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Molecular dynamics study of the formation of a nanocrystalline structure during crystallization and devitrification of nickel nanoparticles

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Abstract: This work is devoted to the study of factors affecting the characteristics of the nanocrystalline structure formed during the rapid cooling of nickel nanoparticles from the melt and during devitrification as a result of heating from low temperatures of particles with an amorphous structure using the method of molecular dynamics. The influence of the temperature change rate from $5 \cdot 10^{11}$ to 10^{13} K/s and the particle diameter from 1.5 to 11 nm on the features of the resulting structure, the amount of stored energy, the temperature of the onset of crystallization and devitrification was considered. It is shown that with an increase in the cooling rate in the case of the simulation of crystallization and the heating rate in the simulation of devitrification, the density of defects and the amount of stored energy in the final structure of nanoparticles increase. The temperature of the onset of crystallization also depended on the rate of temperature change: the lower the rate, the higher the crystallization temperature and the lower the devitrification temperature. As the particle diameter decreases, the crystallization temperature decreases, while the devitrification temperature, on the contrary, increases.

Keywords: molecular dynamics, nanoparticle, crystallization, devitrification, nickel

1. Introduction

Metal nanoparticles have a unique set of physical, chemical, and optical properties, due to which they have high prospects for their application in such areas as microelectronics, optoelectronics, and plasmonics [1,2], medicine and biology [3, 4], chemical catalysis, and fabrication of gas sensors [5, 6]. In the manufacture of nanoparticles, much attention is paid to the control of the phase state, size and shape of particles due to their critical influence on useful properties [7-10]. In view of this, it is of great importance to study the factors affecting the mechanisms and kinetics of phase transitions, as well as the final structure of particles. Great interest has been given recently to particles with a high level of disorder in the atomic structure, i.e. having an amorphous or nanocrystalline structure [11-14]. They possess high stored energy and have a unique electronic structure, which makes them promising in the fields of catalysis, biomedicine, optics, and electronics [15-17].

A nanocrystalline structure, that is, the polycrystalline one with a relatively small grain size from nanometers to tens of nanometers with a high density of nonequilibrium grain boundaries, can be obtained not only by severe deformation, but also by sufficiently rapid cooling, when the recrystallization process is suppressed during the grain growth and many small grains form [18,19]. Using computer simulation, in [20-23], for example, it was shown

that nanoparticles of pure metals upon cooling at a rate of about 10^{12} K/s from the molten state crystallized with the formation of a nanocrystalline structure with a high density of grain boundaries and an average grain size of only about a few nanometers. At a cooling rate of more than 10^{13} K/s, in [20,22], homogeneous crystallization no longer had time to occur, and the particles cooled in the molecular dynamics model had an amorphous structure.

This work is devoted to the study of factors affecting the characteristics of the nanocrystalline structure formed during the rapid cooling of nickel nanoparticles from the melt and during devitrification as a result of heating from low temperatures of particles with an amorphous structure using the method of molecular dynamics. The influence of the temperature change rate and the particle diameter on the features of the resulting structure, the amount of stored energy (energy that can be released during the rearrangement of the structure), the temperature of the onset of crystallization and devitrification is considered. The choice of nickel particles as an example is due to their wide practical application, they are used, for example, in catalysis [24, 25] and in the manufacture of fuel cells [26].

2. Description of the model

To describe interatomic interactions in nickel in the molecular dynamics model, the EAM potential from [27]

was used, where it was obtained based on comparison with experimental data and *ab initio* calculations for various properties of nickel. This potential well reproduces a wide range of mechanical and structural-energetic properties [27,28], it has shown itself well in various molecular dynamics studies and has been successfully tested for various metal properties, including melting, crystallization, and selfdiffusion in the melt [22,23,28].

