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Palladium clusters deposited on the heterogeneous substrates

Kun Wang[a,b], Juanfang Liu[a,b,*], Qinghua Chen[a,b]

[a] College of Power Engineering, Chongqing University, Chongqing 400044, China
[b] Key Laboratory of Low-grade Energy Utilization Technologies and Systems, Ministry of Education of PRC, Chongqing 400044, China

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ABSTRACT

To improve the performance of the Pd composite membrane prepared by the cold spraying technology, it is extremely essential to give insights into the deposition process of the cluster and the heterogeneous deposition of the big Pd cluster at the different incident velocities on the atomic level. The deposition behavior, morphologies, energetic and interfacial configuration were examined by the molecular dynamic simulation and characterized by the cluster flattening ratio, the substrate maximum local temperature, the atom-embedded layer number and the surface-alloy formation. According to the morphology evolution, three deposition stages and the corresponding structural and energy evolution were clearly identified. The cluster deformation and penetrating depth increased with the enhancement of the incident velocity, but the increase degree also depended on the substrate hardness. The interfacial interaction between the cluster and the substrate can be improved by the higher substrate local temperature. Furthermore, it is found that the surface alloys were formed by exchanging sites between the cluster and substrate atoms, and the cluster atoms rearranged following as the substrate lattice arrangement from bottom to up in the deposition course. The ability and scope of the structural reconstruction are largely determined by both the size and incident energy of the impacted cluster.

1. Introduction

Hydrogen energy is one newly clear energy resources. The purity of hydrogen is an important index to the hydrogen energy, so that the purification of hydrogen from gas mixtures would be a crucial process in both existing and prospective uses of hydrogen. The separation membrane is one of the most effective and powerful technologies of improving the hydrogen purity. In which, the Pd membrane and Pd alloys membrane, particularly, the Pd composite membrane have been the research focus [1–4]. In addition, the Pd membrane has been also utilized in the hydrogenation and dehydrogenation reactions [5,6]. To fabricate the Pd membrane, except for sputtering deposition and chemical vapor deposition [7–9], the cold gas dynamic spraying (CGDS), a newly surface treatment technology, was proposed in our laboratory. In the cold spraying, the microscopic Pd particles are accelerated (to 500–1200 m/s) [10–12] by the supersonic gas stream through a converging-diverging nozzle and then deposited on a metal substrate. In order to improve the membrane performance prepared by the cold spraying, it is essential to study the deposition process of Pd particles on the metal substrates.

Compared with the larger experimental consumption, computational modeling may be a good choice to investigate the deposition process. The molecular dynamics (MD) method has been usually applied to investigate the transient phenomena emerging in the impact process and explore the microscopic evolution of the film growth on the substrate [13–17]. Del Popolo et al. [18,19] simulated Pd clusters deposited on the Au(111) surface and did the corresponding experiment. They found that the Pd clusters dissolution occurred at the cluster edges rather than layer by layer. Guo et al. [20] investigated the growth of Pd islands on a Ni(111) substrate and observed the growth followed a 2D mechanism when the Pd coverage was less than 0.4 monolayer above which the 3D islands appeared. Rojas et al. [21] studied the structure and stability of the Pd adlayers on the Au($h\,k\,l$) and Pt($h\,k\,l$) surfaces at different coverage degrees, and found the Pd films grew epitaxially and pseudomorphically along the substrate crystallographic orientation. Vandoni et al. [22] determined the implantation and fragmentation of small Ag_n clusters (n = 1–19) deposited on a Pd(1 0 0) surface with higher energies. And then they studied the collision of a single Ag7 cluster on the Pd(1 0 0) substrate by using the embedded-atom-method (EAM) inter atomic potential function [23]. These experiments were also analyzed by the MD simulation and quan-

* Corresponding author at: College of Power Engineering, Chongqing University, Chongqing 400044, China.
E-mail addresses: cqdxwk@126.com (K. Wang), juanfang@cqu.edu.cn (J. Liu), qhchen@cqu.edu.cn (Q. Chen).

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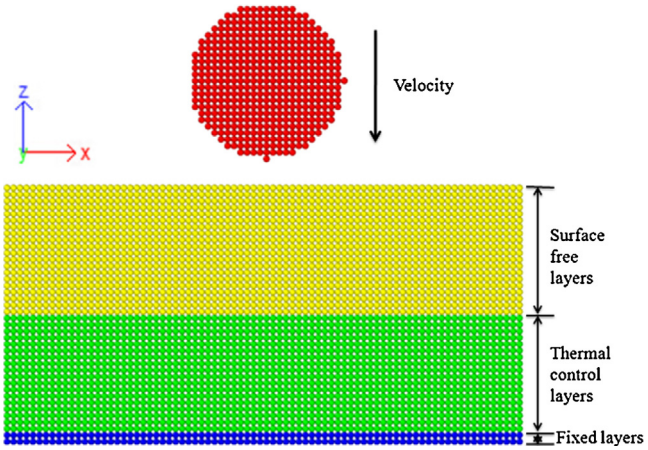

Fig. 1. Schematic of the computational model.

titatively reproduced [24]. Hou et al. [25] studied the deposition of the low-energy Au cluster beam on the Au(1 1 1) surfaces. The simulated film morphology was in excellent agreement with their experimental measurements [26]. Araghi et al. [27] investigated the effects of the cluster size, incident energy and the substrate temperature on the impact of the Co cluster on the Cu substrate. Hong et al. [28,29] simulated the film-growth process of small Fe and Co clusters on the Cu substrate with low energies. Their results showed that the surface roughness reduced and the interface intermixing increased with increasing the incident energy. Hwang et al. [30] found that increasing the atom number per cluster could increase the surface roughness.

