ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 14, № 4 (2013) С. 886-890

PHYSICS AND CHEMISTRY OF SOLID STATE
V. 14, № 4 (2013) P. 886-890

УДК 539.213

ISSN 1729-4428

A.B. Lysenko, I.V. Zagorulko, T.V. Kalinina, A.A. Kazantseva

Conditions of Crystal Nucleation Processes Suppression at the Quenching from a Liquid State

Dnieprodzerzhinsk State Technical University, 51918, Dnieprodzerzhinsk, Dnieprostroevska str., 2,
e-mail: ablysenko@ukr.net

The estimation method of the melt critical cooling rate u_{-}^{*} at which the nucleation processes are completely suppressed and fixed truly amorphous structure that does not contain "quenched nuclei" crystalline phase, is suggested. The calculations of u_{-}^{*} values were performed for materials with significantly different glass forming ability: pure metals (Al, Ni), alloy $Fe_{80}B_{20}$ and the bulk amorphized alloys ($Mg_{65}Cu_{25}Y_{10}$ and $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$). It is shown that to prevent the crystallization in the pure metals melts are necessary cooling rates ~ 10^{13} - 10^{14} K·s^{-1}. Applied to the bulk amorphized alloys u_{-}^{*} values are decreased up to ~ 10^{4} K·s^{-1} that indicates the principal possibility of truly amorphous states obtaining in the products of rapid quenching with the cross sections to about ~ 130 μm.

Key words: quenching from a liquid state, melt cooling rate, truly amorphous state, nucleation frequency.

Стаття поступила до редакції 25.05.2013; прийнята до друку 15.09.2013.

Introduction

According to modern physical conceptions based on the results of the experimental [1 - 3] and theoretical [4 - 6] investigations, metallic glasses (MG) obtained by rapid quenching of melts are not amorphous materials in the strict sense of the word. According to the classification proposed by Glezer A.M. [7] they have an amorphous-nanocrystalline structure which consists of a glassy matrix with inclusions of so-called "quenched nuclei". It follows that in manufacturing of MG predominantly suppresses the processes of crystals growth while the action of nucleation mechanism does not ceases. Contrariwise, in the literature there are some publications [3, 8, 9], which reported obtaining truly amorphous structures without quenched nuclei.

Thus, the data presented in the modern literature does not provide an unambiguous answer to the question about the possibility of complete suppression of crystallization processes in the rapid quenching products. This shows the relevance of specially designed studies of a truly amorphous materials obtaining problem.

In this paper the algorithm for design-theoretical analysis of the conditions of formation of amorphous structures without nanoscale inclusions of the crystalline phase, by which we obtain estimates of the critical cooling rate which causing complete suppression of nucleation processes, for materials with significantly different glass-forming ability.

I. Characteristics of used model

The physical model of complete suppression of crystallization construct based on the condition that during the melt cooling from the melting point T_m to the glass transition temperature T_g in the unit of volume is formed less than one crystal nucleus. In the formalized form this condition was represented by the relation:

$$\frac{1}{u_{-}^{*}} \int_{T_g}^{T_m} I(T)dT < 1 \qquad (1)$$

where u_{-}^{*} is the critical cooling rate of the melt (constant for a given material); *I (T)* is the homogeneous nucleation rate.

The temperature dependences $I(T)$ set by the equations of the classical theory of crystallization [10] taking into account the effect of non-stationary size distribution of heterophase fluctuations [11].
In the result a final inequation by the instrumentality of which defines the value of u_{-}^{*} were obtained:

$$\frac{1}{u_{-}^{*}} \int \frac{N_V D(T)}{a_0^2} \exp\left[-\frac{16pV_m^2 s^3}{3kT\Delta G_m^2(T)}\right] \exp\left[-\frac{3p^2 V_m h(T) u_{-}^{*}}{RT(T_m \cdot T)}\right] dT < 1 \qquad (2)$$

where N_n is the number of atoms per unit volume; D –

diffusion coefficient of the atoms at the interphase boundary; a_o – interphase boundary thickness (atomic diameter); k – Boltzmann constant; V_m is the molar volume; h – dynamic viscosity of the melt; R is the gas constant; s – the specific free energy of the interface crystal-melt; ΔG_m is the molar free-energy difference of the liquid and crystal phases.

