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Preparation and oxidation properties of biomorphic porous carbon derived from native bamboo

Pengzhao Gao*, Shiting Huang, Weiei Gong and Wenxiang Wang
College of Materials Science and Engineering, Hunan University, Changsha 410082, P.R.China

A biomorphic porous carbon (BPC) was prepared by carbonized native bamboo under an Ar atmosphere through a controlled heating process. Microstructural properties of BPC were studied by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). The pyrolytic behavior of bamboo and non-isothermal oxidation properties of BPC were studied by thermogravimetric analysis (TGA). Experimental results show that BPC has a porous interconnected honeycomb microstructure, with a multi-peak pore size distribution, and is a typical non-graphitizable carbon. With an increasing carbonization temperature, the (002) peak of the XRD spectrum becomes stronger, the interplanar spacing decreases, the structure of BPC slowly evolved towards that of ideal graphite, and also the density increases, and bulk porosity decreases. The non-isothermal oxidation properties of BPC exhibit a self-catalytic characteristic, which is discussed through a schematic model.

Key words: Biomorphic porous carbon, Structure properties, Self-catalytic.

Introduction

Design of novel ceramic materials with specific functional properties and structures by mimicking the hierarchical cellular structure of wood has recently gained particular interest [1-3]. Among which, bamboo has very reasonable structures which gives it many excellent properties, such as good carrying capacity, good toughness, etc. Furthermore, biomaterials have very fine and special structures rather than complicated compositions, which are distinctly different from what we seek for ceramic materials with high toughness through composition control. So, the complicated and reasonable structure of natural biomaterials can give us an important insight into making better structure materials through biomimetic design [4]. And also the microstructure of bamboo exhibits a hierarchical cellular structure formed on its growth [5]. The two structural properties make bamboo wood-derived porous ceramics widely applicable in many fields, such as for high-temperature- resistant exhaust gas filters, catalyst carriers, advanced micro-reactor systems, and waste water treatment, etc.

For wood-derived porous ceramics, the microstructural properties and oxidation stability of the porous carbon material can have an important influence on the structure and performance of the ceramics produced. However, little work has been done to study the microstructure and thermal oxidation properties of BPC.

TGA methods (thermogravimetry, differential thermogravimetry) are widely used in the process of studying the thermal oxidation properties of carbon materials [6, 7]. The results of thermal analysis can supply very useful information on the oxidation mechanisms of these types of materials and their thermal oxidation stability.

In the present study, a biomorphic porous carbon (BPC) material was obtained from carbonizing bamboo under an inert atmosphere. The structural properties of the BPC were investigated by XRD, SEM and EDS techniques. The pyrolytic behavior of bamboo and non-isothermal oxidation properties of BPC were investigated by TGA.

Experimental

Material preparation

Native bamboo was purchased from Changsha Wood Co. (Changsha, P.R.China). The material was shaped, dried at 120 °C for 48 h, and subsequently carbonized at 800, 1200, 1500 and 1700 °C (aim temperatures) for 4 h, under an Ar atmosphere with a flow-rate of 50 ml·minute^{-1} in a graphite heater furnace. Four types of BPC with different microstructures were obtained. The heating process from room temperature to the aim temperature was determined through a study of the pyrolytic behavior of bamboo.

Characterization of BPC

The extent of carbonization of BPC was estimated by X-ray diffraction (XRD, D5000, Siemens). An X-ray Diffractometer using nickel filtered Cu K_α radiation produced at 30 kV and 30 mA was used. Scanning speeds were 2° minute^{-1} to record all the possible profiles and for calculations of XRD parameters. From the position of the (002) peak ($2\theta_{(002)}$) in the X-ray diffractogram,

*Corresponding author:
Tel : +86-731-88822269
Fax: +86-731-88823554
E-mail: gaopengzhao7602@hnu.edu.cn

the $d_{(002)}$ interplanar spacing was determined using the Bragg equation:

$$d_{(002)} = \frac{\lambda}{2sin\theta_{(002)}} \quad (1)$$

Density and bulk porosity, which referred to the volume fraction of the pores of the BPC, was calculated by the Archimedes method.

