Carbon 114 (2017) 59–69

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Large diameter pitch-based graphite fiber reinforced unidirectional carbon/carbon composites with high thermal conductivity densified by chemical vapor infiltration

Xian Zhang [a, b], Xuanke Li [a, b, c, *], Guanming Yuan [b], Zhijun Dong [b], Guozhi Ma [c], Brian Rand [c, d]

[a] The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan, Hubei 430081, PR China
[b] The Hubei Province Key Laboratory of Coal Conversion & New Carbon Materials, Wuhan University of Science and Technology, Wuhan, Hubei 430081, PR China
[c] The Research Center for Advanced Carbon Materials, Hunan University, Changsha, Hunan 410082, PR China
[d] School of Mechanical, Aerospace and Civil Engineering, The University of Manchester, Manchester, M13 9PL, UK

ARTICLE INFO

Article history:
Received 22 July 2016
Received in revised form
25 November 2016
Accepted 29 November 2016
Available online 1 December 2016

ABSTRACT

Carbon/carbon (C/C) composites of high thermal conductivity have been prepared by chemical vapor infiltration (CVI) processing from novel graphite fibers of large diameter (~50 μm). The fibers bundles were used to fabricate two types of unidirectional cylindrical C/C composites by a CVI densifying process. One type was initially bonded with phenolic resin impregnation, cured, carbonized and graphitized before subsequent CVI densification (ICCG + CVI). In the second process the bundles were densified by CVI processing only. Both types of composite were further densified by secondary CVI treatment. The microstructure of the C/C composites and the relative contributions of fiber and matrix were investigated. The CVI matrix is highly crystalline and oriented around the fibers and, after secondary CVI treatment and graphitization, densities of the C/C composites prepared by the ICCG + CVI and CVI processes are 1.65 and 1.72 g/cm^3, respectively. The axial thermal conductivities of the two C/C composites are as high as 569 and 675 W/m K, respectively. Simple mixture rules have enabled the thermal conductivity of the CVI matrix itself to be estimated to be of the order of 1200 W/m K, consistent with the highly crystalline nature of this phase and significantly higher than that of the highly oriented large diameter fibers themselves.

1. Introduction

Carbon/carbon (C/C) composites are extensively used as thermo-structural materials, for instance, the friction material in aircraft brakes [1], nose-cones of ballistic missiles, leading edges in high-performance aerospace vehicles, turbine rotors, rocket engines and other high-temperature components [2,3]. Their key thermophysical and thermomechanical properties are low density, high specific strength, high specific modulus, high thermal conductivity, high temperature stability, low coefficient of thermal expansion, superior thermal shock resistance and corrosion resistance, excellent high-temperature friction and wear characteristics and biocompatibility [4–9].

With the development of aerospace industries and high power electronic devices, heat dissipation issues become more and more critical. C/C composites with high thermal conductivity are important thermal management materials [10–14] including heat sinks, heat exchangers and solar lenses in aircraft, phased-array antennae of space-based radar on satellites, compact electronic components in high-performance instrumentation chambers, and plasma facing components of fusion devices [15–17]. They are especially suitable for the applications that need to transfer heat along one specific orientation because of their anisotropic thermal conductivity. It is well known that the thermal conductivity of C/C composites is structure sensitive. The graphite crystal size, orientation, crystallinity and volume fractions of carbon fiber and matrix carbon as well as the architecture, voids and defects of the C/C composites, all have significant influence on the fundamental

* Corresponding author. The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan, Hubei 430081, PR China.
E-mail address: xkli8524@sina.com (X. Li).

http://dx.doi.org/10.1016/j.carbon.2016.11.080
0008-6223/

thermal performance of the C/C composites [18–23]. Mesophase pitch-based fibers possess high thermal and electrical conductivity and are often the preferred reinforcement with either mesophase derived or CVI matrices [11,24–29]. Thermal conductivities as high as 890 W/m K were developed from ribbon shaped fibers of high conductivity and a mesophase matrix but these ribbons are relatively fragile when graphitized [30]. It was shown by Lu et al. [31] that large diameter round fibers (~50 μm) could show higher graphitizability than the common small diameter ones due to a lower degree of oxidative stabilization in the central core which allows some relaxation and the development of increased 'in-plane' coherence length which is so critical to the thermal conductivity [32].

The purpose of this study is to investigate the potential of such fibers for the production of unidirectional C/C composites of high axial thermal conductivity. It was decided to use CVI processing as the method of densifying the composite as this matrix can be highly graphitizing also. It is also well known [33–35] that the pyrolytic carbon and graphite so deposited can align well with the fibers and should contribute significantly to the unidirectional properties of the composite. An estimate of the relative contributions of fiber and matrix to the overall composite thermal conductivity is made here using simple mixture rules. Finally, it is often common to use a phenolic resin based carbon to rigidise the fiber preform prior to CVI carbon deposition and here we compare the composites produced with and without this prior treatment.

