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A first principles kinetic Monte Carlo investigation of the adsorption and mobility of gadolinium on the (100) surface of tungsten

Adib J. Samin*, Jinsuo Zhang

Nuclear Engineering Program, Department of Mechanical and Aerospace Engineering, The Ohio State University, 201 W. 19th Avenue, Columbus, OH 43210, USA

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ABSTRACT

An accurate characterization of lanthanide adsorption and mobility on tungsten surfaces is important for pyroprocessing. In the present study, the adsorption and diffusion of gadolinium on the (100) surface of tungsten was investigated. It was found that the hollow sites were the most energetically favorable for the adsorption. It was further observed that a magnetic moment was induced following the adsorption of gadolinium on the tungsten surface and that the system with adsorbed hollow sites had the largest magnetization. A pathway for the surface diffusion of gadolinium was determined to occur by hopping between the nearest neighbor hollow sites via the bridge site and the activation energy for the hop was calculated to be 0.75 eV. The surface diffusion process was further assessed using two distinct kinetic Monte Carlo models; one that accounted for lateral adsorbate interactions up to the second nearest neighbor and one that did not account for such interatomic interactions in the adlayer. When the lateral interactions were included in the simulations, the diffusivity was observed to have a strong dependence on coverage (for the coverage values being studied). The effects of lateral interactions were further observed in a one-dimensional simulation of the diffusion equation where the asymmetry in the surface coverage profile upon its approach to a steady state distribution was clear in comparison with the simulations which did not account for those interactions.

1. Introduction

Surfaces possess distinct electronic and atomic properties when compared to the bulk of the material and are the site for a variety of processes such as redox reactions, adsorption, and catalysis among others which have indispensable technological applications [1]. Tungsten surfaces are important and have recently been investigated for a variety of reasons [2–5]. They are promising as plasma facing material and exhibit favorable properties for the divertor application in nuclear fusion reactors [6,7]. Tungsten microelectrodes and electrodes are also used in neuroprosthetic applications and other implants which require long term viability of the tungsten surfaces and their protection against corrosion [4,8]. In addition, tungsten surfaces are found to be stable in the range of redox potentials of various actinides thereby enhancing their promising role in pyroprocessing applications for recycling nuclear fuels [9,10]. These surfaces also have potential applications in thermophotovoltaic systems [11] and are used to investigate the process of oxidative dissolution through the formation of complexes on the surface of the metal [12].

In pyroprocessing of used nuclear fuel treatment, it is important to separate uranium and plutonium from lanthanide fission products based on their electrochemical properties. Cyclic voltammetry is one of the primary tools currently used to investigate the kinetic and electrochemical properties of different lanthanide fission products [13,14] in the molten salt for pyroprocessing. However, the analysis of the recorded signals is not straightforward due to the deposition of lanthanides on the electrode surface (typically tungsten). Furthermore, it was also observed [3] that surface phenomena such as the adsorption isotherm are generally not accurately described with continuum level models since these cannot capture interatomic interactions and other atomic scale processes. Therefore, it is important to investigate the surface-related phenomena from a more fundamental point of view.

In this work, the adsorption of gadolinium (one of the lanthanide fission products) on the tungsten (100) surface will be

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* Corresponding author.
E-mail address: samin.2@osu.edu (A.J. Samin).

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investigated. The favorable adsorption sites on the tungsten surface will be determined. In addition, a mechanism for surface diffusion is proposed and the surface diffusion of gadolinium on the tungsten surface and the concentration profile evolution are calculated.

2. Computational details

2.1. Density functional theory (DFT) calculations

Spin polarized density functional theory calculations were carried out using the Vienna ab initio simulation package (VASP) [15,16] with the implementation of the Projector-Augmented-Wave (PAW) pseudopotentials [17,18]. A generalized gradient approximation (GGA) exchange correlation functional was used as parameterized by Pardew, Burke and Ernzerhov [19]. In the treatment of the electronic structure of Gd, the intra-atomic Coulomb repulsion was accounted for through the use of a Hubbard U via a GGA + U functional and the value of $U_{eff} = 6$ eV was utilized [20,21]. The valence electron eigenfunctions were expanded in a plane-wave basis set with an energy cutoff of 450 eV and a Methfessel-Paxton smearing of the first order of width 0.1 eV was used in the simulations [22]. The W(100) surface was represented by a p(4 × 4) surface supercell and a five-layer slab which was separated by a vacuum with a thickness of about 22.19 Å to minimize interactions with slab images. The bottom three layers were fixed at bulk positions while the positions of atoms in the top two layers were allowed to relax. Reciprocal length integrations were performed using a (3 × 3 × 1) Monkhorst-Pack [23] Γ-centered k-point grid. The convergence criterion for the electronic self-consistent calculation was set to 10^{-7} eV. Furthermore, the structure was allowed to relax until the forces acting on the atoms were less than 0.01 eV/Å.

