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THE GROWTH KINETICS OF METALLIC CRYSTALS. RESULTS OF SIMULATIONS

The correct values of the surface kinetics coefficients were obtained for systems of Al, Cu, and Ni metals at sufficiently large sizes of nanocrystals in initial conditions. The simulation based on the molecular dynamics method was performed with applying our program for parallel computing and the LAMMPS program. We used the potentials of the embedded atom type. We applied NVT ensemble, but the volume of samples was not constant as they had free surfaces (they were smaller than the main cell). Our results showed that the classical Wilson-Frenkel model was not able to describe quantitatively the temperature dependence of the kinetics coefficients, and the Broughton, Gilmer and Jackson equation was valid at temperatures close to the melting point, not lower than 100 - 200 K. The temperature dependencies of the diffusion coefficients for these metals in the supercooled liquid state were analyzed. Discrepancies in the results of our simulation and the literature data were discussed.

Keywords: kinetics of crystallization, supercooled metals, diffusion, interfaces.

Получены корректные значения коэффициентов поверхностной кинетики для систем металлов Al, Cu, и Ni при задании сравнительно больших размеров нанокристаллов в начальных условиях. Моделирование по методу молекулярной динамики было выполнено с применением нашей программы для параллельных вычислений и программы LAMMPS. Были использованы потенциалы типа "погруженного" атома. Мы применяли NVT ансамбль, но объем образцов не был постоянным, поскольку они имели свободную поверхность (были меньше, чем основная ячейка). Наши результаты показали, что классическая теория Вильсона-Френкеля не в состоянии количественно описать температурную зависимость кинетических коэффициентов, а уравнение Броугхтона, Гилмера и Джексона справедливо при температурах, близких к температуре плавления, не ниже 100 - 200 К. Проанализированы температурные зависимости коэффициентов диффузии для указанных металлов в переохлажденном жидком состоянии. Обсуждены расхождения между результатами нашего моделирования и литературными данными.

Ключевые слова: кинетика кристаллизации, переохлажденные металлы, диффузия, межфазные поверхности.

Отримані коректні значення коефіцієнтів поверхневої кінетики для систем металів Al, Cu, Ni за порівняно великих розмірів нанокристалів в початкових умовах. Моделювання за методом молекулярної динаміки було виконано із застосуванням нашої програми для паралельних обчислень і програми LAMMPS. Були використані потенціали типу "зануреного" атома. Ми застосовували NVT ансамбль, однак об'єм зразків не був постійним, оскільки вони мали вільну поверхню (були меншими за основну комірку). Наші результати продемонстрували, що класична теорія Вільсона-Френкеля не в змозі кількісно описати температурну залежність кінетичних коефіцієнтів, а рівняння Броугхтона, Гілмера і Джексона є справедливим за температур, близьких до температури плавлення, не нижче 100 - 200 К. Проаналізовані температурні залежності коефіцієнтів дифузії для цих металів у переохолодженому рідкому стані. Обговорені розбіжності між результатами нашого моделювання та літературними даними.

Ключові слова: кінетика кристалізації, переохолоджені метали, дифузія, міжфазні поверхні.

Introduction

The kinetics of solidification controls the microstructure development of materials. It is therefore essential to have detailed understanding and knowledge of the kinetics during solidification of melts for improving production of metallic materials. To match the value of the surface kinetics coefficient, intensive convection was ensured by electromagnetic devices in some experimental works.

It is known long ago that the surface kinetic coefficient β_T in the ratio $\beta_T = v/\Delta T$ (v is the growth velocity, $\Delta T = T_m - T$, T_m - is the melting temperature) is the value of order 1 m/(s·K) for pure metal at the temperatures near the melting point T_m [1-3]. In the large temperature intervals it is better to consider the dependence of growth velocity on the surface supersaturation $v(\sigma)$ ($\sigma = \Delta\mu/kT$ is the relative supersaturation). In accordance with Wilson–Frenkel theory [4,5] this dependence for a pure material can be written as

$$v = \beta_s [1 - \exp(-\Delta\mu_T / kT)] \quad (1)$$

where β_s is the kinetics coefficient, $\Delta\mu_T$ is the difference of chemical potentials of two phases at the temperature T . Furthermore, the coefficient β_s can be expressed in terms of the diffusion coefficient D of the liquid [6]:

$$\beta_s \cong 6f_1 aD / \lambda^2 \quad (2)$$

where λ corresponds to an elementary diffusive jump distance of particles in the liquid, a is the interatomic distant, prefactor f_1 represents the fraction of collisions with the crystal that contributes to the growth of the crystal. It is assumed that the diffusion coefficient can be expressed by an Arrhenius law, $D = D_0 \exp(-Q/kT)$. However, some experimental data for pure metals (see Ref. [7]) allow arguing that their crystallization is not thermally activated.

