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Abstract

The interaction of edge plasma with material surfaces raises key issues for the viability of the International Thermonuclear Reactor (ITER) and future fusion reactors, including heat-flux limits, net material erosion, and impurity production. After exposure of the graphite divertor plate to the plasma in a fusion device, an amorphous C/H layer forms. This layer contains 20-30 atomic percent D/T bonded to C. Subsequent D/T impingement on this layer produces a variety of hydrocarbons that are sputtered back into the sheath region. We present molecular dynamics (MD) simulations of D/T impacts on amorphous carbon layer as a function of ion energy and orientation, using the AIREBO potential. In particular, energies are varied between 10 and 150 eV to transition from chemical to physical sputtering. These results are used to quantify yield, hydrocarbon composition and eventual plasma contamination.

1. Introduction

Understanding the erosion of amorphous hydrogenated carbon (aC:H) is of fundamental importance for the International Thermonuclear Reactor (ITER) [1,2]. Carbon coatings will likely be used at the divertor plates and possible in regions of the first wall. Elements with higher atomic number (like tungsten), have lower erosion rates, but could lead to much larger *bremsstrahlung* and recombination radiation than carbon. Improved understanding of C erosion in the regime relevant to ITER (H, D, T bombardment, from 0 to 200 eV) may lead to strategies to mitigate erosion and, in addition, may provide clues to the problem of tritium retention that will affect C coatings in ITER.

Experimental data on carbon erosion is growing [3,4,5], but still there are large variations in the data due to different preparation techniques, experimental setup, etc. In addition, there are several models [6,7,8] that fit some of the available data, but a complete description of the erosion process is still lacking. Typically, if erosion is due to a highly energetic collisional process, it is called physical sputtering. On the other hand, if erosion is dominated by bond-breaking at relatively low energies, it is called chemical sputtering. In addition, the chemical erosion by energetic ions is different from the one resulting from chemical etching by "thermal" ions, giving for instance a large isotopic effect. Of course, the distinction between "chemical" and "physical" processes does not establish clear boundaries, and many erosion events are difficult to classify. Typically, for erosion of aC:H by energetic H, D, or T, the boundary between chemical and collisional processes is located around 20-40 eV. Collisional contributions to sputtering are usually calculated using binary collision approximation (BCA) codes, like SRIM [9]. These codes are extremely fast, but cannot include any chemical effects, and therefore

predict no erosion below ~20-40 eV, which contradicts the experimental data. In the last decade, molecular-dynamics simulations (MD) using empirical potentials [10,11] or tight-binding [12] have provided new clarity to the atomic scenarios for erosion below 35 eV, where chemical erosion dominates. All MD simulations of sputtering using empirical potentials have used the REBO [13] potential to describe hydrocarbon interactions. A more recent potential, AIREBO [14], improves the REBO potential by adding long range and torsional forces. However, to the best of our knowledge, there are no erosion simulations with AIREBO up to date. Here we present the first such simulations, including extension of the energy range up to 150 eV, allowing a comparison with the experimental data well into the physical sputtering regime.

The paper is organized as follows. In Section 2 we describe in detail the molecular-dynamics simulations, including the preparation of our computational samples, and the potentials employed. In Section 3 we present the results obtained for the carbon sputtering yields calculated under different conditions. The results of the simulations will be summarized in section 4.

2. Molecular-dynamics simulations

In this section, we describe the methodology used to study the effects of ion impacts on an aC:H target. In our simulations, we used a three-dimensional 34.03 Å ×19.65 Å ×50.00 Å computational cell with periodic boundary conditions along the three directions (x, y and z). In order to simulate a free surface at the top of the aC:H target, we introduced a vacuum region of thickness ~7 Å. Individual D/T ions were directed onto the target at predetermined angles $0 \leq \theta \leq 75°$ and energies $3 \leq E \leq 150$ eV in random locations, where θ is measured as the angle between the impinging particle and the surface normal (z axis). Since the ions possess relatively large kinetic energies, they frequently reflect off the surface or eject other surface C or H ions back into the vacuum. All such reflected or ejected ions were removed from our simulation cell when they reached our topmost boundary. The interactions between C-C, C-H, and H-H were described based on the adaptive interatomic reactive empirical bond order potential (AIREBO). More details are given below.

