



ELSEVIER

Journal of Nuclear Materials 290–293 (2001) 158–161

Journal of
nuclear
materials

www.elsevier.nl/locate/jnucmat

Energy distributions of CD_4 and CD_3 chemically released from graphite by D^+ and D^0/Ne^+ impact

E. Vietzke *

Institut für Plasmaphysik, Forschungszentrum Jülich GmbH, Euratom Association, Trilateral Euregio Cluster, D-52425 Jülich, Germany

Abstract

Time-of-flight (TOF) experiments were performed to determine the energy distributions of CD_4 and CD_3 chemically released from graphite by energetic D^+ ion impact or by a synergistic reaction of Ne^+ ions and D atoms at temperatures near 800 K and room temperature (RT). The energy distribution of CD_4 chemically released from graphite at 800 K by 400 eV D^+ impact can be fitted by two Maxwell–Boltzmann (MB) distributions, one corresponding to the target temperature (800 K) and a faster one (40%) corresponding to 2000 K. In the synergistic reaction of D^0 atoms and 3 keV Ne^+ ions impacting on graphite at 830 K nearly all formed CD_3 are released by an MB distribution corresponding to 830 K. At room temperature, the time-dependent behavior of the CD_4 signal, after stopping the D^+ or the Ne^+ irradiation in the synergistic reaction case, indicates that no physical sputtering process is involved in this reaction. During synergistic reaction of graphite at room temperature with D^0/Ne^+ , the released CD_4 can be fitted by two MB distributions corresponding to 1200 and 285 K. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Carbon; Chemical erosion; Ion irradiation; Surface effects

1. Introduction

Graphite materials are candidates for parts of future fusion devices such as ITER. For an understanding and modeling of the impurity content and impurity transport in the plasma boundary of fusion devices the impurity sources have to be known. Of particular importance are the formation yields and the energy distribution of the released particles. The latter determines their penetration depth into the plasma. Furthermore, the energy distribution of chemically released hydrocarbons is important in identifying their formation mechanisms, which are key contributions to chemical erosion model development.

Chemical erosion of graphite has been studied in great detail under well-defined ion and atom beam conditions. Erosion yields have been accurately determined and the results have been reviewed [1–3] and tabulated [4]. Here, the discussion will be restricted to

the main reaction products, methane and the methyl radical. Two types of reactions have been identified in the chemical erosion of carbon by hydrogen ion bombardment (reviewed in [5]): a *thermal driven reaction* with yield maximum at 800 K and a *surface reaction* dominating at room temperature (RT) and low ion energies. A similar classification was also suggested for the synergistic reaction during simultaneous bombardment of graphite by energetic ions and atomic hydrogen, leading to CH_3 release via thermal reaction and CH_4 release via surface reaction [7]. Based on these results, the following model for the thermal reaction was suggested. Thermalized ions, reacting with open bonds at the implantation depth, form CH_3 which on its way to the surface captures an H to form CH_4 [6,7]. The mechanism of the first step in the thermal erosion process, i.e. the formation of CH_3 , was elucidated in detail by Horn et al. [8,9]. The second step in the thermal erosion process, the release process of CH_4 , has not yet been identified. In the thermal reaction, only a small dependence on the hydrogen isotope was observed [12].

In contrast, in the surface reaction a larger isotope effect has been seen [10,11]. It is interpreted as an

* Tel.: +49-2461 61 3113; fax: +49-2461 61 2660.

E-mail address: e.vietzke@fz-juelich.de (E. Vietzke).

ion-induced desorption process analogous to physical sputtering of CH_3 from $\text{CH}_3\text{-C}$ complexes of the hydrogenated graphite surface [5,12].

This observation was the main motivation to perform the present study to provide a better understanding of the reaction processes. Energy distributions of chemically eroded molecules have only been published so far for CO from graphite and BO from B_4C during O^+ irradiations [13]. Here, time-of-flight results are presented for the energy distribution of chemically released CD_4 and CD_3 from graphite by energetic D^+ impact or by a synergistic reaction due to Ne^+ and D^0 atoms for both types of reactions mentioned above.

