Preparation of Silicon Carbide hollow fiber Membrane in Low Temperature by Precursor Pyrolysis

Man Xu¹,², Mengke Guan¹, Shulin Wang¹,²,* and Mengyu Wu¹

¹School of Material Science and Engineering, Wuhan Institute of Technology, Wuhan 430074, China
²Energy Saving Materials and Membrane Technology Research Institute, Wuhan Institute of Technology, Wuhan 430074, China

*Corresponding author e-mail: 1799195482@qq.com

Abstract. The silicon carbide (SiC) powder is covered with polycarbosilane (PCS), N-Methyl pyrrolidone (NMP) is a solvent, polyethersulfone (PES) is a bonding aid, using phase-phase and solid-phase sintering process combined with a step-by-step molding to prepare a symmetrical structure of silicon carbide hollow fibers, and determine the membrane's perforation and purification and purity of the water distribution and the circumference of the membrane. The results show that the SiC membrane tube is a finger-hole structure layer-spongy structure layer-finger-hole structure structure, the optimal sintering temperature is at 1200 ℃, the size of the prepared ceramic membrane aperture is concentrated in about 0.9 μm, and the pure water flux is 2.832 m³ / (m².h).

1. Introduction

In recent years, the outer diameter of the hollow fiber microtube structure membrane is generally less than 2mm, which has attracted wide attention. In addition to the advantages of the traditional ceramic membrane itself, the new hollow fiber ceramic membrane prepared by phase conversion method has the characteristics of large density per unit volume filling, simple preparation process, low cost, equipment miniaturization, simple structure and self-supporting body membrane, so the research of hollow fiber ceramic membrane is paid more attention. In recent years, it has become one of the main research hotspots in the field of solid state chemistry and inorganic membrane technology, and the research and development of new hollow fiber ceramic membrane has great potential to solve the bottleneck of the development of ceramic membrane technology. Compared with the flat and tube ceramic membranes, the new hollow fiber ceramic membrane has a very high accumulation density, large effective filtration area per unit volume membrane, controllable microstructure, and high...
membrane permeability. Therefore, hollow fiber ceramic membrane will replace the traditional plate
and tube membrane and organic hollow fiber membrane, etc., in the corrosive fluid filter, high
temperature membrane reactor, solid oxide fuel cell, membrane contact reactor, catalyst carrier or
composite membrane support body mouth and other fields have a broad application prospects [3-4]. The
phase conversion method induced by solution impregnation has been initially proved to be one of the
most effective methods for the preparation of hollow fiber ceramic membrane. Combining phase
conversion with high temperature sintering process [5], the permeability of the membrane is expected to
be significantly improved by the dry and wet spinning of one step molding and the preparation of
self-supported asymmetrical hollow fiber ceramic membrane, which is expected to be significantly
improved due to the thin wall and microstructure control.

The advent of polycarbosilane (PCS) makes it possible to prepare silicon carbide membrane
materials at low temperatures. König [6] and so on will be SiC powder into the PCS positive
n-Hexane solution, the preparation of organic slurry, directly coated on the surface of the silicon carbide support
membrane, in 900 ℃ PCS can be completely decomposed to produce amorphous SiC, bonded silicon
carbide particles to form SiC membrane.

This text paper studies a preparation method of silicon carbide hollow fiber membrane containing
binder PCS, using PCS to cover silicon carbide particles, on the basis of this powder, adding PES and
NMP, preparing non-water-based silicon carbide slurry, and using low-temperature liquid phase
sintering, the preparation of a pure SiC hollow fiber membrane

2. Experimental

2.1 Experimental raw materials

The silicon carbide powder used in this experiment are produced by Henan Yakun Group, SiC fine
particle powder particle size is 1.2um, polyethersulfone (PES), N-Methyl pyrrolidone (NMP),
polycarbosilane (PCS), and n-Hexane. The industrial-grade polyethersulfone, produced by BASF
Chemical Corporation of Germany, was purchased as a polymer solvent by The Chinese
Pharmaceutical Group Shanghai Chemical Reagents Co., Ltd. at a low melting point below (-20℃)
and chemically pure NMP. The outer solidification bath of the spinning molding process and the gel in
the core liquid are tap water.

