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SOME PROBLEMS OF CRYSTALLIZATION THEORY CONNECTED WITH RESULTS OF SIMULATIONS

Results of simulations of nucleation and growth of metal crystals obtained in recent years are considered. They are essentially contradicted with some fundamentals of classical crystallization theory. In particular, crystallization theories do not take in consideration the real structure of supercooled melts and size effects, which diminish the thermodynamic driving force for phase transition to zero at sufficiently small nucleus sizes. As growth rates strongly depend on crystal size, only simulating the systems with sufficiently large nanocrystals in initial conditions allows obtaining the correct values of surface kinetics coefficients. Results of such simulations give an evidence of changes in the crystal growth mechanism at large supercoolings. Under the conditions turns of clusters in front of the crystallization zone contribute significantly to growth kinetics.

Keywords: cluster structure, nucleation, kinetics of crystallization, supercooled metals, diffusion, interfaces.

Наводяться результати з моделювання процесів зародження та росту кристалів металів, отримані за останні роки. Вони фактично суперечать деяким основам класичної теорії кристалізації. Зокрема, в теорії кристалізації не береться до уваги реальна структура переохолоджених розплавів і розмірні ефекти, які зменшують до нуля термодинамічну рушійну силу для фазового переходу при досить малих розмірах зародків. Швидкості росту сильно залежать від розміру кристалів, тільки імітація систем з досить великими нанокристалами в початкових умовах дозволяє отримати вірні значення коефіцієнтів поверхневої кінетики. Результати моделювання дають відомості щодо змін у механізмі росту кристалів при високих переохолодженнях. За таких умов повороти кластерів перед фронтом кристалізації істотно впливають на кінетику росту.

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

Приводятся результаты по моделированию процессов зарождения и роста кристаллов металлов, полученные за последние годы. Они фактически противоречат некоторым основам классической теории кристаллизации. В частности, в теории кристаллизации не принимается во внимание реальная структура переохлажденных расплавов и размерные эффекты, которые уменьшают до нуля термодинамическую движущую силу для фазового перехода при достаточно малых размерах зародышей. Скорости роста сильно зависят от размера кристаллов, только имитация систем с достаточно большими нанокристаллами в начальных условиях позволяет получить правильные значения коэффициентов поверхностной кинетики. Результаты моделирования дают сведения касательно изменений в механизме роста кристаллов при больших переохлаждениях. В этих условиях повороты кластеров перед фронтом кристаллизации существенно влияют на кинетику роста.

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

1. Introduction and Details of Simulations

Crystallization processes such as nucleation and kinetics of solidification influence the microstructure formation in materials. Understanding and knowledge of these processes are important for the production of materials. Nowadays simulations by the method of molecular dynamics (MD) describe properties of great number of materials sufficiently correctly. Therefore, the results of crystallization process simulations are worthy of the analysis and application for improving the technologies of material production.

The crystallization of amorphous alloys occurs, as a rule, during a rather long-term temperature annealing. It is unreal to simulate all stages of such processes by the MD method. However, crystallization centers (CC) can arise for accessible machine time in the model of supercooled melt alloy if the total concentrations of added components do not exceed 10 at. % or in the case of intermetallic phase forming from the alloy melts of suitable compositions.

We studied a structure formation in supercooled melts of pure metals and alloy melts, appearance of crystallization centers (CC) and crystal growth kinetics. Models with free surfaces were obtained in result of fusion of crystals with free surfaces (16384, 131072 atoms) and quenching of liquids to temperatures of annealing. The oblong crystal with periodic boundary conditions along one axis was set in initial conditions for studying of growth kinetics of nanocrystals. A half of samples were made amorphous artificially by repeated random displacements of atoms; a random distribution of atoms of the second component was set. After the relaxation annealing the data of simulations during the further annealing were periodically saved. The MD simulations were fulfilled through applying programs for parallel computing, mainly, the LAMMPS codes (large-scale atomic-molecular massively parallel simulator) with using the known potentials of embedded type (EAM potentials). In addition, we can view many clusters of different kinds. Identification of clusters was fulfilled with the help of LAMMPS (*compute cna/atom* and *pe/atom*) and also programs for visualization VMD and OVITO.

