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Sintering behavior of porous SiC ceramics

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Abstract

Yeast, a new pore former, was adopted to fabricate porous SiC ceramics for the first time. The dispersion and stability of slurry were found to depend strongly on the content of glycerol. In this work, the change of components of porous SiC ceramics in sintering process has been investigated in detail. It was also found that sintering behavior of porous SiC ceramics showed a great difference with the change of the content of sintering aid (Al_2O_3) and the optimal content of Al_2O_3 was 5–10 wt.%. In addition, the sintering temperature and hold time had great influence on sintering properties of porous SiC ceramics.

Keywords: A. Sintering; B. X-ray methods; C. Mechanical properties; D. SiC; D. Al_2O_3

1. Introduction

Porous ceramics have been found many applications including catalyst supports, filters for molten metals and hot gases, lightweight cores for sandwich panels, radiant burners, dust or soot collectors, heat exchangers, refractory linings for furnaces, and porous implants in the areas of biomaterials and so on.

Pores in porous SiC ceramics can be made by burning out the pore former in sintering process. In general, there are two kinds of pore former, inorganic materials (such as NH_4HCO_3 [1], C powder [2–5], and so on) and organic materials (such as starch [6,7], PVA [8–10], PVB [11]). As for these organic materials, they are only common organic compounds and polymers. There are few reports about using microorganisms as pore former. Yeast is a kind of microorganism and mainly contains C, H, O, N, P, S elements. The purpose of the present work is to fabricate porous SiC ceramics using yeast as pore former and to investigate their sintering behavior.

2. Experimental procedures

Commercial silicon carbide (SiC) powder ($\rho = 3.18$ g/cm^3, $d_{50} = 21.4\,\mu$m) was chosen as the major material, and Al_2O_3 powder ($\rho = 3.97$ g/cm^3, $d_{50} = 15.0\,\mu$m) was added as a sintering aid. Clay was put in as agents for shaping and sintering. Ethanol was used as dispersion media and glycerol was used as both dispersion media and stabilizing agent. The ratio of weight of materials to that of alumina ball (used as grinding media) is 1:2. All the materials above were kept milling for 12 h in a plastic bottle. Then, yeast ($d = 350$–$450\,\mu$m) was put into the bottle and blended with the slurry for 30 min. The slurry was dried for 7 h to form powder and the powder was pressed to form rectangular samples [2]. Firing of the samples was conducted in a programmable box furnace. The samples were first heated at a heating rate of 1 °C/min from 0 to 900 °C to burn out the yeast, and then heated to sintering temperature at a heating rate of 5 °C/min with a 1–5 h soaking for sintering of the ceramic powder in air.

The porosity, bulk density and skeletal density of yeast were measured by mercury porosimetry (Model PoreSizer 9320, Micrometrics Instrument Group, Norcross, GA). The struts and the image of fracture surface of porous SiC ceramics were observed by scanning electron microscopy (SEM) and the porosity and bulk density were measured by Archimedes' method. The specimens with a dimension of approximately 36 mm × 8 mm × 6 mm were used to test the flexural strength in Instron 8501 materials testing machine by three-point flexure, using a span of 30 mm and a crosshead speed 1 mm/min. Phase analysis of the combustion products was performed by X-ray diffraction (XRD).

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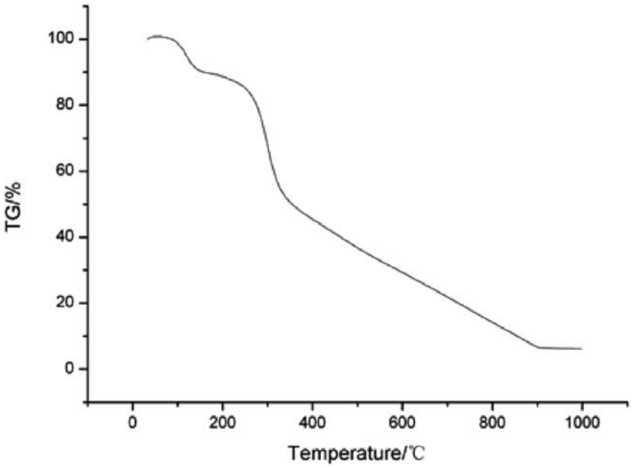

Fig. 1. TG curve of yeast at a heating rate of 10 °C/min.