Transition states for Gd diffusion on the W(100) surface were determined using the climbing nudged elastic band method [24]. The calculation of the activation barrier on a potential energy surface was carried out using a single image with a spring constant of 5 eV/Å. Zero-point energies (ZPE's) were also quantified through calculating the normal-mode vibrational frequencies and associated zero-point energies of the adsorbate Gd and local W atoms at the minima and transition states.

2.2. Kinetic Monte Carlo (KMC) simulations

In kMC simulations the time evolution of the system is described by a stochastic trajectory and the system states along this trajectory are connected by processes with certain probabilities. Here, we use a lattice kinetic Monte Carlo where adsorption sites are mapped onto a lattice and the system can evolve by allowing the adsorbate Gd atoms to hop between neighboring adsorption sites. Within the quantum version of harmonic transition state theory [25] the microscopic rate constant for a hop is given by:

$$k_{IF} = \Gamma_{IF}\, exp(-E_a/k_B T) \tag{1}$$

In equation (1), k_{IF} is the hopping rate from an initial site I to a final site F, Γ_{IF} is the hopping frequency at infinite temperature, k_B is the Boltzmann constant, T is the temperature of the simulation and E_a is the activation energy barrier for hopping from the given initial site to the final site under consideration. The infinite temperature hopping rate may be estimated as [25]:

$$\Gamma_{IF} = \frac{\prod_{i=1}^{3} f(h\nu_{I,i}/2k_B T)}{\prod_{j=1}^{2} f(h\nu_{TS,j}/2k_B T)} \tag{2}$$

In equation (2) the function f is given by $f(x) = \sinh(x)/x$, and ν_I, and ν_{TS} are the normal mode frequencies at the initial and transition state site respectively. Finally, the activation energy barrier may be approximated as [26,27]:

$$E_{a,IF} = E_{cl,IF} + \varepsilon_{zp}^{TS} - \varepsilon_{zp}^{I} + \frac{1}{2}(\Delta E) \tag{3}$$

In equation (3), $E_{cl,IF}$ is the classical energy barrier for the hop from the initial to the final state. This classic barrier is defined by the difference in energy between the initial state and the transition state which represents a saddle point in the potential energy hypersurface. The quantities ε_{zp}^{TS} and ε_{zp}^{I} are the zero point energies of the system at the initial site and the transition state site respectively. Finally, the lateral Gd-Gd interactions in the adlayer were accounted for in the last term by including the effect of two-body interactions. The pair interactions were extracted from DFT calculations and the expression for ΔE is:

$$\Delta E = \varepsilon_{nn}{*}\left(N_{fnn} - N_{inn}\right) + \varepsilon_{nnn}{*}\left(N_{fnnn} - N_{innn}\right) + \ldots \tag{4}$$

where ε_{nn} and ε_{nnn} are the interaction energy parameters for nearest neighbors and next nearest neighbors and N_{fnn} and N_{inn} are the number of nearest neighboring Gd atoms in the initial and final state and similarly N_{fnnn} and N_{innn} are the number of next nearest neighboring Gd adsorbed atoms in the initial and final state. The interaction parameters were determined through DFT calculations via:

$$\varepsilon = E^{tot}(W, Gd_2) - E_{clean} - 2\left[E^{tot}(W, Gd) - E_{clean}\right] \tag{5}$$

where E_{clean} is the total energy of the clean slab, $E^{tot}(W, Gd_2)$ is the energy of the slab with two adsorbed Gd atoms (which are either located in the nearest neighboring adsorption sites or next nearest neighbor adsorption sites), and $E^{tot}(W, Gd)$ is the total energy of the tungsten slab with one adsorbed gadolinium atom.

At each step of the kMC simulation, a gadolinium atom in the adlayer may hop from a hollow site on the W(100) surface to one of its four nearest neighbors (distance a). Each kMC move included obtaining the rates (k_i) for all the possible transitions from the current configuration. A choice for the hop was selected by generating a random number to perform the hop according to the condition:

$$\sum_{i=1}^{j-1} k_i \le rK \le \sum_{i=1}^{j-1} k_i \tag{6}$$

In the equation, r is the generated random number and K is the sum of the rates of all possible hopping processes. The clock is then advanced by $-\ln(\sigma)/K$ where σ is another random number. Finally, the recorded trajectory may be calculated from a kMC simulation on a surface from the equation:

$$D = \lim_{t \to \infty}\left[\frac{1}{4t}\left\langle |\boldsymbol{R}(t) - \boldsymbol{R}(0)|^2 \right\rangle\right] \tag{7}$$

Table 1
Ab initio calculated adsorption energies, magnetization, and distance from the tungsten surface for Gd on distinct sites on the p(4 × 4) W(100) surface.

Adsorption Site	On-Top	Bridge	Hollow
Adsorption Energy (eV)	−1.54	−2.62	−3.133
Magnetization (μ_B)	8.71	8.74	8.90
Distance from surface (Å)	2.55	2.04	1.92