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Journal of Nuclear Materials 337–339 (2005) 857–861

journal of nuclear materials

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Low-energy tritium ion erosion of graphite

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Abstract

Chemical erosion of pyrolytic graphite was measured over the temperature range 300–950 K, using a mass-analyzed tritium ion beam. The T_2^+ beam was produced by cycling 10 Ci (1 mg) of T_2 gas through the ion source from source getter to pumping getter and back. The T_2^+ beam current was up to 0.66 μA ($\sim 10^{18} T^+/m^2s$) at energies of 50–500 eV/T^+. Hydrocarbon formation rates were measured in the residual gas using quadrupole mass spectroscopy. C_xT_y hydrocarbon formation yields were similar to those obtained for H^+ and D^+ (0.002–0.1). As with H^+ and D^+, the T^+-induced yields at 200–250 eV/T^+ tend to peak at about 700–800 K, with a shift to lower temperature and flatter distributions at lower ion energies.

PACS: 28.52.Fa; 42.40.Hf; 79.20.Rf; 81.05.Uw
Keywords: Tritium; Chemical erosion; Carbon-based material; Erosion and deposition; Ion–surface interaction

1. Introduction

Graphite and other carbon-based materials are prime candidates for use as plasma-facing materials in the divertor of next-step fusion devices such as ITER [1]. It is important to be able to predict the rates of erosion by particle impact, since this may determine the component lifetime and the rate of tritium codeposition. While an extensive database exists for erosion of carbon due to H^+ and D^+ impact [2–9], there are no published data on chemical erosion by tritium, which will comprise half of the fuel in a fusion reactor. Tritium measurements are more difficult and more expensive to make because of the radioactive nature of tritium: safety and regulatory considerations place significant restrictions on experimental procedures and the available tritium supply (10 Ci = 1 mg = 370 GBq). The University of Toronto Tritium Laboratory [10] is an ultra-high vacuum facility equipped with a mass-analyzed low-energy ion gun suitable for T^+-impact erosion measurements.

Previous chemical erosion measurements in similar experiments with H^+ and D^+ [6,11,12] show relatively small isotopic effects (typically, the deuterium to hydrogen yield ratio is in the range 1.2 to 2). The general trends of yield vs. energy and yield vs. temperature were similar for bombardment by both H^+ and D^+ – with D^+-induced chemical erosion yields being up to two times higher under some energy-temperature conditions: e.g., 300 K graphite at <25 eV, or 600–800 K graphite at >50 eV [6]. Chemical sputtering by high plasma flux densities also revealed no significant isotope effect [13]. In contrast, mass-loss measurements suggest that the erosion yield at 300 K due to D^+ is up to five times greater than that of H^+, for energies <50 eV [8]. The reasons for this disagreement are still being debated [1,8].

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doi:10.1016/j.jnucmat.2004.09.050

Modeling suggests that components of chemical sputtering involving elastic-collision-induced bond breaking of precursors in the near surface might be expected to show higher erosion rates with higher incident ion masses [6,11,12]. This was approximated as a square-root of mass dependence, indicating that going from mass 2 (D) to mass 3 (T) should have a very small effect on chemical erosion yields.

The objective of the present study was to make the first ion beam measurements of chemical erosion yields for T^+ irradiation of graphite and assess the extent of isotopic effects on erosion by comparing the hydrocarbon yields for all three isotopes of hydrogen.

2. Experiment

2.1. Experimental facility: tritium laboratory

2.1.1. Ultra-high vacuum system

All experiments were performed in an ultra-high vacuum system equipped with three-stage pumping. The tritium source chambers and the gun's ion source chamber were pumped by zirconium alloy getters, type ST-172 (SAES Getters, USA); the deceleration lens stage, separated from the ion source by a 1 mm diameter aperture, was pumped with a CTI-100 cryopump; and the target chamber, separated from the deceleration lens stage by a 5 mm diameter aperture, was pumped by a 150 ℓ/s Leybold turbomolecular pump, backed by a scavenger getter to prevent loss of tritium through the pump exhaust. In addition, a scavenger getter was operated in the target chamber to keep the tritium pressure low enough for stable operation of the quadrupole mass spectrometer (QMS). The vacuum system is similar to the one described in more detail by Haasz and Youle [10]. The base pressure in the vacuum system was $<10^{-7}$ Pa after a 24 h bakeout at 400 K. The target chamber walls were then conditioned for 24 h in 10^{-2} Pa of H_2, in the presence of a hot tungsten filament, which created a flux of H atoms, leading to reductions of background H_2O and hydrocarbons.