The morphology and quantitative elemental analyses of the BPC were characterized by scanning electron microscopy (SEM, JEOL, JSM-6700F) equipped with an energy dispersive X-ray spectroscope (EDS, Oxford).

The pyrolytic behavior of bamboo was characterized using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in flowing Ar of 50 ml·minute^{-1} with a heating rate of 10 K·minute^{-1} from room temperature to 800 ºC. The initial mass of a sample was about 7.0 mg.

TGA and DSC were performed on a TGA-DSC (model Netzsch Thermische Analyzer STA 409C) thermal analyzer with alumina powder as the reference sample.

The oxidation properties of BPC were measured using thermogravimetric analysis (TGA) in flowing air of 50 ml·minute^{-1} with heating rates of 10, 15 and 20 K·minute^{-1} from room temperature to 700 ºC.

Results and Discussion

Pyrolytic process of bamboo converted to biomorphic porous carbon

Bamboo may be converted into a porous carbon that retains its anatomical features by a controlled thermal pyrolytic process. In order to study the pyrolytic behavior of bamboo, some small pieces were heated in the thermal analyzer in an Ar atmosphere. As is known, the three major components of bamboo, namely hemicellulose, cellulose and lignin, break down in a stepwise manner [8, 9].

Fig. 1 shows the TG-DTG and DSC curves of bamboo dried at a temperature range of 25-800 ºC. It can be seen that weight loss of bamboo proceeds in two stages. The first stage starts at 30 ºC, end at about 100 ºC, reaches a maximum rate (*da/dT* stand for the reaction rate) at 56.7 ºC, the weight loss is about 7%, which may be the removal of moisture.

The second stage starts at 186.3 ºC, reaches a maximum rate at 328.1 ºC and it is almost terminated at 600 ºC, minimal weight loss occurs afterwards, the weight loss in this stage is about 70%. During the second step of weight loss, the organic groups in bamboo decompose in four steps: (1) the decomposition of hemicellulose in bamboo takes place at around 190-280 ºC and a large amount of hydroxyl groups are dislocated from hemicellulose and cellulose, accompanied by the evolution of water which escapes; (2) 200-250 ºC, cellulose is drastically decomposed whereas the net structure of lignin remains stable, with the exception of the dislocation of methoxyl groups from lignin; (3) 250-400 ºC, the net structure of lignin collapses, up to about 390 ºC, followed by which more positions in the aryl groups are substituted; (4) for bamboo carbonization, the aromatization of residual carbon has approximately been completed at a temperature as high as 600 ºC. But the fusion of aromatic rings possibly does not occur [10].

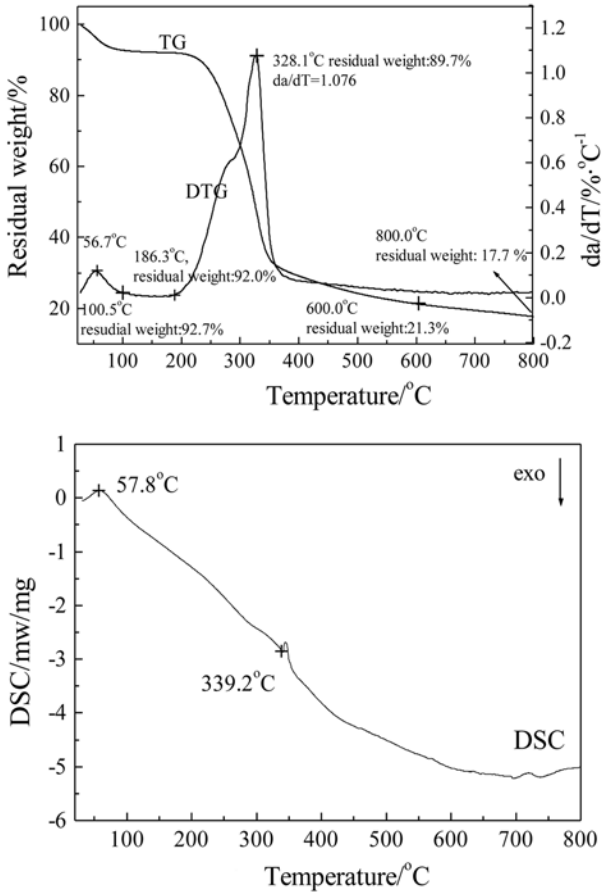

Fig. 1. TG-DTG and DSC curves of bamboo dried in an Ar atmosphere.

