Effect of final pyrolysis temperature on the mechanical and thermal properties of carbon foams reinforced by aluminosilicate

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ABSTRACT

Carbon foams with phenolic resin as precursor and aluminosilicate as reinforcement were prepared at different final pyrolysis temperatures. The microstructures, mechanical and thermal properties of the foams were investigated by scanning electron microscopy, mechanical testing and the laser flash method, respectively. The results show that the cells are mainly open with incomplete cell membranes, and the aluminosilicate particles are located in cell walls. The surface of cell openings becomes rougher as the final pyrolysis temperature increases. The ultimate compressive strength increases from 0.45 to 1.74 MPa when increasing the final pyrolysis temperature from 1100 to 1550 °C. The thermal conductivity ranged from 0.37 to 0.52 W m⁻¹ K⁻¹ at room temperature and decreases with increasing the final pyrolysis temperature. The occurrence of the mullite phase plays a key role in the changes of the mechanical properties and thermal conductivity of the foams.

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1. Introduction

Carbon foams are porous carbon materials with many advantages such as low density, high specific modulus and strength, high applicable temperature (up to 3000 °C in an inert atmosphere), large surface area, and controllable thermal and electrical conductivity [1]. These particular features determine their many potential applications such as sandwich panels, battery electrodes, catalyst support and filters, high-temperature thermal insulation and thermal management [2,3].

Recently a kind of resin-derived carbon foam material with aluminosilicate as additive was reported in our previous work [4]. The compressive strength of the newly developed foams was higher as much as 60% than that of the pure carbon foams. The oxidation resistance property of new foams reaches the best performance as the additive content is about 11 wt%.

Nevertheless, so far there have been no reports of research on the influences of preparation parameters on the properties of aluminosilicate-reinforced carbon foams. As we all know, the final pyrolysis temperature (FPT) is a main influencing factor on the microstructure and phase composition of the foams. Thus, the properties of this material such as the mechanical strength and thermal conductivity will change with the value of FPT.

The purpose of the present investigation is to reveal the influences of FPT on the microstructure and properties of the aluminosilicate-reinforced carbon foams. At first, several groups of foam specimen with a certain content of aluminosilicate particles as additive were prepared at different FPTs. Then, the microstructure, mechanical properties and thermal conductivity of these specimens were investigated using scanning electron microscopy (SEM), mechanical testing, and the laser flash technique, respectively. Finally, the relationship between these properties and FPT, the mechanism of deformation and thermal conduction in the foams were discussed.

2. Experimental

2.1. Materials

Phenolic resin was chosen as the precursor in this work (manufactured by Beijing FRP Institute). Sodium bicarbonate (AR grade), p-toluene sulfonic acid (AR grade), and Tween 80 (AR grade) were selected as foaming agent, catalyst, and surfactant, respectively. These chemical agents were purchased from Beijing Jinwen Chemical Reagents Company. Aluminosilicate was selected as additive (provided by a company in Baotou city, Inner Mongolia Autonomous Region, China). This material is mainly composed of SiO₂ and Al₂O₃ with particle size of about 50–150 μm.

2.2. Processing

First, a sample of phenolic foam sized of about 200 × 200 × 300 mm³ was fabricated using chemical bubbling method with phenolic resin, polysorbate-80, sodium bicarbonate and p-toluene

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sulfonic acid as precursor, surfactant, foaming agent and catalyst, respectively. Another additive introduced in the mixture was aluminosilicate with amount about 10 wt% of the precursor. The mixture was treated by ultrasonic for the dispersion of the additive. The foaming agent had not been added until the aluminosilicate was dispersed well in the phenolic resin. After the curing process the phenolic foam was cut into tens of specimens with different shape and size for different measurements. The specimens with homogeneous pore distribution were selected out and divided into four groups. Then, the four specimen groups were carbonized with different FPTs according to a certain temperature schedule shown in Fig. 1. All specimens were heated under vacuum environment with a rate of about 140 °C h⁻¹ when the temperature was below 300 °C and a low rate of 30 °C h⁻¹ while the temperature was above 300 °C to avoid the occurrence of cracks. They were held at 300 °C for 1 h to allow the decomposition of organic compounds from the foam specimens and maintain at different FPTs from 1100 to 1550 °C for 3 h. Finally, the specimens naturally cooled to room temperature with a rate of about 60 °C h⁻¹. The processing parameter and characterization of the specimen groups of carbon foams are listed in Table 1.

