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New weight-loss measurements of the chemical erosion yields of carbon materials under hydrogen ion bombardment

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Abstract

Total erosion yields of graphite and carbon materials under hydrogen and deuterium bombardment measured with the weight-loss method are presented for ion energies between 15 eV and 8 keV in the temperature range 300 to above 1000 K. The temperature of the maximum of the chemical erosion increases from below 600 to above 850 K with ion energies from 15 to 300 eV. Chemical erosion yields obtained by weight-loss measurements exceed yields measured mass-spectrometrically always by a factor of about two. Collector experiments show that a fraction of the eroded particle sticks to walls and, therefore, reduces the yield measured by mass spectrometry. A synergistic effect of neutrals in the ion beam on the chemical erosion yield can be excluded. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Graphite and carbon materials are widely used as plasma facing materials in today's thermonuclear fusion experiments due to their superior thermo-mechanical properties and the low radiation of carbon ions from the central plasma. Major disadvantages of carbon materials are, however, the high chemical reactivity of carbon with energetic hydrogen ions leading to large erosion and the ability of carbon to trap hydrogen, especially in codeposited layers [1]. Therefore, in the most recent ITER design [1] the use of carbon is restricted to surface areas of extreme heat loading, such as divertor plates and protection limiters. But for transient events like disruptions, carbon materials appear to be substituted by any other material for the divertor plates.

The main processes of the chemical erosion seem to be understood [2–8]. Models for describing the erosion of carbon by hydrogen isotopes exist [4–7] even if some aspects are still under discussion, e.g., the flux dependence [7].

In this paper, we focus on another open aspect: Why are erosion yields obtained from weight-loss measurements larger than those obtained from the hydrocarbon production measured by mass spectrometry? Different explanations are discussed as for example the influence of fast neutrals in the decelerated ion beam, of the usage of D_3^+ instead of D^+ ions or the reduced detection probability of the eroded particles (e.g., radicals) in mass spectrometry due to wall collisions and sticking. For different hydrocarbon radicals the surface loss probability β is reported to vary widely between zero and unity, e.g., for CH_3 and C_2H the values of β are $\ll 0.01$ and 0.9, respectively [9–12].

We present new data of the temperature dependence of the total erosion yield measured by the weight-loss method for ion energies between 15 and 300 eV in the temperature range 300 to above 1000 K. Also a collection of new and published data is given showing the ion impact energy dependence of the yield for hydrogen and deuterium bombardment at room temperature and of the maximum yield of the temperature dependence. In addition, collector measurements and experiments were made with a suppressed amount of neutrals.

2. Experimental

The erosion measurements were performed at the Garching high current ion source [13] which was

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adjusted to produce mass-separated ion beams of D_3^+ and H_3^+ in the energy range 1–8 keV (mainly 3 keV). These ions were slowed down by biasing the target to the chosen impact energy. D^+ and H^+ were used for the high ion energies up to 8 keV. For all total yield data presented here the ion beam hit the surface perpendicularly (incident angle = 0°). The bombardment spot had sizes between 0.3 and 0.8 cm^2 depending on the impact energy. The ion current decreased from above 120 μA for high ion energies (>1 keV per D) to 40–80 μA for impact energies above 150 eV D_3^+ down to about 20–40 μA at the minimum impact energy of 45 eV D_3^+. This corresponds to flux densities of about $1–6 \times 10^{19}$ D m^{-2} s^{-1}. For H bombardment the ion current was always higher than for D corresponding to flux densities of about $4–8 \times 10^{19}$ H m^{-2} s^{-1}.

The total erosion yield was determined by measuring the weight loss in situ with a Mettler vacuum-microbalance (sensitivity ±1 μg) and the total ion charge. In order to get the temperature dependence of the total yield the targets were heated (up to 1200 K) by electron bombardment from the rear. The temperature was controlled by an infrared pyrometer.

