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LETTER

Reducing the microcracks of mesophase-pitch-based carbon foams by long-time-coking method

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Carbon fiber-reinforced composites have existed for many years [1, 2]. They represent an attempt to incorporate the exceptional mechanical properties of carbon fiber into a polymer, metal, ceramic, carbon char or pitch matrix. The fibers act as the major load-bearing elements and the matrix serves to transfer load to the fiber network. Although this composite is attractive because its high performance, the carbon fiber-reinforced composite technology is limited by the complexity of the fabrication process and the expensive carbon fibers [3, 4]. Carbon foam derived from mesophase pitch precursor can be considered to be an interconnected network of graphitic ligaments or struts having the similar structure of carbon fiber, they represent a potential alternative for carbon fiber as a reinforcement in the structural composite [5]. The carbon fiber from mesophase pitch has been achieved [6], however the carbon foam appeared to be quite fragile. It is postulated that this may be caused by two reasons [7]: (1) the graphitic planes in the ligaments are not aligned along the length of the ligaments, and (2) the presence of defects especially the microcracks in both ligaments and junctions. In this letter, a long-time-coking method, to our best knowledge, was applied firstly for preparing the carbon foam and found that the microcracks were significantly reduced and the graphitic planes were highly aligned in both ligaments and junctions.

In this study, a Mitsubishi AR naphthalene-based synthetic mesophase pitch with a softening point of 275 °C was used as precursor and the stabilization methods of high temperature but short time [5], low temperature but long time and oxidization [8] were applied respectively to investigated the effects of different preparation methods on the microcracks of the carbon foams. In the experiment, the AR mesophase pitch powders were loaded in a mold and then the mold was placed in a stainless steel reactor which was pressured by nitrogen until the final pressure 1 MPa. The reactor was heated at a heating rate of 4 °C/min up to 460 °C and soaked for 1, 5, 7, 9, 11 h, respectively. The as-obtained green foams were carbonized at 1000 °C for 15 min, and named as CCF5, CCF7, CCF9, CCF11, respectively except the foams soaked 1 h which were oxidized prior to carbonization at the same carbonization conditions and named as OCF. In another separate cycle the reactor was heated at the same heating rate directly up to 550 °C and carbonized at the same conditions as above mentioned, the as-received carbon foams name as CCF550.

For comparison of the structures under optical microscopy, the as-obtained carbon foams were embedded in epoxy resin and then ground and polished according to usual method. The investigation of the obtained foam/resin bulks was carried out on a Nikon E600 POL polarized light microscope and typical micrographs were captured by an in-situ Nikon DXM1200 digital camera.

Figure 1 shows the optical micrographs of OCF and CCF550, as can be seen that both ligaments and junctions exhibit many microcracks and multicolored

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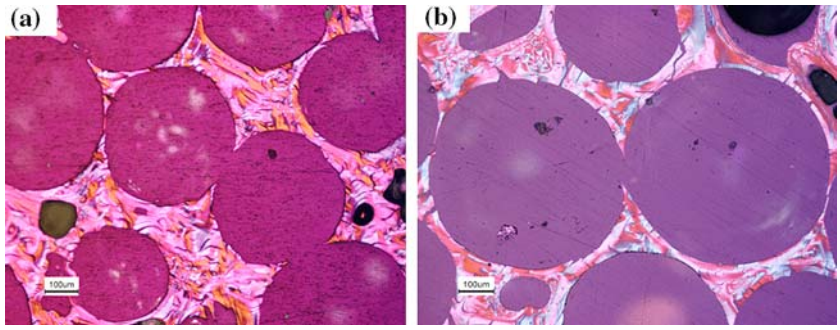

Fig. 1 Optical micrographs of (**a**) OCF; (**b**) CCF550

regions, and it is evident that the microcracks in monochromatic regions are significantly less than that in multicolored regions indicated by the Figs. 1a and 2d. So it is believed that the anisotropic thermal expansion coefficient of these multicolored regions is probably the reason of the microcracks. In the process for making OCF, because of the oxidization, the molecules of mesophase pitch were cross-linked and thus inhibited the rearrangements of the mesophase domains during subsequent carbonization confirmed by the multicoloured regions in the Fig. 1a. According to method developed by Klett [5], the pitch precursor can be heated directly to a high temperature and then got a sufficient coke, but the low-molecular-weight compounds reacted not sufficiently and were embedded in the parent precursor because of short holding time, and these compounds continuously evaporated during carbonization causing the microcracks indicated in the Fig. 1b.