2.3. Microstructure measurements

The foam specimens were sprayed by Eiko IB3 Ion Coater at first. The surface morphologies of the foams such as cell size, cell shape, and the dispersion of the aluminosilicate, were obtained using SEM (JEOL JSM-6460LV).

The room temperature X-ray diffractograms of the foams were recorded using X-ray diffractometer (Rigaku D/max2200) with Cu Kα radiation (λ=0.15406 nm). The X-ray diffraction (XRD) patterns were recorded in the angular range of 10°~80° with a step size of 0.01° using monochromatic X-rays.

2.4. Mechanical properties tests

Compression testing was performed on a microcomputer-controlled electron universal testing machine (model CMT5504, New Three Points Corporation in Shenzhen, China). Specimens (15 × 15 × 15 mm) were compressed between two stainless steel platens with a crosshead speed of 1.5 mm min⁻¹. The displacement is followed by a laser extensometer. The compressive yield strength (σ) was calculated by Eq. (1).

\[ \sigma = \frac{F}{A} \]  

(1)

where \( \sigma \) is the compressive yield strength, \( F \) is the yield load, \( A \) is the cross-section area. All the results were calculated based on the average of several tests and the number of specimens for each point was no less than seven.

2.5. Thermal conductivity measurements

The thermal properties of the foams were measured by the laser flash method. An instrument typed of NETZSCH LFA 427 was applied to measure the thermal diffusivity of the foams from room temperature about 20 °C to a high temperature of 800 °C. Specimens with a diameter of 12–13 mm and a thickness of 3–4 mm were used for testing. Thermal conductivity, \( \lambda \), is determined by Eq. (2).

\[ \lambda = \rho C \alpha \]  

(2)

where \( \rho \) is specimen’s density, \( C \) is specific heat and \( \alpha \) is the thermal diffusivity. There was no less than five specimens were measured for each point.

3. Results and discussion

3.1. The microstructure of the foam specimens

As listed in Table 1, the bulk density of the foam specimens was about 0.17 g cm⁻³. The weight loss caused by the reactions including pyrolysis, fasculation and rearrangement in the carbonization process is about 60%, and the FPT has no significant effect on the weight loss.

Fig. 2 shows the SEM photographs of the foams from specimen groups No. 1, No. 2, No. 3 and No. 4, with FPT of 1100, 1250, 1400 and 1550 °C, respectively. It can be seen that the foam cells present spherical shape and non-uniform size with diameter of about 200–300 μm. This is due to the fact that in the foaming process competitive growth and surface tension are two main factors to create foams with spherical cells. The foam cells are mainly open with incomplete cell membranes, and each cell is sealed off from its neighbors partly. There are three phases in the foam specimens: the carbon matrix, the aluminosilicate, and the internal voids or pores. The aluminosilicate particles are dispersed in the carbon binder and the matrix of the foams, which can be seen more clearly in Fig. 2c. Moreover, the voids are not present at the junctions but located in cell membranes or cell walls of the carbon foams.

It can also be seen in Fig. 2 that the surface of cell walls in foams from group No. 1 and No. 2 with FPTs of 1100 and 1250 °C respectively is smooth (Fig. 2a and b). Nevertheless, the surface of cell openings becomes rough with increasing FPT. This can be seen more obviously at the edge of cavities or voids in specimen from group No. 4 with FPT of 1550 °C (Fig. 2d). This can be explained by the fact that there are two types of cell openings [5,6]. One type of openings formed in the foaming process is smooth. During the foaming process of the phenolic resin, the surface tension draws the materials into the cell edges, and a thin skin framed with thicker edges is formed. The other type of opening appears to be coarse, generated by brittle fracture of the cell walls in carbonization process. As a result, the surface of part opening goes into rough when the FPT increases from 1100 to 1550 °C.
Unlike pitch-derived carbon foams with large anisotropic flow domain aligned parallel to the cell wall [3], the resin-derived foams are of glassy carbon structure due to lacking of graphic structure. Likewise, the foam samples fabricated with resin as precursor have not anisotropic but isotropic properties.

