STUDY ON THE INFILTRATION PROCESS AND MICROSTRUCTURE TRANSITION OF 2D C/C COMPOSITES

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Abstract

2D needle-punched fiber felt was infiltrated by a kind of rapid isothermal chemical vapor infiltration technique. The infiltration process and texture transition of the as-received C/C composites were investigated. The porosity and the variations of the cumulative pore volume were determined by a mercury porosimetry. The texture was observed under a polarized light microscope. The results show that the relative mass gain of the sample increases linearly with the infiltration time at the initial stage until 20h, and subsequently the increasing rate of the relative mass gain decreases gradually with the prolonging of infiltration time. Three layers of pyrocarbon were formed around fibers. Low-textured pyrocarbon was obtained at the initial stage. With the densification duration, high-textured pyrocarbon was formed on the surface of low-textured pyrocarbon. Low-textured pyrocarbon was produced again during the later densification. The texture transition is ascribed to the variation of the ratio of Cumulative inner surface area to volume of pores.

Keywords: C/C composites; ICVI; Pyrocarbon; Mercury porosimetry; Polarized light microscope.

Introduction

Isothermal chemical vapor infiltration (ICVI) is currently a major process for producing carbon/carbon (C/C) composites in the aerospace industry. But this process has been considered to be strongly diffusion-limited since it was developed in the 1960s, which results in a long densification period. To overcome this problem, some new techniques have been developed such as thermal gradient CVI, pulse CVI，forced flow thermal gradient CVI and film boiling CVI[. However, these techniques can not replace the ICVI process for mass production, especially for the preparation of brake disks for aircraft brakes. Therefore research on the ICVI, which is mainly focused on the improvement of infiltration rate and control of texture structure, has never been ceased in recent years. In our previous work, the conventional ICVI furnace was improved, which reduced the densification period of ICVI to 125h at ambient pressure using 2D needle-punched carbon felt as perform. It has been found that the texture of the pyrocarbon around fibers changes abruptly even if the infiltration temperature, the total pressure, the partial pressure, and the residence time keep constant. This special phenomenon was also reported by and. However, up to now, the reason for the abrupt change of the pyrocarbon texture has not been explained deeply.

The aim of the present investigation is to analyze the infiltration process and the reason of the

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texture transition of pyrocarbon around fibers detailedly. 2D needle-punched carbon felts were infiltrated by improved ICVI process at ambient pressure for different time. Methane was used as precursor. The infiltration temperature，the partial pressure of methane and the residence time of gases were kept constant. The relative mass gain, accumulated pores volume and the ratio of cumulative inner surface area to volume of pores (As/Vr) of as-obtained samples as a function of densification time were systematically investigated.

Experimental

Preparation of C/C composites

The preform used in the experiment was 2D needle-punched fiber felt, of which the volume fraction of carbon fibers was 28.7 % and the architecture was 00/900/00/900. The density of fibers was 1.72g/cm3. The pores are distributed inside fibers, among fiber bundles and among fiber layers as shown in Fig.1. The preform size was 60 mm(height)×45 mm(length)×11mm(thickness). Acording to the length of the felt, the infiltration depth amounts to 22.5mm. Natural gas was used as precursor with methane volume fraction of 98%. Using nitrogen as the diluent gas, an improved infiltration furnace consulting reference was applied to manufacture C/C composites by new technology. The chemical vapor infiltration of the preforms was performed in ambient pressure. The infiltration time was varied by 5h, 10h, 15h, 20h, 25h, 30h, 50h, 75h, 100h and 125h at a constant temperature, methane partial pressure and residence time. The samples were cut in accordance with Fig.2 for measurement.

