Effects of SiC Micro-Powder Content on Properties of RSiC Porous Ceramics Supports

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Abstract. The sintering mechanism of recrystallized silicon carbide (RSiC) is mainly “the evaporation-condensation process” of silicon carbide. In the process of sintering, no liquid phase is generated and the samples almost do not shrink. After sintering, the pore connectivity of the specimens comes excellent, so the gas permeability of the RSiC porous ceramic supports is very good. The influences of SiC micro-powder content on the properties of the supports were investigated. Specifically, the open porosity, cold modulus of rupture, hot modulus of rupture at 1200°C, pore size distribution, and gas permeability of samples were measured. The microstructure and phase composition of samples were also analyzed by SEM and XRD. Our results show that RSiC porous ceramic supports with not-too-high apparent porosity but excellent permeability and mechanical properties at room and high temperature can be prepared by simply adjusting the amount of SiC micro-powder.

1. Introduction

Porous ceramic composite membranes can be used to separate operations at high temperatures and in harsh environments. They are widely used because they have attractive properties that include excellent thermal stability, corrosion resistance, and mechanical strength [1-6]. Porous ceramic composite membranes generally consist of three parts: supports, transition layers, and membrane layers. The supports are essential to the application of porous ceramic membranes. They must have large porosity (>30%), high gas permeability, a narrow range of pore sizes, good mechanical properties, and corrosion resistance [7-9]. Most recent research on porous ceramic supports has focused on oxides (for example: Al₂O₃ and mullite) or oxide-bonded SiC porous ceramics [10-12]. Compared with oxide or oxide combined with SiC supports, recrystallized silicon carbide (RSiC) porous ceramic supports have many advantages, such as high gas permeability, good high-temperature mechanical properties, excellent thermal shock resistance, and resistance to corrosion by H₂, CO, etc. [13].

RSiC ceramics are prepared by using SiC powder with different particle sizes and high purity as raw material, without adding sintering aid, and sintering at high temperatures (2200 ~ 2450°C) [14]. The principal sintering mechanism of RSiC is the “evaporation-condensation process” of silicon carbide [15]. In China, researches on RSiC ceramics focus on high-temperature structural materials, electro-thermal materials, and porous ceramic skeletons [16]. However, there are few reports on RSiC porous ceramic supports. In this study, we prepared RSiC porous ceramics supports by dry-pressing method, using SiC coarse powder and SiC micro-powder as raw materials.
2. Experimental

2.1. Raw materials
Commercially available SiC coarse powder (99.7 wt.% purity, d_{50} = 100.0 μm, Shandong Huarong New Materials Co., Ltd, Weifang, China) provided skeleton material for the support. SiC micro-powder (99.4 wt.% purity, d_{50} = 2.5 μm, Shandong Huarong New Materials Co., Ltd, Weifang, China) was used as bonding material. Polyvinyl alcohol (PVA, analytical purity, Henan Hengxie Chemical Reagent Co., Ltd, Henan, China) was used as binder for green bodies.

2.2. Samples preparation
Porous SiC ceramic membrane supports were prepared according to the process shown in Figure 1. First, SiC coarse powder and micro-powder were mixed in different mass ratios and dry blended in a high-speed mixer (R02, Maschienfabrik Gustav Erich) for 60 min at 1000 rpm. The blending was then continued for 5 minutes with 3 wt% PVA solution (4 wt.% aqueous solution) to obtain a homogeneous mixture. This mixture was uniaxially pressed into a circular sheet (Φ 50×50 mm²) and a plate-like (25×25×150 mm³) green body under a pressure of 100 MPa, using a steel die. Compositions of the specimens used in this study are listed in Table 1. The green bodies so obtained were placed in an oven at 120°C until the mass stabilized. Finally, the dried specimens were heated to remove PVA at 700°C for 4 h, and sintered in an argon atmosphere at 2300°C for 3 h, followed by furnace cooling.