A. Interatomic potentials.

As originally developed, the REBO potential was exclusively short-ranged, i.e. two atoms interact only if they are separated by a distance less than a covalent-bonding cutoff of 2.0, 1.7, an 1.8 Å for C-C, H-H and H-C bonds respectively [13]. The REBO potential has been very successful in describing intramolecular interactions in carbon and hydrocarbon materials. However, REBO does not incorporate any way to successfully treat intermolecular interactions (e.g. dispersion, short-range repulsion). This shortcoming is circumvented in AIREBO by including a Lennard-Jones (LJ) potential. To preserve the reactive character of the potential (altered by the strong repulsive barrier usually associated to LJ potentials), a switching scheme that accounts for chemical characteristics of the system is also included in AIREBO [14]. The other new component of the AIREBO potential is a term dependent on dihedral angles modified to conserve the chemical reactivity of the potential. This is a four-body term introduced to create a barrier to rotation around bonds so as to preserve the chemical structure of complex polymers (C_xH_y, $x>2$). This is especially important when simulating amorphous systems. In this

manner, the total energy can be expressed as: $E^{AIREBO} = E^{REBO} + E^{LJ} + E^{tors}$. Both the switching functions associated with E^{LJ} and the multi-body character of E^{tors} make the addition of these terms substantially costly from a computational standpoint. In their paper explaining their AIREBO potential, Stuart *et al.* [14] indicate that the LJ and torsion interactions are only small perturbations on the REBO terms, which dominate in calculations of structural and energetic properties. In dynamical simulations involving bond dissociation and formation, the E^{LJ} and E^{tors} contributions may be significant. In this paper, prior to conducting any further sputtering simulations, we set out to study the relative importance of each one of these terms on the physical parameter of interest: the carbon sputtering yield Y_C.

We have performed simulations by switching on (T) and off (F) the two new AIREBO contributions (LJint, tors), plus a third term involving LJ long-range corrections (LJcorr). This last term is a constant additive correction by which the tail of the attractive potential brings a small additional contribution to the cohesive energy [15]. This last correction is complementary to using LJ interactions and thus if LJint is turned off (F), LJcorr is necessarily off as well. In order to describe energetic collisions appropriately, at very short distances we have splined the "universal" or ZBL potential [16] to the pair potential in REBO.

B. Amorphous hydrogenated carbon samples

The creation of a satisfactory aC:H substrate is a key task that involves multiple simulation steps. Generally, samples no larger than 500 atoms have been used in the literature [10-12]. The final structure onto which the annealing procedure is performed contains 2025 atoms. Our procedure is outlined here: i) first we equilibrate the system (crystalline graphite) at temperatures between 4000 and 5000 K; ii) with the graphite in a quasi-liquid state, we substitute C atoms by H atoms randomly until a concentration of 25% at. H is reached (to mimic the 0.25-0.4 H:C structure observed in experiments [17]); iii) then we do a series of 1-ps annealing/quenching operations in decrements of 500K until the final desired temperature of 500K is reached.

Two different samples were prepared by following the procedure previously described. The first was obtained by annealing only with the REBO term, i.e. an FFF condition (neither LJint nor tors nor LJcorr interactions). The second one was annealed using a TTT condition (full AIREBO). Figure 1 shows the computational cell after the annealing process for the latter condition. Samples prepared under FFF conditions contain a considerable number of non-equilibrium chemical configurations that increase their surface reactivity. On the other hand, these configurations are not present on samples annealed under TTT conditions. This mainly results from the contribution from the torsional term which limits the deviation from optimum dihedral configurations.

3. Results

As described earlier, T ions were impinged on the crystal at random surface locations and at fixed energies and angles. Following the ion impingement, the system was allowed to relax for 0.5-2.0 ps and the C, H, and C_xH_y ion sputtering yields were measured separately. A minimum of 2000 impingement simulations were performed for each energy and angle in order to establish meaningful sputtering yield statistics, resulting in errors of 10-20% in our final sputtering yields. The carbon sputtering yield

(Y_C) is defined as the number of C_xH_y molecules that exit the surface unequivocally during the timescale of the simulation at hand. Prior to determining the impingement condition a sensitivity analysis of the effect of terms in the interatomic potential was carried out to find a compromise between numerical accuracy and computational efficiency.

A. Sensitivity Analysis of Interatomic Potential.

This sensitivity analysis will enable us to calibrate the relative contribution of each AIREBO term so as to optimize the use of our computational resources. To our knowledge, this is the first sensitivity study performed under dynamical conditions for these hydrocarbon potentials. Table I shows results of carbon sputtering yield obtained at two different angles (30 and 45°) and 100 eV for REBO (FFF) and the full AIREBO (TTT). As one can see, results depend substantially on the type of annealing performed on the sample. The FFF target has a non-equilibrium structure and thus results obtained on it are somewhat spurious. It is evident how Y_C varies considerably when TTT is used vs. FFF for this case (almost threefold). This is related to the fact that the surface changes its morphology towards more favorable configurations when TTT is employed, which enhances the reactivity of the atoms with the impinging particles, leading to higher sputtering yields. As for the TTT case, the differences are ±30%, which indicates that the relevant parameter for the sputtering calculations is the structure of the target. Therefore, we conclude that the best compromise to optimize computational resources vs. numerical accuracy is to use the TTT-annealed target (with full AIREBO) with FFF (REBO) tritium bombardment. This sensitivity study may differ at much lower energies, and further simulations are in progress.

