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The effect of zirconium addition on the microstructure and properties of chopped carbon fiber/carbon composites

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Abstract

Carbon/carbon composites containing zirconium were prepared using chopped carbon fiber, mesophase pitch and Zr powder by the traditional process including molding, carbonization, densification and graphitization. The influence of Zr on the microstructure and properties of the composites were investigated. Results show that Zr can improve the interface bonding, promote more perfect and larger crystallites and enhance the conductive/mechanical properties of the composites. The high in-plane thermal conductivity of 464 W/(m K) and excellent bending strength of 83.6 MPa was obtained for a Zr content of 13.9 wt% at heat treatment temperature(HTT) of 2500 °C. However the conductive/mechanical properties of the composites decrease dramatically for an higher HTT of 3000 °C. SEM micrograph of the fracture surface for the composites shows that lower disorder crystallite arrangement of fiber and carbon matrix come into being in the composites during HTT of 3000 °C, which should be responsible for the low properties. Correlation between the content of Zr and the microstructure and properties are discussed.

Keywords: Carbon/carbon composites; Mesophase pitch; Microstructure; Mechanical properties; Thermal conductivity

1. Introduction

Carbon/carbon (C/C) composites with high thermal conductivity have been one of attractive candidates for heat dissipation with sufficient development of high thermal conductivity fiber [1]. At present, C/C composites with high thermal conductivity have been extensively studied by using ultra high thermal conductivity fiber such as vapor grown carbon fiber (VGCF) and mesophase pitch-based continuous carbon fiber as reinforcement [2–4]. But these fibers are expensive, and with continuous fiber that need woven or knitted, which will add complexity and cost on the fabrication of C/C composites. These limited their application widely.

Considering the comparatively cheap of short fibers, and C/C composites with it have simple fabricated process and low price, chopped carbon fiber/carbon composites with high in-plane thermal conductivity at room temperature have been developed in our previous work using 6 mm mesophase pitch-based carbon fiber as functional fiber, mesophase pitch as binder by a series of processes including molding process, carbonization, densification and graphitization [5]. But its highest thermal conductivity of 385 W/(m K) is low comparatively than the level reported in [2–4] .

Many carbon materials with high thermal conductivity are obtained by using starting materials that are readily graphitizable and by using as high a heat treatment temperature (HTT) as possible. Zr element can accelerate the graphitization of carbon and adding some amount of Zr in carbon can get higher degree of graphitization and higher thermal conductivity at a certain HTT [6,7], and also can improve bending strength and resistance to ablation properties [7,8]. However, there is less information to microstructure and properties of C/C composite with Zr additive.

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In the present work, chopped carbon fiber/carbon composites containing zirconium have been developed to obtain higher thermal conductivity and other better properties. Effects of Zr addition on the microstructure and thermal/mechanical properties of chopped carbon fiber/carbon composites with HTT of 2500 °C were described. The properties and microstructure of the composites were also investigated at higher HTT of 3000 °C.

2. Experimental

2.1. Fabrication of C/C composites containing zirconium

Dialead K223SE chopped mesophase pitch-based carbon fiber (produced by Mitsubishi Chemical Co. diameter 11 μm, length 6 μm, thermal conductivity 20 W/(m K)) were dispersed in water with AR mesophase pitch powder (<150 μm, produced by Mitsubishi Gas Chemical Co., Inc. softening point 280 °C,anisotropic content 100%) and Zr powder(<100 μm) in exiting of the surface activity agent (the mass ratio of pitch to fiber was 0.8). Then, mixture was hot-molded under 50 MPa pressure at 300 °C. Next, molded samples were carbonized at 900 °C for 1 h in a nitrogen atmosphere to gain low density C/C composites. And then six general coal tar pitch impregnation/carbonization (PIC) cycles were performed on density C/C composites. Finally, all samples were treated at 2500 °C for 1 h. Basic compositions of the resulting materials see Table 1.