Calculations were carried out for materials with different glass-forming ability: pure metals Al, Ni, one of which (Ni) is fixed in the amorphous state at extremely high (~ 10^{10} K·c^{-1}) cooling rates of melt, alloy $Fe_{80}B_{20}$, characterized by midrange of glass-forming ability [12], and also well-known bulk amorphized alloys $Mg_{65}Cu_{25}Y_{10}$ and $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ [13, 14].

As is seen from the relation (2), the value of the integrand expression is determined substantially by the temperature dependences of three parameters: the diffusion coefficient D, the energy stimulus of crystallization ΔG_m and melt viscosity h.

The diffusion coefficient was determined by the previously calculated values of viscosity using the Stokes-Einstein equation:

$$D = \frac{k\,T}{3pa_o h} \qquad (3)$$

In its turn, the temperature dependences of the viscosity were approximated by the empirical equation of Vogel-Fulcher-Tamman [15]:

$$h(T) = A\exp\left(\frac{B}{T - T_o}\right) \qquad (4)$$

where A, B, T_o - constants depending on the nature of a material.

Calculating details of the temperature dependences $h(T)$ and $\Delta G_m(T)$ for pure metals are given in the paper [16]. For alloy $Fe_{80}B_{20}$ the dependence $I(T)$ was estimated by the ratio proposed in [12]. For Mg- and Zr-based bulk glass-forming alloys we used the dependences of supercooled melts viscosity presented in [13] and [17] and experimental data [13, 18] allowing to calculate the values $\Delta G_m(T)$. The specific free energy of the interface crystal-melt σ for all of the materials was evaluated according to the method of [19].

II. Results and analysis

The results of the settlement analysis are summarized in the table. It can be seen that the selected for investigation materials are characterized by essentially different values of the critical cooling rate u_{-}^{*} causing suppression of nucleation. For pure metals analyzable parameter is ~ 10^{13} - 10^{14} K·s^{-1} which corresponds to a critical thickness of the rapidly quenched foils l^{*} ~ (4 - 9)·10^{-5} μm [20]. Listed values of the melt cooling rates and layer thicknesses can not be achieved by the modern methods of rapid quenching indicating the impossibility of obtaining observable metals in a truly amorphous state.

For alloy $Fe_{80}B_{20}$ an action of homogeneous nucleation mechanism is terminated at melt cooling rate of the $u_{-}^{*} \approx 5\cdot10^{10}$ K·s^{-1} ($l^{*} \approx 0{,}88$ μm). Similar values u_{-}^{*} and l^{*} lies at the limit of possibility of the traditional methods of quenching from the liquid state. Hence, guaranteed obtaining of rapidly cooled samples of alloy $Fe_{80}B_{20}$ not containing "quenched nuclei" is low-probability.

As can be seen from the table, during quenching from the liquid state of Mg- and Zr-based alloys which are inclined to the formation of bulk metallic glasses, truly amorphous structures fixed at a relatively small values of the critical cooling rate of ~ 10^{7} and $3\cdot10^{4}$ K·s^{-1}, i.e. in the layers with thickness of ~ 4 and ~ 125 μm, respectively. These results lead to the conclusion that the principal possibility of experimental verification of the effect of the complete suppression of homogeneous nucleation processes during rapid cooling of easily glass-forming alloys $Mg_{65}Cu_{25}Y_{10}$ and $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$.

The tabular data analysis shows that one of the reasons for significant differences for critical speeds of rapid quenching of materials are very high maximum values of stationary nucleation frequency for pure metals ($I_0^{\max} \approx 10^{34} - 10^{36}$ m^{-3}·s^{-1}), which are achieved at the deep reduced supercoolings of melt ($\Delta T_r^0 \approx 0{,}44$ - $0{,}49$). With increasing of glass-forming ability of the material, parameters $I_0^{\max}$ and ΔT_r^0 are decreased, reaching values of ~ $4.31\cdot10^{17} - 1.26\cdot10^{10}$ and ~ 0.33 and 0.29 for alloys $Mg_{65}Cu_{25}Y_{10}$ and $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$.

