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УСТОЙЧИВОСТЬ ПЕРЕОХЛАЖДЕННЫХ РАСТВОРОВ КРИСТАЛЛИЗАЦИОННЫХ СИСТЕМ В КЛАССИЧЕСКОЙ ТЕОРИИ ОБРАЗОВАНИЯ НОВОЙ ФАЗЫ

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Обобщены теоретические и экспериментальные оценки устойчивости растворов кристаллизационных систем к переохлаждению. Обсуждаются общие закономерности кинетики процесса кристаллизации с позиций классической теории образования и роста частиц новой фазы. В ходе анализа кинетической диаграммы процесса периодической гомогенной кристаллизации выявлено три характерных периода – период устойчивости к переохлаждению, период роста кристаллов и период рекристаллизации. Установлена природа процессов, определяющих длительность характерных периодов. Обоснована применимость математического аппарата классической теории образования новой фазы для вычисления основных и частных функционалов кристаллизационной системы. Приведены соотношения, позволяющие вычислить основные и частные функционалы устойчивости кристаллизационной системы к переохлаждению. Проанализировано влияние категории кристаллизационной системы на величины предела переохлаждения и экстремума индукционного периода периодической гомогенной кристаллизации. Представлены параметры устойчивости к переохлаждению пересыщенных водных растворов некоторых классов неорганических и органических веществ при периодической гомогенной кристаллизации. Сделаны выводы относительно положения экстремумов основных и частных функционалов кристаллизационной системы. Правильность выводов подтверждена анализом экспериментальных данных по кинетике кристаллизации ряда неорганических и органических веществ из водных и водно-органических растворителей. На примере процесса периодической гомогенной кристаллизации витамина группы B_1 тиаминбромида из водно-этанольного раствора построен полный ряд положений экстремумов основных и частных функционалов кристаллизационной системы. Отмечены закономерности влияния содержания органического компонента в бинарном растворителе на функционалы устойчивости кристаллизационной системы.

Ключевые слова: кристаллизационная система, сингония кристаллов, предельное переохлаждение, индукционный период, фазообразование, ячейка полного смешения

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STABILITY OF SUPERCOOLING SOLUTIONS OF CRYSTALLIZATION SYSTEMS IN CLASSICAL THEORY OF NEW PHASE FORMATION

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Theoretical and experimental evaluations of crystallization systems solutions stability to overcooling were summarized. The general regulariries of the kinetics of the crystallization process are discussed from the standpoint of the classical theory of the formation and growth of new-phase particles. During the analysis of the process of periodic homogeneous crystallization kinetic diagram, three characteristic periods were revealed: the period of resistance to supercooling, the period of crystal growth, and the period of recrystallization. The nature of the processes determining the duration of the characteristic periods has been established. The applicability of the mathematical apparatus of the new phase formation classical theory for calculating the basic and particular functionals of the crystallization system is substantiated. Relations are given that make it possible to calculate the main and particular functionals of the crystallization system stability for supercooling. The analysis of crystallization system category influence on the magnitude of limit supercooling and periodic homogenous crystallization induction period extreme was made. Parameters of the resistance to supercooling of supersaturated aqueous solutions of inorganic and organic substances certain classes under periodic homogeneous crystallization are presented. Conclusions are drawn regarding the position of the main and particular functionals extrema of the crystallization system. The correctness of the conclusions is confirmed by an analysis of the experimental data on the crystallization kinetics of a number of inorganic and organic substances from aqueous and aqueous-organic solvents. On the example of periodic homogeneous crystallization process of the vitamin B1 thiamin bromide from the water-ethanol solution, a complete series of the crystallization system main and particular functionals extremum positions the are constructed. The regularities of the influence of the organic component concentration in a binary solvent on the stability functionals of the crystallization system are noted.

Key words: crystallization system, syngony, limit supercooling, induction period, phase formation, complete mixing cell

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Earlier [1], based on the analysis of large arrays of experimental data, we have identified relatively stable categories of crystallization systems (CS) by the nature of the crystallized substance and solvent. It was shown, that the classification affiliation of the CS determines the position and magnitude of the main functionals and activities of the CS, which can be used to select the design and mode parameters of the crystallizers to be designed, as well as to optimize the functioning continuous crystallization plants.