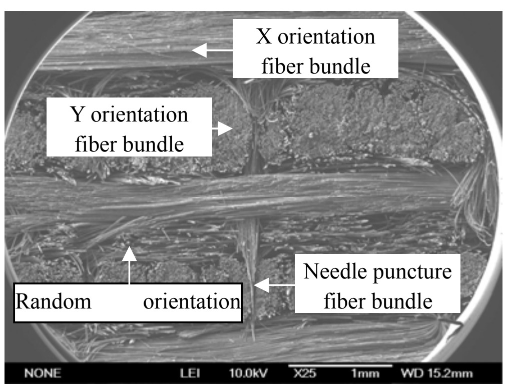
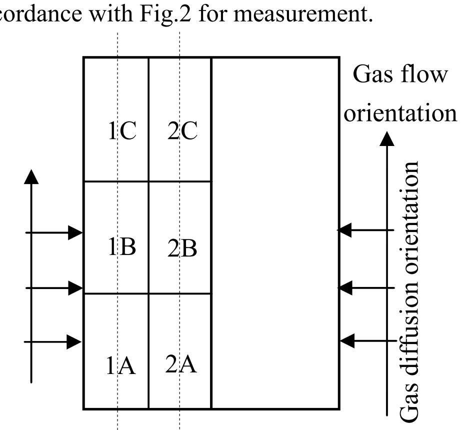


Fig. 1 The image of 2D needle-punched fiber felt



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Characterization of C/C Composites

A 9310 mercury porosimetry made in US was used to determine the porosity and cumulative pore volumes of the as-received samples 1B and 2B at different infiltration time. The As/Vr was calculated in accordance with the following formulas:

$$A_s/V_r = \frac{\textit{Cumulative pore surface area per gram}}{\textit{Cumulative pore volume area per gram}} \ldots\ldots\ldots \qquad (1)$$

The initial As/Vr of preform was calculated by the following formulas:

$$\left[A_s \big/ V_r \right] = 2\frac{1-P_0}{P_0}\cdot\frac{1}{r_0} \qquad (2)$$

where P0 is the porosity of preform and r0 is the initial radius of fibers, which was 4μm in our experimental.

The texture of the as-received samples 1A and 2C at different infiltration time was observed under a Leica DLM polarized light microscope.

Results and discussion

Study of infiltration process

Fig. 3 shows the relative mass gain of the preform vs. the infiltration time, from which the relative mass gain of the preform increases with the prolonging of the infiltration time. Additionally, the curve can be roughly divided into two stages. Before 20 hours, the relative mass gain of the preform increases linearly with the densification time. After 20 hours, the increase rate of the relative mass gain reduces gradually. Fig. 4 shows the open porosity as a function of the infiltration time. It can be seen that the porosity of the samples is also reduced with the prolonging of the infiltration time. However, the porosity in the initial stage of densification decreases rapidly while that decreases slowly in the final stage, which conforms to the relative mass gain trend of the preform. That the porosity of the sample 1B is slightly lower than that of the sample 2B proves further that there exists weak diffusion limited in the improved ICVI techniques. The correlation between the accumulated pore volumes and pore radius distribution of the samples 1B and 2B is shown in Fig 5. As the infiltration time increases from 5h to 125h, the accumulated pore volumes of the sample 1B and 2B both decrease gradually and their difference becomes smaller and smaller. During the end of densification, the accumulated pore volume of sample 2B is still higher than that of sample 1B (Fig.5(c)). The relationship between the bulk density of the samples and the infiltration time is shown in Fig. 6, and the bulk density distribution as a function of the distance from the center of preform is shown in Fig. 7. In the initial stage of densification, the bulk density increases with the infiltration time. Later, the increasing rate of bulk density is gradually reduced. After 100h, no apparent changes occur. From Fig.7, there is nearly no density difference between the inner region and the outer one in the initial stage of densification. However, with the proceeding of densification, the bulk density difference gradually increases, though the final bulk density difference of the samples between the inner region and outer one is only 0.05g/cm3 or so.

