



Molecular dynamics modeling of chemical erosion of hydrocarbon films

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ABSTRACT

The erosion of hydrocarbon layers at room temperature due to co-bombardment of energetic (150 eV) argon ions and thermal atomic hydrogen is investigated. Using molecular dynamics simulations a mechanism has been identified explaining the experimentally observed increase of the physical sputtering yield. The surface erosion process is primarily a physical sputtering mechanism, enhanced by the screening effect of hydrogen atoms. This causes emission of unsaturated hydrocarbon molecules from the surface within a few picoseconds after ion impact and a superthermal energy distribution of the emitted molecules.

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1. Introduction

Carbon is among the favorite materials for the first wall of present day fusion experiments due to its favorable thermo-mechanical properties. However, atomic hydrogen as well as energetic species from the fusion plasma cause erosion of the plasma-facing carbon tiles. The erosion products are then redeposited at other locations in the vessel. The formation of co-deposited layers in remote areas contributes to the permanent retention of hydrogen isotopes present in the experiment (eg radioactive tritium), which is a potentially limiting constraint in the long-term operation of fusion reactors [1–3].

As of now there is no real substitute for carbon for handling high heat fluxes in the divertor strike-point zone of tokamaks and in the start-up scenario of ITER the divertor area with the highest thermal loads consists of CFC tiles.

Quantitative and qualitative understanding of the erosion mechanism in co-bombardment situations is, therefore, urgently desired.

The interaction of hydrogen with carbon-based plasma-facing components (PFCs) leads to their erosion by both momentum transfer processes (physical sputtering) and chemical reactions [4]. In order to understand the influence and interaction of the different processes of carbon erosion various experiments have been performed. The kinetic energy and the chemical reactivity were supplied by two independent particle fluxes, a beam of energetic argon ions and another beam flux of thermal hydrogen atoms [5–9]. The experiments showed that the resulting erosion rates at moderate energies were higher than both the expected physical

sputtering rate as well as the chemical erosion rate due to the hydrogen atoms, which in some experimental cases was zero due to the sample being at ambient temperature. In order to indicate that both momentum transfer processes and chemical reactions play a role for this enhanced erosion, it is commonly referred to as *chemical sputtering* [4]. In particle beam experiments [6–9] the erosion yield was studied for different Ar energies and a varying hydrogen to argon flux ratio of between 0 and ~500. It was observed that the additional flux of hydrogen atoms leads to a dramatic increase in the sputtering yield. However, the atomistic picture of the erosion process is not accessible by these experiments. Therefore, in the present study, we perform molecular dynamics simulations to gain insight into the details of this synergistic erosion process.

2. Molecular dynamics simulation method

A molecular dynamics simulation code, Hydrocarbon Parallel Cascade (HCPaCas version V3.22), has been used which employs a fifth-order predictor–corrector Gear algorithm to calculate the positions and velocities of particles using adaptive time steps [10]. The a-C:H samples were prepared by annealing a collection of carbon and hydrogen atoms using the Brenner potential for C–H and C–C interactions [11,12] and DFT-based pair-potentials for the Ar interactions [13]. The sample preparation was similar to the preparation method given in [14] and is described in more detail in [15]. After several heating cycles between 300 K and 4000 K with periodic boundary conditions in all directions to obtain an annealed amorphous sample the periodic boundary condition in z-direction was removed. To mitigate the effects of the ‘box opening’ a surface bombardment with low energy (5 eV) Ar atoms was applied followed by additional 12 ns for equilibration of the sample.