2. Experimental

2.1. Raw materials

A commercial naphthalene-derived mesophase pitch produced by Mitsubishi Gas Chemical Corporation was directly used as a raw material to produce the pitch fibers by melt spinning. The mesophase pitch has 100% anisotropic content, a softening point of 265 °C and a high carbon yield of about 80% (heat-treated under nitrogen atmosphere at 900 °C for 3 h). Liquid phenolic resin purchased from Shanghai East China University of Science and Technology was used as the impregnating agent to initially densify some of the graphite fiber bundles.

Molten mesophase pitch was extruded through a spinneret with 20 holes of 450 μm diameter under pressurized nitrogen of 0.2 MPa at a spinning temperature of 320–330 °C, and the extrudates were then drawn through a winding drum at rotational speed of 40 m/min controlled by a servo motor to form round-shaped pitch fibers.

The as-spun pitch fibers were stabilized at 220–240 °C in an O_2 atmosphere for 10 h at a flow rate of 200 ml/min. The stabilized fibers have a slightly higher carbonization yield of about 84%, in comparison to that of mesophase pitch. The obtained stabilized fibers were subsequently heat-treated to 1000 °C for 1 h under a N_2 atmosphere and then were heat-treated at 3000 °C in an Ar atmosphere to acquire highly oriented graphite fibers with the diameter of about 50 μm. The graphitized fibers with a large diameter were used as the raw material for the preparation of the C/C composite.

2.2. Preparation of one-dimensional cylindrical C/C composites

One-dimensional cylindrical C/C composites with a resin/CVI matrix, the ICCG + CVI process, were produced as follows: Firstly, the graphite fiber bundles with bulk density of around 1.02 g/cm^3 tied with nylon cable were impregnated with liquid phenolic resin under vacuum and subsequently solidified at 150 °C for 0.5 h. The impregnation and solidification processes were repeated 8–10 times and then the cylindrical C/C composite was carbonized in the crucible furnace to 1000 °C (Fig. 1a). Subsequently, the C/C composites were heat-treated at 3000 °C for 15 min and polished to remove the phenolic resin carbon (PRC) from both the outside of the longitudinal plane and the two ends of the C/C composites. Finally, the C/C composites with a density of about 1.27 g/cm^3 were further densified by a CVI treatment and subsequent carbonization at 1000 °C for 1 h followed by graphitization at 3000 °C for 15 min to produce the sample with the density of 1.48 g/cm^3 as shown in Fig. 1b. The CVI process was performed at a temperature range of 950–1000 °C for a long period using propene as the carbon precursor gas and nitrogen as the carrier gas at a volumetric ratio of about 1:3 [36].

One-dimensional cylindrical C/C composites were also produced by a direct CVI process, i.e., without prior impregnation by phenolic resin. The graphite fiber rods were first tightened by nylon cable ties, which were then gradually replaced by T300-3k PAN-based carbon fiber bundles. The prepared fiber rods (shown in Fig. 2a), with bulk density of about 1.09 g/cm^3, were densified by the CVI process. The cylindrical C/C composites prepared by the first CVI treatment are shown in Fig. 2b. After graphitization treatment at 3000 °C for 15 min, the T300-3k fiber shells were peeled off to obtain the cylindrical C/C composites as shown in Fig. 2c. The average density of the graphitized C/C composites prepared by this CVI process is 1.60 g/cm^3.

In order to explore the influence of secondary CVI densification, the C/C composite products prepared by the ICCG + CVI and CVI processes were polished to remove external pyrolytic carbon (PyC) and open the closed pores at the surface of the products. They were then densified again by a secondary CVI treatment, carbonized at 1000 °C and graphitized at 3000 °C. The average bulk densities of the C/C composites prepared by the ICCG + 2CVI process and the 2CVI process are 1.65 and 1.72 g/cm^3, respectively.

2.3. Characterization of the unidirectional cylindrical C/C composites

The C/C composite specimens were made into a size of 10 × 10 × 4 mm by cutting and polishing along both the longitudinal and transversal directions. XRD structural analyses and the thermal diffusivity measurement were both performed along the two directions. The textural diagram of the as-prepared test specimen from the one-dimensional C/C composite is shown in Fig. 3.

The structural preferred orientation was determined by X-ray diffraction (XRD, Philips X ′ Pert MPD Pro, Holland) analysis using Cu K_α radiation (λ = 1.54056 Å) at an accelerating voltage and applied current of 40 kV and 30 mA, respectively. Microstructure, morphology, and texture of the C/C composites were imaged with a NOVA 400 NANO field emission scanning electron microscope (SEM) and a Carl Zeiss AX10 polarized light microscope (PLM) in

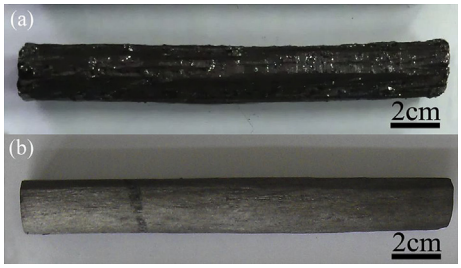

Fig. 1. The optical photographs of the graphite fiber rods, (a) after impregnation with fluid phenolic resin and curing at 150 °C for 0.5 h, (b) after CVI process and heat treatment at 3000 °C for 15 min. (A colour version of this figure can be viewed online.)