig. 6 Flow curve of the slurry used in preparing SiC RPCs

and decreasing shear stress versus shear rate curves. The curve exhibits a distinct thixotropy loop and a characteristic shear-thinning behavior that is just required by the present application.

Properties and structures of SiC RPCs

With optimal slurry, SiC RPCs was prepared by a preset roller method. The properties of SiC RPCs sintered at different temperatures are shown in Table 1. It is essential to study the strut porosity of the sintered ceramic as it determines the strength of the reticulated porous body. The strut open porosity was measured by crushing the sintered reticulated porous body. Table 1 shows that the strut open porosity decreases when sintering temperature rises from 1,100 to 1,300 °C. The higher the sintering temperature, the more the liquid phase is and the lower its viscosity is. Thus, the liquid phase fills in pores and makes the products compact. Therefore, the strut porosity decreases sharply with sintering temperature and reaches to the minimum value at 1,300 °C. It also can be seen by the microstructure of the fracture surface of the struts (in Fig. 7). With increasing of the sintering temperature, the combination of the particles becomes more compact, and the amount and size of pores in the samples decreased. At higher temperature, the oxidation of SiC powders as shown in Table 1 increased sharply, which led to plenty of bubbles in the struts. Therefore, the porosity of the strut increased.

Table 1 also gives the mechanical properties of SiC RPCs. The compressive strength of SiC RPCs increased significantly with increase of sintering temperature increased and reached the maximum value at 1,300 °C. The compressive strength of open cell

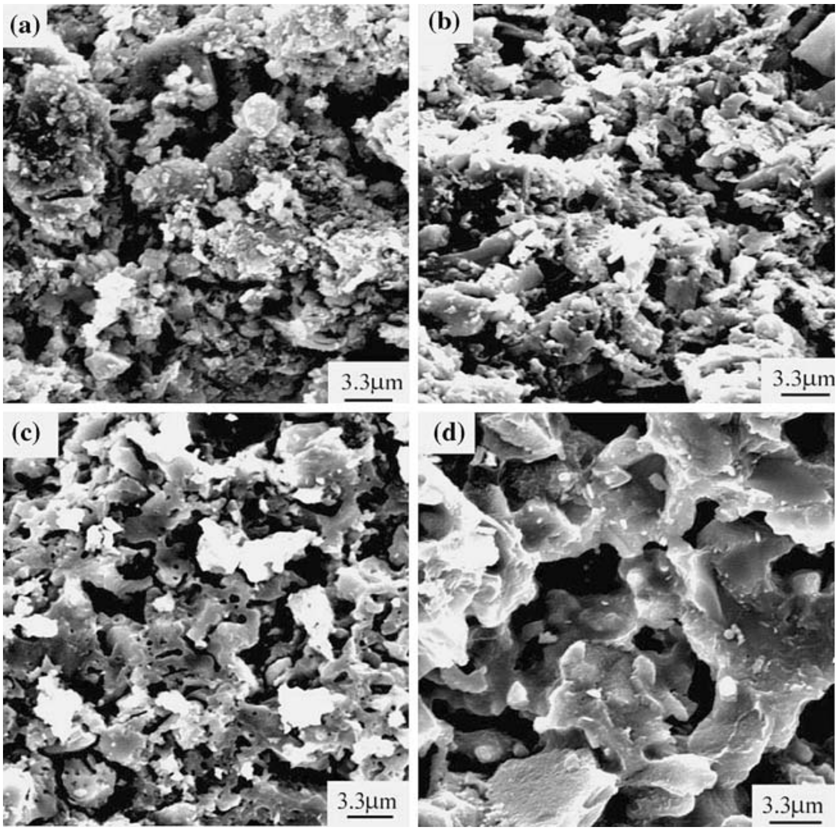


Fig. 7 SEM photos of SiC RPCs with different sintering temperature for 3 h (**a**) 1,100 °C; (**b**) 1,200 °C; (**c**) 1,300 °C, and (**d**) 1,450 °C

Table 1 Properties of SiC RPCs sintered at different temperatures for 3 h

Sintering temperature/°C	Oxide rate of SiC/wt%	Bulk density ρ_b/g cm^{-3}	Relative density ρ_b/ρ_s	Strut porosity/%	Compressive strength/MPa
1,100	10.04	0.40	0.12	41.35	0.33 ± 0.13
1,200	15.36	0.37	0.12	37.26	0.35 ± 0.17
1,300	23.76	0.43	0.16	7.53	0.79 ± 0.08
1,400	44.68	0.44	0.18	24.37	0.69 ± 0.10
1,450	52.08	0.48	0.19	11.58	0.51 ± 0.04