The micrographs of carbon foams prepared by long-time-coking method are given in Fig. 2. These micrographs reveal that there are less microcracks in both ligaments and junctions as compared with those in the Fig. 1, and the graphitic planes are highly oriented parallel to the surface of the bubbles and along the axis of the ligaments, indicated by the large monochromatic regions in the Fig. 2d. The lack of oxidization and long holding time allow the mesophase domains to grow very large during processing, producing very large monochromatic regions in the foam. It is believed that the multicolored regions is caused by random orientation of the domains and these regions will serve to reduce the overall thermal conductivity and mechanical performance [9], but carbon foams prepared by long-time-coking method can develop large monochromatic regions and thus the performance will be significantly improved, experimental results listed in Table 1 show that the specific compressive strength of carbon foams soaked for 5 h and 11 h are 6.33 MPa and 11.38 MPa, respectively. It should be noted that the deformation of the spherical bubbles may be caused by the long holding time.

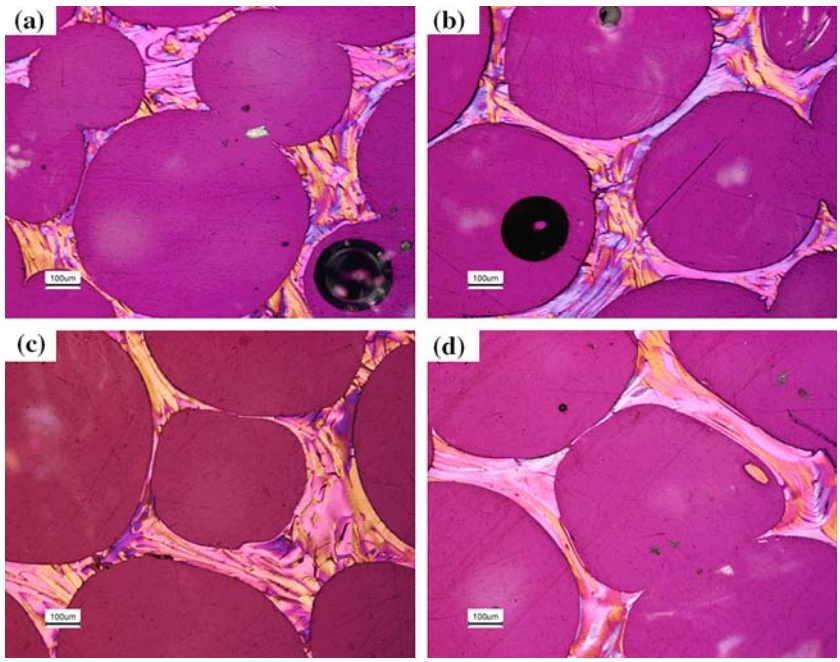

Fig. 2 Optical micrographs of (**a**) CCF5; (**b**) CCF7; (**c**) CCF9; (**d**) CCF11

Table 1 Properties of carbon foams prepared under different conditions

Properties	OCF	CCF550	CCF5	CCF7	CCF9	CCF11
Bulk density (g/cm^3)	0.350	0.213	0.224	0.243	0.270	0.219
Specific compressive strength[a] (MPa)	6.57	7.30	6.33	6.74	7.87	11.38

[a] Specific compressive strength defined as Compressive strength divided by Bulk density

From above analyses, it can be considered that the long-time-coking method is effective for improving the performance of mesophase-pitch-based carbon foams. After comparing the micrographs in Figs. 1 and 2, a conclusion can be drawn that carbon foam prepared by long-time-coking-method exhibit few microcracks and highly aligned graphitic structure, and this method can be used effectively for preparing pitch-based carbon materials.

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