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

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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_2, C_2, W_2, 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.

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 temperature [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 [6–9]. 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 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 [16–18]. 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

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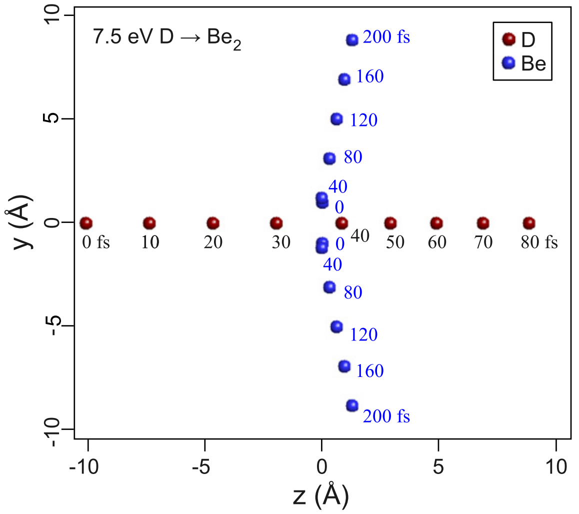

Fig. 1. Trajectory snapshot plot of swift chemical sputtering mechanism for the case of a 7.5 eV D ion impacting against the midpoint of a Be–Be dimer. The small numbers next to the atoms indicate the time in fs when the atom position was recorded. Note that for clarity the positions of the D atom are shown more frequently than the Be ones. (For interpretation of color mentioned in this figure the reader is referred to the web version of the article.)

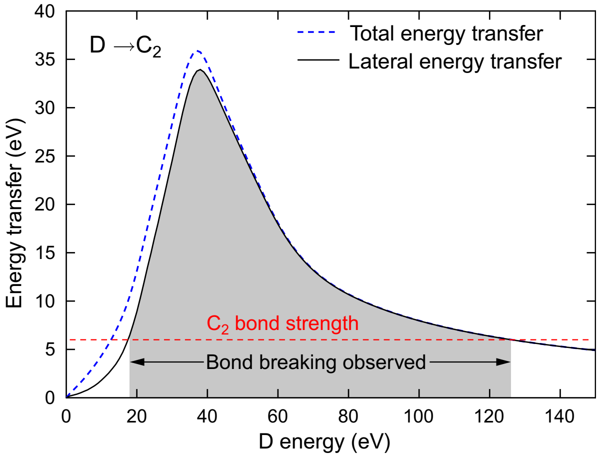

Fig. 2. Energy transfer from a D ion to the two atoms in a C dimer. Shown separately is the total energy transferred to the dimer and the lateral energy transfer. The latter quantity was obtained by subtracting the final kinetic energy for motion in the z direction from the total energy of the dimer. 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. (For interpretation of color mentioned in this figure the reader is referred to the web version of the article.)

chemical bond towards the middle of it, see Fig. 1. The momentum transfer in the y (lateral) direction can be written as

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

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 [20–22], 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$_2$, C$_2$, W$_2$, 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 [16–18], 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 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