Molecular Dynamics Modeling of the Processes of Surface Metallization*

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In the present study molecular dynamics simulations were performed for collisions of nanoclusters with each other and with the substrate for determining the mechanism of formation of bound states depending on the cluster size and impact velocity. A highly efficient parallel code for three-dimensional molecular dynamics was developed. This code is based on a spatial domain decomposition algorithm with one-dimensional parallelization and involves an additional subdomain load balancing algorithm that can save a considerable amount of computational time.
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I. INTRODUCTION

Improving the quality of materials, as well as their operational characteristics becomes particularly important now. A possible way to solve this problem is application of multifunctional protective coatings. As a result, extensive experimental and theoretical research of a wide class of processes was initiated, beginning from synthesis of nanopowders to their applications in practice. An example could be surface metallization by means of deposition of metal nanopowders from the gas phase.

Because of the space and time scales of these phenomena, experimental investigations of elementary processes, such as the dynamics of collisions of individual clusters with each other and with the substrate surface, are rather difficult. Therefore, the main tool for studying these processes is theoretical modeling. The molecular dynamics method has appropriate space and time scales. With this method, the mechanism of formation of nanostructures can be studied in detail at the subatomic level, and thermomechanical characteristics of these structures can be obtained.

A collision of a high-velocity cluster with a cold solid substrate is the main elementary act of coating formation in the deposition (spraying) process. For this reason, the most important aspect of studying micro-level processes inherent in deposition is a detailed investigation of physical and chemical effects that take place in high-velocity collisions of nanoclusters with each other and with the substrate surface.

II. PHYSICAL SYSTEM

As a physical system, we considered collisions of large spherical cuprum clusters with each other and with the substrate. The total number of atoms in the system var-

FIG. 1: Dependences of the kinetic temperature (A), total force acting on the left cluster from the right one (B), center of the mass velocity of the right cluster (C) and the distance between center of the mass of the clusters (D). Initial velocity 50 m/s. Cluster diameter is 100 Å.

ied from 88,230 to 709,214 for collisions of clusters and reached 275,846 atoms for the case of deposition onto the substrate.

Interaction of atoms inside each cluster and between atoms of different clusters and the substrate is described by a many-body EAM potential [1]. The atomic trajectories are calculated with a velocity Verlet algorithm.

The most difficult problem in molecular dynamics simulation is a long time needed for calculation, even for comparatively small systems of atoms [2]. The basic method of solving this problem is the use of highly efficient parallel scaled codes. In the present study we implemented a scaled algorithm based on one-dimensional parallelization with additional subdomain load balancing algorithm [3].

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FIG. 2: Dependences of the kinetic temperature (A), total force acting on the left cluster from the right one (B), center of the mass velocity of the right cluster (C) and the distance between center of the mass of the clusters (D). Initial velocity 500 m/s. Cluster diameter is 100 Å.

III. RESULTS AND DISCUSSIONS

A. Cluster collision

The velocity of the clusters was varied in numerical experiments in a wide range from 50 to 600 m/s. To analyze the phenomena at the microlevel, we use the following physical parameters: components of the total force acting on the left cluster from the right cluster, components of the center of mass of the right cluster, and distances between the centers of mass of the clusters. As the physical processes considered are characterized by strong thermodynamic nonequilibrium, we additionally introduced the total kinetic temperature and the kinetic temperature in the contact region, which is determined from the kinetic energy of random motion of atoms. The kinetic temperature allows us to determine whether there is substance melting after the impact interaction. The value of the kinetic temperature is found by means of a physical analysis of the system of atoms located in a sphere of radius 7 Å with the center at the point of contact of the nanoclusters.

For clusters of diameter 100 Å (88,230 atoms), the bound state is not formed for velocities below 250 m/s, and a typical pattern of expansion of nanoclusters (their motion away from each other) is observed. As the threshold value of the interaction velocity is exceeded, the clusters become bound. As an example, Fig. 1 shows the results of cluster collisions with a velocity of 50 m/s (the clusters move away from each other) and Fig. 2 shows the results for 500 m/s (the clusters form a bound structure). The time evolution of the kinetic temperature in the contact region shows that no melting occurs in the contact region, i.e., large nanostructures in the gas phase can be formed not only due to condensation, but also due

FIG. 3: Dependences of the kinetic temperature (A), total force acting on the left cluster from the right one (B), center of the mass velocity of the right cluster (C) and the distance between center of the mass of the clusters (D). Initial velocity 50 m/s. Cluster diameter is 200 Å.

to collisions.

Numerical experiments performed for large-size clusters (diameter 200 Å, 709,214 atoms) show that the behavior of the physical parameters is qualitatively similar for high and low velocities for both physical systems. As an example, Figs. 3 and 4 show the time evolution of the parameters for interaction velocities of 50 and 500 m/s.

It should be noted, however, that the threshold velocities of interaction are principally different. Thus, clusters of diameter 100 Å are not bound at interaction velocities below 250 m/s, whereas a bound structure is formed at this velocity from clusters of diameter 200 Å.

Thus, we can conclude that an increase in nanocluster mass and size leads to reduction of the threshold value of velocity necessary for the formation of the bound structure. This phenomenon is directly related to the possibility of collision energy dissipation to internal degrees of freedom. As an example of the bound structure formed as a result of high-velocity interaction, Fig. 5 shows the dynamics of the collision of clusters of diameter 200 Å with a velocity of 500 m/s.

B. Deposition of clusters onto the substrate

The material of the nanoclusters and the substrate was identical, and the interaction between the atoms inside the substrate and nanocluster and between the atoms of the substrate and nanocluster was described by the EAM potential. The simulations in numerical experiments were performed for clusters 20 Å and 50 Å in diameter to determine the effect of the cluster size on the deposition capability in the range of velocities from 10 to 600 m/s.

