Thermal-Insular Carbon Foam Prepared From Phenolic Resin

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A thermal-insular carbon foam with low density, high strength and low thermal conduction coefficient was successfully prepared from the phenolic resin by using foaming and then carbonization process. A series of carbon foams with various densities and structures were obtained，and the properties of as-prepared carbon foams were investigated in the paper. The structure and properties of the resultant carbon foam were characterized by scanning electron microscopy (SEM), mercury adsorption, compressive strength and thermal diffusion coefficient measurements. Results showed that as-prepared carbon foams had relatively low bulk densities of 0.15-0.55g/cm^3 and high compressive strength of 4.6-29.5MPa .The pore distribution of these carbon foams changes from 0.07μm to 1.50μm, and there was little change in the pore size of these carbon foam . Thermal diffusion coefficients of all samples were in the range of 0.18-0.29mm^2/s and had little change at the temperature from25℃to 300℃.

Keywords

Phenolic resins；Porous carbon；Diffusion；Carbonization

1．Introduction

Porous materials have been studied for many years. The carbon foam composed of hollowed carbon microspheres or pours is a peculiar porous carbon materials with low density and excellent mechanical and thermal properties which derived from various precursors such as pitches, resin, polymer, wood and coal，etc carbonized at high temperature. Carbon foams were first developed by the researchers of the US Air Force Materials Laboratory in the late 1960s [1]. These carbon foams were thermally stable, low in weight and density, chemically pure，low thermal expansion, resist thermal stress and shock, and relatively inexpensive. These carbon foams are attractive for many aerospace and industrial applications. Other applications for carbon foam include porous electrodes, high-temperature insulation, filters and demisters, storage batteries, scaffolds, and acoustic control.

Recently, with the development of science and technology, many kinds of carbon foams were prepared and applied. Due to their light weight and potential tailorability of their physical and mechanical properties over a wide range, carbon foam materials have received a great deal of attention. But most research on carbon foam only focus on pitch ,coal, etc . There was little research on carbon foam derived from phenolic resin.

Phenolic resin was a kind of instantantous resistant high temperature and insulation thermal materials applied to space aerocraft, rocket, missile and plane field [2]. The phenolic foam with high carbon yield is one good precursor of carbon foam [3].Due to average thermal conduction coefficient was in between 0.02-0.04w/mk[4], the beginning insulation thermal material applied on the head of the missiles was the phenolic foam. In English and Europe, phenolic foam was a important thermal insulation and heat preservation material [5,6].

The carbon foam prepared from the carbonization of phenolic foam will possesse the synthetic properties of carbon and phenolic foam material and is a good low-weigh and high-strength thermal-insulator material applied under higher temperature harsh condition. So the research and preparation of carbon foam from phenolic resin will be of significance. But in the process of preparation , big pore size , disuniform pore distribution , brittle, difficult carbonization or craze in carbonizing are problems which must to be resolved. In the paper , by first foaming and curing under a high pressure and then carbonizing covered in admixture, a kind of carbon foam derived from phenolic resin with low density, high strength , little and uniform pore size and low thermal conduction coefficient was successfully obtained.

2. Experiment

2.1 Preparation of carbon foam derived from phenolic resin

The preparation of carbon foam had two steps .First step was foaming and curing processes to form phenolic foam precursor. Firstly, the formaldehyde Phenol, foaming agent, cruring agent and stabilizing agent were soluted by ethanol in a vessel, then putted in a high pressure kettle. Under 0.8-1.5MPa pressure ,the solution was heated. When the solution was heated to 180-220□, the pressure of kettle was released to atmospheric pressure at a rate of 0.1-0.3MPa /h. Finally，the solution was heated up to 280-300□ and maintained for 5-6h, and a precursor was obtained. In the second step, the resulted precursor was covered in the mixture of coke and artificial graphite powder and then was heated to 800□ at the rate of 1-2℃/min and maintained for 0.5-1h in N_2 atmosphere in a carbonization stove. When the carbonization process finished, carbon foam derived from phenolic resin was successfully obtained .

2.2 Sample characterization

SEM

The inter and surface structure of the carbon foams were observed by using a field emission scanning electron microscope （LEO438VP）.

Pore structure

In the paper, the pore distribution, pore size and bulk density of the carbon foams were observed and studied by using a mercury adsorption (Micrometritics Autopore Iv 9500).

Thermal properties

The thermal diffusion coefficients of all samples were measured by using the measuring apparatus(NETISCH LFA447).

The thermal conduction coefficients of all samples were calculated by $\lambda = Cp \cdot \alpha \cdot \rho$

where λ = thermal conduction coefficients

Cp= specific heat

α = thermal diffusion coefficients

ρ =bulk density .

Mechanical properties

The compressive strengths of the carbon foams were measured by material testing machine.

3. Result and discussion

3.1 The influence of the concentration of phenolic resin in solution on the properties of the carbon foam .

A series of carbon foams with various density and structure were obtained by the adjustment of the concentration of phenolic resin in solution . The properties of carbon foams were showed in table 1.