The amount of neutrals in the beam, not decelerated by the target bias, was determined by measuring the weight loss of a gold target at 60 eV deuterium impact energy (180 eV D_3^+). Gold is only eroded by physical sputtering and the deuterium impact energy of 60 eV is below the threshold for physical sputtering of gold [13]. Therefore, the measured weight loss can be assigned to the physical sputtering of the neutral deuterium atoms of 1 keV, which provides a flux of about 3% of the ion flux with the knowledge of their yield. This value is in very good agreement with a previous determination measuring the secondary electrons emitted inside a Faraday cup [14]. The neutrals in the beam are mainly produced in the outlet of the magnet area before they pass through the target bias. Thus, by aligning the ion beam of the chosen mass not only with the magnetic deflection, but also with an additional electrostatic deflection, the amount of the neutrals hitting the target could be reduced below the detection limit of about 0.3%. Due to this alignment the ion current and correspondingly the flux density, decreased to about one-half of the usually obtained value. This alignment was used for some total yield measurements on graphite.

The chemical erosion yields versus the target temperature were obtained by measuring the methane mass signal (CD_4) in the residual gas with a quadrupole mass spectrometer. During ion bombardment the target temperature was increased in steps and held for 6 min to ensure steady-state conditions. In order to obtain the chemical erosion yields, the CD_4 signals were calibrated for all target temperatures and impact energies with the same factor. This factor was gained by setting the maximal CD_4 signal (around 850 K) of the temperature dependence at 1 keV deuterium bombardment equal to the chemical erosion yield of 0.1. This yield of 0.1 was determined from the weight-loss measurement subtracting the physical sputtering part [4,5]. In doing this, the contributions of heavier hydrocarbons (C_xH_y, $x > 1$) are considered as they are produced at 1 keV. But the changes of the ratio of heavier hydrocarbons to methane with ion impact energy and target temperature are neglected [15,16]. The published ratios from different laboratories vary between 0.2 and 1 for 1 keV deuterium bombardment at around 800 K [16,17]. For lower energies, ratios above 2 were reported [16]. Additional to the heavier hydrocarbons, changes in the amount of emitted radicals have to be kept in mind.

Pyrolytic graphite of Union Carbide with the surface parallel to the graphite planes was used as target for most of the presented measurements. A fine-grain graphite (EK76, Ringsdorff) was used as target material for the 50 eV weight-loss data in Figs. 1 and 2. The yields from a broad variety of graphite's and carbon materials [13] are specially marked in Fig. 3.

Additional measurements were done using the collector technique. As collectors, strips of papyex graphite (Le Carbon-Lorraine, Ref. No. 497-30121) with an aluminium layer of about 800 nm thickness were used. They were placed circularly around the target. The pyrolytic graphite target was bombarded with 30 and 50 eV deuterium (90/150 eV D_3^+). The physically sputtered and chemically eroded particles as well as reflected deuterium reached the collectors and created detectable a-C:D layers. These layers were analysed with MeV ion beam techniques. The amount of deposited carbon was measured using proton enhanced backscattering (PES) of 1.735 MeV protons (cross-sections, see [18,19]). The amount of deuterium was measured with 0.79 MeV ^3He ions using the nuclear reaction $D(^3He,p)^4He$. More details of the experimental set-up can be found in [13,19,20].

3. Results and discussion

3.1. Temperature dependence of the erosion yields

In Fig. 1, the discrepancy between the chemical erosion yields obtained from weight-loss measurements and CD_4 production are shown for 50, 100 and 200 eV. The contribution of physical sputtering calculated with the revised Bohdansky formula [4,5,22] has been subtracted from the weight-loss data. The chemical erosion yields obtained from the CD_4 production are much lesser than 50% of those from the weight-loss measurements and include the contribution of heavier hydrocarbons as they occur at 1 keV. In order to take into account the increased contribution of heavier hydrocarbons at lower energies [15,16], the yields have to be scaled by a factor 2

