THE FABRICATION OF CARBON-CARBON BY A RAPID DENSIFICATION PROCESS —CHEMICAL LIQUID-VAPOR INFILTRATION

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Introduction

The two routes (liquid impregnation and CVD or CVI) for the preparation of C/C both require quiet long processing time to achieve high density desired; because of many cycles of the first method and very low deposition rate of the latter. These limitations add considerably to the cost of the components and limit the application of C/C materials. Although it is possible to reduce the processing time by employing thermal CVI[1]or FCVI[2], a new process, we call it rapid chemical liquid-vapor infiltration deposition(CLVD), is simple, much faster and allows rapid densification to obtained. This process is invented by Frances[3] and can overcome some limitations presented above. The main advantages of such technique include reducing the processing time significantly.

Here we report the results of the study on such rapid process using the experimental device which leads to C/C and the mechanism on rapid densification by CLVD.

Experimental

The cyclohexane(CYH) and kerosene(KEE) are chosen as matrix precursor due to their low cost. The carbon felt(0.12g/cm³) has been used in this work for the facility to cut desirable shaped samples and for its low cost and flexibility which allows easy handling. The preforms (carbon felt disks) ,each 160mm(od) × 80mm(id) × 10mm(thick),are placed around the heater mandrel which is connected to an electric power. Composites are prepared at the temperature range from 900°C to 1100°C in a water —cooled chamber within 3 hours. The heating apparatus in our study is constituted by radiation, the heating rate is controlled by adjusting the working electric current and voltage of electric power which supply 8.4~14.5KW. The temperature gradient(800-900°C) inside preforms is measured by several thermocouples placed along radial direction of preforms. The thermocouple closed to the outer border of preforms is employed identifying when the densification process is achieved.

The porous disks to be densified were immersed in liquid precursor which is heated at a temperature superior to the pyrolyzing temperature. When the temperature of the liquid precursor in contact with hot substrate (ie. the heater) and preforms reaches to boiling point, the liquid precursor vaporized violently, with increasing temperature, then begin cracking and the carbon deposit is produced first inside of the preforms, because of the thermal gradient existing within the preforms, in which the deposited zone move from inner to outer.

Results and mechanism of densification

Table 1 give the operating conditions and some properties such as bulk density and calculated porosity for the composites prepared by CLVD process. Preliminary densification runs show that deposition temperature above 940°C is found to be suitable for carbon deposition. The disk density was increased from 0.12g/cm³ to above 1.70 g/cm³ within 3 h using KEE, while using CYH as precursor ,from 0.12g/cm³ to 1.51g/cm³ just in 0.7h. Table 2 summarizes the rate of weight gain, deposition rate and moving rate of deposition front. In the case of KEE, the deposition rate and rate of weight gain are lower than that in the case of CYH. The highest carbon pick up rate is 0.72g/min , average value of each disk is 0.54g/min,the highest deposition rate on fiber surfaces is 64μm/h on process conditions. The microstructure of the deposited carbon under polarized-light microcopy is that rough-laminar and smooth carbon deposit exists at the same time in preforms. The microstructure of the different composites prepared using KEE as precursor is found very little difference from that of CYH as precursor, it appears that the microstructure of the deposited carbon do not depend on the nature of aliphatic hydrocarbon precursors.

We analyze the mechanism of the rapid densification based on the experiment. Compared with the classical process such as CVD or CVI, a great difference of new process lies in a direct contact existing between the substrate and the precursor. Furthermore, it appears that of the problem due to the diffusion of the reactive species is not the a limiting step because of the presence of the boiling liquid inside the preforms, in other words, fibers of carbon felt have been "surrounded" by the liquid due to the large porous or tunnel inside the felt full filled with precursor. The precursor concentration of the region closed to the fiber surfaces is so high that the rate of chemical reaction is very high, hence the rate of carbon deposited is quite rapid. On the other hand, because of the boiling and vaporizing liquid, in the high temperature region (closed to the heater), there exists a transitional zone which consists of a liquid boundary and a vapor boundary, between which the precursor concentration(C_T) is much lower than that

(C_L)of the zone outside of the liquid boundary, this leads to a great concentration gradient between liquid region and deposition region (transitional zone) which result in the rapid diffusion or infiltration of the liquid precursor from liquid carbon source zone to the transitional zone(deposition zone) through liquid boundary(see Figure 1). For all these reasons, a high diffusion flow in the liquid-vapor reactive medium is formed, which explain a fact that such deposition process is governed not by the diffusion of precursor but chemical reaction related to carbon deposition.

