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Effect of oxygen and hydrogen on microstructure of pyrolytic carbon deposited from thermal decomposition of methane and ethanol

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ABSTRACT

Chemical vapor infiltration (CVI) is the most extensive industrial preparation of carbon/carbon (C/C) composites. Precursor affects the CVI process considerably. In the present study, using carbon fiber bundles as preforms, methane and ethanol as precursors, the C/C composites were densified by decomposition of various gases in CVI. The thickness and texture of deposited pyrolytic carbon (PyC) were characterized by polarized light microscopy (PLM). The microstructure of PyC was analyzed by Raman spectroscopy. The morphologies of PyC were characterized by scanning electron microscopy (SEM). The composition of PyC was detected by X-ray photoelectron spectroscopy (XPS). Adding hydrogen in methane precursor resulted in a sharp decrease in the deposition rate and texture of PyC. Mixture of methane and ethanol as the precursor improved the deposition rate and texture remarkably. Besides, O element in ethanol was not remained as a constitution of PyC, and it was removed before the formation of PyC.

1. Introduction

Carbon/carbon (C/C) composites have been widely used for their excellent performance [1–3]. In recent years, various methods have been developed to control the synthesis of C/C materials, including some catalytic reactions [4,5]. However, chemical vapor infiltration (CVI) is still the most commonly used process for industrial production of C/C composites. It has the characteristics of no damage to fibers, high purity of carbon matrix, simple process equipment and the ability to simultaneously densify a number of complex shaped preforms. However, due to quite a lot of factors and the pretty fast reaction rate at high temperature, the deposition process is extremely complex [6–9]. Similarly, the properties of C/C composites obtained by different precursors also have large difference.

From the point of view of microstructure, C/C composites prepared by CVI process usually have four typical textures under polarizing microscope: high texture (HT), medium texture (MT), low texture (LT) and isotropic carbon (ISO) [10]. Among them, HT has a small ablation rate, low friction, wear rate and other good mechanical properties at high temperature for meeting the industrial needs [11]. Therefore, for the densification process of C/C composites, it is the main approach of previous research to obtain high textured PyC by controlling process parameters. Up to now, it has not yet been completely achieved controlling of PyC texture. Although the high texture can be obtained, the variation range of process parameters is narrow and difficult to control [12]. Widening the range and reducing the difficulty of controlling parameters have become the main problems to be solved.

It was found that adding ethanol in the precursor can be conductive to control the deposition process [13]. Pyrolysis reaction of ethanol was preliminary explored, and then using ethanol as a precursor obtained PyC with high texture completely [14]. It was found that ethanol had no corrosive effect on carbon fibers and matrix, which shown its great potential as a precursor in CVI process [15]. At present, the effects of adding ethanol precursor on the microstructure of PyC have not been studied, which will be demonstrated in the present study.

Becker et al. [16] reported that addition of hydrogen decreased the deposition rate evidently and inhibited the pyrolysis reaction. Besides, a hydrogen inhibition model of carbon deposition was proposed [17]. Xiong et al. [18,19] found that the addition of hydrogen in CVI process was beneficial to obtain HT carbon and uniform density distribution. Therefore, the effect of hydrogen on the CVI process needed to be further verified. Compared to hydrogen which is a typical reductive gas, the oxygen in ethanol should improve oxidability of the hydrocarbon precursor. In the present study, the microstructure of PyC under oxidizing and reducing gases atmosphere was observed. Finally, the reaction mechanisms were analyzed.

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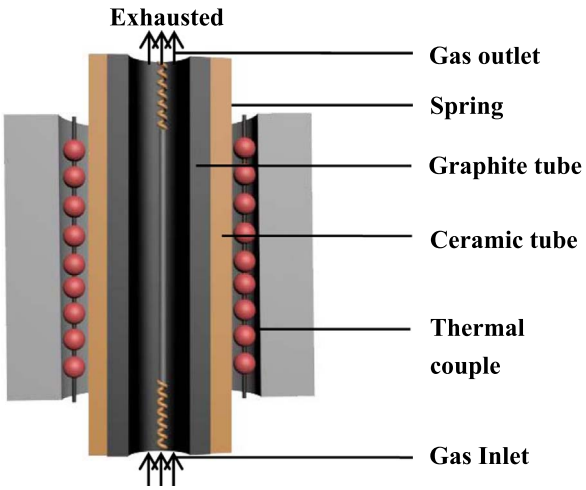

Fig. 1. Schematic diagram of the deposition reactor and graphite mold.

2. Experimental procedures

2.1. Chemical vapor infiltration

A scheme of the infiltration reactor is presented in Fig. 1. To achieve better control of gas flow and residence time, 24 K bundles of carbon fibers (Toray T700SC) were densified within a graphite tube holder with an inner diameter of 18 mm. In this paper, the PyC was deposited in a temperature of 1150 °C from gases mixture. Among them, methane (CH_4) and ethanol (C_2H_5OH) were used as precursors, as well as hydrogen (H_2) was used as additive gas. In addition, nitrogen (N_2) was used as carrier gas. The purity of methane, hydrogen, nitrogen was 99.999%. The ethanol steam was obtained by gasification of absolute ethanol (AR), and its purity was 99.7%. The infiltration and residence time were 20 h and 0.07 s, respectively. Under maintaining the partial pressure of C atom in the initial deposition gases, the following experimental schemes were designed, as shown in Table 1. The experimental procedure is: firstly, both ends of the carbon fiber bundles were tensioned and fixed to the center of the graphite mold by a spring, as also shown in Fig. 1. Then the fiber bundles were infiltrated at 1150 °C and 7 kPa. The infiltrated carbon fiber bundles were removed from the reactor, and the densified parts of bundles were cut into several small pieces along the axis of bundles to determine texture and average deposition rate.

