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Dynamics of small mobile helium clusters near tungsten surfaces

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ABSTRACT

We report the results of a systematic atomic-scale analysis of the dynamics of small mobile helium clusters in tungsten, near tungsten surfaces. These helium clusters are attracted to tungsten surfaces due to an elastic interaction force that drives surface segregation. As the clusters migrate toward the surface, trap mutation and cluster dissociation are activated at rates higher than in the bulk. These kinetic processes are responsible for important structural, morphological, and compositional features in plasma-exposed tungsten, including surface adatoms, near-surface immobile helium–vacancy complexes, and retained helium content. Detailed results are presented for di-helium and tri-helium clusters near low-Miller-index tungsten surfaces.

The implantation of helium (He) atoms has significant implications for the surface morphological evolution and the near-surface structural evolution of plasma facing components (PFCs) in nuclear fusion reactors; due to its thermomechanical properties, tungsten (W) is an important PFC material. Helium ion exposure in linear plasma devices or tokamak plasmas is known to cause formation of microscopic features, termed as "fuzz" or "coral," on the surface of plasma-exposed materials after only a few hours of plasma exposure [1–7]. Although the precise formation mechanisms of such complex surface morphologies remain unknown, they are mediated by the dynamics of He atoms and the aggregates that form in the PFC near-surface regions. In W, such interstitial He atoms are very mobile and aggregate to form clusters of different sizes [8–13]; the smallest of these clusters also are mobile [13] and their diffusional transport mediates the evolution of surface morphology and near-surface structural evolution.

A fundamental understanding of the underlying He cluster dynamics, as well as cluster–cluster, cluster–defect, and cluster–surface interactions is required in order to develop accurate coarse-grained models that efficiently predict long-term PFC structural and surface morphological evolution due to plasma exposure. Toward this end, the purpose of this Letter is to analyze small mobile He cluster dynamics in near-surface W and to identify the kinetic processes activated in the near-surface region. We find that these cluster reactions lead to formation of W surface adatoms, immobilized He–vacancy complexes near the surface, and He desorption from the surface and, therefore, have significant impact on surface morphology, near-surface structure, and He retention in the material.

Our analysis is based on molecular-statics (MS) and molecular-dynamics (MD) simulations, as well as computation of optimal reaction pathways using the open-source program LAMMPS [14]. In the MS simulations, conjugate-gradient energy minimization is employed. The important aspects of the MD simulations are detailed below. Energy landscapes along optimal reaction pathways are constructed using the climbing-image nudged elastic band (CI-NEB) method [15,16]. In the computations, the interactions between W atoms are described according to the Embedded Atom Method (EAM) potential of Finnis and Sinclair [17] as modified by Ackland and Thetford [18] and by Juslin and Wirth [19]. W–He pair-wise interactions are described according to the pair potential of Juslin and Wirth [19] and He–He interactions are described by the pair potential of Beck [20] as modified at short distances by Morishita et al. [21]. Simulations based on these potentials have reproduced accurately results from first-principles density functional theory (DFT) calculations for the formation energies and ground-state configurations of He point defects and self-interstitial atoms in W [19]. For small He–vacancy clusters, the predictions of the potentials for the binding energies are in excellent qualitative agreement with the DFT results, although the vacancy binding energy is slightly but systematically overestimated by the potentials [19]. MD simulations based on these interatomic potentials have been used in previous studies to explore helium implantation effects on tungsten surface evolution [11–13,22]. In general, the interatomic potentials employed in this study are considered very reliable for analyzing the dynamics of small mobile helium clusters in tungsten.

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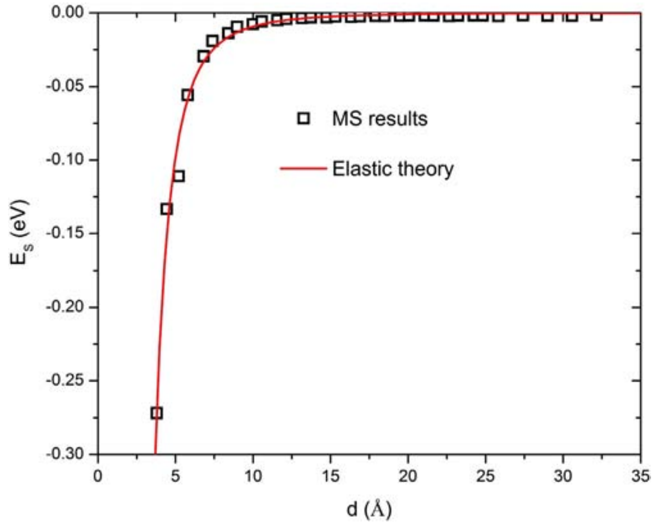

Fig. 1. Potential energy profile (open squares), $E_s(d)$, from MS simulations for the interaction of a He_3 cluster with the W(100) surface in the near-surface region as a function of the distance d of the cluster from the surface. The zero-energy level corresponds to the cluster formation energy in the bulk material, i.e., at a practically infinite distance from the surface, realized asymptotically. The solid line represents a least-squares fit to the simulation results according to elasticity theory.

