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Journal of Nuclear Materials 313–316 (2003) 77–81

journal of nuclear materials

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# Molecular dynamics simulations of the effect of deuterium on tungsten erosion by oxygen

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## Abstract

Chemical erosion of tungsten is one of the critical issues for its use as tokamak armor material. Oxygen impurities in the SOL plasma may deteriorate the good tungsten performance. The regime at the divertor surface heated up to 1500 K is investigated, with SOL particles arriving with energies below the sputtering threshold. Oxygen can form the molecules $WO_2$ and $WO_3$ under deuteron bombardment. The tungsten erosion is assumed due to the sublimation of the $WO_3$ molecules. To calculate this process the classical atomic dynamics analysis code (CADAC) is developed. As a new numerical method, time step clusters are introduced which allow significant acceleration of the calculations, especially for assemblies of atoms of large mass ratios, keeping the conservation of momentum and energy. First results are presented based on a solution of simplified equations for molecular surface densities, with kinetic coefficients obtained by CADAC. The deuteron bombardment significantly reduces the erosion because it destroys the $WO_2$ molecules and removes oxygen due to oxygen sputtering.

*PACS:* 52.40.H
*Keywords:* Plasma–wall interaction; Divertor; Tungsten; Oxygen; Molecular dynamics simulations; Chemical erosion

## 1. Introduction

Tungsten is one of the favorite materials for ITER tokamak divertor armor. Its advantage is high cohesive energy, from which follows rather large threshold energy for deuterium–tritium (DT) sputtering: $E_{\mathrm{thr}}^{\mathrm{DT}} \approx 150$ eV [1]. Tungsten erosion has to be small because tungsten atoms penetrating into the core plasma can cause radiation collapse. Therefore, DT ion energies must be well below $E_{\mathrm{thr}}^{\mathrm{DT}}$ near the divertor wall. Tungsten erosion, however, could also occur due to major plasma impurities such as oxygen [2] coming to the wall. Experimental investigations and computer simulations of physical tungsten sputtering due to oxygen impact have been reported in [3–5]. The threshold energy of oxygen impact is $E_{\mathrm{thr}}^{\mathrm{O}} \approx 40$ eV, which sets an additional constraint. In previous comprehensive calculations for tungsten chemical erosion, equal high temperatures of the wall and the nearby gas were assumed [6]. In this study the erosion due to the sublimation of volatile complexes $WO_3$ created from impurity atoms trapped at the divertor surface heated by deuterium plasma of the scrape-off layer (SOL) up to the temperature of 1500 K is modeled.

The chemical erosion problem appears after the physical sputtering is suppressed and therefore a limitation of $10^2$ eV for D and 20 eV for O impact energies is assumed to be provided at the wall. From the small $E_{\mathrm{thr}}^{\mathrm{O}}$ a severe restriction of a few eV on the electron temperature $T_e$ follows in order to minimize the additional increase of energies of O ions of charges $z$ by about $3T_e z$ in the pre-surface electrostatic sheath [7]. Due to weak electron–ion energy exchange and substantial cooling of electrons by the wall it may be possible to achieve the necessary regime with rather low $T_e$ despite of the rather

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PII: S0022-3115(02)01585-4

hot ions. In addition, the sheath may capture scattered ions, and ionized erosion particles can impact again on the wall with a bright energy spectrum, but in this preliminary study, the sheath and redeposition processes are not considered. As shown in [3], at small $T_e \approx 5$ eV the changes in the sputtering yield by redeposition impact are not significant.

## 2. Kinetic equations at the surface

Because metal electrons neutralize ions at the surface, only the neutral atoms are assumed to strike it. The bombarding fluxes $j_D$ and $j_O$ of deuterium and oxygen atoms are assumed to be given. The oxygen atoms trapped at the surface occupy available sites of the tungsten surface density $n_W \approx 10^{15}$ cm$^{-2}$, until deuteron impacts cause their sputtering. If the oxygen atoms are stopped at the occupied sites, they create the complexes $WO_2$ or $WO_3$, thus lessening the binding of the involved tungsten atoms to the lattice. These molecules can sublimate or be destroyed by fast deuterons.