Fig. 3 displays the XRD patterns of carbon foams from these four groups with different FPTs. It is obvious that there are three peaks at 2θ values of 38.2°, 44.5° and 78.1° in the XRD patterns. These three peaks are contributed by aluminum crystal planes (111), (200) and (322) because the powder specimen was loaded into a cylindrical aluminum specimen holder as the diffraction scan was run. It can also be seen the intensity of peak nearly 38.2° is relatively low when the FPT is low, i.e. 1100 and 1250 °C, shown in XRD patterns of specimens from groups No. 1 and No. 2. When the FPT increases to 1550 °C the intensity of this peak becomes higher. This can be explained by the fact that in conditions of the same additive content the relative peak intensity of background to matrix carbon becomes larger as the FPT increases. Meanwhile, the intensity of peak at 2θ values of 44.5° and 78.1° also increases with increasing FPT. In addition, peaks before 2θ values of about 35° in specimen from group No. 1 are attributed to the compounds in aluminosilicate, mainly the silica dioxide and the alumina. With the FPT increasing from 1100 to 1250 °C, the peaks of the mullite phase (2SiO2–3Al2O3) begin to appear with 2θ values of 16.4°, 26.2° and 33.1°. Moreover, the intensity of these peaks increases with improving the FPT from 1250 to 1550 °C, which can be observed clearly in local amplification patterns from 10° to 35° in Fig. 3. The crystalline parameters such as diffraction angle, diffraction intensity, lattice spacing and full-width half-maximum (FWHM) of mullite in different carbon foam specimens are compiled in Table 2. The results show that the FWHM and the lattice spacing d_{210} decrease when the FPT increases, indicating that the crystallinity of mullite is increased. This is very helpful to improve the mechanical properties of the foams on account of that mullite is a compound with a relatively high strength. The relationship between mechanical properties and microstructure of the foams with different FPTs will be discussed in Section 3.2.2.

### 3.2. Mechanical properties of the foam specimens

#### 3.2.1. Load–strain curve of the carbon foams

Fig. 4 shows the compressive load–strain curves of the foam specimens with different FPTs. According to the results reported by

<table>
<thead>
<tr>
<th>Specimen group</th>
<th>FPT (°C)</th>
<th>2θ (deg.)</th>
<th>Intensity (cps)</th>
<th>FWHM (deg.)</th>
<th>d_{210} (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 1</td>
<td>1100</td>
<td>22.99</td>
<td>232.2</td>
<td>0.3012</td>
<td>4.354</td>
</tr>
<tr>
<td>No. 2</td>
<td>1250</td>
<td>26.17</td>
<td>364.8</td>
<td>0.2625</td>
<td>3.403</td>
</tr>
<tr>
<td>No. 3</td>
<td>1400</td>
<td>26.22</td>
<td>471.6</td>
<td>0.2408</td>
<td>3.396</td>
</tr>
<tr>
<td>No. 4</td>
<td>1550</td>
<td>26.24</td>
<td>743.1</td>
<td>0.2217</td>
<td>3.394</td>
</tr>
</tbody>
</table>

Fig. 2. SEM micrographs of the foams with FPT of (a) 1100 °C (b) 1250 °C (c) 1400 °C and (d) 1550 °C.

Fig. 3. XRD patterns of the foams with different FPTs.

Table 2

<table>
<thead>
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1550 °C the intensity of this peak becomes higher. This can be explained by the fact that in conditions of the same additive content the relative peak intensity of background to matrix carbon becomes larger as the FPT increases. Meanwhile, the intensity of peak at 2θ values of 44.5° and 78.1° also increases with increasing FPT. In addition, peaks before 2θ values of about 35° in specimen from group No. 1 are attributed to the compounds in aluminosilicate, mainly the silica dioxide and the alumina. With the FPT increasing from 1100 to 1250 °C, the peaks of the mullite phase (2SiO2–3Al2O3) begin to appear with 2θ values of 16.4°, 26.2° and 33.1°. Moreover, the intensity of these peaks increases with improving the FPT from 1250 to 1550 °C, which can be observed clearly in local amplification patterns from 10° to 35° in Fig. 3. The crystalline parameters such as diffraction angle, diffraction intensity, lattice spacing and full-width half-maximum (FWHM) of mullite in different carbon foam specimens are compiled in Table 2. The results show that the FWHM and the lattice spacing d_{210} decrease when the FPT increases, indicating that the crystallinity of mullite is increased. This is very helpful to improve the mechanical properties of the foams on account of that mullite is a compound with a relatively high strength. The relationship between mechanical properties and microstructure of the foams with different FPTs will be discussed in Section 3.2.2.
Bruneton and Shen [7,8], carbon foams exhibit a multi-stage deformation response consisting of linear elastic loading section, a plateau region and graceful failure when subjected to compressive loading. However, there is only one foam group, i.e. No. 1, agrees with this discipline completely, which can be seen in Fig. 4. The load–strain curves of the rest three specimen groups No. 2, No. 3 and No. 4 just only show linear stage and plateau region. This could be explained by the foam structure and phase composition.