2.1.2. Tritium ion gun

The ion source was an electron-impact extraction type (SPECS IQE 12/38) with a modified Wien filter to select the desired ion beam (see [6] for more detail). [Post T_2^+ irradiation thermal desorption of the specimen showed that the dominant desorption species were T_2 and CT_4, confirming that the beam was T_2^+, and was not contaminated with H.] The maximum T_2^+ beam current was obtained with an initial beam energy of 1000 eV. The ions were then decelerated in a five-element electrostatic lens, with transmission close to 100% for net beam energies of $>75\ \text{eV}/T_2^+$ ion. The beam spot size was about 3–4 mm in diameter, resulting in a flux density of $\sim10^{18} T^+/m^2\,s$ with 0.66 μA of T_2^+. Due to variations in the ion source plasma and beam optics, the ion energy had an uncertainty of ±10 eV (5 eV/T^+). Secondary electron suppression was accomplished by making the specimen the final element of the deceleration lens, with a bias ranging from 0 V (for net 1000 eV T_2^+) to +925 V (for net 75 eV T_2^+). The final aperture (at ground potential) before the specimen was larger than the beam diameter (5 mm vs. 3–4 mm), so that with careful steering of the ion beam, secondary electron emission from this aperture was minimal. In addition, the last lens element before the aperture was biased +400 to +500 V, and thus would attract secondary electrons produced on the upstream face of the aperture plate.

2.1.3. Graphite specimen

A single graphite specimen (as-deposited pyrolytic graphite, HPG99, by Union Carbide) was used for all experiments. This polycrystalline graphite exhibits both micro and macro porosity, has a mosaic spread of ~30°, and a density of 2200 kg/m^3. The specimen temperature was varied by resistive heating and was measured with an optical pyrometer, which was calibrated against a tungsten–rhenium thermocouple. Prior to the T_2^+ irradiation experiments the specimen was annealed in situ at 1150 K for 10 min.

2.1.4. Quadrupole mass spectroscopy

Chemical erosion during T_2^+ irradiation of graphite was measured by quadrupole mass spectroscopy. The QMS was a Leybold Transpector, set to monitor selected masses rather than the entire spectrum, in order to speed up data collection. The QMS was calibrated before and after the experiments with three calibrated leak bottles containing CH_4, C_2H_4 and C_3H_6. Other hydrocarbon yields were calibrated relative to these three using ratios determined in earlier experiments [14]. An additional calibration was performed on the same system with three calibrated leak bottles containing CD_4, C_2D_4 and C_3D_6, in order to measure isotope effects on the QMS sensitivity to hydrocarbons. It was found that the cracking patterns of H-hydrocarbons and D-hydrocarbons are the same, to better than 10%. However, the QMS is 1.67 times more sensitive to CD_4 than to CH_4, and 1.5 times more sensitive to C_3D_6 than to C_3H_6, but 1.8 times more sensitive to C_2H_4 than to C_2D_4. As a first approximation, the sensitivity to C_xT_y was taken to be the sensitivity to C_xD_y. This introduces some uncertainty into the absolute values of the yields, which we estimate as ± a factor of two for individual hydrocarbons (based on the above variations from H- to D-hydrocarbons) and ± a factor of 1.5 for the total erosion yield (since the comparison of H- and D-hydrocarbon sensitivities showed that some of the sensitivities were similar for both H and D, and some changed in opposite directions). The absolute yields for the six hydrocarbons measured (CT_4, C_2T_2, C_2T_4, C_2T_6, C_3T_6 and C_3T_8) were determined from the measured cracking patterns, relative sensitivities, and QMS signals at masses 21, 30, 33, 36, 39 and 51, as described in [11]. The uncertainty in the measurements is dominated by the uncertainty in projecting the deuterated hydrocarbon calibration to tritiated hydrocarbons.

