

# Mechanism of swift chemical sputtering: comparison of Be/C/W dimer bond breaking

K. Nordlund<sup>a,\*</sup>, C. Björkas<sup>a</sup>, K. Vörtler<sup>a</sup>, A. Meinander<sup>a</sup>, A. Lasa<sup>a</sup>, M. Mehine<sup>a</sup>, A. V. Krasheninnikov<sup>a,b</sup>

<sup>a</sup>Department of Physics, P.O. Box 43, FI-00014 University of Helsinki, Finland

<sup>b</sup>Department of Applied Physics, P.O. Box 1100, FI-00076 Aalto University, Finland

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## Abstract

Current and future tokamak-like fusion reactors include the three elements Be, C, and W as the plasma-facing materials. During reactor operation, also mixtures of all these elements will form. Hence it is important to understand the atom-level mechanisms of physical and chemical sputtering in these materials. We have previously shown that athermal low-energy sputtering of pure C and Be can be understood by the swift chemical sputtering mechanism, where an incoming H (or D or T) ion enters between two atoms and pushes them apart. In the current Article, we examine the model system of D impacting on a single dimer to determine the detailed mechanism of bond breaking and its probability for the Be<sub>2</sub>, C<sub>2</sub>, W<sub>2</sub>, WC, BeW, and BeC dimers. The results are found to correlate well with recent experiments and simulations of sputtering of the corresponding bulk materials during prolonged H isotope bombardment.

**Keywords:** Swift chemical sputtering, Mixed materials, Ion irradiation

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## 1. Introduction

The interactions between ions with kinetic energies of the order of 1 – 100 eV with materials are an interesting borderline between physics and chemistry. Since the energies involved are comparable or only slightly higher than the strengths of chemical bonds, chemical effects can be expected to give a significant contribution to material erosion in this energy regime. This issue is particularly important due to the ongoing development of the ITER fusion reactor, where ions in this energy range will interact with complex Be/W/C-based plasma facing materials.

Several types of chemical effects have indeed been reported in this system. Numerous experiments have shown that any carbon-based first wall material in the divertor part of the reactor erodes with high yields at energies clearly below the physical sputtering threshold (see e.g. [1, 2]). While this anomalous erosion can at high temperatures be understood by hydrogen-induced formation of volatile species that desorb by thermal activation [3, 4], the effect does not show any temperature dependence between liquid nitrogen and room tempera-

ture [5], showing that a thermally activated mechanism cannot be the full explanation.

Molecular dynamics computer simulations have shown that (at least part of the observed) carbon and beryllium erosion can be explained by a special type of chemical sputtering: the incoming energetic ion enters between two carbon atoms, forcing them apart if its kinetic energy is low enough that it spends a substantial amount of time between the atoms [6, 7, 8, 9]. If one of the carbon atoms is only loosely bound to the surface, this can cause sputtering of it, along with any hydrogen which may be bound to it. Also sputtering of larger molecules is possible [7]. Several aspects of this “swift chemical” sputtering of carbon have been examined by computer simulations, such as its angular dependence [10], effect of electronically excited states [11], cobombardment with plasma impurities [12] and the effect of sample structure [13]. The simulated and experimental sputtering yields have also been found to be in good agreement with each other [14, 15]. For Be the fractional sputtering yields of BeD molecules have been shown to be in excellent agreement with experiments [9].

In the current paper, we first present an analytically-based explanation of the sputtering mechanism for the model system of a H ion impacting on a dimer. We then carry out simulations of D ions impacting on dimers

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\*Corresponding author. Tel: +358 9 191 50007; fax: +358 9 191 50610

Email address: kai.nordlund@helsinki.fi (K. Nordlund)