B. Carbon sputtering data

We have simulated the impact of tritium atoms with the target surface at a number of angles, namely $\theta = 0, 30, 45, 60$ and 75°, and in the 5-150 eV energy range. Figure 2 shows the whole angular spectrum at high incident energies (50, 100 and 150 eV). The figure clearly shows how the strong dependence on the angle of incidence at 150 eV is mitigated to a nearly energy-independent behavior at 50 eV. In general, Y_C increases with angle as for high θ's ('grazing' angles) since the damage is localized on the surface where atoms are more likely to be dislodged. Experiments by Eckstein and co-workers using D bombardment [18] also find a flat dependence on the sputtering yield at 50 eV, although their yield is about 3.5 times larger than our calculations. In addition, they find an increase in the yield with angle at energies of 350 eV and higher, but there is no data for intermediate energies.

Of particular interest is the comparison of our results with other simulations and experimental data. Fig. 3 shows a comparison of our results with several molecular dynamics and tight-binding calculations [11,12] and with experimental data in pyrolitic graphite [3]. Although there is considerable noise in the data, our results agree reasonably well with those of ref. [11], labeled "Kresheninnikov2002", where both the tight binding and the empirical potential results display similar low-energy behavior as our data. Since these data were taken at a substrate temperature of 300K with deuterium and our data at 600K with tritium, one might expect their results to be somewhat lower than our results. The other simulation results [11], labeled "Salonen2001", were also obtained at 300K

with tritium but do not agree so well with the other MD data. It is not yet clear what the explanation for this discrepancy may be, although Salonen *et al.* used a Maxwellian energy distribution for the impinging D and T ions on a substrate significantly smaller than ours. The high-energy tail of the distribution may have had a dominant effect. The experiments and our simulations were performed using monoenergetic ions.

At higher energies, where physical sputtering dominates over chemical sputtering, our results are in reasonable agreement with the experimental data. A possible explanation for the difference at low energy between our simulations and the experiments of Mech *et al.* [3] is that the full contribution to chemical sputtering may not be taken into account in MD simulations. The rate constant for some chemical reactions that may have strong contributions to the total carbon yield is well beyond our simulated timescale (several ps). It is worth mentioning that the sputtered C is seen to escape the surface either as monoatomic C (~70%) or associated to H atoms forming simple molecules (CH, CH_2 and CH_3 mostly). In order to capture the full post-impact sputtering, longer timescales and/or coarser methods (such as Monte Carlo or rate theory models) need to be implemented, and we are already carrying out preliminary calculations for near-surface chemistry using our MD results as input.

4. Summary and conclusions

We have performed MD simulations of C sputtering in *a*C:H using the AIREBO potential. Our results demonstrate that, for the regime where physical sputtering dominates, the surface morphology has a stronger effect than the interatomic potential terms that we investigated. Preliminary simulations at 5-30 eV with AIREBO also indicate huge variations in the yield depending on the sample structure/size, as previously reported for REBO potential simulations [12].

We have covered the polar angle/incident energy parameter surface in detail and have seen that, at low energies, the carbon yield is almost independent of the incident angle, in agreement with recent experiments. Our high-energy data displays reasonably good agreement with experimental results obtained under similar conditions. At lower energies, chemical effects are predominant and the MD timescales are not sufficiently long to capture the sputtered molecules stemming from delayed chemical reactions. Carbon sputtering rates can have a strong impact on the properties of the plasma in a fusion chamber. Preliminary calculations with UEDGE [19] show that a factor of two reduction in the C sputtering coefficient can change the ion density in the plasma by more than a factor of two, even though the amount of C in the plasma is only a few percent.

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Tables

Table I: Carbon sputtering yield ($\times 10^{-2}$) on two different targets (annealed and non-annealed) for an incidence T angle of 30° and 45°. Results are for two extreme cases: considering all AIREBO interactions (LJint=T, tors=T, LJcorr=T) and solely the REBO potential (FFF).