The CVI technique of C/C composites is extremely complicated. There exist the gas-phase reactions (homogeneous reactions) and gas-solid phase reactions (heterogeneous reactions) as well as the competition between them. If the gas-phase reaction is dominant, the diffusion limited will appear, which will lead to a long densification period. This disadvantage exists in traditional ICVI techniques. If the gas-solid reaction is dominant, the infiltration rate is rapid. In this study, an improved ICVI technique was adopted to infiltrate the 2D needle-punched fiber felt. By adjusting the gas flow volume, the shorter residence time of the gas in the reaction zone was obtained to control the pyrolysis reaction of precursor outside the preform. As a result, the densification period is much shorter than that of traditional ICVI techniques. In the initial stage of densification, the relative mass gain of the preform and the increase of the bulk density are in proportion with the infiltration time owing to the lower diffusion resistance of the flowing gases and the larger specific surface area of the preform. With the proceeding of densification, the volume of the porosity becomes smaller gradually as shown in Fig. 5, which results in the diffusion limited due to the narrower tunnel of diffusion as shown in Fig. 5.

Therefore, the increasing rates of the relative mass gain of the preform and the bulk density are declined gradually. By the end of densification, the gas diffusion tunnel becomes far smaller and the diffusion way becomes the Knusen diffusion such that the increasing rates of the relative mass gains of the preform and bulk density become far smaller. At this time, the crust of pyrocarbon will be formed on the surface of the perform, resulting in the further increasing of density difference between the inner region and the outer one, as shown in Fig. 7. Under such a condition, the bulk density of the sample in the inner region cannot be enhanced obviously even if the infiltration time prolongs continuously.

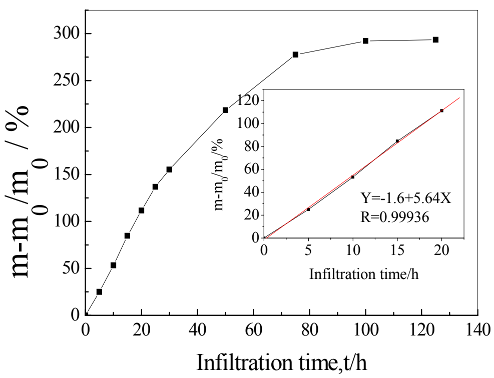


Figure 3. Relative mass gains of the preform as a function of the infiltration time .

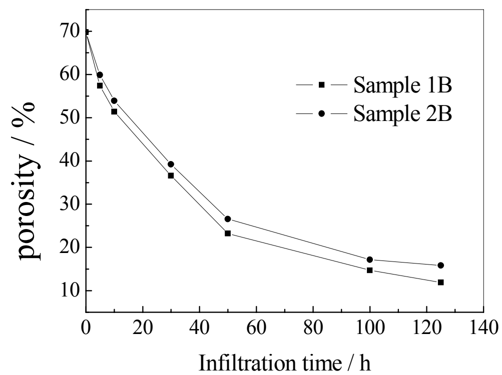
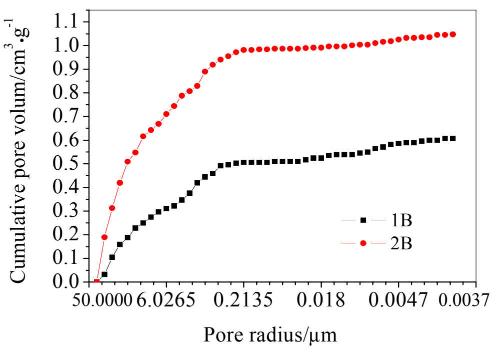


Figure 4. The open porosity as a function of the infiltration time.



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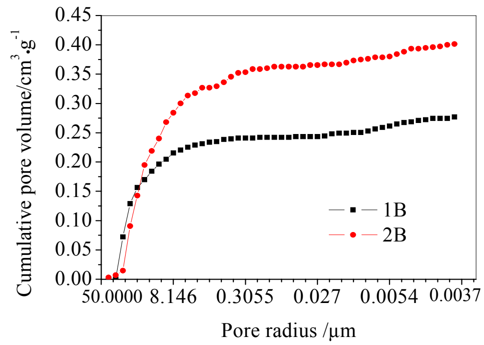

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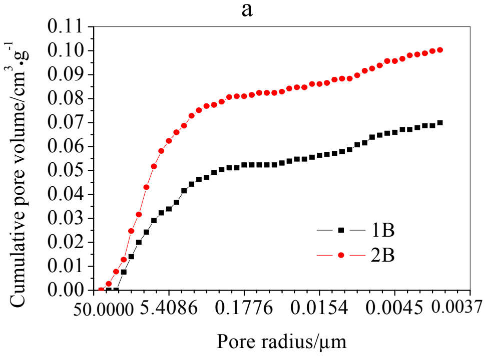

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Figure 5. Cumulative pore volumes as a function of the pore entrance radius of perform infiltrated.
(a) 5h, (b) 30h, (c) 125h.