It can be seen that two slight peaks exists in the DSC curve, an endothermal peak at 57.8 ºC corresponds to the stage of removal of moisture and the exothermal peak at 339.2 ºC corresponds to the maximum pyrolytic rate. The pyrolytic process of the three major components of bamboo do not have a distinct region, the DSC curve of bamboo has no strong peak.

The TG-DTG curves for bamboo is similar in its nature to that of maple wood. But the DSC curve shows slight differences due to differences in chemical contents of bamboo and maple wood [11].

From the TG-DTG curves of dried bamboo, it can be seen that between room temperature and 600 ºC, almost 95% of the total weight loss occurs due to evolution of H_2O, CO_2, and volatile hydrocarbon species from decomposition reactions via the open pore channel system of bamboo. Thus, in order to retain the anatomical features of the material, the prolyitc process of bamboo used in this experiments was a slow heating rate of 2 K·minute^{-1} between room temperature to 600 ºC and a higher rate of 5 K·minute^{-1} up to the aim temperature.

XRD and porosity analysis of BPC

Fig. 2 shows the XRD patterns of BPC obatined by carbonization at various temperatures. Two broad diffraction bands are observed, indicating that the BPC is amorphous.

For the BPC obtained at 800 °C, it can be seen that there are two main analogous graphitic peaks corresponding to a broad (002) peak and a lower intensity (10*l*) peak, being suggestive of the development of hexagonal network layers stacked roughly parallel to each other, i.e. a turbostratic structure [12], which indicates the regularity of carbon in BPC is poor.

Judging from the weak intensity and broadness, the peak (002) profile of BPC consists of three components that correspond to amorphous (B), turbostratic (T) and graphitic (G) components. With an increase of the carbonization temperature, the T and G components increase and the B component decreases [13].

From Fig. 2, it can also be seen that the (002) peak becomes stronger, shifts to larger 2θ angles, and has a smaller full-width at half-maximum intensity with an increase in the carbonization temperature from 800 to 1700 °C, as expected for non-graphitizable carbonized cellulose[12], which means that the T and G components became larger. This implies that the regularity of the carbons in the porous carbon became better; consequently their structure became more rigid and stable.

The narrowing of the (002) peak is indicative of developing atomic order in the BPC. It is noted that the profile of the (10*l*) peak changes from a symmetric one below 1500 °C to asymmetrical for 1700 °C, revealing the turbostratic nature of BPC. However, it seems that three-dimensional crystallinity was almost not developed even after carbonization at 1700 °C because the (004) peak and the splitting of (10*l*) peak to (100) and (101) peaks can hardly be observed.

The $d_{(002)}$ value is traditionally used to estimate the degree of graphitization of carbon. In general, growing disorder in a material is reflected in increased values of $d_{(002)}$ [14]. As shown in Fig. 2, the (002) interplanar spacing

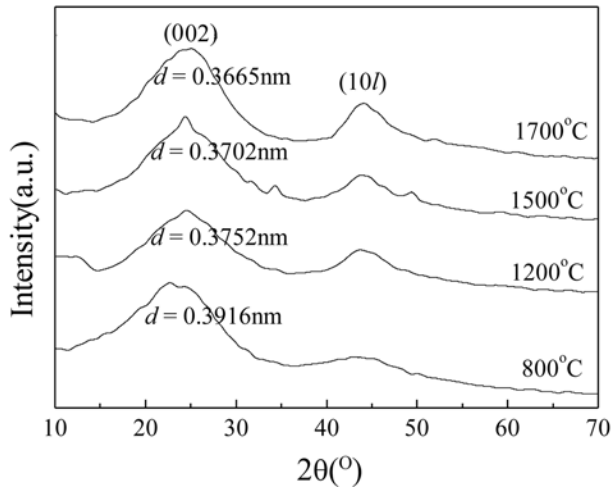

Fig. 2. XRD patterns of BPC treated at different temperatures.