In the linear stage, the cell edges and cell walls of the foams are elastically distorted. As for the cell structure, the cell membranes are weak, which can be proved from the voids in Fig. 2. Thus the stiffness of the foams derives mostly from that of the cell edges. The linear elasticity of the foams is controlled by cell edge bending and cell face stretching. After the end of the elastic threshold the plateau region appears. The peak value denotes the point of crack initiation. During compression, the initial crack occurs at the weakest location and then propagates, so cell edges of the foams are broken. Then the compressive load goes down slowly for further compression. As a result, layered crushing mode of failure occurs in foams [9]. The plateau is associated with collapse of foam cells by brittle crushing of the brittle foam. When the strain exceeds a certain value, the foams are destabilized and fails. This phenomenon displays very well on specimen group No. 1 and a visible failure stage appears. This can be explained by the fact that the average density of specimen group No. 1 is a little lower than that of the rest three groups and the cell edges are easy to crack but not collapse. This point can lead to a large decrease of compressive load in condition of no detectable strain variation. However, the rest specimen groups No. 2, No. 3 and No. 4 show a gradual failure under a compressive load. There are two reasons for this phenomenon. One is that the bulk density of these groups is larger than that of group No. 1. The other is that mullite increases when increasing the temperature from 1250 to 1550 °C. Mullite has high strength and good heat shock characterization especially at high temperature. Furthermore, this phase stops the propagation of the cracks thus the foams are toughened. As a result, the ultimate compressive strength of the foam specimens increases from 0.45 to 1.74 MPa with improving the FPT from 1100 to 1550 °C.

Moreover, the ultimate compressive strength of foams can be relative to the factors about foam structure. The thickness of cell wall and the length of cell edge are used to describe the foam structure. The relationship among thickness of cell wall, length of cell edge, bulk density of specimens follows Eq. (3).

\[
\left(\frac{t}{l}\right)^2 \propto \left(\frac{\rho}{\rho_s}\right)^k
\]

where \(t\) is the thickness of the cell wall, \(l\) is the length of the cell edge, \(\rho\) is the bulk density, \(\rho_s\) is the true density of the foam, and \(k\) is a constant between 1 and 2 [10]. As the data compiled in Table 1, the average density of specimen group No. 1 is the lowest one among all groups, which implies a thinner cell wall and longer cell edge. As a result, specimen group No. 1 has the minimum compressive strength of about 0.45 MPa.

Another important parameter for this material is Young’s modulus. It can be seen in Fig. 5 that Young’s modulus (elastic modulus) of the foams reaches a maximum on group No. 3 with FPT of 1400 °C. This could be explained by that the modulus is usually the sum of three contributions: cell edge bending, membranes stresses and the compression of the cell fluid [11]. Surface tension can draw the phenolic resin into the cell edges in the foaming process, leaving only a thin membrane across the faces of the cells. Furthermore, there is no fluid trapped within the cells as shown in Fig. 2. As a consequence, the stiffness derives mostly from that of cell edges. Among these four foam groups No. 3 has the highest bulk density thus this group possesses the highest elastic modulus.

