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Carbon erosion mechanisms in tokamak divertor materials: insight from molecular dynamics simulations

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Abstract

While there is much experimental and theoretical interest in the surface physics of amorphous hydrogenated carbon under hydrogen bombardment, the atomic-scale interactions taking place under low-energy ($E \sim 10$ eV) particle bombardment still remain obscure. We now describe an erosion mechanism for low-energy ions, which leads to carbon erosion yields much higher than expected from physical sputtering alone, and also find that the erosion yield from this mechanism is highly sensitive to the detailed surface structure. We show that this sensitivity can explain why the erosion of tokamak divertor carbon surfaces has been shown to decrease sharply at extremely high hydrogen fluxes ($\sim 10^{19}$ ions/cm^2 s). The high-flux hydrogen bombardment produces a very high hydrogen content at the sample surface, which lowers the carbon sputtering yield by an order of magnitude by decreasing the carbon bond collision cross-section. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Amorphous carbon; Molecular dynamics; Sputtering; Tokamak

1. Introduction

The erosion of carbon by intensive hydrogen bombardment has been recently shown to decrease sharply at very high fluxes ($\sim 10^{19}$ ions/cm^2 s) [1]. This effect can not be explained by standard sputtering or erosion models, yet understanding it is central for selection of fusion reactor divertor materials, and formulation of sputtering models for high-flux conditions. In fact, a central reason to the difficulty of understanding this effect is that ordinary sputtering and erosion models are ill suited for describing the hydrogen isotope interactions at kinetic energies around 10 eV, as this energy regime is well beyond that of ordinary chemistry, but also well below that described accurately by irradiation physics. Furthermore, erosion of carbon atoms and small molecules from amorphous hydrogenated carbon (a-C:H) surfaces by $\sim$10 eV hydrogen ions is known to occur at yields much higher than expected by physical sputtering [2,3]. This low-energy sputtering, often called chemical sputtering, is assumed to be due to some sort of bond-breaking mechanism, but qualitative understanding of how bond breaking actually takes place, as well as of the factors contributing to it, is missing [2,4].

Molecular dynamics (MD) computer simulations [5], however, can treat realistically both the many-body collisional phase and subsequent thermalization involved in the problem. Using an empirical hydrocarbon potential energy function, we have initiated the use of molecular dynamics methods for studying the hydrogen–a-C:H surface interactions in carbon-based divertor materials.

2. Method

The atomic-scale interactions of hydrogen ions [1] impinging on a-C:H surfaces were studied with classical

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[1] The classical MD simulations can not take account of the charge state of atoms. Here we use the term ion to denote the incoming particle regardless of its charge state, and the term atom to denote any particle in the sample or sputtered out from it.

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MD simulations. The interatomic forces were calculated using the empirical Brenner–Beardmore many-body potential energy function, which is a modified version of the original Brenner hydrocarbon potential [6,7]. We chose the parameter set II of the original potential formulation, since it gives a more accurate C–C bond stretching constants, as well as a later modified parametrization [8]. Simulation cells consisting of 500–2000 atoms were prepared with a H/C ratio of 0.4, matching the experimental hydrogen saturation value of bulk a-C:H at 300 K [9,10]. The fractions of the sp^2 and sp^3 hybridized carbon atoms in the cells were 50–65% and 25–40%, respectively. [2] The atoms within a distance of 2 Å from the bottom of the cell were held fixed and the top atom layers were equilibrated at 300 K. Periodic boundary conditions were applied in the directions perpendicular to the surface normal.

The incident ion (H, D or T) energy was either selected randomly from the Maxwell–Boltzmann energy distribution for some root mean square (rms) energy, or kept constant for each incident ion. The incident ion was assigned a velocity towards the surface with a steep off-normal angle between 0° and 20°. For each ion impact, the atoms in the cell were shifted at random in the directions perpendicular to the surface normal. In order to keep the substrate temperature constant, and to embed the kinetic energy brought into the cell by the ion, the temperature was scaled to 300 K within 2 Å from the borders using the method by Berendsen et al. [11]. The impact cascades were followed for 2–3 ps, after which another ion was shot at the same original surface (non-cumulative simulations) or at the surface produced in the previous bombardment event (cumulative simulations). Typical simulation runs consisted of 2000–6000 incident ion impacts.

