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New insights into the early stages of thermal oxidation of carbon/carbon composites using electrochemical methods

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ABSTRACT

Highly graphitic carbon/carbon (C/C) composites are susceptible to high temperature air oxidation, e.g., when they are employed in aircraft brakes, and yet little is understood about the initial stages of oxidation damage. The present work demonstrates, for the first time, that aqueous, room temperature, electrochemical methods can be used to understand the early stages of thermal oxidation of C/C composites after exposure to air at 300–700 °C. Electrochemistry is shown to be significantly more sensitive to detection of the initial changes in the C/C composite structure and the evolution of its surface area, as compared with traditional bench-top methods. Cyclic voltammetry experiments, carried out in sulfuric acid solutions, revealed that thermal corrosion initiates at temperatures as low as 400 °C, which is more than 200 °C lower than the temperature at which changes can be seen as both the carbon mass loss and pore volume increase in this work. Time-dependent potential scan rate data and AC impedance analysis have revealed new insights into the evolution of pores in these materials, demonstrating that the initial thermal corrosion process is dominated by the lengthening of pre-existing mesopores and micropores, rather than the formation of new pores.

1. Introduction

Carbon/carbon (C/C) composites are commonly employed as engineering materials because of their light weight, high temperature stability, thermal shock resistance, toughness, high specific strength, and high-speed friction characteristics [1–3]. A number of companies have taken advantage of these properties in the large volume production of aircraft wheel brake heat sinks. In particular, a high carbon density, along with a high degree of graphitization within the composite, is desirable because of the resulting increased strength, heat transfer rates, wear resistance [2,3] and oxidation resistance [4], and decreased uptake of water-born contaminants that decrease friction properties. However, to achieve good braking friction and an appropriate vibration response, the porosity of these materials should be closer to 7–17%.

High temperature oxidation, with the formation of CO and CO_2 gases and subsequent deterioration of the structural properties, is a particular concern for graphitic materials applied in aircraft and vehicle brakes [1–3,5], as well as in nuclear reactors [6]. The rate of oxidation of a C/C composite has a complex dependency on temperature, degree of graphitization, surface characteristics, surface area, pore structure, and pressure [4,6–9]. These rates have been reported to transit from surface controlled (kinetic) oxidation at lower temperatures, to pore diffusion controlled at intermediate temperatures, and to gas transport limited (thermal) at higher temperatures [10,11]. In all regimes, changing pore features, such as their density, length, and diameter, as well as surface roughness, will directly influence O_2 transport and reaction rates, and thus will influence the O_2 gradient within the C/C sample [11].

Although rapid, diffusion controlled oxidation of graphitic C/C composites will occur at >700 °C at atmospheric pressures [12,13], the oxidation of nanoporous carbons may show signs of diffusion control even down to 450 °C, as is reported during the thermal oxidation of glassy carbon [14]. In addition, the chemical nature of carbon surfaces changes due to the formation and loss of surface oxygen complexes at elevated temperatures [15]. Thus, improving the understanding of the nanostructural changes as a function of temperature is recognized as a significant challenge [10].

The thermal activation of carbon in the presence of oxidizing agents, such as CO_2, is often used to significantly increase their

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surface area and micropore volume for supercapacitor applications [16–19]. Thus, it is logical to assume that air oxidation of C/C composites may undergo a similar, but faster small pore evolution process, especially within tight pores, where slow mass transport of oxygen or of gas phase corrosion products could lead to a local build-up of CO and CO_2. For carbon capacitors in aqueous solutions, the nature of these small pores can be elucidated using gas sorption methods [16–23] and then correlated with electrochemically determined charge capacity [16,21–23]. Although quantifying this correlation can be difficult, partly as capacitive properties may depend on ion-pore and ion-wall interactions at the micropore scale [16,21,24], it is clear that electrochemistry is a very sensitive analytical tool for understanding the relative changes to a carbon pore structure, as well as for assessing the mass transport limitations that occur within the porous carbon structure.

In this work, we demonstrate, for the first time, that aqueous electrochemical methods can be used to assess the state of C/C composites that are composed of a graphitized, polyacrylonitrile (PAN)-derived fiber mesh, subsequently densified with repeated cycles of chemical vapour infiltrated (CVI) carbon, as a function of thermal oxidation conditions. Electrochemistry is demonstrated to be significantly more sensitive for detecting the initial changes to the C/C composite structure, especially as compared to traditional bench-top methods [13,25,26], allowing the evolution of the surface area to be monitored as the C/C composites are systematically thermally oxidized. Cyclic voltammetry studies of these materials in aqueous sulfuric acid solution after exposure to high temperature air showed that measurable thermal oxidation begins at temperatures as low as 400 °C, which is 200 °C lower than the temperature at which changes can be seen as both the carbon mass loss and pore volume increase in this work. It is also revealed that the initial thermal oxidation corrosion of C/C composite proceeds via the lengthening of pre-existing micropores/mesopores, rather than the development of new pores. Further oxidation at >500 °C continues by competition between the lengthening and widening of small pores, although the formation of completely new micropores/mesopores is also probable.