Table 1 : The properties of a series of carbon foams

Sample	1	2	3	4	5
Concentration(g/mL)	0.10	0.15	0.22	0.30	0.35
Density (g/cm^3)	0.15	0.23	0.37	0.43	0.55
Average pore diameter(μm)	1.50	0.70	0.10	0.09	0.07
Compressive strength(MPa)	4.6	9.8	13.8	18.9	29.5

Table 1 showed the influence of the concentrations of phenolic resin in solution on the density ,pore texture and pressure strength of the carbon foams .In the process of preparation, the preparation of precursor of carbon foam was of important and essential. The structure and properties of carbon foam were mostly depended on the structure and properties of phenolic foam [7.8]. So the structure and properties of carbon foam was decided by the structure of precursor. From table 2, it can be seen that with the concentrations of resin increased form 0.10 to 0.35g/mL, the density ,the pressure strength of carbon foams increased from 0.15 to 0.55g/cm^3, 4.6 to 29.5MPa respectively, and but the average pore diameter decreased form 1.50 to 0.07μm. The concentration of resin also was the viscosity of solution. It is well known that, the viscosity of solution has a important influence on foaming. With viscosity increased, it was of necessity that the pore size and well of carbon foam precursor became less and thicker respectively. These changes influenced the structure and properties of carbon foam. So as a result, with the viscosity increased, density and compressive strength of carbon foam increased.

3.2 SEM

SEM microphotographs of the carbon foam prepared with 0.37g/cm^3 bulk density were showed in Figure 1 .Form these SEM microphotographs，it can be seen that the texture of carbon foam was porous, reticulate and uniform. These SEM microphotographs also evidenced that the pore sizes of carbon foam were little and the pore size distribution was uniform and the average pore diameter of the carbon foam with 0.37g/cm^3 was approximate 0.1μm .

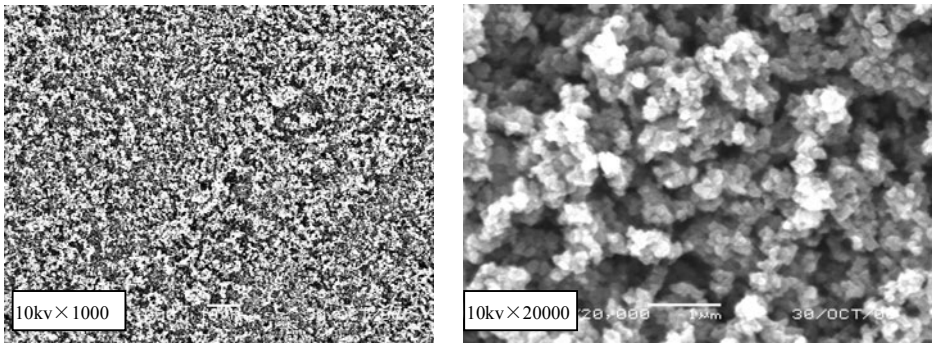

Fig1： SEM microphotographs of phenolic carbon foam with 0.37g/cm^3

3.3 Pore structure

The pore structure of carbon foams with 0.15 to 0.55 g/cm^3 were showed in figure 2.

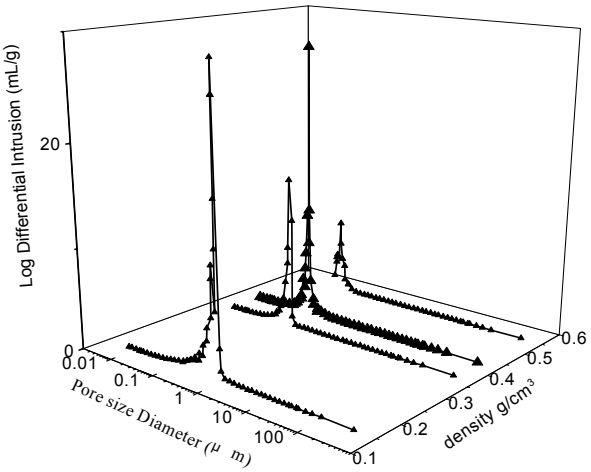

Fig 2: The pore texture of these carbon foams prepared

Figure 2 showed the pore texture of these carbon foams prepared from 0.15 to 0.55g/cm^3. From figure 2, it can be seen that pore sizes and pore distributions of these carbon foams. With bulk density increased, average pore size of these carbon foams decreased. The average pore diameter of all sample changed from 0.07μm to 1.50μm, and the pore distributions of all carbon foam samples were very uniform .When the density was 0.15g/cm3 , the most pore sizes were little and the average pore diameter was only 1.50μm, and with density increased the pore size changed more little and more uniform . From figure 2, it also be seen that around 99% pores of any one carbon foam distributed in a very narrow range, and there was little change in the pore size. Figure 1 and Figure 2 both explained that why the carbon foam with low bulk density relatively possessed a high strength .