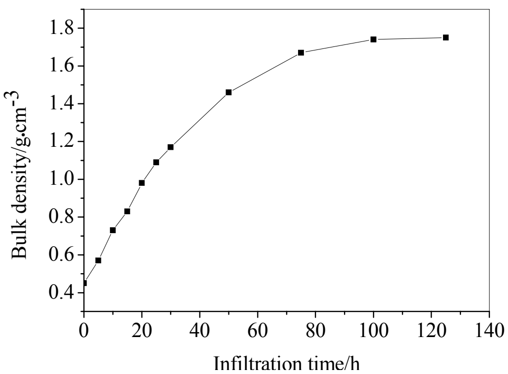

Figure 6. Bulk density as a function of infiltration time.

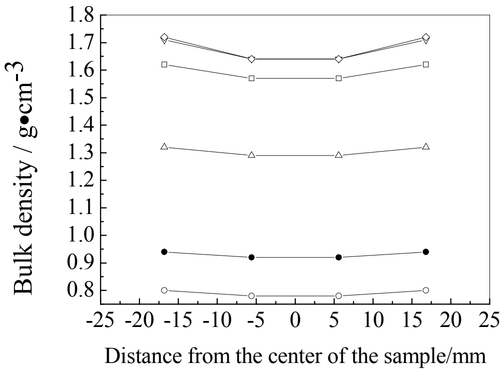

Figure 7. Bulk density as a function of the distance from the center of the samples infiltrated at different infiltration time.
○5h, ●10h, △50h, □75h, ▼100h, ◇125h

Texture

With respect to C/C composites, controlling their texture is as important as the rapid uniform densification because ideal structure endows these composites with good properties. Fig.8 shows the texture of the sample 1A after different densification time. In the initial densification (0-5h), a layer of low-textured (LT) is infiltrated on the fiber surface as shown in Fig. 8(a), in which no optical activities can be found under a polarized light microscope. The color of the matrix is almost the same as that of the fiber. When the infiltration time reaches 20h, a layer of high-textured (HT) as shown in Fig. 8(b) is formed that possesses representative characteristic of HT, for example high reflectivity and the irregular extinction cross under the polarization. Meanwhile, HT becomes thicker as the densification time proceeds. The pores have been filled by HT when the infiltration time is 75h as shown in Fig. 8(c). By the end of densification, a layer of LT has been produced on the HT surface among fiber bundles as shown in Fig. 8(d). From Fig.9, the pyrocarbon textures of the sample 2C are similar to those of the sample 1A after infiltration for the same time. During experiments, the infiltration temperature, the partial pressure of the precursor and the residence time of the gas remain constant. Thus, the variation of the texture is only attributed to the variation of As/Vr ratios. Consequently, the variation of As/Vr ratio as a function of densification time was investigated as shown in Fig. 10. The As/Vr ratio first increases apparently and then slightly decreases and increases again with the prolonging of the densification time. In the initial stage of densification, most of fibers are not joint with one another, so the total surface area of the pores increases and the volume decreases with the thickening of pyrocarbon on the fiber surface, leading to the increasing of As/Vr ratio obviously. As the densification time is about 20h, fibers inside the fiber bundles are connected by pyrocarbon, resulting in the reduction of the As/Vr ratio. After 25h, the pyrocarbon infiltration mainly takes place in larger pores among fiber bundles. Under such a condition, pores can be approximately regarded as hollow spheres. Then As/Vr is equal to 16/3R. Therefore, with the densification proceeding, the radius of the sphere becomes smaller gradually, resulting in the increasing of As/Vr ratio.

