

Molecular Dynamics Simulation of Nickel Crystallization from Melt Containing Crystal Nuclei

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Abstract—Nickel crystallization from melt with crystal nuclei has been simulated by the molecular dynamics method. A model used in simulation contains a relatively large number of atoms, and a computational cell has the form of a sheet with 12 deliberately introduced crystal nuclei (small cylindrical crystalline areas with rigidly fixed atoms). The use of crystal nuclei has been dictated by the fact that crystallization from melt in the molecular dynamics method is difficult to simulate at cooling rates typical of this method. The orientation of the crystal lattice in nuclei was set randomly but so that tilt boundaries resulting from crystallization had a $\langle 100 \rangle$ or $\langle 111 \rangle$ misorientation axis. The computational cell first melted and then was kept at a constant temperature of 1500 K for a long time. The growth of crystal nuclei did not depend on their orientation, and the growth rate was roughly the same. As a result, the grain size was also nearly the same. The grain structure was perfect and regular, indicating that defects in the crystallizing material arise last, namely, at grain boundaries and triple junctions. Disclinations and any significant local stresses at triple junctions were not observed. During crystallization, the free volume concentrated largely at grain boundaries and triple junctions (mostly at the latter). In addition, relatively small subgrains sometimes arose during crystallization near triple junctions. The subgrains were, as a rule, in tension, and their orientation differed from that of neighboring grains. They rapidly “healed up,” being absorbed by growing neighboring grains.

Keywords: molecular dynamics, triple junction, grain boundary, free volume, crystallization

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INTRODUCTION

Triple junctions at grain boundaries differ in properties from boundaries forming them. According to experimental data [1–5], diffusion near a triple junction is much more intense than along grain boundaries. The triple junction often has a “loose” structure (sometimes with amorphous inclusions [6]); that is, it has a greater free volume than forming grain boundaries [5, 7, 8]. Certainly, it should be borne in mind that systems of grain boundaries and their corresponding triple junctions resulting from melt crystallization and intense plastic deformation differ considerably. For example, the fraction of so-called nonequilibrium grain boundaries and other extra defects in the latter case is higher [9–11]. In this article, the point at issue is triple junctions due to metal crystallization.

Earlier [12], it was shown that the formation of excess free volume in crystallization-induced triple junctions is most probably associated with the holding (“confinement”) of the liquid phase on meeting three crystallization fronts. As a result, excess free volume concentrates in the triple junction after crystallization. Figure 1 schematically shows the confinement of free

volume in triple junctions during crystallization. The movement rate of the crystallization front is an order of magnitude lower than the speed of sound; therefore, defects arising during pure metal crystallization form, as a rule, last. They appear at junctions of variously oriented crystal phases, i.e., at grain boundaries and triple junctions. It is noteworthy that triple junctions crystallize first. By the instant three crystallization fronts meet (Fig. 1), the density of the liquid phase remaining at the junction, which had no time to crystallize, is lower than the density of the crystal phase. Because of the lack of atoms needed to form an “ideal” triple junction, an excess free volume arises, which concentrates mostly at the triple junction during crystallization.

It was also mentioned [12] that when the excess free volume concentrates at triple junctions, sometimes relatively small crystal subgrains (from one to several nanometers across) arise. The subgrains were in tension, and their orientation differed from that of neighboring grains (Fig. 2).

We think, however, that our model used in [12] is not free of disadvantages. First, the computational cell size was insufficiently large: the capacity of the cell was

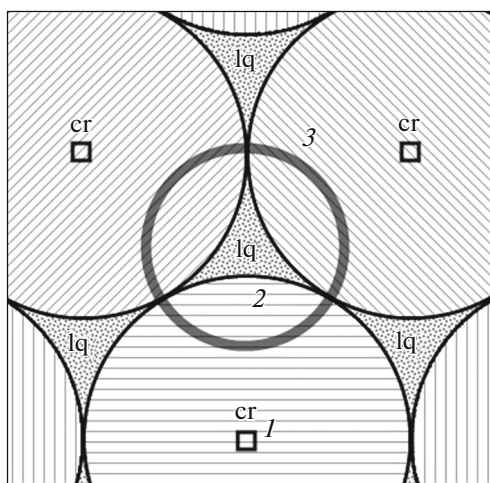


Fig. 1. Schematic representation of the polycrystalline structure during crystallization at the instant crystallization fronts meet and liquid phase volume is confined. “cr” and “lq” stand for “crystal phase” and “liquid phase,” respectively; 1, crystallization center; 2, crystallization front; and 3, calculation cell boundary in the molecular dynamics model [12].