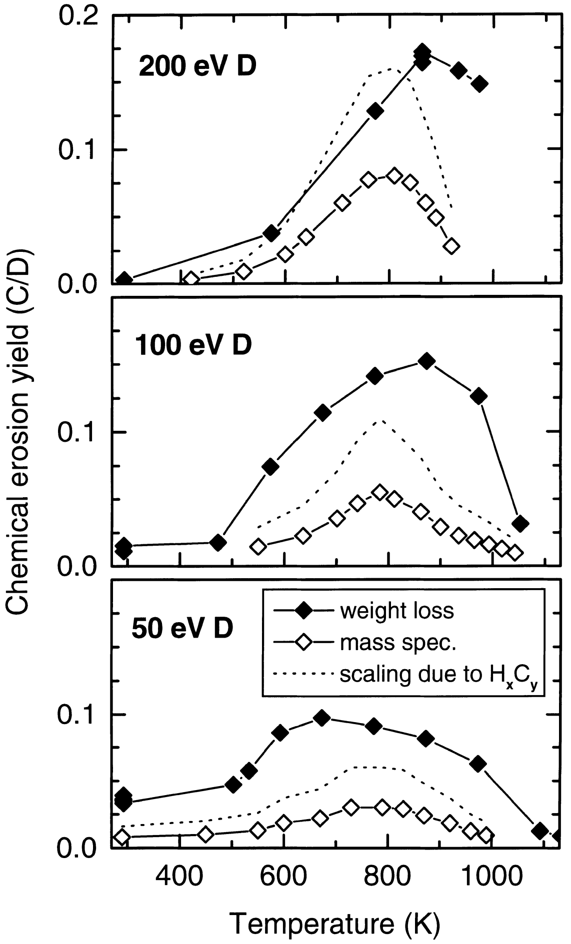

Fig. 1. Temperature dependence of the chemical erosion yield of D on C obtained by measuring weight loss (filled) and CD_4 production (open, calibrated to a yield of 0.1 for 1 keV) at flux densities of 1–6 × 10^{-19} m^{-2} s^{-1} and at normal incidence (new and published data [21]). The increased contribution of heavier hydrocarbons for deuterium impact energies below 1 keV are taken into account by approximate scaling of the mass spectrometry data with a factor 2 (dashed lines). Note that physical sputtering [4,5,22] has been subtracted from the weight-loss data.

(dashed curves). Even then, a significant difference remains especially at the lowest impact energies.

It is well known, that the maximum yield of the temperature dependence decreases with decreasing ion impact energy [4–7,15]. Additionally the temperature of that maximum (T_{max}) shows, especially for the weight-loss data, a drastic shift with decreasing impact energy of about 250 K from above 850 to below 600 K, a behaviour not yet reported up to now. The mass spectrometry data in Fig. 1 show, if any, a very small shift. A quite larger shift of about 100 K for mass spectrometry data and an explanation are reported in [15]. Fig. 2 summarises the temperature dependence of the total erosion yield for different ion impact energies of hydrogen and deuterium obtained from weight-loss measurements.

