Boron-containing carbon aerogels: excellent mechanical and thermal insulation properties

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Abstract. The boron-containing carbon aerogels with excellent properties are reported: The precursor of carbon aerogels was modified by boric acid. Compared with the unmodified carbon aerogels, the compressive strength of the prepared carbon aerogels has been significantly improved, reaching 4.57 MPa. The density of the carbon aerogels is between 0.253-0.287 g/cm\textsuperscript{3}, and the thermal conductivity is also kept at a low level of 0.057-0.062 (W m\textsuperscript{-1} k\textsuperscript{-1}). Excellent mechanical and thermal insulation properties make the prepared carbon aerogels have a good application prospect.

1. Introduction

Since Pekala [1] used high-temperature pyrolysis of organic aerogels to obtain carbon aerogels, carbon aerogels have become a research hotspot of thermal insulation materials, due to their rich porosity, high surface area, low density and unique high temperature stability under inert atmosphere [2]. However, the low density and low thermal conductivity of carbon aerogels are also accompanied by a decrease in compressive strength [3]. The neck of the particles will suffer from brittle fracture under pressure because of the weak connection between carbon aerogels nanoparticles, which limits its application in high-temperature thermal insulation materials [4]. In order to improve the compressive strength, compositing with fiber reinforced materials become a common method. However, although the compressive strength of this carbon aerogel composite material can be improved, an increase in density and thermal conductivity would usually happen [5,6]. so the balance between thermal conductivity, density and compressive strength performance needs to be adjusted. Therefore, the design and preparation of high strength and low thermal conductivity carbon aerogels is still a major challenge in the field of carbon aerogel technology.

Boron is commonly used to improve the heat resistance of phenolic resins. B element is doped into the molecular chain of phenolic resin by chemical reaction. Boron can be converted into B\textsubscript{2}O\textsubscript{3} and B\textsubscript{4}C at high temperature to improve thermal protection [7]. Although the study of boron modification on the thermal insulation performance of phenolic resin is relatively thorough, there are almost no reports about the performance of boron-modified phenolic aerogels as precursors of carbon aerogels.

In this work, boron-containing carbon aerogels with high compressive strength, low density and low thermal conductivity were successfully prepared by sol-gel and carbonization of boric acid modified phenolic. The mechanical and thermal insulation properties of the boron-containing carbon aerogels were studied.
2. Experimental part

Phenolic resin solution was prepared by the polymerization of resorcinol and formaldehyde. Firstly, the boron-modified phenolic aerogel was prepared. Different proportions of boric acid and phenolic resin were dissolved in ethanol and stirred evenly by magnetic stirring. The specific composition was shown in Table 1. The compositions were transferred to a closed polytetrafluoroethylene reactor for gelation. The gelation temperature is 110°C for 24 hours. Then the prepared wet gel was put into a supercritical drying kettle for supercritical drying, and the boron-modified phenolic aerogel was prepared.

The prepared boron-modified phenolic gel was put into a vacuum atmosphere furnace, heated to 900 °C at a rate of 5°C/min in Ar atmosphere, and held for 2 hours for carbonization. The prepared carbon aerogel is labeled as B-C-X (X is the mass ratio of boric acid to novolac phenolic). Corresponding phenolic precursor aerogel is labeled as B-N-X.

Table 1 Experimental scheme, the prepared carbon aerogels density and BET specific surface area in this work

| Samples    | H3BO3:NR (Mass ratio) | Apparent density (g/cm³) | BET Surface area (m²/g) | Micropore area (m²/g) |
|------------|-----------------------|--------------------------|-------------------------|-----------------------|
| B-C-1/3    | 1:3                   | 0.287                    | 6.675                   | 0.325                 |
| B-C-1/6    | 1:6                   | 0.266                    | 26.587                  | 1.989                 |
| B-C-1/9    | 1:9                   | 0.264                    | 48.788                  | 18.109                |
| B-C-1/12   | 1:12                  | 0.253                    | 54.486                  | 19.854                |

3. Results and discussion

 FTIR transmission spectra of pure phenolic aerogel and boron-modified phenolic aerogel are shown in Figure 1(a). Compared with the unmodified phenolic aerogel, the new peak at 1363cm⁻¹ after boron modification is mainly due to the formation of the B-O-C stretching vibration[8], indicating that B element has been successfully connected to the main chain and it is not a simple physical mixing. The peak at 3224cm⁻¹ is the stretching vibration peak of B-O in unreacted boric acid. The XPS curve of carbon aerogel in Figure 1(c)(d) can also prove this result. The two low energy regions of B1 at peak 185.48 eV and B2 peak at 187.11 eV are mainly attributed to the existence of B-C and BC₂O bond, and
the 195.15 eV at B5 peak is due to the existence of residual B-OH group, and the two main high-energy differences are B3 peak at 190.83 eV and B4 peak at 192.44 eV[9]. These are B-O and B-O-C bonds respectively.