2. Cluster Structure of Supercooled Melts

The time dependences of numbers of different clusters and energy of atom interaction in supercooled melts were studied. For example, Fig. 1 shows the concentrations of clusters in supercooled models of $Al_{90}Ni_{10}$ melt alloy plotted versus time. There are many different clusters in this melt alloy. Their measurable values depend on limits for displacements of atoms from equilibrium positions and assumed dispersion in orientations of atom bonds in different techniques. A relaxation time that is necessary to come close to equilibrium concentrations of clusters and time of initial decrease of potential energy to a stable value are roughly $40 \div 60$ ps. The cluster structure of the models depends on potentials that are used. Sometimes there is a great many of icosahedral clusters. If we take into account all atoms in such clusters, their number reach the total number of atoms. It is clear that more stable icosahedral clusters (with smaller interaction energy) cannot become the crystallization centers during their life. Therefore, a fore-factor near the exponent in the classical equation for the rate of nucleation is undoubtedly overstated. This leads to the overstating of the activation energy for atoms joined into crystals or overstating of the crystal-melt surface tension which values are often chosen for fitting experimental results in the framework of classical theory.
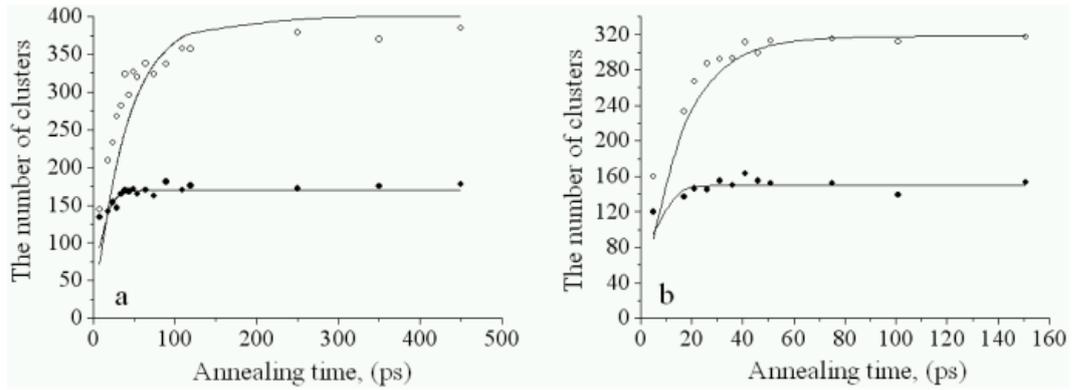
Fig. 1. Changes of quantities of clusters during relaxation annealing of the Al-10Ni alloy; a – T=500 К, b – T=650 К; ● – FCC-clusters, ○ – icosahedrons, full lines are calculated by Eq. $N(t) = N_{max}(1-\exp(-t/\tau))$. The best fit of simulation data (lines) was obtained for the following values of τ: $\tau = 40$ ps at $T = 500$K and $\tau = 15$ ps at $T = 650$K in the case of the icosahedral clusters.