3. Results and discussion

3.1. The character of yeast

Yeast belongs to microorganism and is mainly composed of C, H, O, N, P, S. The surface of yeast has many pores. The result measured by mercury porosimetry shows that the porosity is 29.66%, the bulk density is 1.1062 g/cm^3, and the skeletal density is 1.5727 g/cm^3. Therefore, some slurry is adsorbed on the surface of yeast.

Yeast completes its pyrolysis at higher temperature than general pore former, which relieves the closing of pores, without deleterious residua and reaction with the green body. Thermogravimetric analysis (TGA) of the yeast is performed in air in order to determine the thermal decomposition range. Fig. 1 shows TG curve of yeast at a heating rate of 10 °C/min. It is observed that the yeast is decomposed in three steps in air. In the first step (100–200 °C), there is only a little change in weight. In the second step (200–900 °C), decomposition is basically completed through oxidation and generates much gas, resulting in a dramatic loss in weight. At temperature >900 °C, the weight remains constant.

3.2. Effect of the content of glycerol on sintering

Gravity has great influence on the dispersion of slurry due to the great difference of the densities of all the materials. Yeast and other materials are easy to settle if only ethanol is used as dispersion media. Because the densities of these materials are different, the rates of sedimentation are different and slurry splits into many layers after short time. In order to solve the problem, glycerol is adopted as stabilizing agent to decrease the influence of gravity. The glycerol has high viscosity (1499 mPa s) and can bind in the pores on the surface of yeast. Then, it binds other materials in slurry and forms into uniform density grains. After milling with alumina balls, these grains are dispersed uniformly to form high stability slurry without farther aggregation. These grains are negatively charged. The negative charges generate repulsion among the grains and make the grains disperse uniformly. In addition, sedimentation of these grains becomes difficult because of the high viscosity of slurry with glycerol. Then, the slurry has high stability.

Table 1
Comparison of properties of sintered porous SiC ceramics with different content of glycerol

Content of glycerol (%)	Porosity (%)	Bulk density (g/cm^3)	Flexural strength (MPa)
26.8	61.4	1.10	16.8 ± 1.2
23.1	64.0	0.97	14.6 ± 1.5
18.9	63.4	0.99	11.3 ± 1.2
16.7	62.1	1.04	8.3 ± 1.1

The content of glycerol has great influence on sintering and pressing. Table 1 shows the porosity, bulk density and flexural strength of porous SiC ceramics (sintered at 1300 °C with 3-h hold) with different glycerol content. With the increase of glycerol content, the porosity and bulk density change little but flexural strength increases sharply. With increase of glycerol content, sintered samples become tighter due to fewer defects and less easy to collapse. The surface also shows fewer bubbles. This is because the viscosity of slurry increases with the increase of glycerol content. Then, different density materials are more difficult to segregate into different layers and the stability of the slurry improves. After drying, more uniform powder is formed and more SiC and Al_2O_3 are bound onto the surface of yeast particles. In the green body, glycerol takes up more space and decreases the air. So, increasing the content of glycerol improves the sintering of porous SiC ceramics and makes the strut denser. But, too much glycerol makes it difficult to dry and press. In this work, the optimal content of glycerol is 25–30 wt.%. In this range, there are no bubbles on the surface of sintered products.

3.3. The component change in sintering

In this work the main materials were SiC and Al_2O_3 and they were sintered in air. The components changed during the sintering process. The differential scanning calorimetry (DSC) and TG analysis of dried green powder were performed in the work. From TG-DSC curve of green powder (Fig. 2), the component change can be seen clearly. Near 217.8 °C, there is an endothermic peak in DSC curve and dramatic loss in weight also shows in TG curve because of the volatilization of glycerol. From 217.8 to 1176.1 °C, some loss in weight still appears because some materials are burned out. At 1176.1 °C, the DSC curve shows an exothermic peak and the weight of powder stops decreasing and begins to increase. The reason is that at this temperature SiC begins to oxidize. The oxidation of SiC proceeds by either or both of the reactions [12,13]:

$$\mathrm{SiC(s)} + \tfrac{3}{2}\mathrm{O_2(g)} \leftrightarrow \mathrm{SiO_2(s)} + \mathrm{CO(g)} \quad (1)$$

$$\mathrm{SiC(s)} + 2\mathrm{O_2(g)} \leftrightarrow \mathrm{SiO_2(s)} + \mathrm{CO_2(g)} \quad (2)$$