2. Experimental

The time-of-flight (TOF) results were obtained in a beam apparatus, using line-of-sight mass spectrometry and mechanical chopping of the emitted hydrocarbons from the target. Details of the experimental set-up and data evaluation are described in previous papers on TOF measurements [13,14]. In brief, specimens (3 mm wide, 0.2 mm thick and 50 mm long) were bombarded by deuterium ion beam at 60° incident angle with respect to the normal or simultaneously by neon ion beam at 0° incidence combined with a deuterium atom beam under 45° incident angle. Beam energies and fluxes were: 1.2 keV D_3^+ and $1.8 \times 10^{19} \text{ D}^+/\text{m}^2 \text{ s}$; 3 and 5 keV Ne^+ and $2 \times 10^{19} \text{ Ne}^+/\text{m}^2 \text{ s}$; 2500 K ($\approx 0.22 \text{ eV}$) D^0 and $3 \times 10^{19} \text{ D}^0/\text{m}^2 \text{ s}$. The ion beam was not mass selected; 78% of the ions were D_3^+ , i.e. 86% of single D's were ejected in form of D_3^+ . For the '50 eV D^+ ' results, a 1.2 keV D_3^+ beam was decelerated by a target potential of +1050 V with a flux of $5\text{--}9 \times 10^{18} \text{ D}^+/\text{m}^2 \text{ s}$.

The emitted particles were periodically chopped by a motor-driven disk with a trapezoidal transmission pulse (HWFMT = 13 μs , repetition time 700 μs) and were directly detected after a flight path of $s = 15 \text{ cm}$ by a differentially pumped line-of-sight quadrupole mass spectrometer (QMS) aligned at 90° with respect to the incident atom beam direction.

As mentioned in [13], the ratio of the reemitted fluxes of two Maxwell–Boltzmann distributions can be directly derived from the ratio of the TOF maxima values (within 2% for the distribution used here).

3. Results

3.1. Thermal reaction at around 800 K

Fig. 1 shows the TOF spectrum of CD_4 formed in the reaction of 400 eV D^+ with graphite at 800 K. A broad distribution is observed clearly above the thermal distribution with respect to the target temperature. This

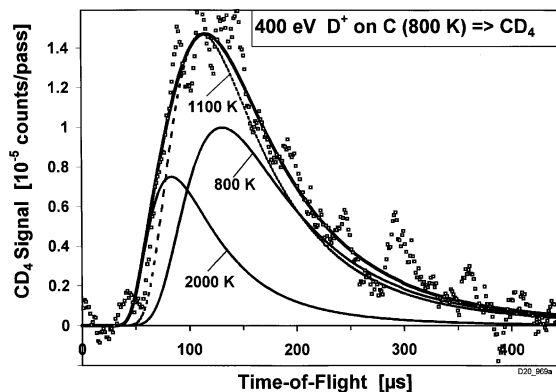


Fig. 1. Time-of-flight spectrum of CD_4 released from graphite at 800 K by 400 eV D^+ bombardment. Thin lines are calculated MB distributions at the given temperatures, and the thick one is the sum of the two calculated distributions. The TOF spectrum of CD_4 was fitted to two MB distributions for 800 and 2000 K. The dashed line is an MB distribution at 1100 K, shown for comparison only.

TOF spectrum cannot be fitted by a single Maxwell–Boltzmann (MB) nor by a sputter [15] distribution. A good fit is obtained by using two MB distributions at 2000 K and T_{target} ; 40% of the emitted CD_4 is associated with the 2000 K temperature.