3. Nucleation and size effects

The formation of nuclei in metal melts under large supercooling differs essentially from the classical scheme, which assumes the large possibility of appearance of very small nuclei from several atoms. The results of simulations give an evidence of slow ordering in some small area of pure or multicomponent supercooled melts (close to 1 nm) without their growth up to the moment at which curved rows of atoms become nearly straight (Fig. 2).
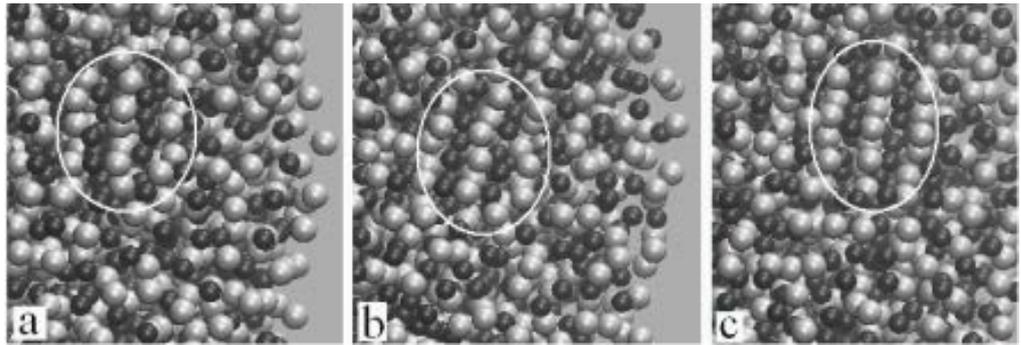
Fig. 2. Successive images of the model, which show the consecutive stages of forming of the crystallization center in $Al_{50}Ni_{50}$ alloy melt; T=1000 K, times of annealing: a – 77, b – 87, c – 107 ps; atoms Al are light grey, Ni – dark grey.

In multicomponent systems, the areas with atoms only of the main component should exist for forming nuclei of initial crystals. Therefore, the rate of nucleation will be minimal in the case of homogeneous distribution of atoms of added components. In the case of presence of a component with very small diffusivity (we studied the alloy Al-5Ni-2.7Y), the nucleus of aluminum, if it is formed, cannot grow as atoms of yttrium (large grey atoms in Fig. 3) are practically immovable. The local radial pair distribution function (RPDF) show that the nucleus structure is improved with time. However, the total RPDF is typical for amorphous phase until the total volume of nanocrystals is less than the volume of the amorphous phase.