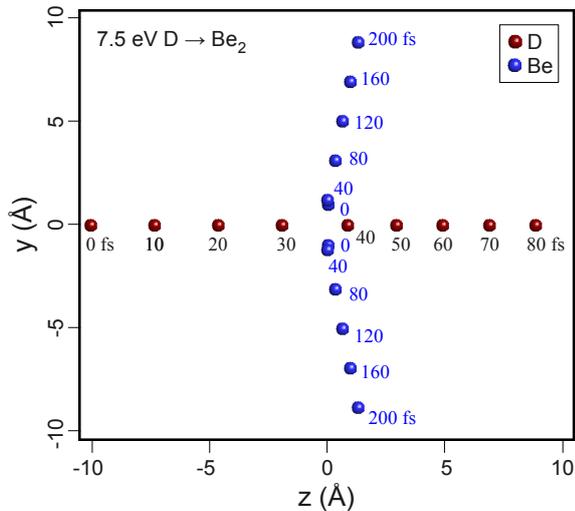


Figure 1: (Color online) Trajectory snapshot plot of swift chemical sputtering mechanism for the case of a 7.5 eV D ion impacting against the midpoint of a Be-Be dimer. The small numbers next to the atoms indicate the time in fs when the atom position was recorded. Note that for clarity the positions of the D atom are shown more frequently than the Be ones.

consisting of all the ITER-relevant elements Be, C, and W as well as their mixtures, using an interatomic potential for the quaternary H-Be-C-W system recently developed by us [16, 17, 18]. The results are finally compared to experimental and simulation results of chemical sputtering of realistic Be, C, and W materials.

## 2. Analytical description of mechanism

The physico-chemical origin of the swift chemical sputtering can be understood by considering the model system of one H isotope ion colliding with a dimer [8]. The most symmetric case possible is the one where the H atom moves perpendicular to the chemical bond towards the middle of it, see Fig. 1. The momentum transfer in the  $y$  (lateral) direction can be written

$$p_y = \int_{-\infty}^{\infty} f_y(t, E_{kin}^H) dt \approx \bar{f}_y \bar{\tau}, \quad (1)$$

where  $f_y$  is the force acting on the carbon atoms and  $E_{kin}^H$  the initial kinetic energy of the H atom. The integral can be qualitatively evaluated as a product  $\bar{f}_y \bar{\tau}$ , where  $\bar{f}_y$  is an effective average force during the collision, and  $\bar{\tau}$  an effective average time the H atom spends in the area of the C-C bond.

If the kinetic energy of the H ion  $E_{kin}^H$  is low, the H atom returns back without entering the region between

the C atoms. Then  $\bar{f}_y$  and the  $y$  momentum are small and the bond is not broken. When the initial kinetic energy of the impinging particle is high enough for the H atom to stay for a (relatively) long time  $\bar{\tau}$  in the region between the atoms, the bond breaks. If the initial kinetic energy of the impinging particle is further increased, the bond breaking ceases. The reason is that although  $\bar{f}_y$  is large, the particle spends too little time in the region between the carbon atoms to cause any bond breaking ( $\bar{\tau}$  is short). Thus there is a finite energy window in which the bond breaking can occur (cf. Fig. 2). The characteristic time of this process is very short, of the order of 10 fs. Because the mechanism involves atom bonding, requires kinetic energy, and is rapid, we named it “swift chemical sputtering” [19].

To rule out dependence on the choice of potential, we have shown that the effect occurs as described above using three varieties of the Brenner potential [20, 21, 22], for Si [23], as well as in a tight-binding quantum mechanical framework [8].

## 3. Methods

For the current Article, we carried out a systematic set of simulations of D ions impacting towards the midpoints of Be<sub>2</sub>, C<sub>2</sub>, W<sub>2</sub>, WC, BeW, and BeC dimers. The interactions between the atoms were in all cases described with our interatomic potential for the H-Be-C-W system [16, 17, 18], implemented in the PARCAS classical molecular dynamics code [24]. We note that for some of the materials involved, the dimer properties do not exactly match the experimental ones due to necessary compromises made in the potential development. However, the material comparison can still give valuable insights into how the swift chemical sputtering mechanism depends on dimer bond distance and strength.

