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Effects of particle grading composition of SiC on properties of silicon-bonded SiC porous ceramics

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Abstract
Silicon-bonded silicon carbide (SBSC) porous ceramics had been prepared by mixing two different particle size of SiC powder (coarse and fine) as aggregates for silicon carbide porous ceramics, adding metallic Si as the binder phase and firing at 1450 °C under argon atmosphere. Various combinations of SiC mixtures consisting of two different particle size and packing density were prepared, and the samples were investigated to understand apparent porosity, bending strength, pore size distribution, and microstructure. The result showed that mixing an appropriate proportion of SiC coarse and fine powders could not only improve the pore size distribution of SBSC porous ceramics but also significantly increase the bending strength compared with the single-particle size sample. The system had the highest free packing density when the ratio of coarse to fine SiC size was >2 and the coarse powder content was 60–70 wt%. The optimal bending strength, and apparent porosity were 37.53 MPa and 37.11% respectively when mixing 70 wt% of coarse powder (50.8 μm) and 30 wt% of fine powder (9.5 μm) and sintered at 1450 °C in an argon atmosphere. The material created had 100.3% increased bending strength, and 0.99% decreased porosity compared with the single-particle size sample (50.8 μm).

1. Introduction
SiC porous ceramics are widely used in gas filtration and purification, catalyst carrier, thermal insulation, and other fields due to their high-temperature resistance, corrosion resistance, good thermal shock resistance and high strength [1–7]. The main preparation methods of SiC porous ceramics are (1) particle packing; (2) adding pore-forming agent; (3) template method; (4) direct foaming, etc [8–11]. The particle packing method is a common method for preparing SiC porous ceramics, which involves the self-melting method and the addition of the binding phase method. The self-melting method is made from high-purity SiC of different particle sizes, mixed in a certain ratio and sintered at high temperatures (around 2300 °C). The addition of a binding phase method means that the SiC powder (coarse and fine) is sintered at a lower temperature (around 1500 °C) by adding a binder phase with a lower melting point to the SiC mixture [12]. Silicon-bonded silicon carbide (SBSC) porous ceramics refer to filling Si as a bonding phase between SiC particles so that porous ceramics can be prepared at a lower temperature [13]. SBSC porous ceramics are currently widely used in Diesel particulate filters (DPF). However, the lower bending strength limits further development of new products for particle filters and other applications. Song [14] prepared Si-bonded SiC ceramics with Si as the binder at 1700 °C. Xing [15] designed S-SiC ceramics with excellent mechanical properties by using 25 wt% SiC powder (D50 = 0.5 μm) and 75 wt% SiC powder (D50 = 4.6 μm), but the porosity was lower than 30%.

Particle packing methods are greatly influenced by the size of SiC powder and particle size distribution because the pore within SiC porous ceramics is formed from SiC powder accumulation. Therefore, the pore size can be controlled, and the strength of ceramic products can be improved by the proper particle grading.
composition of SiC powder [16–19]. However, it is difficult to obtain porous ceramics’ high strength and high porosity simultaneously. When other conditions are constant, the increase in porosity will decrease bending strength [20].

In this paper, SiC porous ceramics were prepared using silicon metal powder as the binder. The effects of different silicon carbide powder particle grading composition on the free packing density, apparent porosity, pore size distribution, bending strength and microstructure of SBSC porous ceramic blends were systematically investigated.