3.2.2. Effect of the FPT on compressive strength and elastic modulus

Fig. 5 illustrates the ultimate compressive strength and elastic modulus as functions of FPT. It can be seen that the ultimate compressive strength increases with increasing FPT. Although the bulk density of these four groups is pretty much the same of about 0.17 g cm⁻³, the foam group No. 4 with FPT of 1550 °C exhibits the highest ultimate compressive strength of 1.74 MPa. This value increases substantially by 291% comparing with that of the group No. 1 pyrolyzed at FPT of 1100 °C. In the pyrolysis process complex phase transformation takes place on aluminosilicate which is located in the cell walls as observed in Fig. 2. Some new phases such as mullite begin to occur on specimen group No. 2 with FPT of 1250 °C as shown in Fig. 3. The XRD patterns in Fig. 3 and the lattice parameters in Table 2 suggest that the diffraction peak intensity of mullite increases when increasing the temperature from 1250 to 1550 °C. Mullite has high strength and good heat shock characterization especially at high temperature. Furthermore, this phase stops the propagation of the cracks thus the foams are toughened. As a result, the ultimate compressive strength of the foam specimens increases from 0.45 to 1.74 MPa with improving the FPT from 1100 to 1550 °C.

As we know, the thermal conductivity of reticulated vitreous carbon is very low. Fig. 6 illustrates the thermal conductivity of the foam specimens with different FPTs at various testing temperatures.
The results were calculated by Eq. (2) used the data of foam density, heat capacity and thermal diffusivity measured in the tests. It can be seen in Fig. 6 that the thermal conductivity at room temperature decreases from 0.52 to 0.37 W m\(^{-1}\) K\(^{-1}\) with the FPT increases from 1100 to 1550 °C. Furthermore, the thermal conductivity of the foams enhances to some extent with increasing the testing temperature from room temperature to 800 °C, no matter what the FPT is.

According to theory of thermal physics, there are four parameters to influence the thermal conductivity of the foams. The relationship among these parameters can follow by Eq. (4).

\[ \lambda = \lambda_s + \lambda_g + \lambda_c + \lambda_d, \]  

(4)

where \( \lambda_s \) is the conduction through solids, \( \lambda_g \) is the conduction through gas, \( \lambda_c \) is the convection within the cells, and \( \lambda_d \) is the radiation through the cell walls and the voids. In the resin-derived foams the volume fraction of the solid phase is very low. Thus the heat conduction through both the glassy carbon and pores are very poor. The small cell size will suppress the convection and reduce the radiation by absorption and the repeated reflection from the cell walls. Therefore, the whole system exhibits a very low thermal conductivity, which makes the foams a prime choice for thermal insulation.

Nevertheless, it is difficult to determine quantitatively the influencing factors of the foam’s thermal conductivity especially on specimens with high porosity, even though a finite element analysis on specimens with high porosity, even though a finite element analysis

![Fig. 6. Thermal conductivity of the foams with different FPTs as a function of testing temperature.](image)

The influence of FPT on the microstructure, mechanical and thermal properties of aluminosilicate-reinforced carbon foams was investigated. It has been shown the foam cells present spherical shape and non-uniform size with diameter of about 200–300 μm. The surface of part opening in carbon foams goes into rough as the FPT increases from 1100 to 1550 °C. Simultaneously, the peaks of the mullite phase begin to appear. The ultimate compressive strength of foam groups increases from 0.45 to 1.74 MPa when increasing the FPT from 1100 to 1550 °C. The elastic modulus of the foams reaches a maximum at FPT of 1400 °C. The thermal conductivity drops from 0.52 to 0.37 W m\(^{-1}\) K\(^{-1}\) with increasing FPT from 1100 to 1550 °C, in virtue of the occurrence and content increase of the mullite phase.

4. Conclusions

The influence of FPT on the microstructure, mechanical and thermal properties of aluminosilicate-reinforced carbon foams was investigated. It has been shown the foam cells present spherical shape and non-uniform size with diameter of about 200–300 μm. The surface of part opening in carbon foams goes into rough as the FPT increases from 1100 to 1550 °C. Simultaneously, the peaks of the mullite phase begin to appear. The ultimate compressive strength of foam groups increases from 0.45 to 1.74 MPa when increasing the FPT from 1100 to 1550 °C. The elastic modulus of the foams reaches a maximum at FPT of 1400 °C. The thermal conductivity drops from 0.52 to 0.37 W m\(^{-1}\) K\(^{-1}\) with increasing FPT from 1100 to 1550 °C, in virtue of the occurrence and content increase of the mullite phase.

Acknowledgments

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References