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Determining the waiting times for the first nucleus appearing in the results of examination of the volume of the models, we found that they are essentially smaller than the times at which perceptible changes in internal energy of the system because of crystallization become visible.
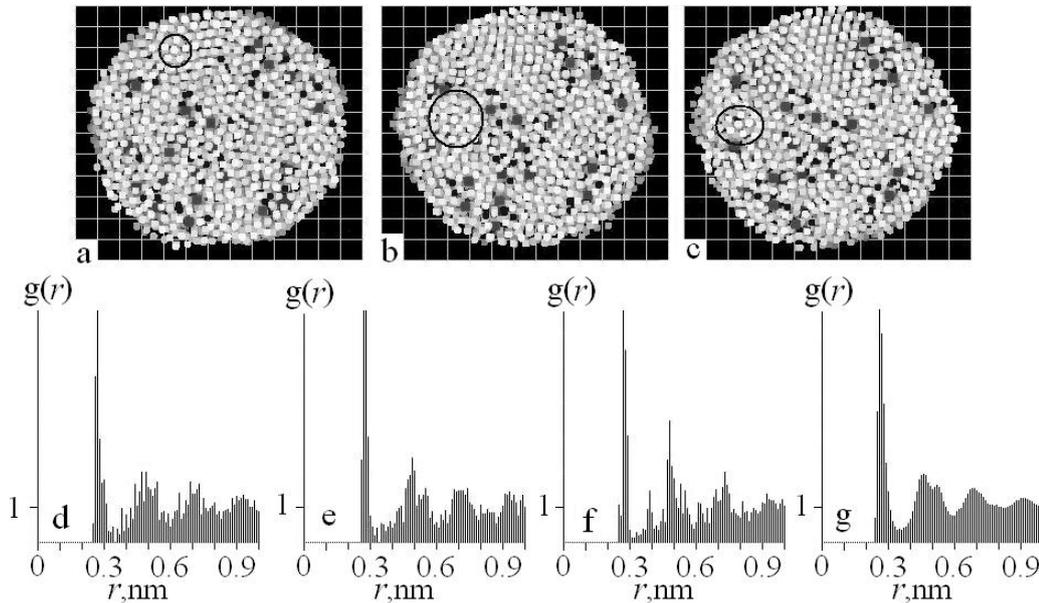
Fig. 3. Structure formation in the model of alloy Al-5Ni-2.7Y [2],
Ni-atoms are the smallest, Y-atoms are the largest; icosahedral clusters are evolved by circles,
T=650 K, for a, b, c – time t = 1600, 2500 and 3500 ps; d, e, f are the LRPDF from central part of the
CC; (g) is the common RPDF for t =3500 ps.
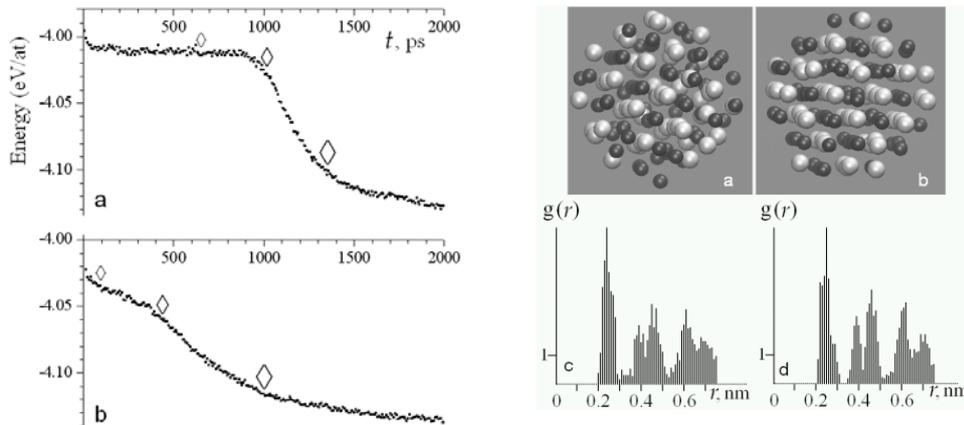
Fig. 4. The time dependences of the internal potential energy [3] for the $Al_{50}Ni_{50}$ system;
a – T=1200 K; b – T=1100 K; a small mark ◊ marks the first nucleus appearance.

Fig. 5. Images of atoms from the central part of the growing crystallization center (a,b) and local
RPDFs from these areas (c,d) [3], T=1200 K, a – the crystal size (diameter) is 1.5 nm, b – 2.5 nm.

Analyzing the structure and internal energy of small crystallization centers, we found that they are size dependent, the internal energy of crystallization centers per one-atom decreases during their growth. The internal energy is such as in the amorphous phase at the size of nucleus of order 1 nm (in diameter). This means that the

thermodynamic force for crystallization, i.e. the difference of chemical potentials of the amorphous phase and crystallization centers (CC) with the imperfect structure, is size dependent also, and it goes to zero at diminishing size of nuclei. The free surface energy is also size dependent; it also becomes negligible. The unstable nucleus can exist for some time as the driving force for its dissolution is also very small. The thermodynamic analysis of nucleation for such case was fulfilled in Ref. [1]. In addition, we found that the rate dependences of small CC on their size are stronger than they can be predicted if the Gibbs–Thomson shift to the relative supersaturation is taken into account only.

4. Surface kinetics

In accordance with Wilson–Frenkel theory, the dependence of crystal growth rate on the supersaturation ($\sigma = \Delta\mu_T/kT$) for pure metals can be written as

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

where β_s is the kinetics coefficient, $\Delta\mu_T$ is the difference of chemical potentials of two phases at the temperature T. The coefficient β_s can be expressed in terms of the diffusion coefficient D of the liquid [4]: $\beta_s \cong 6 f_1 a D / \lambda^2$ where λ corresponds to an elementary diffusive jump distance of particles in the liquid, a is the interatomic distant, prefacor f_1 represents the fraction of collisions with the crystal that contributes to the growth of the crystal. Authors [5] 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:

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

where f_2 is a constant, close to 1.