The flux of trapped oxygen atoms is given by $Aj_O$ with $A$ being the trapping coefficient. Surface densities of the molecular complexes $n_{WO}$, $n_{WO_2}$ and $n_{WO_3}$ determine the fractions of the areas covered either by pure surface tungsten atoms or by the molecules. For instance, the $WO_2$ surface fraction is equal to $n_{WO_2}/n_W$, and the pure surface fraction $n_{W0}/n_W$, with $n_{W0} = n_W - n_{WO} - n_{WO_2} - n_{WO_3}$ being the surface density of the sites not occupied by O atoms.

The rate $dn_{WO_3}/dt$ of generation of the molecules $WO_3$ at the surface given by $Aj_O n_{WO_2}/n_W$ is proportional to the fraction occupied by the $WO_2$ molecules. Similarly the other sources of the molecular complexes can be expressed. Finally the equations for the surface densities take the form

$$\frac{dn_{WO}}{dt} = Aj_O\frac{n_{W0}}{n_W} - \frac{n_{WO}}{n_W}Aj_O - \sigma_{sput}n_{WO}j_D + 2\sigma_{WO_2}n_{WO_2}j_D, \tag{1}$$

$$\frac{dn_{WO_2}}{dt} = \frac{n_{WO}}{n_W}Aj_O - \frac{n_{WO_2}}{n_W}Aj_O - \sigma_{WO_2}n_{WO_2}j_D,$$
$$\frac{dn_{WO_3}}{dt} = \frac{n_{WO_2}}{n_W}Aj_O - \frac{n_{WO_3}}{\tau^{sub}}. \tag{2}$$

The cross-sections $\sigma_{sput}$ and $\sigma_{WO_2}$ describe the oxygen sputtering and the destruction of the $WO_2$ molecules. At wall temperatures of 1500 K only the tungsten trioxide can sublimate significantly [8] therefore the tungsten erosion is assumed due to $WO_3$ and described with the sublimation time $\tau^{sub}$ that is assumed to be small enough for neglecting the destruction of $WO_3$.

A stationary solution ($d/dt = 0$) to Eqs. (1) and (2) is obtained. Introducing the dimensionless parameters $\eta = \sigma_{WO_2}n_W j_D/(Aj_O)$, $\varepsilon = \sigma_{sput}/\sigma_{WO_2}$, $\delta = Aj_O\tau^{sub}/n_W$, $x = n_{WO}/n_W$, $y = n_{WO_2}/n_W$ and $z = n_{WO_3}/n_W$ the equations are transformed as $1 - x - y - z = x + \varepsilon\eta x - 2\eta y$, $x = y(1+\eta)$, $z = y\delta$. Eliminating $z$ and $x$, an expression for $y$ is obtained to be used for the tungsten erosion flux $j_W$:

$$j_W = \frac{n_{WO_3}}{\tau^{sub}} = \frac{n_W}{\tau^{sub}}z = Aj_O(3 + \varepsilon\eta + \varepsilon\eta^2 + \delta)^{-1}. \tag{3}$$

The parameter $\delta$ is assumed negligibly small, which gives an upper estimate for $j_W$.

## 3. The simulation method and the code CADAC

The calculation of $\sigma_{sput}$, $\sigma_{WO_2}$, and $A$ is carried out using the classical molecular dynamics (MD) simulation method with pair potentials [9]. This approach for obtaining the kinetic coefficients may be only the first step in this direction, because the basic implications of the pair potential approximation remain rather uncertain. For light projectile ions, the first principle potentials are derived only for interaction energies much larger than $10^2$ eV [10]. For energies of a few eV some empirical potential functions are available for the involved interactions, but they have been suggested for two-atomic systems [9]. Hence, for the many-body interactions at the surface considered in this work, neither available potential would be a good choice. In such situation the classical MD simulation, which is a rather general method available for the problem in question, can rely on some reasonable combinations from the two opposite limits.

In the Newton equations $d\mathbf{p}_i/dt = \mathbf{F}_i$ and $d\mathbf{r}_i/dt = \mathbf{p}_i/m_i$ describing the time evolution of $N$ atoms of masses $m_i$, positions $\mathbf{r}_i$, and momentums $\mathbf{p}_i$, the forces $\mathbf{F}_i$ are constructed from the sum of potential functions $V_{ij}(r)$, $r = |\mathbf{r}_i - \mathbf{r}_j|$, with $1 \leqslant i < j \leqslant N$.

