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O_2 erosion of graphite tile substrates

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Abstract

The removal of codeposited tritiated carbon films from the next generation of fusion reactors may rely on the use of baking in an O_2 environment to remove the films. In the present study, we have investigated the effect of baking in O_2 on graphite tile substrate materials. After baking five types of graphite in 2.1 kPa O_2 for 100 h at 623 K, no change in mass was observed. An upper limit on the erosion rate was calculated to be $\sim 4 \times 10^{-10}$ C/O_2, whereas the codeposited films obtained from tokamaks have erosion rates as high as 10^{-5} C/O_2. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The next generation of fusion reactors currently calls for the use of carbon-based materials for some plasma-facing components [1]. However, the use of carbon leads to tritium inventory issues related to the trapping of tritium in codeposited carbon/hydrogen layers formed on nearby surfaces [2]. Such layers must be removed regularly for safety and other considerations. One of the methods being considered for the removal of such films [2] is to heat surfaces to temperatures of 523–623 K in an environment of O_2 gas. The use of O_2 gas will allow the films to be removed from remote surfaces, not just those with a line of sight to the plasma chamber, and also will not be affected by magnetic fields. There is concern, however, that the substrate graphite tiles may also be eroded by the O_2 exposure. To answer this concern, we have exposed various types of graphite specimens (Union Carbide HPG99, Ringsdorff EK98, POCO AXF-5Q, UCAR ATJ and Dunlop 2D C/C) to O_2 at 623 K, and monitored the mass as a function of O_2 exposure time.

1.1. Review of graphite oxidation

A substantial body of literature is available on the oxidation of graphite exposed to air, pure O_2 gas and O_2 molecular beams. All of this work, however, has been done at temperatures >750 K, and thus is not of great value in estimating yields in tokamaks at temperatures closer to 600 K, but the results do put the measurements of the present study in perspective.

Difficulties exist in the comparison of results, as many types of experiments have been performed, and results have been presented in several different ways. Yields, C/O_2, are rarely given. In this report, we give yields normalized by the O_2 flux to the geometric surface. In some instances, erosion rates were related to the BET or other specific surface area, and it was necessary to convert areas.

The various sources uncovered in the course of this review are given in Table 1, and the yields are plotted in Fig. 1. The data tend to fall in two general regions, with a separation at ~1000 K. This form does not follow exactly the 'classical' three regions of erosion as identified in [3–5]; however, the middle region may be obscured by the scatter in the data. Above 1000 K, there is a relatively weak temperature dependence, with yields either increasing somewhat with increasing temperature [4–7], or having a maximum at ~1400 K [8–10]. The existence of a maximum in the erosion yield appears to be associated with the nature of the surface being oxi-

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Table 1
Published results on the thermo-oxidation of carbon materials in air or O_2 gas

Reference	Materials	Experimental technique	Temperature range	O_2 exposure	Yields reported as
Okada and Ikegawa [6]	Artificial graphites	Mass loss	973–2273 K	1 atmosphere air	$mg/cm^2/s$ (apparent surface area)
Duval [8]	Graphites and non-graphites	Cryo-condensation of CO_2 and CO converted to CO_2	1109–2100 K	$5 \times 10^{-5} - 3 \times 10^{-3}$ Torr O_2	CO/O_2 (geometric surface area)
Lang and Magnier [14]	Porous graphite	Differential CO and CO_2 infrared absorption measurements and Mass loss	893 K	Dry air	$g/m^2/h$ (BET area, BET area $= 0.56$–$3.1 m^2/g$)
Olander et al. [7,9]	Pyrolytic graphite (prism and basal planes), Union Carbide	Line-of-sight mass spectrometer	300–2375 K	O_2beam, 10^{16} O_2/cm^2s	Reaction probability, CO/O_2, CO_2/O_2
Rodriguez-Reinoso et al. [12]	Highly oriented pyrolytic graphite (Union Carbide)	Mass loss	973–1073 K	20 Torr O_2	$\mu m/min/cm^2$ (initial edge surface area)
Vietzke et al. [10]	Pyrolytic graphite Union Carbide HPG	Line-of-sight mass spectrometry	970–1570 K	O_2beam, 9×10^{15} O_2/cm^2s	CO/O_2
McKee [11]	C/C composite sheet	Mass loss	773–1273 K	Flowing air	$\mu m/cm^2/s$ (geometric surface area)
Bacos et al. [4,5]	2D C/C composite	Mass loss	1073–2273 K	Flowing air	g/g/s specific surface area $0.03 m^2/g$, (specific surface area)/(geometric surface area) ~ 660
Penzhorn et al. [13]	EK98 fine grain graphite Dunlop 2D C/C composite	Time to complete combustion	1053 K	Flowing air	mg/h
Davis and Haasz [18]	EK98 fine grain graphite HPG99 pyrolytic graphite	Mass loss	913–1033 K	1 atmosphere air	C/O_2 (geometric surface area)

