Study of the melting nanocrystalline aluminum by the molecular dynamics method

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ABSTRACT
Using molecular dynamics simulation, a study of the melting of aluminum with a nanocrystalline structure obtained as a result of severe plastic deformation was conducted. It is shown that the melting of nanocrystalline aluminum begins at a lower temperature than monocrystalline aluminum. The higher the density of grain boundaries and other defects, and, accordingly, the higher the excess energy, the lower the melting temperature. In the presence of defects, melting proceeds heterogeneously and begins primarily from the grain boundaries and free surface. In a pure crystal that did not contain any defects or free surface, melting in the model proceeded homogeneously. When studying recrystallization in nanocrystalline aluminum, it was found that its intensity is greatly influenced by the free surface: the restructuring of the structure near it occurred faster than in the bulk of the material.
KEYWORDS
molecular dynamics • melting • nanocrystalline structure • recrystallization

Introduction

In recent decades, much attention has been paid to ultrafine-grained and especially nanocrystalline materials, which include polycrystals with an average grain size of less than 100 nm. They have unusual physical and mechanical properties, associated mainly with a large volume fraction of grain boundaries compared to the usual coarse-grained state [1–4]. They are obtained by different methods, including intense plastic deformation, sintering of nanopowders, condensation from the gas phase, etc. A common property of nanocrystalline materials is a high degree of nonequilibrium structure and large values of excess, or stored, energy [1–4].

One of the examples of the manifestation of excess energy in nanocrystalline materials, apparently, should be considered the experimentally observed decrease in the ignition temperature of the high-temperature synthesis reaction during the production of intermetallic compounds after preliminary mechanical activation treatment of the initial mixture of powders [5–10]. As a result of such processing, the initial mixture is subjected to intense mechanical action, as a result of which a nanocrystalline structure with a high

concentration of structural defects is often formed in metals [8–10]. Under normal conditions, the ignition temperature coincides with the melting temperature of aluminum, but after mechanical activation treatment it decreases significantly [5–10]. Among the main reasons for this decrease are the relatively high values of excess energy due to the high concentration of grain boundaries and other defects in the mixture after mechanical activation, the high diffusion mobility of atoms in nanocrystalline materials, as well as a possible decrease in the melting point of nanocrystalline aluminum compared to conventional coarse-crystalline aluminum.

As for the latter, in [11–14], using computer modeling, it has been shown that melting is not a homogeneous process, it begins, as a rule, from free surfaces and grain boundaries. In this case, the melting of the structure near the interfaces began in the mentioned works at lower temperatures than for a pure crystal. The nanocrystalline structure has a relatively high proportion of nonequilibrium grain boundaries, which, obviously, should be reflected in the overall melting process and the temperature at which the phase transition begins. When studying phase transitions in nanoparticles [15–17], we actually observed a noticeable decrease in the melting temperature of metal particles with a nanocrystalline structure.

This work is devoted to the study, using molecular dynamics simulation, of the melting of aluminum with a nanocrystalline structure obtained as a result of severe plastic deformation. The effect of excess energy on the melting temperature was considered. The melting mechanism was studied under conditions of the presence and absence of a free surface along with grain boundaries. The work also considered the influence of the initial excess energy and free surface on the intensity of recrystallization.

Description of the model

To describe interatomic interactions in the molecular dynamics model, the EAM potential from [18] was used, where it was obtained based on comparison with experimental data and *ab initio* calculations of various properties of aluminum. This potential well reproduces a wide range of mechanical and structural-energetic properties [18–20]. It has proven itself in various molecular dynamics studies and has been successfully tested in modeling various processes, including melting, crystallization and self-diffusion in the melt [18–24]. This potential has been repeatedly used to simulate the melting of aluminum [22–24]. It reproduces this phase transition quite well and gives a melting temperature relatively close to the reference value – 990 K for an ideal crystal with a free surface [22,23].

