Preparation and Properties of Porous SiC/SiC Composites

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Abstract. The purpose of this study was to investigate the preparation and properties of porous SiC fiber reinforced SiC matrix (SiC/SiC) composites. SiC/SiC composites were prepared by polymer impregnation pyrolysis (PIP) progress with polycarbosilane (PCS) as impregnate and SiC fiber as reinforcement. The pores of the composites were pre-introduced by regulating the distribution of yarns during the braiding of the fiber preform. The apparent porosity, pore structure and the tensile strength were studied and compared with the laser drilling composites. The results show that the properties of the composites pre-perforated by fiber preforms are superior to the composites drilled by laser.

1. Introduction

With the rapid development of aeronautics and astronautics, working temperatures of the aircrafts are getting higher and higher that even exceed the limit of superalloys. New generation of thermal structure materials are urgently needed. Advanced ceramics such as SiC have low density, high temperature tolerance, high oxidation resistance and high corrosion resistance, which have been potential candidates. Although advanced ceramics materials have such superior physical-chemical and mechanical properties, the biggest shortcoming of them is their low toughness. Once a small crack occurs in the ceramics, it will propagate rapidly, resulting in disastrous accidents [1]. There are many ways to overcome shortcomings of ceramics, and the most efficient way is to combine ceramics with ceramic particles, fibers, or whiskers to obtain ceramic matrix composites. The most outstanding one is the fiber reinforced ceramic matrix composites, especially continuous fibers like carbon fibers or SiC fibers, which could reach superior toughness. While as the limit to antioxidant capacity of carbon fiber, C/SiC composites are more inclined to use for thermal structures with limited lifetime, especially in the aerospace sector. In view of the excellent oxidation resistance of SiC fiber, SiC/SiC composites can be used for long life thermal structures, which are considered as one of the most potential thermal structural materials used for aircraft engine, which not only attain excellent thermal and mechanical properties, but also excellent oxidation resistance[2-5].

In the field of high-performance engines, the turbine inlet temperature of the aero-engines with a weight ratio of 10 is currently exceeding 1500 °C, and the average temperature of the turbine inlets of the aero-engines with a thrust-to-weight ratio of 12-15 is being developed up to 1800 °C. The environment temperature in the engine is so high that the parts often require cooling. Film cooling is an effected way that cool air bled from film hole attach to the surface to prevent hot free-stream gas. So preparation of film pores is a key technology which greatly affected the cooling effect. SiC/SiC composites are typical difficult-to-machine materials due to their own natures such as high hardness and anisotropy. How to prepare pores that meet the process requirements has become an urgent
problem to be solved. The traditional method of preparing film pores is mechanical drilling or laser drilling. Mechanical drilling can obtain a good precision of the hole diameter, but there are problems such as serious tool wear and generation of defects, and the efficiency is very low. Laser drilling has high efficiency, but the pore has taper and the surface of the inner wall of the pore is delaminated and cracked due to the existence of the heat affected zone. It should be noted that the above two methods belong to the removal type processing, which will cause damage to the fiber and matrix, resulting in a significant decrease in material properties [6]. While the porous SiC/SiC composites prepared in this paper provide a new idea for the preparation of film pores that can avoid material damage.

2. Methodology

2.1. The raw materials
The raw materials used for the experiment include SiC fiber (purchased from Liya New Materials Co.ltd, China) and PCS (purchased from Liya Chemistry Co.ltd, China).

2.2. Materials preparation
The fiber preforms are braided in 2.5D structure, and interlocks are formed by winding weft and warp yarns, and the fiber bundles are interwoven at a certain angle in the direction of thickness, so that the material has better integrity, good shear performance and strong designability. 2.5D braided composite material avoids the disadvantages of poor performance between layers of 2D braided composite material and complex technology of 3D braided composite material, reduces the manufacturing cost, shortens the production cycle, and is easy to prepare rotary components, such as head cone, shell and other complex structural parts. During the braiding of the fiber preforms, regular arrangement of pores is formed by adjusting the arrangement of the warp yarns.

