



# Preparation of carbon/carbon composite by pyrolysis of ethanol and methane



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## ABSTRACT

A high textured carbon/carbon (C/C) composite was prepared using the mixture gas of ethanol and methane as the precursor by isothermal chemical vapor infiltration. The preform was infiltrated at 1180 °C with the gas pressure from 2 to 10 kPa. For 85 h infiltration, the average bulk density is up to  $1.8 \pm 0.02 \text{ g cm}^{-3}$ . The texture of the infiltrated carbon was studied by polarized-light microscopy and characterized with the aid of the extinction angle. Texture and fracture morphology of the pyrolytic carbon matrix were observed using scanning electronic microscope. C/C composites with high textured pyrolytic carbon matrix and high density were obtained by pyrolysis of ethanol and methane. This indicates the mixture of ethanol and methane is a promising candidate of the precursors for the preparation of C/C composites.

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## 1. Introduction

Carbon/carbon (C/C) composites have attracted particular attention in aeronautic and astronautic fields because of their wear resistance, ablation resistance, high thermal stability and excellent mechanical properties under high temperature [1–3]. Many researchers have reported that tribology and ablation characteristics of C/C composites are greatly related to the textures of the pyrolytic carbon matrix [4–7]. The textures of pyrolytic carbons were determined according to their optical activity and the extinction angle ( $A_e$ ) with polarized light microscopy (PLM) [8,9]. Textures of pyrolytic carbon can be defined as isotropic ( $A_e \leq 4^\circ$ ), low texture (LT,  $4^\circ \leq A_e < 12^\circ$ ), medium texture (MT,  $12^\circ \leq A_e < 18^\circ$ ) and high texture (HT,  $A_e \geq 18^\circ$ ) [10]. Generally, the HT pyrolytic carbon produced by isothermal chemical vapor infiltration (ICVI) is desired because it has good ablation resistance and excellent tribological properties [4–6]. Therefore, it is desired to obtain C/C composites with high textured pyrolytic carbon matrix.

As a renewable fuel, ethanol can contribute to energy and environmental protection [11]. It is expected to be a promising candidate of hydrocarbon precursors. Ethanol was used by Yan and Zhang to prepare C/C composites [12,13]. A homogeneous HT pyrolytic carbon was obtained in a wide temperature range of 1000–1200 °C with pressure range of 3–10 kPa. The density of the composites was  $1.67 \text{ g cm}^{-3}$  after 114 h. The temperature and

pressure range is larger than that of other hydrocarbon precursors (methane, propene, etc.). A larger range of technological parameter can decrease the production difficulty and increase the qualified rate. This implies that ethanol is superior to other precursors. However, ethanol has a high chemical activity when decomposed, corresponding to a high deposition rate of pyrolytic carbon at early stage of the chemical vapor infiltration (CVI) process. In addition, the higher molecular weight results in a lower diffusivity compared with methane. The high deposition rate and low diffusivity eventually lead to increase of the unfilled micropore in C/C composites.

A wide range of hydrocarbon precursors have been used to prepare C/C composites by CVI [14–18]. Methane is the most common one of all, which has the smallest molecular weight among all of hydrocarbons. This results in its high diffusion coefficient, which is favorable to the densification of C/C composites. Nevertheless, the high textured pyrolytic carbon can be only yielded in a small temperature and pressure range using methane as the precursor [16,17]. In addition, in mass production, it is difficult to keep uniformity and stabilization of the products in a large CVI furnace, which will decrease the production efficiency.

Above all, HT pyrolytic carbon can be made from ethanol in a wide range of temperature and pressure by CVI, but the density of the obtained composites is low. In addition, methane is favorable to the densification of C/C composites. To improve the preparation efficiency of C/C composites with HT pyrolytic carbon matrix, methane was introduced to ethanol. The mixture gas was used as the precursor of pyrolytic carbon. The preparation of C/C

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composites by ICVI using ethanol mixed with methane as the precursor was studied.

## 2. Experimental procedure

### 2.1. Material preparation

Preforms of the composites are polyacrylonitrile-based (PAN-based) two dimensional needle-punched integrated felt with dimensions of  $\Phi$  70 mm  $\times$  10 mm. They are made up of layers of 0° non-woven carbon fiber cloth, 90° non-woven carbon fiber cloth and short-cut mat layer after needle-punching in Z direction step by step. Initial relative porosity of the preforms is 75%. The PAN-based carbon fibers have a typical density of 1.76 g cm<sup>-3</sup>. The preforms were infiltrated by ICVI at 1180 °C.

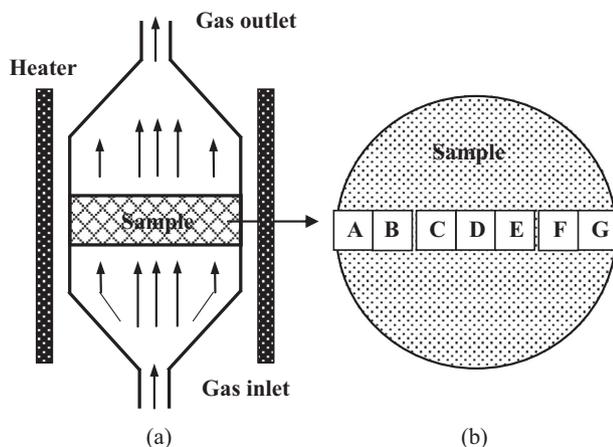
During the preparation process, the preforms were placed in a self-designed device (Fig. 1(a)). The deposition pressure was 2–10 kPa. Ethanol vapor carried by nitrogen were mixed with methane. The mixture gas was used as the precursor of pyrolytic carbon. Nitrogen was used as the carrier and diluent gas. Due to a pressure gradient between the top and bottom surface of the preform, the precursor would flow through it. Pure methane was used as the precursor at the same deposition conditions for comparison.