3.4 Thermal property

The data of thermal properties of carbon foams with 0.15 to 0.55 g/cm^3 were showed in table 2 and the change curves of thermal diffusion coefficients of carbon foams with temperature changed from 25 to 300℃ were showed in figure 3.

Table 2: The thermal diffusion and thermal conduction coefficients of carbon foams at 25℃.

Sample	1	2	3	4	5
Density (g/cm^3)	0.15	0.23	0.37	0.43	0.55
Thermal diffusion coefficient (mm^2/s)	0.18	0.20	0.24	0.27	0.29
Thermal conduction coefficient(W/mK)	0.019	0.033	0.063	0.082	0.113

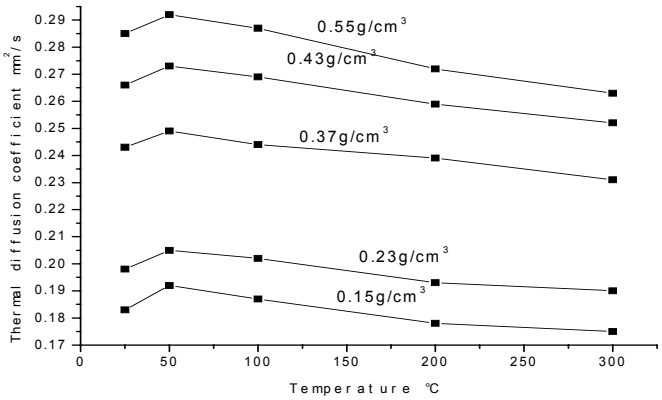

Fig 3: The changes of thermal diffusion coefficient of the carbon foams prepared with temperature change

Table 2 showed the thermal diffusion and thermal conduction coefficients of carbon foams at temperature 25℃ .Figure 3 showed the changes of thermal diffusion coefficient of the carbon foams prepared with various density from 0.15 to 0.55 g/cm^3

with temperature changed from 25 to 300℃. From Table 2 and Figure 3, it can be seen that the thermal property of carbon foam was closely related with density, and with density increased, the thermal diffusion and thermal conduction coefficients increased. And it also can be seen that the thermal diffusion coefficient of the sample with 0.15 g/cm^3 density was only 0.18mm^2/s and the thermal conduction coefficient of the same sample also was only 0.019 W/mK at 25℃, and when the density of sample was up to 0.55g/cm^3, the thermal diffusion coefficient and thermal conduction coefficient of the sample was up to 0.29 mm^2/s and 0.113 W/mK respectively . From Figure 3, it can be seen that with temperature increased, the thermal diffusion coefficients of carbon foam first increased and was up to maximum at 50℃ and then decreased , and all samples had same change trend. These data also showed that the thermal diffusion coefficients of carbon foams had little change with the temperature change from 25℃ to 300℃ and showed that the kind carbon foam had excellence thermal stability.

It is well known that, the thermal properties of carbon foam are closely relate with the pore microstructure. When density increased , pore size decreased and structure changed more compact. These changes decreased the heat convection and brought the increases of thermal diffusion coefficient . Form above tables and figures , a conclusion that the carbon foam derived form phenolic resin by using the process was a porous carbon material with excellent thermal insulation property can be obtained.

Conclusion

1) The concentration of phenolic resin is a important factor of influence on the structure and property of Carbon foam. By changing the concentration of phenolic resin in solution, a series of carbon foams with various structures and properties can be obtained.

2) The pore diameter of all carbon foam by this process was very little and the pore distribution was very uniform , and there was little change in the pore size of any one carbon foam .

3) Carbon foam derived from phenolic resin by using this process is a good insulation thermal carbon material with high strength, low density and excellence thermal insulation property.

Reference

[1] Ford W. Method of making cellular refractory thermal insulating material. US patent 3121050, 1964.

[2] Bruneton E，Tallaron C，Gras-Naulin N，et la．Evolution of the structure and mechanical behaviour of a carbon foam at very high temperatures[J]．Carbon，2002，40：1919～1927．

[3]Knop A,Seheib W. Chemistry and Applied of Phenolic Resins. NewYerk, Springer -Verlag, 1979

[4] dos Reis M J，Silverio F，Tronto J，et a1．[J]．J of Physics and Chemistry of Solids，2004，65：487-92．

[5] Shutov F A．Processing and Application of Phenolic Foams[J]．Cellular Polymers，1984，3(2)：94～95．
[6] Valgin V D．Study on Fire-resistant Phenolic Foams[J]．Euro-plastics Monthly，1973；46(7)：57～58．
[7]Kwon Y W ，Yoon S H，Sistare P J．Compressive failure of carbon-foam sandwich composites with holes and/or partial delamination [J]．Composite Structures，1997，38：573～580．
[8]Rode A V，Elliman R G，Gamaly E G，et la．Electronic and magnetic properties of carbon nanofoam produced by High-repetition-rate laser ablation[J]．Applied Surface Science, 2002, (197-198): 644～649．