The study was carried out using the own software package for molecular dynamics calculations MDR [29]. Nickel nanoparticles were first created in the model by cutting a ball of a given size from a crystal. Diameter of the particles varied from 1.5 to 11 nm: 1.5, 1.75, 2, 2.25, 2.5, 3, 3.5, 4, 5, 6, 7, 8, 9, 10, and 11 nm. For particles with a diameter of less than 1.5 nm, it was difficult to determine the moment of the onset of crystallization, while for particles with a diameter of more than 11 nm, the influence of the free surface was already relatively small. The computational cells in the form of a rectangular parallelepiped with periodic boundary conditions contain one particle [30-32]. Vacuum was simulated around the particle.

After the creation of the initial crystalline round particle, structural relaxation was carried out at a constant temperature of 500 K for 20 ps. This duration was quite sufficient to establish an equilibrium state of the atomic structure of the particles for the given temperature. To keep the temperature constant and control its value during gradual changes in the main computer experiments, a Nose-Hoover thermostat was used. The resulting single-crystal particles were used as starting particles for modelling gradual heating. For particles of each size, heating at a constant rate from a single-crystal state to a temperature significantly higher than the melting point, cooling from the melt to normal temperatures (for modelling of crystallization) and heating of an amorphous particle from low temperatures to a temperature above the melting point were carried out.

To conduct the last series of computer experiments and simulation of devitrification, amorphous particles were first created by ultrafast (with a rate of the order of 10^{16} – 10^{17} K/s) cooling of particles melted in the first series of experiments (when heated above the melting point). When the metal is cooled at such a rate, homogeneous crystallization does not have time to occur and an amorphous structure is formed. The quality of the amorphous structure was checked using diagrams of the radial distribution of atoms and the average energy of atoms in a nanoparticle (this will be discussed in more detail in the next section). In addition, the destruction of the crystal structure of the particles and their crystallization, as a rule, were clearly visible visually, as well as when using a crystal phase visualizer.

The change in temperature during heating and cooling was carried out at a constant rate by a corresponding change in the velocity modules of all atoms in the model. Three rates $\Delta T/\Delta t$ were considered in the work: $5 \cdot 10^{11}$, 10^{12} , $5 \cdot 10^{12}$ and 10^{13} K/s. It is known that when melts are cooled at a rate above $10^{13}-10^{14}$ K/s, homogeneous crystallization in pure metals does not have time to occur, and in this case metallic glasses are obtained [11,33]. At the same time, as will be seen below, the rate of 10^{12} K/s is sufficient for homogeneous crystallization to occur.

3. Results and discussion

To analyze of the structural state of nanoparticles, the average potential energy of nickel atoms in a particle was used as the main characteristic. Figure 1 shows examples of temperature dependences of the average atomic energy for particles with diameters of 8 nm (Fig. 1a) and 2.5 nm (Fig. 1b) upon heating from the single-crystal state (curves numbered 1 in the figures), and reverse cooling from the melt (curves 2) and heating from the amorphous state (curves 3) with four different rates of temperature change $5 \cdot 10^{11}$, 10^{12} , $5 \cdot 10^{12}$, and 10^{13} K/s.

With increasing temperature, the energy increases almost linearly, which is due to thermal vibrations of atoms and thermal expansion. Phase transitions, melting and crystallization, are accompanied by a change in the average energy (increase in melting and decrease in crystallization), which becomes sharper as the rate of temperature change decreases. The melting-crystallization phase transitions, as is known, do not occur instantaneously. The crystal-liquid front moves at a finite velocity, depending on temperature, atomic mobility, and the presence of impurities, and, as a rule, is about several tens of meters per second [34,35]. In connection with the foregoing, we determined the temperatures of phase transitions by the moment of their onset (shown by arrows in Fig. 1).

