Preparation of SiC\textsubscript{f}/SiC Composites with Low Porosity by Liquid Composite Moulding-Pyrolysis Process

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Abstract. Traditionally, Polymer infiltration and pyrolysis (PIP), chemical vapor infiltration (CVI) and melt infiltration (MI) are main processes to fabricate continuous silicon carbide fiber reinforced silicon carbide matrix (SiC\textsubscript{f}/SiC) composites, one of attractive potential high temperature structural materials. However, long preparation period and high porosity are still problems for further applications. Especially, porosity is crucial to the mechanical properties. Liquid composite moulding-pyrolysis (LCMP) used liquid SiC precursor to decrease the open porosity to 5\% with no more than 11 cycles of infiltration and pyrolysis. Mechanical properties like bending strength was investigated with different thickness of pyrolytic carbon (PyC) interface and pyrolysis cycles. The bending strength reached 585 MPa with 200 nm PyC interface under 1200\degree C pyrolysis temperature. Thus, LCMP process offers exciting opportunities to improve performance of SiC\textsubscript{f}/SiC composites.

1. Introduction
Continuous silicon carbide fiber reinforced silicon carbide matrix (SiC\textsubscript{f}/SiC) composites have been considered to be potential high temperature structural materials for fusion energy systems and advanced gas turbine engineering in aerospace vehicles\cite{1-5} because of their high strength, high modulus, pseudo-ductile fracture behavior, inherent low activation characteristics under severe environments and excellent thermal stability. PIP\cite{6-10}, comparing with other traditional methods including CVI \cite{11-15} and MI\cite{16-19}, has obvious advantages on fabricating complex shape products and controlling density. However, high porosity is still a critical problem to influence mechanical properties.

The final density of a ceramic matrix composites (CMC) is important to its behavior and properties, especially with regard to protecting the interface between fiber and matrix from oxygen attack and to produce a proper sharing of any applied load between the fibers and matrix. Distributed bulk porosity is obviously related to density of the material, since an increase in porosity will reduce the density of the material. So more and more researchers focus on decreasing porosity, one method is combining different methods, and another one is focusing on the precursor. Xie \textit{et al}. used nearly 18 cycles PIP process to get high density\cite{20}, Zhang \textit{et al}. combined CVI and PIP to solve the problems caused by using single method \cite{21}, high density SiC\textsubscript{f}/SiC composites were achieved by these methods, but high cost. Itoh \textit{et al}. from Mitsui Chemicals, compounded a transparent precursor, and the viscosity was 70 mPa\textsuperscript{s} \cite{22}. Kotani \textit{et al}. added SiC powders in the PVS precursor, fabricating SiC\textsubscript{f}/SiC composites

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with 400 MPa~600 MPa bending strength [23-24].Hu et al. synthesized a series of polycarbosilane precursor, which was suitable for fabricating composites, but too expensive [25]. All above, liquid precursor was attracted much researches to solve the porosity problem by LCMP process.

Since porosity were mainly from insufficient infiltration, volume contraction after high temperature pyrolysis and different thermal expansion coefficient between SiC fiber and matrix, Liquid SiC precursor can be used to decrease the porosity because of low viscosity and high ceramic yield. Thus, LCMP process added curing step to decrease the weight loss during pyrolysis, providing an effective method to improve mechanical properties.

2. Materials and Methods

2.1. Materials
Silicon carbide fiber was obtained from Fujian Torch Electron Technology Co., Ltd, which diameter was 13 micrometer and tensile strength was 280 MPa. The fiber was weaved to special size. Liquid SiC precursor was obtained from Institute of Chemistry Chinese Academy of Sciences, and its viscosity was nearly 50 cP at room temperature.

2.2. Preparation
The process of LCMP are divided into three parts: Firstly, using CVI to achieve a PyC interface on SiC fiber preform. Secondly, curing in the specific model after first precursor infiltration. Finally, recycling the pyrolysis and precursor infiltration to achieve densification.

2.3. Characterizations

2.3.1. Density and porosity test. Density and open porosity of SiCf/SiC composites were investigated by Archimedes methods, water was used to test the density and open porosity, final result was the average of three samples, the design formulas were shown in the following:

\[ \rho = \frac{m_1 \times \rho_1}{m_3 - m_2} \]  
\[ \theta = \frac{m_3 - m_1}{m_3 - m_2} \]

\( \rho_1 \) was the density of water under test condition, \( \rho \) was the volume density of SiCf/SiC composite, \( m_3 \) was a wet weight, \( m_2 \) was an immersed, hanging weight, \( m_1 \) was a dry weight and \( \theta \) represent open porosity.