2. Experimental

2.1. Preparation of SBSC porous ceramic

Coarse α-SiC powder \( (D_{50} = 50 \, \mu m, \geq 99\%) \) and fine α-SiC powder \( (D_{90} = 10 \, \mu m, \geq 99\%) \) (Shandong Jiefeng Materials Co., China) and silicon powder \( (\sim 23 \, \mu m, \geq 99\%, \) Shandong HanZun New Energy Technology Co., China) were used as raw materials, and poly vinyl alcohol solution (1788, Macklin Biochemical Co.) was used as adhesive. The coarse and fine silicon carbide powders were graded on standard sieves (Nanjing Xiongchen Industry & Trade Co., China) with mesh sizes of 200, 250, 280, 325, 450, 600 and 800 to obtain powders with narrow particle size distribution with the average particle size of 9.5 \( \mu m, 19.7 \, \mu m, 30.2 \, \mu m, 40.6 \, \mu m, 50.8 \, \mu m, 61.3 \, \mu m \text{ and } 71.9 \, \mu m, \) respectively (shown in Tab.1). The porous ceramics prepared with a single particle size of SiC powder have low strength. In contrast, porous ceramics prepared by the gradation of two different particle sizes of SiC have a higher performance. Different sizes and different proportions of coarse powder and fine powder were mixed to obtain SiC powder with a double particle size distribution. Then 4:1 ratio of prepared SiC powder mixture and Si powder were milled for 24 h. After that, the dried mixtures were granulated with 5 wt\% poly vinyl alcohol solution (7 wt\%, 1788, Macklin Biochemical Co., China; Decomposition temperature 400 °C–700 °C) as binder and pressed into a strip \( (50 \, mm \times 6 \, mm \times 6 \, mm) \) of green sample under a pressure of 4 MPa. Finally, the raw samples were held at 700 °C under air atmosphere for 1 h to expel the PVA and then sintered under argon atmosphere at 5 °C/min to 1450 °C for 1.5 h to obtain SBSC porous ceramics.

2.2. Characterization

The powder’s free packing density (loose density) was measured by Ricko FZ54–4 powder density meter. The microstructure and morphology were analyzed by scanning electron microscope (SEM, JSM-6510, Japan). The three-point bending strength was tested with an electronic universal testing machine, the support span was 30mm and the crosshead speed was 0.5 mm/min. Average bending strength (MPa) was obtained from 5 samples. The apparent porosity and bulk density were calculated by the Archimedes method. The pore size distribution was measured by a mercury porosimeter (GT-60, Quant Grome, USA).

3. Results and discussion

3.1. Influence of particle grading composition of SiC on the packing density of SiC powders

SiC powder with \( D_{50} = 10 \, \mu m \text{ and } D_{90} = 50 \, \mu m \) as raw materials was graded. Selected standard sieves with mesh numbers of 200, 250, 280, 325, 450, 600 and 800 and assembled them in descending order of mesh number from bottom to top. Weighed 100 g of silicon carbide powder, started sieving from a 200 mesh sieve, and collected the SiC powder on each sieve after sieving, and the powder was divided into 7 particle size ranges, and the powder was divided into 7 particle size ranges. The particle size of the powder after grading was shown in table 1.

Due to the large difference in density between SiC and Si, the experiments were conducted to study the packing density of SiC powders with two particle sizes first. On this basis, the packing density of Si-SiC blends was studied. All possible particle gradation options were designed based on the seven particle sizes \( M_1 \text{ to } M_7 \) of SiC powder in table 1, as shown in table 2.

Different particle gradation schemes in table 2 were chosen to investigate the free packing density of two different particle sizes of SiC particles at different ratios. Figure 1 shows the effect of coarse powder addition on the packing density of SiC powders at different particle gradations. From figure 1, it can be seen that the packing density of the powder increased with the increase of the coarse powder content, and the free packing density of the system was larger when the proportion of coarse powder was 60 wt% – 80 wt% and the proportion of fine powder was 20 wt% – 40 wt%. When there was an excess of coarse powder and less fine powder, fewer fine particles entered the coarse particle gap, which led to loose powder packing and a lower packing density. This is in good agreement with Furnas’ model of the gradation of the two-particle sizes [21]. He concluded that for a system with two types of particles, the volume fraction of fine particles should be:
with the above studies, we investigated the particle gradation of SiC coarse and particle grading composition on the packing density of Si-SiC mixed powder was only studied. In combination density of the Si-SiC system is shown in ratio greater than 2. With a total SiC powder of 100 wt%, the effect of SiC coarse powder addition on the packing SiC coarse powder content was 60 \% to 70 \% which is consistent with the actual experimental results. The packing density of the powder is mainly related to the coarse powder particle size and fine powder particle size ratio, and the coarse powder particle size has a greater influence on the packing density after grain composition. When the SiC coarse powder was M7, the packing density varied from 0.9 g cm\(^{-3}\) to 1.37 g cm\(^{-3}\), and the optimum packing density of M7 was the largest, reaching 1.35 g cm\(^{-3}\). This is since the packing density of the mixed powder is mainly determined by the coarse particles, with the fine particles filling in the gap of the coarse particles, and the maximum packing density is higher when the coarse particles have a larger particle size. When the ratio of particle size of coarse and fine particles of SiC powder was less than 2, the improvement of the packing density of the grade-matched powder was not obvious. As shown in figure 1(c), the powder packing density of the M3-M4 grading system increased from 0.9 g cm\(^{-3}\) to 1.1 g cm\(^{-3}\). This was because the particle size of M3 and M4 powder were 50.8 \(\mu m\) and 40.6 \(\mu m\) respectively, the gap size formed by the stacking of the two powders was less than 40.6 \(\mu m\), resulting in the M4 powder particles not being able to fill into the gap, which made it impossible for the SiC powder to achieve the ideal state of tight buildup. Therefore. It is generally best to choose a coarse to fine powder particle size ratio greater than 2.