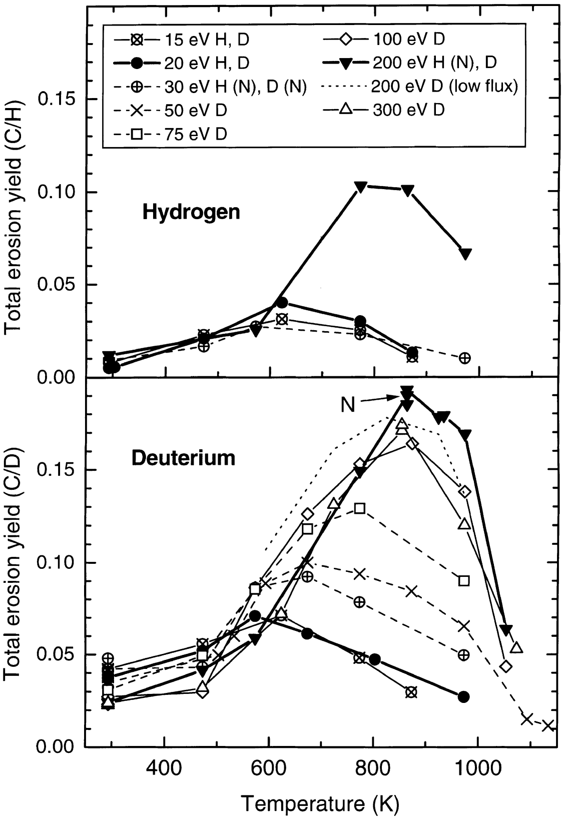

Fig. 2. Temperature dependence of the total erosion yield of H (top) and D (bottom) on graphite obtained by measuring the weight loss at ion impact energies between 15 and 300 eV with flux densities of 1–8 × 10^{-19} m^{-2} s^{-1} and at normal incidence. The dotted curve was measured with a reduced flux of 0.7 × 10^{-19} m^{-2} s^{-1} (about one-tenth of the maximum obtainable flux). The single data point and the series labelled with 'N' are measured with a reduced amount of neutrals (for more details see in the text).

The dependence of the temperature T_{max} on flux density is reported for total erosion yields in [4,5] and for mass spectrometric data in [15]. But in our experiment the variation in the flux density for the different impact energies is too small to be the reason for the observed shift [4,5]. This was also verified by comparing the total erosion yield for 200 eV at maximum flux with data at a flux of about a factor of 10 lower, shown in Fig. 2. A shift of about 50 K is observable, as expected from earlier results [4,5]. Therefore, only a small contribution to the shift results from the flux variation.

The difference in the shift with impact energy of T_{max} between weight-loss and mass-spectrometric measure-

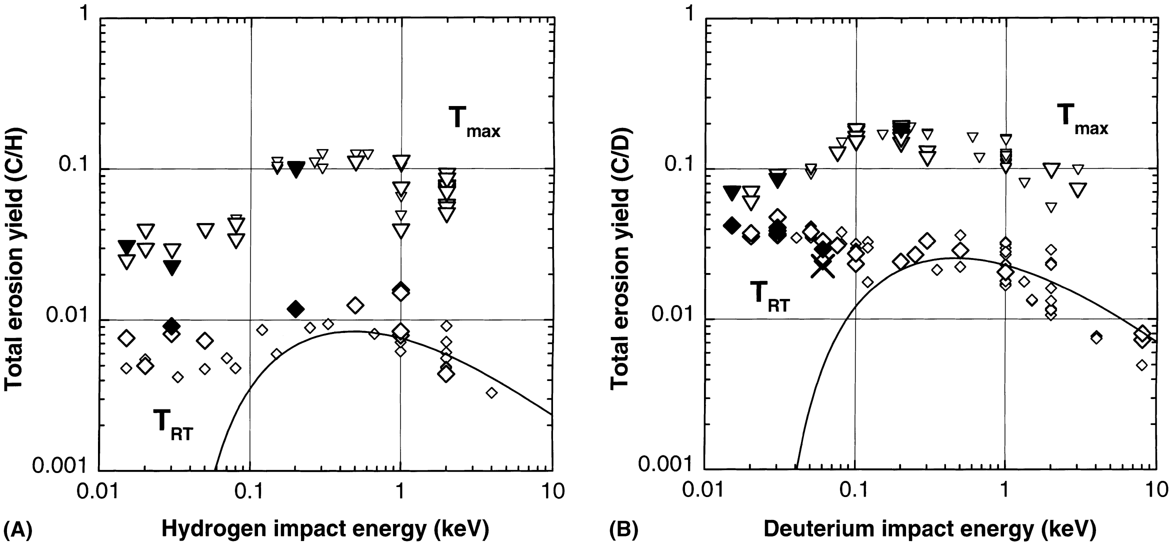

Fig. 3. Impact energy dependence of the total erosion yield of H (left) and D (right) on C obtained by measuring the weight loss at flux densities of 1–8 × 10^{-19} m^{-2} s^{-1} and at normal incidence. Big symbols: pyrolytic graphite of Union Carbide with the surface parallel to the graphite planes. Small symbols: variety of different carbon materials (new and published data [13]). Filled symbols: measured with a reduced amount of neutrals (for more details see in the text). Cross: measured with D^+ instead of D_3^+ ions and reduced amount of neutrals. Lines: physical sputtering calculated by the revised Bohdansky formula [4,5,22]. Data labelled with T_{max} (triangles) are measured at temperatures around the maximum of the temperature dependence and data labelled with T_{RT} (diamonds, cross) are measured near 300 K.