The fiber preforms are coated with a pyrolytic carbon interphase with thickness of about 100 nm through thermal chemical vapor infiltration process with propane gas as carbon source. Then the SiC ceramic matrix are incorporated into the preforms through the PIP progress with PCS as impregnant. The PIP cycles repeat until the final weight increment of the prepared composites is not beyond 1% and SiC/SiC composites are completed as is shown in Figure 1.

![Figure 1. The preparation scheme of SiC/SiC composites.](image)

2.3. Characterization methods
The apparent porosity is measured by Archimedes technique as in equation (1), where \( \rho_1 \) is the density of maceration liquid under experimental conditions; \( m_1 \) is the dry sample quality; \( m_2 \) is the quality of the sample after fully dipping in the liquid; \( m_3 \) refers to the air quality of the sample after fully impregnating and drying the surface. The sample must be washed and dried before testing.

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\pi_a = \frac{(m_2 - m_1)\rho_1}{m_3 - m_2} \times 100\%
\]  

(1)

The pore structure and morphology is characterized by digital radiography and CT and SEM.
The tensile test specimens are cut from composites according to the standard ASTM C1275 with the nominal dimensions in Figure 2. Room temperature tensile tests are taken on an electronic universal testing machine. The tests are carried out with 0.5 mm/min crosshead speed at room temperature (25°C). For each kind of composites, five specimens are measured. Average tensile strength of the five specimens in the tests is used to evaluate the tensile strength of the composites.

**Figure 2.** The tensile test specimen with nominal dimensions in millimeters.

3. Results and discussion

3.1. The apparent porosity of the composites

In this study, according to the mechanism of pore formation, the pores in the SiC/SiC composites can be divided into three categories. (1) There are some original pores in the preforms that are not fully filled by PCS due to inadequate impregnation and these pores are retained until the composites are completed. Especially when the pore size is small or the channel connecting the pore with the outside world is small, it is difficult or takes a long time for the precursor solution with high viscosity to fully enter the pore, so the matrix cannot fill the pores. Most closed pores fall into this category. (2) Some smaller pores were caused by pores and cracks in the matrix caused by volume shrinkage of precursor after pyrolysis. On the one hand, during the pyrolysis of precursor, small molecules will escape and leave pores. On the other hand, during the pyrolysis of precursor, the volume will shrink by about 50%, resulting in pores. (3) During the braiding of the fiber preforms, regular arrangement of pores is formed by adjusting the arrangement of the warp yarns. Compared to the first two categories of pores, these holes are too large to be fully filled and eventually remain, forming the porous materials. The apparent porosity can effectively reflect the content of the third type of pores.

| Sample Number | Fiber Volume Fraction (%) | Warp Arrangement   | Apparent Porosity (%) |
|---------------|----------------------------|--------------------|-----------------------|
| 1             | 50                        | Average distribution | 16                    |
| 2             | 49                        | Reserved pores      | 22                    |
| 3             | 45                        | Average distribution | 15                    |
| 4             | 43                        | Reserved pores      | 28                    |

In this paper, by setting up different warp arrangement rules, the porous materials with different pore contents are obtained, and their apparent porosity is shown in Table 1. Sample 1 and sample 3 are the traditional uniform arrangement of warp yarns, which means there is no prefabricate pores, and the apparent porosity reflects the first and second categories of pores. Sample 2 and sample 4 obtain the third category of pores by adjusting the arrangement of warp yarns, and thus show significantly larger apparent porosity. By comparing sample 1 with sample 2 and sample 3 with sample 4, it can be found that materials with different porosity can be obtained by adjusting weaving parameters with almost no
change in fiber volume fraction. At the same time, it can be found that the lower fiber volume fraction can obtain a larger range of porosity regulation.

3.2. The pore structure and morphology
Figure 3 is the digital radiography image of sample 1 and sample 2. It can be clearly seen from the figure that the warp yarns in sample 1 are evenly arranged, while the warp yarns in sample 2 are arranged in a group of two closely connected warp yarns, which are evenly arranged. It can also be seen from the Figure 3 that obvious pores remain between different groups of warp yarns in sample 2.