The computational cell had the shape of a parallelepiped with dimensions of 14.3, 14.0 and 11.7 nm at 0 K along the *x*, *y*, *z* axes, respectively (Fig. 1) and contained 124416 atoms. The initial structure corresponded to an ideal fcc aluminum crystal (Fig. 1(a)). To obtain a nanocrystalline structure containing a high density of defects, intense plastic deformation was simulated. Intense deformation was carried out by alternating uniaxial compression and tension by 15 % along all three axes, followed by shear deformation also alternately along all axes by 15 %. During deformation, the temperature of the computational cell increased. To avoid its melting and recrystallization, the computational cell was sharply cooled after each stage of deformation.

Figure 1(b) shows the structure of the computational cell after deformation using a crystalline phase visualizer based on the CNA (Common Neighbor Analysis) method [25]. As can be seen, it contains a high density of defects and a large number of small grains.
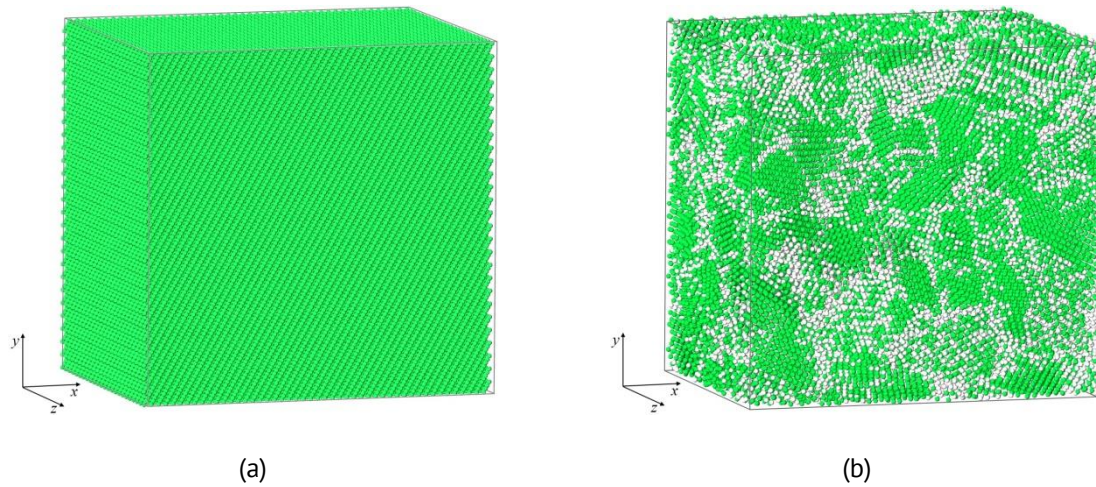

(a) (b)

Fig. 1. Obtaining an initial deformed structure: a) starting computational cell; b) the cell after severe plastic deformation. Atoms whose immediate environment corresponds to the first coordination sphere of the crystal lattice are colored green; white atoms – the crystal lattice has not been identified

In this work, three variants of the nanocrystalline structure were considered, which were obtained as a result of relaxation of the structure shown in Fig. 1(b), for 200 ps at different temperatures: 500, 600 and 700 K (Fig. 2). During the relaxation process, the concentration of defects and the number of grains decreased, and their average size increased. Excess, or stored, energy was estimated as the difference between the average potential energies of an atom in the structure under consideration and in an ideal crystal. That is, this is the energy that can be released during the restructuring of the structure into an ideal crystal, per one atom. For the computational cells shown in Fig. 2, the stored energy was equal to 0.14, 0.10 and 0.08 eV, respectively, for the structures in Fig. 2.
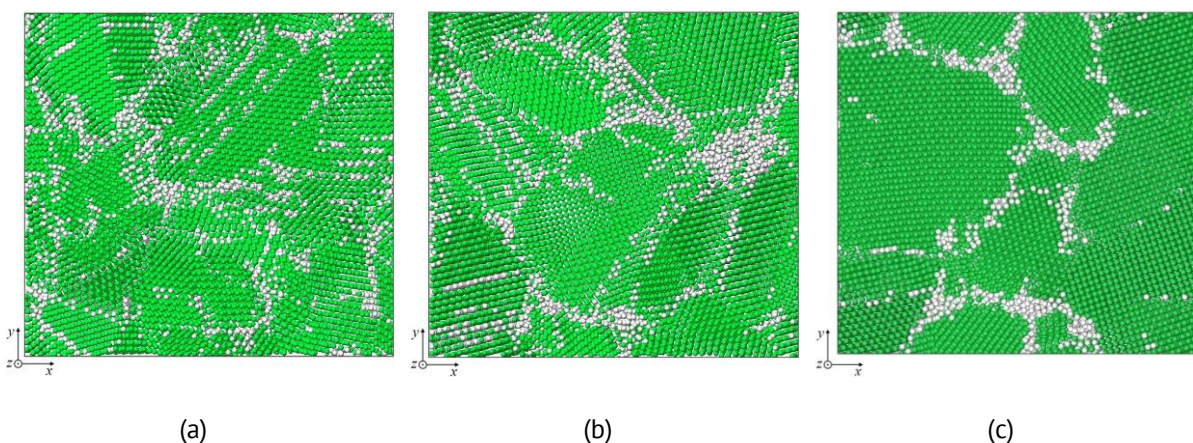