The low-tonnage processes of crystalline substances production by the crystallization method in dispersed media are, as a rule, periodic. On the kinetic diagram of such a process (Fig. 1), we can distinguish three time intervals [2]: - the interval of resistance to supercooling I, the interval of crystals growth II and the recrystallization interval III. The duration of the interval of resistance to supercooling is determined by the processes of autogenesis - the formation of the stable germs with a certain size - (moment t₁) and autocatalysis processes - the formation of new germs due to the self-priming effect of the CS (up to t₂). The total duration of the stability interval is usually treated as an induction period.

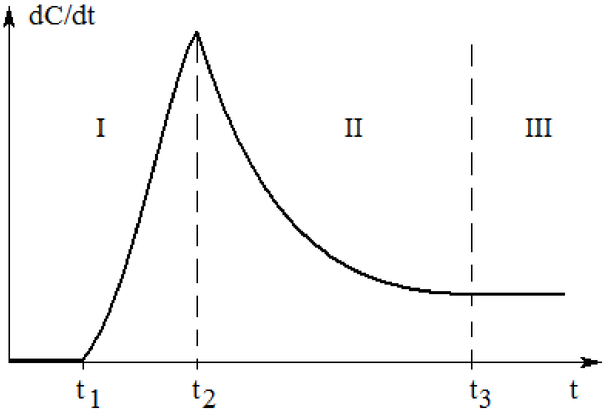

Fig. 1. The time dependence of the change in a concentration C of CS solution in a cource of the periodic crystallization

Рис. 1. Временная зависимость скорости изменения концентрации С раствора КС в ходе периодической кристаллизации

Despite the indisputable successes of the experimental methods for studying the induction period of CS, at the present time [3,4] there is a great need for theoretical methods for calculating it, allowing one to predict the magnitude of the limiting supercooling and the corresponding sizes and surface energy of the germs. Quantitative estimates of these values can be obtained by analyzing of the basic and particular stability functionals of CS. The classical theory of homogeneous crystallization considers the positions and values of the limiting supercooling (supersaturation) and the crystallization rate extremum at the instant of moment t₂ as the basic functionals of the CS stability. The limiting size of the germs at the moment t₁ and the time t₃ of the given yield of the crystallized product will be considered as particular functionals. The present paper generalizes the results of physical and numerical experiments on the stability of CS to supercooling (supersaturation) studying. An analysis of a rather large number of CS of various nature has shown that the dependences of the formation rate α and the crystal size r on the supercooling are well described by the unified Frenkel's [5] and Thomson's [6] relations:

$$\alpha = L\cdot\exp\left(-\frac{A_\alpha + D_\alpha \dfrac{T_0^2}{\Delta T^2}}{T_0-\Delta T}\right); \qquad (1)$$

$$r = 9{,}255\cdot10^{-9}\sqrt[3]{\frac{D_\alpha}{A_\alpha}}\cdot\frac{T_0}{\Delta T}\cdot\sqrt[3]{\frac{M\cdot\Delta E_\alpha}{\rho_T q}}\,. \qquad (2)$$

The work of A_r, spent on the formation of a new phase germs (characterizes the Gibbs energy [7]) and the number of molecules n_r of the crystallizable substance in the germ can be estimated using the following relationships:

$$A_r = \frac{D_\alpha}{A_\alpha}\cdot\left(\frac{T_0}{\Delta T}\right)^2\cdot\frac{\Delta E_\alpha}{N_0}; \qquad (3)$$

$$n_r = 2\frac{D_\alpha}{A_\alpha}\cdot\left(\frac{T_0}{\Delta T}\right)^3\cdot\frac{\Delta E_\alpha}{q}. \qquad (4)$$