The As/Vr ratio controls the competition between the gas-phase pyrolysis reactions and gas-solid heterogeneous reactions. The larger As/Vr ratio means the smaller pore volume and the larger surface area, which is beneficial to the gas-solid heterogeneous reactions. On the contrary, the smaller As/Vr ratio signifies the smaller surface area and the larger pore volume, which is beneficial to the gas-phase reactions. According to the Particle-filler mode and G-T model， when the proportions of aromatic molecule Particle (such as benzene, anthracene, naphthalene and other aromatic molecules) and small linear molecule filler (acetylene as the major component) in a gas mixture reach an optimal value scope, HT texture pyrocarbon can be formed. Otherwise, the lower–textured (LT or MT) pyrocarbon will be formed for the excess of the amount of aromatic molecule or small linear molecule. The reason of the transition texture is to be discussed by combining the Particle-filler mode and As/Vr ratio variety as follows.

In the initial stage of densification, a layer of LT is first infiltrated on the fiber surface due to the lower As/Vr ratio of preform, which is in favor of the sufficient pyrolysis reaction in the gas phase. After 25h, the As/Vr ratio increases gradually. The pyrolysis reaction is restricted, which leads to the reduction of amount of aromatic molecules. At this time, the ratio of the larger aromatic molecules to the smaller linear molecules in the gases is in an optimum scope such that the HT is formed on the surface of LT as shown in Fig. 8b and Fig. 8c. In the later densification period, the pore radius becomes smaller and smaller and the pores inside the fiber bundles are nearly full of pyrocarbon. At this time, As/Vr ratio is far great, which is not in favor of the gas-phase reaction and the gas diffusion way is changed from Fick diffusion to Knusen one. The amount of gases that diffuse into the pores is much small and the surface area of the pores is still much large. Therefore, the gas-phase pyrolysis reaction of precusor in pores cannot take place sufficiently resulting in the excess of small linear molecules, so LT is formed on the surface of HT.

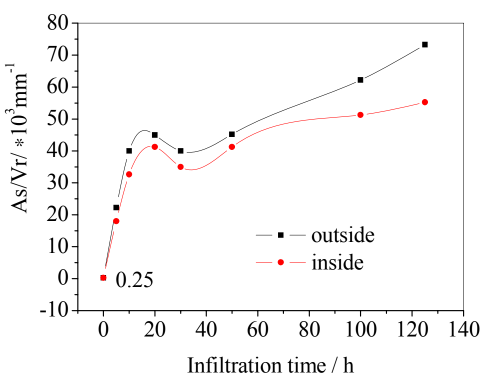

Fig. 10 The surface area/volume ratio as a function of the infiltration time determined for pore entrance diameter larger than 0.0037μm

