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Oxidation kinetics and mechanisms of carbon/carbon composites and their components in water vapour at high temperatures

Fei Qin *, Li-na Peng, Guo-qiang He, Jiang Li, Yong Yan

Science and Technology on Combustion, Internal Flow and Thermal-structure Laboratory, Northwestern Polytechnical University, Xi'an, Shaanxi 710072, PR China

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ABSTRACT

Thermogravimetric analysis and scanning electron microscopy were used to study the oxidation kinetics of four-direction carbon/carbon composites and their components (fibres and matrices) in a H_2O–Ar atmosphere at high temperatures. The oxidation processes were restricted to reaction-limited oxidation. The rate of mass loss was estimated for the four-direction carbon/carbon composites and their components at high temperature. The pressure exponent for the reaction of the carbon/carbon composites with H_2O was 0.59, and the pre-exponential factor and activation energy for the reactions of H_2O with the carbon/carbon composites, carbon fibres and matrices were determined.

1. Introduction

The advantages of carbon/carbon (C/C) composites, such as light weight, high specific strength and modulus, remarkable thermal stability and excellent thermal shock resistance, have resulted in their increased application in rocket nozzles, thermal protective systems for re-entry vehicles, supersonic aircraft nosetips and airplane brake disks [1–3]. In these applications, C/C composites often experience oxidation in oxidizing atmospheres at high temperatures, which causes a sharp degradation of the performance. The use of C/C composites in industrial applications is limited because of their increased sensitivity to oxidative environments. Therefore, numerous investigations have been performed to determine methods to protect C/C composites against oxidation [4–6].

Recently, the oxidation behaviour of C/C composites has been experimentally characterized in numerous reports [7–15], which focus on the oxidation process, recession rate measurements and oxidation morphology. However, the oxidation kinetics of C/C composites remains a complex problem in which kinetics parameters play an important role. Libby and Blake [16] studied the oxidation of solid carbon particles in a H_2O and CO_2 atmosphere at high temperatures and obtained the reaction kinetics parameters through experimentation and theoretical calculation. Chelliah et al. [17] used graphite to conduct oxidation tests at high temperatures and obtained the kinetics parameters for the oxidation of $C_{(s)}$ and H_2O. Fuller et al. [18] obtained the activation energy for the reaction between C/C composites and H_2O at temperatures ranging from 800 to 1300 °C. Opila [19] studied the pressure exponent for the reaction between T-300 fibres and water vapour, which was limited by the chemical reaction and mass transfer. Guo et al. [20] performed an oxidation test on a 2D C/C composites in air at temperatures ranging from 745 °C to 900 °C and obtained the kinetics parameters for oxidation at low and high temperatures. Lachaud et al. [21] obtained the intrinsic reactivities of C/C composites, carbon fibres and matrices in air at 625 °C. Opeka et al. [22] obtained that the vapor pressure considerations provide significant insight into the relatively good oxidation resistance of ZrB_2- and HfB_2-based ceramic materials at 2000 °C and above. Chen et al. [23] performed an oxidation test on C/SiC composites by oxy-acetylene flame with the temperature of 2900 and 3550 °C, and the main oxidation behaviour was obtained. Zou et al. [24] obtained a heterogeneous microstructure of C_f/ZrC composites by X-ray diffraction, scanning electron microscopy, electron backscattering diffraction, and transmission electron microscopy.

Many researchers have performed reactions between air and C/C composites. However, the oxidation kinetics and oxidation mechanisms of reactions between water vapour and C/C composites at high temperatures are required for propulsion systems and the re-entry of spacecraft. The oxidation behaviour and kinetics of four-direction C/C composites and their components (fibres and matrices) in a H_2O–Ar atmosphere were explored in this study. The oxidation morphology and microstructure, as well as the oxidation mechanism of the C/C composites are analyzed and discussed.

* Corresponding author at: School of Astronautics, Northwestern Polytechnical University, Xi'an, Shaanxi 710072, PR China. Tel./fax: +86 29 88494163.
E-mail address: qinfei@nwpu.edu.cn (F. Qin).

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2. Experimental

2.1. Materials

Uncoated 4D C/C composites and their components were investigated in this study. The reinforcements were T300 PAN-based carbon fibres, and coal-tar pitch was used as the precursor to form the matrix. The same four-direction composites preform was used as previously described in Refs. [22,23]. The structural features of this preform are listed in Fig. 1. Carbon fibres that were 2.0 mm wide and 0.6 mm thick were preformed into hexagonal shapes with three directional axes, *W*, *X* and *Y*, which were aligned along the same plane at 120°. The preform was impregnated with coal-tar pitch before heat treatment and subjected to a series of densification cycles, which included high-pressure impregnation, carbonization and graphitization, to achieve the desired density (1.93–1.94 g cm^{-3}). Details of the heat treatment process are provided in [24].

2.2. Sample preparation

In this study, a C/C composites sample was processed into a cuboid with dimensions of 30 mm × 9 mm × 9 mm.