(a) (b) (c)

Fig. 2. Sections of the considered computational cells obtained as a result of relaxation for 200 ps at different temperatures: (a) 500 K; (b) 600 K; (c) 700 K

For comparison, computational cells containing a free surface and without it were considered. In the second case, periodic boundary conditions were used along all axes; in the first case, free conditions were used at the ends along the x-axis, that is, a free surface was simulated. In both cases, the NPT canonical ensemble was simulated using the Nose-Hoover thermostat. The time integration step was 2 fs.

To determine the melting point, the method of gradual heating was used to plot the dependence of the average potential energy of atoms on temperature [12,26–28]. Heating was carried out at a rate of 10^{12} K/s. At lower speeds, the results were strongly influenced by recrystallization, which was especially intense at temperatures close to the melting point. On the other hand, at higher heating rates it was more difficult to determine the melting point.

Results and Discussion

Figure 3 shows the dependences of the average atomic energy on temperature for the nanocrystalline structures under consideration when heated at a constant rate of 10^{12} K/s in the absence and presence of a free surface. For comparison, curves (indicated by number 4) obtained by heating an ideal crystal are shown.

The melting temperature of the crystal in the absence of a surface and any defects (curve 4 in Fig. 3(a)) turned out to be significantly higher (1140 K) than the melting temperatures found for the other structures under consideration. In this case, the melting process proceeded homogeneously, that is, almost simultaneously throughout the entire volume of the computational cell, and therefore the increase in atomic energy at the moment of melting appears sharper in Fig. 3(a) compared to other cases.

If there were grain boundaries or surfaces in the computational cell, melting began at them, after which the liquid-crystal interface moved away from the defects into the rest of the volume. The crystal-liquid front, as is known, moves with a finite speed that depends on temperature and, as a rule, amounts to several tens of meters per second [29,30].

Figure 3 clearly shows that the melting point of aluminum with a nanocrystalline structure is lower than that of monocrystalline aluminum. Moreover, the higher the defect density, the smaller the grain size and the higher the stored energy, the lower the melting temperature. This dependence manifested itself to a greater extent in the absence of a free surface (Fig. 3(a)). In the case of the presence of a surface, the melting temperatures of the considered variants of the structures turned out to be close, which, firstly, is explained by the large contribution of the surface as an additional site of initiation of melting, and, secondly, by more intense recrystallization in comparison with cells without a surface. Due to the recrystallization, the average energy of atoms initially decreased with increasing temperature. For structures with a higher density of grain boundaries and other defects, and correspondingly containing more stored energy, recrystallization, as can be seen from the graphs in Fig. 3, proceeded more intensely.

