

## Deposition of Pyrolytic Carbon using Ethanol as Precursor in Chemical Vapor Infiltration

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**Abstract:** Using ethanol as the precursor of pyrolytic carbon, chemical vapor infiltration of a carbon fiber felt with an initial bulk density of  $0.47\text{ g/cm}^3$  was performed at the temperature of  $1125^\circ\text{C}$  and the pressure of  $20\text{ kPa}$ , resulting in a bulk density of  $1.67\text{ g/cm}^3$  after densification of 114h. Extinction angles from  $19.5^\circ$  to  $20.5^\circ$  for various regions in the densified sample are determined, which correspond to a high-textured carbon, leading to flexure strength of  $137\text{ MPa}$ . Analysis of 2D texture distribution suggests that ethanol is a promising carbon source to synthesize carbon-carbon composites with homogeneously high-textured pyrolytic carbon.

**Key words:** carbon-carbon composites; ethanol; chemical vapor infiltration; pyrolytic carbon; microstructure

Chemical vapor infiltration (CVI) of pyrolytic carbon has been widely used for fabricating carbon-carbon composites. The precursors for the pyrolytic carbon in CVI process are mainly hydrocarbons, such as methane, propylene and cyclohexane, *etc*<sup>[1-3]</sup>. Other non-hydrocarbon precursors have not received proper attention. Being an environmentally friendly derivative of hydrocarbon, ethanol has been extensively used in the field of pyrolysis and combustion as an alternative of fossil-based fuels<sup>[4]</sup>. In addition, ethanol has also been used to produce carbon nanotubes *via* thermal pyrolysis<sup>[5]</sup>. Thus, it is worth to try ethanol as the precursor of pyrolytic carbon in the CVI of carbon-carbon composites.

## 1 Experimental

A disk carbon fiber felt with initial bulk density of  $0.47\text{ g/cm}^3$  and fiber volume fraction of 27.3% were used as preform. The disk felt was in the dimension of 67mm in diameter and 10mm in thickness. The deposition of pyrolytic carbon from ethanol was carried out using an isothermal forced-flow CVI reactor. The schematic of the reactor was shown in Fig. 1. During the infiltration processing, ethanol was evaporated, diluted and carried by  $\text{N}_2$  gas with flow rate of  $1.4\text{ L/min}$ . The deposition was operated at  $1125^\circ\text{C}$  under reduced pres-

sure of  $20\text{ kPa}$ . After densification for 114h, composite disks with bulk density of  $1.67\text{ g/cm}^3$  were obtained. Then the disks were cut to several small specimens for various characterization and tests. High temperature heat treatment (HTT) was performed at  $2500^\circ\text{C}$  for 1h to graphitize the deposited pyrolytic carbon. The crystal lattice parameters were determined using a X-ray diffractometer (PANalytical X'Pert Pro) with  $\text{CuK}\alpha$  radiation. The lattice spacing ( $d_{002}$ ) of the graphitized pyrolytic carbon were tested and calculated by Bragg's law to identify the texture of the pyrolytic carbon accurately. The graphitization degree ( $g$ ) of the heat-treated pyrolytic carbon was calculated using equation " $g(\%) = \frac{0.3440 - d_{002}}{0.3440 - 0.3354} \times 100\%$ "<sup>[6]</sup>.

Polarized-light microscopy (PLM) was employed to study the texture of the deposited pyrolytic carbon inside the carbon-carbon composites. The flexural strength of the composites was evaluated by three-point bending test using a universal testing machine (Instron 1195, England). The loading span in the bending test was 40mm in width, and the sample size was  $55\text{ mm} \times 10\text{ mm} \times 4\text{ mm}$ . After testing, scanning electron microscope (SEM, JSM-6700F) was used to observe the morphology of the fractured surface.