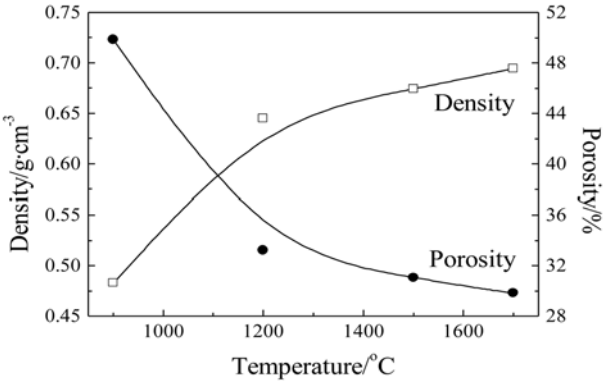

Fig. 3. Bulk porosity and density of BPC treated at different temperatures.

of the crystalline decreases with an increase in the carbonization temperature, which means the structure of BPC slowly evolved towards that of ideal graphite. Crystalline graphite exhibits a sharp peak and an interplanar spacing close to 0.3354 nm [15]. All $d_{(002)}$ values of BPC are much higher than that of ideal graphite, indicating the non-graphitizable characteristics of BPC. These results suggest that BPC carbonized at experimental temperatures is not composed of a completely graphitized carbon, but has a turbostratic structure [16, 17]. The graphene layers became more extended, their spacing closer, and the graphene stacks higher with an increase in the carbonization temperature [16].

Fig. 3 shows the bulk porosity and density of BPC obtained by carbonization at different temperatures. It can be clearly seen that the porosity increases and density decreases with an increase of the temperature.

Microstructural characterization of BPC

Fig. 4 shows SEM images of BPC (carbonization at 1200 °C). A microstructure similar to a blood vessel can be seen in the porous carbon (see Fig. 4(a), (b)), which comes from the cells of the dead bamboo. There are many micropores in the cell wall, which afford the wood routes to transmit nutrient and water. After burning in an inert gas, the organic cell walls turned into carbon. The cell cavities are connected by these micropores in the cell wall. As seen in Fig. 4(a), (c), the microstructure of the BPC prepared shows hollow channels of various diameters that originate from tracheid cells which are parallel to the axis of the bamboo. The channels can be classified into three groups, depending on their cross-sectional area: large channels (noted by "A"), medium-sized channels (noted by "B"), and small channels (noted by "C"), which form honeycomb structures. The average diameter of each group of cells is 100 mm for the large cells, 25 mm for the medium-sized cells and 6 mm for the small cells. Most of the cellular pores show a round or elliptical shape.

Table. 1 displays the EDS data of the BPC (carbonization at 1200 °C). It can be seen clearly that the main element of BPC is carbon; the K, Ca and Mg may be from the inorganic salts absorbed in the bamboo growth process.