### 3.2. Influence of particle grading composition of SiC on the packing density of Si-SiC blended powders

Silicon metal powder was introduced based on the gradation scheme in table 2, with a mass ratio of 8:2 between SiC and Si (23 \(\mu m\)) powder. Since the Si content was kept constant during the experiments, the effect of SiC particle grading composition on the packing density of Si-SiC mixed powder was only studied. In combination with the above studies, we investigated the particle gradation of SiC coarse and fine powders with a particle size ratio greater than 2. With a total SiC powder of 100 wt\%, the effect of SiC coarse powder addition on the packing density of the Si-SiC system is shown in figure 2.

As shown in figure 2, with the increasing SiC coarse powder, the packing density of Si-SiC mixed powder first increased and then decreased. In general, the packing density of Si-SiC powders can reach a maximum when the SiC coarse powder content is 60–80 wt\% and the SiC fine powder content is 20–40 wt\%. The Si-SiC blended powders with high packing density are as follows: M7-M1, M6-M1, M5-M1, of which the M5-M1 system has the maximum powder packing density. In contrast, the M1-M2 system has the lowest powder packing density. Compared to the pure SiC powders described above, the SiC grain composition resulted in a relative decrease in

### Table 1. Particle size and number of the graded powder.

| Particle size(\(\mu m\)) | 9.5 | 19.7 | 30.2 | 40.6 | 50.8 | 61.3 | 71.9 |
|---------------------------|-----|------|------|------|------|------|------|
| Number                    | M1  | M2   | M3   | M4   | M5   | M6   | M7   |

### Table 2. Grains composition scheme and size ratio of SiC powder.

| Number       | The particle size of coarse powder (\(\mu m\)) | The particle size of fine powder (\(\mu m\)) | Particle diameter ratio | Number       | The particle size of coarse powder (\(\mu m\)) | The particle size of fine powder (\(\mu m\)) | Particle diameter ratio |
|--------------|-----------------------------------------------|---------------------------------------------|-------------------------|--------------|-----------------------------------------------|---------------------------------------------|-------------------------|
| M7-M8        | 71.9                                         | 61.3                                        | 1.17                    | M3-M4        | 50.8                                         | 40.6                                        | 1.25                    |
| M7-M9        | 71.9                                         | 50.8                                        | 1.41                    | M4-M5        | 50.8                                         | 30.2                                        | 1.68                    |
| M7-M10       | 71.9                                         | 40.6                                        | 1.77                    | M5-M6        | 50.8                                         | 19.7                                        | 2.58                    |
| M7-M11       | 71.9                                         | 30.2                                        | 2.38                    | M6-M7        | 50.8                                         | 9.5                                         | 5.35                    |
| M7-M12       | 71.9                                         | 19.7                                        | 3.64                    | M7-M8        | 50.8                                         | 5.35                                        | 9.5                    |
| M8-M9        | 61.3                                         | 50.8                                        | 1.21                    | M4-M5        | 40.6                                         | 30.2                                        | 1.34                    |
| M8-M10       | 61.3                                         | 40.6                                        | 1.51                    | M5-M6        | 40.6                                         | 30.2                                        | 1.34                    |
| M8-M11       | 61.3                                         | 30.2                                        | 2.03                    | M6-M7        | 30.2                                         | 9.5                                         | 3.18                    |
| M8-M12       | 61.3                                         | 19.7                                        | 3.11                    | M7-M8        | 19.7                                         | 9.5                                         | 2.07                    |

\[
\varphi_f = \frac{1 - \varphi_c}{1 - \varphi_c + \frac{\varphi_c}{\varphi_f}}
\] (1)