The main calculated relations used in the analysis are given in [1]. To determine the ultimate supercooling of ΔT_1 and the surface energy of particles of size r_1 (here and below, the numerical indexes for the variables correspond to the time points in Fig. 1), the principle of the minimum entropy production ΔS* and the variational method of nonequilibrium thermodynamics [8] were used. In this approximation, under the condition $\alpha = 1$, equation (1) becomes the expression for ΔT_1:

$$\Delta T_1^3 - \left(\frac{A_\alpha}{\ln \alpha/L} + T_0\right)\cdot\Delta T_1^2 - 2D_\alpha T_0^2 = 0\,, \qquad (5)$$

And the condition of the extremum of the absolute volume rate of separation of the new phase at the end of the induction period $r_2^3\alpha_2$ [9] leads to the expression for ΔT_2:

$$3\Delta T_2^4 - \left(A_\alpha - 6T_0\right)\Delta T_2^3 + 3\Delta T_2^2 T_0^2 + 3D_\alpha\Delta T_2 T_0^2 - 2D_\alpha T_0^2 = 0\,. \qquad (6)$$

Using the equations of the classical kinetics crystallization theory $\alpha = K\Delta C^m$ [2], and taking into account the results of the analysis of the experimental data [10], it is possible to estimate the autogenesis time t_1 and the time to reach a given relative yield v of the crystallized product t_3:

$$t_1 = \frac{1}{K\Delta C_1^m}; \qquad (7)$$

$$t_3 = -t_2 \frac{1}{v} \ln(1-v), \qquad (8)$$

where ΔC_1 is the absolute supersaturation of the CS corresponding to the limiting overcooling ΔT_1 and t_2 is the end time of the induction period, which corresponds to the yield of the crystallized product v_2:

$$t_2 = \frac{3v_2}{2\pi r_2^3 \alpha_2}. \qquad (9)$$

Statistical analysis of the physical and numerical experiments data [1] made it possible to establish some general regularities of the crystallization kinetics due to the category of the crystallographic system [11], as well as a combination of the natural properties of the crystallized substance and the solvent.

In this case it is established:

- the character of the dependence of the total crystals number on the time N (t), and also the kinetics of crystal growth parameters are determined by the category of the crystallographic system (Fig. 2);

- the positions of the limit ΔT_1 and the extremum ΔT_2 are in the relation $\Delta T_2 > \Delta T_1$;

- the effect of autocatalysis of CS is directly proportional to the category of the crystallographic system and inversely proportional to the ratio A_α/D_α; The position of the rate of germs formation extremum (according to ΔC) is determined by the average concentration of the CS solution in the induction period.

A typical example illustrating this regularity is the process of periodic homogeneous crystallization of vitamins B_1 group from a water-ethanol solution [12]. For an aqueous solution of thiamine bromide at T = 343 K, ΔT_1 = 7,6 *K* and ΔT_2 = 33,8 K were determined experimentally. Then, the complete set of the basic and particular CS functionals extrema positions, taking into account [1], takes the view:

$$\Delta T_{\max(\alpha)} > \Delta T_{\max(\alpha/\beta)} > \Delta T_2 > \Delta T_{\max(\alpha\beta^3)} >$$
$$> \Delta T_{\max(\beta/\alpha\beta^3)} > \Delta T_{\max(\beta)} > \Delta T_1$$

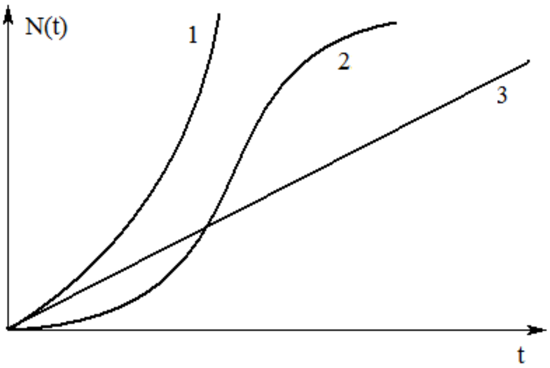

Fig. 2. Time dependencies of the total number N of the crystals for 1 - higher 2 - moderate and 3 - the lowest crystallographic system category

Рис. 2. Зависимости полного числа кристаллов N от времени для 1 – высшей, 2 – средней и 3 – низшей категории кристаллографических систем

The building of such a series for any CS can be of considerable help in improving the structural and technological complex of the crystallization unit and optimizing the number of steps of the crystallizer with both internal and external recycling of the liquid (solid) phase. Examples, confirming the correctness of these conclusions are given in Tables 1, 2. It should be noted that for a CS on the base of binary solvents, the composition of the solvents has a certain effect on the CS stability to overcooling. In this case, the course of the CS stability functionals parameters dependences on the concentration of the organic component (which reduces the solubility of the crystallizable substance [13]) in a solvent, qualitatively repeats the dependence of the ratio A_α/D_α.