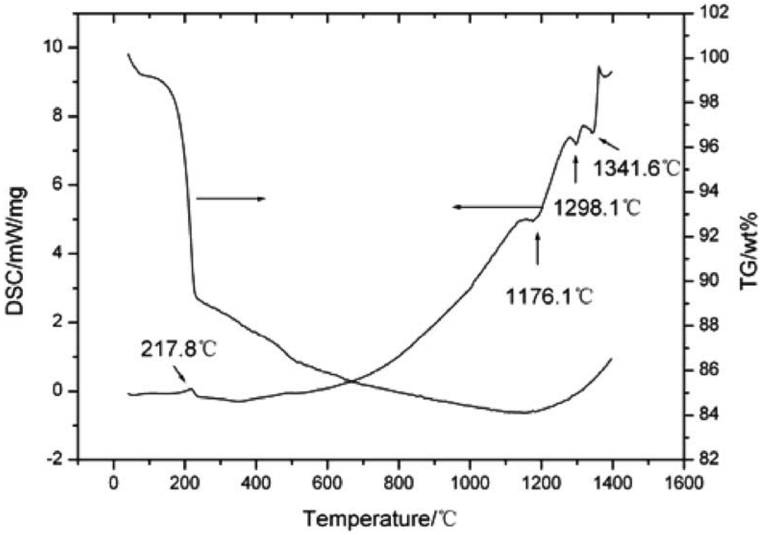

Fig. 2. TG-DSC curve of the dried powder at a heating rate of 10 °C/min.

From 1176.1 to 1300 °C, the weight of powder increases because of the continued oxidation of SiC. At 1298.1 °C, an exothermic peak exists in the DSC curve. In Fig. 5c, there is a mullite peak in the XRD pattern but not in Fig. 5b. These indicate that mullite formation reaction ($3Al_2O_3 + 2SiO_2 \leftrightarrow 3Al_2O_3 \cdot 2SiO_2$) occurs at 1298.1 °C. There is also an exothermic peak at 1341.6 °C. The oxidation of SiC proceeds vigorously generating more SiO_2 at this temperature. These results reveal that the main phases of the sintered body are SiC, SiO_2, alumina, and mullite, which also can be seen from Fig. 3 (the image of struts in sintered porous SiC ceramics at 1300 °C with 3-h hold). For struts in sintered porous SiC ceramics, energy dispersive spectroscopy (EDS) analysis shows that the main phases are coincident to the reaction products discussed above. In Fig. 3, part 1 is mainly Al_2O_3, part 2 is mainly SiC, part 3 is mainly mullite and part 4 is SiO_2.

3.4. Effect of the content of Al_2O_3 on sintering

Al_2O_3 is used as sintering aid. The content of Al_2O_3 has great influence on sintering. In this work, the content of Al_2O_3 is investigated at 5, 10, 15, 20, and 30 wt.%. Fig. 4 shows the XRD patterns of the sintered SiC porous ceramics with (a) 5 wt.% Al_2O_3, (b) 10 wt.% Al_2O_3, (c) 15 wt.% Al_2O_3, (d) 20 wt.% Al_2O_3, (e) 30 wt.% Al_2O_3. In all these XRD patterns, there are four main phases present (SiC, Al_2O_3, mullite, SiO_2), in agreement with the EDS analysis

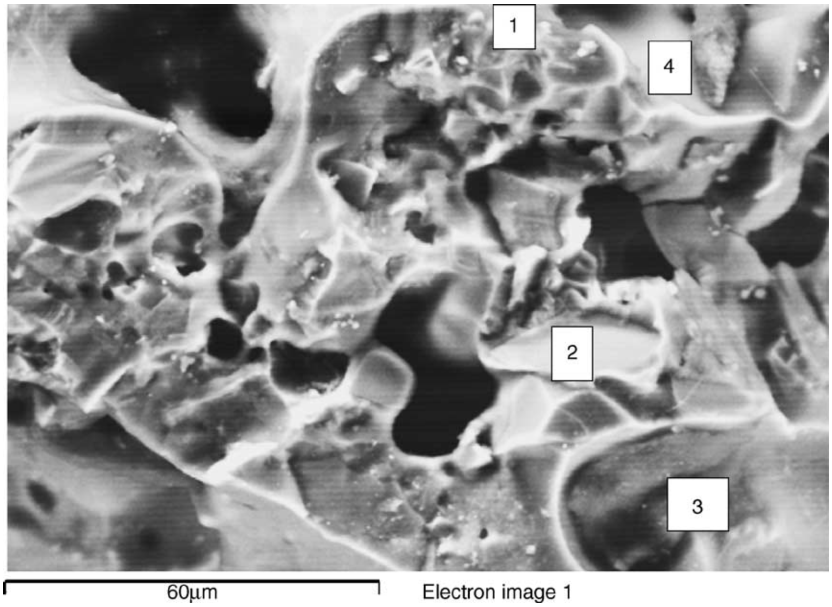

Fig. 3. SEM image of the fracture surface of the struts in SiC porous ceramics.

