The microstructure of isotropic pyrocarbon obtained by isothermal chemical vapor deposition

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Introduction

Isotropic pyrocarbon, deposited onto a hot substrate via pyrolysis of hydrocarbon species in chemical vapor deposition apparatus (CVD), has been widely applied in heart valves and nuclear fuel particles coating [1-3]. Some preparation methods, such as fluidized bed CVD and tumbling bed CVD, have been applied to manufacture isotropic pyrocarbon. But the substrate in fluidized bed chemical vapor deposition is constantly moving in the reaction tube, so the deposition condition is totally different (Close the inlet, the residence time and temperature is short and low). The reaction tube in tumbling bed chemical vapor deposition was rotated by a variable motor and the substrate was moved and tumbled with the rotating of reaction tube, so the residence time was hard to determine and gas flow pattern was greatly influenced.

Compared with fluidized bed and tumbling bed CVD, the substrate and reactor tube in our experiment are both stationary. The residence time, the gas flow pattern could be determined easily. As long as proper gas inlet pipe, gas distributor and reactor tube are schemed out, isotropic pyrocarbon could deposited steadily. In this paper, we investigated the deposition of pyrolytic carbon at 1200℃ in hot wall reactor.

Experiments

The hot wall chemical vapor deposition reactor was made from a 180mm long graphite tube with 62mm outer diameter and52mm inner diameter. The diagram of the reactor is shown in Fig.1. The deposition substrate, a 2mm thick graphite plate (60mm×40mm), was cleaned by ethanol in ultrasonic cleaning machine and was placed on a support pillar fixed in the reactor. The deposition temperature was 1200℃ and natural gas acting as precursor gas is pumped in and outflow from the bottom and top of the reactor and its volume flow rate was 0.10m^3/h, 0.15 m^3/h and 0.20 m^3/h.

The density of the pyrocarbon was measured using the Archimedes methods in ethanol. The morphology and microstructure of pyrocarbon was observed by scanning electron microscopy (SEM, JOEL JSM-6460) and transmission electron microscopy (TEM, JEM-3010). Texture was examined quantitatively by measuring the orientation angle resulted from azimuthal intensity scans of selected area electron diffraction patterns (SAED) via the method proposed by Bourrat et al [4]. Raman analysis was carried out by single spot (about 1μm) measurements, using a 50× objective lens

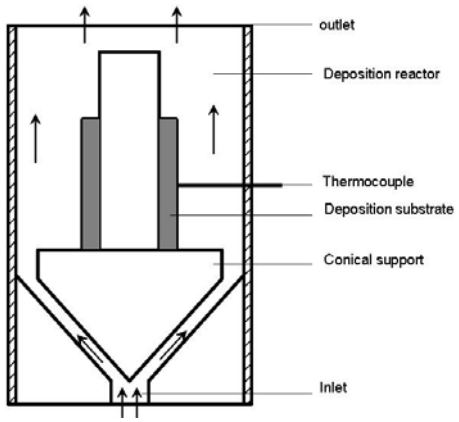

Fig.1 The diagram of the deposition apparatus and reactor chamber

Results and Discussion

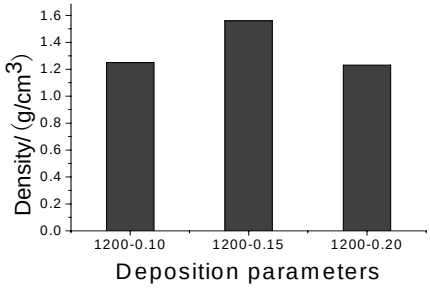

Fig.2 The density of the products obtained at different deposition parameters

It could be seen from Fig.2 that the density of the products increase first and then decrease as the gas flow rate increase. As the gas flow rate increases, the residence time of the reactant decrease and the concentration of aromatic hydrocarbon species decrease. The ratio between aromatic and linear hydrocarbon species increases gradually [5]. When the gas flow rate is 0.15 m^3/h, the ratio is in proper range and the density of the product is high (1.56g/cm^3).