ments could be possibly explained by strong changes in the contribution of C_xH_y molecules and radicals with temperature. But only weak changes are found in the temperature dependence of the C_xH_y molecules [15]. Therefore, it is expected that the ratio of hydrocarbon radicals to molecules varies with hydrogen impact energy [4,5] (see below). The superposition of the contribution of the different hydrocarbon molecules and radicals, each with different temperature dependence, would easily produce a shift in T_{max} as well as a change in the shape of the temperature dependence of the yield.

3.2. Ion impact energy dependence of the erosion yields

A complete data collection of the impact energy dependence of the total erosion yield of hydrogen and deuterium on carbon materials is shown in Fig. 3 obtained by weight-loss measurements at the Garching high current ion source [13]. The data labelled with T_{max} are the total yields measured at temperatures near the maximum of the temperature dependence. For impact energies above 100 eV all presented data are measured between 800 and 920 K, below 100 eV the lowest temperature is 570 K. Only for impact energies above 1 keV with a large deposited power by the ions, the target temperature of the data labelled with T_{RT} is higher than room temperature, but always lower than 400 K. In this collection the difference between different carbon materials is not significant for both hydrogen isotopes. The variation is within the error bar of the reproducibility of individual measurements.

The main features of the impact energy dependence are described by the model of chemical erosion presented in [4–8] although the above mentioned shift of T_{max} is not included.

3.3. Isotope effects of the erosion yields

The total erosion yield data in Figs. 2 and 3 show clearly an isotope effect with D yields being higher than H yields. The isotope effect is implemented in the existing models [4–7]. The isotope mass is involved in the chemical erosion due to the production of radiation damages enhancing the thermally activated chemical erosion and due to the kinetic ejection of loosely bonded hydrocarbons at low impact energies. It should be noted that a much smaller isotope effect is observed by mass spectrometry [6,15].

3.4. Synergistic effect by neutrals

A possible cause of the difference observed between yield measurements by weight loss and by mass spectrometry of carbon for low ion impact energies may be the small percentage of high energy neutrals (1 keV) in the ion beam. Although the sputtering by neutrals alone does not contribute more than a few percent to the measured yield, a synergistic enhancement of the yield from low energy ions due to simultaneous impact of energetic neutrals can not be ruled out [3]. Therefore, some measurements were performed with a reduced amount of neutrals.

Total yield data, also shown in Figs. 1 and 3, are obtained with a reduced amount of neutrals. The yields are identical within the errors of the weight-loss measurement. A synergistic effect of a few percent of high-energy neutrals (here 1 keV) in the flux of low-energy ions is not observable and, therefore, can be neglected. Especially the amount of neutrals in the ion beam could not explain the discrepancy of mass spectrometry and weight-loss data.

Linked to the synergistic effect by neutrals a measurement was performed with D^+ instead of D_3^+ and with a reduced amount of neutrals (cross in Fig. 3). The ion flux was one-eighth of the usual one. A change in the yield was not observable. The neutralisation and dissociation of the D_3^+ ions into D atoms upon impact with possible variations of, e.g., energy or excitation states does not show an effect on the chemical erosion process.

3.5. Sticking of the eroded particles

A possible origin of the discrepancy between weight loss and mass spectrometry is the loss of eroded atoms and molecules to the vessel surfaces before detection in the mass spectrometer [9–12]. The build-up of carbon layers from chemically eroded species is also of great interest for the hydrogen inventory in the codeposited layers observed in fusion devices [1,12]. In order to determine the sticking of the eroded particles, collector experiments are presented in Fig. 4. Carbon was clearly deposited in both measurements, with 60° and with 0° incident angle of the deuterium beam. A homogeneous carbon background was subtracted from the measured carbon content due to surface contamination on the Al collector found prior to the deposition of 2 and 1.5×10^{20} C/m^2, respectively. In the case of 60° impact the deuterium density confirms the angular distribution of carbon. The ratio D to C is about 0.5. A deuterium depletion due to the analysing ion beam has been observed, suggesting that the layers are more likely soft a-C:D films than hard films [23,24].