Where \(\varphi_f\) is the volume fraction of fine particles, \(\varphi_c\) and \(\varphi_f\) are the relative density of the coarse and fine powders, respectively. Using this formula, the mass fraction of coarse particles to reach the theoretical maximum free packing density is 60 wt\% to 70 wt\%, which is consistent with the actual experimental results.
the packing density of the Si-SiC blended powders due to the addition of Si powders with less density than SiC, which impacted the effect of the particle gradation.

3.3. Influence of particle grading composition of SiC on the properties and structure of SBSC porous ceramics

(1) The effect of the amount of SiC fine powder on the properties of SBSC porous ceramics

Figure 3 shows the effect of the amount of SiC fine powder on the apparent porosity, bulk density, and bending strength of SBSC porous ceramics for different grading schemes. In general, the bulk density and bending strength of SBSC porous ceramics increased and then decreased as the SiC fine powder content increased. In contrast, the apparent porosity first reduced and then increased. This was because as the SiC fine powder gradually increased, the SiC fine powder filled into the SiC coarse particle voids, the packing slowly tightened and the molten silicon gradually infiltrated between the particles, enhancing the bond between the SiC powders. When the SiC fine powder content exceeded the optimum value, the excess SiC fine powder could not enter the voids, resulting in a reduction in the overall packing density, which led to a loosening of the particle.
packing in SBSC porous ceramics, a reduction in mechanical properties and an increase in apparent porosity \cite{22, 23}.

When the SiC fine powder content was 30wt\%, as the particle size of the SiC coarse powder increased, the bulk density of the ceramic product gradually increased, the porosity decreased and the bending strength of the product first increased and then decreased. Combined with figure 2, it can be seen that when the SiC coarse powder particle size was larger, the free packing density of the Si-SiC hybrid powder was higher and the compacted density of the blank was also higher, resulting in a tight bond between the porous ceramic particles, which led to a reduction in porosity and an increase in bulk density. However, when the SiC coarse powder particle size was M3, the apparent porosity did not change significantly and the bulk density and bending strength of the product was relatively low. From figures 2(c) and (d) above, it could be seen that the packing density of the M3-M1 graded powder was less than that of the M5-M1 graded powder. This is probably because the pores formed by the accumulation of M3 powder are relatively small, and it is difficult for M1 powder to enter the pores, thus forcing the tightly packed M3 particles to separate. So the bulk density and bending strength of the M3-M1 porous ceramic were smaller.

In summary, the Si-bonded SiC porous ceramics reached a maximum bending strength of 37.53 MPa, a bulk density of 1.955 g cm\(^{-3}\) and an apparent porosity of 37.11\% when the SiC particle grading composition was M5-M1 in a ratio of 70 : 30 (mass percent). However, the Si-bonded SiC porous ceramics prepared from the single-particle size SiC powder with a particle size of 50 \(\mu\)m had a bending strength of 18.73 MPa and apparent porosity of 38.1\%. Compared to the single-particle size sample, the porosity of the graded SBSC porous ceramic was only 0.99\% lower, while the bending strength increased by 18.8 MPa, an increase of up to 100.3\%. The particle grading composition had a significant effect on the bending strength of porous ceramics.

4. The effect of the amount of SiC fine powder on the microstructure of SBSC porous ceramics

Si-bonded SiC porous ceramics were prepared from two particle sizes of SiC powder, M5 and M1. Five samples of each formulation were prepared and the sample with the best bending strength of each formulation was taken for SEM analysis. Figure 4 shows the cross-sectional SEM images of Si-bonded SiC ceramics with different SiC
Figure 3. Effect of SiC fine powder addition on the properties of SBSC porous ceramics at different gradations.