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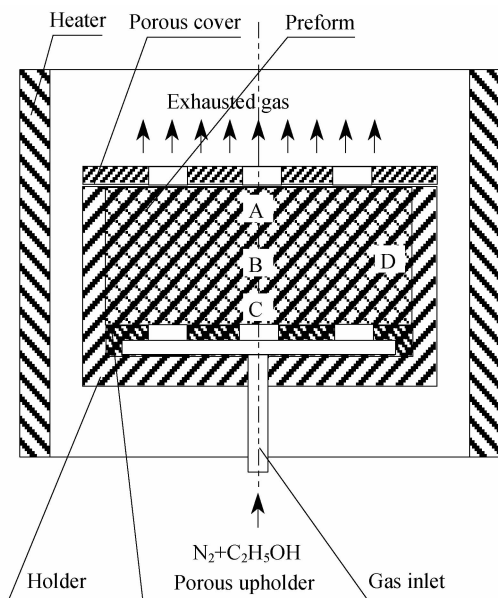


Fig. 1 Schematic diagram of the infiltration reactor  
A, B, C, D was marked for the region analyzed with PLM

## 2 Results and discussion

Figure 2 shows the increase of the density of carbon-carbon composites with the infiltration time. The

density of carbon-carbon composites increases from  $0.47\text{ g/cm}^3$  to  $1.67\text{ g/cm}^3$  within 114h. After the pyrolytic carbon deposits inside the pores, there is less space left for the subsequent deposition, and the mass transport of ethanol vapor to the center part of the sample becomes more difficult which also lead to the decrease of the densification rate. Thus, the densification rate declines gradually with the increase of the deposition time.

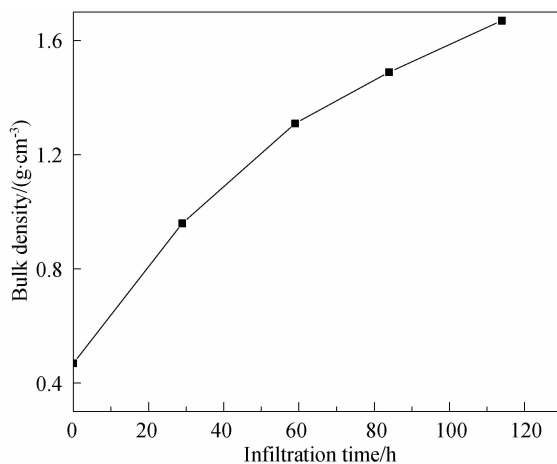


Fig. 2 Increase of density of carbon-carbon composites with the infiltration time