no greater than 30000 atoms. Obviously, resulting grains were fine. Second, the nickel crystallization was simulated at a relatively low thermionic cathode temperature, 800 K. In this study, we tried to remediate these disadvantages. The application of the OpenCL technology in the in-house developed MDR program made it possible to increase computational cell sizes by an order of magnitude.

MODEL DESCRIPTION

Simulation was carried out by the molecular dynamics method. A computational cell for nickel had

the form of a sheet with 12 deliberately introduced crystal seeds (nuclei)—small cylindrical crystalline areas with rigidly fixed atoms (in Fig. 3 they are painted dark gray and marked by 1). Crystal nuclei were used because crystallization from melt in the molecular dynamics method is difficult to simulate at cooling rates typical of this method. The fact is that cooling rates necessary for the formation of a crystal structure from melt must be very low in terms of molecular dynamics: on the order of 10^{12} K/s [13]. At cooling rates typical of molecular dynamics (10^{15} – 10^{16} K/s), crystallization has no time to occur and an amorphous structure arises [13].

Crystal nuclei in the computational cell were equally distant from each other (Fig. 3). The orientation of the crystal lattice in nuclei was set randomly but so that tilt boundaries resulting from crystallization had a $\langle 100 \rangle$ or $\langle 111 \rangle$ misorientation axis. Computational cells contained about 240000 atoms. Their thickness along the Z axis (Fig. 3) was about 25 Å, and the height and width were 360 and 300 Å, respectively. Boundary conditions along the X and Z axes were taken to be periodic, and those along the Y axis were free. Under such conditions, the volume of the computational cell could vary with temperature and during crystallization.

Nickel–nickel interaction was described in terms of the Cleri–Rosato potential [14]. This potential proved itself in calculations of the structural and energy characteristics of metals by the molecular dynamics method [15–18]. The time step of integration in the molecular dynamics method was equal to 5 fs. The temperature in the model was set through atomic initial velocities according to the Maxwell distribution.

Crystallization in the molecular dynamics model was simulated as follows. First, the computational cell

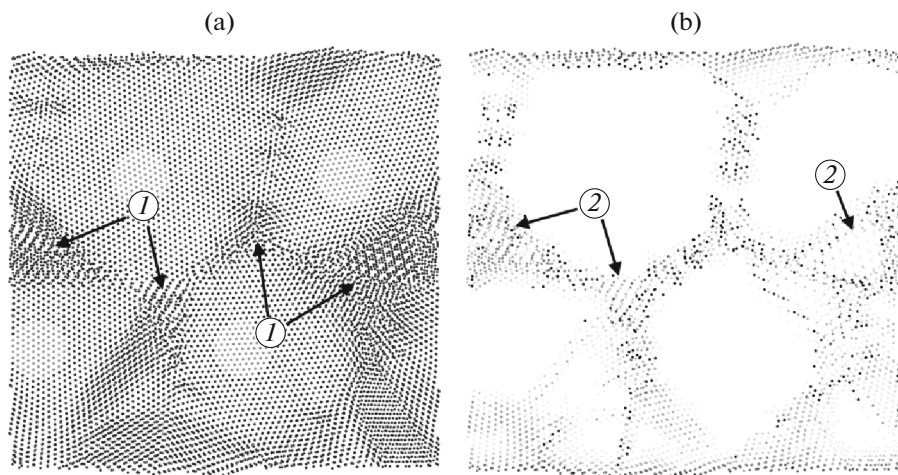


Fig. 2. (a) Computational cell and (b) visualization of mean distances to the nearest atoms within 2000 ps after the crystallization simulation in the presence of four crystal nuclei: (1) concentration and confinement of free volume and (2) stretched crystal subgrains at triple junctions [12].

was melted by keeping it at 3000 K (with the crystal structure in nuclei being fixed). Then, the temperature in the thermostat was lowered by 1500 K and crystallization was simulated. When different temperatures were set, all interatomic distances varied according to the thermal expansion coefficient, which was predetermined for the potential used.