Fedorov [3] had listed in his book some results of known experimental data concerning the kinetics coefficients for growth of metal crystal from pure melts and the coefficients of self-diffusion in these melts. After re-counting of β_T to β_s , we can see that these values are much greater than ones that can be evaluated according to Eq. (2) at $f_1 \cong 1$. But the sizes of growing crystals and surface supercoolings are not known exactly at measurements of experimental velocities. These quantities are known exactly at simulations.

In recent years, MD simulations have been applied extensively to study kinetics and thermodynamic properties of crystal-melt interfaces. It is important that nowadays simulations give values of many physic-chemical properties, including diffusivity that coincides well with the experimental values. The results of simulations for the Lennard-Jones liquid [7], for Cu and Ni [8] and for gold [9], did not confirm the dependence (1) for the surface kinetics. The kinetics coefficients calculated on the base of previous simulation results differed essentially from estimations on the basis of Wilson-Frenkel theory. For example, the authors of [9] have obtained the values $\beta_{T100} = 18.8 \pm 1.0 \text{ cm}\cdot\text{s}^{-1}\text{K}^{-1}$; $\beta_{T110} = 12.6 \pm 1.0 \text{ cm}\cdot\text{s}^{-1}\text{K}^{-1}$ and $\beta_{T111} = 7.0 \pm 1.0 \text{ cm}\cdot\text{s}^{-1}\text{K}^{-1}$ for different orientation of gold crystals. The authors of [10] have obtained for Ni-crystals significantly smaller anisotropy and somewhat higher values of β_T for low index $\{100\}$, $\{110\}$, and $\{111\}$ interfaces: $\beta_{T100} = 35.8 \pm 2.2$, $\beta_{T110} = 25.5 \pm 1.6$, and $\beta_{T111} = 24.1 \pm 4.0$ in units of cm/(s K).

The authors of [7] connected the kinetic coefficient with the average thermal velocity $(3kT/m)^{1/2}$ to explain the results of simulations of crystal growth in the LJ liquid:

$$v = f_2 (3kT / m)^{1/2} [1 - \exp(-\Delta\mu_T / kT)] \quad (3)$$

where f_2 is a constant of the first order.

Later, Mikheev and Chernov [11] have developed the density functional theory of freezing for the case of crystal-melt interface, which is rather diffuse on atomic scale. They proposed estimation, $v=(kT/m)^{1/2} \Delta T/T$, after simplifications of their results.

In this work, we present the simulation results concerning the growth of metal crystals from pure melts. The data are obtained in the large intervals of supercooling, including the growth from the amorphous state. In addition, we consider the size effect in crystal growth, i.e. the dependence of growth velocity on the crystal size. Our models have free surfaces and contain sufficiently many atoms.

Details of the simulation

The MD simulations were fulfilled using our program for parallel computing and the LAMMPS codes (large-scale atomic-molecular massively parallel simulator) [12]. In the case of LAMMPS, we included into the data file the tables of EAM potentials converted by C.A. Becker (see <http://www.ctcms.nist.gov/potentials/>) into the dynamo format (each table from 10000 points). In our program, the EAM tables from 5000 point each were used. Parallel calculations were fulfilled by means of Graph processors (NVIDIA graphics-cards) with the help of GPU software included in LAMMPS and CUDA software.

All simulations employed the Verlet algorithm [13] with a time step of 1.5 fs. The weak thermostating for isothermal annealing was chosen in all cases; in our program, a multiplier to velocity of atoms was $1 \pm 0.001 \sqrt{|T - T_t|/T}$ (T is a instantaneous temperature, T_t is the set temperature, sign “+” if $T < T_t$).