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After the preparation steps the sample with the dimensions of $14 \times 14 \times 28 \text{ \AA}^3$ had 930 atoms with an H/(H + C) ratio of 0.38 and a density of 1.750 g/cm^3 . This corresponds to a-C:H layers deposited from ethylene plasma discharges with typical parameters of H/(H + C) = 0.39 and a density of 1.7 g/cm^3 [16]. The fractions of threefold and fourfold coordinated carbon atoms were 60% and 37%, which is in good agreement with the experimental data for a-C:H films with properties intermediate between hard and soft [17]. The sample was bombarded with monoenergetic 150 eV Ar atoms at an angle of 45° with respect to the surface normal and at random azimuthal angles. The Ar interactions with carbon and hydrogen atoms were modeled using additive pair-potentials. The bombarding atoms were initialized at a height of 7 \AA above the surface, which is beyond the largest cutoff radius of 4.5 \AA of all the potentials used in this simulation. The Ar bombardment simulations were run for 5 ps. In the sample, the energetic argon atoms were typically thermalized within 0.5 ps after the impact, and thereafter the sample was relaxed for another 4.5 ps. Monoenergetic hydrogen atoms of 0.5 eV energy were incident upon the Ar bombarded surface with 45° polar and random azimuthal angles. The simulation time for a single H bombardment was 5 ps, and 50 H atoms were incident for each Ar atom. This number (50) was determined in such a way that an increase in the number of hydrogen atoms had no detectable impact on the simulation with the present argon energy of 150 eV since the total amount of near-surface hydrogen was in saturation; additionally incident H atoms were either reflected from the sample or simply replaced hydrogen atoms already present on the surface. Also, abstraction of H_2 -molecules could be observed, but the total number of hydrogen atoms showed only small fluctuations around the saturation value. In 11 simulation sets, consisting each of 13 cumulative repetitions of the (1 Ar + 50 H) cycle plus a final Ar impact, the surface was bombarded by a total of 7150 hydrogen atoms and 154 Ar atoms.

For comparison two additional sets of cumulative bombardment runs were also performed with only Ar atoms and with only H atoms, respectively. In those cases the time between successive impact events was kept the same as for the co-bombardment simulations.

3. Results

The results of the three different simulation set-ups are given below:

3.1. Hydrogen only

In the case of H-alone simulations the number of carbon atoms of the initial sample is unchanged by the additionally offered hydrogen, i.e. no erosion occurred. The increase in the hydrogen content is restricted to the upper part of the sample (3 \AA), forming a thin, hydrogen-enriched layer which has also been observed in other simulations [18]. Nevertheless, a comparison of the C–C bond statistics between the initial sample and the sample after H exposure reveals that the carbon network is not affected by this increase of surface H content, because most of the hydrogen atoms are added to the already existing open bonds in the initial sample.

3.2. Argon only

In the case of physical sputtering by Ar bombardment, an average loss of 11 C atoms has been observed, which corresponds to an erosion yield of 0.8 C/Ar . The Ar bombardment increases the number of carbon atoms with a lower carbon coordination number at the expense of fourfold coordinated carbon atoms. At the same

time, the upper part is depleted of hydrogen since the average loss ratio is C:H = 1:2. This depletion has also been noticed by, e.g. Beardmore and Smith [19], however at Ar energies of 1 keV.

3.3. Co-bombardment

Here on average 24 carbon atoms were lost, corresponding to an yield of 1.7 C/Ar . The incident hydrogen is incorporated into the surface layer maintaining its supersaturated condition as can be deduced from the $N_{\text{H}}/N_{\text{C}}$ -ratio raising from initially 0.62 to 0.72 in the upper half of the sample. Taking into account the reduced number of C atoms in the sample, the bond distribution also indicates the increased appearance of terminal C atoms in addition to the changes induced by the physical sputtering processes. In Fig. 1 the variation of the carbon coordination number (number of C–C bonds) is plotted as a function of Ar impact events for the Ar|H case. The number of bonds is normalized to the number of carbon atoms present in the samples for each Ar bombardment event. It can be seen that the numbers of singly and doubly coordinated atoms are increased at the expense of threefold and fourfold coordinated atoms. The analysis of the sputtered species for the Ar-alone and Ar|H cases are shown in Fig. 2. The erosion histogram shows the fraction of different ejected hydrocarbon radicals normalized to the total number of events. It can be seen that the fraction of C_xH_y , where $x > 3$, is small in both cases. Nevertheless, the fraction of eroded C_3 - and larger molecules is significantly higher if additional hydrogen is present. Also the temporal profile of carbon atoms ejected in the form of C_xH_y molecules is different with respect of the Ar only situation. A molecule specific inspection of the emission time reveals that most of the smaller hydrocarbons (C_1H_y) were ejected within 1 ps after the Ar impact. Most of the larger molecules were eroded at later times ($>2.5 \text{ ps}$), contributing to the high fraction of eroded carbon atoms in the case of Ar|H simulations. In the Ar-alone case, the lack of molecules with more than three C atoms prevents the occurrence of any late emissions. The kinetic energy of the eroded molecules is above the thermal energy in almost all cases and the emission is therefore a direct consequence of the ion impact in both the cases. The energy of the higher hydrocarbons ($x > 3$) is also above the thermal range (0.5–2 eV). The pronounced high energy tail in the Ar|H simulations (not shown) is a consequence of the more pronounced occurrence of loosely bound carbon atoms.

