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Radiation damage in WC studied with MD simulations

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Abstract

Studying radiation damage in tungsten carbide (WC) is of importance due to its applications in fusion reactors. We have used molecular dynamics to study both deuterium induced sputtering and modification of WC surfaces and collision cascades in bulk WC. For collision cascades in bulk WC we note a massive recombination and major elemental asymmetry for the damage. Studying the erosion of WC surfaces, we find that C can erode through swift chemical sputtering, while W does not sputter more easily than from pure W. The amorphization of the surface and the D-content due to the D bombardment is important for the damage production and sputtering process.

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1. Introduction

Tungsten carbide (WC) is a much used material in wear resistant parts such as cutting and mining tools and drill bits due to its hardness and temperature resistance. Tungsten, carbon and tungsten carbide are also planned to be used in the divertor of fusion reactors such as ITER [1]. The divertor is the part of the reactor to which particles from the plasma are directed and it will be under intense heat load by low-energy (1–100 eV) hydrogen isotopes, mainly deuterium, as well as impurity plasma particles and high energy particles.

Molecular dynamics (MD) is well suited for studying the time and length scales of initial damage production and sputtering, which are not easily accessible to experiments. Collision cascades in bulk materials give important information on the damage produced by the energy transfer from an irradiating particle to the material. Studies have been done on many materials [2–5], but only a few on multi-elemental such as metal alloys [6,7] and compound semiconductors [8,9]. WC is of particular interest due to its extraordinary differences in mass and chemical properties of the constituent elements.

The erosion of divertor surfaces is very important in fusion reactors as eroded particles and molecules cool down the plasma. Especially heavier elements must sputter as little as possible. Tungsten is a metal and it only erodes through physical sputtering with a threshold of around 200 eV [10], while carbon is known to also sputter through chemical sputtering [11]. Thus it is interesting to examine in which way a ceramic-like WC acts under irradiation and what the sputtering yields for W and C are from the surface. Some experiments have been performed on sputtering of WC [10], but MD simulations can be used to study the sputtering events in more detail.

2. Method

All MD simulations were performed using the PARCAS code [12], equilibrating the systems to 300 K for 5–10 ps using the Berendsen temperature and pressure control [13]. We use a Tersoff type potential recently developed for this purpose in our group [14]. For the bulk cascade

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simulations a recoil energy of 0.4–5 keV was given to an atom in a random direction, near the centre of the sample, which contained up to 153,600 atoms for the highest energy. Periodic boundary conditions were used and if the energy of an atom in the border region exceeded 10 eV, the simulation was stopped and a new recoil, in the same direction but farther from the border, was started instead. Defects were found by searching for atoms outside spheres of radius 0.25 of the nearest neighbour distance, and the atom type of the defect was noted. Clusters of defects were defined to include nearest neighbour atoms sites of the opposite atom type and second nearest neighbour sites of the same atom type.

For sputtering simulations boxes of 1920 atoms were used for simulations of crystals. These were constructed using periodic boundaries in two directions and opening a (0 0 0 1) surface and fixing the bottom of the sample in the third. Both W- and C-terminated surfaces were simulated. Amorphous samples containing 1000 atoms with tungsten content between 50% and 90% were also used. The surfaces were bombarded cumulatively with 10–2000 eV deuterium ions with an angle of incidence randomly chosen between 0° and 20° for 2000 impacts with annealing runs between the bombardments. The box size was deemed to be sufficiently large, though higher energy deuterium could move through the whole simulation cell, corresponding to a situation where the damage takes place deeper in the bulk. The use of deeper boxes for a large number of impacts would have been computationally challenging.

3. Results and discussion

Up to 90% of damage caused by collision cascades in bulk WC was observed to recombine in the cascade, as can be seen in Fig. 1. This is a much more pronounced effect than that in other non-metallic materials such as Si [15]. In Fig. 2 we note that most of the remaining defects are carbon, especially for isolated defects where almost no tungsten Frenkel pairs can be found. To explain this elemental asymmetry we first explored whether the mass and size differences of W and C are enough to affect the cascades, using the binary collision approximation [16] code SRIM-2003 [17]. 5 keV SRIM cascades show about three times more W than C isolated defects, in contrast with MD results. Low-energy ballistic effects, such as shown to be important for GaN [18] were ruled out by simulating the average threshold displacement energy [19], which turned out to be similar for W and C recoils, 24 ± 3 eV and 20 ± 2 eV, respectively.