Apart from the details given above, the simulations follow normal surface cascade modeling procedures [12]. Since MD simulations follow the motion of all atoms in the system [5], the erosion yields and species will be obtained by counting atoms which leave the substrate, and the cumulative simulations will also provide a description of hydrogen buildup during prolonged irradiation.

3. Results and discussion

3.1. Hydrogen shielding

In the first cumulative simulation runs, the cell was impinged on by 1 eV (rms) hydrogen ions [13]. The high rate (2×10^{25} ions/cm^2 s) of ion incidence led to a strong hydrogen buildup on the cell surface, which did not slow down until a supersaturated [3] value of $H/C \approx 0.54$ was attained (Fig. 1). After this the hydrogen content in the cell increased only very slightly, as the surface was already very coated with hydrogen. The slight increase was due to hydrogen–hydrogen replacement collisions of impinging ions driving hydrogen atoms into unsaturated regions deeper in the a-C:H cell. No carbon sputtering was observed in these simulation runs. When the rms energy of the impinging atoms was raised to 10 eV, a similar increase of the hydrogen content in the cell was seen as in the previous case. The rate of increase in the hydrogen content before obtaining the supersaturation value was nearly the same in both cases. However, the fluctuation of the hydrogen content at the surface was much stronger in the higher energy bombardment, which also led to significant carbon erosion. The supersaturated value of 10 eV bombardment was $H/C \approx 0.56$. Discussion on the stability and relaxation of the hydrogen shielding, as well as comparison with the experimental and simulation fluxes, was given in an earlier paper [13].

We studied the effect of the hydrogen shielding on the carbon erosion yield by running series of non-cumulative simulations with ion rms energy of 10 eV. A significant difference in the carbon yield between the bombardment of an unsaturated surface and the bombardment of a supersaturated surface was observed. With an unsaturated surface, the carbon yield was ~0.01, whereas with a supersaturated surface, the carbon erosion yield was suppressed to ~0.001. This sharp drop was due to the hydrogen coating leading to a decreased C–C bond collision cross-section.

3.2. Bond-breaking mechanism

The atomic-scale interactions leading to carbon erosion in our modeling were studied in detail with non-cumulative bombardment simulations of the same unsaturated surface. Since hydrogen atoms only form a single bond, it is the C–C bonds that bind the surface carbon atoms to the bulk carbon network. The carbon erosion mechanism in our simulations was the breaking of those C–C bonds by the incident ion (Fig. 2). Since the ions had not enough kinetic energy to directly kick the carbon atoms from their atom sites by elastic collisions, the sputtering took place in a different manner. The ions penetrated into the region directly between the carbon atoms, i.e. the covalent bond. The carbon atoms were then forced apart from each other by a strong repulsion that was caused by the repulsive part of the potential energy function. The repulsive push occurred very rapidly and the carbon network did not have time

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[2] This includes the surface atoms.

[3] By supersaturation we mean, in the present context, hydrogen contents in a-C:H significantly higher than the experimentally observed equilibrium ratio of 0.4.