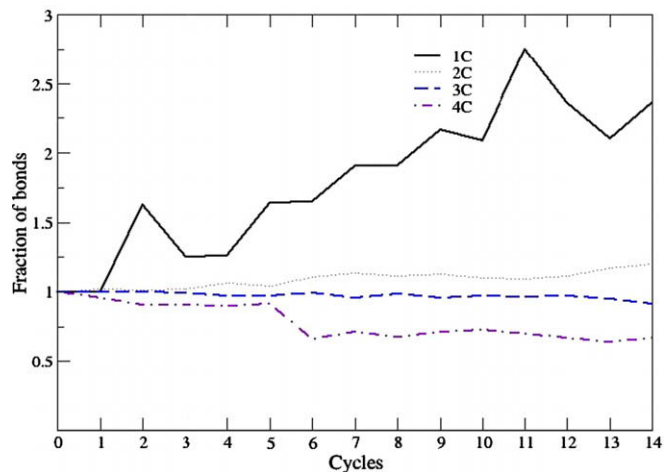


Fig. 1. The variation of the carbon coordination number (C–C bonds, ranging from 1 to 4, labeled as 1C, 2C, 3C and 4C, respectively) as function of the Ar + H-cycles normalized with respect to the initial values.

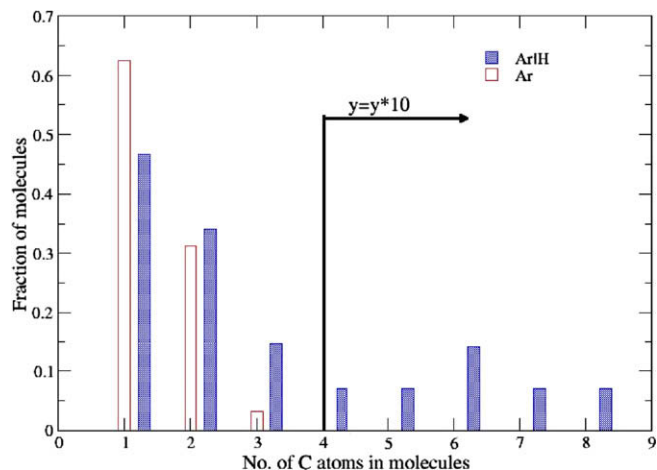


Fig. 2. Comparison of the number of carbon atoms in the sputtered molecules for (a) Ar + H-cycles (Ar|H) and (b) argon only bombardment (Ar).

4. Discussion and conclusion

We observed the ejection of unsaturated radicals from a-C:H layers at 300 K surface temperature with a yield of 1.7 as compared to 0.8 for normal physical sputtering. This can be attributed to the abundance of hydrogen in the top layers of the film.

The process of erosion can be described as follows: Ar atoms create open bonds within their penetration range (mean range $\sim 8 \text{ \AA}$) resulting in the formation of linear hydrocarbon chains. The fractions of singly and doubly coordinated atoms are increased at the expense of threefold and fourfold coordinated atoms, as shown in Fig. 1. The damage created is mostly in the top layers, the depth profile of the displaced atoms being in good agreement with TRIM.SP calculations [6].

The open bonds thus formed on the top layers are passivated due to hydrogen bombardment in the case of the Ar|H simulations, resulting in hydrogen-rich upper layers as indicated by the increase of the H/C ratio in the upper half of the film. In the case of pure Ar bombardment, impact induced chains of carbon atoms get eventually re-attached to some other open bond locations.