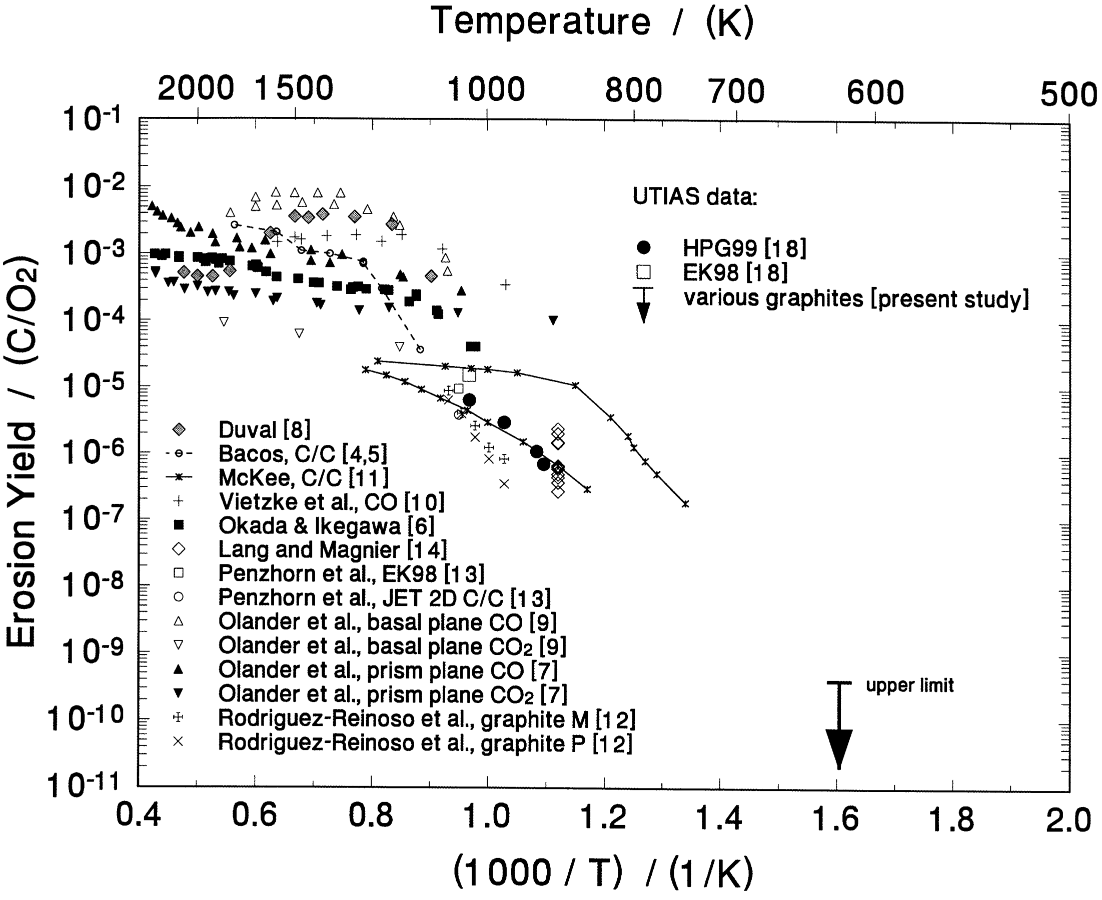

Fig. 1. Temperature dependence of the oxidation of various graphites.

dized; Olander et al. observed a maximum in the erosion yield for the basal plane [9], but not for the prism plane [7] of the same type of graphite. Other differences between the basal and prism planes were noted, such as differences in the relative amounts of CO and CO_2 produced [7,9]. Below 1000 K, the results tend to indicate a stronger temperature dependence [11,12], with the yields decreasing with decreasing temperature. The data of Penzhorn et al. [13] are of interest in that the two materials studied were also part of the present study.

Several reasons exist for the large spread in experimental results. Firstly, oxidation rates are quite sensitive to the type of graphite studied. For example, in the study of C/C composites by McKee [11], a large variation of yields (up to an order of magnitude) was observed, even for composites produced in a similar manner. Not surprisingly, a study by Lang and Magnier [14] on graphites with different BET surface areas gave results which also varied by an order of magnitude. Results on highly oriented pyrolytic graphite [12] tended to give the lowest yields. Yields were also found to be dependent on the O_2 pressure [8] or O_2 beam flux [7,9].

Some of the results by Olander et al. [7] require attention. Above 1000 K, their results tend to agree with the other high temperature studies [4–6,8,10]; however, the data point at 900 K, $Y \sim 10^{-4}$ CO_2/O_2, is very much out of place. Even more troubling is their report of a room temperature erosion yield of $\sim 10^{-5}$ CO/O_2. The authors in [7] believed this to be a true chemical reaction. If this is so, the observed unusually high yield could possibly be related to the use of an O_2 beam, where the beam molecules could be at a temperature (not stated in [7]) between 300 and 1200 K. The 10^{-5} value was also the limit of their sensitivity. In one particular case, the room temperature yield was measured to be 10^{-3} CO/O_2 (as high as the yield at 2000 K!), a value much larger than the system sensitivity, and also clearly related to the modulated O_2 beam. It was believed that this large yield was due to the contamination of the specimen with tungsten from the filament of the electron beam heater [7]. This may be a further indication that tungsten and carbon are a bad combination when oxygen exposure at elevated temperatures is a possibility. In the study of doped graphites by Chen et al. [15], the oxidation of a W-doped graphite in air proceeded at a rate much higher than that seen for other doped or pure graphites, and led to the rapid disintegration of the specimen.