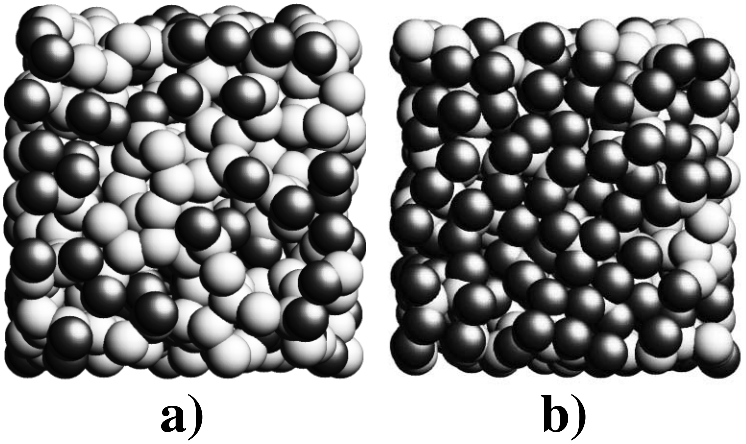

Fig. 1. Simulation cell surface seen from above at the start of the 1 eV cumulative hydrogen bombardment (a) and after 6000 incident ions (b). The dark spheres represent hydrogen atoms, and the light spheres represent carbon atoms. The supersaturated hydrogen coating leading to a decreased C–C bond collision cross-section can be clearly seen.

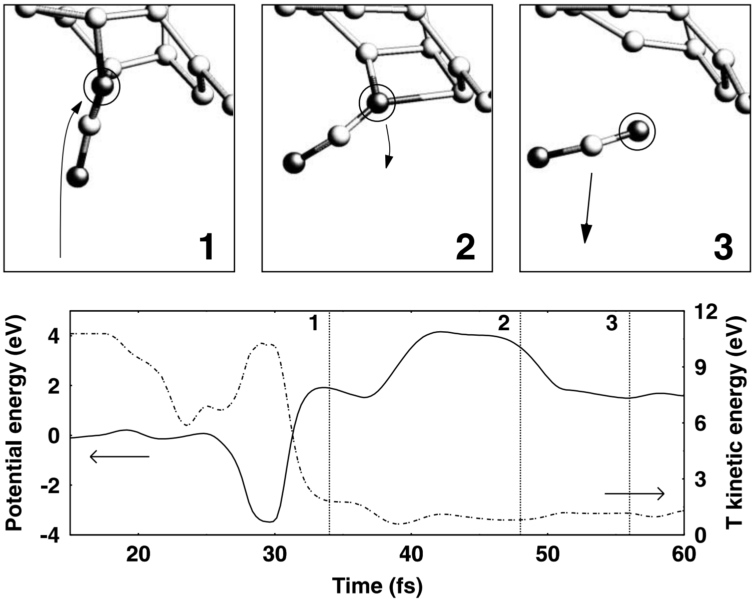

Fig. 2. Illustration of the carbon sputtering mechanism observed in our simulations. The movement direction of the impinging tritium ion (circled) is designated by the thin arrow. The light spheres represent carbon atoms and the darker ones, T atoms. (1) The T ion enters the space between the two carbon atoms. (2) The two carbon atoms are forced apart by the tritium ion between them and the C–C bond is broken. (3) The carbon atom leaves the sample with the two tritium atoms bonded to it. The graph below the snapshots shows the total potential energy of the two carbon atoms whose bond is broken, and the kinetic energy of the impinging tritium ion. The total potential energy at the start of the simulation has been chosen as the zero potential energy. The dashed lines show at what time the snapshots (1)–(3) have been made.

to relax to a new fully bonded equlibrium configuration. The separation, and consequently C–C bond breaking, could be further enhanced by the impacts of the incident ion with the surface carbon network atoms. Although in our case the hydrogen ion did not enter the exact midpoint of the C–C bond, the energetics of this process (c.f. Fig 2) correspond well to ab initio calculations, which have shown a relaxed bond-centered hydrogen configuration in diamond having an energy of about 5 eV above the perfect lattice configuration [14,15].

The determining factor for which hydrocarbon molecules were sputtered away from the surface was the depth of the broken C–C bond. The dangling hydrocarbon chain above the broken bond left the surface.

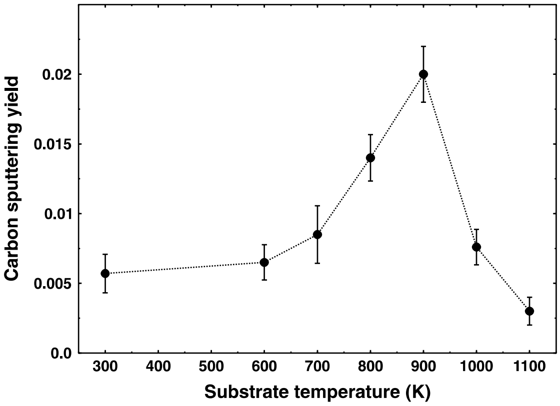

Fig. 3. Carbon sputtering yield as a function of temperature in non-cumulative T bombardment simulations for one substrate simulation cell. From [16].