Furthermore, close porosity was calculated by the following formula.

\[ \theta_c = 1 - \theta - \frac{\rho}{\rho_m} - \left(1 - \frac{\rho_f}{\rho_m}\right) \times \alpha_f \] 

\( \rho_f, \rho_m \) represent SiC fiber and SiC matrix respectively, \( \theta_c \) was close porosity of SiCf/SiC composite.
2.3.2. Mechanical properties test. Bending strength were measured by test machine C45.105 from MTS Co., Ltd, America at both room temperature and 1200°C. Samples with a rectangle shape (length was 36 mm, width was 4mm and thickness was 3 mm) were prepared for bending test.

2.3.3. Scanning Electron Microscopy (SEM). The microstructure was tested by S-4800 from HITACHI Co., Ltd, Japan. The thickness of PyC interface and the microstructure of bending strength were analyzed by SEM.

2.3.4. Thermo Gravimetric Analysis (TG). The ceramic yield was analysed by STA 449F3 from NETZSCH, Germany, the test atmosphere was Ar, with flow rate was 200 mL/min, and the heating rate was 10°C/min from room temperature to 1400°C.

![Figure 2](attachment:image.png)

Figure 2. TG graph of Liquid SiC precursor from room temperature to 1400°C.

![Figure 3](attachment:image.png)

Figure 3. Different states during LCMP process. (a) liquid precursor at room temperature, (b) curing state, (c) after pyrolysis.

3. Results and discussion

3.1. Ceramic yield of precursor

Figure 2 shows three weight loss stages during temperature increase. The first weight loss temperature was around 200°C, which mainly from volatilized small molecule polymer. The following stage caused by the reaction between Si-H and Si-C, releasing lots of CH₄ and H₂. The last weight loss stage was caused by gradually released H₂ and crystalline. However, the final ceramic yield was still above 70 wt%. High ceramic yield means less infiltration times, so fabricating period was shorten during LCMP process.
Furthermore, a typical pyrolysis process under 1200°C were tested by neat precursor, as shown in Figure 3. Liquid precursor was shown in Figure 3a, the precursor was yellow. The state after curing was shown in Figure 3b, which was just a little bubbles on the surface of curing sample. Figure 3c shows pyrolysis result, the shape was kept after curing, without any damage. The rough surface was caused by the gas produced during pyrolysis.

| Table 1. Results of several pyrolysis of neat liquid precursor. |
|---------------------------------------------------------------|
| Curing ratio (wt%) | Mass after pyrolysis (g) | Ceramic yield (%) |
|-------------------|--------------------------|-------------------|
| 1                 | 98.1                     | 24.044            | 81.8              |
| 2                 | 98.4                     | 4.661             | 80.3              |
| 3                 | 98.0                     | 5.810             | 82.1              |

Comparing results from Table 1 with Figure 1, ceramic yield reached to 80%, while curing ratio were more than 98 wt%, the reason was different heating rate. The heating rate during TG-DSC test was 10 °C /min, much faster than pyrolysis process, so the small molecule polymer volatilized much more before curing, leading to lower ceramic yield.

3.2. Interface

The thickness of PyC interface on perform were controlled by infiltration time and deposition rate. Interface was crucial to mechanical properties, not only because transfer stress from matrix to fiber, but also protect fiber from oxygen and other chemical damage[26]. An uniform PyC interface was fabricated shown in the Figure 4, analyzed by SEM. Figure 4a showed PyC interface around the fiber, while no defect shown in Figure 4b.

Figure 4. SEM graphs of PyC interface on a fiber under different times. (a) 5000×, (b)50000×.

Figure 5. Weight increse and volume fill with pyrolysis increase. (a) weight increase, (b) volume fill.
3.3. Densification

Figure 5 shows weight increase and volume fill during LCMP process. A fast weight increase before 3 cycles was shown in Figure 5a, the weight gain rate reached 40 wt%, which means nearly 20% volume was filled after first pyrolysis. The weight increase gradually and weight gain rate decrease, almost no change shown after 9 cycles of pyrolysis, because the porosity was nearly filled. Figure 5b shown the experimental values were always closed to the theoretical value, even caught up with theoretical value after 4 cycles. The reason was matrix shrink during pyrolysis.