![Diagram](Image)

**Figure 1.** Process flow chart for the preparation of porous SiC ceramic supports.

| Sample No. | SiC micro-powder:coarse powder (mass) | PVA aqueous solution (wt.%) |
|------------|--------------------------------------|-----------------------------|
| A30        | 30:70                                | 4%                          |
| A40        | 40:60                                | 4%                          |
| A50        | 50:50                                | 4%                          |
| A60        | 60:40                                | 4%                          |
| A70        | 70:30                                | 4%                          |
| A85        | 85:15                                | 4%                          |
| A100       | 100:0                                | 4%                          |
2.3. Characterization

The phase composition and microstructure of the porous RSiC ceramic supports were analysed by X-ray diffraction (XRD, X’Pert Pro, Philips, Eindhoven, Ni, Cu Kα radiation) and by a scanning electron microscope (SEM, EVO-18, ZEISS, Germany) coupled with energy dispersive X-ray spectroscopy (EDS, X-Max 50, Oxford, UK).

The open porosity was determined by the Archimedes method with distilled water as the liquid medium. The modulus of rupture was measured by a three-point bending test (HWOR-02/16, Sinosteel Luoyang Institute of Refractories Research Co., Ltd., Luoyang, China), and the hot modulus of rupture was tested in air at 1200°C. Gas permeability was measured by a porous ceramic gas permeability tester (TQD03-3, Sinosteel Luoyang Institute of Refractories Research Co., Ltd., Luoyang, China). Permeability (K) of the sample can be evaluated by using the equation [17]:

\[
K = \frac{\eta Q}{A \Delta P}
\]

(1)

where \(\Delta P\) is the pressure drop from the entrance to the exit of the sample, \(A\) and \(L\) are, respectively, the cross-sectional area and the thickness of the sample, \(Q\) is the volumetric flow rate, and \(\eta\) is the dynamic viscosity of \(N_2\). The thickness and diameter of the samples tested were both 50 mm. \(\Delta P\) and \(Q\) were measured by a porous ceramic gas permeability tester. The permeability was then calculated from the slope of the line plotted for \(\Delta P\) vs. \(Q\) using equation (1). For the dynamic \(N_2\) viscosity \(\eta\) we used \(1.78 \times 10^{-5} \text{ Pa} \cdot \text{s}\) at room temperature.

3. Results and discussion

3.1. Phase composition

The XRD results for the sample A60, SiC, the micro-powder, and the coarse powder are shown in Figure 2. The phase composition of the sample A60 is the same as that of SiC alone—either coarse or micro-powder—indicating that the RSiC ceramic supports are composed of SiC alone.

![Figure 2. XRD patterns of the sample A60, the SiC micro-powder and the coarse powder.](image)

3.2. Microstructure

The sintering mechanism of RSiC consists mainly of the “evaporation-condensation process” of silicon carbide. However, SiC can produce only very few gaseous molecules. The “evaporation” of SiC is not simply the gasification of SiC, but is the decomposition of SiC in the presence of SiO₂. Usually, there is a thin layer of SiO₂ on the surface of SiC micro-powder, and the “evaporation-
condensation” process of SiC is realized with the help of SiO₂. At 2300°C, the reaction of SiC and SiO₂ can be represented as follows[18]:

\[
\text{SiO}_2(g) \rightleftharpoons \text{SiO}(g) + \frac{1}{2} \text{O}_2(g) \quad (2)
\]

\[
\text{SiC}(s) + \text{SiO}(g) \rightleftharpoons 2\text{Si}(g) + \text{CO}(g) \quad (3)
\]

The equation for the overall reaction is

\[
\text{SiC}(s) + \text{SiO}_2(g) \rightleftharpoons 2\text{Si}(g) + \text{CO}(g) + \frac{1}{2} \text{O}_2(g) \quad (4)
\]

In the overall reaction [Equation(4)] , the forward reaction can be regarded as “the SiC evaporation process”, and the inverse reaction can be regarded as “the SiC condensation process”. The sintering mechanism of RSiC ceramic supports is illustrated schematically in Figure 3.