It was observed that the QMS was no more affected by the T_2 background gas than it was by H_2: long exposure to either species slowly reduced the sensitivity of the electron multiplier, but it recovered after several months of outgassing. During the experiments the background T_2 pressure was kept as constant as possible in order to minimize QMS sensitivity changes. The uncertainty associated with this effect is estimated to be <10%. Since the QMS sensitivity was affected by the background pressure during the experiments, the leak-bottle calibrations were performed at similar pressures.

2.2. Experimental procedure

2.2.1. Tritium supply to the ion gun

The ion gun and the procedures for erosion measurements were similar to those used in [6], except for the added complexity of working with tritium. T_2 gas was fed into the ion source by heating up a 'source' getter to temperatures of 870–1170 K, at which temperatures the getter released absorbed T_2. After passing through the ion source, where the gas pressure was about 0.8 Pa, most of the T_2 was pumped by the 'pumping' getter. The 'pumping' getter was heated to about 570 K – warm enough to allow for rapid diffusion of tritium into the getter material, but cool enough to keep the partial pressure of T_2 (in equilibrium with the getter surface) low so that the getter would pump it. During each 10–70 min cycle, the 'source' getter temperature would be gradually raised in order to keep the T_2 pressure in the source near the point where the source would produce the maximum beam current, 0.66 μA of T_2^+ at 0.8 Pa. At the end of each cycle, the 'source' getter would be cooled to 570 K, the 'pumping' getter would be heated to 870 K, and valves would be closed or opened so as to switch the 'source' getter into 'pumping' getter mode, and vice versa. Unfortunately, with each cycle the getters would pick up some background H_2 gas, diluting the T_2. Furthermore, some of the T_2 would be pumped by the vacuum system walls, and some would be pumped onto the cryopump – leading to a gradual reduction of the available T_2. Some of the T_2 in the deceleration lens chamber would pass through the differential pumping aperture into the target chamber, where a turbomolecular pump and another pumping getter would keep the gas pressure just below the QMS operating limit of 1.3×10^{-3} Pa. At this pressure, the T_2 gas causes an increase in some of the QMS signals by up to a factor of two, so the calibrations with the leak bottles had to be performed with similar gas pressures.

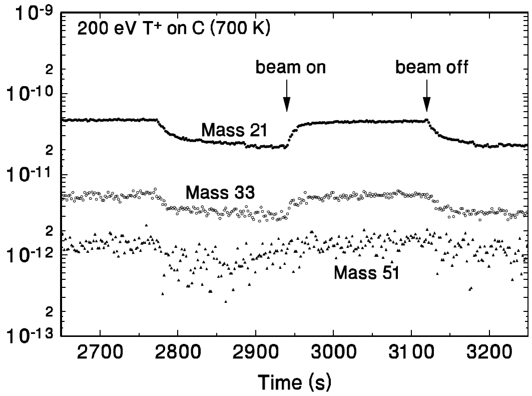

Fig. 1. Typical QMS trace of masses 21, 33, and 51, at 700 K for 400 nA of 400 eV T_2^+ (200 eV/T^+).

For each 10 Ci shipment of tritium, the ion source could be operated for up to 10 cycles before the amount of tritium on the source getter dropped to the point where the needed ion 'source' pressure could not be maintained. This amounted to about 6 h of cumulative operating time. Results from four tritium shipments are reported here. Typical QMS traces of three masses are shown in Fig. 1; the sharp steps are due to the T_2^+ beam being cycled on and off. The more gradual increases are due to increases in the 'source' getter temperature, causing the T_2 pressure (and the QMS signals) to increase.