2. Experimental methods

2.1. Sample preparation

C/C composite samples consisted of graphitized, polyacrylonitrile (PAN) fiber mesh that were densified with three cycles of chemical vapour infiltrated (CVI) carbon and were then further partially graphitized under N_2 at 1800 °C, with the objective of obtaining a rough laminar microstructure for the CVI carbon matrix. Each 1/2″ × 1/2″ × 1/4″ sample was rinsed sequentially with deionized water, acetone, and absolute ethanol, and then dried at 80 °C for at least 48 h. All samples were then heat treated three times at 900 °C (3 °C min^{-1} ramp rate) for 2 h and finally at 900 °C for 1 h, all under flowing nitrogen. This was done so that each sample was conditioned using the same initial thermal history, leading to more consistent electrochemical analysis results.

The physical properties of these samples, determined prior to air oxidation, are given in Table 1, with 30 samples used for volume and size measurements, 27 samples for carbon density measurements, and 344 samples used in the mass and porosity measurements. The variation found among samples is mainly due to the graded porosity resulting from the manufacturing process. As mentioned in the introduction, many factors, such as the degree of graphitization and the texture of the carbon matrix, the defects in the C/C composite, gas flow, oxygen partial pressure, and temperature will all significantly influence the oxidation behavior of the C/C composite. Although all carbon composite samples studied in our work originated from one manufacturing batch and thus should be composed of identical materials, should have been manufactured under the same conditions, and have similar degrees of graphitization, these samples still have variable porosities and microstructures. Thus, in order to perform a meaningful comparison of thermal oxidation rates, we had to carefully limit the number of independent variables investigated. For this work, we chose the thermal oxidation temperature to be that variable and keep other factors the same, with emphasis on the early stages of thermal oxidation damage, as this is an issue that is not discussed well in the literature for graphitized and semi-graphitized carbons.

Table 1
Typical properties of the C/C composite samples.

Property (units)	Value (standard deviation)
Nominal size (cm)	1.263 (0.016) × 1.252 (0.021) × 0.635 (0.001)
Nominal volume (cm^3)	1.005 (0.018)
Mass (g)	1.6799 (0.0741)
Nominal density (g cm^{-3})	1.67 (0.05)
Porosity (%)[a]	15.78 (2.58)
Carbon density (g cm^{-3})[b]	1.995 (0.010)
Surface area (m^2 g^{-1})[c]	0.25
C (%)[d]	98.28
H (%)[d]	0.27
N (%)[d]	0.13
Residue (%)[d]	1.32
2θ/FWHM(002) (°)[e]	26.15/0.74
2θ/FWHM(100) (°)[e]	42.71/2.23
d (002) (Å)[e]	3.407
L_c (Å)[e]	111.01
L_a (Å)[e]	78.27

[a] Obtained using Archimedes method. Values ranged from *ca.* 11–22%.

[b] Helium pycnometry data.

[c] N_2 sorption (BET) data.

[d] From CHN elemental analysis.

[e] Calculated from the XRD patterns (not shown here) of a ground powder sample, based on the Scherrer equation. Interlayer spacing [d (002)] and apparent crystallite size [L] along the c-axis and a-axis are given, based on the 002 peak and K values of 0.91 and 1.84, respectively.

Thus, samples were thermally oxidized by placing them (with the smaller area side facing down) into a 9 cm × 1.8 cm × 1 cm deep alumina boat located on top of the 1 inch diameter tube furnace (Lindberg/Blue) K-type thermocouple, and then heating the assembly in stagnant laboratory air between room temperature and target oxidation temperatures of 300, 400, 500, 600, or 700 °C at a ramp rate of 3 °C min^{-1}. Each sample was held at the target oxidation temperature for 4 h and was subjected to only one thermal oxidation test, with multiple samples studied at each target temperature. Images of unoxidized and 700 °C thermally oxidized samples are shown in Fig. 1. No visible geometrical size changes were observed, and evidence of oxidation damage was difficult to discern by a low powered optical microscope.

2.2. Characterization

2.2.1. Structural methods

The mass of the C/C specimens, before and after thermal corrosion, was measured using a 4-digit analytical balance with a sensitivity of 0.1 mg. The corresponding porosities were determined using the Archimedes method and vacuum infiltration of absolute ethanol. The solid density of selected samples was determined using helium pycnometry (Micromeritics AccuPycII 1340). Gas sorption, before and after thermal corrosion, was carried out with an ASAP 2010 Micromeritics sorptometer. Due to the inherently low surface areas of these C/C samples, masses in the 4–6 g range were routinely analyzed, which required combining 3 to 4 samples from a given thermal oxidation temperature study. The