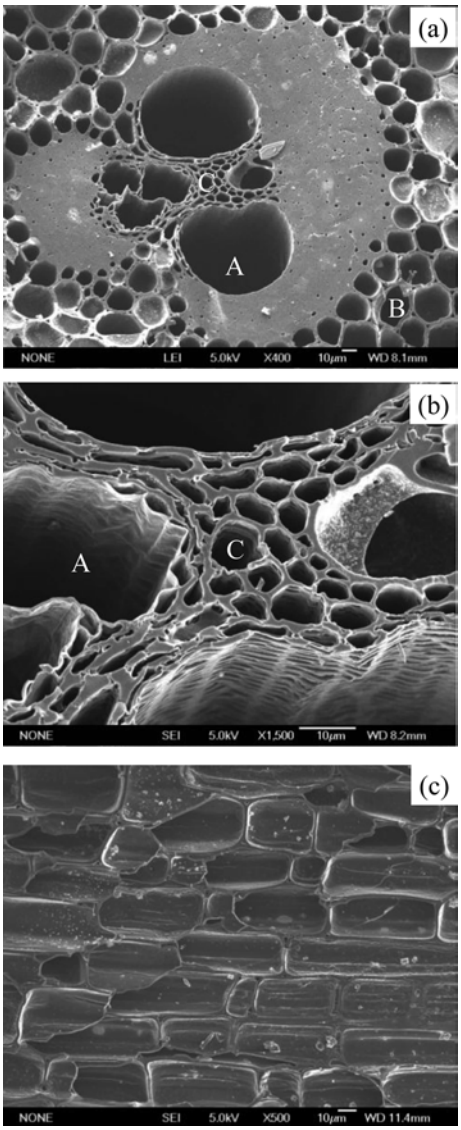

Fig. 4. SEM micrographs of (a, b) cross sections perpendicular to the axial direction and (c) a cross section parallel to the axial direction of a biomorphic porous carbon (BPC).

Table 1. EDS data of BPC

Element	C	K	Ca	Mg	Total
Weight/%	96.24	1.86	1.27	0.63	100.00
Atom/%	98.69	0.59	0.39	0.36	100.00

Non-isothermal oxidation properties of BPC

Fig. 5 shows the TG-DTG curves of BPC (carbonization at 1200 °C) with different heating rates in an air atmosphere. From the TG curves, it can be clearly seen that the oxidation weight-loss of BPC increases with an increase of the temperature, and the initial and final temperatures of the oxidation reaction increase when the heating rate increases.

From the DTG curves, irrespective of the heating rate, it is easy to see that the oxidation rate (*da/dT*) of BPC increases at first and then decreases with an increase of the temperature.

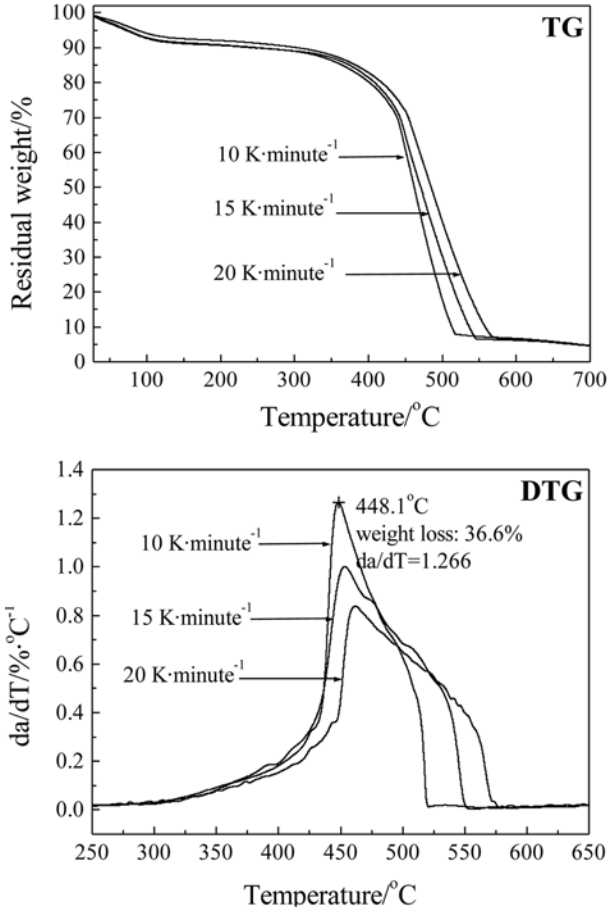

Fig. 5. TG-DTG curves of BPC with different heating rates in an air atmosphere.

Combined with the TG and DTG curves, it can be seen that the oxidation rate increases at first and then decreases with an increase of the weight-loss, it is up to a maximum when the weight-loss is 36.6% for 10 K·minute^{-1}. Thus, the characteristic of this reaction is "self-accelerating", according to Ref [18].

Fig. 6 shows a schematic model of the BPC oxidation weight-loss process. The BPC has a turbostratic microstructure (as known from the XRD pattern shown in Fig. 2) and has a few unsaturated carbon atoms (which could react with oxygen, Abbr as: ACA) on the BPC material and atmospheric interface. Thus, the BPC material has the lowest oxidation rate in the initial oxidation stage (see Fig. 6(a)).

As the oxidation reaction proceeds, the chemical bond (C-C-C-C-C) of the material should be broken off by the oxidation to form more unsaturated carbon atoms, thereby increasing the ACA. Thus, with an increase of the weight-loss, the amount of ACA increases (Fig.6 (b)), the reaction rate increases also. So the "self-accelerating" characteristic is displayed [18].

