Letter to the Editor

Isotropic pyrocarbon deposited at 1250 °C by means of thermal gradient chemical vapor deposition

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ABSTRACT

Isotropic pyrocarbon was fabricated at 1250 °C via thermal gradient chemical vapor deposition. The density of the deposit was measured using Archimedes methods and the microstructure was examined by polarized light microscope and scanning electron microscope. The results showed that the density of the deposit was about 1.85 g/cm^3 and it was constituted of spherical pyrocarbon grains which was about 0.6–0.8 μm in diameter and compacted densely and there are some microcracks in the deposit.

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1. Introduction

Pyrocarbon is a quasi-crystalline carbonaceous material which is deposited on hot substrate by pyrolysis of hydrocarbons, such as methane, ethylene, ethane, and benzene [1] and has been widely used as rocket nose cones and nozzles, matrices of carbon fiber composite materials and biomaterials, etc. [2,3].

According to the difference of microstructure, pyrocarbon could be distinguished into two kinds: anisotropic and isotropic pyrocarbon. So far, isotropic pyrocarbon has been successfully applied into nuclear energy field as coating materials. In BISO-coated fuel particles, porous isotropic pyrocarbon layer is used to coat the fuel particles to store the fission product gases and protect the dense isotropic pyrocarbon layer against the damage of fission recoil nuclei. Dense isotropic pyrocarbon layer acts as a pressure vessel to prevent the dispersion of fission product gases as well as a barrier to hinder the migration of other fission products [4–6].

At present, fluidized bed chemical vapor deposition is always employed to fabricate isotropic pyrocarbon layers. But compared with fluidized bed chemical vapor deposition, the deposition rate of pyrocarbon in thermal gradient chemical vapor deposition is more rapid. And fuel particles could be made into required shape rather than in fluidized state [7]. However, rare attempts are made to prepare isotropic pyrocarbon via gradient thermal chemical vapor deposition. Thereby preparing for further research of depositing pyrocarbon on fuel particles, isotropic pyrocarbon is deposited on graphite substrate at high temperature by gradient thermal chemical vapor deposition.

2. Experiment

2.1. Deposition parameters

Deposition was carried out in a thermal gradient CVD apparatus and natural gas was used as carbon source (the ingredients of natural gas are as following: 98% CH_4, 0.3% C_3H_8, 0.3% C_4H_{10}, 0.4% other hydrocarbons, and 1% N_2). The diagram of the thermal gradient CVD apparatus could be seen in [8] and the substrate was a 600 (height) × 100 (width) × 20 (thickness) mm high strength graphite plate which was wrapped by several layers of graphite paper. The flow rate of natural gas was 0.5 m^3/h at temperature rise period and the depositing temperature was 1250 °C, the depositing time 60 h, and natural gas flow rate 2.5 m^3/h.

2.2. Structure observation

The microstructure of the deposit was observed on Leica DMLP polarized light optical microscope after coarse grinding, fine grinding and polishing with diamond paste. The fracture surface of the deposit was examined on a Supra 55 scanning electron microscope (SEM).

3. Results and discussion

3.1. Optical microstructure

The optical microstructure of the deposit is shown in Fig. 1. Fig. 1(A) and (A') correspond to the deposits under normal and polarized light, respectively. Under normal light, the microstructure of the deposit is homogeneous and pyrocarbon crystallites compact densely. However, there are porosities and microcracks

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inside. Under polarized light, the deposit is composed of two kinds of components: regenerative pyrocarbon which possesses apparent growth feature and isotropic pyrocarbon which does not have optical activity. The crystallites size of regenerative pyrocarbon decreases gradually along the deposition direction.

3.2. Fracture surface

Fig. 2 is the micrograph of the fracture surface of the deposit. Fig. 2(B), (C) and (D) correspond to the magnifications of the rectangle area in Fig. 2(A), (B) and (C), respectively. From Fig. 2(A), it could be seen that laminar pyrocarbon which is shaped in pebble in its surface view deposits onto the substrate. Then, there is a progressive transition of the microstructure of pyrocarbon from laminar to grain along the deposition direction (White arrow shown in Fig. 2(A)). In Fig. 2(B), the grain size decreases gradually until it reaches a stable size. Fig. 2(C) is the magnification of the fine grains in Fig. 2(B). It could be seen that the isotropic pyrocarbon is consti-

tuted of spherical shape grains. The size of the grains is about 0.6–0.8 µm and there are porosities among the aggregated spherical grains in Fig. 2(D).