To characterize the interaction of small He clusters with the surface, we performed MS simulations to obtain the relaxed structure and energetics for clusters in the near-surface region as a function of distance from the surface. Fig. 1 shows the results of this analysis for a tri-He cluster near the W(100) surface (open squares). The solid line represents a least-squares fit to the computational results according to elastic theory for the interaction of an inclusion with the surface (boundary) of a continuous elastic medium [23–27]. The elastic interaction potential is expressed by $E_s(d) = -A / d^3$, where d is the distance of the cluster (inclusion) from the surface and A is a material property, the surface segregation strength, that is determined at a given thermodynamic state by the elastic constants of the material and the surface crystallographic orientation; the negative sign indicates an attractive interaction. The excellent fitting of the MS results by the elastic potential $E_s(d)$ shown in Fig. 1 validates and parameterizes the elastic theory and provides an approach to computing the surface "sink strength" A. We carried out MS simulations for all the small mobile He_n clusters, $1 \leq n \leq 7$, near W(100), W(110), and W(111) surfaces and found similar results with those of Fig. 1, namely, that the He cluster interaction energies with low-index W surfaces agree well with elastic theory, in which the sink strength A increases with increasing cluster size n. These results for all the clusters and surface orientations studied will be reported in a forthcoming publication.

The aforementioned results indicate that small mobile He_n clusters in near-surface regions of tungsten are attracted to and migrate to the surface by drift due to the thermodynamic driving force for surface segregation in addition to Fickian diffusion; this driving force, $\mathbf{F}_s(d) = -\nabla E_s(d) = (3A/d^4)\mathbf{n}$, where $\mathbf{n}$ is the unit vector normal to the surface, is described very well by elasticity theory for the respective cluster and surface orientation. This thermodynamic driving force, $\mathbf{F}_s$, affects directly the flux of He_n clusters by contributing to their total flux the drift flux component $D_n C_n \mathbf{F}_s / (k_B T)$, directed toward the surface, where D_n and C_n are the diffusion coefficient and concentration of the mobile He_n cluster, respectively, k_B is Boltzmann's constant, and T is temperature. This understanding of near-surface cluster dynamics due to the cluster–surface physical interaction motivates the investigation of other kinetic processes beyond diffusion and drift, namely, rate processes that may be activated as the clusters approach the material surface. Consequently, we carried out targeted MD simulations of small-He cluster dynamics in the near-surface region for the systematic identification and detailed characterization of such kinetic processes. Increasing the fluxes of the He_n clusters toward the surface increases the rates of all such near-surface kinetic processes.

Here, we focus on the di-He (He_2) and tri-He (He_3) clusters in W and report results on their dynamics near the W(100) surface. For each cluster, we generated several hundreds of one-ns-long trajectories at two temperatures, $T = 1000$ K and $T = 1200$ K, in supercells containing $N = 4000$ W atoms (we used $N = 5120$ and 6144 for the W(110) and the W(111) surfaces, respectively); periodic boundary conditions were applied in the principal directions of the surface plane, with the surface treated as a free surface. In each trajectory, the small He cluster in the initial configuration was placed at a distance from the surface such that the cluster felt the attractive elastic interaction with the surface, typically ~10 atomic layers below the surface plane. The stability of the resulting configurations (for a small sample of each MD simulation outcome) was confirmed by analyzing much longer MD trajectories (~100 ns). The clusters were relaxed (energy minimization) at practically the same distance from the surface plane for each MD trajectory and the trajectories were initialized randomly at each temperature. Although there is bias for cluster migration toward the surface in the initial configuration, the thermodynamic driving force is not strong at this distance of the cluster from the surface. Most of the kinetic events (cluster reactions) recorded occur typically within the first few hundred picoseconds of the trajectory; however, in some trajectories, the clusters had to migrate for longer times before a reaction event was recorded.

The outcomes of the MD analysis for the He_2 and He_3 clusters near W(100) are summarized in Table 1. These outcomes are the products of the kinetic processes identified and expressed as cluster reactions in Table 1. All of these stable configurations are reported in Appendix A [28]. We identified four different outcomes for He_2 and five different outcomes for He_3. The corresponding kinetic processes identified are trap mutation, trap mutation followed by cluster dissociation,

Table 1
List of reactions undergone by the He_2 and He_3 clusters near the W(100) surface. The integer index l indicates the lattice plane where He_m–V complexes are formed; $l = 1$ corresponds to the surface plane and l increases with increasing depth below the surface. The relative probabilities of occurrence for all of these reactions from analysis of MD trajectories at $T = 1000$ K (522 and 504 MD trajectories at n = 2 and 3, respectively) and $T = 1200$ K (288 and 659 MD trajectories at n = 2 and 3, respectively) are also listed.

He_n	Reaction	Relative probability ($T = 1000$ K)	Relative probability ($T = 1200$ K)
n = 2	$W + He_2 \rightarrow He_2\text{–}V(l = 4) + W_s$	0.6%	0.8%
	$W + He_2 \rightarrow He_2\text{–}V(l = 3) + W_s$	74.3%	74.2%
	$W + He_2 \rightarrow He\text{–}V(l = 3) + W_s + He_{(g)}$	4.8%	5.9%
	$W + He_2 \rightarrow W + 2\ He_{(g)}$	20.3%	19.1%
n = 3	$W + He_3 \rightarrow He_3\text{–}V(l = 5) + W_s$	12.3%	15.6%
	$W + He_3 \rightarrow He_3\text{–}V(l = 4) + W_s$	84.3%	71.7%
	$W + He_3 \rightarrow He_2\text{–}V(l = 3) + W_s + He_{(g)}$	0.2%	1.7%
	$W + He_3 \rightarrow He\text{–}V(l = 3) + W_s + 2\ He_{(g)}$	2.6%	9.9%
	$W + He_3 \rightarrow W + 3\ He_{(g)}$	0.6%	1.1%