ВІСНИК
ДОНБАСЬКОЇ НАЦІОНАЛЬНОЇ АКАДЕМІЇ БУДІВНИЦТВА І АРХІТЕКТУРИ

Актуальні проблеми фізико-хімічного матеріалознавства
Випуск 2013-4(102)

UDC 541.64:542.62:546.23

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TOPICAL PROBLEMS OF THE NUCLEATION KINETICS AND MASS CRYSTALLIZATION OF SUPER-COOLED MELTS AND SOLUTIONS

The paper contains a short list of the nucleation and mass crystallization classical characteristics of super-cooled melts and solutions. There are given the basic problems of this kind of phase transformation and the principles the team of the Department of Physics and Physical Material Science of the Donbas National Academy of Civil Engineering and Architecture followed in their investigation. There was created a cluster-coagulation model of crystallization based on the following stages: nucleation, nucleus coagulation, growth and coalescence. A crystallographic table of the chemical elements was developed, with phase transformations in the condensed state being specified. This table served as the basis for the cluster-coagulation model development.

nucleation kinetics, mass crystallization, super-cooled melts, super-cooled solutions, interrelationship between crystal structure and liquid phase

A lot of information on crystallization, both in the form of specific investigations of this or that substance and in the form of the monograph summaries, has been stored; its only listing would take a sufficiently large place. Its analysis gives an accurate account of the functional mechanisms of mass crystallization and monocrystal growth and of the scientifically substantiated control of a structure and solid phase properties. Nevertheless, these very papers are indicative of numerous contradictions in the results obtained for the same substances with the use of different methods and techniques which means that there is no systematic approach to the investigation of different substances taking into account the periodicity of the molecular and crystal structure, polymorphism, isomorphism etc.

The crystallization process consists of a series of successive phases: nucleation, nucleus growth, coalescence of nuclei and the so-called mass crystallization. The mechanisms of each phase of solidification are well known [1].

The nucleation theory on the crystallization of melts was created by Gibbs, Volmer and Kossel [2]. It is based on the assumption that as a result of fluctuation in the super-cooled phase the energy barrier of nucleation conditioned by crystal surfacing can be overcome.

Keeping in mind these assumptions and the theory of the absolute rate of reactions, Tornball and Fischer [3] derived a classical formula for the nucleation rate

$$I = \left(1/V\right) dN/dt = \left(N_0 kT/h\right) \exp\left(-\left(\Delta G + \Delta G_\eta\right)/nkT\right). \tag{1}$$

Rate I shows a number of nuclei generating of N non-crystallized molecules per second as a result of a single act of crystallization, k is the Boltzmann constant, h is the Planck constant, n is the number of molecules in a nucleus. The second member in the exponent of equation (1) is the free energy of activation ΔG_η of the processes of crystallizing element diffusion through a phase boundary for a short distance.

For vitrification-prone substances, ΔG_η is found from formula $\Delta G_\eta = kT\left(a + b/(T - T_c)\right)$, where a, b – *const*, T_c is the vitrification temperature.

The quantity ΔG specifies the Gibbs energy change when a critical nucleus is generated. The difference of the Gibbs energies ΔG of the coexisting phases is indicative of the direction of the phase transformation and is equal to the work of a new phase formation, for example, in the transition melt (L) → crystal (S) ($A_{S,L} = \left|\Delta G\ \right| = \left|G_L - G_S\right|$).

In the expansion of function $\Delta G = \Delta G\left(\Delta T^-\right)$ into a series, the following equation is derived:

$$\Delta G = \frac{\Delta H_L}{T_L}\Delta T + \frac{\left(C_{p_S} - C_{p_L}\right)}{2T_L}\Delta T^2 + \frac{1}{6T_L}\left(\frac{\partial C_{p_S}}{\partial T} - \frac{\partial C_{p_L}}{\partial T}\right)\Delta T^3 + \ldots, \qquad (2)$$

where C_{p_S}, C_{p_L} – are heat capacities of solid and liquid phases.

This work for a critical nucleus size l_k of a cube-shaped crystal stable to a further growth is equal to $A_k = 32\sigma_{SL}^3 / \Delta\mu_V^3 = 32\sigma_{SL}^3 / T_L^2 / \rho^2 \Delta H_{SL}^2 \left(\Delta T^-\right)^2$ and the critical nucleus size itself is equal to:

$$l_k = 4\sigma_{SL} / \Delta\mu_V = 4\sigma_{SL} T_L / \rho\, \Delta H_{SL} \Delta T^-, \qquad (3)$$

where $\Delta\mu_V$ is a chemical potential change in a phase transformation, σ_{SL} is the inter-phase surface energy on the melt-crystal boundary, T_L and ΔH_{SL} are melting temperature and enthalpy, ρ is density, ΔT^- is a pre-crystallization super-cooling.