3.3. Density

The thickness of the deposit is about 3 mm and the density at various positions is measured using Archimedes methods in ethanol and the result is shown in Fig. 3. The density of the deposit is high (more than 1.85 g/cm^3) and the fluctuation is small.

3.4. Discussion

In this experiment, the residence time of precursor gas was very long, about 110 s (τ_s estimated $= V_r/Q_0(T/T_0)(P/P_0)$, Q_0 is the flow rate of the precursor gas under T_0, P_0), which effected the microstructure of the deposit greatly. When natural gas entered into thermal gradient chemical vapor deposition apparatus, methane
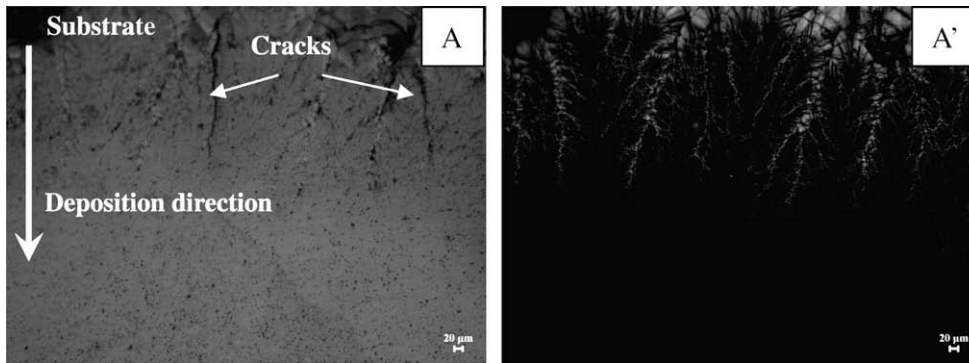

Fig. 1. (A) and (A') are the optical microstructure of the deposit under normal and polarized light. White arrow shows the deposition direction.
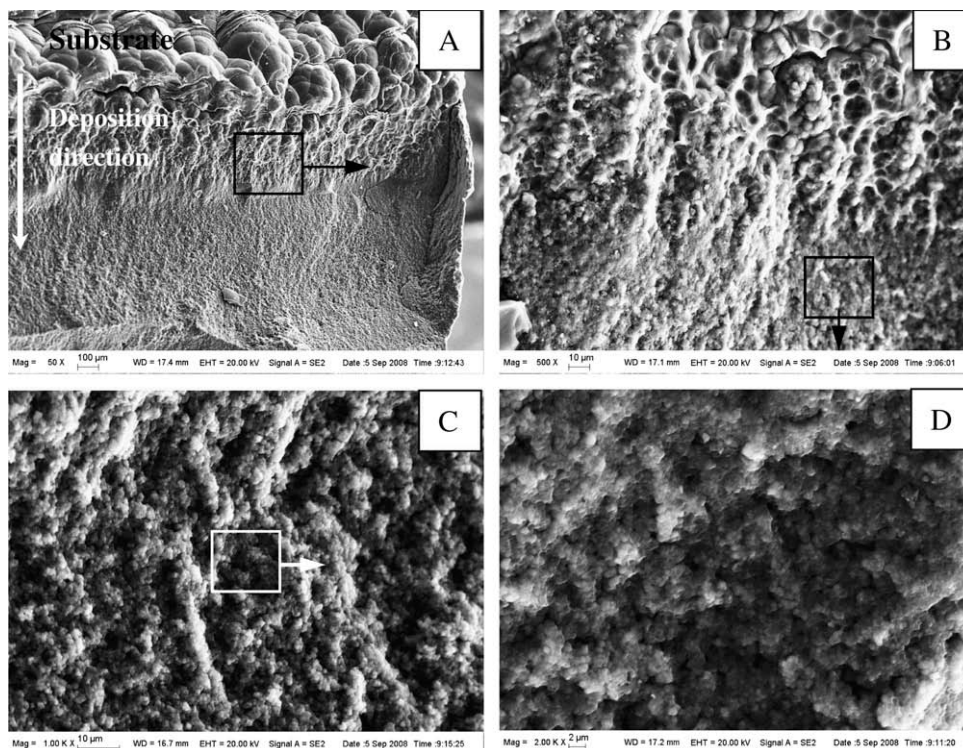