We applied NVT ensemble (constant number of atoms, volume of the main cell, and temperature), but the sample volume was not constant as they have free surfaces (were smaller than the main cell). The first step before simulations was preparing of samples for simulations. Initial form of models was created in the auxiliary program. All atom coordinates were passed in LAMMPS or in our program, and their melting was accomplished (fully or partly). Two forms of samples were prepared. Kinetics of growth of small crystallization centers (after nucleation) was studied in spherical samples with a free surface (nanodrops of 16384 atoms). They were formed in a result of fusion of an ideal crystal given in initial conditions at a temperature above the melting temperature in 100-200 K over a period of time >50 ps. Then they were quickly (1–2 ps) cooled to the chosen temperature of annealing (to obtain statistics for “one” temperature, the set temperatures for annealing were different slightly, 0.1 – 0.2 K). For analyzing the results of simulations, we use the program that enables viewing with the step in one angstrom all sections of the model with coordinates of atoms from saved files. The strong dependence of growth velocities on the size of crystallization centers was found in [14].

To study growth kinetics of nanocrystals, oblong samples (of 32768 atoms) in the form of cylinder with the structure of crystal phase were set in initial conditions (periodic boundary conditions along one axis were applied). Then their larger part was transformed into amorphous state by the way of many random displacements of atoms with further quick heating above melting point and then quick cooling to the chosen temperature. The nanocrystals of 5–7 nm in size (for them, the size effect is not as essential as for small crystallization centers) with initial interfaces of (100), (110) or (111) crystal type were able to grow at the constant temperature.

In addition, we can view many clusters of different kinds. Identification of clusters was fulfilled with the help of LAMMPS software or in results of procedure running, which determined the number of nearest neighbors and angles with nearest neighbors for every atom, and gives a color for atom visualization dependently on a cluster type (see Ref. [14]).

The values of the diffusion coefficients for Al and Ni and Cu at different temperatures were determined by measurements of mean-square displacements of atoms for the same potentials, which were used for studying of growth.

Results and the discussion

Relaxation processes occur in the supercooled melts after setting a certain temperature for annealing. The waiting time for appearance of crystallization center is larger than the time of relaxation. However, the measurements of growth velocities in oblong specimens should be fulfilled after the structure relaxation. The results of simulations for determination of diffusivity in melts of metals and growth velocities with using modern potentials are in a good agreement with experimental data. Therefore, a quantitative comparison of such data with predictions of theories is already opportune. The table 1 contains simulated and experimental data on kinetic coefficients β_T and β_S at the melting temperatures, the values of magnitudes D_0 and activation energy Q , which determine the temperature dependencies of the diffusion coefficients, and the values of the coefficients f_1 and f_2 that are chosen for best fitting of kinetic coefficients by Eqs. (1) and (3). It is necessary to note that the values of D_0 and activation energy Q are determined for not terrific supercoolings of liquid – roughly up to 200 K. Data of Ref. [19] give an evidence of the Arrhenius type dependence (constant Q) for copper in the large temperature period. It is unlikely as essential changes in a structure of materials take place near the glass-transition temperature.

Table 1

The simulated and experimental data on kinetic coefficients β_T and β_S at the melting temperatures, the values of magnitudes D_0 and activation energy Q

Material	$\beta_T, \text{m}/(\text{sK})$	$\beta_S, \text{m}/\text{s}$	$D_0 \cdot 10^8, (\text{m}^2/\text{s})$	Q, K	$\Delta H, \text{K}$	T_m, K	f_1	f_2
Al _{sim}	0.50±0.02 (our)	369	4.45	2617	1288	975	6	0.3
Ni _{sim}	0.30±0.02 (our)	366	7.5	5480	2075	1600	9	0.475
	0.39 [15]	549	8.6 [15]	5751	2098	1718 [15]	6.9	0.64
Ni _{exp}	0.2 [16]	284	7.7 [17]	5499	2098	1728	3.36	0.33
Cu _{sim}	0.65 (our)	592	4.5	3600	1301	1175	12	0.8
Cu _{exp}	1.58 [18]	2149	5.7 [19]	3883	1352	1356	29	2.96

It is clear that Eq. (3) approximates better the values of the kinetics coefficient near the melting temperature (the value of f_2 is closed to 1). Fig. 1 shows the temperature dependences of the growth velocities for Ni, Al and Cu obtained as results of simulation and also the curves calculated according to Eqs. (1) and (3) with prefactors that give the best fit at the melting point. We calculated the difference of chemical potential of two phases according to the equation $\Delta\mu = \Delta H (1 - (T/T_f)^2)/2$ which fits better such dependencies [14] than the Spaepen equation. The full lines in Fig. 1 give the temperature dependence of velocities calculated according to Eq. (1).