2.2 Experimental process

On the basis of the forming of the dry and wet method, the hollow fiber ceramic membrane was
prepared by using the phase conversion method induced by solution impregnation and low
temperature sintering technology. The process is as follows:

A certain amount of PCS powder is completely dissolved in n-Hexane, and a certain amount of SiC
powder is added. The mass ratio of PCS and SiC is 1: 30. Grind with a mortar until the n-Hexane is
completely evaporated, and the PCS will form a coating on the SiC surface floor. According to the
ratio of m (PES): m (NMP): m (raw material powder) is 2: 8: 5, an appropriate amount of PES is
dissolved in NMP and added to the PCS package The coated SiC powder is mixed uniformly to obtain
a casting film slurry. In order to uniformly disperse the solid particles in the polymer solution, the cast
film slurry needs to be continuously stirred for more than 24 hours. The casting film slurry should be
prepared under air humidity of less than 55%, otherwise the PES will harden with water when the polymer is dissolved, and a casting film slurry meeting the requirements cannot be prepared.

The prepared cast membrane slurry is added to the slurry tank on the spinning device, the residual bubbles are removed by vacuum, and the core liquid (water, internal gel) is applied, and the nitrogen pressure (1 bar) is applied to squeeze the cast membrane slurry into the nozzle after the vacuum. Fiber wet membrane extruded from the nozzle through 5cm dry spinning course (air gap) immersed in the outer solidification bath (water) for 24h or more to ensure that the solvent and non-solvent exchange and phase conversion process is fully carried out, forming hollow fiber membrane raw blanks.

The degassing process should be guaranteed for more than two hours, otherwise the bubbles in the cast membrane slurry are not exhausted, then the extruded membrane tube is easy to deform, or even break. Figure 1(a) is the gas 1h when SiC hollow fiber ceramic membrane raw blank, Figure 1(b) degassing 1h SiC hollow fiber ceramic membrane blank map, which can be intuitively seen in the slurry bubbles for extruded SiC hollow ceramic fiber membrane tube harm.

After the gel solidification of the hollow fiber membrane precursor to be dried at room temperature, and then at 5 °C/min to 650°C to remove the organic polymer and other volatile substances, and then at 5 °C/min heat ingress to 1200 °C insulation, and finally natural cooling to room temperature to get hollow fiber ceramic membrane sample. This experiment uses the XD-5A X-ray diffraction analyzer produced by Japan's Tsushima Company to analyze samples at different burned temperatures, and characterizes the sample profile of the JSM-5510LV-type scanning electron analyzer produced in Japan.

3. Results and discussion

3.1 Phase analysis of SiC hollow fiber membrane

Figure 2 is an XRD diagram of the SiC hollow fiber tube. As shown in Figure 2, the fiber tube is mainly composed of SiC with a spatial point group of P63mc (186), but also contains a small amount of 3C-SiC, SiC hollow fiber tube after sintering, no change in the phase, indicating that the PCS has been cracked to produce β-SiC[7], at 1000°C, the product (006) The diffraction peak of the crystal surface is 0.273°, the diffraction peak is the characteristic diffraction peak of β-SiC, indicating that PCS has cracked the production of β-SiC, but the degree of silicon carbide crystallization is low, basically glass-state silicon carbide, glass-state silicon carbide makes the original silicon carbide particles bond with each other, and make the ceramic membrane and the support body bonding each other, on the one hand to provide the strength of the membrane, on the other hand to reduce the pores
of the membrane. The product at 1200°C can clearly observe that the characteristic diffraction peak is slightly higher than the characteristic diffraction peak of the product at 1000°C, at which time PCS is cracked to produce a slightly better crystallization degree of β-SiC, but according to the surface of the hollow fiber tube did not appear powder and other phenomena, indicating that PCS cracking produced silicon carbide or belongs to glass-state silicon carbide.

![XRD patterns of SiC hollow fiber membranes at different sintering temperatures](image)

Figure 2. XRD patterns of SiC hollow fiber membranes at different sintering temperatures

3.2 Membrane performance analysis of SiC hollow fiber membrane

The porosity rate of SiC hollow fiber membrane at different sintering temperatures was determined by density method. The pore rate of SiC hollow fiber membrane with a sintering temperature of 1000°C was measured at 30.38%, and the pore rate of SiC hollow fiber membrane with sintering temperature of 1200°C was 25.16%. This is mainly due to the sintering process, with the increase in sintering temperature, PCS cracking produced a large number of glass-state SiC so that the original SiC particles bond to each other, thereby reducing the film pores, making the specimen more dense, the porosity reduced.

