Initiation of the Explosive Crystallization Process in Amorphous Alloys of the Fe-Zr System by Pulse Laser Treatment

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In the work, a series of theoretical calculations were carried out to analyze the possibility of the process of explosive crystallization during laser treatment of binary amorphous alloys of the Fe-Zr system. The calculations were carried out within the framework of the modified theory of homogeneous crystallization for binary alloys, which takes into account the work associated with the concentration fluctuation. Calculation of the characteristics of the crystallization process was performed for two modes: slow heating at a speed of 0.16 K/s and an instant laser pulse, while it was considered that the amorphous tape was heated by a laser beam to a certain temperature within 10^{-6} seconds. The integral curve of the temperature dependence of the volume part of the crystalline phase during slow isothermal annealings is characterized by the presence of a «shelf», which indicates the two-stage crystallization process. The temperature range of crystallization at slow heating (0.16 K/s) is 90 K. We analyze the peculiarities of the crystallization process of amorphous alloys under the influence of laser treatment. The high heating rates, achieved by the laser treatment of amorphous alloys, create a number of differences in the course of crystallization processes compared with crystallization during slow isothermal annealings. According to the calculations, impulse heating to temperatures below 550 K does not cause crystallization. After 551 K, there are significant changes in the crystallization kinetics. At 552 K, the crystalline phase part has reached the value of 8 %. In the interval from 552 K to 553 K, there is a sharp jump in the value of the crystal phase proportion from 8 % to 99 %, that is a complete crystallization of the amorphous alloy occurs. The calculations carried out have shown that explosive crystallization may occur during the pulsed laser annealing of binary amorphous alloys of the Fe-Zr system. The temperature at which explosive crystallization is possible due to the laser pulse was less than 60 K for the temperature of the beginning of intensive crystallization at slow heating.

Keywords: Explosive crystallization, Pulsed laser annealing, Amorphous alloy, Relative integral free Gibbs' energy, Volume part of crystalline phase.

1. INTRODUCTION

The amorphous metal alloys of the Fe-Zr system are characterized by a wide range of unique physical properties and are widely used as the latest functional materials; so the study of the peculiarities of their crystallization process has an important fundamental and applied value. Since amorphous alloys are thermodynamically unstable systems, it is necessary to investigate the regularities of the crystallization process under the influence of various external factors.

One of these factors is impulse laser treatment. The use of pulsed laser treatment can significantly increase the rate of thermal impact on metals and alloys: up to $(10^4\text{-}10^6)$ K/s using the most common pulsed and continuous technological lasers, and in some cases up to $(10^9\text{-}10^{10})$ K/s. Under such influence, crystallization must occur instantaneously throughout the volume of the amorphous tape (explosive crystallization) [1]. The phenomenon of explosive crystallization in amorphous metallic alloys is characterized by the intensive isolation of the latent heat of crystallization at the boundary of the phase separation, which is accompanied by the self-heating of the crystallization front.

The phenomenon of explosive crystallization is intensively studied both theoretically and experimentally. In addition to the apparent physical interest in this phenomenon, the study of the nature of explosive crystallization is also important in connection with the increasing use of amorphous materials in modern technology. Indeed, explosive crystallization, initiated by a rather strong local energy momentum, can extend to the entire volume of amorphous material at high velocity [2]. It is very important that the appearance of explosive crystallization can occur at temperatures substantially lower than the temperature of crystallization during isothermal annealing. This fact must be taken into account when choosing amorphous materials for practical application. The problem of research is related to the theoretical analysis of the possibilities of the process of explosive crystallization during laser treatment of binary amorphous alloys of the Fe-Zr system.

2. EQUATION FOR THE DESCRIPTION OF THE CRYSTALIZATION KINETICS IN THE Fe-Zr SYSTEM

A series of theoretical calculations were carried out to analyze the possibility of the process of explosive crystallization during laser treatment of binary amorphous alloys of the Fe-Zr system. The calculations were carried out within the framework of the modified theory of homogeneous crystallization for binary alloys, which takes into account the work associated with the concentration fluctuation. An important characteristic of the crystallization process of amorphous alloys is the volume part of the crystalline phase $X(t)$ at a given time, which for the binary systems is described by the differential equation [3]:

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$$\frac{dX(t)}{dt} = (1 - \sum_{i=1}^{k} X_i(t)) \frac{4}{3} \pi \langle J_{0i} U_i^3 \rangle (t - t_{0i})^3$$

$$\langle J_{0i}, U_i^3 \rangle = \int_0^1 J'_{0i}(C_2) U_i^3(C_2) dC_2 \qquad (1)$$

where k is the number of crystalline phases; U_i is the linear crystal growth rate of the i-th phase; J_{0i} is the initial nucleation frequency, which corresponds to $\sum_{i=1}^{k} X_i = 0$; t_{0i} is the start time of the crystallization of the i-th phase.