Transformation of dependences identified by calculations leads to the fact that at a given rate of QLS time of the melt cooling from the material melting temperature to temperature of stationary nucleation maximum, and also number of crystallization centers formed during this time decreased and thus increases the probability of complete suppression of nucleation processes.

Besides parameters $I_0^{\max}$ and ΔT_r^0 are an important criterion for propensity of melts to form a truly amorphous structures are sensitivity of nucleation kinetics to the regime of melt cooling. To illustrate the effect of these criteria specifying different cooling rates of melts the non-stationary frequency nucleation from the reduced supercooling was calculated and compared with graphs $I_0(\Delta T_r)$ (figs. 1 - 3). It can be seen that the presented series of dependencies $I(\Delta T_r)$ possesses qualitatively similar dome-like character, but differ by significantly lower maximum values of nucleation frequency for easily glass-forming Zr-based alloy. Furthermore, for this alloy calculated curves $I(\Delta T_r)$ exhibits a higher sensitivity to cooling conditions than similar dependence for Al (fig. 1) and alloy $Fe_{80}B_{20}$ (fig. 2). Indeed, as can be seen from fig. 3, an evident

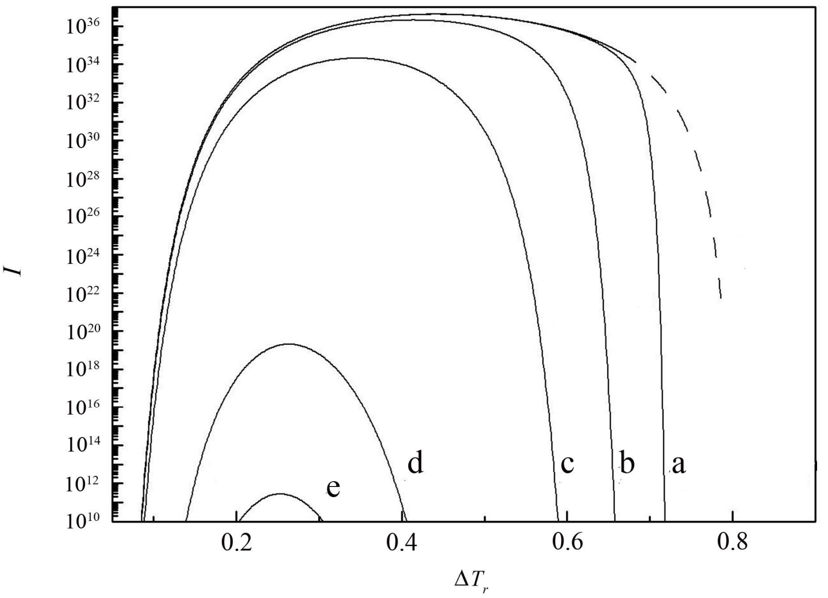

Fig. 1. Dependences of stationary nucleation (dotted line) and nonstationary nucleation (solid lines) frequency from the reduced supercooling for pure Al at various cooling rates (K·s^{-1}): 10^{10} (a); 10^{12} (b); 10^{13} (c); 10^{14} (d); $1.5 \cdot 10^{14}$ (e)