2.2.2. Wall contribution to the QMS signals

The wall contribution is the portion of the signal due to the effects of reflected ions on hydrocarbon emissions from the target chamber walls. The total signal observed at any one mass (with the beam on the target) is the sum of the *background signal* + *the wall contribution* + *the true signal due to erosion of the specimen*. In this set of experiments the chamber walls were conditioned with hydrogen, and the wall contribution was primarily composed of C_xH_y molecules. This means that at several key masses, e.g., mass 21 (CT_3), mass 33 (C_2T_3) and mass 51 (C_3T_5), there was little or no wall contribution. [Note that the breakup of the CT_4, C_2T_4, etc., hydrocarbons in the QMS leads to the signals at masses 21, 33, etc., which were monitored and calibrated to obtain the erosion yields.] Over the 6-h run time possible with the 10 Ci load of T_2, this wall contribution did not appear to increase significantly due to the fact that the walls were already saturated with H-hydrocarbon precursors from conditioning with hydrogen atoms. However, the presence of H on the walls leads to the possibility that the tritiated hydrocarbons might exchange a T-atom for an H-atom during one of the many collisions with the wall between the time the tritiated hydrocarbon

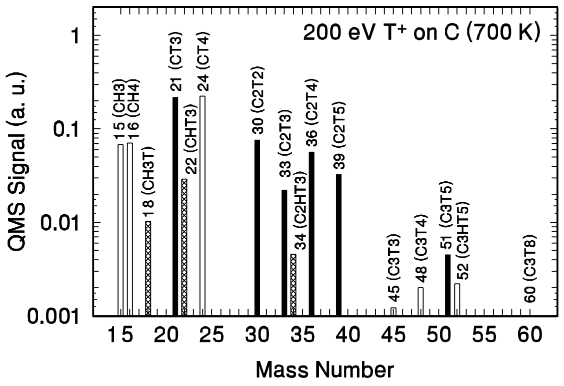

Fig. 2. Net QMS signals for 400 nA of 400 eV T_2^+ incident on graphite at 700 K, after subtracting the signals with the beam off. Solid bars indicate peaks that were used in the erosion yield analysis; hatched bars indicate peaks corresponding to mixed isotope hydrocarbons. The primary hydrocarbon associated with each peak is indicated.

was released from the specimen and when it was detected in the QMS; similarly, hydrocarbon radicals emitted from the specimen might pick up an H-atom during a collision with the wall. For this reason, we monitored several key masses which would indicate the presence of ‘mixed’ molecules: hydrocarbons containing both H and T atoms. The ratios of M22:M24 (CT_3H:CT_4) and M34:M36 (C_2T_3H: C_2T_4) were generally <0.2:1, indicating that the probability of mixed molecule generation was relatively small. Fig. 2 shows a partial spectrum of the net QMS signal (beam on – beam off) for 400 nA of 400 eV T_2^+ (200 eV/T^+) on graphite at 700 K.

3. Results and discussion

Fig. 3 shows hydrocarbon formation yields for 200 eV H^+, 200 eV D^+, and 200–250 eV T^+ impacting on graphite at temperatures of 300–950 K. The yields for H^+ and D^+ were adapted from [6]. [Here we refer to incident species as H^+, D^+, and T^+, even though the molecular ions are only singly charged.] The T^+ yields have larger scatter, but are generally similar to those for H^+ and D^+, both in terms of magnitude and the shape of the curve. Fig. 4 shows a temperature profile of the total chemical erosion yield (i.e., sum of the C atoms in the measured hydrocarbons) for 200–250 eV/T^+, compared to 200 eV/H^+ and 200 eV/D^+ yields from [6]. Within the scatter of the tritium data, the erosion yields are essentially the same for T^+ as for H^+ and D^+, with maximum yields around 700 K. One point at 700 K is much lower than the others, for no obvious reason. Within this scatter, the square root of 3/1 and 3/2 model prediction [12] for T vs. H and T vs. D isotopic effects, respectively, would not be discernible.