FIG. 4: Dependences of the kinetic temperature (A), total force acting on the left cluster from the right one (B), center of the mass velocity of the right cluster (C) and the distance between center of the mass of the clusters (D). Initial velocity 500 m/s. Cluster diameter is 200 Å.

The substrate had to satisfy the following requirements in simulations. Its mass should be much greater than the mass of the clusters (tend to infinity in the limit). The substrate size should be such that the unloading wave in the substrate returns to the contact region in a time much greater than the time of the cluster-substrate collision. In the numerical experiments described below, the substrate consisted of 111,656 atoms (Fig. 6).

To simulate an infinite substrate with an unchanged spatial position, we used the well-approved procedure of artificial viscosity acting on the substrate atoms. This procedure also allowed us to simulate dissipation of energy imparted by the cluster into the infinite substrate. At the initial time, the cluster velocity was defined, which was a controlled external parameter. At the initial stage of research, the clusters moved perpendicular to the substrate. The following physical parameters were chosen as the basic characteristics for analyzing the process of deposition of the clusters onto the substrate: the kinetic temperatures (this term is used to emphasize the nonequilibrium state of the cluster in the course of the collision) determined from the kinetic energy of random motion of atoms, the kinetic temperature in the contact region, and the components of velocity of the center of mass of the cluster. The estimate of the kinetic temperature in the contact region allows us to determine whether there is substance melting after the impact interaction with the substrate. The value of the kinetic temperature is found by means of a physical analysis of the system of atoms located in a hemisphere of radius 7 Å with the center at the point of contact of the nanocluster and the substrate.

The numerical experiments show that the nanoclusters 20 Å and 50 Å in diameter formed a bound structure

FIG. 5: Nanocluster collision, side view in the XY plane. Initial velocity is 500 m/s. A: initial moment, B: time 40 ps.

FIG. 6: Deposition of cluster (diameter is 50 Å) onto a substrate, side view in the XY plane. Initial velocity is 500 km/s. A: initial moment, B: time 80 ps.

with the substrate at all velocities in the examined range. It was found that an increase in the size of the deposited cluster does not lead to any principal changes in the physical pattern of the phenomenon, though certain reduction of fluctuation effects should be noted. It was also found that there is no thermodynamic equilibrium at the moment of the cluster impact onto the substrate.

The translational temperature T_Y is the first component to increase, earlier than transversal temperature $T_{X,Z}$. In the course of the process evolution, however, the components of the kinetic temperature become equalized owing to redistribution of energy between all translational degrees of freedom, and the temperature smoothly

FIG. 7: Dependences of cluster kinetic temperature (A) and kinetic temperature in the contact region (B) versus time. Cluster diameter is 50 Å. Initial velocity is 500 m/s.

FIG. 8: Side view in the XY plane. Clusters diameter is 50 Å. Initial velocity is 500 m/s. A: initial moment, B: time 100 ps.

decreases owing to heat transfer to the substrate.

Figure 7 shows the time evolution of the total kinetic temperature and the kinetic temperature in the contact region. The temperature rapidly increases (almost to 900 K) at the collision moment, then the temperature drastically decreases (at times of 10^{-13} - 10^{-12} s), and finally the temperature reaches a constant asymptotic value owing to heat transfer to the substrate.

Thus, the physical basis of the formation of the bound state of the nanocluster-substrate system is similar to the case with a collision of clusters considered previously. The cluster forms the bound state with the substrate owing to the emergence of metallic bonds between the cluster and substrate atoms rather than owing to melting.

To study the deposition of nanoclusters onto the substrate in more detail and to develop a realistic model of the physical and chemical processes of detonation deposition, we performed numerical experiments on deposition of two nanoclusters.

FIG. 9: Dependences of the kinetic temperature for both clusters (A), the distance between center of the mass of the clusters (B), Y-components of the mass velocity (C: first cluster, D: second cluster) versus time.

Figure 8 illustrates the numerical experiment performed. Cluster 2 with a velocity of 500 m/s was deposited onto the substrate with a previously deposited cluster 1. The direction of cluster 2 was perpendicular to the substrate, but cluster 2 was shifted with respect to cluster 1 in the horizontal projection to simulate a more realistic case with a tangential impact (Fig. 8).

It follows from the dependences of the kinetic temperature on time that the impact interaction of the impacting cluster with the already deposited cluster leads to a drastic increase in the kinetic temperature of the deposited cluster approximately during 10^{-12} s and its subsequent smooth reduction due to energy dissipation into the substrate (Fig. 9).

Simultaneously, the kinetic temperature in the impacting nanocluster smoothly increases, and the kinetic temperatures of both clusters reach identical asymptotic values after a certain relaxation time. The cluster melting does not occur. It should be noted that the normal components of mass velocity of both clusters become equalized much faster (Fig. 9).

IV. CONCLUSIONS

For high-velocity interaction of two nanoclusters, an increase in their mass and size was found to result in a lower threshold value of velocity necessary for the bound state formation. Numerical experiments also showed that the bound state between nanoclusters was generated owing to metallic bonding in the absence of melting in the contact region.

Investigation of deposition of nanoclusters onto a substrate demonstrated that an increase in mass or size of nanoclusters had no effect on the physical pattern of the phenomena studied. Certain attenuation of fluctuation effects, however, should be noted. Deposition of nan-

oclusters onto the substrate occurred in the entire examined range of velocities, and the physical grounds of the bound state formation were identical in both nanocluster-nanocluster and nanocluster-substrate systems.

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