Molecular dynamics simulation of nanocluster deposition on the metal substrate

Andrey V. Utkin[1,a], Igor F. Golovnev[1] and Vasily M. Fomin[1]

[1] Khristianovich Institute of Theoretical and Applied Mechanics SB RAS, Institutskaya Str., 4/1, 630090, Novosibirsk, Russia

[a] utkin@itam.nsc.ru

Keywords: Molecular dynamics; nanocluster deposition.

Abstract. In the present study molecular dynamics simulations were performed for collisions of nanoclusters with the substrate for determining the mechanism of formation of bound states depending on the cluster size, impact velocity and angle of incidence. A highly efficient MPI parallel code for three-dimensional molecular dynamics was developed.

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. A collision of a high-velocity cluster with a cold solid substrate is the main elementary act of coating formation in the 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 the substrate surface. This issue is hard to examine experimentally because of the space and time scales and the main research tool is theoretical modeling. Molecular dynamics method, owing to its space and time scales, offers a unique possibility for detailed subatomic-level studies of both the specific features of the mechanism of formation of nanostructures and conditions that affect these mechanisms.

Physical system.

As a physical system, we considered collisions of large spherical copper clusters with the substrate. The total number of atoms in the system reached 275,846 atoms. Interaction of atoms is described by a many-body EAM potential [1]. The atomic trajectories are calculated with a velocity Verlet algorithm. In the computations, the value of the time step 0.1 fs was chosen on the basis of accuracy requirements. 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.

Results and discussion.

Deposition of clusters onto the substrate. Normal impact angle.

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. 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. 1, A,B).
To simulate an infinite substrate with an unchanged spatial position, we used the well-approved procedure of artificial viscosity acting on the substrate atoms [3]. 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. 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.

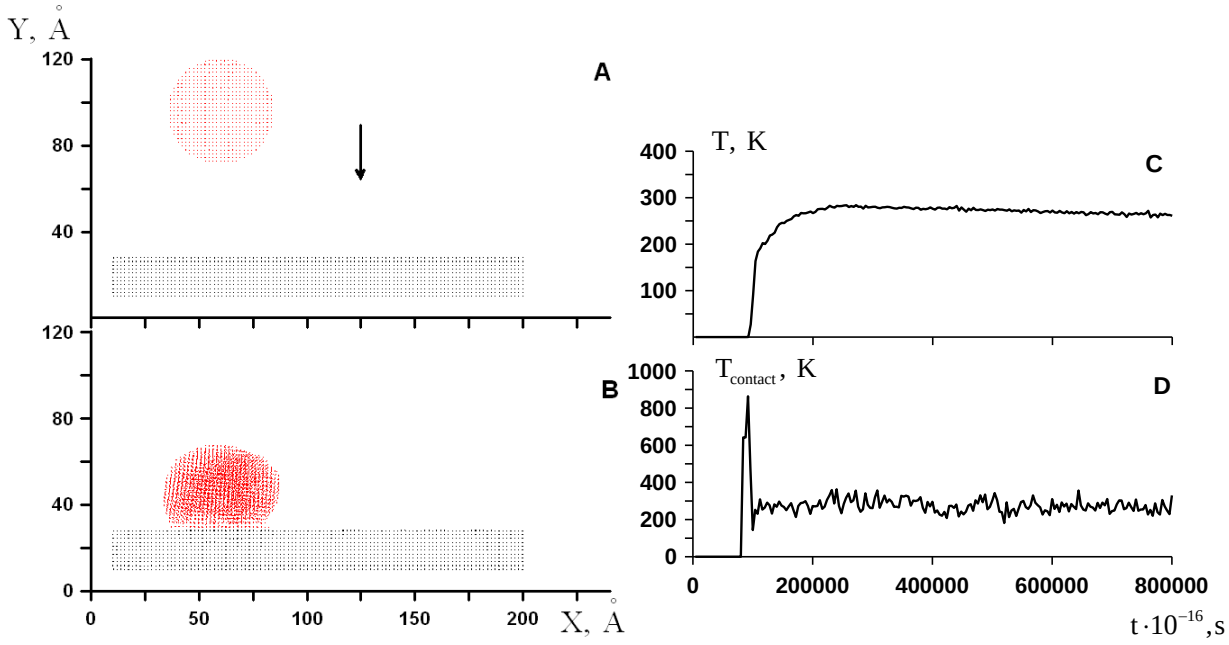

Fig.1. Initial (A) and final (B) positions of the cluster and substrate in the XY plane. Dependences of cluster kinetic temperature (C) and kinetic temperature in the contact region (D) versus time. Cluster diameter is 50 Å. Initial velocity is 500 m/s.

The value 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 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 decreases owing to heat transfer to the substrate.