### 2.2. Characterization of C/C composites

Samples for measuring density were cut from the composites according to Fig. 1(b). The density of the samples was determined by the Archimedes principle. The textures of the pyrolytic carbon were observed by polarized light microscopy using a Leica DMLP microscope. Three-point bending test was carried out in accordance with Q/GB 95–92 [19] to characterize the mechanical properties of the composites. The test was carried out on a MTS CMT5304-1KN universal test machine. The force and position accuracy is  $\pm$ 0.5%. The loading head radius is 0.5 mm. Samples with dimensions of 55 mm  $\times$  10 mm  $\times$  4 mm were cut from the composites along the direction paralleled to the non-woven carbon fiber cloth. The span was 40 mm. The loading speed is 0.5 mm/min. Morphology of the fractured surface of the sample was observed using a ZEISS SUPRA 55 scanning electron microscope (SEM).

## 3. Results and discussion

The average density of the sample is  $1.8 \pm 0.02$  g cm<sup>-3</sup> after 85 h infiltration. The density is higher than that of the composites pre-



**Fig. 1.** Schematic of the infiltration device (a) and sampling positions for measuring density (b). (A)  $d = 30$  mm, (B)  $d = 17.5$  mm, (C)  $d = 5$  mm, (D)  $d = 0$  (E)  $d = 5$  mm, (F)  $d = 17.5$  mm, (G)  $d = 30$  mm,  $d$  is the distance away from the center.

pared from pure ethanol with more time cost (Table. 1) [12,13] and is close to that of the composites prepared from pure methane (Table. 1) [16,17]. As the addition of methane into pure ethanol precursor, the densification rate of C/C composites is improved. The methane plays an important role in the densification because it has higher diffusion coefficient [20] which favors the diffusion depth and infiltration depth. Compared with ethanol (larger molecular weight and lower diffusion coefficient), methane is favorable for the densification of the sample inside. As lower diffusion coefficient, ethanol is more unfavorable to fill the inside pore. In addition, relatively more close pores would yield. These factors affect the densification of the composites. The addition of methane in the ethanol precursor seems to be effective.

The internal density distribution curve was shown in Fig. 2. It can be seen that the density decrease gradually from center to edge. The density in the central position (position D) is  $1.85 \pm 0.02$  g cm<sup>-3</sup>, which is the highest among those in other positions. The density difference between the central position (position D) and outer position (position G) is  $0.14$  g cm<sup>-3</sup>, which is related to the flow distribution of the precursor. As shown in Fig. 1, the precursor gas flow into the infiltration device from the only middle hole. The gas residence time would not be homogeneous while passing through different sections of the sample. Most of the gas would pass around the middle region of the sample, leading to a shorter residence time. The opposite situation occurred at the outer positions. Longer residence time would bring larger molecule (aromatic hydrocarbons). This would be adverse to diffusion of the precursor. Thus, the outer position has the lowest density. Based on this mechanism, it is likely to reduce the density difference between central and outer position by reforming the infiltration device. However, the densification rate is higher than that of the processes with pure ethanol as the precursor.

Fig. 3 shows the PLM images of the composites. It can be shown that the pyrolytic carbons fill most of the pores between carbon fibers. Only a few relatively large pores are not completely filled. There are some cracks between pyrolytic carbon layers surrounding different carbon fibers (labeled by solid arrows in Fig. 3(a) and (b)). The cracks may be formed during cooling process as the thermal expansion coefficient of the pyrolytic carbon layer has certain orientation leading to a nonuniform contraction.

The images of position D is shown in Fig. 3(a). Fibers, pyrolytic carbon and pores can be clearly distinguished. The fibers display black as they are not sensitive to light, while the pyrolytic carbon has high optical activity and exhibits irregular and rough extinction crosses corresponding with the typical characteristics of HT pyrolytic carbon [8]. Compared to literature [12,13], optical characteristics of the pyrolytic carbon prepared from the mixture precursor are similar to those. The texture of the pyrolytic carbon is verified to be HT with  $A_e$  of  $22 \pm 0.5^\circ$  [8], while  $19.5^\circ$ – $20.5^\circ$  in literature [12,13]. Pyrolytic carbon in position G (Fig. 3(b)) has the same  $A_e$  to that in position D, which indicates that C/C composite with uniform HT pyrolytic carbon can be obtained from the mixture precursor. The addition of methane has almost no influence on the formation of high textured pyrolytic carbon. Based on particle-filler model [21], aromatic hydrocarbons are the molecular particles and small linear hydrocarbons, with ethine as the major

**Table 1**  
Time and final density of CVI with different precursor.

Precursor	Time (h)	Final density (g cm <sup>-3</sup> )
Ethanol + CH <sub>4</sub>	85	$1.80 \pm 0.02$
Ethanol	96	1.47
Ethanol	114	1.67
Methane	120	1.84 (max.)

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