The nucleation rate for binary systems J'_i is described by the distribution functions of the crystalline nuclei that arise at certain concentrations, that is

$$J'_i(C_2) = N \frac{D}{a^2} \exp\left[-\frac{16\pi\sigma^3 V_0^2}{3kT\left(\Delta G^{\alpha-i}(C_2) - 2\left|\Delta G^{\alpha-\alpha}(C_2)\right|\right)^2} \right]$$

$$\Delta G^{\alpha-i}(C_2) = \Delta G^{\alpha}(C_2) - \Delta G^{i}(C_2); \qquad (2)$$

$$\Delta G^{\alpha-\alpha}(C_2) = \Delta G^{\alpha}(C_2) - \Delta G^{\alpha}(C_{20}),$$

Here, $\Delta G^{\alpha}(c_2)$ and $\Delta G^{i}(c_2)$ are the concentration dependences of the relative integral Gibbs free energy of the amorphous (α) and crystalline (i) phases; c_{20} is the initial concentration of the second component in the α-phase; c_2 is an arbitrary concentration of the second component in the α- and i-phases; σ is the surface tension at the boundary of two phases, V is the molar volume, N is the number of atoms per unit volume; a is the atomic diameter; D is the diffusion coefficient.

Taking into account that during crystallization in the binary system several stable formations are formed, as well as the possible occurrence of metastable phases, equation (2) is generalized to

$$J_i = \int_0^1 J'_i(c_2) dc_2 , \qquad (3)$$

where $i = \beta, \gamma, \delta, \varepsilon$ are the crystalline phases.

The total nucleation frequency J of different types will be written in the form

$$J = \sum_{i=1}^{k} J_i , \qquad (4)$$

where k is the number of stable and metastable phases occurring during crystallization. The linear crystal growth rate in the case of binary alloys is described by the equation

$$U_i = \frac{D}{a}\left(1 - \exp\left(-\frac{\Delta G^{\alpha-i} - \left|\Delta G^{\alpha-\alpha}\right|}{RT} \right) \right). \qquad (5)$$

Equation (1) is solved by methods of numerical integration, from which all values $X_i(t)$ are determined for the system; $X(t) = \sum_{i=1}^{k} X_i$.

The main parameter that determines the crystallization kinetics of binary alloys is the concentration

dependences of the Gibbs free energies of the amorphous and crystalline phases that arise in the process of phase formation. The relative integral Gibbs free energy of the amorphous phase is described by the following expression [4]:

$$\Delta G^{\alpha}\left(c_{Zr}, T\right) = f_{\Delta H} + RT\left(c_{Zr}\,ln\,c_{Zr} + \left(1 - c_{Zr}\right) \times \right.$$

$$\times ln\left(1 - c_{Zr}\right) - 10.7\left(0.5 + \frac{3.5 \times 10^5}{T^2} \right) f_{\Delta V/V0} \right) + \qquad (6)$$

$$+ \frac{\Delta H_0^{Fe}\left(T_0^{Fe} - T\right)}{T_0^{Fe}}\left(1 - c_{Zn}\right) + \frac{\Delta H_0^{Zr}\left(T_0^{Zr} - T\right)}{T_0^{Zr}} c_{Zr}$$

In equation (6), the functions ΔH_0^{Fe}, ΔH_0^{Zr}, T_0^{Fe}, T_0^{Zr} are the enthalpy and melting temperature of iron and zirconium. Functions $f_{\Delta H}$ and $f_{\Delta V/V_0}$ give an opportunity to take into account the experimental dependences $\Delta H(c_{Zr},\,T)$ and $\frac{\Delta V}{V_0}(c_{Zr}, T)$ for different temperatures and concentrations and are analytically described by the following relationships:

$$f_{\Delta H, \Delta V/V_0} = \frac{a_{\Delta H, \Delta V/V_0}(1 - c_{Zr})c_{Zr}}{1 + b_{\Delta H, \Delta V/V_0} c_{Zr}} , \qquad (7)$$

$$a_{\Delta H, \Delta V/V_0} = \frac{\beta_{\Delta H, \Delta V/V_0}}{\alpha_{\Delta H, \Delta V/V_0}{}^2} , \quad b_{\Delta H, \Delta V/V_0} = \frac{1 - 2\alpha_{\Delta H, \Delta V/V_0}}{\alpha_{\Delta H, \Delta V/V_0}{}^2} ,$$

where $\alpha_{\Delta H}$ is the position of the concentration dependence of enthalpy extremum $\Delta H(c_{Zr},\,T)$, $\beta_{\Delta H}$ is the modulus of this value at the extremum point, $\alpha_{\Delta V/V_0}$ is the position of the concentration dependence of extremum $\frac{\Delta V}{V_0}(c_{Zr}, T)$, $\beta_{\Delta V/V_0}$ is the modulus of this value at the extremum point. These parameters are determined from experimental and calculated data [4-6].