Fig. 2 shows the TOF spectrum of CD_3 , the main reaction product in the synergistic reaction of D^0 and 3 keV Ne^+ with graphite at 830 K. The TOF spectrum is nearly fitted by an MB distribution at the target temperature, together with a small component ($\approx 10\%$ of flux) at 2000 K. No correction was made for the cracking of CD_4 since this yield at 830 K is smaller than 3% of the CD_3 yield [6].

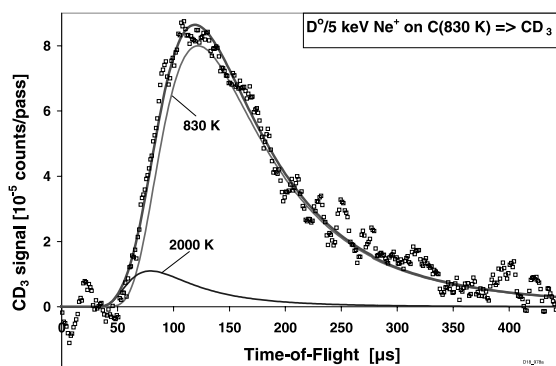


Fig. 2. Time-of-flight spectrum of CD_3 released from graphite at 830 K by $\text{D}^0/3 \text{ keV Ne}^+$ bombardment. Thin lines are calculated MB distributions for the given temperatures, and the thick one is the sum of the two calculated distributions.

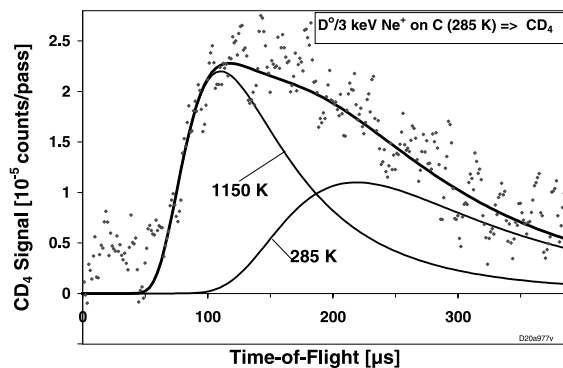


Fig. 3. Time-of-flight spectrum of CD_4 released from graphite at room temperature by $\text{D}^0/3 \text{ keV Ne}^+$ bombardment. Thin lines are calculated MB distributions for the given temperatures, and the thick one is the sum of the calculated distributions.

3.2. Surface reaction at room temperature

Fig. 3 shows the TOF spectrum of CD_4 from the synergistic surface reaction D^0 and 3 keV Ne^+ on graphite at 285 K. No sputter distribution is observed. The TOF spectrum can be fitted by two MB distributions at 1150 and 285 K. Although the TOF spectrum of CD_4 from the 50 eV D^+ irradiation of graphite at 285 K was very noisy, it seemed to be similar to the one in Fig. 3.

Further information on both of these surface reactions can be obtained from the time traces of the CD_4 QMS signal after stopping the ion irradiation. In Fig. 4

the results of many sequences are seen, whereby in each sequence the ion irradiation was on for 100 ms and off for 100 ms. The restart of the ion irradiation in the next sequence occurs always at time zero. In Fig. 4(b) the D_2 reemission is also shown. The steady-state reemission level of D_2 is reached very fast, implying that the deuterium concentration in the sample surface is not the reason for the slow build up of the conditions causing the formation of CD_4 . The same time trace of the CD_4 signal is seen – clearly in the opposite direction – by stopping the ion irradiation. Interesting for the question whether the surface reaction is a physical sputtering process of $\text{CH}_3\text{-C}$ complexes is the behavior of the CD_4 signal directly after stopping the ion irradiation. This part is seen in the inserts of the figures where the time scale is magnified. No abrupt decrease of the CD_4 occurs as expected from physical sputtering and as it has been seen for BO from the reaction of O^+ on B_4C [13]. The CD_4 signal decreases with time constants of 8 and 39 ms in Fig. 4(a) and 4 and 19 ms in Fig. 4(b), respectively. It should be added that no CD_3 is formed in the reaction of 50 eV D^+ on graphite at 285 K.