Figure 4. SEM images of SBSC porous ceramics with different contents of SiC fine powder: (a) 10 wt%, (b) 20 wt%, (c) 30 wt%, (d) 40 wt%.
As can be seen in figure 4, as the M1 powder content increased, the large pores were filled and became progressively smaller, which accounted for the increase in packing density and bulk density. In addition, the disappearance of the large holes avoided the collapse of the holes during sintering, resulting in a more uniform distribution of the pore structure and a more stable SBSC porous ceramic support body. The decrease of the distance between particles led to the gradual enhancement of the bond between molten Si and SiC particles. From the experimental results in figures 2(c) and 3(c), we know that the maximum packing density and bending strength were achieved when the SiC coarse powder M5 content was 70 wt% and the SiC fine powder M1 content was 30 wt%. This means that the particles are stacked in the most compact state and that the particles bind best to each other, which is evident in figure 4(c). As the SiC fine powder content continued to increase, in addition to some of the fine powder filling into the large particle gap, the remaining fine powder accumulated with each other, forming smaller diameter stomata, as in figure 4(d). However, the uneven particle size distribution of the pores directly destroyed the otherwise more stable support structure. The schematic diagram of microstructure evolution by increasing content of SiC fine particles is shown in figure 5.

5. The influence of the amount of SiC fine powder on the pore size distribution of SBSC porous ceramics

Si-bonded SiC porous ceramics were prepared from two SiC powders, M5 and M1. Figure 6 shows the effect of SiC fine powder addition on the pore size distribution of the porous ceramics, where the SiC fine powder additions were 0 wt% (F0), 10 wt% (F1), 20 wt% (F2), 30 wt% (F3), 40 wt% (F4). As can be seen from the graph, the average pore sizes were 6.47 μm (F0), 4.64 μm (F1), 3.68 μm (F2), 2.43 μm (F3) and 2.40 μm (F4).
respectively. As the SiC fine powder content increased, SiC fine powder gradually filled the gap between the large ones when the SiC coarse powder formed close packing, the large pores in the product were reduced, the number of small and medium-sized pores increased and the pore size distribution became wider [24]. From figures 2(c) and 3(b), it can be seen that the packing density and bulk density were maximum when the SiC coarse powder (M5) content was 70 wt%, and the SiC fine powder (M1) content was 30 wt%, which means that the silicon carbide particles are closely packed at this point. So, the average pore size of SBSC porous ceramics decreased significantly to 2.43 μm because the SiC particles were tightly packed and the large pore size was filled with SiC fine powder. In this case, the porous ceramic had the most uniform distribution of pores and a stable pore structure, which resulted in the highest bending strength as shown in figure 3(c). When the SiC fine powder content was too high (40 wt%), the pore size distribution of the product became wider, resulting in an uneven distribution of pore sizes within the product, which affected the bending strength of SBSC porous ceramics.

6. Conclusions

SBSC porous ceramics were prepared using particle-graded SiC as raw material and silicon powder as the binder, applying a particle stacking model to guide experiments at 1450 °C under argon atmosphere. The effect of SiC particle grading composition on the packing density and sintering properties of the SiC-Si system was investigated. The optimum SiC particle grading composition scheme was determined and Si-bonded SiC porous ceramics with superior properties were prepared. The following main conclusions were drawn.

(1) For the two different particle size SiC systems, the free packing density of the system is larger when the size ratio of coarse to fine particles is >2 and the percentage of coarse powder is 60–70 wt%; the actual experimental results are in general agreement with the results obtained from the Furnas’ theoretical model.

(2) For the SiC-Si mixed powder system when SiC: Si = 4:1 (mass ratio) and the content of SiC fine powder is around 20 wt%~30 wt%, the stacking of the system is relatively tight; the effect of M5-M1 particle grading composition is significant.

(3) The particle sizes of SiC coarse and fine powders are 50.8 μm and 9.5 μm, and the mass ratio is 70:30. The properties of Si bonded SiC porous ceramics are the best, with the bending strength of 37.53 MPa, bulk density of 1.955 g cm⁻³, apparent porosity of 37.11%, and average pore size of 2.43 μm.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Declaration of interest statement

No conflict of interest exits in the submission of this manuscript, and manuscript is approved by all authors for publication. I would like to declare on behalf of my co-authors that the work described is original research that has not been published previously.