As is known, the amount of newly generated ACA is determined by the amount of C-C bonds and surface area of the material, which all decrease with an increase of the

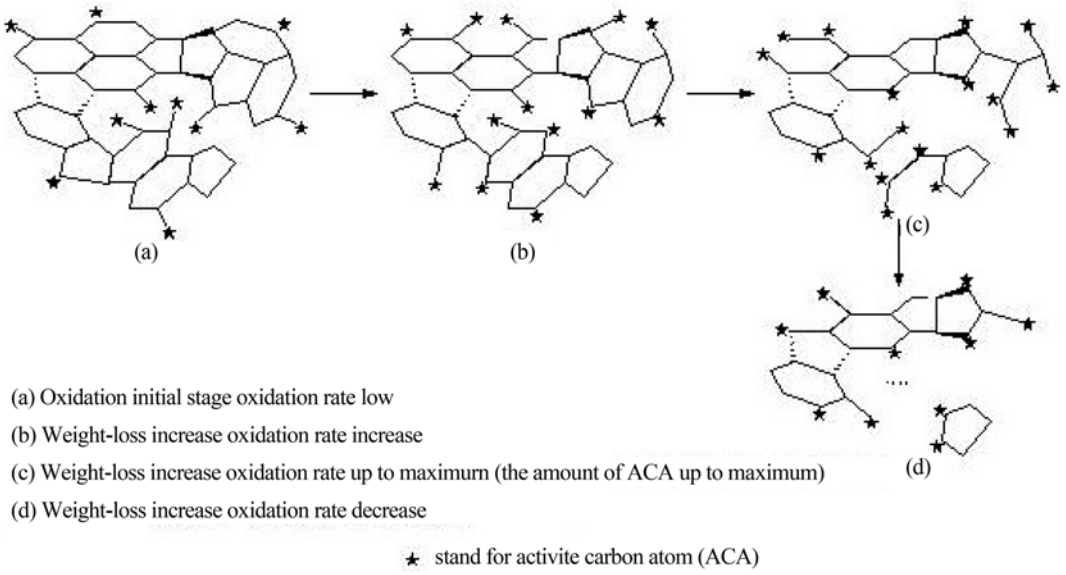

Fig. 6. A schematic model of the BPC oxidation weight-loss process.

temperature and oxidation weight-loss. At the same time, with an increase of the reaction rate, more ACA is consumed.

Namely, with an increase of the temperature, weight-loss and oxidation rate, the amount of newly generated ACA decreases and that of consumed ACA increases. When the amount of consumed ACA is equal to that of the generated ACA, the reaction rate reaches its maximum (Fig. 6 (c)) (weight loss equals to 36.6% for 10 K·minute^{-1}). And then the amount of ACA starts to decrease (Fig. 6(d)) with an increase of the weight-loss.

Conclusions

In the present study, biomorphic porous carbon (BPC), which retains bamboo's anatomical features, was prepared by carbonizing native bamboo under an Ar atmosphere through a controlled heating process. The microstructural characterization and oxidation properties of BPC were investigated. The results are summarized as follows:

(1) The pyrolytic process of bamboo proceeds in two stages: (1) the first stage starts at 30 ºC, end at about 100 ºC, the weight loss is about 7%, which may be the removal of moisture;(2) the second stage starts at 186.3 ºC and terminates at 600 ºC, the weight loss is about 70%, due to evolution of H_2O, CO_2, and volatile hydrocarbon species from decomposition reactions of the organic components of bamboo. A minimal weight loss occurs up to 600 ºC.

(2) The BPC has a porous interconnected honeycomb microstructure, has a multi-peak pore size distribution, and is a typical amorphous carbon. With an increase in the carbonization temperature, the (002) peak of the XRD spectrum becomes stronger, the interplanar spacing decreases, the structure of BPC slowly evolved towards that of ideal graphite, and also the density increased and bulk porosity decreased.

(3) The non-isothermal oxidation properties of BPC exhibit a "self-accelerating" characteristic.

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