Our simulations with different cells showed that the difference in surface structure can lead to considerable differences in carbon yield. The crucial factor is how many C–C bonds a carbon atom at the surface has. A carbon atom with only one or two carbon bonds erodes more easily than one with several carbon bonds.

The sensitivity of the yield to the surface structure also can lead to a strong temperature effect in the yield. Changes in the number of carbon atoms with 1, 2 or 3 carbon bonds right at the surface can lead to strongly differing yields at different temperatures, see Fig. 3. We note that the maximum in the yield occurs at about 800–900 K, which lies in the same temperature range of 600–900 K, where the maximum is observed experimentally [2]. The reasons behind the modified surface structure will be discussed elsewhere [17].

Our simulations runs with constant incident ion energies ranging from 5–30 eV gave sputtering yields of the order of ~0.001–0.01. The physical sputtering yield can be estimated with the TRIM program, which only considers binary ion–atom collisions [18,19]. The yields given by TRIM were an order of magnitude smaller than the ones given by our simulations. Thus, it is clear that the yields of the order of magnitude observed in our modeling can not possibly be explained by physical sputtering alone.

4. Conclusion and acknowledgements

We have shown how the high-flux ion bombardment of an a-C:H surface can lead to a highly increased hydrogen content on the sample surface. This hydrogen coating very efficiently suppresses carbon sputtering from the surface. We have also presented a new sputtering mechanism by low-energy ions. The carbon sputtering yield observed in our low-energy ion bombardment simulations was considerably higher than the one given by physical sputtering, estimated with a binary ion–atom collision program. Since the bond-breaking mechanism requires only a localized bond, the mechanism can be expected to be present in low-energy ion bombardment of other covalently bonded materials.

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References

[1] A. Kallenbach et al., Nucl. Fus. 38 (1998) 1097.
[2] J. Roth, C. Garcia-Rosales, Nucl. Fus. 36 (1996) 1647 and references therein.
[3] A. Annen, W. Jacob, Appl. Phys. Lett. 71 (1997) 1326.
[4] W. Jacob, Thin Solid Films 326 (1998) 1 and references therein.
[5] R. Smith (Ed.), Atomic and Ion Collisions in Solids and at Surfaces: Theory, Simulation and Applications, Cambridge University, Cambridge, UK, 1997.
[6] D.W. Brenner, Phys. Rev. B 42 (1990) 9458.
[7] K. Beardmore, R. Smith, Philos. Mag. A 74 (1996) 1439.
[8] D.W. Brenner, private communication.
[9] J. Roth et al., J. Nucl. Mater. 93&94 (1980) 601.
[10] B.L. Doyle et al., J. Nucl. Mater. 103&104 (1981) 513.
[11] H.J.C. Berendsen et al., J. Chem. Phys. 81 (1984) 3684.
[12] J. Tarus et al., Phys. Rev. B 58 (1998) 9907.
[13] E. Salonen et al., Phys. Rev. B 60 (1999) 140005 Rapid communications.
[14] T.L. Estle, S. Estreicher, D.S. Marynick, Phys. Rev. Lett. 58 (1987) 1547.
[15] C.H. Chu, S.K. Estreicher, Phys. Rev. B 42 (1990) 9486.
[16] E. Salonen, K. Nordlund, J. Keinonen, C.H. Wu, Europhys. Lett., in press.
[17] E. Salonen, K. Nordlund, J. Keinonen, C.H. Wu, submitted for publication.
[18] J.P. Biersack, L.G. Haggmark, Nucl. Instrum. Meth. 174 (1980) 257.
[19] J.F. Ziegler, 1998, SRIM-98 computer code, private communication.