Figure 4 shows sections of nanocrystalline aluminum with a structure corresponding to Fig. 2(c) (3 in Fig. 3(b)), in the presence of a surface at different moments of the melting process. The figure clearly shows that melting begins at the boundaries of grains and the surface, that is, where the atoms are in shallower potential wells compared to an ideal crystal.
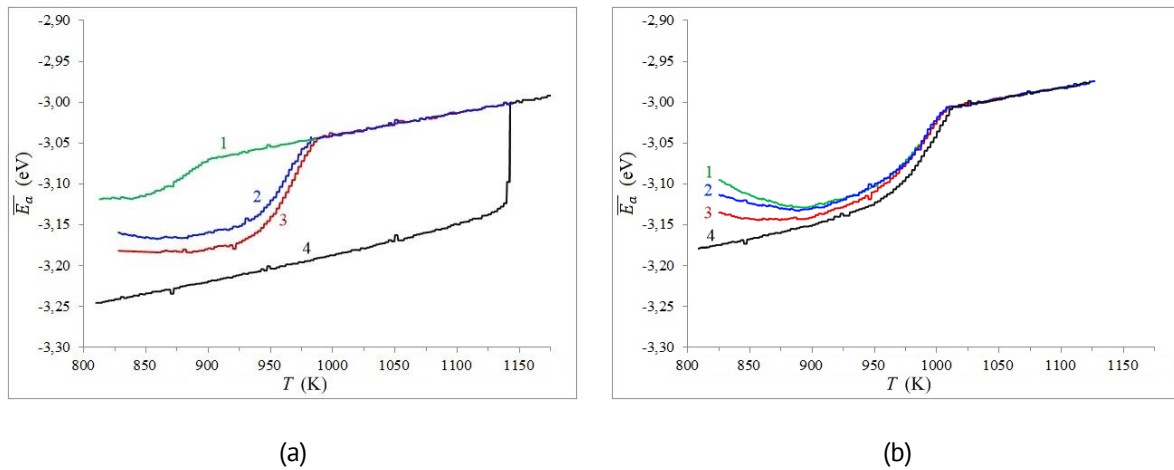
(a) (b)

Fig. 3. Dependences of the average potential energy of atoms on temperature during heating at a rate of 10^{12} K/s under conditions without (a) and in the presence of a free surface (b). 1, 2, 3 – dependencies for cells with structures shown in Fig. 2(a-c), respectively; 4 – for an ideal crystal
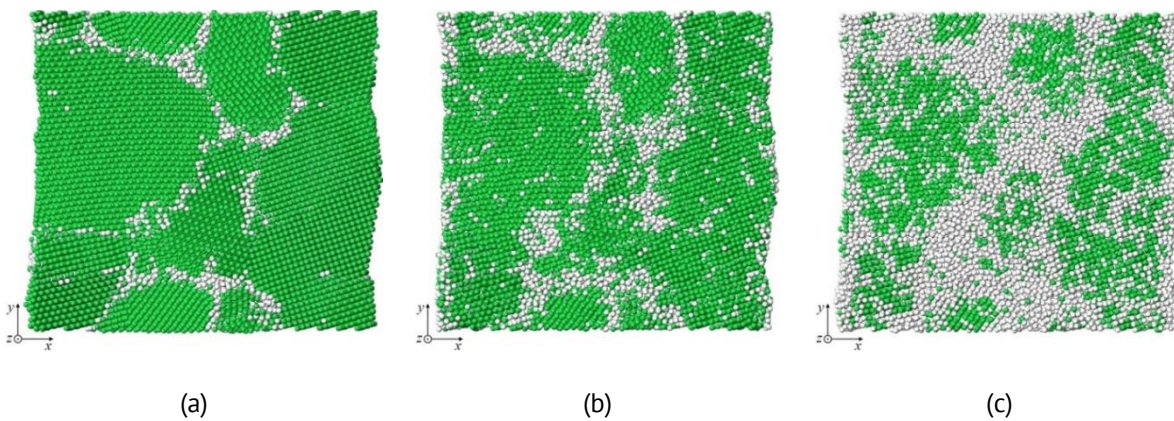

(a) (b) (c)

Fig. 4. Melting from grain boundaries and surface: (a) initial structure; (b) at a temperature of 950 K at a time of 5 ps; (c) at a temperature of 970 K at a time of 10 ps