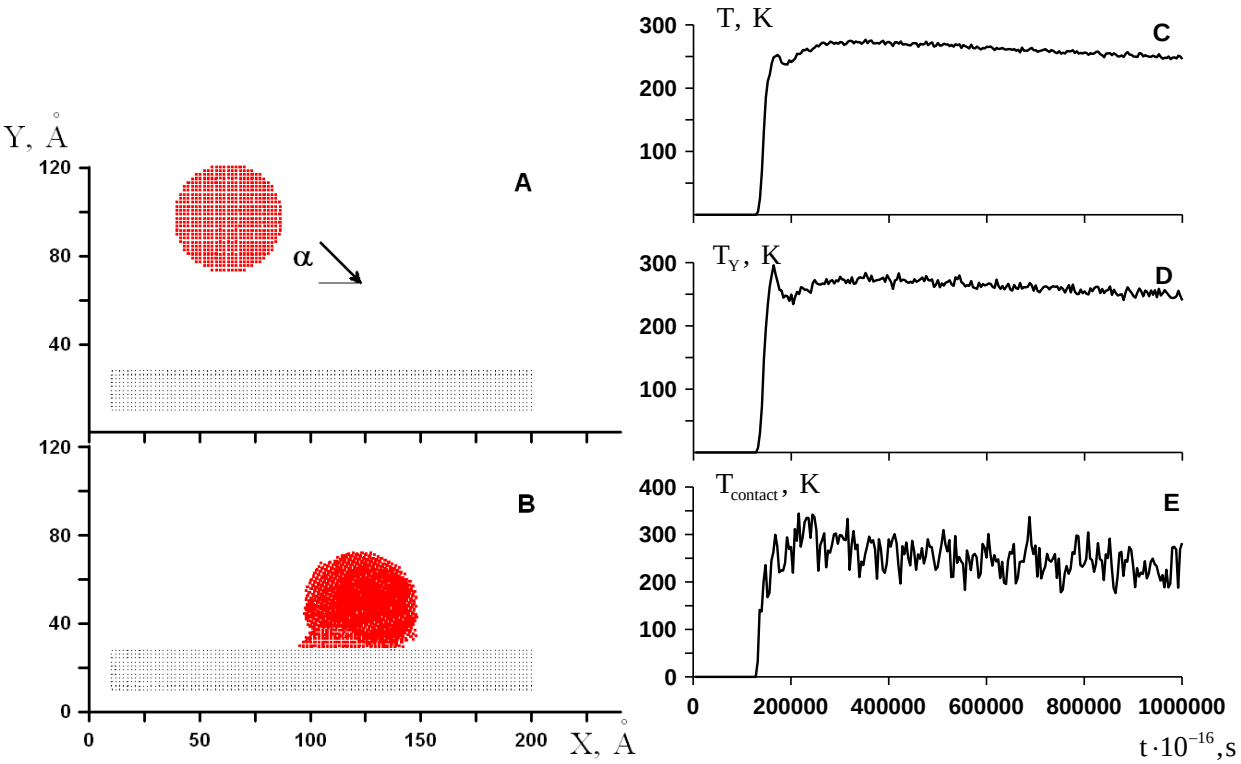

Fig.2. Initial (A) and final (B) positions of the cluster and substrate in the XY plane. Dependences of cluster kinetic temperature (C), Y–component of cluster kinetic temperature (D) and kinetic temperature in the contact region (E) versus time. Impact angle $\alpha = 45^{\circ}$. Initial velocity is 500 m/s

Fig. 1 (C, D) 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 0.1-1 ps), and finally the temperature smoothly decreases by almost linear law due to heat transfer to the substrate.
Thus, 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.

Effect of the cluster impact angle on the process of deposition onto the substrate.
Based on the previously approved research methods, the cluster-substrate interaction with different impact velocities and impact angles other than normal was numerically simulated.
As an example, Fig. 2 (A, B) shows the phenomenon in projections onto the XY plane for the cluster velocity of 500 m/s and impact angle $\alpha = 45^{\circ}$.
As in previous studies with deposition of a cluster moving normal to the substrate, a bound state is found to form between the cluster and substrate material. The impact of the cluster on the substrate leads to a drastic increase in the X and Y components of the kinetic temperature.
approximately during 3 ps with subsequent equalization of all three components in 10 ps after the impact. The values of the kinetic temperature of the cluster and the kinetic temperature in the contact region do not reach the threshold value of the melting temperature.

Figure 3 shows the results of numerical simulations for the cluster velocity of 500 m/s and impact angle $\alpha = 32^{\circ}$. It is clearly seen that the deposited cluster is partially destroyed during the impact.

