The role of the vacancy complexes of nanocompacted aluminum particles on the formation of structure during heat treatment

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Abstract.

The boundaries of thermal stability of the initial face-centered cubic (fcc) phase in perfect aluminum clusters with a diameter up to 3 nm have been investigated by the molecular dynamics method using a modified tight binding (TB-SMA) potential. Based on the performed computer analysis, it has been concluded that, in most cases, for aluminum clusters with sizes up to D = 2.5 nm, the most stable configuration is the structure with pentagonal symmetry. With a further increase in the number of atoms, the fcc structure becomes more stable. The influence of the degree of disorder of nanocompacted aluminum particles up to 4 nm in diameter on the formation of a crystal structure during heat treatment has been analyzed. It has been shown that, under the effect of the temperature factor, the clusters undergo a transition from the initial fcc phase to other structural modifications, including those with pentagonal symmetry, even in the case of clusters with fairly large sizes.

1. Introduction

Investigation of the physical properties of metal nanoparticles with characteristic nanometer-scale sizes is an important problem from both the fundamental and applied points of view due to great prospects for their practical applications. In particular, the technological base for structural and functional nanomaterials, in many cases, includes ultra-fine metal powders [1–3], which can be considered as the main raw materials for producing compact nanocrystallites. Among the basic methods for synthesizing nanoparticles that form the base of nanopowders are the technique using gas phase condensation, precipitation from colloidal solutions, low-temperature plasma, cathode sputtering, molecular beams formed by different sources of heating, electric explosion, mechanical dispersion, and some others.

Despite the great variety of methods used for synthesizing nanocrystalline particles, the experimental investigation of their structure and properties is still very complicated [4]. One of the main reasons for these difficulties is the high reactivity of nanoparticles due to their highly developed surface, which can contain up to 50% of all the atoms of the particle. In this respect, of great scientific and technical interest are currently not single nanoparticles (nanoclusters) but compacted nanocrystalline materials, which are often more convenient for the investigation and application [1].

The vast majority of the currently available technologies used for synthesizing these materials have employed various types of compaction, often with the subsequent high temperature sintering [1]. Avoiding contact with the environment in the production of nanopowders and their compaction makes it possible to exclude the contamination with different impurities. However, particles of the compacted nanomaterial prepared by this method contain numerous stacking faults, the main of which are vacancies and pores. Investigations of the density of compacted samples showed that the overall degree of structural disorder in such materials due to the presence of different types of vacancy defects can vary in the range from 5 to 30%. There is no doubt that these single defects and their complexes can have a significant influence on the formation of the internal structure of nanomaterials at the atomic level. The use of high pressures and temperatures during the compaction of nanopowders makes it possible to decrease their residual porosity and to increase the relative density of the

synthesized materials. However, this method cannot completely solve the problem of the production of defect-free nonporous compact nanopowders.

Among the nanoparticles used now or in the near future, special attention should be paid to small particles, nanoobjects with different types of spatial structure, which allow us to determine the dependence of the observed physical and chemical properties of their structure. Thus, in order to more accurately determine the real structure of this material, it is of interest to investigate the dynamics of the influence of heat treatment on individual nanoparticles of the material. Indeed, for the understanding of the specific features of the formation of the structure and properties of nanomaterials, it is very important to consider the structural phase transformations occurring in these objects during heating and cooling. The thermal stability threshold of the nanostructure is highly dependent on many factors. Some of them are well known (for example, the state of grain boundaries), but some yet to be determined. Since it is very difficult to perform real experiments of this level, the main purpose of the present work is to investigate the formation of the internal structure in individual structural units of nanocompacted aluminum with the use of computer simulation techniques.

2. The computer model

For the simulation of clusters, there are two basic numerical methods that complement each other, namely, the Monte Carlo method and the molecular dynamics (MD) method. The Monte Carlo method is very effective for studying macroscopic properties of a system. This method is successfully used to investigate the order–disorder of atoms, crystal growth, annealing of radiation defects, dislocation slip through a system of obstacles, etc.