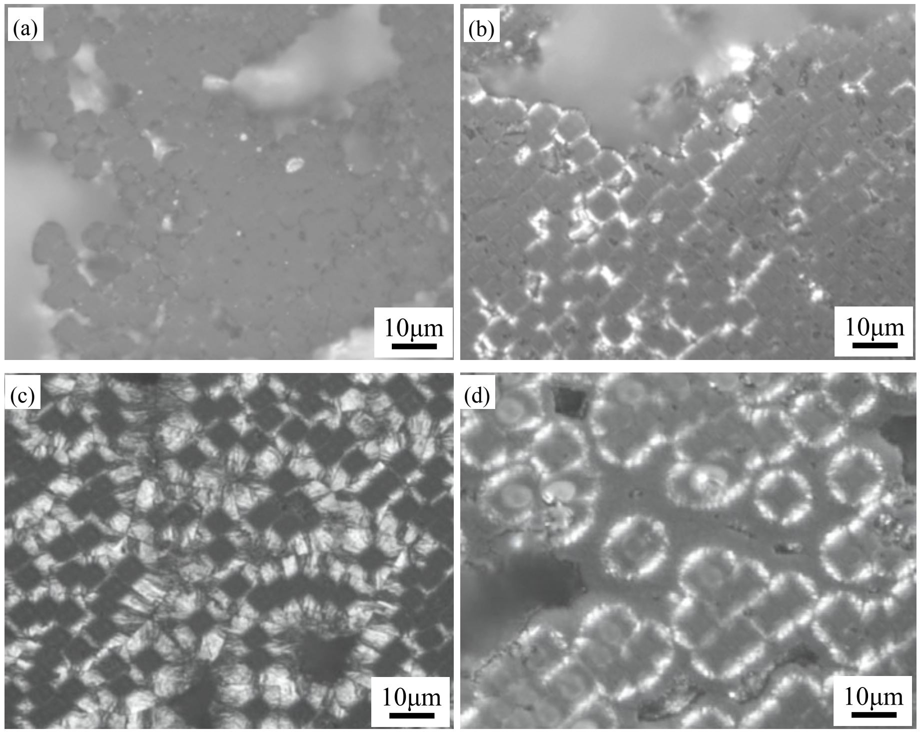

Fig. 8 The polarized light microscopy of resultant samples 1A.
The infiltration time of 5h(a), 20h(b), 75h(c) and 125h(d).

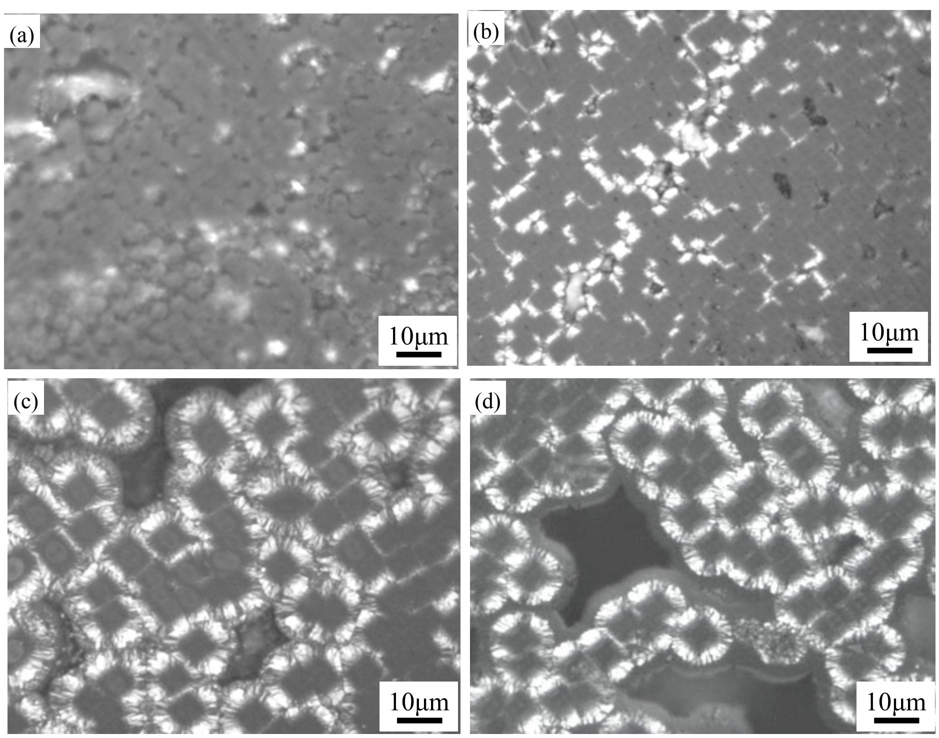

Fig. 9 The polarized light microscopy of resultant samples 2C.
The infiltration time of 5h(a), 20h(b), 75h(c) and 125h(d).

Conclusions

(1) In the initial stage of densification of C/C composites, the relative mass gain of the preform increases linearly with the densification time. As the densification proceeds, the increasing rate of the relative mass gain of the preform becomes slower and slower.

(2) The porosity and accumulated pore volume gradually reduces and the difference of the accumulate pore volume between the interior and the exterior of the sample gradually decreases as the densification proceeds.

(3) The As/Vr value first increases apparently and then decreases and increases again with the prolonging of the densification time. The transition of the texture around fiber is ascribed to the As/Vr variation of preform.

Acknowledgements

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