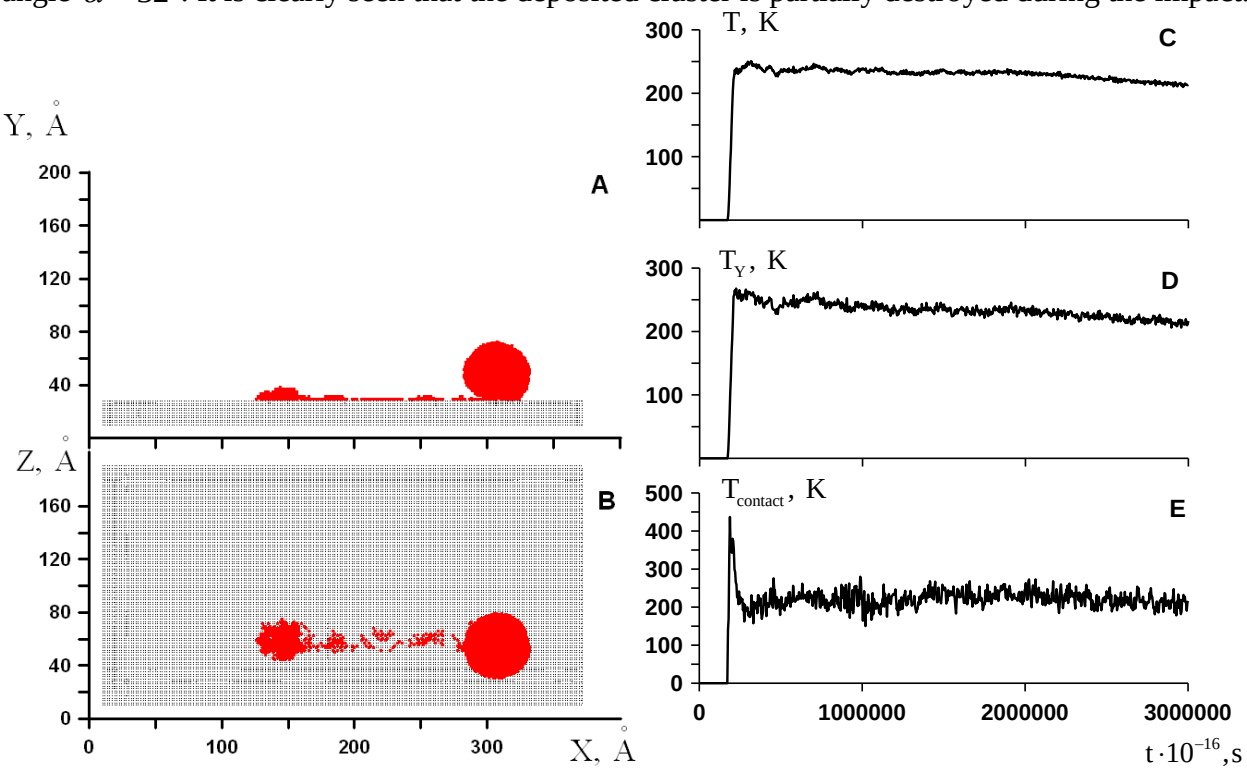

Fig.3. Final position of the cluster in the XY (A) and XZ (B) planes. Dependences of cluster kinetic temperature (C), Y–component of cluster kinetic temperature (D) and kinetic temperature in the contact region (E) versus time. Impact angle $\alpha = 32^{\circ}$. Initial velocity is 500 m/s

The cluster atoms in the contact region were "spread" over the substrate (braking distance), and a bounded structure is formed between the remaining basic fragment of the cluster and the substrate. As in previous experiments, the values of the kinetic temperature of the cluster and the kinetic temperature in the contact region do not reach the threshold value of the melting temperature (Fig. 3, C, D, E). The formation of a plane trace from the cluster material on the surface results in better coating of the surface, which is confirmed by experiments on cold gas-dynamic spraying [4].

Detailed studies of the effect of the impact angle in a wide range of its values made it possible to determine a critical minimum angle between the velocity vector and the surface; if the impact angle is smaller than the critical value, deposition of clusters does not occur, which is also consistent with experimental data of cold gas-dynamic spraying.

Numerical experiments showed that the critical angle of impact for the cluster velocity of 500 m/s is $\alpha = 24^{\circ}$. Additional studies of the effect of the impact velocity revealed that the critical minimum angle depends on velocity. An increase in the deposited cluster velocity was found to decrease the critical angle. Thus, the critical impact angle is $\alpha = 32^{\circ}$ for the impact velocity of 300 m/s, $\alpha = 30^{\circ}$ for 400 m/s, $\alpha = 22^{\circ}$ for 700 m/s, and $\alpha = 17^{\circ}$ for 800 m/s.

Changes in the cluster and substrate structure during deposition.

Stress tensor components were used to analyze the structural changes in the substance. To determine the stress tensor components, the components of the total force acting on each surface atom of the substrate from the side of all atoms of the deposited cluster were found.