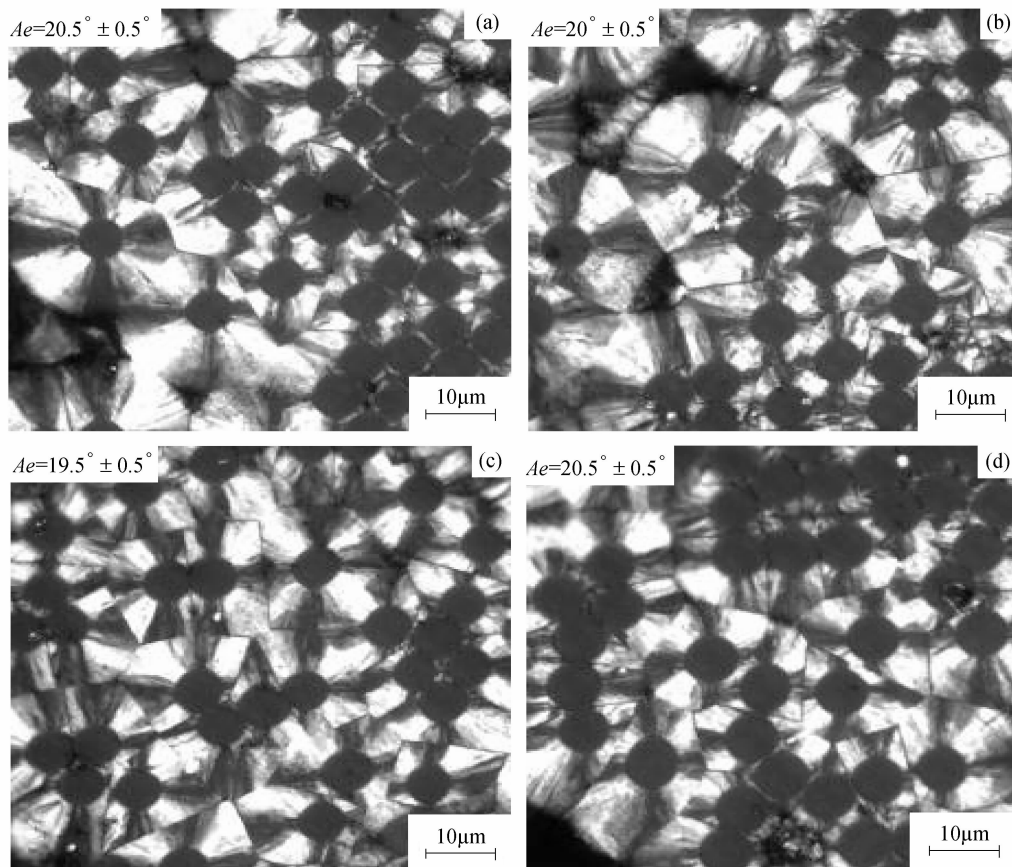


Fig. 3 Polarized-light micrographs in the different regions of carbon-carbon composite disk  
(a), (b), (c) and (d) correspond to A, B, C, and D regions in Fig. 1, respectively

The textures of the deposited pyrolytic carbon can be identified by PLM, as shown in Fig. 3. The four micrographs correspond to the pyrolytic carbon deposited at different positions in Fig. 1. It is clear that fibers at all regions are surrounded by concentric pyrolytic carbon exhibiting irregular extinction crosses and strong optical reflectance under polarized light. The extinction angle ( $A_e$ ) in the texture structures can be measured as  $(20.5^\circ \pm 0.5^\circ)$ ,  $(20^\circ \pm 0.5^\circ)$ ,  $(19.5^\circ \pm 0.5^\circ)$  and  $(20.5^\circ \pm 0.5^\circ)$  at different positions, corresponding to the high textured pyrolytic carbon<sup>[7]</sup>. As is well known, due to the complexity of mass transport and chemical reactions inside the carbon fiber preforms during the deposition, the texture of pyrolytic carbon in carbon-carbon composites are normally the mixture of high texture, medium texture and low texture structure<sup>[8]</sup>. It is difficult to form homogeneous high-textured pyrolytic carbon in CVI of carbon-carbon composites. Therefore, it is really interesting that the pyrolytic carbon matrices deposited from ethanol are all high textured inside the carbon-carbon composites, which is an obvious advantage for their mechanical and frictional properties<sup>[9]</sup>.

The X-ray diffraction patterns of the deposited and the HTT specimens are shown in Fig. 4. The lattice spacing  $d_{002}$  for the pyrolytic carbon deposited in center of the sample is calculated to be 0.3452nm. After high temperature heat-treatment, this specimen exhibits a graphite-like  $d_{002}$  of 0.3362nm, corresponding to the typical value of the high-textured pyrolytic carbon. The graphitization degree ( $g$ ) of the HTT pyrolytic carbon calculated is 90.7%, indicating good graphitization character of the deposited pyrolytic carbon.

Carbon fiber felts lay out a nearly homogeneous three-dimensional structure and thus are ideally suitable

for investigating CVI processes<sup>[1]</sup>. But its fiber volume fraction of 27.3% is too low to offer satisfied flexural strength. However, with ethanol precursor, the obtained carbon-carbon composite specimens still have a high flexural strength of 137MPa in the three-point bending test, which benefits from the structure of high-textured pyrolytic carbon in the composites. Figure 5 gives the SEM morphology of the fracture surface after bending test. Figure 5 (a) indicates that carbon fibers are surrounded by layered pyrolytic carbon matrix. The enlarged micro-graph in Fig. 5 (b) demonstrates that the carbon matrix consists of thick and regular graphite-like layers without apparent cracks, which is also a key feature of the high-textured pyrolytic carbon<sup>[10]</sup>.