4. Discussion and conclusions

In modeling chemical erosion in fusion devices, mostly a thermal distribution with respect to the target temperature of the formed hydrocarbons is assumed. This would imply only a minor error for the thermal reactions since the average temperature in Fig. 1 is $\approx 1100 \text{ K}$ for a target temperature of 800 K. However,

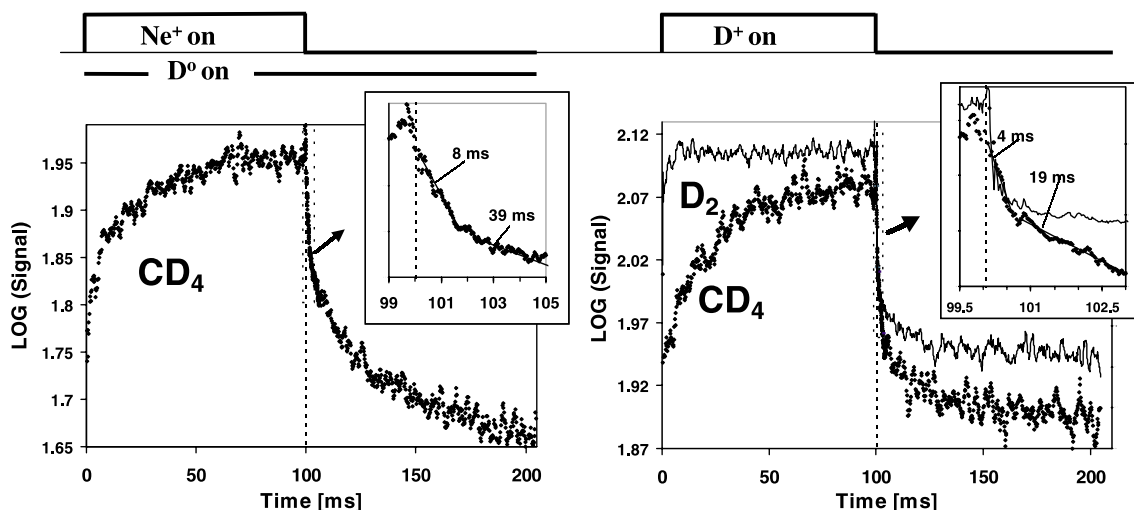


Fig. 4. The logarithm of the CD_4 QMS signals of many sequences, as a function of time, from graphite at room temperature irradiated by $\text{D}^0/3 \text{ keV Ne}^+$ (left) and 50 eV D^+ (right), whereby in each sequence the ion irradiation was on for 100 ms and off for 100 ms. The D^0 bombardment was continuously on. The inserts, magnified in time, show the decrease of the signals and the time constants subsequent to ion irradiations.

much more important for the quantitative modeling of the chemical erosion is the fact that *the surface reaction is not a sputtering process*. Even if only a binding energy of 1 eV is assumed as mentioned in [5] the average velocity of the hydrocarbons would be four times larger than the superthermal component in Fig. 3.

What are the implications of the new findings for the understanding of the reaction process itself? The first step in the thermal reaction at around 800 K, the thermal release of CD₃, is in complete agreement with the present results. In the synergistic reaction shown in Fig. 3, nearly all CD₃ formed at the surface are released with an MB distribution of the target temperature. For the D⁺ ion reaction at ≈800 K (Fig. 1) there are two processes involved with the final product CD₄ [6]. In a first step, CD₃ thermally formed at the implantation depth will adsorb at internal surfaces. The second step, the release of CD₄ from the CD₃ adsorbed complex is not quite clear. It seems that it is an ion-induced effect but not a physical sputtering process since the energy distribution has no sputtering component and the emission continues even after the ion irradiation is stopped [6]. Presumably, this ion-induced effect is due to the creation of defects followed by an annealing with the CD₃ adsorption complexes. A detailed mechanism explaining the release of such components with slightly overthermal energy is not available.

