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Microstructure of carbon fiber preform and distribution of pyrolytic carbon by chemical vapor infiltration①

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Abstract: The carbon/carbon composites were made by chemical vapor infiltration(CVI) with needled felt preform. The distribution of the pyrolytic carbon in the carbon fiber preform was studied by polarized light microscope(PLM) and scanning electronic microscope(SEM). The experimental results indicate that the amount of pyrolytic carbon deposited on the surface of chopped carbon fiber is more than that on the surface of long carbon fiber. The reason is the different porosity between the layer of chopped carbon fiber and long carbon fiber. The carbon precursor gas which passes through the part of chopped carbon fibers decomposes and deposits on the surface of chopped carbon fiber. The pyrolytic carbon on the surface of long carbon fibers is produced by the carbon precursor gas diffusing from the chopped fiber and the Z-d fiber. Uniform pore distribution and porosity in preform are necessary for producing C/C composites with high properties.

Key words: carbon/carbon composites; chemical vapor infiltration; carbon fiber preform; porosity; pyrolytic carbon

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1 INTRODUCTION

Carbon/carbon(C/C) composites have been used in aerospace applications because of its low density, high strength, low thermal expansion, excellent tribological properties and capability of withstanding temperatures over 3 000 ℃ in many environments. For example, missile nose tips, solid rocket moter throats, rocket nozzles and aircraft brake disc[1, 2], are all made from C/C composites. The fabrication of C/C composites are completed by forming carbon matrix in the internal pores of a carbon fiber preform. There are two kinds of methods for producing C/C composites. One is the impregnation-carbonization[3], the other is the chemical vapor deposition (CVD)[4-6] or chemical vapor infiltration (CVI)[7]. The former is to impregnate the preform with liquid phase carbon precursor, such as resin, pitch, into the internal pores of carbon fiber preform, then, the impregnation carbon fiber perform is carbonized and graphitized. The latter is to introduce gas phase carbon precursor, such as methane, propane, propylene, and benzene from the inside to the outside of the preform, then the carbon precursor gas is decomposed and deposited on the surface of carbon fiber at high temperature. Therefore, all densification process relates to the flowing and deposition of carbon precursor in the preform. The pore distribution and the porosity in the preform will influences the flow property of carbon precursor, the properties of the deposited carbon and the final properties of the composites. At present, the studies in the field of C/C composites mainly focus on the densification technology and theory of CVI or CVD process, such as ISO-thermal gradient CVI[8], force flow-thermal gradient CVI[9-11], rapid direction diffused CVI[12], thermal gradient-pulse flow CVI[13] and pulse chemical infiltration[14]. However, very few studies deal with the influences of the pore distribution and porosity in the preform on the deposited carbon distribution. In the present study, the influences of the pore distribution and porosity of the preform on the deposited carbon by CVI are studied.

2 EXPERIMENTAL

2.1 Preparation of carbon fiber preform

The needled felt was utilized as carbon fiber preform to fabricate the aircraft brake disc in present study. The long carbon fiber is 12K-PAN based T700 from TOHO RAYON, Japan. The chopped carbon fiber is 12K-PAN based T700 from TORAY, Japan. The schematic diagram of needled felt is shown in Fig. 1.

In Fig. 1(a), part A is the chopped carbon fiber web, part B and C are long fibers in X and Y direction. The needled felt consisted of superposed ABAC layers repeatedly and needled fibers or Z-d