However, not all grain boundaries are equally likely to initiate melting. As it turned out, this depends on the energy of boundary formation, that is, again on the stored energy. For example, in the case of boundaries with low formation energy, that is, low-angle boundaries with a high density of coinciding nodes, special boundaries, and especially twins, melting occurs less intensely than at other boundaries.
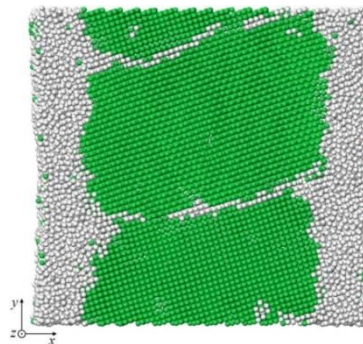

Fig. 5. Melting from the surface in the presence of low-energy grain boundaries

For a computational cell with a low-energy grain boundary, a relatively small difference in the average atomic energy from the average atomic energy in a cell without defects was characteristic. In addition, when using the crystalline phase visualizer for such boundaries, the number of atoms whose environment did not correspond to the crystal (white atoms in the figures) was noticeably smaller than in the case of high-angle boundaries. Figure 5 shows an example where it is clearly visible that the melting front comes from the free surface (left and right), while two low-energy boundaries remain almost unmolten.
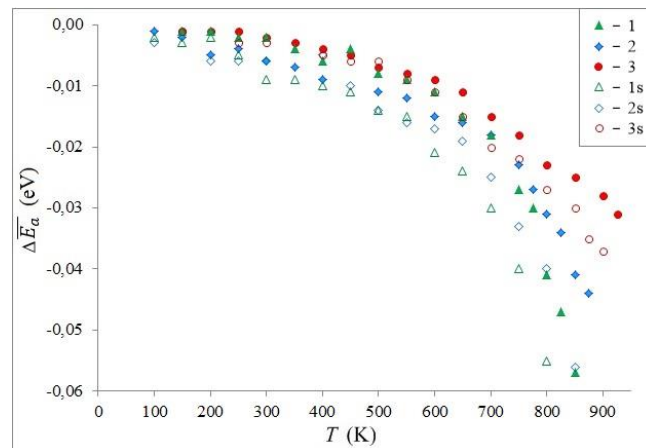

Fig. 6. Dependence of the change in the average energy of an atom during relaxation for 200 ps on temperature. Filled markers - when there is no surface, unfilled - when there is a free surface. The numbering of markers coincides with the numbering of curves in Fig. 3

When simulating heating, intense recrystallization was observed, during which a decrease in the concentration of defects and grain growth occurred. We conducted an additional study of the decrease in stored energy in the cells under consideration during relaxation at different temperatures. The results are shown in Fig. 6. Based on the research data, one can judge the stability of the nanocrystalline structure depending on various factors. So, first of all, with increasing temperature and, especially when approaching the melting temperature, recrystallization occurs more intensely. Secondly, a structure that initially has a higher excess energy, that is, containing more nonequilibrium defects, is reconstructed faster. In addition, we noticed a significant influence of the free surface. In its presence, recrystallization proceeded relatively more intensely (open markers in Fig. 6), which is apparently explained by the contribution of surface diffusion, which, as is known, proceeds faster than in the bulk.

Conclusions

Using molecular dynamics simulation, a study of the melting of aluminum with a nanocrystalline structure obtained as a result of severe plastic deformation was conducted. It is shown that the melting of nanocrystalline aluminum begins at a lower temperature than monocrystalline aluminum. Moreover, the higher the density of grain boundaries and other defects, and, accordingly, the higher the excess energy, the lower the melting temperature. In the presence of defects, melting proceeds heterogeneously

and begins primarily from the grain boundaries and free surface, after which the melting front moves towards the rest of the volume. In a pure crystal that did not contain any defects or free surface, melting in the model proceeded homogeneously and began at a temperature significantly higher (150 K) than in the case of the presence of grain boundaries or surfaces.

Grain boundaries with relatively low energy of formation (i.e., high density of coincident nodes) are less likely to initiate melting than high-angle boundaries.

When studying recrystallization in nanocrystalline aluminum, it was found that it occurs more intensely as the temperature approaches the melting point, as well as when it contains a larger number of nonequilibrium defects. In addition, the free surface had a significant effect on the intensity of recrystallization. The restructuring of the structure near it occurred faster than in the bulk of the material.

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