Furthermore, there is no surface crusting occurred in this rapid process attributed to the large temperature gradient and the high rate of the diffusion, which allows the depositing front moving from inner to outer of the preform steadily, at the same time the temperature gradient decreases until the whole preform is densified completely.

Conclusion

The novel process allows so fast a densification rate that reduces significantly the total densification time of porous C/C preform by less a factor of one percent compared to the classical process such as ICVI. C/C composites with the density as high as 1.74g/cm³ were obtained. The highest rate of weight gain and deposition rate of the fiber surface obtained in present work is respectively 0.72/g/min and 64µm/h, which is two order of magnitude faster than the typical value of 0.1~0.25µ m/h for the ICVI process. This approach allows the operating temperature a little lower than that in ICVI. Rough laminar and smooth deposited carbon microstructure were observed under crossed polarizers.

It is much faster than others because the chemical reaction on deposition take place in a liquid-vapor medium which produce a high diffusion flow that leads to the fact that the deposition process is governed by chemical reaction kinetics. Another reason is that the temperature gradient within the preform allows the deposition front continuously and rapidly moving from inner to the outer surface of preform, which means that no surface crusting occurred. Hence, the process avoids any machining of the composites to reopen porosity. However, the equipment for the new process is less complicated than that used in chemical vapor deposition or infiltration due to the gaseous precursor instead of liquid carbon source. These features are great industrial advantages.

References

[1] I.Goleck, R.C.Morris. Rapid densification of porous carbon-carbon composites by thermal - gradient CVI. App.Phys.Letter. 1995;66(5):2334-2336.
[2] J.S.Lewis, W.J.Jackey, S.Vaidyaraman. Model for prediction of Matrix Microstructure for C/C composites prepared by forced flow-thermal gradient CVI. Carbon 1997;35(1): 103-112.
[3] Michel Houdayer, Jean Spitz, Danh Tran-Van. Process for the densification of a porous structure, US patent 4472454, 1984.

Table 1. Operating conditions and properties of the densified composites

Run No.	Deposition time (h)	Deposition temperature °C	Bulk density (g/cm³)	Total porosity (%)
KEE				
K-9	2.75	>940	1.74	10.00
K-3	2.5	>970	1.71	11.16
K-7	1.5	>950	1.67	11.56
K-6	1.0	>920	1.34	31.55
CYH				
C-7	0.7	>980	1.48	26.00
C-8	0.7	>960	1.51	23.26
C-4	0.7	>940	1.44	27.68

Table 2. Efficiency of densification by CLVI process

Run No.	Rate of weight gain (g/min)	Deposition [a] rate (µm/h)	Densification [b] rate (mm/h)
K-9	0.54	49	23.74
K-3	0.50	46	24.04
K-7	0.45	41	16.37
K-6	0.47	44	21.97
C-7	0.64	56	25.34
C-8	0.72	64	19.63
C-4	0.52	53	25.09

a--moving rate of deposition front along radial direction of disk;
b—deposition rate on fiber surface.

$\Delta C = C_L - C_T >> 0$, $\Delta T = T_T - T_L >> 800°C$
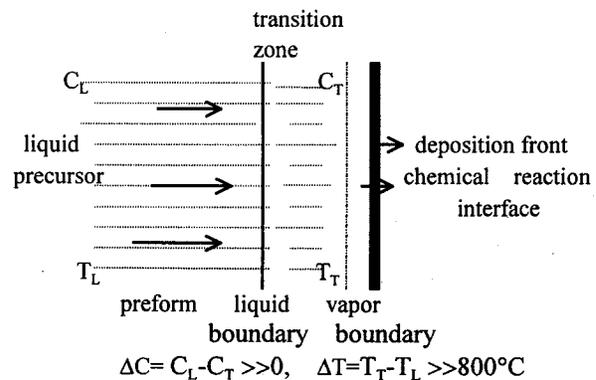
C_L-- the concentration of precursor outside of the preform,
C_T-- the concentration of precursor in transition zone,
ΔT-- the thermal gradient exiting in preform.

Fig.1   The formation of a high diffusion flows in liquid-vapor reactive medium during densification