The choice of simulating only impacts towards the midpoint introduces a high level of symmetry to the elemental systems. Without this symmetry, the H may form a bond to one of the dimer atoms, making bond breaking easier, as has been recently shown explicitly by Reinhold *et al.* in detailed simulations of bond breaking in non-symmetric configurations and for D impacting on larger molecules [25]. This is also reflected in our results for non-elemental systems, where the symmetry is broken and in some cases bond-breaking was observed for incoming ions with energy less than the bond strength (see below). However, as the focus of the current paper is to provide a comparison of dimers composed of different elements in a maximally simple

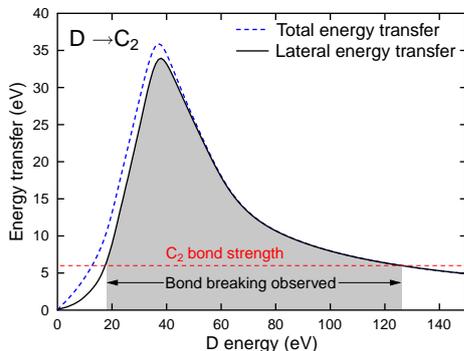


Figure 2: (Color online) Energy transfer from a D ion to the two atoms in a C dimer. Shown separately is the total energy transferred to the dimer and the lateral energy transfer. The latter quantity was obtained by subtracting the final kinetic energy for motion in the  $z$  direction from the total energy of the dimer. The gray area illustrates the energy interval where bond breaking was observed in the simulations. The red horizontal dashed line shows the energy of the dimer bond. Note that the positions of the gray area and red dashed line are determined independently.

system, results are shown only for ions directed towards the midpoint.

Energy conservation was monitored automatically during all simulations, and the time step was chosen adaptively [26] to ensure conservation to an accuracy of 0.0001 eV/atom or better through the entire simulation run. The dimer was initially placed centered on the origin, with the dimer axis oriented along the  $y$  axis (lateral direction). The incoming D dimer was placed at  $z = -10$  Å and given a kinetic energy in the positive  $z$  direction towards the midpoint of the dimer. The boundary conditions were kept open in all dimensions. No electronic stopping, temperature or pressure control was used in the simulations.

The ion energy was scanned from 0 to 200 eV, and the end result of the simulations automatically analyzed for bond-breaking (defined as either one of the dimer atoms having zero potential energy in the end of the simulation) and for whether the D atom was reflected backwards or transmitted through the dimer.

## 4. Results and discussion

### 4.1. Carbon

The results for D impacting with a carbon dimer are shown in Fig. 2. The gray area in the figure illustrates the energy interval where bond breaking was observed in the simulations. The red horizontal dashed line shows

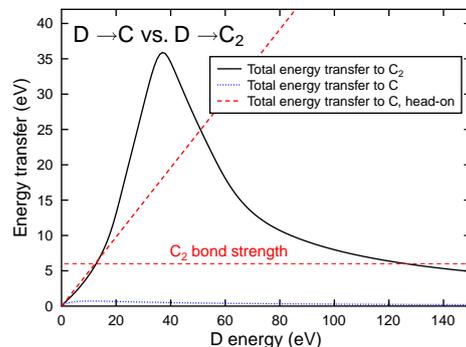


Figure 3: (Color online) Comparison of energy transfer from a D ion to the two atoms in a C dimer and a single C atom. The “total energy transfer to C” was calculated for the same lateral distance (impact parameter) from the ion to the C nucleus as in the dimer case. In the “head-on” case the impact parameter was zero.

the energy of the dimer bond. Note that the positions of the gray area and red dashed line were determined independently. The excellent agreement between the gray region and the positions where the red line crosses the lateral energy transfer curve confirms the argument of the analytical model that the crucial factor behind the bond breaking is the momentum (and hence kinetic energy) transfer from the ion to the atoms in the dimer. Bond breaking occurs only in a limited energy window, confirming the analytical argument that at high enough energy, the momentum transfer goes down and the bond breaking ceases.

A similar model calculation can also be used to establish that the energy transfer mechanism is not the same as in a binary collision characteristic of physical sputtering. We reran the same calculation as described above, but removing one of the dimer atoms. Thus the calculation contains only 2 atoms and corresponds to solving the classical binary scattering integral for an impact parameter that is half the bond length of the C-C dimer bond distance. The results are illustrated in Fig. 3, which shows that the energy transfer to the single atom is dramatically weaker than to the dimer, and in fact never exceeds the bond strength of 6 eV. The figure also shows the energy transfer to a dimer can be even larger than that from D to C in a binary head-on collision. This shows that at low energies, swift chemical sputtering can be expected to be a more significant source of energy transfer and hence sputtering than binary collisions.