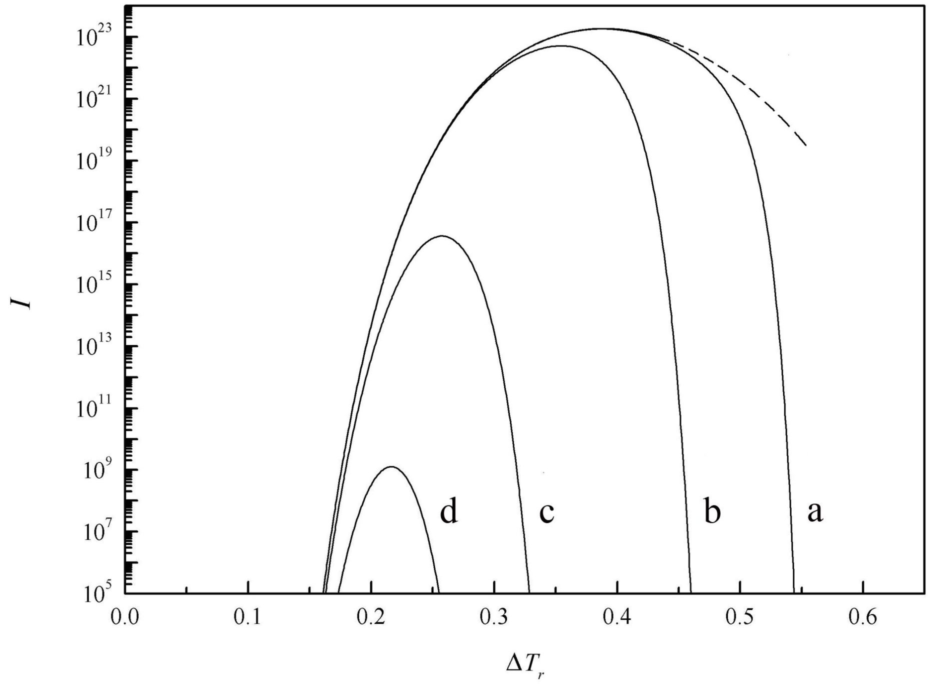

Fig. 2. Dependences of stationary nucleation (dotted line) and nonstationary nucleation (solid lines) frequency from the reduced supercooling for alloy Fe$_{80}$B$_{20}$ at various cooling rates (K·s^{-1}): 10^{6} (a); 10^{8} (b); 10^{10} (c); $5 \cdot 10^{10}$ (d)

decrease of the maximum values of the nucleation frequency and shift of the maximum of $I(\Delta T_r)$ dependence towards lower values ΔT_r observed even at cooling rates $u_-^* \approx 10^2$ K·s^{-1}. At the same time dependencies $I(\Delta T_r)$ for alloy Fe$_{80}$B$_{20}$ undergo similar changes at cooling rates $u_-^* \approx 10^8$ K·s^{-1} (fig. 2), and at quenching of the molten aluminum nucleation processes start to slow down only at extremely high values of $u_-^* \approx 10^{12}$ K·c^{-1} (fig. 1).

The described changes of nucleation processes kinetics leads to a significant reduction of the dependences $I(\Delta T_r)$ maximum with increasing of the melt cooling rate. For example, at critical regimes of rapid quenching the maximum values of non-stationary nucleation frequency reduced in comparison with the

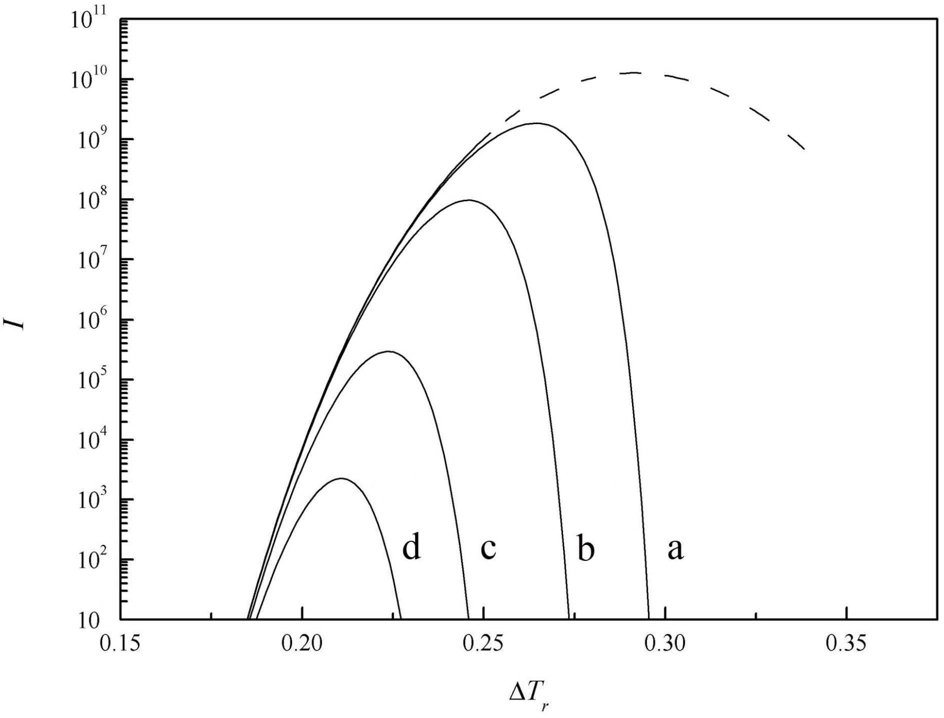

Fig. 3. Dependences of stationary nucleation (dotted line) and nonstationary nucleation (solid lines) frequency from the reduced supercooling for alloy $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ at various cooling rates ($K \cdot s^{-1}$): 10^2 (a); 10^3 (b); 10^4 (c); $3.3 \cdot 10^4$ (d)