The dotted lines in Fig. 1 show the temperature dependence of velocities calculated according to Eq. (3). Those and other lines go close to the experimental dots near the melting point because the coefficients f_1 and f_2 are chosen from such condition. However, the coefficients f_1 is too large in comparison with (1). Analyzing the temperature dependences of growth velocities, we see that the Wilson-Frenkel theory with such great

coefficients, $f_1 \sim 10$, fits better the calculated data in wide temperature intervals. Thus, the simulated data concerning the growth velocities in the large temperature intervals give evidence of the thermo-activated growth.

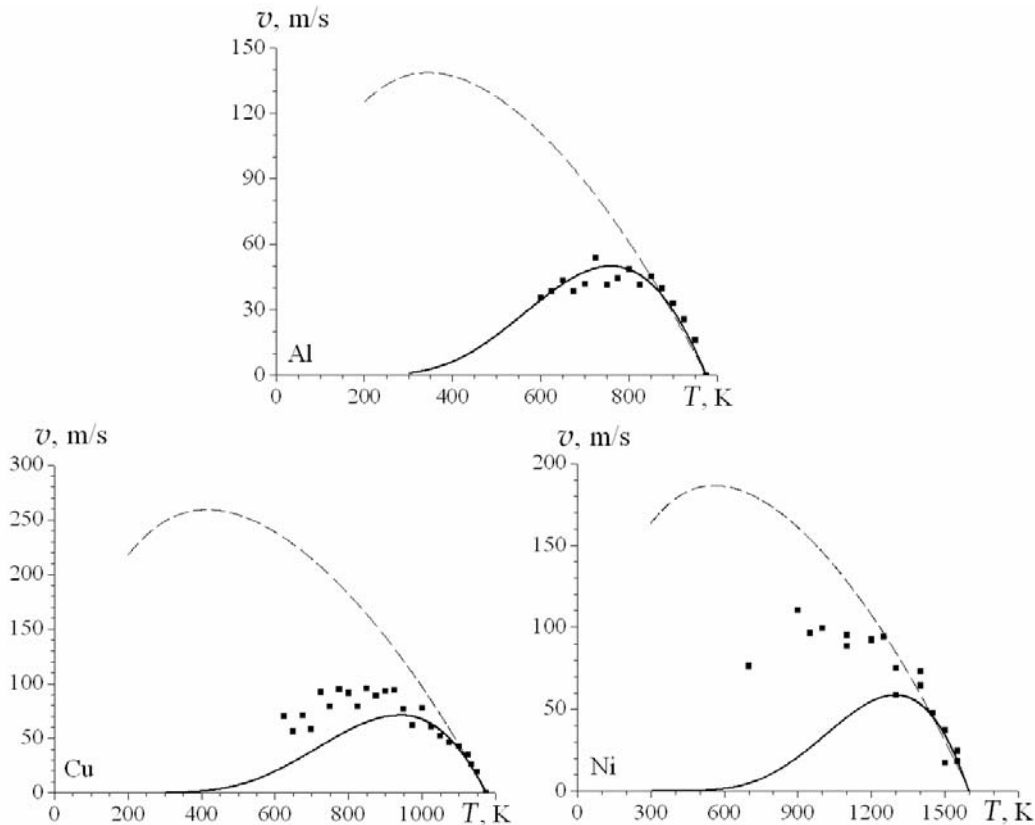


Fig. 1. The simulated growth velocities of single crystals and calculated data.

Full lines are calculated according to the Wilson-Frenkel theory; dotted lines are calculated according to the Broughton, Gilmer and Jackson equation.

Conclusions

The Broughton, Gilmer and Jackson equation for the evaluation of growth velocities is valid at the temperatures close to the melting points (not lower than 100-200 K from them). The simulated data concerning the growth velocities in the large temperature intervals give nevertheless an evidence of the thermo-activated growth. However, the values of the kinetics coefficient are much larger that is predicted by the Wilson-Frenkel theory for pure metals. For definitive conclusion about temperature periods, in which the first or second theory works better, it is necessary to carry out a careful study of diffusivity for these metals in the large temperature intervals and determine the temperature dependences of the activation energy Q .

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