Since ballistic effects cannot explain the effects, we instead look at the high formation energy of W Frenkel pairs compared to the formation energy of C Frenkel pairs, about 15 eV and 3 eV, respectively [14]. These values show that it is energetically very favourable for tungsten defects to recombine. Hence almost all isolated W Frenkel pairs recombine, while the relatively stable C defects remain to

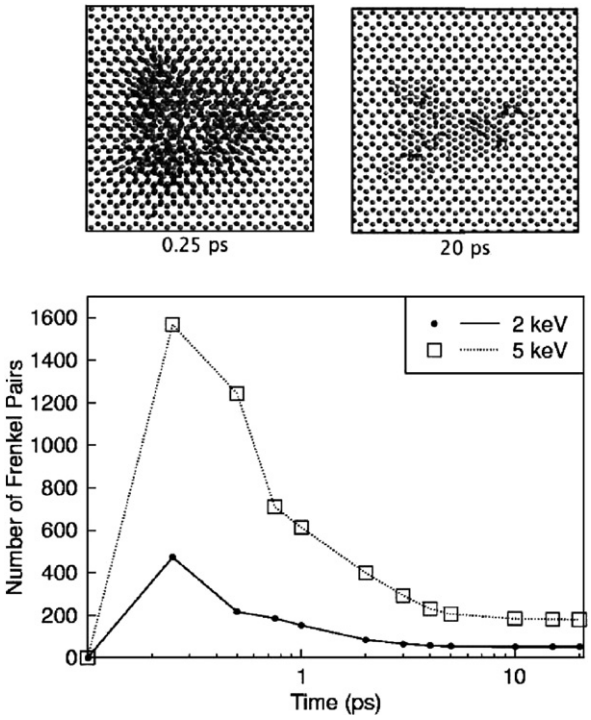

Fig. 1. Frenkel pair production as a function of time in 2 keV and 5 keV W-recoil cascades in WC. The figure also shows snapshots, taken at 0.25 ps (left) and at 20 ps (right), of a 5 keV cascade, where it can be visually seen that most of the damage recombines. The lighter spheres represent C atoms and the darker ones W atoms.

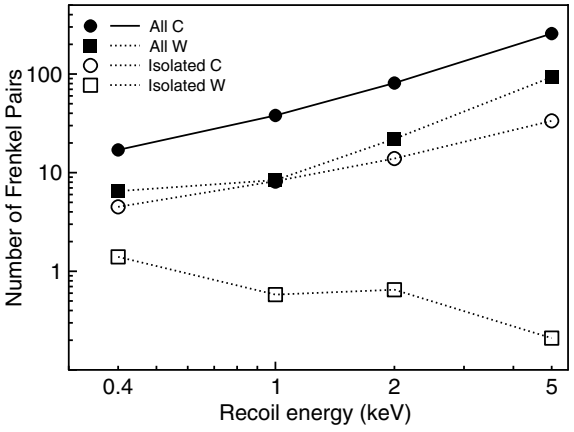

Fig. 2. Total and isolated defects after 0.4 keV, 1 keV, 2 keV and 5 keV W-recoil cascades. The isolated Frenkel pairs are not part of a defect cluster.

a larger degree. The relatively large release of energy to the material from W defect recombinations prolong the heat spike, giving defects more time to recombine before the cascade region fully solidifies, enhancing the remarkably large recombination.

Looking at the deuterium bombardment of WC surfaces, the sputtering yields of carbon from WC surfaces are largest at around 100 eV where it is about 0.1, after which it starts to go down due to the deuterium channelling through the box. The W- and C-terminated surfaces both

exhibit similar sputtering yields, as in both cases the surfaces amorphizes, but the C-terminated surface sputtering yield is larger as the first surface layer more easily reacts with incoming deuterium. It is noteworthy that a small sputtering yield is observed even at 10 eV, where physical sputtering is impossible. The process and amount of chemical sputtering of C from WC is very similar to that in pure C. Tungsten does not sputter from WC surfaces more than from pure tungsten, which is very important for plasma–wall interactions in fusion reactors. The amorphization is visualised in Fig. 3 with snapshots of the samples after 2000 bombardments for different energies.