The fine quality of the limit potentials in the appropriate energy ranges becomes irrelevant in the intermediate situation where the simplicity of the approximations seems to be preferable. Therefore the Bohr potential $V_B$ and the Morse potential $V_M$ [9] are chosen to be applied. The potential parameters are taken from [9,11,12]. For the pairs W–W the modified Morse potential [11] is applied which models the tungsten lattice interactions quite well. For W–D, O–D, and D–D interactions it was realized that the Bohr and Morse potentials are replacing each other rather consistently: at 10 eV $V_B$ dominates and at −2 eV $V_M$ dominates. If one would change significantly one of them, this consistency would be destroyed. For this situation the linear combination $V = V_B + V_M$ represents the interatomic potential $V$ sufficiently. For W–W, W–O, and O–O interactions also $V = V_B + V_M$ is used, albeit at energies below $10^2$ eV the Bohr potentials contribute negligibly. Fig. 1 shows these interatomic potentials $V_{ij}(r)$.

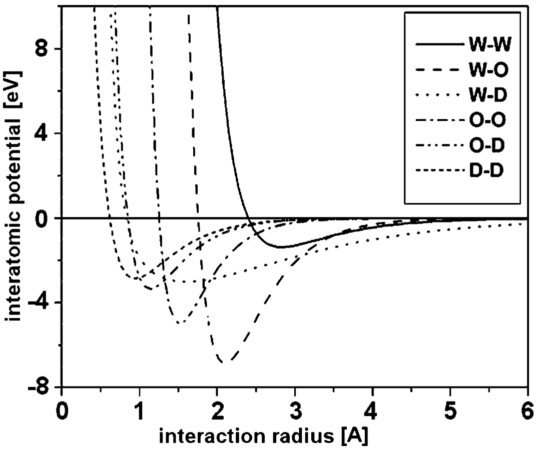

Fig. 1. The interatomic potentials used in the calculations for the assemblies of tungsten, oxygen and deuterium atoms.

The Newton equations are approximated with a simple finite-difference scheme of second order in the time step $\Delta t$:

$$\mathbf{p}(t+\Delta t) = \mathbf{p}(t) + \mathbf{F}\left(t+\frac{\Delta t}{2}\right)\Delta t, \tag{4a}$$

$$\mathbf{r}(t+\Delta t) = \mathbf{r}(t) + \frac{\mathbf{p}(t)+\mathbf{p}(t+\Delta t)}{2m}\Delta t. \tag{4b}$$

Given appropriate initial conditions, the time evolution of the atomic system is calculated step by step, with exact momentum conservation and small energy non-conservation errors, which is important as the only essential feature of the background quantum system the Newtonian model can tackle.

The time step values depend on the atomic masses $m$ and kinetic energies $E$. The interatomic field imposes a limitation $\Delta r_{\max}$ on atomic displacements, which according to Eq. (4b) results in $\Delta t < (m/E)^{1/2}\Delta r_{\max}$. This means that the positions of a few incident deuterium or oxygen atoms must be updated much more frequently than that of many tungsten lattice atoms. With ordinary algorithms (see e.g. [9]), all atoms would be computed with a same smallest $\Delta t$ and thus the lattice atoms would waste processor time. Moreover, during the impacts the interatomic forces for a few atoms significantly increase resulting in an additional decrease of $\Delta t$ according to Eq. (4a).

The simplicity of the scheme of Eq. (4) allows the implementation of individual time steps $\Delta t$ for each atom, which increases the calculation speed drastically. The atomic assembly is divided into several indexed groups, the 'time step clusters', with equal individual $\Delta t$ in each group. The atoms of the 0th cluster have some maximum step $\Delta t_{\max}$ and the step of $j$th cluster is given by $\Delta t_j = \Delta t_{\max}/2^j$ $(j = 0,\ldots,J)$. In the course of the calculation, the atoms automatically change the clusters when necessary for required accuracy. $\Delta t_{\max}$ and the required number of clusters $J$ are variable, which additionally improves energy conservation and performance. This concept is introduced in this paper for the first time.