Table

The calculated values of the nucleation frequency and the critical cooling rate for investigated materials

№	Material	u_-^*, $K \cdot s^{-1}$	l^*, m	I_0^{max}, $m^{-3} \cdot s^{-1}$	$\Delta T_r(I_0^{max})$	I^{max} at u_-^*, $m^{-3} \cdot s^{-1}$	$\Delta T_r(I^{max})$
1	Al	$1.5 \cdot 10^{14}$	$4.1 \cdot 10^{-11}$	$4.1 \cdot 10^{36}$	0.44	$2.0 \cdot 10^{11}$	0.26
2	Ni	$5.0 \cdot 10^{13}$	$9.5 \cdot 10^{-11}$	$3.8 \cdot 10^{34}$	0.49	$2.67 \cdot 10^{12}$	0.26
3	$Fe_{80}B_{20}$	$4.8 \cdot 10^{10}$	$8.8 \cdot 10^{-7}$	$1.8 \cdot 10^{23}$	0.39	$1.26 \cdot 10^{9}$	0.22
4	$Mg_{65}Cu_{25}Y_{10}$	$1.1 \cdot 10^{7}$	$4 \cdot 10^{-6}$	$4.3 \cdot 10^{17}$	0.33	$7.6 \cdot 10^{5}$	0.21
5	$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$	$3.3 \cdot 10^{4}$	$125 \cdot 10^{-6}$	$1.3 \cdot 10^{10}$	0.29	$2.2 \cdot 10^{3}$	0.20

value of I_0^{max} about 25 orders of magnitude for Al, 14 orders for alloy $Fe_{80}B_{20}$ and 7 orders of magnitude for alloy $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (table).

Despite this, the observable pure metals retain a high nucleating ability which explains the high level of the corresponding values u_-^*. Conversely, the maximum of $I(\Delta T_r)$ dependences for alloys $Mg_{65}Cu_{25}Y_{10}$ and $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ is reduced to values of about ~ 10^3 – 10^6 m^{-3} s^{-1} which creates a real conditions for the complete suppression of crystallization under quenching from the liquid state conditions.

Conclusions

1. An algorithm for estimation of the metal melts critical cooling rate u_-^* which providing nucleation processes suppression and fixing of truly amorphous structures without inclusions of "quenched nuclei" of crystalline phases.

2. By calculations is ascertained that for complete prevention of crystallization in pure metal melts are necessary cooling rates of ~ 10^{13} – 10^{14} $K \cdot s^{-1}$ which can not be achieved by known methods of quenching from the melt. When using the bulk amorphized alloys the

values $\overset{*}{u}_{-}$ are reduced up to $\sim 3\cdot 10^{4}\,\mathrm{K\cdot c^{-1}}$ which indicates about the principled possibility of obtaining a truly amorphous states in the products of rapid quenching with the cross sections up to ~ 130 μm.

3. The main factors that increase the tendency of alloys to absolute amorphization are relatively low ($I_0^{\max} < 10^{20}\,\mathrm{m^{-3}\cdot s^{-1}}$) values of stationary nucleation frequency and pronounced tendency of nucleation processes slowing with the growth of melt cooling rate.

Лисенко О.Б. - доктор фізико-математичних наук, доцент, завідувач кафедри фізики конденсованого стану;
Загорулько І.В. - аспірант кафедри фізики конденсованого стану;
Калініна Т.В. - старший викладач кафедри фізики конденсованого стану;
Казанцева Г.О. - аспірант кафедри фізики конденсованого стану.