We have determined the growth rates and diffusivities of pure metals: Al, Ni, and Cu in the wide temperature intervals. Figure 6 shows the results obtained for Ni and Cu. The differences of chemical potentials of two phases were calculated according to the equation $\Delta\mu = \Delta H (1 - (T/T_f)^2)/2$ which fits better such dependencies [1] than the Spaepen equation. In the wide temperature ranges, Arrhenius law cannot fit the diffusion coefficients. The dependences $\ln D$ on $1/T$ show it unambiguously. It is connected with strong changes in structure during the glass transition. At low temperatures, the $D(T)$ dependences correspond to essentially smaller activation energies; it is connected most likely with a change of diffusion mechanism.
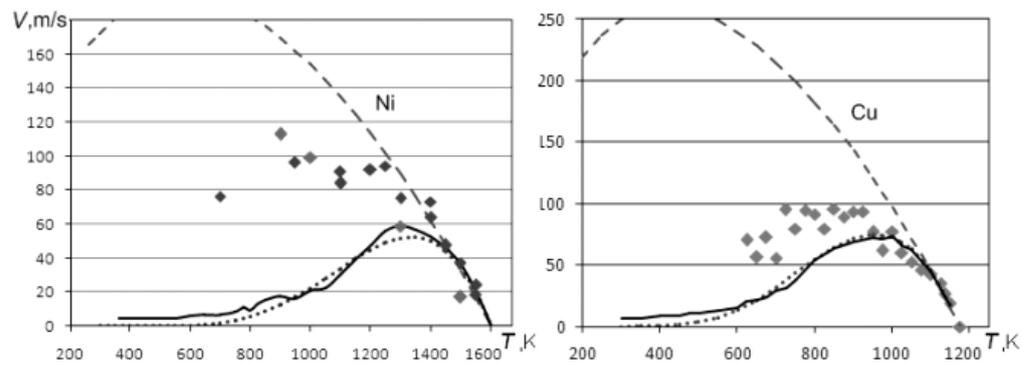
Fig. 6. Simulated growth rates (points) plotted versus the temperatures and calculated data,
—— – by Eq (2);   —— – by Eq.1 with real diffusion coefficients: ······ – by Eq.1 with the Arrhenius dependence $D(T)$.

The full line in Fig. 4 shows the values calculated according to Eq. (1) with $f_1 = 8.5$ for Ni and $f_1 = 14$ for Cu; the dotted lines are calculated by Eq. (1) with using the dependence $D(T)$ of Arrhenius type with parameters determined at high temperatures; the dashed lines are calculated by Eq. (2) with $f_2 = 0.8$ and 0.5. The Eq. (1) fits calculated rates near the melting points because we used too high values of the coefficient f_1. At the middle and low temperatures, both theories fall. Studying the interface structure of growing crystals gives evidence that the main contribution to the growth rates at low temperatures is provided by attachments of clusters existing in front of the interface after their turns or changes in their structure.

5. Conclusions

Thus, a bimolecular model of nucleation does not take in consideration the real structure of supercooled liquids and real structure of small nuclei, i.e. size effects, which diminish to zero the thermodynamic driving force for phase transition at sufficiently small nucleus size. The cluster structure of liquids limits the number of possible places for forming of nuclei and limits the growth rate of small crystallization centers. The growth rate of crystals depends strongly on their size. Only simulating the systems with a sufficiently large nanocrystal in initial conditions allows obtaining the correct values of the surface kinetics coefficients. Crystal growth mechanism changes at increasing of supercoolings of melts. The classical Wilson-Frenkel model is not able to describe the temperature dependence of the kinetics coefficients on a quantitative level. The Broughton, Gilmer, and Jackson equation is valid only at the temperatures close to the melting point (not lower 100÷200 K). Turns of clusters in front of crystallization zone contribute significantly to growth kinetics at large supercoolings.

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