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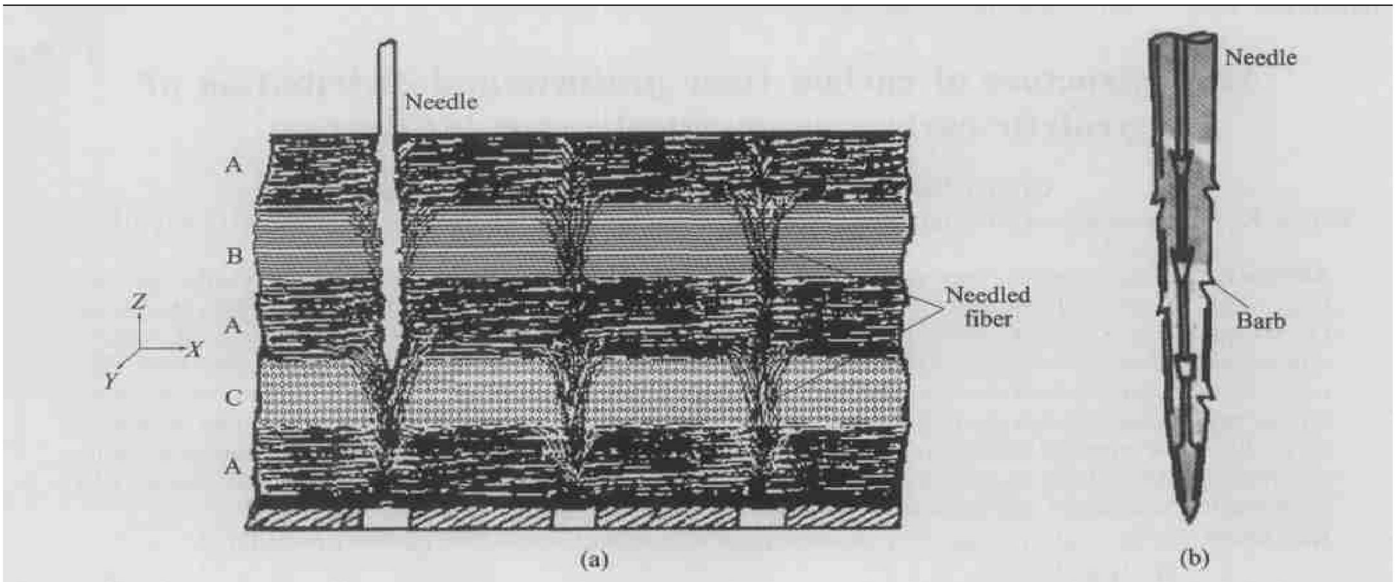

Fig. 1 Schematic diagrams of needled felt(a) and shape of needle(b)

fibers. Many needles penetrated perpendicularly into the superposed layers, when they moved down and passed through the layers of chopped carbon fibers firstly. The part of chopped carbon fibers were carried down into the layers of long fibers and the layer of chopped fibers. When the needles were up, the carried fibers were left as the needled fibers owing to the needle moving direction was in the same direction of their barbs as shown in Fig. 1(b). With the increase of needle density, more *Z*-direction fibers were penetrated into the felt and the frictional forces among the carbon fiber in all the layers become larger and larger. The carbon fiber felt was fabricated using a number of superposed layers connected by the friction between Z-d and other fibers (long or chopped fibers). Finally, the felt with a density of (0.6 ±0.03) g/cm^3 was cut in form of d146 mm/40 mm × 20 mm.

2.2 Chemical vapor phase densification process

The preform was densified by using the pressure-gradient CVI process. Propene was used as precursor and nitrogen as the carrier gas. The densification temperature ranged from 800 ℃ to 1 000 ℃ at low pressure. Finally, the density of C/C composites was up to 1.85 g/cm^3 after 4 cycles of CVI and machining. After high temperature treatment at 2 300 ℃ the C/C composites were made.

2.3 Determination of microstructure

After cutting and polishing, the growing of deposited carbon at different positions of the C/C composite samples were observed by metalloscope. The cross section and the properties of CVI deposited carbon were observed by SEM.

3 RESULTS AND DISCUSSION

The chemical vapor infiltration (CVI) process is that the carrier gas and hydrocarbon gas flow through the inside to the outside of the preform by pressure-force or other method. For a given condition, the hydrocarbon molecular collide the surface of carbon fiber and the carrier gas molecular, and decompose during flowing through the preform. The hydrogen atoms of hydrocarbon form hydrogen molecular and other gas molecular to eliminate. The carbon atoms deposit on the surface of carbon fiber in the form of solid phase so as to make the preform density increase and the porosity decrease. After 4 cycles of CVI and machining, the density of C/C composites is up to 1.8 g/cm^3.