After the membrane layer is burned, the bore size distribution and pure water flux test are carried out, and the test results are shown in the figure below. Figure 3 shows the aperture distribution of the silicon carbide support and the membrane burned, as can be seen from the figure, the aperture distribution range of 1000°C is 1.0 to 2.2μm, and the aperture size of the membrane layer of 1200°C is distributed between 0.7 and 1.3μm, mainly concentrated near 0.9μm, indicating that the size of the membrane body aperture is more uniform, and the result of the same pore rate is consistent, and the SiC hollow fiber membrane of 1200°C is more dense.

![Pore-size distribution of SiC hollow fiber membranes at different sintering temperatures](image)

Figure 3. Pore-size distribution of SiC hollow fiber membranes at different sintering temperatures

Using pure water penetration device to test the pure water permeation flux of SiC hollow fiber membrane with a sintering temperature of 1200°C, the pure water permeation flux of sintering temperature is obtained by Figure 4, when the cross-membrane pressure difference is 1bar, the average
amount of pure water flux of the membrane layer is 2.382 m$^3$ / (m$^2$ h), and over time, the pure water flux value is getting smaller and smaller, may be that the membrane hole is blocked by the contaminants in the test equipment, or because the structure of the membrane is destroyed due to excessive pressure.

![Figure 4. Pure water flux of SiC hollow fiber membrane](image)

3.3 Microstructure analysis of SiC hollow fiber membrane

Figure 1(b) and 5 show samples of SiC hollow fiber membrane blanks and sintered. From Figure 1(b), it can be seen that the raw blank sample of SiC hollow fiber membrane obtained by phase legal system is smooth on the surface, and the raw blank has good toughness and continuity. Figure 5(a) is in accordance with a certain temperature procedure sintered after the sample, the experiment obtained a certain strength of SiC hollow fiber membrane tube.

During the experiment, the scanning electron microscope was used to observe the shape of SiC hollow fiber membrane, and Figure 5(b) was a section and surface profile of SiC hollow fiber ceramic membrane at 1200°C. From Figure 5(c), it is clear that the SiC hollow fiber membrane forms a dense surface layer near the inner and outer surface, presenting a finger-hole-like structure; the asymmetrical structure of the SiC hollow fiber membrane tube is due to the different phase-separation processes taking place on the inner and outer surface and middle region of the membrane tube. The nascent wet membrane extruded from the spinning head, the inner surface of which first came into contact with the core liquid water, the solvent polyethersulfone and water between the transfer of the process of rapid occurrence, causing a transient phase, the outer wall of the membrane after extruding from the dead head after a period of about 5cm air gap is immediately immersed into the water, polyethersulfone and water also occurred in the instantaneous phase, instant phase due to rapid reaction, generally form a finger-hole structure, the middle part of the wet membrane of the polyethersulfone and water transfer exchange is relatively slow, mainly due to the wet membrane surface phase curing to hinder the diffusion of water to the inside of the wet membrane, the slow phase-separation process, slow phase-separation generally formed a spongy structure.

From Figure 5(c) it can also be seen that the inner and outer surface of SiC hollow ceramic fiber membrane is a finger-hole-like structure, the inner surface aperture is 5-10μm, the appearance face diameter is 10-15μm, the middle layer is loose porous spongy structure, the aperture is about 0.6-1μm.

Figure 5(d) is a SEM analysis of the SiC hollow fiber membrane layer, as shown in the figure, the membrane layer after 10000 times amplification, you can see the SiC particles between the obvious bonding, it is speculated that SiC generated from PCS cracking acts as a binder, SiC particles free accumulation formed about 2 μm aperture, explaining PCS cracks at 1200°C produces a glass-state SiC that binds the original SiC particles to each other, so carbon and silicon are derived from the
glass-state SiC produced by PCS cracking, providing strength for the formation of hollow fibrous fibrous membranes.

Figure 5. SEM images of SiC hollow fiber membranes
(a) sintering samples, (b) cross-section (c) fiber wall, (d) outer surface

4. Conclusion
(1) In the process of preparation of cast membrane slurry to ensure that the air humidity is less than 55%, the experimental raw materials to avoid the existence of combined water, cast membrane slurry bubbles to be eliminated, otherwise can not be made uniform cast membrane slurry, so that can not prepare a complete smooth SiC hollow fiber ceramic membrane blank.
(2) The precursor polycarbosilane in the vacuum atmosphere 1200 ℃ insulation 1h can get the glass state SiC, so that SiC particles bond with each other, reduce the pores between the membranes.
(3) With the increase of sintering temperature, the pore rate of the SiC membrane tube decreases. The prepared silicon carbide ceramic membrane tube appears as a spongy structure layer of the hole structure. The asymmetrical structure of the hole structure layer is beneficial to improve the permeability of the membrane.

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