Additional insight can be obtained by plotting the  $z$  coordinate of the ion as a function of time, see Fig. 4.

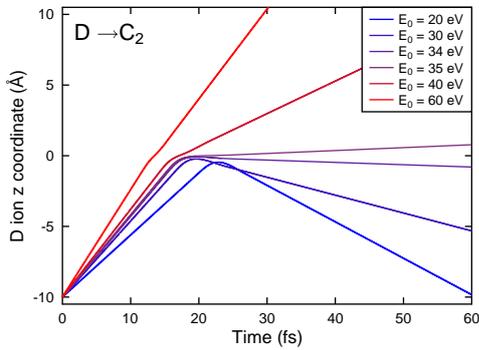


Figure 4: (Color online)  $z$  coordinate of D atom while it collides with a  $C_2$  dimer.

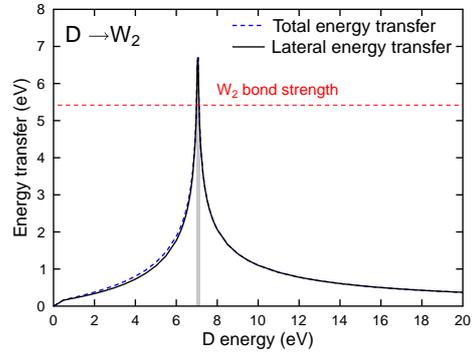


Figure 6: (Color online) As Fig. 2, but for W.

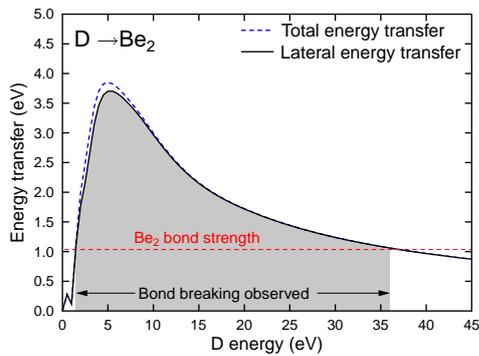


Figure 5: (Color online) As Fig. 2, but for Be.

The plot illustrates how the ion gets slowed down when it enters between the dimer atoms, and either is transmitted through the dimer or reflected back. Note that the  $z$  coordinate does not necessarily perfectly correlate with whether the ion passes through the dimer, because some kinetic energy in the  $z$  direction is also passed to the dimer. For the same reason, the maximum energy transfer may also be at a slightly different energy. For the particular case illustrated in Fig. 4, the ion was reflected backwards up to an energy of 34 eV, but transmission through the bond only occurred at 36 eV. The maximum total energy transfer occurred at 37 eV, when the ion transferred 35.89 eV to the dimer (i.e. was left itself with only 1.11 eV of kinetic energy).

#### 4.2. Comparison of materials

The calculation of the energy transfer was repeated for all the possible dimers in the ternary Be-C-W sys-

tem. The results are illustrated in Figs. 5 – 7.

Figure 5 shows that similar to C, also the Be-Be dimer bond can break by energy transfer from a D. However, both the energy transfer and the energy needed for bond breaking is much lower than for C-C. The reason to this is the different H-Be interaction and that the Be-Be bond energy is much weaker (about 1 eV vs. 6 eV for carbon).

In W (Fig. 6) the probability for bond breaking is negligible, due to the strong W-W bond and the large mass difference between D and W making momentum transfer inefficient. The mass effect was confirmed by running a test simulation with the mass of D set to the same as W, while keeping the chemical interactions the same as for D-W. These calculations showed bond breaking in a very wide energy interval of 9 – 64 eV. The energy transfer is enough to break the bond only in a very narrow energy window. This implies that in a practical situation, where it is highly unlikely the D would impact on the midpoint of a bond, the probability for swift chemical sputtering of pure W should be extremely low.

Figure 7 shows the energy transfer and bond breaking probability for D impacting on the mixed WC, BeW and BeC dimers. Here the behaviour is more complex, because both the mass difference and different interactions introduce an asymmetry to the system. Monitoring of the atom trajectories showed that the D ion interacted in complex trajectories with the dimer, and in some cases became attached to one of the atoms that was initially in the dimer (hashed region in the plots). This explains the complex energy dependency of the energy transfers. However, in spite of these complications, the energy transfer and bond strength still match very well, showing that also for mixed systems the bond breaking can be understood in the swift chemical sputtering formal-

ism.