The micrographs of C/C composites are shown in Fig. 2. Fig. 2(a) reveals the image in the adjacent part between the long and chopped fibers. Part A is the area of long carbon fibers, part B is the area of chopped fiber web. From this result, it can be seen that the deposited carbon between long and chopped fibers exhibits an obvious difference. The pyrocarbon deposited on the chopped fibers is more than that on the long fibers. But the deposited carbon on the surface of long fibers near the chopped fibers is more than that on internal fibers.

Fig. 2(b) reveals the image in the adjacent part between long, chopped, and *Z*-direction fibers. Part A and B are the parts of long and chopped fibers respectively. Part C is the Z-d fibers, part D is a pore. This picture still proves the above result. And the carbon deposited on the surface of Z-d fiber is the same as that on chopped fibers.

To observe the deposited carbon in different part in detail, the SEM observation was done. Fig. 3 shows the fracture surface of C/C composites. It is

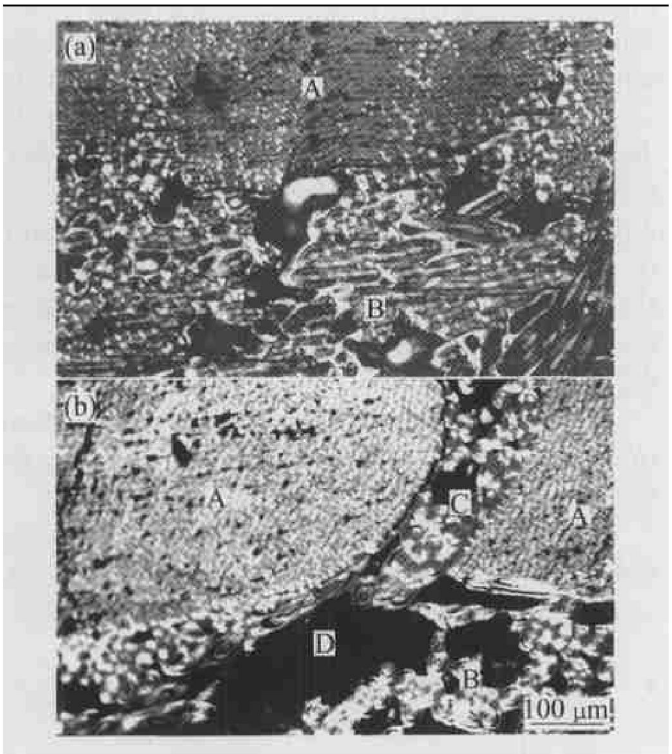

Fig. 2 Micrographs of C/C composites

revealed that the deposited carbon in different parts in the preform is not the same. The quantity of deposited carbon in chopped fibers is more than that in long fibers. The SEM results are the same as that of the optical microscope.

The long fibers(1-D) in the preform is stitched on the under chopped fiber layer by Z-d fibers. These fibers are in compact state, as shown in Fig. 4(a)[15]. The content of carbon fiber in 1-D state is higher and the content of porosity is lower than those in other state.

The content of carbon fiber is calculated according to the following equation:

$$V_{f\ \max} = \frac{\frac{\pi r^2}{2}}{2r\sin\frac{\pi}{3}} = 0.909$$

where r is the radius of carbon fiber; $V_{f\ \max}$ is the maximum content of the carbon fiber.

And, the content of porosity is calculated as

$1 - V_{f\ \max} = 1 - 0.909 = 0.091$

The fibers in chopped web are in the form of 3-D state, as shown in Fig. 4(b). The content of carbon fiber is calculated by

$$V_{f\ \max} = \frac{3\times\pi r^2\times 4r}{(4r)^3} = 0.589$$

And, the content of porosity is

$1 - V_{f\ \max} = 1 - 0.589 = 0.411$

From the calculation above, it can be seen that the porosity in the part of chopped fibers is 4.5 times than that in long fiber web.