Table 2
Comparison of properties of sintered porous SiC ceramics with different content of Al_2O_3

Content of Al_2O_3 (%)	Porosity (%)	Bulk density (g/cm^3)	Flexural strength (MPa)
5	61.4	1.10	16.8 ± 1.2
10	60.8	1.11	15.2 ± 0.9
15	63.9	0.99	12.9 ± 1.1
20	61.7	1.09	11.2 ± 0.8
30	59.5	1.18	9.1 ± 0.5

of struts and reaction products of equations. From Fig. 4, it can be seen that the intensities of Al_2O_3 peak become higher with the increase of Al_2O_3 content. This means that the peak intensity on the XRD patterns can show the change in the population of the phases in the composition to some extent. Table 2 shows the porosity and bulk density changes little but flexural strength decreases obviously with the increase of Al_2O_3 content. The reason is that more Al_2O_3 promotes melting green materials and thereby causes more SiC to oxidize. Then, more gas releases and the struts have more defects. It is found that the optimal content of Al_2O_3 is 5–10 wt.%.

Table 3
Influence of sintering temperature on porosity, bulk density, flexural strength of sintered SiC porous ceramics

Sintering temperature (°C)	Porosity (%)	Bulk density (g/cm^3)	Flexural strength (MPa)
1300	61.4	1.10	16.8 ± 1.2
1200	65.6	0.96	9.5 ± 1.6
1100	68.5	0.93	7.6 ± 1.4

3.5. Effect of the sintering temperature and hold time

Table 3 shows that porosity decreases, density increases and flexural strength increases when sintering temperature rises from 1100 to 1300 °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. In addition, the components also change. Fig. 5a–c show the change of phases at different temperature. At 1100 °C, there are only two kinds of phases, SiC and Al_2O_3. SiO_2 peak appears at 1200 °C and mullite peak is found at 1300 °C. The results show SiC is oxidized from 1100 to 1200 °C and mullite is generated from 1200 to