However, the screening effect of hydrogen atoms in Ar|H case makes the closing of long hydrocarbon chains difficult even if there are available binding sites. Although this effect is hard to quantify it is clearly visible in the simulations. The subsequent Ar impacts cause further breaking of C–C bonds resulting in the detachment of unsaturated molecules from the sample. The bond breaking was either by direct bombardment or by the knock-on atoms. Since the top atoms of the linear carbon chains are covered with hydrogen in the Ar|H case, the broken molecule fails to re-attach to any other available bonding site. Hence, the unsaturated molecule comes out of the sample. As can be seen from the temporal distribution of the eroded particles, all of the molecules were ejected

within 5 ps after Ar impact. The kinetic energy distribution of the eroded particles shows that the ejected molecules are not thermalized.

The analysis of the sputtered species in each case shows that the fraction of radicals having more than four carbon atoms is low, which is in agreement with the existing results for co-bombardment simulations performed with low energy noble gas ions and hydrogen atoms (5 eV and 10 eV) on a-C:H films [20] using the same interaction potentials.

In conclusion the mechanism which leads to the yield enhancement in the simulations can be described as *hydrogen enhanced physical sputtering*.

The chemical and momentum transfer effects involved in the erosion process can be clearly distinguished. The eventual ejection of C_xH_y radicals is entirely a momentum transfer effect. However, the steric repulsion which arises due to excess hydrogen on the surface in our simulations is purely chemical in origin and is responsible for the increased sputtering yield. Diffusion effects are not prominent on the simulation time scales.

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References

- [1] J. Roth, J. Nucl. Mater. 266–269 (1999) 51.
- [2] M. Mayer, V. Rohde, A. von Keudell, ASDEX Upgrade Team, J. Nucl. Mater. 313–316 (2003) 429.
- [3] G. Federici et al., Nucl. Fusion 41 (2001) 1967.
- [4] W. Jacob, J. Roth, in: R. Behrisch, W. Eckstein (Eds.), Sputtering by Particle Bombardment, Springer, Berlin, 2007, p. 329.
- [5] E. Vietzke, K. Flaskamp, V. Philipps, J. Nucl. Mater. 111&112 (1982) 763.
- [6] C. Hopf, A. von Keudell, W. Jacob, J. Appl. Phys. 94 (2003) 2373.
- [7] C. Hopf, A. von Keudell, W. Jacob, Nucl. Fusion 42 (2002) L27.
- [8] C. Hopf, W. Jacob, J. Nucl. Mater. 342 (2005) 141.
- [9] W. Jacob, C. Hopf, M. Schlüter, Phys. Scripta T124 (2006) 32.
- [10] K. Nordlund, J. Keinonen, Phys. Rev. Lett. 77 (1996) 699.
- [11] D.W. Brenner, Phys. Rev. B 42 (1990) 9458.
- [12] D.W. Brenner, Mater. Res. Soc. Bull. 21 (2) (1996) 36.
- [13] K. Nordlund, N. Runeberg, D. Sundholm, Nucl. Instrum. and Meth. B 132 (1997) 45.
- [14] P. Träskelin, K. Nordlund, J. Keinonen, J. Nucl. Mater. 357 (2005) 1.
- [15] P.N. Maya, U. von Toussaint, C. Hopf, New J. Phys. 10 (2008) 023002.
- [16] Th. Schwarz-Selinger, A. von Keudell, W. Jacob, J. Appl. Phys. 86 (1999) 3988.
- [17] J. Robertson, Mater. Sci. Eng. R37 (2002) 129.
- [18] E. Salonen, K. Nordlund, J. Tarus, T. Ahlgren, J. Keinonen, C.H. Wu, Phys. Rev. B (Rapid Commun.) 60 (1999) 14005.
- [19] K. Beardmore, R. Smith, Nucl. Instrum. and Meth. B 102 (1995) 223.
- [20] P. Träskelin, K. Nordlund, J. Keinonen, Nucl. Instrum. and Meth. Phys. Res. B 228 (2005) 319.