Figure 3. Digital radiography image of sample 1 and sample 2.

Figure 4 is the CT image of sample 2. CT scanning and reconstruction of the structure of sample 2 showed that the prefabricated pores in the fiber preform are well preserved during the preparation of SiC/SiC composites. Figure 5 is the real picture of sample 2, and its profile also confirms this conclusion. Why these pores are preserved is an interesting question. This is because in fiber preforms, small pores are usually preferred for filling, especially between single filaments. Small pores require fewer PIP cycles than large ones to achieve the same density, so at the same PIP cycles, the filling of the larger pores lags behind the small pores. In addition, the size of the small pore is more conducive to the development of capillary force, so that the matrix filling degree in the small pore is higher and more compact. At the same time, the densification of larger pores is delayed due to the fact that larger
pores usually act as escape channels for gases and small molecules. Since the prefabricated pores are the largest in size, they are the slowest to fill and are ultimately preserved.

![Real picture of sample 2.](image)

### 3.3. Results of tensile tests

Table 2 lists the tensile strength of the SiC/SiC composites. The three groups of test specimen have similar fiber volume fraction and are prepared by the same PIP process. Specimen 1 and specimen 3 are the traditional uniform arrangement of warp yarns, which means there is no prefabricate pores. The only difference between specimen 3 and specimen 1 is that specimen 3 uses laser to drill pores after the preparation, so that its apparent porosity is close to that of specimen 2. Specimen 2 obtain the prefabricated pores by adjusting the arrangement of warp yarns.

| Test Specimen Number | Fiber Volume Fraction (%) | Warp Arrangement | Apparent Porosity (%) | Tensile Strength (MPa) |
|-----------------------|---------------------------|------------------|-----------------------|-----------------------|
| 1                     | 45                        | Average distribution | 15                    | 212                   |
| 2                     | 43                        | Reserved pores    | 28                    | 201                   |
| 3                     | 45                        | Average distribution | 27                    | 175                   |

![The typical morphology of laser drilling pores.](image)

The tensile strength of specimen 2 is 5.2% lower than that of specimen 1, which can be concluded that the average arrangement of warp yarns can provide better mechanical properties. While the tensile strength of specimen 3 is 17.5% lower than that of specimen 1. This means that to obtain the same amount of pores, specimen 3 needs to sacrifice more mechanical properties. Another way to calculate, with a similar amount of pores, the tensile strength of specimen 2 is 14.9% higher than that of specimen 3, which shows great advantages. The reason for this result is that the integrity of fibers and matrix of specimen 3 is destroyed after the laser drilling, and the processing defect causes the decline
of mechanical properties of the composites. Figure 6 shows the morphology of the pore wall made by laser. It can be seen that the fibers and matrix are cut off at the position of the pore, and the pore wall has lamination, micro-crack and other defects, which directly leads to the decline of the mechanical properties.

4. Conclusions
This paper provides a new method to obtain pores in SiC/SiC composites, which is to prefabricate pores in the braiding process of fiber preforms by regulating the distribution of yarns, and retain them in the subsequent material preparation process to form porous SiC/SiC composites. In the case of similar apparent porosity, this new method can obtain less mechanical property damage compared with laser drilling method, because this prefabrication technique does not destroy the integrity of fibers and matrix, while the drilling method will cause the damage of fibers and matrix. This technique can be applied to the fabrication of SiC/SiC composites film holes in order to obtain better properties of components.

References
[1] Naslain R 2004 Composites Sci. and Technol. 64 155-70
[2] Mingwei C, Haipeng Q, Jian J, Xiuqian L, Yu W and Hao Z 2013 Key Engineering Materials 544 43-7
[3] Schmidt S, Beyer S, Knabe H, Immich H, Meistring R and Gessler A 2004 Acta Astronautica 55 409-420
[4] Guangde L, Yong L, Guoqiang Y and Xin M 2016 Ceramics International 42 12901-6
[5] Xin M, Haifeng H and Haipeng Q 2018 Rare Metal Materials and Engineering 47 58-61
[6] Weijie X and Mingwei C 2016 Journal of Synthetic Crystals 6 1534-8