If all deposited carbon comes from physically sputtered atoms (6% of the total erosion yield for 50 eV deuterium as calculated by TRIM.SP [25]), the shape of the polar distribution at 0° incident angle should be approximately a cosine distribution. However, the measured areal density has not the cosine shape; it has a nearly isotropic value of 3.5×10^{20} C/m^2. This value is much higher than an estimation for the maximum of a cosine distribution of 1.4×10^{20} C/m^2 at the 0° polar angle. For an angle of incident of 60° the distribution should be peaked near 60° in forward direction (positive polar angle) and should drop clearly for negative angles, as a calculated distribution by TRIM.SP [25] indicates (only physical sputtering).

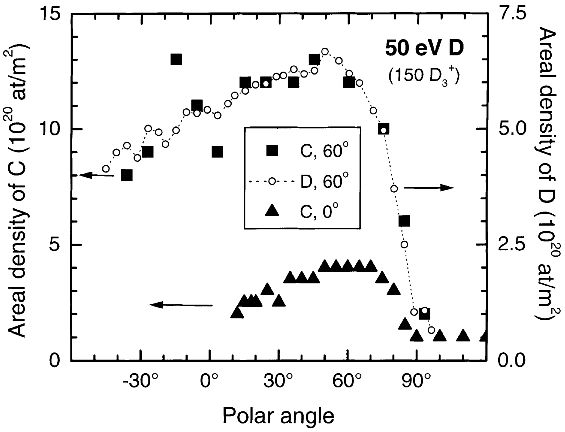

Fig. 4. Polar distribution of the areal density of deposited carbon and deuterium. The incident angle of the 150 eV D_3^+ ions was 60° and 0°. The mass loss of the target was 33 μg and 55 μg, respectively. The distance of the circular collector from the target centre was 19 mm. Target and collectors were at room temperature.

The measured data at 60° impact seem indeed to be peaked, which would suggest a kinetic process for the chemical erosion [4,5]. But the drop at negative polar angles is too low suggesting, similar to normal incidence, that other processes contribute. For example, several reflections of the eroded particles at the walls before the deposition would produce a more isotropic distribution. This suggestion is encouraged by the non-zero signals above 90° and also by the published sticking coefficients of hydrocarbon radicals [9–12].

The ratio of deposited carbon to eroded carbon is not sufficiently quantifiable from the measured data, because the integration over a full hemisphere requires better knowledge of the angular distribution and the influence of the experimental geometry (e.g., reflections). Nevertheless, assuming a rotational symmetric angular distribution of the deposited carbon, we can extrapolate the collector to a half sphere. This would account for at least a quarter of the eroded carbon deposited on the half-spherical collector. Surely, part of the chemically eroded particles is deposited somewhere on the vessel surfaces and does not reach the mass spectrometer. This contributes to the discrepancy between weight-loss and mass-spectrometry measurements. If carbon is lost to the surfaces in multiple reflections, as indicated by the broad distribution, this contribution may become even more significant for the residual gas analysis. Total erosion yields from mass spectrometry can only be determined using advanced techniques as the line-of-sight geometry or threshold spectroscopy.

4. Summary

Our new weight-loss measurements of the total erosion yield of graphite and carbon materials by hydrogen and deuterium bombardment show:

- The temperature of the maximum of the chemical erosion increases from below 600 to above 850 K with ion energies from 15 to 300 eV. This shift is larger than the shift measured by mass spectrometry (250 K compared to 100 K) and could possibly be explained by the dependence of the contribution of hydrocarbon molecules and, especially, radicals on hydrogen impact energy and target temperature.
- A synergistic effect of neutrals in the ion beam on the erosion yield can be excluded by varying the amount of neutrals in the ion beam between 3% and below 0.3%.
- From collector measurements it is clearly shown that a fraction of the chemically eroded particles (e.g., radicals) stick to the vessel surfaces and will not reach the mass spectrometer. This appears to be the main reason why the chemical erosion yield measured by mass spectrometry is lower than that measured by the weight-loss method.