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References

[1] Adler J 2005 Ceramic diesel particulate filters Int. J. Appl. Ceram. Tec. 2 429–39
[2] Vogt U F et al 2007 Macroporous silicon carbide foams for porous burner applications and catalyst supports J. Phys. Chem. Solids. 68 1234–8
[3] Wood S and Harris A T 2008 Porous burners for lean-burn applications, Prog. Energy. Combust. 34 667–84
[4] Colombo P 2006 Conventional and novel processing methods for cellular ceramics Philos. Trans. A. Math. Phys. Eng. Soc. 364 109–124
[5] Gomez–Martin A et al 2016 Permeability and mechanical integrity of porous biomorphic SiC ceramics for application as hot gas filters Mater. Des. 107 450–60
[6] Carvalho A C et al 2015 A new source for production of ceramic filters Mater. Lett. 145 250–52
[7] Dey A et al 2015 Permeability and nanoparticle filtration assessment of cordierite-bonded porous SiC ceramics Ind. Eng. Chem. Res. 52 18362–72
[8] Wang S F et al 2010 Fabrication, structure and properties of porous SiC ceramics with high porosity and high strength. Adv. Mat. Res 105-106 608–11
[9] Jana D C, Sundararajan G and Chattopadhyay K 2016 Effect of porosity on structure, young’s modulus, and thermal conductivity of SiC foams by direct foaming and gelcasting J. Am. Ceram. Soc. 100 312–22
[10] Streitwieser D A et al 2005 Application of the chemical vapor infiltration and reaction (M-R) technique for the preparation of highly porous biomorphic SiC ceramics derived from paper J. Eur. Ceram. Soc. 25 817–28
[11] Luyten J et al 2003 New processing techniques of ceramic foams Adv. Eng. Mater. 5 715–8
[12] An Z B et al 2019 Synthesis and formation mechanism of porous silicon carbide stacked by nanoparticles from precipitated silica/glucose composites J. Mater. Sci. 54 2787–95
[13] Liu T L et al 2020 Effects of SDBS and ZrO2 additives on the microstructure and properties of silicon-bonded SiC porous ceramics Ceram. Int. 46 2910–4
[14] Song I H et al 2012 Effects of silicon particle size on microstructure and permeability of silicon-bonded SiC ceramics J. Ceram. Soc. Jpn. 120 370–4
[15] Xing Y Y et al 2018 Grain Composition on Solid-state-sintered SiC Ceramics J. Inorg. Mater. 33 1167–72
[16] Wu H B et al 2014 Processing, microstructures and mechanical properties of aqueous gelcasted and solid-state-sintered porous SiC ceramics J. Eur. Ceram. Soc. 34 3469–78
[17] Guo W M et al 2016 Tuning pore structure of corrosion resistant solid-state-sintered SiC porous ceramics by particle size distribution and phase transformation Mater. Design. 100 1–7
[18] Zhou P P et al 2018 Microstructures and performance of CaO-based ceramic cores with different particle size distributions for investment casting Mater. Res. Express. 5 2
[19] Xu C S et al 2019 Preparation and properties of sic porous ceramics with double-particle size Mater. Res. Express. 5 851 1
[20] Rice R W 1993 Evaluating porosity parameters for porosity–property relations. J. Am. Ceram. Soc. 76 1801–8
[21] Furnas C C 1931 Grading aggregates I-mathematical relations for beds of broken solids of maximum density Ind. Eng. Chem. 23 1052–28
[22] Zhang S, Liu W Y and Granata G 2018 Effects of grain size gradation on the porosity of packed heap leach beds Hydrometallurgy. 179 238–44
[23] Wickland B E et al 2006 Design and evaluation of mixtures of mine waste rock and tailings Can. Geotech. J. 43 928–45
[24] Chen C et al 2019 Microstructure and properties of diamond/SiC composites via hot molding forming and CVI densifying. Adv. Eng. Mater. 21 (Germany: Wiley-VCH Verlag) 5