In order to investigate the influence of additive for the composites at higher temperature, some samples were treated at 3000 °C for 0.5 h.

2.2. properties testing and microstructure characterization

The density of the samples was determined on mass and geometry. Thermal conductivity at room temperature was measured by the thermal gradient method. The measuring method and the instrument is the same with the literature [9]. The electrical resistivity was determined by a DC four-probe method. The bending strength was tested by three-point bending method.

X-ray diffraction (XRD) patterns were obtained in X-ray diffractometer (Rigaku-D/maxγ-A, Cu Kα, $\lambda = 0.15418$ nm, 40 kV, 60 mA) and XRD crystalline parameters (d_{002}, g, La and Lc) of the composites were calculated by same formulas with [5], where d_{002} is the graphite interlayer spacing, g is the degree of graphitization, La is the average crystallite diameter and Lc is the average crystallite thickness.

Surface and fracture topography of the samples was observed by LEO438VP scanning electron microscopy (SEM). The particle size and distribution of the additive were determined using the E-contrast in the backscattered electrons (BE).

Table 1
Basic composition of C/C composites containing zirconium

Material (wt%)	CM-Z0	CM-Z5	CM-Z10	CM-Z15	CM-Z20
Zr raw additive	0	5	10	15	20
Zr content	0	3.5	7.1	10.8	13.9
Fiber content	40.8	39.7	38.6	36.9	33.7
Carbon matrix 1	26.4	27.1	25.0	24.1	21.7
Carbon matrix 2	32.8	29.7	29.3	28.2	30.7

Note: Carbon matrix 1 from mesophase pitch; carbon matrix 2 from coal-tar pitch.

3. Results and discussion

3.1. Effect of Zr on the microstructure of C/C composites (HTT of 2500 °C)

The study of preparation shows that Zr element almost has no loss during a series of processes including molding, carbonization, densification and graphitization.

XRD phase analysis (Fig. 1) demonstrates that Zr in the composites exists only in the form of zirconium carbide (ZrC), which is the same as in Zr-doping graphite [6–8].

From the BE images (Fig. 2), it can be seen that ZrC in the composites shows a uniform dispersion and their dimensions are sub-μm, and a large quantity ZrC will be formed and ZrC grain become larger with much addition of Zr.

Table 2 lists crystal parameters of C/C composites containing zirconium and also pure composites (CM-Z0) by the same process to understand the role of Zr. Compared with CM-Z0, the C/C composites containing Zr exhibit lower the graphite interlayer distance (d_{002}), higher the degree of graphitization (g) and larger crystallite size (La, Lc) in all case. A tendency of reduced d_{002} and increased g, La and Lc of the composites with increase of Zr concentration was also observed. These show that the microstructure of the composites transits to perfect graphite and Zr as the catalyst accelerates the graphitization of the carbon fiber and carbon matrix during the heat treatment at high temperatures. Fig. 3 shows the fracture morphology of

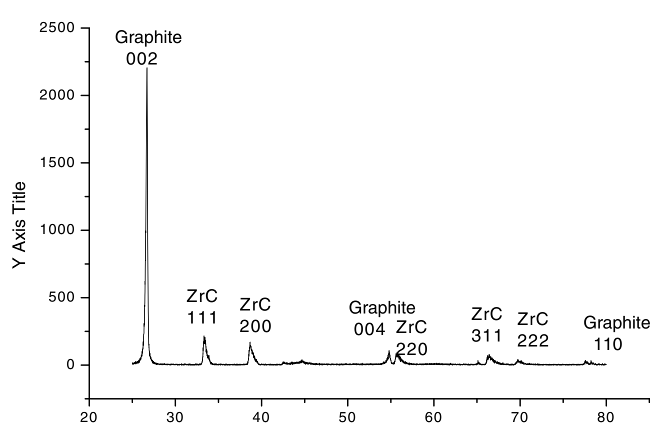

Fig. 1. XRD pattern of CM-Z20.