It should be noted that crystallization fronts in the given model have a near-cylindrical, rather than near-spherical, form. This form was taken deliberately to highlight the collisions of crystallization fronts and liquid phase confinement. In addition, computational cells adopted here are sheets several lattice parameters thick; that is, they represent a sort of slice or section of a 3D material, yet remaining a 3D model.

RESULTS AND DISCUSSION

Figure 3 exemplifies a crystallizing computational cell. Growing crystal grains are distinctly seen in this figure. Crystals grow with roughly the same rate irrespective of orientation (according to [19], this rate is several tens of times lower than the speed of sound in metals). Therefore, grown grains are almost equal in size, as is seen in Fig. 4. Figure 4 shows the final structures of computational cells with $\langle 111 \rangle$ (Fig. 4a) and $\langle 100 \rangle$ (Fig. 4b) tilt boundaries upon the crystallization simulation. To make the images of the structure more distinct, computational cells after the main computer experiment were cooled to a temperature close to 0 K. The obtained structures were studied with a visualizer of mean distance to the nearest atoms. This instrument gives an idea of the presence of local stresses and, indirectly, the free volume distribution. For each atom, its mean distance to the nearest neighbors was calculated. If the mean distance differed from this distance in an ideal crystal insignificantly, the atom was not colored (it remained light gray). Otherwise, it was painted grayscale, the greater the free volume around, the darker the shade of gray.

It is seen in Fig. 4 that resulting crystal grains are free of defects. Their structure is perfect and regular, indicating that during crystallization defects arise last, specifically, at grain boundaries and triple junctions. It should be noted that visually the width of grain boundaries is roughly the same. It was shown [20] that it equals about 5 Å when determined from the diffusion permeability of boundaries. Disclinations and any considerable local stresses at triple joints were not observed.

Low- and high-angle boundaries depicted in Fig. 4 markedly differ. The free volume is distributed periodically in the former and continuously in the latter. Low-angle tilt boundaries represent periodically arranged edge dislocations [15], whereas in high-angle ones dislocations become indiscernible.

As previously [12], we focused attention primarily on whether the free volume is confined at triple junc-

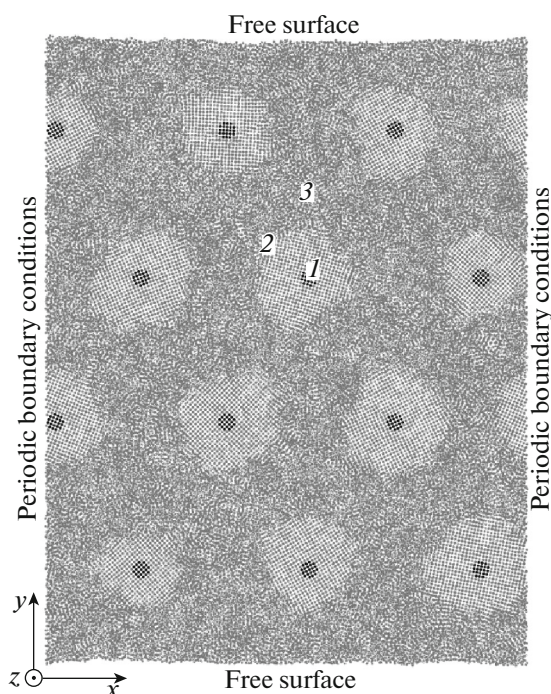


Fig. 3. Computational cell used for crystallization simulation: (1) crystallization nuclei, (2) crystallization front, and (3) liquid phase.

tion during crystallization. It can be seen in Fig. 4 that the free volume indeed concentrates at junctions to a greater extent than at grain boundaries. It should however be borne in mind that the free volume during diffusion may partially move away along grain boundaries toward the free surface. In addition, it may penetrate into boundaries in the case of junction migration (see, for example, [21]). Yet, these results suggest that triple junctions are preferred for free volume concentration.

Comparing the above results with those reported in [12], one can see an important difference: in the given model subgrains in tension are absent in the final structure. Such subgrains appeared during crystallization but eventually healed up, being absorbed by growing grains. Their presence in the final structure in [12] may be associated with a (i) low temperature of the thermostat at which crystallization was simulated (this temperature was insufficient for the normal evolution of the crystal structure) and (ii) short simulation time (insufficient for healing up stretched subgrains).