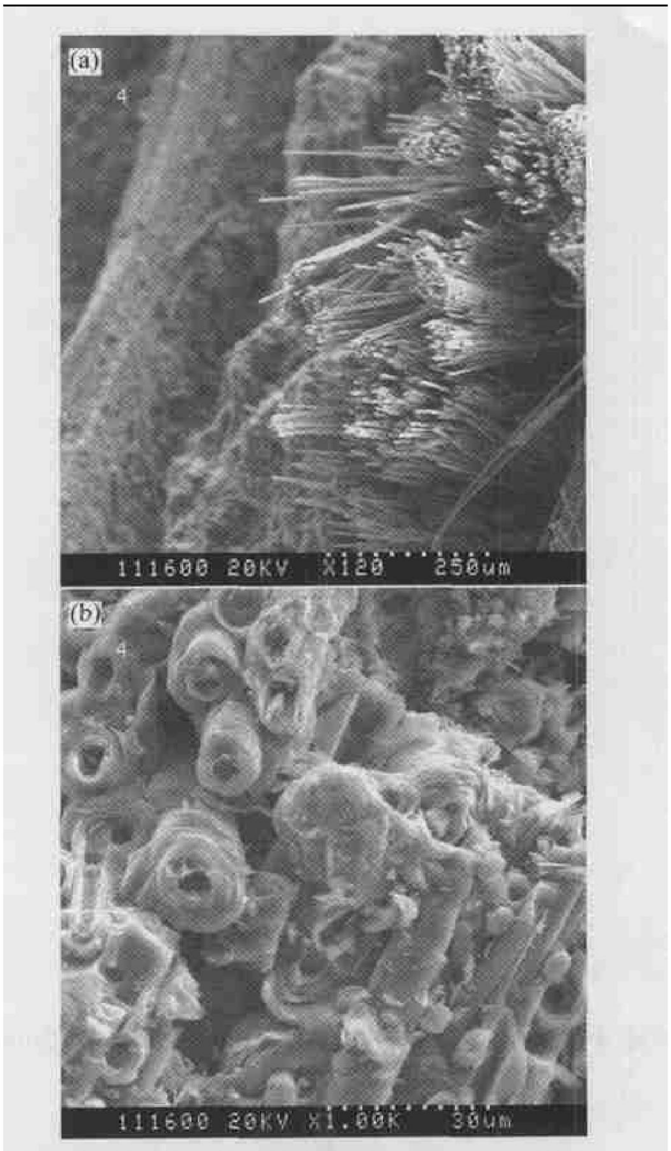

Fig. 3 SEM images of different part in preform
(a) —Long fibers; (b) —Chopped fibers

On the condition of low pressure in the furnace, the pressure in the annular outside of the preform is lower than that of inside, so a pressure gradient exists between inside and outside of the annular preform. The carbon precursor gas and carrier gas pass through the preform from inner to outer by the pressure force, as shown in Fig. 5.

At high temperature, when the gases of carbon precursor and carrier flow through the preform, they will firstly (or mainly) pass though the part which have high porosity and constantly collide with the carrier gases molecular and carbon fiber surface, the hydrogen atoms are eliminated and carbon atoms deposit on the carbon fiber surface. At the same time, the gases will diffuse into the long fiber layer. The quantity of gases flowing through the low porosity is not more.

Owing to the lower porosity of long carbon fiber web without Z-d fiber existing, the deposited carbon clogs and blocks out the gas passage by the