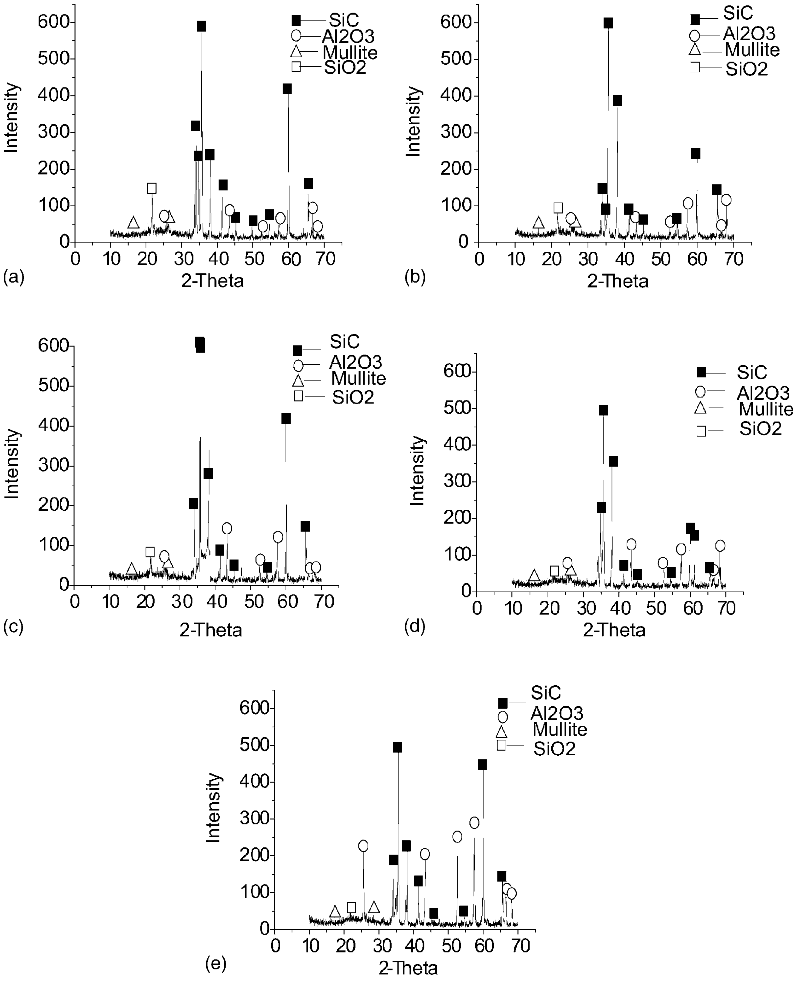

Fig. 4. XRD patterns of the sintered SiC porous ceramics with different Al_2O_3 content. (a) 5 wt.% Al_2O_3, (b) 10 wt.% Al_2O_3, (c) 15 wt.% Al_2O_3, (d) 20 wt.% Al_2O_3, (e) 30 wt.% Al_2O_3.

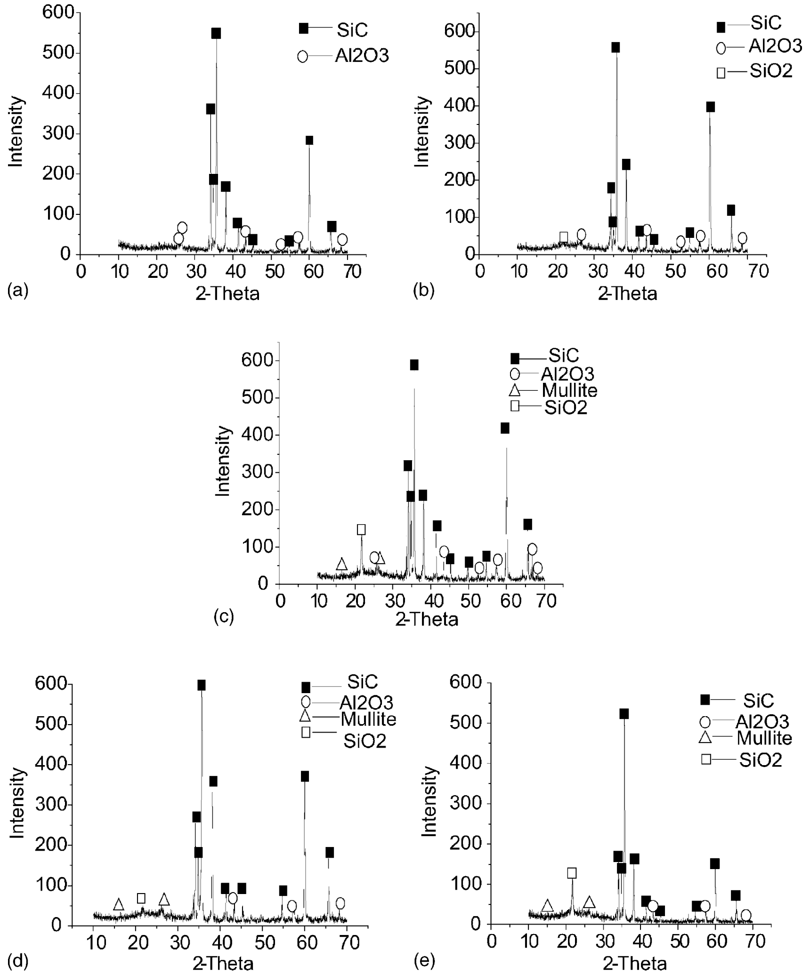

Fig. 5. XRD patterns of the sintered SiC porous ceramics heated at different temperature with different hold time: (a) sintering at 1100 °C with 3-h hold, (b) sintering at 1200 °C with 3-h hold, (c) sintering at 1300 °C with 3-h hold, (d) sintering at 1300 °C with 1-h hold, (e) sintering at 1300 °C with 5-h hold.

1300 °C, which is consistent with the TG-DSC analysis of dried powder. At 1400 °C, plenty of bubbles cover the surface of sintered products. This is because viscosity of the liquid phase decreases sharply with temperature increasing and the liquid phase flows over the surface to form bubbles due to high pressure CO or CO_2 [14,15]. So, the sintering temperature should be chosen at 1300 °C. The properties of sintered products at 1400 °C have not been investigated here because the products are over-sintered.