The above results indicated that the cluster size and incident energy have a significant effect on the film growth and the deposition configuration. Comparing to ion beams (or single atom, small clusters), the large clusters have much stronger influences due to much higher energy density and stopping power when impacted with the same incident velocity [31–33]. However, comparison of the large clusters deposited on the different substrates and the corresponding formed interfacial configurations have least been found in the existing literature. The aim of this paper is to explore the deposition morphology, interfacial characteristics and microscopic binding mechanism of the large Pd cluster deposited on the disparate substrate (Cu, Pd, Ni, Fe, Ta) surfaces. Furthermore, one oversize Pd cluster was constructed to elucidate the structural reconstruction of the larger cluster.

2. Simulation method

The model was depicted in Fig. 1. The spherical cluster is composed of 3568 Pd atoms with the radius of 4.67 nm. The dimension of the substrate is $40a_0 \times 40a_0 \times 20a_0$, and a_0 is the lattice constant of the substrate material. Along the z direction, the top half atom layers of the substrate were defined as the free layer to reflect the bombardment process. The bottom two layers were acted as the fixed layer, and the atoms are static to hinder the movement of the substrate mass center due to the bombardment of the incident clusters. The other layers were the thermal control layer and maintained a constant temperature of 300 K by the Nose-Hoover method [34,35].

The following EAM potential function [36] was adopted to describe the atomic interaction of the deposition system

$$E = \frac{1}{2}\sum_{i,j,i\neq j}\phi_{ij}(r_{ij}) + \sum_{i}F_i(\rho_i)$$

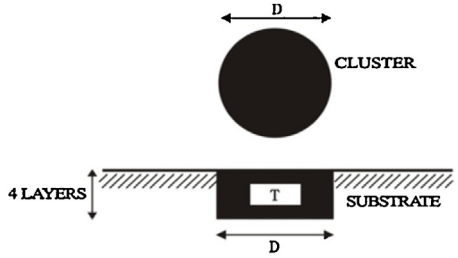

Fig. 2. A characteristic region of the substrate.

where ϕ_{ij} represents the pair potential energy between the atom i and j separated by a distance r_{ij}, and F_i is the energy resulted from embedding an atom i into a local site with the electron density ρ_i which is calculated by

$$\rho_i = \sum_{j,j\neq i} f_j\left(r_{ij}\right)$$

here $f_j\left(r_{ij}\right)$ is the electron density at the site of the atom i arising from the atom j at a distance r_{ij} away. The specific form and corresponding parameters of the potential function in Ref. [36]. were adopted. In the simulation, the cut-off distance was used to improve the computation efficiency.

Periodic boundary conditions were applied in the x and y directions. The Newton's motion equation of each atom was integrated by the Verlet algorithm [37,38]. The integration time-step was 1 fs. At the starting, the cluster was located on a sufficient position above the substrate surface to avoid the interaction between them. Both the cluster and the substrate were equilibrated for 40 ps before depositing clusters. According to our deposition experiments, the incident velocities of the cluster were set to 700 and 1100 m/s. The simulation runs 80 ps to collect the data.

To judge whether the local melt happened or not inside the substrate, a characteristic region was withdrawn, as shown in Fig. 2. This cylindrical region with the 4 atom-layer depth and the cluster diameter should contain the sufficient substrate atoms to avoid the large fluctuation of the recorded local temperature [39].

3. Results and discussion

3.1. Comparison of the deposition morphology of different substrates

The deposition morphology was firstly observed and the morphology evolution of the Pd cluster deposited on the Ta substrate at the incident velocity of 1100 m/s was presented in Fig. 3. In the figures, only a few sections of the system were shown, and the red balls were the cluster atoms and the yellow were the substrate atoms. According to the morphology evolution, the whole deposition process can be divided into three stages, absorption, collision and relaxation. At the absorption stage, the Pd cluster with a given incident velocity gradually approached the substrate surface from the initial location and almost kept the original spherical structure. As the second stage happened, the cluster collided with the substrate. The cluster atoms on the bottom gradually lost the initial structure, some spread on the substrate surface and some embedded in the substrate. Meanwhile, some substrate atoms were squeezed onto the surface and accumulated around the cluster. At this stage, the cluster and substrate surface atoms interpenetrated each other. Both the cluster and the impacted substrate region were deformed. The impacted substrate region rebound upward, and some cluster atoms were rearranged. Then, the system reached to the maximum expansion, and the relaxation stage was coming. At the end of the deposition, the whole system tended to an equilibrium state. In the