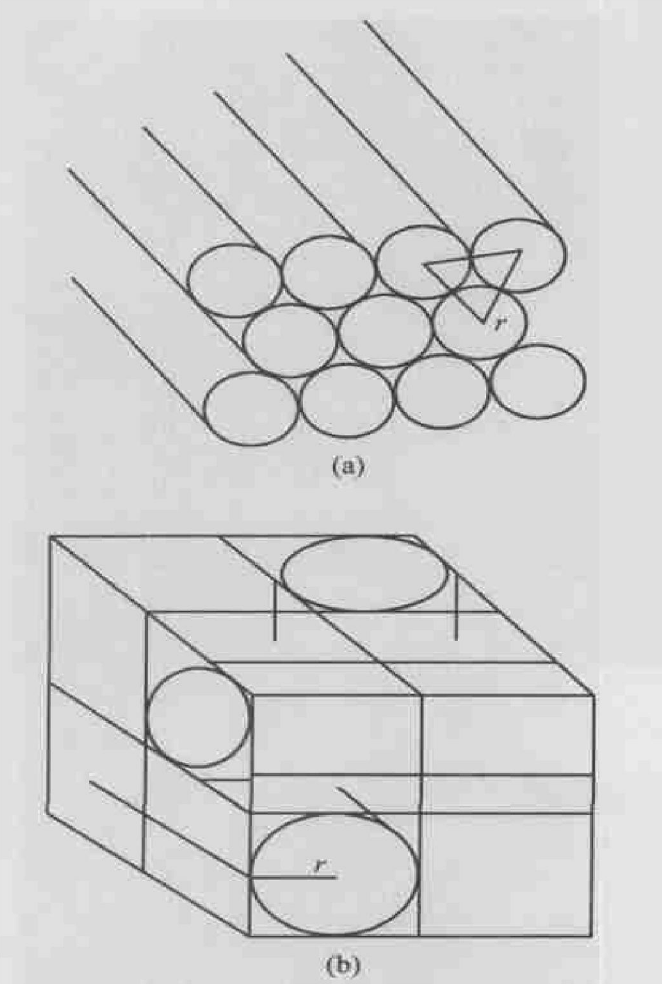

Fig. 4 1-D(a) and 3-D(b) carbon fiber distributing

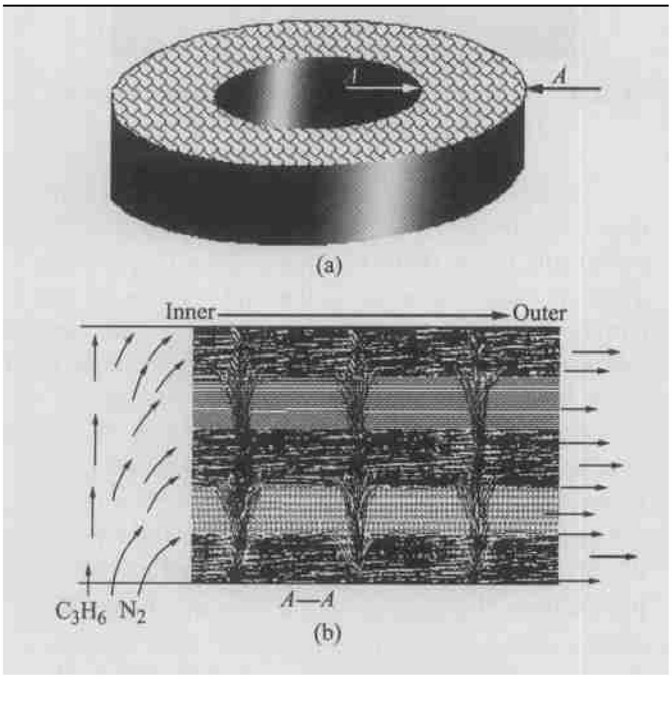

Fig. 5 Sketch of gases flowing through preform

bottle-neck effect, leading to the quantity of deposited carbon on the surface of long carbon fibers decreasing. If the bottle-neck effect occurs on the preform surface, the clog layer of deposited carbon can be cut off by machine, but if it occurs in the inner of preform, the effect cannot be eliminated.

From this result it can be concluded that the deposited pyrocarbon in the part of long fibers mainly comes from the decomposed gas which is diffused from the position of Z-d fibers. The density of needled fiber directly influences the flow of the gases. The higher the density of the preform is, the larger the influence of the Z-d fiber on the depositing process.

In addition, the larger pore in the preform cannot be eliminated by CVI process owing to the bottleneck effect(as shown in Fig. 2(b)).

Therefore, the preform with the uniform pore and porosity is necessary for making the high performance C/C composites.

4 CONCLUSIONS

The deposition of carbon in different parts of carbon fiber preform was investigated. The most of carbon precursor gases flow through the chopped fiber web with high porosity and continually deposit on the carbon fiber surface. The main source of deposited carbon in the long fiber is the decomposition of the gas, which diffuses from the Z-d fibers. The needling density directly influences the flow of gases. The higher the density of the preform, the larger the influence of the Z-d fiber on the deposited process. The preform with uniform pore and porosity is the precondition to make high performance C/C composites.

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