The melting of particles of the same size began at approximately the same temperature at different heating rates. However, the crystallization temperature turned out to be much more sensitive to the cooling rate (curves 2 in the figure): as the cooling rate from the molten state decreased, the crystallization onset temperature increased, and this was more pronounced in the case of relatively small particles (Fig. 1b). At a rate of $5 \cdot 10^{12}$ K/s, crystallization occurred for an 8 nm particle, as seen in Fig. 1a, only partially (this can be seen from the relatively small drop in the average energy of atoms) and did not occur at all for a particle with a diameter of 2.5 nm. As known, homogeneous crystallization consists of two stages: the nucleation of crystalline nuclei and their growth, that is, the movement of the crystallization front. These stages are sequential, and after the formation of stable nuclei, the front moves at approximately the same rate as during melting, which can be seen from the similar slope of the curves in most cases during melting and crystallization.

After crystallization, the average energy of atoms, as a rule, turned out to be higher than for a single-crystal particle (curves 2 and 1). Moreover, this difference increased with increasing particle diameter and cooling rate. This is explained by the formation of defects after crystallization, mainly grain boundaries. With an increase in the cooling rate, the relaxation time of the structure was reduced and more defects remained inside the particle.

The temperature at which devitrification began (drop in curves 3 in Fig. 1) also depended to a large extent on the rate of temperature change and decreased as the heating rate decreased. It should be noted that after the crystallization of an amorphous particle, as in the case of crystallization from a melt, the average energy of the atoms was noticeably higher than the energy of a single-crystal particle, which is again explained by the formation of a polycrystalline structure with a high content of grain boundaries and other defects. For



Fig. 1. (Color online) Temperature dependences of the average potential energy of atoms at different heating/cooling rates of nickel nanoparticles 8 nm (a) and 2.5 nm (b) in diameter. 1 — heating of a single-crystal particle, 2 — cooling of a particle from a molten state, 3 — heating of a particle from an amorphous state. T_m is the melting point, T_c is the crystallization temperature, T_d is the devitrification temperature.

the case of an 8 nm particle and a heating rate of 10^{12} K/s, an interesting effect was observed: at a temperature of about 1200 K, intense recrystallization began, as a result of which the particle got rid of most defects (Fig. 1a shows that the energy after recrystallization became almost equal to the energy of a single-crystal particle).

An important result follows from a comparison of the curves for heating single-crystal and nanocrystalline particles obtained as a result of devitrification (curves 1 and 3 in Fig. 1) — the melting of a nanocrystalline particle occurs at lower temperatures than a single-crystal particle due to the influence of a high concentration of defects, mainly grain boundaries.

Figure 2 shows the atomic structure in the cut of particles with a diameter of 8 nm, crystallized at four different cooling rates. The structure is depicted using a crystal phase visualizer based on the Common Neighbor Analysis (CNA) method [36], which determines whether each atom belongs to one or another crystal structure by analyzing the arrangement of neighboring atoms. Before analysis of the obtained structure, the particles were cooled ultrafast (at a rate of the order of $10^{16}-10^{17}$ K/s) to get rid of the effect of thermal vibrations of atoms.

Figure 2 well illustrates the fact that with an increase in the cooling rate, the density of defects in the final particle is

higher. In the case of the rate of 10^{13} K/s, as seen in Fig. 2 a, the particle did not have time to crystallize and contains a high proportion of the amorphous structure (white atoms). At a cooling rate of $5 \cdot 10^{11}$ K/s, judging by the very close location of dependences 1 and 3 in Fig. 1a, that is, an insignificant difference in the average energy of single-crystal and crystallized particles, the final structure of an 8 nm particle (Fig. 2 d) contains predominantly low-energy grain boundaries (with a high density of the coincidence sites: special boundaries, twins). For example, twins are characterized by a large number of "*hcp* atoms", which in this case show stacking faults [37].

Figure 3 shows cuts of an 8 nm particle obtained during devitrification, that is, during crystallization as a result of heating an amorphous particle from low temperatures. The particle structure was obtained by heating from 200 to 1000 K and subsequent ultrafast cooling. The figure shows the same regularity: the higher the rate of temperature change (in this case, heating), the more defects in the final structure of the particle. At a rate of 10^{13} K/s, a high fraction of an amorphous structure is again observed, and the 8 nm particle crystallized only partially (Fig. 3 a).