The classical atomic dynamics analysis code (CADAC) was developed to bring to reality the time step cluster concept. One principally important element of CADAC is a recursive procedure that organises the cycles of the calculation process. The procedure starts with $\Delta t_{\max}$ for the atoms of the 0th cluster, but before the actual integration of the equations it calls itself again to make up the shorter steps of $\Delta t_{\max}/2$ for the 1st cluster atoms. In turn each call for the 1st cluster is similarly preceded by calls for the 2nd cluster, and so it goes on for all higher clusters. For the atoms of the highest cluster $J$, the procedure integrates the equations making the two smallest steps. This allows the atoms of the cluster $J-1$ to be calculated and thus the procedure continues.

The momentums transferred to any cluster from the higher ones are accumulated in atomic information structures to be used at the calculations for this cluster that in turn will deliver the momentum to the lower ones. Due to this, CADAC keeps constant the momentum of the atomic assembly.

## 4. Calculations and results

The kinetic coefficients for Eq. (3) were calculated with $\Delta t_{\max} = 10^{-15}$ s, $\Delta r_{\max} = 0.1$ A, and the relative change of the atomic momentum was limited to 0.1 per individual time step. In practice, $J$ may reach 10 and thus the smallest cluster time steps $10^{-18}$ s, at average steps of $(3\text{–}5) \times 10^{-16}$ s. For $r > 6.32$ A the functions $V(r)$ are zeroed. The calculation speed due to optimization by the time step clusters increases by several hundred times.

The calculations are done simultaneously at two opposite sides of a 19 A cubical piece of simulated tungsten bcc-lattice. Along the other four sides, the periodical boundary conditions are imposed. The tests are completed, each consisting of $N_0 = 400$ independent impacts of oxygen or deuterium atoms having fixed energies $E_D$ or $E_O$ and a homogeneous angle distribution towards the surface.

The trapped oxygen atoms were counted resulting in $A = 0.2 \pm 0.02$ at $E_O = 20\text{–}100$ eV for the pure surface. The presence of previously accumulated oxygen atoms at the surface leads to a significant increase of $A$. For instance, if $n_{WO} = 0.3n_W$, $A \approx 0.5$ at $E_O = 25$ eV.

The deuteron impacts decrease $n_{WO}$ and thus reduce the oxidation. In the tests, the oxygen atoms at the surface were bombarded by the deuterons with a

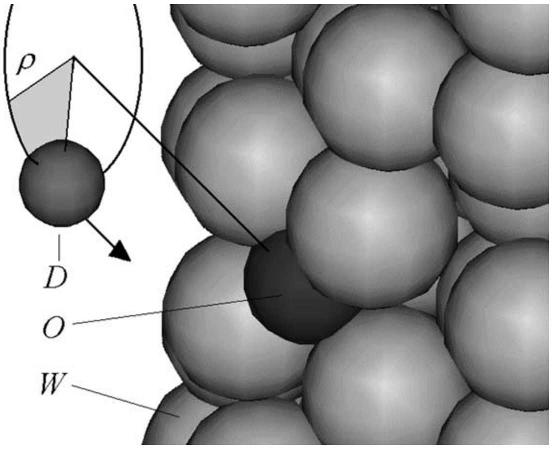

Fig. 2. Impact simulation view: the impact polar angle is shown by the circle sector of radius $\rho$. Projectile velocity shown by the arrow is parallel to the randomly directed ray that originates at the center of the target O.

homogeneously random distribution of the velocity directions and the polar angle of the impact shown in Fig. 2 but at fixed impact parameter $\rho$ and $E_D$. The counted numbers of events of oxygen removal from the surface $N$ produced the oxygen sputtering probability function $P(E_D, \rho) = N/N_0$ that is related to the sputtering cross-section by $P = \partial\sigma_{\text{sput}}/\partial s$, $s = \pi\rho^2$, $\sigma_{\text{sput}}(E_D, 0) = 0$. Making the integration, $\sigma_{\text{sput}} \equiv \sigma_{\text{sput}}(E_D, \infty)$ is approximated at $60 < E_D < 130$ eV with an accuracy of 20% as

$$\sigma_{\text{sput}}(E_D) = 4.5 \times 10^{-20} \times (E_D - 60 \text{ eV}) \text{ cm}. \tag{5}$$

The destruction of $WO_2$ was simulated similarly. The destruction probability function $P(E_D, \rho)$ is obtained to have a local minimum at $\rho = 0$ and an absolute maximum at $\rho \approx 1$–1.5 A depending on $E_D$. The destruction cross-section approximated with an accuracy of 20% is given by

$$\sigma_{WO_2} = 3 \times 10^{-17}(1 + 0.06 \times (E_D - 60 \text{ eV})) \text{ cm}^2. \tag{6}$$