Another important kinetic characteristic is mass crystallization and the related degree of crystallinity η which is dependent on the nucleation rate $I = \frac{1}{V}\frac{dN}{dt}$ (V – volume, N – number of nuclei), nucleus growth rate υ, incubation period τ_1, degree of super-cooling ΔT^-.

The macroscopic description of the dependence of the degree of crystallinity η on time t was given by Kolmogorov, Johnson and Mall Avrami. The Avrami-Kolmogorov equation

$$\eta = 1 - \exp\left[-Z\left(t - \tau_1\right)^n\right], \qquad (4)$$

allows calculating a relative part η of crystallized volume with respect to the whole volume V of a substance:

$$\eta = V_x / V. \qquad (5)$$

Crystallization constant Z is related to nucleation rate I and nucleus growth rate υ. For example, for crystal nuclei $Z = I\upsilon^3$. The Avrami index n characterizes the crystal morphology and the type of crystallization.

Mass crystallization from melts was being theorized on the base of the data obtained for metals and their alloys. This theory is roughly applied for other systems too, both in solidification from melt and for crystallization from melt, vapor and amorphous medium. But in any case, one of the main stages of solidification – the nucleation stage – is scantily known because it is hardly possible to directly observe nuclei, especially in opaque solid substances. That is why in our research of mass crystallization a special attention has been paid to the nucleation issues.

In our research we tried to follow the following concepts:

– investigation of the kinetics of real nucleation and mass crystallization in dependence on the degree of liquid phase super-heating and super-cooling, heat removal velocity, external actions and clearing-up of some important moments of this complex process as applied to different substances has been always an urgent scientific and technical problem since the crystallization conditions are of decisive importance in the formation of the nano-, micro- and macrostructure of crystals and determine their quality and physical-technical properties;

– in the experimental investigations of the kinetics of crystallization of different substances the complex (thermal, X-ray diffraction, optical and other) and systematic studies are to be carried out in the same conditions and the all-round expansion of the nomenclature of the materials (from the simple to complex ones) under study is needed;

– analysis of the research results and development of the ideas on the crystallization of different systems are to be performed from unified positions, namely on the base of the cluster-coagulation model of crystallization suggested and developed by the author in numerous publications. This model is based on the cluster structure of a liquid phase both above and below the temperature of melting. In the process of super-cooling, crystalline nuclei are generated from clusters; these nuclei store up and then coagulate with each other.

All these taken together presuppose an account of various phase transformation and a close interrelationship between a solid body structure and a liquid phase structure.

When dealing with the problem of solid and liquid state of chemical elements, Mendeleev's periodic law and the structural-crystallographic table of the chemical elements created by the author [4] 4 were taken as the base for analysis and generalization.

Analysis of the structural-crystallographic table resulted in the following conclusions:

– at temperature of chemical element melting the high-temperature modification melts. This very modification is formed in the inverse process, i. e. on crystallization;

– in a small zone of melt super-heating above melting temperature, clusters resembling the structure of a high-temperature crystalline modification survive.

As super-heating increases, the short-range order rearrangement takes place in melts and as a result of this different kinds of crystallization (from quasi-equilibrium to non-equilibrium-explosive one) might be observed in cooling;

– on the base of the structural-crystallographic table one can predict new modifications in some chemical elements, a «queue» of polymorphic transformations as temperature and pressure change as well as structural rearrangements of clusters in a liquid phase.

The thermodynamic treatment of crystallization is based on the analysis of the dependence of the Gibbs thermodynamic potential G (Gibbs free energy) on temperature, pressure, concentration etc. In Figure 1 is shown the dependence of the Gibbs energy for crystal G_S and for melt G_L on temperature T for an equilibrium phase transformation taking place at melting temperature T_L. Temperature changing to this or that side of T_L, the difference of the Gibbs energies $\Delta G = G_S - G_L$ reverses sign. At $T > T_L$, $\Delta G > 0$ a liquid phase is stable, and at $T < T_L$, $\Delta G < 0$ a solid phase is stable. Such a phase transition, taking place in point T_L without super-coolings ($\Delta T^{-} = 0$), is equilibrium. In this case, on cooling the melt, the curve $G(T)$ will proceed the path *abe* (Figure 1).

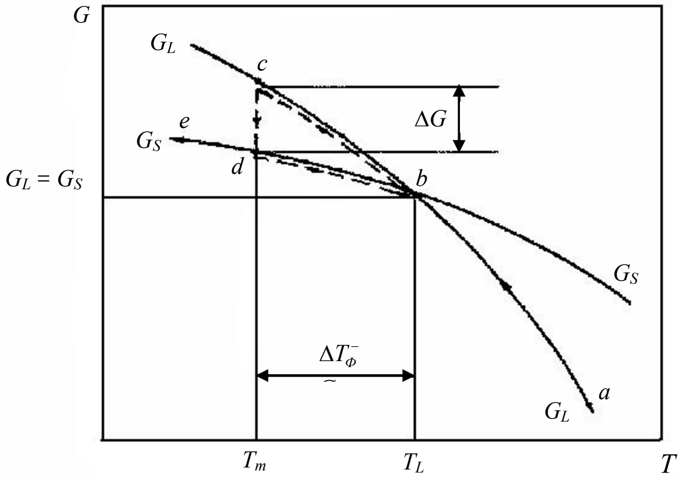

Figure – Dependence of Gibbs energy G on temperature T for solid G_S and liquid G_L phases.