An increase in the density of defects with an increase in the rate of temperature change is obviously explained by a decrease in the duration of the relaxation of the structure. One should expect a decrease in the density of defects, their displacement to the surface, and recrystallization during prolonged relaxation at a sufficiently high temperature.

To mathematically describe the effect of the free surface of nanoparticles on their melting point, a formula is often used based on the assumption that the change in the phase transition temperature is proportional to the ratio of the surface area to the volume of the particle [38, 39], that is, for a round particle, this change should be proportional to $N^{-\frac{1}{3}}$ or d^{-1} , where N is the number of atoms in a particle, and d is its diameter. We used the same assumption to describe the crystallization and devitrification temperatures by adding a correction δ that takes account for the finite thickness of the near-surface layer of the particle:

$$T(d) = T^0 - \frac{A}{d - \delta}.$$
 (1)

Here T and T^0 are the crystallization/devitrification temperatures of a particle and bulk material; *A* is the parameter responsible for the degree of influence of the particle surface on the crystallization/devitrification temperature.

Using formula (1), we constructed approximation curves of the dependences of the crystallization (Fig. 4a) and devitrification (Fig. 4b) temperatures of nanoparticles on their diameter (dotted lines in the figures). As can be seen,



Fig. 2. (Color online) Atomic structure of nickel particles with a diameter of 8 nm in a cut obtained as a result of crystallization at different cooling rates: 10^{13} K/s (a); $5 \cdot 10^{12}$ K/s (b); 10^{12} K/s (c); $5 \cdot 10^{11}$ K/s (d).



Fig. 3. (Color online) Atomic structure of nickel particles with a diameter of 8 nm in a cut obtained as a result of devitrification at different heating rates: 10^{13} K/s (a); $5 \cdot 10^{12}$ K/s (b); 10^{12} K/s (c); $5 \cdot 10^{11}$ K/s (d).



Fig. 4. (Color online) Temperature of crystallization (a) and devitrification (b) of a nickel particle depending on its diameter at different rates of temperature change.

for the temperature change rates of 10^{12} and $5 \cdot 10^{11}$ K/s, the values obtained in the model (shown by markers in Fig. 4) agree well (within the errors) with the approximation curves, which proves the leading role of the free surface not only in the melting process, but also crystallization and devitrification of nanoparticles. Values of parameters for formula (1) in the case of crystallization are as follows: T_c^0 =1170 K, A=450 K·nm, δ =0.4 nm for a rate of 5 · 10¹¹ K/s, and T_c^0 =1170 K, A=580 K·nm, δ =0.4 for a rate of 10¹² K/s.

In the case of devitrification, the phase transition temperature, in contrast to crystallization, decreased with increasing particle diameter. However, as seen in Fig. 4 b, it is also well described by formula (1), but with a negative value of *A*. This can be explained by the relatively higher diffusion of atoms on the surface, which, in the case of small particles, reduces the probability of the formation of stable crystalline nuclei upon heating from the amorphous state. Values of parameters for formula (1) in the case of devitrification: T_d^0 =370 K, *A* = 550 K·nm, δ = 0.4 nm for a rate of 5 · 10¹¹ K/s, and T_d^0 =400 K, *A* = 600 K·nm, δ = 0.4 nm for a rate of 10¹² K/s.

At a temperature change rate of $5 \cdot 10^{12}$ K/s (triangular markers in Fig. 4), the crystallization and devitrification temperatures differed significantly from the values obtained at rates of 10^{12} and $5 \cdot 10^{11}$ K/s, which indicates the transitional nature of the processes under consideration at a given rate — crystallization at $5 \cdot 10^{12}$ K/s has already partially passed, which can also be seen, for example, from the curves in Fig. 1. For particles with a diameter of less than 3 nm, the temperature of the beginning of the phase transition was already difficult to determine, it was not recorded from the curves of the average atomic energy (Fig. 1b).