![Figure 3. Schematic illustration of the sintering process of RSiC ceramic supports.](image)

During sintering, first, because of high chemical reactivity, SiC micro-powder is easy to react with SiO₂ (g) in the forward reaction of Equation 4 to obtain Si (g), CO (g) and O₂ (g). Then, the three kinds of gas diffuse into the neck of the SiC coarse particles to have a reverse reaction of Equation 4 to generate SiC which is deposited due to its low saturated steam here. The reverse reaction produces another product, SiO₂ (g), which continues to react with other SiC micro-powder. The reaction in circles until it is completed. In summary, SiO₂ (g) is equivalent to a "catalyst" or "porter" which "carries" the SiC micro-powder to necks between the SiC coarse particles, thereby realizing the sintering process of RSiC.

The driver of the sintering process is chemical reactivity and the relation of vapor pressure to curvature. The smaller the size of the SiC particles, the higher the activity and the faster the reaction with SiO₂ to form the gas phase. SiC deposits preferentially in necks of SiC coarse particles, because the large radius of curvature in this region leads to low pressure of SiC vapor. In this way, SiC fine particles migrate to the necks of the SiC coarse particles through the "evaporation-condensation process" until all necks of the SiC coarse particles are fully filled or the SiC fine particles are used up. There are no generation of the liquid phase and almost no linear change in the sintering process of RSiC, so the pore connection of the RSiC porous material can be very good.

Figure 4 shows the fracture morphology of specimens with different contents of SiC micro-powder.
It can be seen from Figure 4A30 that SiC coarse particles are bonded to a network, without SiC fine particles appearing. When the content of SiC micro-powder is 40%, well-developed necks between SiC coarse particles are formed, and SiC fine particles do not appear, as shown in Figure 4A40. The network bonded by SiC coarse particles is blocked by SiC fine particles, as shown in Figures 4A60 and 4A70. Figure 4A85 shows that SiC fine particles are connected into a network in which SiC coarse particles are distributed in isolation. When the content of SiC micro-powder is 100% (Figure 4A100), SiC fine particles are bonded to a network, with no SiC coarse particles appearing.

For the purpose of sintering, 40% is the optimum content of SiC micro-powder. When the amount of micro-powder is less than 40%, the development of necks by SiC coarse particles is incomplete. When it is more than 40%, the excessive micro-powders form fine particles by “evaporation-coagulation”, blocking the network structure of the SiC coarse particles. When it is more than 85%, SiC coarse particles are isolated in the network of fine particles, and the material tends to form fine-grained structure. With an increase of the content of SiC micro-powder, the proportion of small pores increases. In addition, it can be seen from Figure 4 that the pore connectivity of all samples comes very good.
3.3. Mechanical properties
The effects of SiC micro-powder content on the cold modulus and hot modulus of rupture of specimens are shown in Figure 5. This figure shows that with an increase in the content of SiC micro-powder, the cold modulus of rupture of the samples increases from 32.0 MPa to 48.5 MPa, then decreases to 24.7 MPa, and then rises to 45.1 MPa. The hot modulus of rupture shows the same pattern of change as that of the cold modulus, although the hot modulus of rupture is everywhere higher than the corresponding cold modulus of rupture.

![Figure 5. The effects of SiC micro-powder content on the cold and hot modulus of rupture of the specimens.](image)

The strength of a specimen is determined mainly by its microstructure (Figure 4). From Figure 4 it can be seen that because necks of SiC coarse particles develop best with 40% SiC micro-powder, the modulus of rupture of the samples (both hot and cold) is highest for that content. With the content of SiC micro-powder increasing from 40% to 70%, the continuity of the network structure formed by SiC coarse particles is destroyed by SiC fine particles, so the strength gradually diminishes. When the content of SiC micro-powder is increased further from 70% to 100%, the fine SiC particles gradually form a continuous network structure, and the structure of the samples tends to be fine-grained, so each modulus of rupture increases.

At 1200°C, the SiO₂ glass phase formed by SiC oxidation is beneficial to the healing of micro cracks in the sample, so the hot modulus of rupture is higher than the cold modulus of rupture of the same formulation [19].

3.4. Pore characteristics and gas permeability
Figure 6 presents open porosity, average pore size, and gas permeability of samples as functions of SiC micro-powder content; also the distribution of pore sizes for A30 through A100.