But under definite conditions, deviations from the specified equilibriums can be observed for the same substances. There are known the effects of crystal super-heating on melting and a considerable super-cooling of a melt on crystallization. In the latter case the Gibbs energy G will proceed the path *abcdbe* as the melt cools. The range of temperatures from T_L up to the crystallization onset T_m is called a pre-crystallization physical super-cooling $\Delta T_{\phi}^{-} = T_L - T_m$, and the liquid state in this range is meta-stable.

The super-cooling quantity is taken into account at the analysis of different thermodynamic and kinetic characteristics of phase transformations: nucleation work, critical dimensions of nuclei and nucleation rate, crystal growth rate, degree of crystallinity and mass crystallization constant. So, the first priority task in the investigation of the crystallization kinetics is the investigation of super-coolings and their being influenced by different factors (thermal prehistory of melts, testing conditions, external actions, impurities etc.).

The basic techniques of studying super-coolings as well as thermal effects under phase transformations are the thermal ones. Of prime importance are the methods developed by the author and his colleagues, which include the method of the cyclic thermal analysis (CTA) with a special sensitivity of thermocouples [5] and a combined method of the CTA and differential thermal analysis (DTA) [6], the method of determining a heat-accumulating material in the form of a mixture of crystalline hydrates on the base of the diagram states [7]. These methods proved to be effective in revealing quite a number of new endo- and exothermal effects described in [8].

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Получено 08.05.2013

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АКТУАЛЬНІ ПРОБЛЕМИ КІНЕТИКИ ЗАРОДКОУТВОРЕННЯ Й МАСОВОЇ КРИСТАЛІЗАЦІЇ ПЕРЕОХОЛОДЖЕНИХ РОЗПЛАВІВ І РОЗЧИНІВ

Донбаська національна академія будівництва і архітектури

Повідомлення складається з короткого переліку класичних характеристик процесів зародкоутворення й масової кристалізації переохолоджених розплавів і розчинів. Наведено основні проблеми цього фазового переходу й принципи, яких дотримується у своїх дослідженнях колектив кафедри фізики й фізичного матеріалознавства Донбаської національної академії будівництва й архітектури. Розроблено кластерно-коагуляційну модель кристалізації, яка заснована на наступних етапах: зародкоутворення, коагуляція зародків, їх ріст і об'єднання. Розроблено кристалографічну таблицю хімічних елементів із вказівкою фазових перетворень у конденсованому стані, на основі якої набувала розвитку кластерно-коагуляційна модель.

кінетика зародкоутворення, масова кристалізація, переохолоджені розплави, переохолоджені розчини, взаємозв'язок структури кристалів і рідкої фази

В. Д. АЛЕКСАНДРОВ

АКТУАЛЬНЫЕ ПРОБЛЕМЫ КИНЕТИКИ ЗАРОДЫШЕОБРАЗОВАНИЯ И МАССОВОЙ КРИСТАЛЛИЗАЦИИ ПЕРЕОХЛАЖДЕННЫХ РАСПЛАВОВ И РАСТВОРОВ

Донбасская национальная академия строительства и архитектуры

В сообщении дан краткий перечень классических характеристик процессов зародышеобразования и массовой кристаллизации переохлажденных расплавов и растворов. Перечислены основные проблемы данного фазового перехода и принципы, которых придерживается в своих исследованиях коллектив кафедры физики и физического материаловедения Донбасской национальной академии строительства и архитектуры. Разработана кластерно-коагуляционная модель кристаллизации, которая основана на следующих этапах: зародышеобразование, коагуляция зародышей, их рост и слияние. Разработана кристаллографическая таблица химических элементов с указанием фазовых превращений в конденсированном состоянии, на основе которой развивалась кластерно-коагуляционная модель.

кинетика зародышеобразования, массовая кристаллизация, переохлажденные расплавы, переохлажденные растворы, взаимосвязь структуры кристаллов и жидкой фазы

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Aleksandrov Valery – DSc. (Chem.), Professor, Head of the Department Physics and Physical Material Science, Donbas National Academy of Civil Engineering and Architecture. Scientific interests: investigation of physical and chemical bases of the kinetics of crystallization of substances: nucleation, crystal growth, mass crystallization to obtain materials with the pre-given structure and properties.