The fibre was assumed to be an isotropic and homogeneous material with a larger specific surface area than the C/C composites. The carbon fibres were tightly bundled to avoid being oxidated completely before the oxidation test temperature has reached its maximum temperature. In this experiment, seven bundles of T300 3 K PAN-based carbon fibres with a total length of 253 mm were folded twice and fixed. Then the carbon fibres were suspended in the oxidation reactor for the oxidation test. The number of fibres in each cross-section was calculated to be 2.73×10^6 per square centimetre. A large amount of closely arranged carbon fibres formed a columnar structure. During oxidation, only the surface of the fibre bundle contacts the oxidizing gas. An electron microscope was used to observe the post-test sample and a decrease in the diameter of the carbon fibre on the sample surface was found. No significant change in the diameter of the inner fibre was observed. This result suggests that under the experimental test conditions, the diffusion of the oxidizing gas inside the sample is negligible. Therefore, the recession of the carbon fibre sample caused by oxidation was assumed to be along the radial direction of the cylinder.

The matrix is an important component of C/C composites. To obtain the kinetics parameters for the reaction of the matrix with the oxidizing gas, the matrix must first be separated from the C/C composites. After analyzing the C/C composite, the dimensions of the matrix were determined to be approximately 1 mm × 1 mm × 2 mm. Because the fibre bundle is tightly connected to the matrix, it is extremely difficult to keep the matrix intact while separating the fibres from the composites with conventional tools. Therefore, a substitute matrix material was used in this experiment that was prepared by the same process of fabricating the C/C composites. This material was produced by impregnation, high pressure carbonization and a high temperature treatment followed by pitch impregnation that was performed at a moderately high temperature. To obtain a large bulk matrix for the C/C composite, the impregnation and carbonization cycle was repeated three to five times followed by graphitization. Because only a small extent of oxidation was observed during the test, the oxidized surface area was assumed to remain constant.

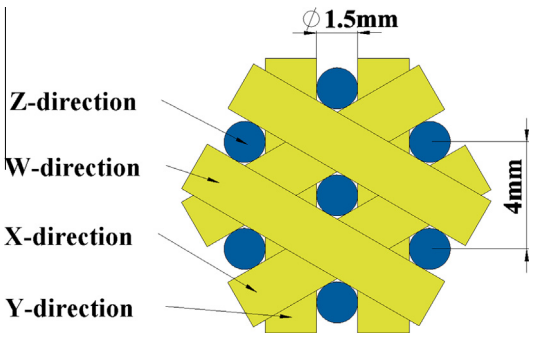

Fig. 1. Diagram of the four-direction C/C composites preform.

2.3. Oxidation test

The objective of this work was to investigate the oxidation reaction of the C/C composites under a high-temperature water vapour and Ar atmosphere. The reaction is written as follow:

$$C_{(s)} + H_2O \leftrightarrow CO + H_2 \tag{1}$$

A thermogravimetric analysis (TGA) reactor was used to conduct oxidation tests on samples containing different phases of carbon. The diagram of the equipment and the working process are shown in Fig. 2. A highly precise magnetic suspension balance with a precision as high as 1×10^{-5} g was installed at the top of the apparatus and used to weigh the samples during testing. The oxidation process should be quasistatic at each temperature, and the temperature of each sample should reach the specified maximum temperature at the minimum mass loss ratio. Therefore, a slow heating rate 5 °C min^{-1} was used.

Ar was injected into the furnace with the water vapour. The partial pressure of the water vapour was obtained as follows:

$$\frac{dV_{H_2O}}{dt} = \frac{P_t}{P_a - P_t}\frac{dV_{Ar}}{dt} \tag{2}$$

$$P_{H_2O} = \frac{\frac{dV_{H_2O}}{dt}}{\frac{dV_{H_2O}}{dt} + \frac{dV_{Ar}}{dt} + \frac{dV'_{Ar}}{dt}} P_a \tag{3}$$

where $\frac{dV_{H_2O}}{dt}$ is the water vapour flow rate, $\frac{dV_{Ar}}{dt}$ is the flow rate of Ar, which transported the water vapour, P_t is the saturated water vapour pressure, P_a is the atmospheric pressure, P_{H_2O} is the water vapour partial pressure and $\frac{dV'_{Ar}}{dt}$ is the flow rate of Ar that was used to adjust the water vapour partial pressure.

To obtain the pressure exponent of the reaction between the C/C composites and water vapour, experiments were performed using different water vapour partial pressures. To transport the water vapour, an Ar flow rate of 100 ml min^{-1} was used in each experiment. The flow rate of Ar was increased from 100 ml min^{-1} to 650 ml min^{-1} and used to adjust the partial pressure of the water vapour. To obtain the pressure exponent, the inner temperature of the furnace was 1100 °C and the range of water vapour partial pressures was controlled from 0.10 to 0.18 atm in the experiment.

To obtain the pre-exponential factor and activation energy of the C/C composite, fibre and matrix, experiments were performed under different operating conditions. The inner temperature of the furnace was ramped from 600 °C to 1400 °C for the oxidation tests of the C/C composites, fibre and bulk matrix. For the oxidation experiments of the C/C composites and its components, the water vapour partial pressure was 0.15 atm.

By controlling the water vapour partial pressure, flow rate and reaction surface area of the samples during testing, a maximum value for the second Damköhler number (*Da*) of 9.23×10^{-4} was attained. *Da* is defined as follows:

$$Da = \frac{\delta_c k}{D} \tag{4}$$