### 4.3. Comparison to other works

The results obtained here are very well in line with previous [7, 27, 9] and ongoing simulation studies of the sputtering of Be/C/W materials. Some of the simulation results are illustrated in Fig. 8. The previous studies and experiments have shown that chemical sputtering of carbon is very pronounced at low energies, and that it occurs with a low but non-negligible probability in Be as well. On the other hand, experiments have not shown any indications of chemical sputtering of W, and neither do our currently ongoing simulations. These observations are fully consistent with the results in Figs. 2, 5 and 6. Although figure 6 indicates that the W dimer bond might be broken by D ions, in a solid W surface each atom has 8-9 “bonds” (i.e. nearest neighbours), and breaking of several of these is extremely unlikely. For the same reason the Be yield can be expected to be much smaller than the C one, consistent with the analysis of number of neighbours presented in [9].

The results for mixed dimers (Fig. 7 indicate that all the types of mixed systems considered here can be expected to sputter chemically. This is consistent with previous and ongoing simulations for WC [27] which show pronounced sputtering at low energies (although at higher energies also other molecular sputtering mechanisms are active [28]), and ongoing simulations in BeC where trajectory analyses show swift chemical sputtering. Simulations of the sputtering of BeW are not yet available, so the present work indicates that chemical sputtering should be also observed in that system.

Regarding sputtering of mixed materials, one has to bear in mind that prolonged bombardment of any mixed carbide material can lead to the formation of loosely bound hydrocarbons on the surface [27]. These could naturally break and lead to carbon sputtering even if the metal-carbide bond would not break so easily. Due to this complication, the results on the bond breaking in the dimer model system cannot be quantitatively correlated to experimental or simulated sputtering yields in the solid materials.

## Conclusions

Using classical molecular dynamics modelling of the model system of D ions impacting on dimers containing the elements Be, C, and W, we have examined the fundamental mechanism and energy dependence of the swift chemical sputtering mechanism. Studies of ion trajectories in C were used to establish that the energy

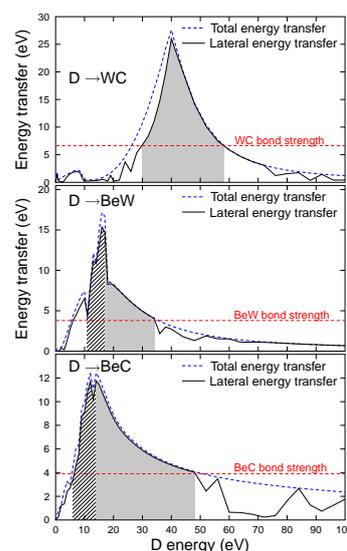


Figure 7: (Color online) As Fig. 2, but for the mixed dimers WC, BeW and BeC. The hashed area shows the energy interval where the dimer bond is broken, but the incoming D remains bonded to one of the atoms that was initially part of the dimer.

transfer in swift chemical sputtering is fundamentally different from that in binary collisions. Comparison of results for the different dimers show that sputtering occurs with a significant probability in all cases except for the  $W_2$  dimer, well in line with experiments and simulations on the sputtering of the same materials in solid phase.

## 5. Acknowledgements

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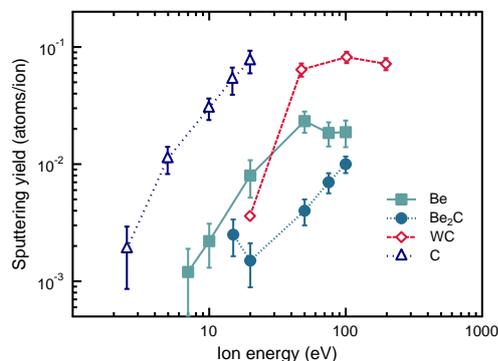


Figure 8: (Color online) Sputtering yields for C, W, Be, WC and Be<sub>2</sub>C obtained by MD simulations in our group. The data for C is from [14], for Be from [9] and for WC from [27].

the same as in [26].

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