2.2. Structural characterizations

The microstructure of PyC was studied with polarized-light microscopy (PLM, Leica DMLP). To detect a micro-zone of the structure of PyC in C/C composites, Raman spectroscopy analyses with Ar ion laser were used, and the laser wavelength was 514 nm. The surface morphology of C/C composites was observed by scanning electron microscopy (SEM, JMS-6460) operated at 20 kV. X-ray photoelectron spectroscopy (XPS, Kratos, Manchester) using an Al monochromatized source was employed to detected the elemental composition of PyC.

Table 1
Experimental scheme for different reaction gases in CVI process of C/C composites.

Experimental number	Temperature/°C	The composition of reaction gases	Infiltration time/h	Residence time/s
S1	1150	CH_4	20	0.07
S2		CH_4+H_2		
S3		$CH_4+C_2H_5OH$		
S4		C_2H_5OH		

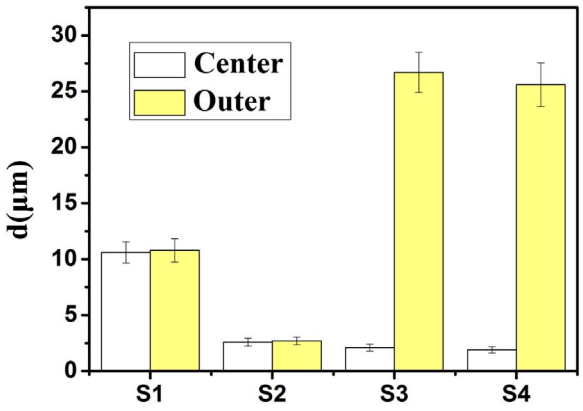

Fig. 2. Deposition thickness of PyC of carbon fiber bundle. The reaction gases of S1-S4 are: CH_4; CH_4+H_2; $CH_4+C_2H_5OH$; C_2H_5OH.

3. Results and discussion

3.1. The thickness of PyC

The deposition rate is characterized using the ratio of the deposited carbon layer thickness and deposition time obtained by the final deposition of carbon fiber bundles. The thickness of deposited carbon layers from sample S1–S4 of carbon fiber bundle is shown in Fig. 2.

Comparing S1 with S2, the deposition thickness of PyC reduces suddenly with hydrogen addition. Therefore, the precursor which possesses hydrogen has a higher deposition rate of PyC. The sharp decrease in the thickness of PyC could be attributed to the addition of hydrogen inhibiting the formation of PyC. For gas-gas homogeneous reactions at high temperature, hydrogen cracks to generate hydrogen atoms reacting with almost all the hydrocarbon gas molecules with high reactivity [20]. Among them, the main reactions are as follows (Eqs. (1) and (2)):

$$H\cdot + R\text{-}H \rightarrow R\cdot + H_2 \quad (1)$$

$$H\cdot + C_nH_{2n} \rightarrow C_nH_{2n+1} \quad (2)$$

The addition of hydrogen to the precursor increases the hydrogen concentration in the gas phase, thus affecting the dehydrogenation of hydrocarbon molecules, which reduces the number of free radicals in the intermediate product. It is not conducive to the condensation reaction between hydrocarbon free radicals and hydrocarbon molecules, thereby affecting the formation of aromatic hydrocarbons in the gas phase. For gas-solid heterogeneous reactions, hydrogen atoms can be chemically adsorbed at the active site of the aromatic carbon plane to form a C-H bond. As the fracture energy of C-H bond is high, it will hinder the formation of new active sites, thus affecting the production rate of PyC [14]. Therefore, with the reaction progress producing hydrogen, the addition of hydrogen in the reactor will make the total content of hydrogen increase in the reactor. The deposition of PyC based on the chemical absorption in the active sites is increasingly difficult.

Because of the large polarity of hydroxyl in ethanol, the electron cloud is biased to O atom and weakens the C-H bond strength, which indicates that ethanol has stronger activity than other hydrocarbon with two C atoms. Therefore, ethanol has a higher deposition rate. In addition, the thickness of PyC using pure methane as precursor is distinct with adding ethanol into precursor. Compared with S1 and S2, PyC thickness of S3 and S4 deposited on the carbon fibers is relatively thicker. It should be pointed out that when the ethanol is added to the precursor, there is a significant difference in the thickness of PyC both inside and outside the carbon fiber bundles. The PyC thickness of outer carbon fibers of S3 is 15 times thicker than that of inner carbon fibers, which can be ascribed to the phenomenon of “sealing hole” if ethanol