ceramics can be expressed by the following general form [18],

$$\sigma_{fc} = C\sigma_{fs}(\rho_b/\rho_s)^{3/2} \qquad (3)$$

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. (3), it is clear that the strut strength is a key parameter, which is decided by the densification of the strut. From Table 1, the strut open porosity decreased as sintering temperature increased and reached the minimum value at 1,300 °C. According to Eq. (3), the compressive strength is also dependent on relative density. With increase of sintering temperature, the relative density of the SiC RPCs increased, leading to improved strength. Both of them led that the compressive strength of SiC RPCs firstly increased and then decreased as sintering temperature increased. It is suggested that the optimum sintering temperature is 1,300 °C, which is at least 100 °C lower than that with Al_2O_3–SiO_2 additives as sintering aids.

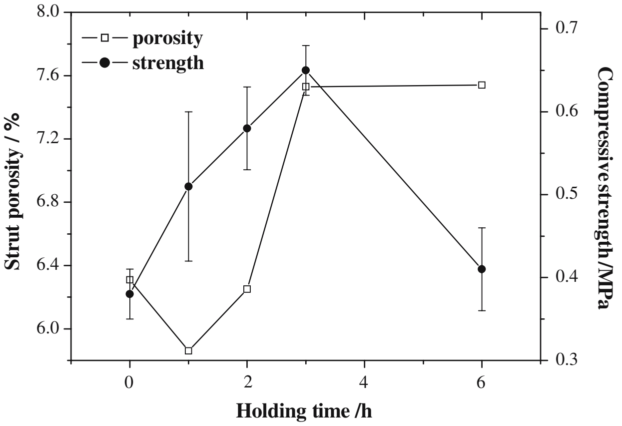
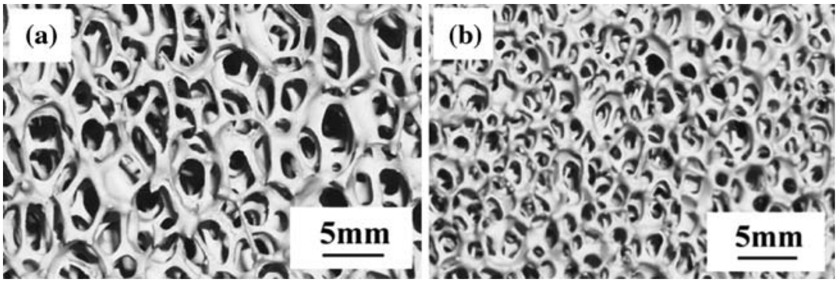


Fig. 8 Properties of SiC RPCs with different holding time

From Fig. 8, the strut open porosity of RPCs decreases very little with increase of holding time and reaches the minimal value up to 1 h holding time. Then it increases with the holding time. However, the value of the strut porosity is almost no variation. This result suggests that holding time has little effect on densification. Compressive strength of RPCs increases with holding time and reaches the maximal value up to 3 h holding time. As holding time beyond 3 h, the compressive strength of RPCs decreases, which may be the reason that plenty of bubbles (caused by superfluous oxidation of SiC) cover the surface of sintered products. Therefore, the optimal holding time is chosen at 3 h.

The macrostructures of SiC RPCs fabricated with 10 and 25 PPI sponges are shown in Fig. 9. It can be seen that the struts of SiC RPCs are very uniform, very thin struts and filled cells are few. Too thin struts are detrimental to the strength of RPCs, and filled cells will decrease the permeability of RPCs. The results show that the selected slurry is very suitable for the coating process. The strut porosities of the products fabricated with 10 and 25 PPI sponge are 8.22% and 7.53%, respectively. The bulk densities of them are 0.29 ± 0.02 and 0.363 ± 0.03 g/cm^3, respectively and the compressive strength are 0.32 ± 0.06 and 0.79 ± 0.08 MPa, respectively. The refractoriness of SiC RPcs is 1,610 °C, which is almost equal to that with Al_2O_3–SiO_2 additives as sintering aids.

Fig. 9 The macrostructures of SiC RPCs sintered at 1300°C for 3 h with different sponges (**a**) 10 and (**b**) 25 PPI



Conclusions

SiC RPCs is fabricated by using MgO–Al_2O_3–SiO_2 additives as sintering aids. The pH value of optimum dispersion of the mixed powders in the presence of silica sol as a binder was found to be around pH = 10. The optimum composite slurry with proper thixotropy was prepared to produce SiC RPCs by the replication process. The results presented in the work show that the optimum sintering temperature is determined to be 1,300 °C, which was at least 100 °C lower than that with Al_2O_3–SiO_2 additives as sintering aids. At the optimal techniques, the obtained PRCs has uniform macrostructure and high refractoriness.

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