[1] N.F. Gadzyra, E.I. Har'kov, I.A. Jakubcov, Metallofizika 11(1), 88 (1989).
[2] A.V. Romanova, A.G. Il'inskij, Amorfnye metallicheskie splavy (Naukova dumka, Kiev, 1987).
[3] J. Z. Jianga, J. Saida, H. Kato, T. Ohsuna, A. Inoue, J. Appl. Phys. Letters 82(23), 4041 (2003).
[4] R. Sellger, W. Loser, Acta Metall. 34(5), 831 (1986).
[5] R. Sellger, W. Loser, G. Richter, Mater. Sci. Eng. 97, 203 (1988).
[6] V.I. Tkach, V.V. Popov, S.G. Rassolov, Metallofiz. i novejshie tehnologii 31(9), 1271 (2009).
[7] A.M. Glezer, E.I. Permjakova, Nanokristally, zakalennye iz rasplava (FIZMATLIT, Moskva, 2012).
[8] A.L. Greer, Acta Metal. 30, 171 (1982).
[9] H.W. Yang, J. Gong, R.D. Li, J.Q. Wang, J. Non-Cryst. Solids. 355, 2205 (2009).
[10] Dzh. Kristian, Teorija prevrashhenij v metallah i splavah. Ch. 1 (Mir, Moskva, 1978).
[11] J.C.A. Vreswijk, R.G. Gossink, J.M. Stevels, J. Non-Cryst. Solids 16, 15 (1974).
[12] V.I. Tkatch, S.N. Denisenko, B.I. Selyakov, Acta metal. mater. 43(6), 2485 (1995).
[13] R. Busch, W. Lin, W.L. Johnson, J. Appl. Phys. 83(8), 4134 (1998).
[14] Y.U. Kim, R. Busch, W.L. Johnson, A.J. Rulison, W.K. Rhim, Appl. Phys. Lett. 68(8), 1057 (1996).
[15] A. Fel'c, Amorfnye i stekloobraznye neorganicheskie tverdye tela (Mir, Moskva, 1986).
[16] A.B. Lysenko, G.V. Borisova, O.L. Kravets, A.A. Lysenko, The Physics of Metals and Metalography 106(5), 435 (2008).
[17] T.A. Waniuk, R. Busch, A. Masuhr, W.L. Johnson, Acta Mater. 46(15), 5229 (1998).
[18] Au-Hui Cai, Hui Wang, Xiao-Song Li, Hua Chen, Yong Zhou, Zheng-Su Wan, Mater. Sci. Eng. A. 435-436, 478 (2006).
[19] K. Mondal, B.S. Murty, Mater. Sci. Eng. A. 454-455, 654 (2007).
[20] A.B. Lysenko, G.V. Borisova, O.L. Kravec, Fizika i tehnika vysokih davlenij 14(1), 44 (2004).

О.Б. Лисенко, І.В. Загорулько, Т.В. Калініна, Г.О. Казанцева

Умови пригнічення процесів зародження кристалів при загартуванні з рідкого стану

Дніпродзержинський державний технічний університет, 51918, Дніпродзержинськ,
вул. Дніпробудівська, 2, e-mail:ablysenko@ukr.net

Запропоновано методику оцінки критичної швидкості охолодження розплавів $\overset{*}{u}_{-}$, при якій повністю пригнічуються процеси зародкоутворення та фіксується істинно аморфна структура, що не містить "загартованих зародків" кристалічної фази. Розрахунки значень $\overset{*}{u}_{-}$ проведено для матеріалів із суттєво відмінною схильністю до склоутворення: чистих металів (Al, Ni), сплава $Fe_{80}B_{20}$ та сплавів, що утворюють масивні металеві стекла ($Mg_{65}Cu_{25}Y_{10}$ и $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$). Показано, що для запобігання кристалізації у розплавах чистих металів необхідні швидкості охолодження $\sim 10^{13} - 10^{14}\,\mathrm{K\cdot c^{-1}}$. Стосовно до сплавів, що легко склуються, значення $\overset{*}{u}_{-}$ зменшуються аж до $\sim 3\cdot 10^{4}\,\mathrm{K\cdot c^{-1}}$, що свідчить про принципову можливість отримання істинно аморфних матеріалів в продуктах швидкого загартування перетинами до ~ 130 мкм.

Ключові слова: загартування з рідкого стану, швидкість охолодження розплаву, істинно аморфні структури, частота зародкоутворення.