As shown in Figure 6(a), open porosity of the specimens increased from 28.9% to 44.2% and average pore size decreased from 23.41 μm to 7.92 μm when the content of SiC micro-powder went from 30 wt.% to 100 wt.%. Because of the large specific surface area of SiC micro-powder, the higher the content of micro-powder, the lower the density of the green body and the higher the open porosity. At the same time, there was almost no linear change in the RSiC sintering process, so the open porosity of the sample increased with the increase of the content of SiC micro-powder. It can be seen From Figure 4 that the proportion of small pores increases with an increase of the content of SiC micro-powder, so average pore size decreases also.
Figures 6(b) and 6(c) show that as the pore diameter of the samples is reduced, the pore size distribution becomes wider as the percentage of SiC micro-powder increases from 30 to 70 wt.% and becomes narrower as the content of SiC micro-powder increases further from 70 to 100 wt.%.

![Graphs showing open porosity and average pore size as functions of SiC micro-powder content.](image)

Figure 6. (a) Open porosity and average pore size as functions of SiC micro-powder content. (b) and (c) Pore size distribution. (d) Gas permeability.

It can be seen from Figure 6d that as the content of SiC micro-powder increases, gas permeability first increases and later decreases, reaching its maximum value of \(40 \times 10^{-12}\) m\(^2\) when the content of SiC micro-powder is 60 wt%. For porous ceramics, the higher the open porosity and the bigger the pore size, the better the permeability of the material[20]. When the content of SiC micro-powder increases, open porosity of the specimens increases, but pore diameter of the samples decreases. When the content of SiC micro-powder is between 30 and 60 wt%, the increase of open porosity has a greater impact on gas permeability, so gas permeability increases. When the content of SiC micro-powder is between 60 and 100 wt%, the decrease of pore diameter has a greater impact on gas permeability of samples, so gas permeability then decreases.

When the content of SiC micro-powder was 60%, the gas permeability of samples was \(40.0 \times 10^{-12}\) m\(^2\) and the open porosity was only 34.5% (Figure 6). The maximum gas permeability of glass-bonded SiC porous materials prepared by Wang B et al. was \(6.5 \times 10^{-12}\) m\(^2\), and the open porosity was 64.7% [21]. The glass-bonded SiC sample prepared by Su Chang Kim et al. has a gas permeability of \(1.0 \times 10^{-12}\) m\(^2\) and an open porosity of 38.0% [22]. Fukushima M et al. prepared a SiC porous ceramic by a gel-freezing method, whose gas permeability was between \(10^{-11}\) and \(10^{-10}\) m\(^2\), and whose open porosity was up to more than 89% [23]. Compared with SiC porous ceramics prepared in other laboratories, our sample A60 had higher permeability but lower open porosity, because the pore connectivity of the sample came very good. In addition, the cold and hot modulus of rupture of specimens were 35.8
MPa and 41.7 MPa, respectively, pore size distribution was narrow, and the pore connectivity was good. The RSiC porous ceramics supports have excellent application prospects in the high-temperature filtration industry.

4. Conclusions
The RSiC porous ceramic supports were prepared by a dry-pressing method in an argon atmosphere at 2300°C for 3 h, using SiC coarse powder (d50=100 µm) and SiC micro-powder (d50=2.5 µm) as raw materials. We examined the effects of the content of SiC micro-powder on the phase composition, microstructure, and other properties. The main conclusions of the study are as follows:

1. By adjusting the content of SiC micro-powder, RSiC porous ceramic supports with narrow pore size distribution, good gas permeability, not-too-high apparent porosity, and excellent mechanical properties at room and high temperatures can be prepared.

2. With an increase of SiC micro-powder content from 30 to 100 wt%, the open porosity of the specimens increased from 28.9% to 44.2%. At the same time, the cold modulus of rupture fluctuated between 24.7 and 48.5 MPa, the hot modulus of rupture fluctuated between 29.0 and 55.1 MPa, and the gas permeability increased and then decreased.

3. When the content of SiC micro-powder was 60%, the specimens showed the best overall properties: an open porosity of 34.5%, 35.8 MPa cold modulus of rupture, 41.7 MPa hot modulus of rupture, 19.26 µm average pore size, and a gas permeability of 40×10⁻¹² m².

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