The molecular dynamics method is the most efficient for the calculation of structural characteristics of point defects, dislocations nuclei, and grain boundaries, as well as for the investigation of the diffusion of atoms. Since the molecular dynamics method allows one to determine dynamic characteristics of a simulated system, it is widely used to investigate structural phase transformations in metals and alloys. It is this technique that is the most adequate to determine the structures of metal clusters with the diameter of our interest, which are stable over a wide temperature range. Other simulation techniques, such as the Monte Carlo method or *ab initio* methods, because of the restrictions on particle sizes, calculations of temperature factors, and others, cannot completely solve the problem. Therefore, for our simulation, we chose the classical molecular dynamics method.

It is well known that in the description of metal nanoclusters is more reliable with the use of a many-body representation of the potential energy function. The main advantage of the many body representation as compared to the simpler pair interaction potential is that it better reproduces some of the main features of metal systems. The many body scheme of constructing the interaction potential overcomes many difficulties encountered in constructing pair interaction potentials by taking into account the band character of metal bonds. In this case, the relatively simple technique for the description of the atomic and electronic structure without recourse to complex *ab initio* calculations is the tight binding (TB) method [5 – 7], in which the ion–ion interaction is described taking into account the band character of the band and the short range repulsive pair potential.

Therefore, after the analysis of different types of representation of the potential energy, the heating of aluminum nanoclusters was simulated using the modified tight binding (TB-SMA) potentials [8] with a fixed cutoff radius corresponding to the fifth coordination sphere. The tight binding potentials are widely used in computer simulation of both macroscopic and nanometer scale objects. Moreover, the potentials proposed by Cleri and Rosato were thoroughly and successfully tested with many thermodynamic parameters [8, 9] and, currently, are among the main potentials used for calculating properties of metal nanoparticles.

The heating of clusters was performed in a canonical ensemble with the Nose thermostat [10]. In the simulation of the canonical ensemble, for which the number of particles N, volume V, and temperature T remained constant (NVT ensemble) and the total angular momentum of the system p was zero, the system was immersed in a thermal reservoir by introducing a random force simulating collisions with virtual particles. During the simulation, the temperature was determined by the average

kinetic energy of the atoms, which was calculated using the Verlet velocity algorithm with a time step $h = 1$ fs.

In order to most accurately investigate the influence of any of the parameters on the change in the structure of clusters, it is necessary, first of all, to minimize the interaction between the particle and its environment. Based on this assumption, we considered the so-called free or isolated clusters, which were placed in thermal reservoir, filled with virtual particles and did not interact with the substrate. The initial objects were spherical fcc aluminum clusters obtained by cutting a sphere from the perfect fcc lattice.
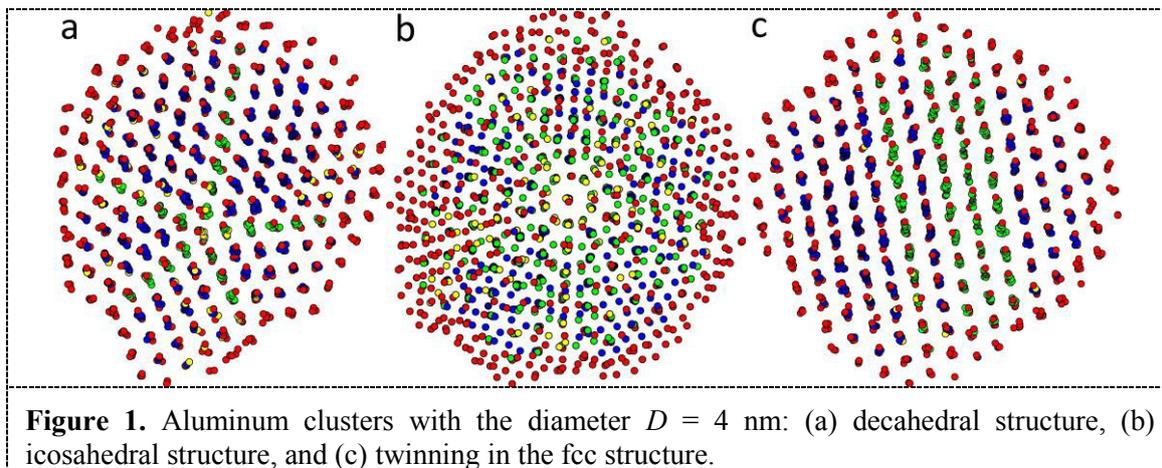
The computer molecular dynamics simulation was carried out with the MDNTP software developed by Dr. Ralf Meyer (Universitat Duisburg, Germany).