Surface condition, tritium energy and incident angle	FFF	TTT
Non-annealed 100 eV 30°/45°	6.26/10.05	2.26/3.16
Annealed 100 eV 30°/45°	0.93/2.04	1.30/1.85

Figure captions

Figure 1: Amorphous C:H layer produced by cooling the liquid by annealing in steps as the temperature is reduced below the melting point with a TTT condition (see text). Carbon atoms are depicted in orange whereas H atoms are blue.

Figure 2: Carbon sputtering yield as a function of θ for three incident energies. The angular dependence decreases with impinging energy.

Figure 3: Comparison of our results for carbon sputtering yield as a function of energy and other simulation and experimental data. Our simulations are for ions incident at 30°, at T=500 K. The data labeled "Salonen 2001" corresponds to ref. [11], for ions impinging at 0°-20° at T=300 K, [11], "Krasheinnikov 2002" to ref. [12], T=300K, and incident angles of 0°-20°. "Mech 1998" refers to the experiments in ref. [3], using normal incidence ions at T=500 K.
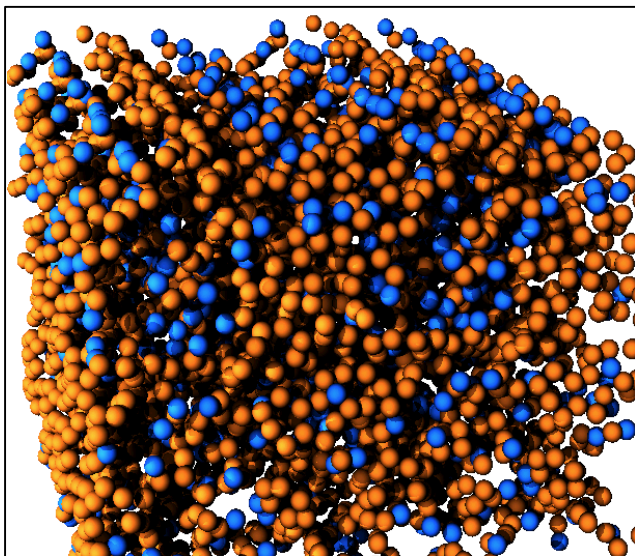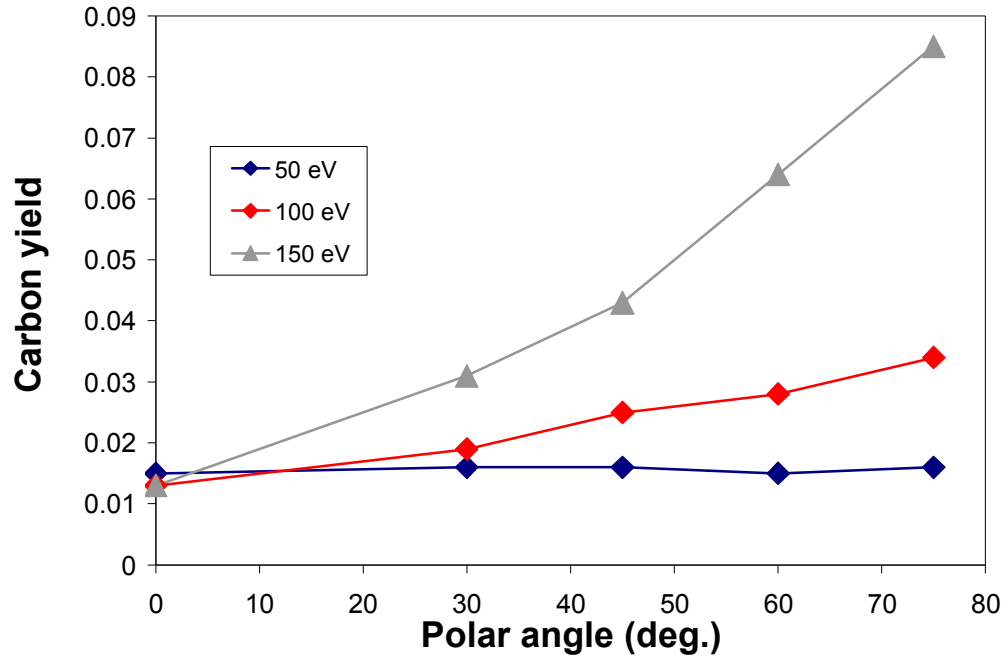
Figure 1

Figure 2

Figure 3

Legend:
- This work, MD, 30 deg, 600K
- Salonen 2001, MD, 30 deg, 300K
- Krasheninnikov 2002, TB, 300K
- Krasheninnikov 2002, MD, 300K
- Mech 1998, QMS, 500K

X-axis: Incident tritium energy (eV)
Y-axis: Carbon yield