Knowing the kinetic coefficients, the tungsten erosion flux $j_W$ Eq. (3) is obtained for a wide range of the input parameters, with $j_A = N_A V_A/2$, $A = D$ or O, $N_A$ the SOL densities, and $V_A = (2E_A/\pi m_A)^{1/2}$ averaged ion velocities. The effective sputtering yield $Y_{\text{eff}} = j_W/j_D$ is shown in Fig. 3. At small impurity concentrations $c_O$ the obtained tungsten erosion fluxes are much smaller than that of Ref. [6], which is attributed to the enhanced oxygen sputtering and the destruction of the molecular complexes by the hot SOL plasma. It is worthwhile to mention that in [5] the oxidation effect was not taken into consideration assuming such mechanism of surface cleaning.

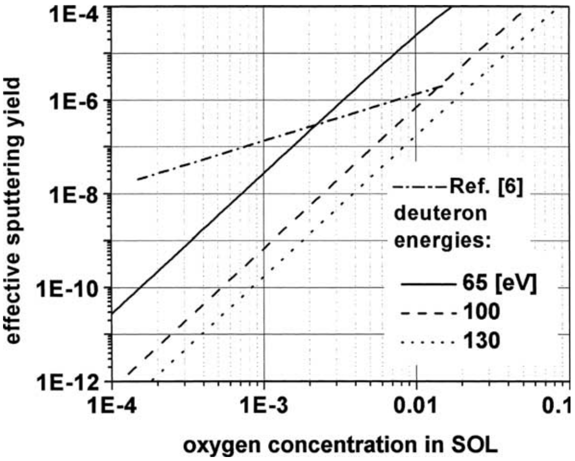

Fig. 3. Dependence of the $WO_3$ sublimation tungsten erosion on the oxygen concentration $c_O = N_O/N_D$ for SOL plasma density $N_D = 10^{14}$ cm$^{-3}$. The oxygen impurity temperature is equal to 20 eV. Retrieving the data of [6], $E_D = 65$ eV was assumed.

For the considered model itself, the most important parameters are the rather high deuterium energy and wall temperature. As to the oxygen impact energies and thus the sheath electron temperature, they can be substantially larger without changing the results significantly in the scope of the validity of the model, which is rather narrow because at an increase of the oxygen energy above $E^{O}_{\text{thr}}$ the physical W sputtering by oxygen will dominate. The sputtering yield by oxygen bombardment at 150 eV measured as $8 \times 10^{-2}$ at 1500 K [4] would correspond to $Y \approx 5 \times 10^{-5}$ of the Fig. 3 at $c_O = 10^{-2}$. With 100 eV oxygen bombardment measured in [3] at $T_e$ of 5 eV and 0.5% O, $Y \approx 3 \times 10^{-5}$ was obtained. These values exceed $Y_{\text{eff}}$ by factors of $10^2$, thus indicating that the physical sputtering will be dominant above the threshold.

## 5. Conclusions

The process of chemical erosion by oxygen coming as a deuterium plasma impurity to a hot tungsten surface was investigated under the conditions excluding the physical sputtering. For this purpose the MD simulation code CADAC was developed. The time step cluster method was introduced which reduces computing time significantly.

The study demonstrates the first application of CADAC for divertor erosion investigations. It was shown that the tungsten chemical erosion flux can be made small compared to the results of Ref. [6], provided that the oxygen impurity concentration is below $10^{-2}$, and the deuterium impact energies are rather high but not sufficient for physical sputtering. The SOL plasma significantly eliminates the WO complexes due to oxygen sputtering and destroys the $WO_2$ complexes, which decreases the production of tungsten trioxide.

More advanced interatomic potentials could be applied, and additional processes could be analyzed. For instance, the oxygen sticking may result in not easily removable complexes and thus in corrosion. The diffusion of the WO complexes along the surface due to the bombardment of DT ions may partially rebuild the destroyed $WO_2$ complexes thus increasing the erosion flux. CADAC seems to be a useful tool for further investigations in this area.

## Acknowledgements

The work was done under EFDA contract TW1-TVP/TUMO1.

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