3. Results and discussion

In the simplest case, a nanocrystalline material consisting of atoms of one type contains two structurally different components: crystalline nanograins and grain boundaries with the width ranging from 0.4 to 1.0 nm [1]. The X-ray diffraction and neutron diffraction investigations of compacted metals demonstrated that the structure of interfaces in nanomaterials is similar to that in conventional polycrystals. Pores were found only in triple junctions, rather than along the entire length of the interfaces, and the density of atoms in the grain boundaries proved to be almost the same as in the crystalline grains [11].

For a physically adequate comparison of the obtained results, at the first stage, we investigated a group of clusters with the internal structure corresponding to the perfect fcc lattice without structural defects. In order to determine the boundaries of thermal stability of different isomeric modifications in aluminum nanoclusters, first of all, we examined the influence of the size of particles and the temperature on the formation of a particular crystal modification. We studied clusters containing 13, 19, 55, 135, 141, 147, 177, 201, 225, 309, 321, 555, 561, and 923 atoms (the diameter D was varied in the range from 0.5 to 3.0 nm). In general, based on the performed computer analysis of the heat treatment processes, it can be argued that, for small defect free aluminum clusters with sizes up to 350–400 atoms, in the majority of the cases, the most stable configuration is the structure with pentagonal symmetry. With a further increase in the number of atoms, the fcc structure becomes more stable in complete agreement with the laws of thermodynamics. However, in the case of aluminum nanoclusters, the geometric magic numbers play a very essential role, which was not observed by us so obviously in the simulation of nickel and copper clusters [12, 13].

At the second stage, we investigated the influence of defects on the formation of the internal structure of clusters. In order to simulate the structure with a desired degree of disorder, some atoms were removed in a random way from the initial cluster. This approach is similar to that described in the work [6], where the role played by pores in nanoparticles during the melting of clusters was analyzed also using the molecular dynamics method (*NPH* ensemble) for perfect fcc alumina clusters with diameters from 2 to 9 nm, which contained pores of different sizes. We also investigated clusters that did not contain pores at the initial stage but with the fractions of the removed atoms (single vacancies) equal to 5, 10, 20, 25, and 30%, which corresponded to real metal nanomaterials produced by the compaction method. For each case of the fixed fraction of vacancies in the cluster, we considered an ensemble of clusters of different sizes. All the clusters were subjected to relaxation at the initial temperature $T = 60$ K for 1 ns. Then, these clusters were heated with a step of 10 K and an exposure time of 0.5 ns.

Figure 1. Aluminum clusters with the diameter $D = 4$ nm: (a) decahedral structure, (b) icosahedral structure, and (c) twinning in the fcc structure.

The results of the simulation demonstrated that single vacancies with the content equal to 5% of the total number of atoms in the cluster led to the formation of small defect regions even at $T = 60$ K. With an increase in the temperature, the size of these regions increased, although, in general, the clusters retained the initial fcc structure. When the fraction of vacancies reached 10% of the total number of atoms in the cluster with the diameter $D = 3$ nm, the fcc structure remained to be the most stable, but with some violation of the order of stacking of atomic planes. With an increase in the cluster size to $D = 4$ nm, the heating resulted in the formation of a nearly perfect fcc structure in only 20% of the computer experiments, the sufficiently defect free fcc structure with the twinning plane was observed in 60% of the numerical experiments, and model clusters had the internal structure with inclusions of different decahedral fragments in 20% of the simulated cases at temperatures $T = 350–460$ K.