After that, the force components were divided by the area assigned to one copper atom on the interface. In the figures below, the blue and red colors are used to indicate the negative and positive characteristics, respectively.

The distribution of the stress tensor component σ_{YX} over the substrate surface, which was obtained by the method described above, is presented in Fig. 4 for normal impact of the cluster and for impact angles $\alpha = 45^{\circ}, 32^{\circ}$.

Noticeable changes in the substrate structure at the place of the cluster impact should be noted (contact spot in the left zone in Figure 4, A, B, C). The appearance of an arc-shaped zone of the changed structure on the left of the contact spot is a consequence of the cluster impact at an angle other than 90°. The thus-performed analysis of the substrate surface after deposition of clusters allows us to conclude that regions both under the adsorbed clusters and under the traces left by the clusters on the surface are stress concentrators. Formation of such structures under external mechanical loads may lead to deterioration of material characteristics and to generation of material destruction spots on these sites [5].

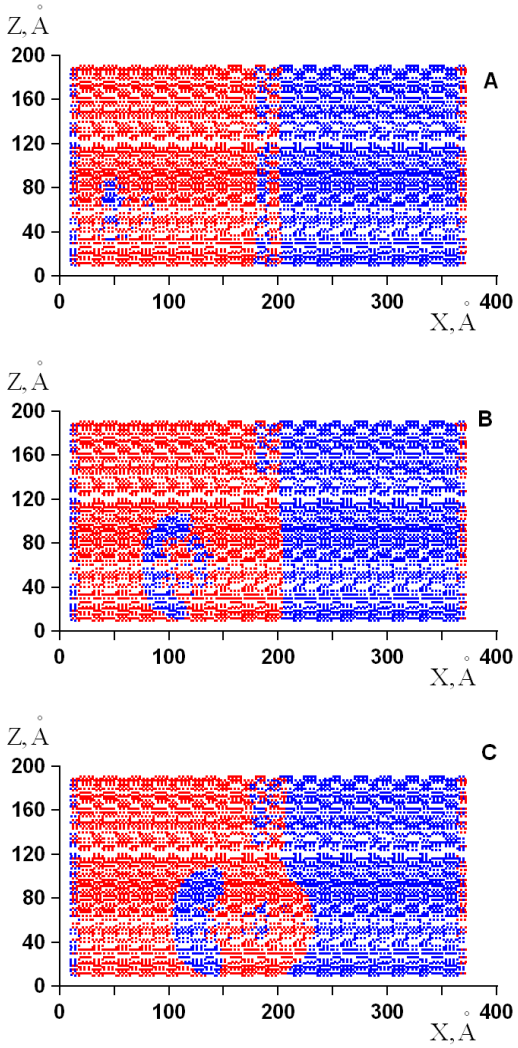

Fig.4. A - normal impact of the cluster onto the surface, B - cluster impact angle $\alpha = 45^{\circ}$, C - cluster impact angle $\alpha = 32^{\circ}$

Summary
Numerical experiments on deposition of the clusters showed that a bound state between the cluster and substrate material is formed due to metallic bonding of the cluster and substrate atoms in the absence of melting in the contact region. Molecular dynamics calculations showed that a tangential impact of the cluster onto the substrate forms a plane trace from the cluster substance on the substrate surface. This situation ensures better coating of the surface, which is confirmed by various experimental data on high-velocity spraying. Detailed studies of the effect of the impact angle in a wide range of its values made it possible to determine a critical minimum angle between the velocity vector and the surface; if the impact angle is smaller than the critical value, deposition of clusters does not occur. An increase in the deposited cluster velocity was found to decrease the critical angle. The analysis of the surface structure after deposition of the clusters showed that areas of stress concentrators appeared both under adsorbed clusters and under the traces left by the clusters on the surface. Formation of such structures can deteriorate the mechanical characteristics of the material under external mechanical loads and lead to generation of material failure sites at these places.

References
[1] R. A. Johnson. Phys. Rev. B., Vol. 39, Issue 17, (1989), pp. 12554–12559.
[2] Y. Deng, R. F. Peierls, C. Riveraz. Journal of Computational Physics, Vol. 161, Issue 1, June (2000), pp. 250-263.
[3] I.F. Golovnev, E.I. Golovneva, V.M. Fomin. Physical mesomehanics, Vol. 6, Issue 5-6, (2003), pp. 41-45.
[4] A.P. Alkhimov, V.F. Kosarev, S.V. Klinkov in Proc. 14th International Conference on the Method of Aerophysical Research, Novosibirsk, Russia, p.58, (2008).
[5] V.E. Panin, V.P. Sergeev, and A.V. Panin, "Nanostructuring of Surface Layers of Structural Materials and Application of Nanostructural Coatings" (in Russian), Russia, Tomsk, Izd. TPU, (2008).