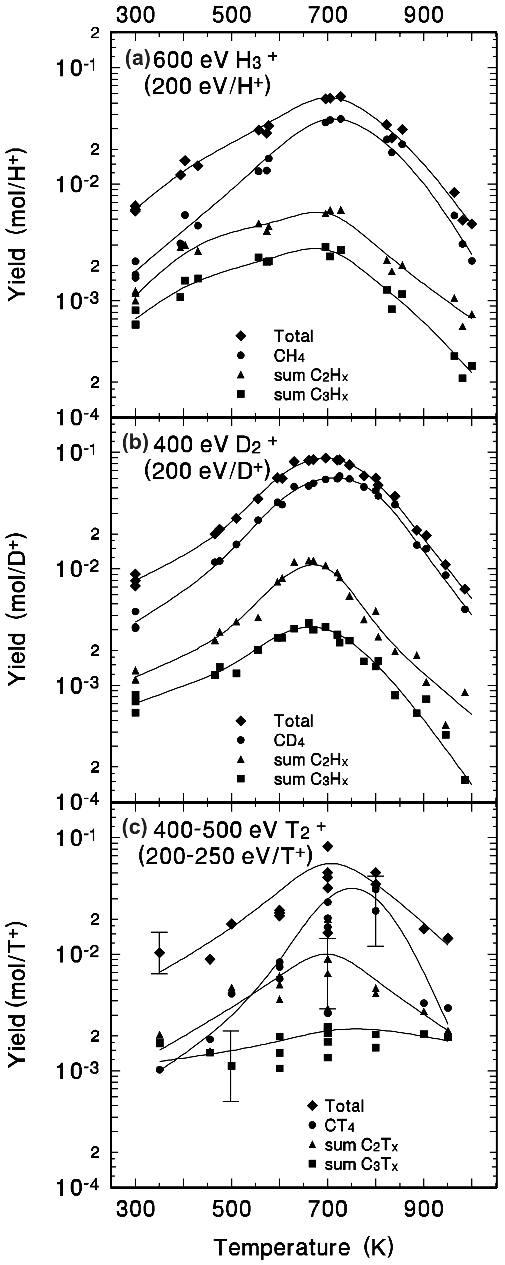

Fig. 3. Hydrocarbon yields as a function of graphite temperature for (a) H^+, (b) D^+ and (c) T^+; (a) and (b) are adapted from [6].

Erosion yields for T_2^+ impacting graphite at 600 K showed no discernable energy dependence (within the experimental uncertainty of about a factor of 2) over the energy range 50–500 eV/T^+; figure not included. In contrast, at 600 K Mech et al. [6] saw a slight increase of erosion yield with increasing ion energy for H^+ and D^+. Attempts to make measurements at lower energies (<50 eV/T^+) have not yet been successful, due to lower erosion yields and lower beam currents at these energies.

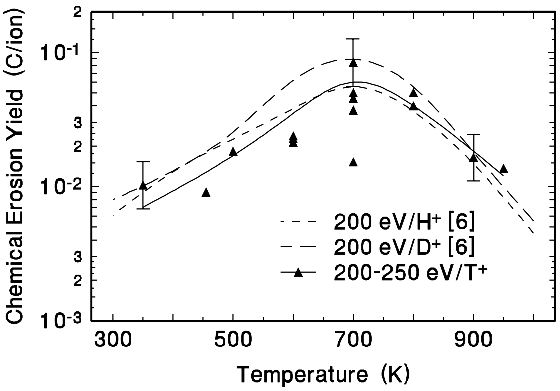

Fig. 4. Total chemical erosion yields (i.e., sum of the C atoms in the measured hydrocarbons) for H^+, D^+ [6] and the current T^+ measurements.

4. Conclusion

This study reports the first measurements of chemical erosion yields of graphite by mass-analyzed, low-energy tritium ions. The key conclusion is that the chemical erosion yields of graphite under H^+, D^+ and T^+ irradiation are very similar in magnitude and temperature dependence. Given the observed absence of a significant isotopic effect for H^+ and D^+ throughout the 10–200 eV energy range [6], and the observed similar yields for H^+, D^+, and T^+ at 200–250 eV, it is a reasonable assumption that no significant isotopic effect is expected for T^+ at energies of tens of eV; this assumption is also supported by the chemical erosion model of Mech et al. [12]. Consequently, the chemical erosion rates for hydrogen and deuterium provide reasonable estimates of carbon erosion due to tritium in a fusion reactor.

Acknowledgments

We gratefully acknowledge funding from the Natural Sciences and Engineering Research Council of Canada and the Canadian Fusion Fuels Technology Project (CFFTP). We thank Charles Perez of our Institute for his help with modifications to the tritium system. We also thank Ray Ilson and Sandu Sonoc of the University of Toronto and Kevin McCrimmon of Chalk River Nuclear Laboratories for their help with tritium safety issues and Gwen Keene and Lloyd Mathias of Ontario Power Generation for their help in obtaining tritium.

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