The deuterium ions implanted in the samples play an important role in the sputtering as most chemically sputtered species are hydrocarbon molecules. Higher energy deuterium ions are retained deeper in the sample. Comparing with simulations with SRIM-2003 which only describes physical sputtering we note similar sputtering yields as the MD simulations at higher energies where chemical sputtering plays a minor role. In Fig. 4 we compare the energy distribution and the range distribution of bombarding deuterium ions using SRIM. As can be seen from the plot, higher energy D give more energy to the atoms in the sample, but the maximum in the range distribution is also deeper in the box. Comparing with the damage production and amorphization degree in Fig. 3, we note that the recoil energy transfer from the deuterium ions is not enough to describe the amorphization of the sample, but that the retained deuterium causes the sample to amorphize more easily at 100 eV than at 200 eV. This is likely related to the major damage recombination effect described above: the presence of D can prevent recombination of Frenkel pairs.

Sputtering experiments use irradiation fluences unavailable to MD simulations due to the huge number of bombardment runs needed and thus WC surfaces in experiments are

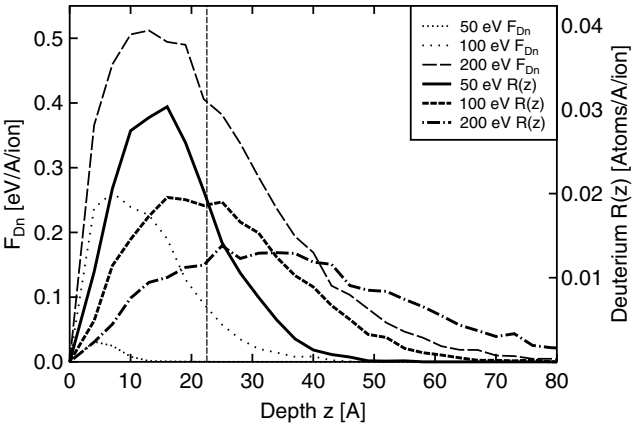

Fig. 4. SRIM analysis of the depth distribution of deposited energy from bombarding deuterium ions (F_{Dn}) (thin lines) and the range of the ions $R(z)$ (thick lines). The vertical line shows the size of the MD simulation box.

largely depleted of carbon which sputter away quickly. Thus we also calculated the sputtering yields at 66 and 300 eV for amorphous WC with 50–90% tungsten, which is how the surface would look after higher fluences even if the experiment started from crystalline WC. We observe that the carbon sputtering yield decrease with increasing tungsten concentration, explaining why sputtering yields seen experimentally are lower [10] than our simulated results.

For 300 eV D bombardment at the lowest available experimental fluences (about 10^{18} ions/cm^2) the concentration c of W in the sample is linear with fluence ϕ [10]. We simulated 50% W crystalline and amorphous WC up to the highest fluences (about 0.03×10^{18}) we can achieve within realistic computation time and note an excellent agreement with experiment for the slope $\mathrm{d}c/\mathrm{d}\phi$. Extracting the experimental data given in Fig. 5 in [10] and fitting a line to it we get $\mathrm{d}c/\mathrm{d}\phi = 63 \pm 10$ at.%. This can be compared with our simulations, in which we get $\mathrm{d}c/\mathrm{d}\phi = 57 \pm 7$ at.% starting

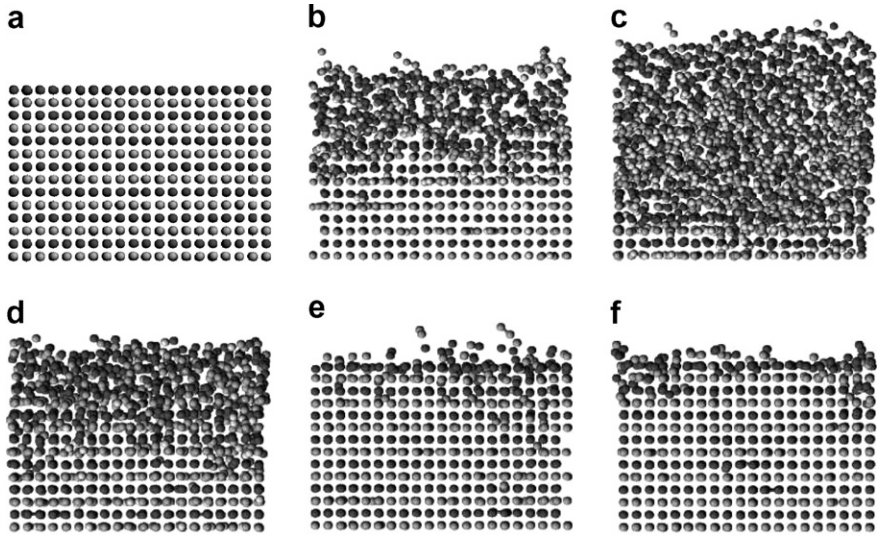

Fig. 3. Snapshots of (a) the initial WC lattice and after cumulative deuterium bombardment at (b) 50 eV, (c) 100 eV, (d) 200 eV, (e) 1000 eV and (f) 2000 eV. The lighter spheres represent C atoms and the darker ones W atoms.

with a crystalline sample and $dc/d\phi = 110 \pm 10$ at.% starting with an amorphous sample. This demonstrates that our model is suitable for describing the sputtering of carbon from WC even though achieving experimental fluence and sample scales is unfeasible. The sputtering results will be presented in detail elsewhere [20].