CONCLUSIONS

Nickel crystallization from melt with crystal nuclei was simulated by the molecular dynamics method. A model used in simulation contains a relatively large number of atoms, and a computational cell has the form of a sheet with 12 deliberately introduced crystal nuclei (small cylindrical crystalline areas with rigidly

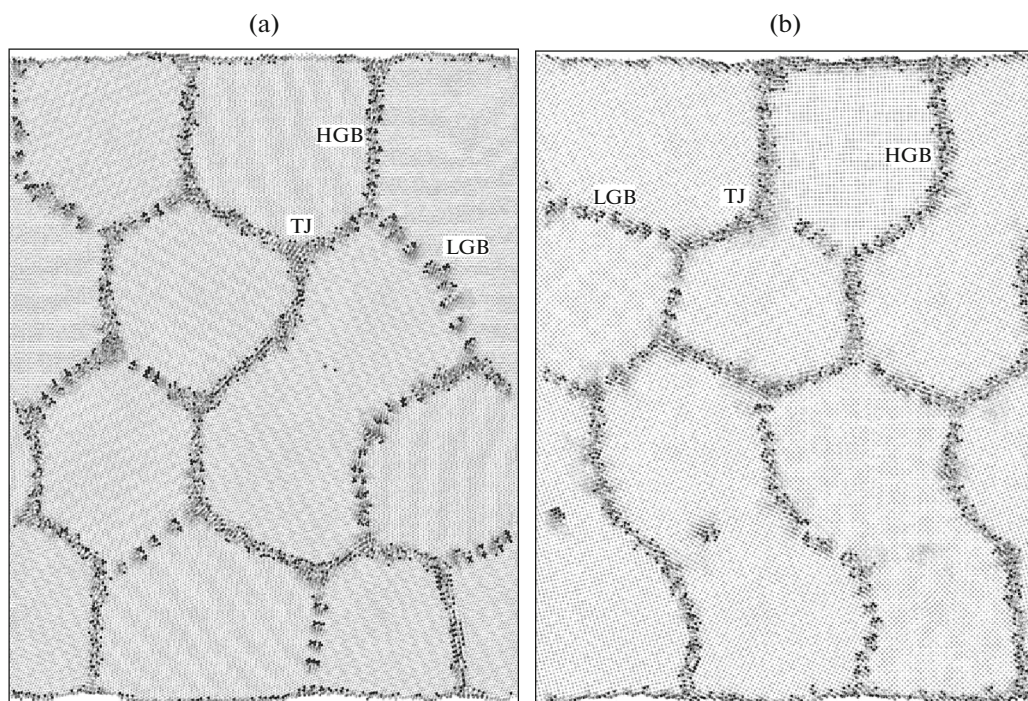


Fig. 4. Free volume distribution in computational cells after crystallization and subsequent cooling: (a) $\langle 111 \rangle$ and (b) $\langle 100 \rangle$ tilt boundaries: LGB, low-angle grain boundary; HGB, high-angle grain boundary; and TJ, triple junction.

fixed atoms). The use of crystal nuclei is explained by the fact that crystallization from melt in the molecular dynamics method is difficult to simulate at cooling rates typical of this method. The orientation of the crystal lattice in nuclei was set randomly but so that tilt boundaries resulting from crystallization had a $\langle 100 \rangle$ or $\langle 111 \rangle$ misorientation axis.

The computational cell first melted and then was kept at a constant temperature of 1500 K for a long time. The growth of crystal nuclei did not depend on their orientation, and therefore the growth rate was roughly the same. As a result, the grain size was also nearly the same. The grain structure was perfect and regular, indicating that defects in the crystallizing material arise last, specifically, at grain boundaries and triple junctions. Disclinations and any significant local stresses at triple junctions were not observed. During crystallization, the free volume concentrated largely at grain boundaries and triple junctions (mostly at the latter). In addition, relatively small subgrains sometimes arose during crystallization near triple junctions. The subgrains were, as a rule, in tension, and their orientation differed from that of neighboring grains. They rapidly “healed up,” being absorbed by growing neighboring grains.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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