For the fractions of the removed atoms equal to 25 and 30% of their total number in the cluster, at the stage of relaxation all the clusters had an amorphous like structure. Upon further heating of model particles, an increase in the primary disorder of clusters with single vacancies up to 25% of the total number of atoms in the cluster led to the growth of structures with pentagonal symmetry. In this case, for the clusters with $D = 3$ nm, the decahedral structure was stabilized in the temperature range $T = 60–220$ K in 30% of the model clusters, whereas the formation of the icosahedral structure was observed in the temperature range $T = 220–340$ K in 50% of the model clusters. Nonetheless, despite the fact that the initial state was amorphous-like, the fcc structure with twinning was observed in 20% of the computer experiments in the temperature range $T = 160–240$ K. With an increase in the cluster diameter to $D = 4$ nm, a sufficiently regular decahedral structure was stabilized in 60% of the computer experiments at temperatures $T = 400–500$ K (Figure 1a), the structures containing only decahedral fragments were found in 30% of the simulated clusters in the temperature range $T = 100–150$ K, and the formation of the defect icosahedral structure was observed in 10% of the model experiments at temperatures $T = 250–300$ K (Figure 1b).

An increase in the cluster diameter to $D = 4$ nm significantly (to 20%) decreased the probability of finding a cluster with the icosahedral structure. Moreover, particles with the decahedral structure were observed in 40% of the performed experiments, and the fcc phase was observed in 20% of the computer experiments (Figure 1c). The remaining 20% of the model clusters had a more complex internal structure with inclusions of several different fragments of the decahedral structure, which competed with each other. As in the case of clusters with the diameter $D = 3$ nm, the formation of the decahedral structure was observed at significantly lower temperatures in the range $T = 80–200$ K, the fcc structure was revealed in clusters at $T = 140–180$ K, the formation of the icosahedral structure proceeded the temperature range of $240–380$ K, and the most complex structure with several decahedral fragments was observed at temperatures of $280–380$ K. In our opinion, these differences in the temperatures of the formation of structural modification in aluminum clusters are associated with different binding energies for different ways of constructing atomic clusters. As is known, it is the

icosahedral structure that has the highest binding energy, which could be judged from the higher melting temperature of the icosahedral clusters as compared to the fcc clusters of the same size. Most likely, it is for this reason that the icosahedral clusters require significantly higher kinetic energies for the transformation of the initially existing amorphous cluster into a well defined icosahedral structure.

4. Conclusions

Based on the performed computer analysis of the heat treatment processes with the use of the molecular dynamics simulation using the modified tight binding (TB-SMA) potential, it can be argued that, in small aluminum clusters with sizes up to $D = 2.5$ nm and without structural defects, in many cases, the most stable configuration is the structure with pentagonal symmetry. With a further increase in the number of atoms, the fcc structure becomes more stable. It was also shown that, in the case of aluminum nanoclusters with the perfect internal structure, the geometric magic numbers play a very significant role.

Thus, the performed molecular dynamics simulation of the heating of aluminum clusters with the content of vacancies from 5 to 30% of the total number of atoms in the cluster demonstrated that the formation of structures with pentagonal symmetry is possible in disordered nanoclusters with a diameter $D = 3$–4 nm, unlike defect free clusters in which, for this size of particles, the fcc structure is more stable. It was found that, for clusters with the diameter $D = 3$ nm, an increase in the number of vacancies leads to an increase in the number of clusters with the icosahedral structure, whereas for clusters with the diameter $D = 4$ nm, the decahedral structure remains predominant. The pentagonal clusters formed during heating, in most cases, have defect structures, in contrast to the fcc particles that are substantially free of packing defects, which was confirmed by the experimental data [14].

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