4. Conclusions

We have studied radiation damage in WC bulk and surfaces. Our results show a preferential defect production and sputtering for the carbon atoms. The large elemental asymmetry in defects after a collision cascade is explained by the big differences in formation energy of W and C Frenkel pairs and can be expected to occur also in other materials with similar differences in defect formation energies. In our deuterium bombardment simulations we found that C sputters from WC through chemical sputtering. The deuterium implanted in the bombardment plays a major role in the damage production and amorphization of the sample.

All results show a major difference between how the carbon and tungsten components in WC are affected by irradiation events, possibly leading to a segregation of W and C during prolonged irradiation. Carbon defects from collision cascades deeper in the material could migrate to the surface, increasing the C-content, while the carbon atoms at the surface sputter away due to low-energy deuterium bombardment.

Acknowledgements

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References

[1] The official ITER webpage: <http://www.iter.org/>.
[2] R.P. Webb, D.E. Harrison Jr., Nucl. Instr. and Meth. B 218 (1983) 697.
[3] T. Diaz de la Rubia, R.S. Averback, R. Benedek, W.E. King, Phys. Rev. Lett. 59 (1987) 1930;
See also erratum:, Phys. Rev. Lett. 60 (1988) 76.
[4] H.M. Urbassek, K.T. Waldeer, Phys. Rev. Lett. 67 (1) (1991) 105.
[5] K. Nordlund, J. Keinonen, M. Ghaly, R.S. Averback, Nature 398 (6722) (1999) 49.
[6] M. Spaczér, A. Almazouzi, R. SchSublin, M. Victoria, Radiat. Eff. Defects Solids 141 (1997) 349.
[7] N.V. Doan, R. Vascon, Radiat. Eff. Defects Solids 141 (1997) 363.
[8] K. Nordlund, J. Nord, J. Frantz, J. Keinonen, Comput. Mater. Sci. 18 (2000) 283.
[9] J. Nord, K. Nordlund, J. Keinonen, Phys. Rev. B 65 (2002) 165329.
[10] H. Plank, W. Eckstein, Nucl. Instr. and Meth. B 124 (1997) 23.
[11] E. Salonen, K. Nordlund, J. Keinonen, C.H. Wu, Phys. Rev. B 63 (2001) 195415.
[12] K. Nordlund, PARCAS computer code, private communication. The main principles of the molecular dynamics algorithms are presented in [15,21]. The adaptive time step and electronic stopping algorithms are the same as in [22].
[13] H.J.C. Berendsen, J.P.M. Postma, W.F. van Gunsteren, A. DiNola, J.R. Haak, J. Chem. Phys. 81 (1984) 3684.
[14] N. Juslin, P. Erhart, P. Träskelin, J. Nord, K. Henriksson, E. Salonen, K. Nordlund, K. Albe, J. Appl. Phys. 98 (2005) 123520.
[15] K. Nordlund, M. Ghaly, R.S. Averback, M. Caturla, T. Diaz de la Rubia, J. Tarus, Phys. Rev. B 57 (13) (1998) 7556.
[16] M.T. Robinson, I.M. Torrens, Phys. Rev. B 9 (12) (1974) 5008.
[17] J.F. Ziegler, SRIM-2003 software package, available online at <http://www.srim.org>.
[18] J. Nord, K. Nordlund, J. Keinonen, Phys. Rev. B 68 (2003) 184104.
[19] K. Nordlund, J. Wallenius, L. Malerba, Nucl. Instr. and Meth. B 246 (2) (2005) 322.
[20] P. Träskelin, N. Juslin, P. Erhart, K. Nordlund, Phys. Rev. B, submitted for publication.
[21] M. Ghaly, K. Nordlund, R.S. Averback, Philos. Mag. A 79 (4) (1999) 795.
[22] K. Nordlund, Comput. Mater. Sci. 3 (1995) 448.