3 Conclusion

High-textured pyrolytic carbon matrix was successfully fabricated by using ethanol as precursor. For industrial application of carbon-carbon composites, high-

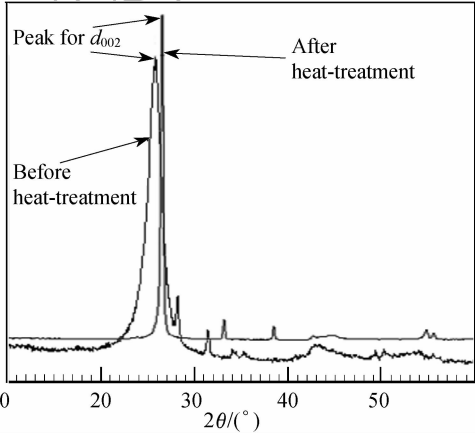


Fig. 4 XRD patterns diffraction of the deposited and the HTT specimens

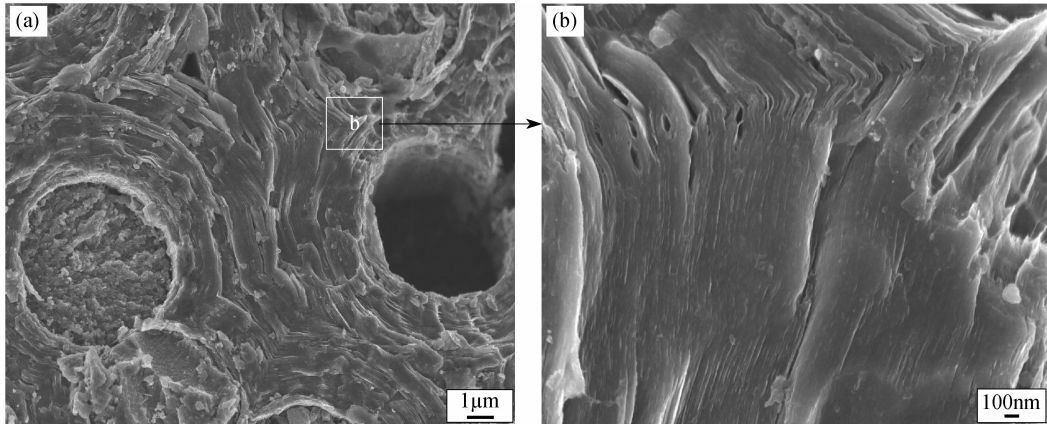


Fig. 5 SEM morphologies of the fracture surface after bending test  
(a) Low magnification; (b) High magnification

textured carbon matrices are normally favourable for the consideration of friction coefficient, anti-ablation and mechanical properties. Consequently, this modification in CVI process shows good potential to improve the performance of carbon-carbon composites.

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## 乙醇热解制备炭/炭复合材料工艺探索及组织特征

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**摘要:** 以密度  $0.47\text{g/cm}^3$  的碳毡为预制体, 乙醇为前驱体, 氮气为载气, 在  $1125^\circ\text{C}$ , 压力为  $20\text{kPa}$  的条件下, 用等温压力梯度化学气相渗透法, 经 114h 致密化, 制备出密度为  $1.67\text{g/cm}^3$  的炭/炭复合材料. 经测试, 材料的弯曲强度为  $137\text{MPa}$ . 偏光显微分析显示: 该材料各区域沉积的基体热解碳组织结构均为高织构, 其消光角为  $19.5^\circ \sim 20.5^\circ$ , 石墨化处理后测得热解碳的  $d_{002}$  为  $0.3362\text{nm}$ . 断口扫描电子显微分析结果也进一步证实获得的热解碳组织为高织构. 表明乙醇是一种极具潜力的制备炭/炭复合材料的前驱体.

**关键词:** 炭/炭复合材料; 乙醇; 化学气相渗透; 热解碳; 组织结构

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