The second step in the D⁺ ion reaction case seems to be also the main reaction channel for the surface reaction at room temperature. First, the reaction product is CD₄ even for the Ne⁺/D⁰ synergistic reaction case at the surface. As seen in Fig. 4, a special structure has to be continuously formed to reach the high reactivity, probably by formation of more soft a-C:D films in the presence of atomic D. Both mentioned effects, the creation of defects resulting in a release of CD₄ and the formation of soft a-C:D films, depend on radiation damage and would explain the isotope effect in the surface reaction by low energetic H⁺ and D⁺. The increase in the reactivity at the restart of the ion pulses seen in Fig. 4 is very surprising since such a surface is strongly hydrogenated. As previously shown [16], such a surface irradiated at room temperature is very reactive if it is exposed to atomic hydrogen at a temperature of 700 K.

If the interferences drawn above are all valid, then the energy distributions of the released CD₄ should be the same during and after stopping the ion bombardment. Verification of this remains to be done which will require a more sophisticated experiment.

In conclusion, for the irradiating species and their respective energies, the ion-induced release mechanism in

the *thermally driven ion reaction* and that in the *surface reactions* seems to be the same one. Only the first step in the thermally driven reaction is different in the two cases.

An important question remains: Is the surface reaction process flux dependent, and if so, what are the consequences for the chemical erosion at high flux densities?

Acknowledgements

The assistance in performing the experiments of Philipp Schlömer and Dejan Jolovic is greatly appreciated. The author also thanks Dr V. Philipps for many useful discussions.

References

- [1] J. Roth, E. Vietzke, A.A. Haasz, *Suppl. Nucl. Fus.* 1 (1991) 63.
- [2] E. Vietzke, A.A. Haasz, Chemical erosion, in: W. Hofer, J. Roth (Eds.), *Physical Processes of the Interaction of Fusion Plasmas with Solids*, Academic, New York, 1996, p. 135.
- [3] J.W. Davies, A.A. Haasz, *J. Nucl. Mater.* 241–243 (1997) 37.
- [4] A.A. Haasz, J.A. Stephens, E. Vietzke, W. Eckstein, J.W. Davis, Y. Hirooka, Particle-Induced Erosion of Be, C, and W in Fusion Plasmas in: R.K. Janev (Ed.), *Atomic and Plasma-Material Interaction Data for Fusion*, vol. 7A, IAEA, Vienna, 1998.
- [5] J. Roth, *J. Nucl. Mater.* 266–269 (1999) 51.
- [6] E. Vietzke, K. Flaskamp, V. Philipps, *J. Nucl. Mater.* 128–129 (1984) 545.
- [7] J. Roth, J. Bohdansky, *Appl. Phys. Lett.* 51 (1987) 964.
- [8] A. Horn, A. Schenk, J. Biener et al., *Chem. Phys. Lett.* 231 (1994) 193.
- [9] M. Wittmann, J. K üppers, *J. Nucl. Mater.* 227 (1996) 186.
- [10] J. Roth, J. Bohdansky, *Nucl. Instrum. and Meth. B* 23 (1987) 549.
- [11] B.V. Mech, A.A. Haasz, J.W. Davis, *J. Nucl. Mater.* 255 (1998) 153.
- [12] B.V. Mech, A.A. Haasz, J.W. Davis, *J. Appl. Phys.* 84 (1998) 1655.
- [13] E. Vietzke, A. Refke, V. Philipps, M. Hennes, *J. Nucl. Mater.* 220–222 (1995) 249.
- [14] E. Vietzke, A. Refke, V. Philipps, M. Hennes, *J. Nucl. Mater.* 241–243 (1997) 810.
- [15] M.W. Thompson, *Philos. Mag.* 18 (1968) 377.
- [16] E. Vietzke, V. Philipps, K. Flaskamp, *J. Nucl. Mater.* 162–164 (1989) 898.