Fig. 2. The SEM micrograph of fracture surface of the deposit. (A) is the micrograph of the area next to the substrate; (B), (C), (D) are the magnifications of the rectangle area in (A), (B), (C), respectively.
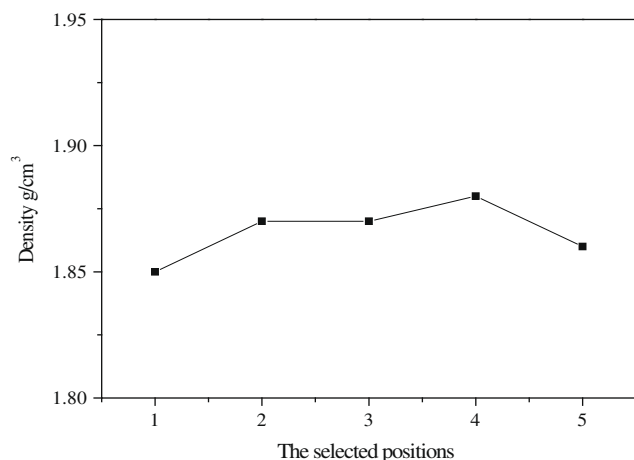
Fig. 3. The density of the deposit at various positions.

as its main component began to undergo complex reactions [2,9–14]. In homogeneous reactions, methane was pyrolysed and methyl radicals were formed fast because of high temperature. A series of free radical reactions resulted of C2 hydrocarbon species [10,11] and different cyclization processes occurred, aliphatic compounds and aromatic species were formed [14]. Cyclization processes were mainly C3 and C4 routs and HACA (hydrogen abstraction and C_2H_2 addition) mechanism.

Surface reactions, which were the fundamentals for the formation of pyrocarbon, were presented as nucleation and growth processes. At the initial stage of surface reactions, the light, aromatic and polyaromatic hydrocarbon species deposited onto the substrate and formed laminar pyrocarbon because of the catalytic influence of the substrate surface. As the thickness of the deposit increased, the catalytic influence of substrate surface was extinguished gradually and the formation rate trended to be stable. The catalytic influence of the substrate surface on microstructure of the deposit could be seen clearly in Figs. 1(A), 2(A) and (B). Aromatic species (benzene, naphthaline, etc.), as the main isotropic pyrocarbon forming species, were mainly formed in homogeneous gas reactions. Homogeneous nucleation of aromatic hydrocarbon species in free volume was favored because of the long residence time, low As/V_R-ratio (about 0.003 cm^{-1}), high temperature and high pressure and the radius of the nucleus of pyrocarbon decreased with increasing temperature, so the particles resulted from the homogeneous nucleation of aromatic hydrocarbon species,

were small and taken into spherical shape. They deposited onto the laminar pyrocarbon by drag force and dehydrogenated and solidified. The size of the particles was so small and the content of hydrogen was so low that it nearly did not have any fluidity, therefore they formed spherical isotropic pyrocarbon (Fig. 2(C) and (D)) and the following growth process largen them. The spherical isotropic grains were almost in the same dimension (about 0.6–0.8 μm) and compacted densely (Fig. 2(D)), that was the reason why the density was so high (more than 1.85 g/cm^3). These results were in accordance with the particle depositing mechanism of pyrocarbon proposed by Lee [15]. It was also proved that fabricating isotropic pyrocarbon by thermal gradient chemical deposition was probable. But the microstructure was deteriorated when the thickness of the deposit was more than 4 mm and there were also cracks in the deposit.

4. Conclusion

Isotropic pyrocarbon has been prepared by thermal gradient chemical deposition furnace at ambient pressure. The density of the deposit is 1.85 g/cm^3 and isotropic pyrocarbon is constituted of spherical grains, which is about 0.6–0.8 μm in diameter and compact densely. This provides a new method to deposit dense isotropic pyrocarbon onto fuel particles for high temperature gas-cooled reactors.

Acknowledgement

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