The carbonization process of boron-modified phenolic aerogels is analyzed by the DTG curve of Fig 1 (b). A relatively rapid weight loss occurs between 0℃ and 100℃, which is mainly due to the presence of adsorbed water. Compared with the unmodified phenolic aerogel, weight loss is more obvious, mainly because B-O-C, B-O-B, B-OH and other boron-containing functional groups have strong hydrophilicity, leading to more adsorbed water. The mass loss rate of aerogels is slow between 100℃ and 400℃ mainly due to the volatilization of some free molecules. Serious mass loss occurred between 400 ℃-800 ℃. As a result of dehydrogenation and decomposition reactions, large amounts of volatile gases are present and significant mass changes can be observed. The emitted gases may include CO, H2O, small molecular hydrocarbons, etc. After carbonization, the residual weight of boron-modified aerogel is 60%, which is more than that of unmodified aerogel. With the progress of carbonization, the carbon aerogel gradually generates B2O3, B2O3 wrap around the skeleton to reduce mass loss. The B-O bond energy is larger than the C-C bond energy, and also increases the heat resistance of carbon aerogels [10].

Figure 2. (a)-(d) SEM images of B-C-X (X=1/3,1/6,1/9,1/12), (e) Nitrogen adsorption-desorption isotherms of carbon aerogel, (f) Pore size distribution of carbon aerogels derived from the BJH method.

The effect of boric acid on the morphology of aerogel is observed by SEM. In Figure 2(a-d), with the increase of boric acid content, the particle size of carbon aerogel increases gradually, as shown in the SEM diagrams of B-C-1/6 and B-C-1/9, and the pores are more evenly distributed. Figure 2(e) shows the nitrogen adsorption/desorption isotherms of carbon aerogel with different boric acid contents, which are obviously type IV isotherm, indicating that the material is dominated by mesoporous structure and there are a few micropores. Figure 2(f) is the pore size distribution calculated by BJH model, showing that the pore size distribution of samples is wider with the increase of boric acid content. Table 1 also shows the distribution of total BET specific surface area and micropore BET. As the carbon aerogel particles become smaller, the specific surface area increases, but the micropore occupies less of the total pore volume.
Figure 3(a) shows that the thermal conductivity of carbon aerogel with boric acid. In general, Carbonization of organic compounds is accompanied by the collapse of micropores, forming macroporous structures, density increase caused by shrinkage of carbon aerogels, leading to the increase of thermal conductivity of aerogels after carbonization. At room temperature, the thermal conductivity of carbon aerogel is mainly contributed by the thermal conductivity of gas and solid. It can be seen from Figure 2 that the distribution of pores and particles in B-C-1/9 samples is uniform, so the thermal conductivity is the lowest. The thermal conductivity of the prepared aerogel is still far lower than that of the carbon fiber and carbon foam fiber sold in the market (0.1-0.25 W·m⁻¹·K⁻¹), and remains at a low level between 0.057-0.062 (W·m⁻¹·K⁻¹).

Figure 3(b) shows the maximum compressive strength of carbon aerogel with different boron content and carbon aerogel without boron. The maximum compressive strength of the unmodified carbon aerogel is only 0.5 MPa, but the maximum compressive strength of carbon aerogel reaches 4.58 MPa after boron modification and the mechanical property have been greatly improved. Compared with other work in Figure 3(d), the prepared carbon aerogel in this work has enhanced compressive strength while maintaining a low density. The participation of boric acid in sol-gel reaction could generate B-O bond with higher bond energy instead of C-C bond, and the carbon skeleton would be wrapped by B₂O₃ in the carbonization process. With the progress of carbothermal reduction reaction, a few B-O-C bonds would gradually transform to B-C bonds with higher bond energy. In addition, carbon aerogels would bend the skeleton instead of breaking while under pressure, due to the flexibility of the B-O bond. Moreover, as shown in Figure 3(c), the "neck" connected between carbon aerogel particles becomes thicker, and the skeleton strength is enhanced. All of these cause the improvement of compression strength.

4. Conclusion
This work presents a simple method to solve the contradiction between high strength and low density and low thermal conductivity of carbon aerogels. After boric acid modification, the prepared carbon aerogels possess excellent comprehensive properties, with density between 0.253-0.287 g/cm³, thermal
conductivity between 0.057-0.062 (W·m⁻¹·k⁻¹) and compressive strength up to 4.58MPa. These properties make Boron-containing carbon aerogels have great application potential in ultra-high temperature insulation materials.

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