Table 1

Stability parameters to overcooling supersaturated aqueous solutions of inorganic substances at the periodic homogeneous crystal tion (T_0 = 323 K)

Таблица 1. **Параметры устойчивости к переохлаждению пересыщенных водных растворов неорганических веществ при периодической гомогенной кристаллизации (T_0=323 К)**

CS category	Substance, yngony	A_α/D_α	ΔT_1,K	ΔT_2,K	t_1,c	t_2,c	t_3,c for v=0,95	$r_1 \cdot 10^{10}$, m	n_{r1}, pieces	$(dv/dt)_2$, 1/c	$\omega_{(dv/dt)2}$ for $\omega_{\Delta T2}$ = 0,7
highest	KCl, I	1.23	10.9	28.5	3.6E-3	0.9	2.7	3.2	2	1.370.28	0.032
moderate	NaN_3 III	2.23	9.8	25.6	3.9E-2	2.8	8.9	3.8	3	0.012	0.048
lowest	$(NH_4)_2SO_4$ IV	5.23	8.2	22.5	1.5E+1	64.2	202.3	5.0	5		0.075

Table 2

Stability parameters to overcooling supersaturated aqueous and aqueous-alcoholic solutions of organic substances at the periodic homogeneous crystallization (T_0 = 323 K)

***Таблица 2.* Параметры устойчивости к переохлаждению пересыщенных водных и водно-спиртовых растворов органических веществ при периодической гомогенной кристаллизации (T_0=323 К)**

Substance, syngony		C_0, %	A_α/D_α	ΔT_1, K	T_2, K	$\omega_{(dv/dt)2}$ for $\omega_{\Delta T2}$ = 0,7	Solvent
$C_{12}H_{22}O_{11}\cdot 7H_2O$	IV	62.5	0.68	7.8	27.0	0.022	H_2O
$(C_{12}H_{17}ON_4S)^+HCl\cdot 1/2H_2O$	IV	55	1.28	5.3	23.9	0.034	
$C_6H_8O_6$	I	38.2	2.28	4.0	22.2	0.048	
$C_{19}H_{21}NO_3$	II	0.16	3.1	3.6	21.4	0.053	
$C_6H_{10}O_3$	IV	93	3.7	3.3	20.5	0.059	
$C_9H_8O_3N_3Cl$	I	0.19	4.12	2.9	20.8	0.056	
$C_{18}H_{32}O_{10}N_2Ca$	IV	40.5	8.7	2.0	14.7	0.085	
$C_{12}H_{22}O_{11}$	V	74	18.4	1.6	14.7	0.085	
$(C_{12}H_{17}ON_4S)+HCl\cdot 1/2H_2O$	IV	49.1	0.66	6.4	26.3	0.024	H_2O
		41.4	1.55	4.4	24.7	0.038	20% C_2H_5OH в H_2O
		32.2	3.46	2.5	21.9	0.057	40% C_2H_5OH в H_2O
		20.1	6.42	1.7	19.5	0.070	60% C_2H_5OH в H_2O
		6.12	7.9	1.4	18.7	0.075	80% C_2H_5OH в H_2O
		0.48	6.45	1.8	19.8	0.071	99,92% C_2H_5OH в H_2O

In conclusion, it should be said that calculating the parameters of the CS germs distribution functions [14] at the stage of autocatalysis, taking into account the experimental data, will allow us to more accurately predict the granulometric composition of the crystallized product in the future, and also to obtain new information on the mechanism of the new phase stable germs formation at the stage of autogenesis.

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