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References

[1] G. Federici, R.A. Anderl, P. Andrew, J.N. Brooks, R.A. Causey, J.P. Coad, D. Cowgill, R.P. Doerner, A.A. Haasz, G. Janeschitz, W. Jacob, G.R. Longhurst, R. Nygren, A. Peacock, M.A. Pick, V. Philipps, J. Roth, C.H. Skinner, W.P. Wampler, J. Nucl. Mater. 266–269 (1999) 14.
[2] J. Küppers, Surf. Sci. Reports 22 (1995) 249.
[3] E. Vietzke, A.A. Haasz, in: W.O. Hofer, J. Roth (Eds.), Physical Processes of the Interaction of Fusion Plasmas with Solids, Academic Press, San Diego, 1996, p. 135.
[4] J. Roth, C. García-Rosales, Nucl. Fus. 36 (1996) 1647.
[5] J. Roth, C. García-Rosales, Nucl. Fus. 37 (1997) 897 (corrigendum to [4]).
[6] B.V. Mech, A.A. Haasz, J.W. Davis, J. Appl. Phys. 84 (1998) 1655.
[7] J. Roth, J. Nucl. Mater. 266–269 (1999) 51.
[8] M. Balden, Phys. Scr. T81 (1999) 64.
[9] P. Kae-Nune, J. Perrin, J. Guillon, J. Jolly, Plasma Sources Sci. Technol. 4 (1995) 250.
[10] M. Shiratani, J. Jolly, H. Videlot, J. Perrin, Jpn. J. Appl. Phys. 36 (1997) 4752 (Part 2).
[11] C. Hopf, K. Letourneur, T. Schwarz-Selinger, W. Jacob, A. von Keudell, Appl. Phys. Lett. 74 (1999) 3800.
[12] A. von Keudell, C. Hopf, T. Schwarz-Selinger, W. Jacob, Nucl. Fus. 39 (1999) 1451.
[13] W. Eckstein, C. García-Rosales, J. Roth, W. Ottenberger, Sputtering Data, Technical Report IPP 9/82, Max-Planck-Institut für Plasmaphysik, Garching, 1993.
[14] H.L. Bay, J. Roth, J. Bodhansky, J. Appl. Phys. 48 (1998) 4722.
[15] B.V. Mech, A.A. Haasz, J.W. Davis, J. Nucl. Mater. 255 (1998) 153.
[16] A.A. Haasz, J.A. Stephens, E. Vietzke, W. Eckstein, J.W. Dawis, Y. Hirooka, Nuclear Fusion Supplement, Atomic and Plasma-Material Interaction Data for Fusion, vol. 7 (1998) and references therein.
[17] J. Roth, E. Vietzke, A.A. Haasz, Nuclear Fusion Supplement, Atomic and Plasma-Material Interaction Data for Fusion, vol. 1 (1991) 63.
[18] R. Amirikas, D.N. Jamieson, S.P. Dooley, Nucl. Instrum. and Meth. B 77 (1993) 110.
[19] M. Mayer, SIMNAR User's Guide, Technical Report IPP9/113, Max-Planck-Institut für Plasmaphysik, Garching, 1997.
[20] M. Balden, M. Mayer, J. Roth, J. Nucl. Mater. 266–269 (1999) 440.
[21] C. García-Rosales, J. Roth, J. Nucl. Mater. 196–198 (1992) 573.
[22] C. García-Rosales, W. Eckstein, J. Roth, J. Nucl. Mater. 218 (1994) 8.
[23] D. Boutard, B.M.U. Scherzer, W. Möller, J. Appl. Phys. 65 (1989) 3833.
[24] M. Balden, M. Mayer, ICRFM-9, Colorado Springs, 1999, J. Nucl. Mater., submitted.
[25] W. Eckstein, Computer Simulation of Ion–Solid Interaction, Springer, Berlin, 1991.