From Table 4, the influence of hold time on the porosity and bulk density of sintered porous SiC ceramics is not very obvious. This result suggests that hold time has little effect on densification. Flexural strength of sintered products with 1-h hold is lower than that with 3-h hold. The flexural strength of sintered products with 3- and 5-h hold are similar. The reason is that oxidation of SiC increases and more SiO_2 appears from 1- to 3-h hold, as shown in Fig. 5d and c. The peak intensity of SiO_2 in Fig. 5d is much lower than that in Fig. 5c. But from 3- to 5-h hold, little oxidation of SiC occurs because almost all the surface of the product is covered by SiO_2. The peak intensities of SiO_2 have little difference in Fig. 5e and c. So, the content of SiO_2 hardly changes. The optimal hold time is 3 h.

Table 4
Influence of hold time on porosity, bulk density, flexural strength of sintered SiC porous ceramics

Hold time (h)	Porosity (%)	Bulk density (g/cm^3)	Flexural strength (MPa)
1	61.6	1.03	13.3 ± 2.2
3	61.4	1.10	16.8 ± 1.2
5	60.1	1.12	17.2 ± 1.5

3.6. *Product with optimal components and techniques*

With all the optimal components and techniques above, porous SiC ceramics are fabricated by adding 60 wt.% yeast powder as pore former. The porosity of the product is 61.4%, its bulk density is 1.10 g/cm^3 and the flexural strength is

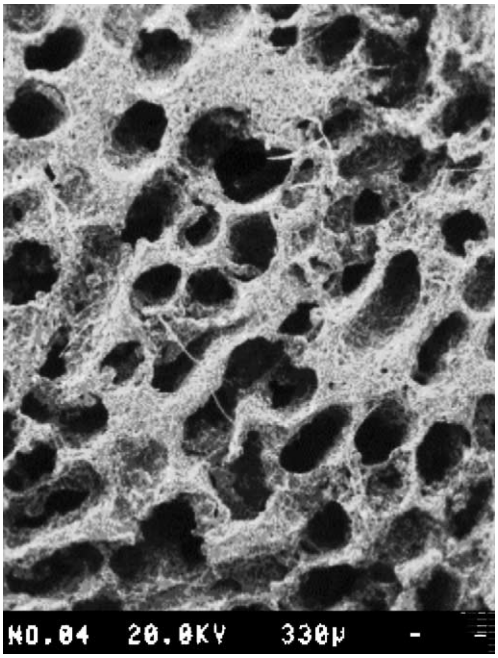

Fig. 6. SEM image of the fracture surface of porous SiC ceramics.

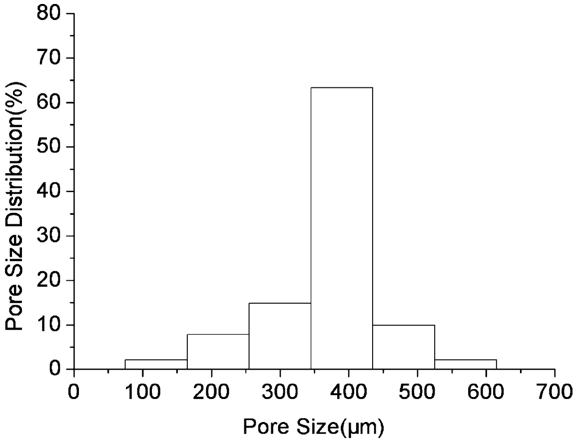

Fig. 7. Pore size distribution of porous SiC ceramics.

16.8 ± 1.2 MPa. Fig. 6. shows the SEM image of the fracture surface of porous SiC ceramics. Through analysis of many SEM pictures by Leica Qwin software, the statistic of pore size distribution is showed in Fig. 7. The main pore size is 340–430 μm, which is close to the size of yeast. The reason is that the shrinkage is very low, only 1.7%. In addition, there are a few pores which size is larger than the yeast size. This is because some pores join together after yeast burned out and are regarded as one pore during analysis.

4. Conclusions

A microorganism, yeast is used as a novel kind of pore former to fabricate porous ceramics successfully. The results presented in this work show that the sintering of porous SiC ceramics is influenced by many factors. Glycerol can improve the dispersion and stability of slurry and then the sintering. The optimal content of glycerol is 25–30 wt.%. As sintering aid, Al_2O_3 has great effect on sintering. The content of Al_2O_3 is chosen from 5 to 10 wt.% because too much Al_2O_3 makes a lot of defects. Sintering temperature and hold time are determined to be 1300 °C and 3 h, respectively, through comparing the properties of porous SiC ceramics at different sintering temperature with different hold time. The final components of sintered products are SiC, Al_2O_3, mullite, SiO_2.

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