The stored energy of crystallized particles was estimated from the difference between the average energy of atoms in them and in single-crystal particles. Figure 5 shows the dependence of the stored energy on the particle diameter and the rate of temperature change. For comparison, data are also given for the pure amorphous state, which was obtained by ultrafast cooling at a rate of $10^{16}-10^{17}$ K/s (by periodically sharp zeroing of the velocities of all atoms), subsequent relaxation at a temperature of 200 K for 20 ps, and final cooling to 0 K.



Fig. 5. (Color online) Stored energy (the difference between the average energy of an atom compared to the energy in a single-crystal particle) depending on the particle diameter and the rate of temperature change. Filled markers — during crystallization, unfilled markers — during devitrification.

To calculate the average energy of atoms, the particles obtained after modeling crystallization and devitrification were also superfast cooled to 0 K (as in the case of obtaining the structures in Figs. 2 and 3) to eliminate the influence of thermal vibrations of atoms.

For the approximation (dashed line in Fig. 5) of the values obtained for amorphous particles, formula (1) again fits well, which indicates the leading role of the free surface in this case:

$$\Delta \overline{E_a}(d) = \Delta \overline{E_a^0} - \frac{A_E}{d - \delta}.$$
 (2)

Values of quantities included in formula (2): $\Delta E_a^0 = 0.17$ eV, $A_r = 0.22$ eV·nm, $\delta = 0.4$ nm.

A pure amorphous structure obviously contains more stored energy, but such particles are also much less stable than nanocrystalline ones: they began to crystallize (devitrify) in the model already at a temperature of about 400 K. For the occurrence of recrystallization and a decrease in the density of defects in nanoparticles, relatively long computer experiments at a sufficiently high temperature were required.

Figure 5 illustrates well that the amount of stored energy increases with an increase in the rate of temperature change, which is explained by the formation of a relatively higher density of structural imperfections during crystallization or devitrification with an increase in the cooling or heating rate. As mentioned above, this is associated with a reduction in the time of the structure relaxation.

It is noteworthy that the values obtained during crystallization (filled markers in Fig. 5) and devitrification (unfilled markers) turned out to be generally close for the same values of the temperature change rate, except for the rate of $5 \cdot 10^{11}$ K/s. The latter, apparently, is explained by the fact that the polycrystalline structure in the case of crystallization is formed at a higher temperature compared to devitrification, and therefore relaxation at the moment of structure formation proceeds more intensively in the first case.

Particles with a diameter of 3 nm and less at velocities of 10^{12} and $5 \cdot 10^{11}$ K/s crystallized either with the formation of a single crystal or with the formation of low-energy grain boundaries (special boundaries, twins) — the average energy of atoms for them turned out to be almost the same as for single-crystal particles. At velocities of $5 \cdot 10^{12}$ and 10^{13} K/s, most of the particles smaller than 2.5 nm in diameter did not have time to crystallize — the stored energy values for them (triangular and square markers) are close to the values for amorphous particles.

4. Conclusion

The study of the factors affecting the characteristics of the nanocrystalline structure formed during the rapid cooling of nickel nanoparticles from the melt and during devitrification as a result of heating from low temperatures of particles with an amorphous structure was carried out by the method of molecular dynamics. The influence of the temperature change rate from $5 \cdot 10^{11}$ to 10^{13} K/s and the particle diameter from 1.5 to 11 nm on the features of the resulting structure, the amount of stored energy, the temperature of the onset of crystallization and devitrification was considered.

As a result of the studies, it was found that the formation of a nanocrystalline structure and, accordingly, the stored energy, can be controlled by varying the cooling rate during crystallization from the melt and the heating rate during devitrification from the amorphous state. With an increase in the rate of temperature change, the final structure of nanoparticles contained more defects and the amount of stored energy increased. The temperature of the onset of crystallization and devitrification also depended on the rate of temperature change: the lower the rate, the higher the crystallization temperature and the lower the devitrification temperature. As the particle diameter decreased, the crystallization temperature decreased, while the devitrification temperature, on the contrary, increased in inverse proportion to the particle diameter.

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