All of the measurements found in the literature, except for the 300 K results of Olander et al., are at temperatures >750 K. This is well above the temperatures proposed for thermo-oxidation in tokamaks, thus providing the incentive for the present study.

2. Experiment

2.1. Graphite specimens

Five types of graphite were used in the study, and their properties are listed in Table 2. The specimens were cut in the shape of rectangular flat plates, with thicknesses ranging from 0.24 to 0.85 mm, and geometric surface areas ~250 mm^2. The specimens (except HPG99 which was exposed to O_2 as received) were prepared by sanding both sides with 600 grit emery paper, followed by polishing with ordinary white paper. Surfaces were blown with He to remove dust, and rinsed with ethanol. A polycrystalline tungsten foil of similar dimensions (but 25 μm thickness) was used as a reference, to guard against the possibility of spurious deposition or erosion processes.

2.2. O_2 exposure at 623 K

Specimens were placed in an ultrahigh vacuum (UHV) system on a stainless steel platform, which had been folded in an accordion shape so that both the top and bottom of the specimens would be exposed to O_2. The whole vacuum chamber was heated to 623 K by external heaters, and the temperature was measured by two copper–constantan thermocouples attached to flanges near the specimen holder. O_2 gas was admitted to the chamber, and held at 2.1 kPa for exposure times ranging from 10 to 50 h, with a cumulative exposure time of 100 h. The procedure for O_2 exposures was identical to that followed in our previous papers on the removal of tokamak films [16,17]. Prior to the O_2 exposures, the specimens were baked in vacuum for 5 h at 623 K to ensure that outgassing did not affect the weight loss measurements. Specimens were weighed before heating, after 1 and 5 h of outgassing, and after 10, 20, 50 and 100 h of O_2 exposure. Specimens were weighed on an Ohaus AP250D electronic balance with a sensitivity of 10 μg. Through repeated measurements, we have estimated the error for our measurements to be ±30 μg.

2.3. High temperature erosion measurements

As a part of some earlier experiments [15], we have measured the erosion of two types of graphite, HPG99 and EK98, when exposed to air at high temperature [18]. Specimens were heated in air either by direct current (data at 973 and 1033 K), or by an infrared spot heater (data at 913 and 923 K). For the direct current heating cases, the specimen temperature was measured by an infrared pyrometer. When the spot heater was used, the temperature was measured by a thermocouple. For these experiments, mass changes were measured with a Mettler AJ100 electronic balance with a sensitivity of 0.1 mg. Mass losses were 0.6–27 mg.

3. Results

The results of the present study, as well as the previous high temperature erosion yields [18] have also been plotted in Fig. 1. The data of [18] are consistent with other studies in the corresponding temperature range. In particular, the data point for EK98 at 1033 K [18] and that of Penzhorn et al. [13] agree very well. The temperature dependence of the HPG99 data [18] is also consistent with the range of literature values.

Table 2
Properties of graphite materials used in the present study

Name	Type	Manufacturer	Density (kg/m^3)	Size (mm^3)
HPG99	As-deposited pyrolytic graphite	Union Carbide Advanced Ceramics	2200	10 × 10 × 0.26
EK98	Fine grain isotropic graphite	Ringsdorff	1860	14.1 × 8.3 × 0.24
AXF-5Q TFTR	Fine grain isotropic graphite	POCO	1780	15.2 × 6.5 × 0.44
TS-1792 (ATJ) DIII-D	Fine grain isotropic graphite	UCAR	1760	11.9 × 11.3 × 0.52
JET Mark I divertor	2D carbon fibre reinforced graphite	Dunlop	(1870 measured)	10.7 × 10.5 × 0.85

Even after 100 h of O_2 exposure at 2.1 kPa, and 623 K, no changes in mass were observed on any of the graphite specimens used in the present study, or on the W-foil reference. Given the accuracy of the mass balance readings, ±30 μg, this gives an upper limit on the erosion yield of $\sim 4 \times 10^{-10}$ C/O_2, which is about three orders of magnitude lower than the next lowest published yield measurement shown in Fig. 1. The result appears to show reasonable consistency with an Arrhenius projection of the higher temperature results, see Fig. 1.

4. Summary

Graphite materials are readily oxidized when exposed to air or oxygen gas at temperatures above ~750 K; however, attempts to measure the oxidation rate at 623 K have not resulted in measurable erosion rates. With erosion yields as high as $\sim 10^{-5}$ C/O_2 for some tokamak codeposits [16], it should be possible to remove tritiated codeposited layers without removing significant amounts of the substrate graphite materials. It appears that the combination of tungsten with carbon may lead to substantially higher oxidation rates, an effect which needs to be further investigated.

Acknowledgements

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