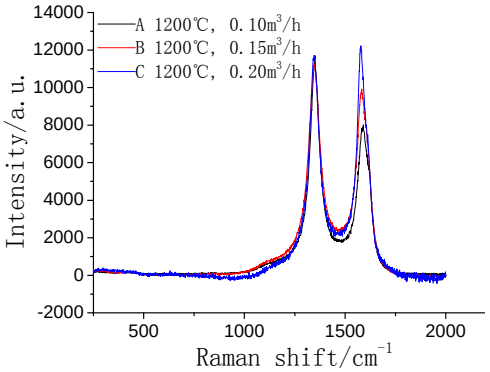

Fig.3 The Raman spectra of the products: A: 1200℃, 0.10m^3/h; B: 1200℃, 0.15m^3/h; C: 120℃0, 0.20m^3/h

Fig.3 shows that the intensities of G band in Raman spectra increase with the increasing of gas flow rate. However, the intensities of the products are almost at the same level. With the increasing in gas flow rate, the concentration of aromatic (linear) hydrocarbon species decreases (increases), the flaws contained in graphene layers decreasing lead to the intensity of the G bands increase gradually.

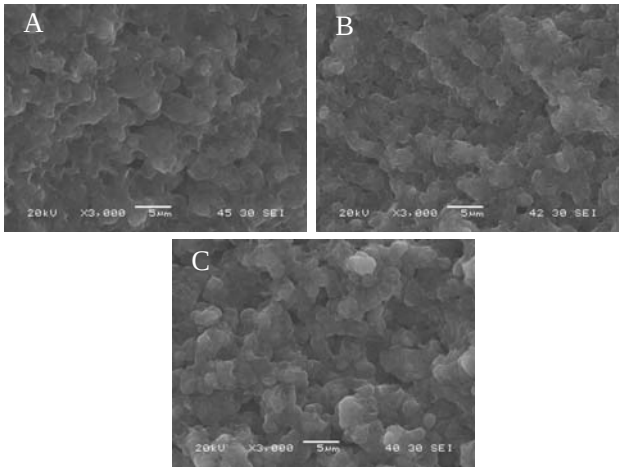

Fig.4 The SEM photographs of the products: A: 1200℃, 0.10m^3/h; B: 1200℃, 0.15m^3/h; C: 1200℃, 0.20m^3/h

The SEM images of the products shown in Fig.4 display that the products are composed of pyrocarbon particles, which is about 1.5～2.5μm. The porosities of the products increase first and then decrease with the increase of the gas flow rate. With the increasing in gas flow rate, the ratio between aromatic and linear hydrocarbon decreases, the porous among the aromatic hydrocarbon species are filled by linear hydrocarbon species. So the porosities are gradually decreased. When the linear hydrocarbon species are dominant, the porosities increase again.

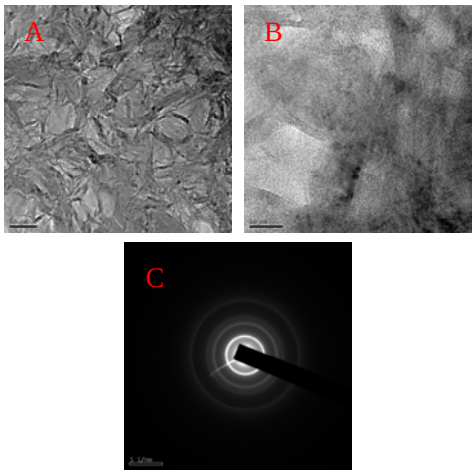

Fig.5 The TEM images and the SAED pattern of the product obtained at 1200℃, 0.15 m^3/h

Fig.5 is the TEM image and SAED pattern of the product obtained at 1200℃, 0.15 m^3/h. It could be found in Fig.6A that the product consists of irregular domains, which is surrounded by fibrous structures. In Fig.6B, the size of the domains is small (about several decade nanometers). The domain is composed of short graphene layers arranged in order. The SAED pattern in Fig.6C is a diffraction circles, which indicates that the orientation angle is 180° and the product is isotropic pyrocarbon.

Conclusions

Isotropic pyrocarbon was fabricated at 1200℃, using natural gas as precursor. The density of the products is 1.25g/cm^3, 1.56 g/cm^3 and 1.23 g/cm^3. The intensity of the G bands increases with the increasing of the gas flow rate. In SEM images, the products is composed of pyrocarbon particles (about 1.5～2.5μm). In TEM, the products consist of irregular domain and fibrous structures. The orientation angle originated from SAED pattern is 180° , which qualitatively shows its isotropic feature.

Acknowledgement

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