Typical cycles from 8 to 11 were investigated to find the relationship between density, open porosity and bending strength at room temperature, as shown in Table 2. With increase of cycles, density gradually increased from 2.42 g/cm³ to 2.52 g/cm³, while open porosity decreased from 9.2% to 4.8%. Liquid precursor was infiltrated to the pores, but volume shrink caused new pores. High density composites were achieved by recycling in LCMP process to improve mechanical properties. Bending strength shown an increase with the density increase before 10 cycles, however, one more cycle cause a decrease from 600 MPa to 545 MPa. The decrease might be caught by modulus matching. After 11 cycles, SiC matrix was too rigid to transfer the stress from outside to the SiC fiber, directly broken happened in matrix instead.

Table 2. Open porosity changes with cycles increase.

| Pyrolysis temperature (°C) | Cycles | Weight gain rate (wt%) | Density (g/cm³) | Open porosity (%) | Bending strength (MPa) |
|----------------------------|--------|------------------------|-----------------|-------------------|-----------------------|
| 1200                       | 8      | 2.6%                   | 2.42            | 9.2               | 334                   |
|                            | 9      | 2.1%                   | 2.46            | 8.2               | 439                   |
|                            | 10     | 1.8%                   | 2.49            | 6.9               | 600                   |
|                            | 11     | 1.4%                   | 2.52            | 4.8               | 545                   |

Figure 6. SEM graphs of samples after bending strength test at room temperature. (a) 8 cycles, (b) 9 cycles, (c) 10 cycles, (d) 11 cycles.

Furthermore, the samples after bending strength were tested by SEM to find the destroyed mechanism. Figure 6 shows no obvious porosity in SiC/SiC composites after 8 cycles, which means LCMP process was efficient to dense. The damage behavior of SiC/SiC composites includes matrix cracking, interfacial debonding, fiber pulling out, fiber fracture and bundle splitting. Comparing with
Figure 6a, 6b, 6d, longer fiber pull out was shown in Figure 6c, which is consistent with the observation from Table 2. More matrix cracking and less fiber pull out, with little interfacial debonding during bending strength test was shown in Figure 6d, which means SiC matrix was too rigid.

3.4. High-temperature Properties
Porosity is often characterized as either open or closed, open porosity is connected to the outside of the part, while close porosity is trapped and closed off from the outside. Open porosity provides a direct path of the external environment to the interior of the CMC, which mainly influence the properties under high temperature. The bending strength of different PyC interface thickness were analyzed under 1200 °C. Samples with 7.2% open porosity decrease a lot from 585 MPa to 451MPa, because more oxygen react with PyC interface through open pores under high temperature. What’s more, the samples with 5.8% open porosity decrease a little.

For close porosity, it might play the role as crack point when the stress putting on. So the less close porosity, the higher bending strength at room temperature. The bending strength of sample with 7.6% close porosity was 585 MPa, while that sample with 9.8% was 547 MPa. Also the thickness of PyC interface between 100 nm to 200 nm seemed suitable for high properties.

Table 3. influence of different thickness of interface and porosity.

| Thickness of PyC interface (nm) | Density (g/cm³) | Open porosity (%) | Close porosity (%) | Bending strength at room temperature (MPa) | Bending strength under 1200 °C (MPa) |
|---------------------------------|-----------------|-------------------|-------------------|-----------------------------------------|-----------------------------------|
| 100                             | 2.54            | 5.8               | 8.6               | 573                                     | 550                               |
| 200                             | 2.53            | 7.2               | 7.6               | 585                                     | 451                               |
| 300                             | 2.5             | 5.9               | 9.8               | 547                                     | 503                               |

4. Conclusion
In conclusion, LCMP process provides an efficient way to get high density SiCf/SiC composites up to 2.54 g/cm³, while the open porosity decrease to less than 5%. Thus, the bending strength at room temperature reached to 585 MPa. During LCMP process, liquid precursor with low viscosity and high ceramic yield were crucial. The open porosity would decrease with the increase of infiltration and pyrolysis cycles, and the mechanical properties would be more excellent. However, modulus matching was also important, too many cycles would decrease the bending strength because the matrix was too grid. The open porosity provides paths for environmental ingress, adversely impacting the material behaviour. So with the advantages on densification, LCMP process has great potential to widespread use in the future.

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