Fig. 1 shows the concentration dependences of the relative integral Gibbs free energies $\Delta G(c_{Zr},\,T)$ for the α-phase and, respectively, for the two crystalline phases (β and γ).

Parameters of the concentration dependences of the relative integral Gibbs free energy of the amorphous phase in the Fe-Zr system were obtained based on the analysis of the state diagram and experimental data [4-6] and were chosen as: $\alpha_{\Delta H} = 0.35$, $\beta_{\Delta H} = -28.8 \cdot 10^3$, $a_{\Delta H} = -235.1 \cdot 10^3$, $b_{\Delta H} = 2.448$, $\alpha_{\Delta V/V_0} = 0.15$, $\beta_{\Delta V/V_0} = -0.3$, $a_{\Delta V/V_0} = -13.3$, $b_{\Delta V/V_0} = 31.11$.

The relative integral Gibbs free energy of the crystalline β and γ phases, which are formed in the Fe-Zr system, is described by the following expression:

$$\Delta G^{\beta,\gamma}(c_{Zr}, T) = A^{\beta,\gamma}(T)(c_{Zr} - c_m^{\beta,\gamma})^2 + \Delta G_0^{\beta,\gamma}(T) , \qquad (8)$$

where $c_m^{\beta,\gamma}$ is the concentration of zirconium, which corresponds to the minimum value of the function $\Delta G^{\beta,\gamma}(c_{Zr},\,T)$, $\Delta G_0^{\beta,\gamma}(c_{Zr},\,T)$ is the minimum value of this function.
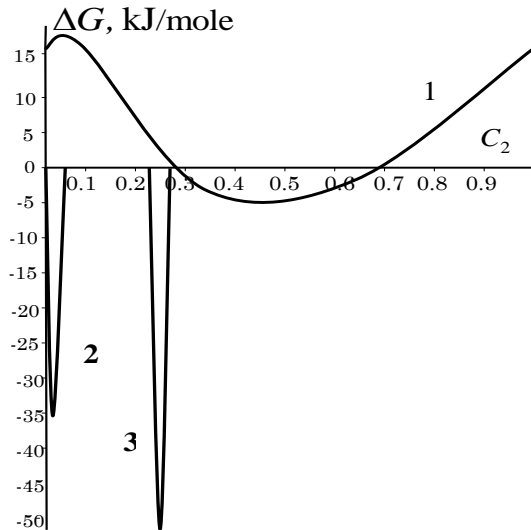
Fig. 1 – Concentration dependence of the integral relative Gibbs free energy of the initial amorphous α-phase (1), crystalline β (2) and γ (3) of the Fe-Zr system

Parameters for calculating the relative integral Gibbs free energy for two crystalline phases observed in the process of phase formation in alloys of the Fe-Zr system are the following:

$$C_m^\beta = 0{,}02, \ C_m^\gamma = 0{,}25, \ A^\beta = -\frac{\Delta G_0^\beta(T)}{(0{,}03)^2} \ A^\gamma = -\frac{\Delta G_0^\gamma(T)}{(0{,}26)^2} \ ,$$

$$\Delta G_0^\beta(T) = -30 \cdot 10^3 + 0{,}1RT \ \text{(J/mole)} ,$$

$$\Delta G_0^\gamma(T) = -44 \cdot 10^3 + 0{,}1RT \ \text{(J/mole)} .$$

According to equations (1)-(8), the concentration dependences of the relative integral Gibbs free energies of the Fe-Zr system α-phase (amorphous phase) and, respectively, the crystalline β- and γ-phases were calculated and constructed. The obtained equations allow us to calculate the characteristics of the crystallization process of alloys of the Fe-Zr system.

3. RESULTS OF CALCULATING THE CRYSTALIZATION PROCESS PARAMETERS OF THE AMORPHOUS ALLOYS OF THE Fe-Zr SYSTEM

Calculation of the characteristics of the crystallization process was performed for two modes: slow heating at a speed of 0.16 K/s and an instant laser pulse, while it was considered that the amorphous tape was heated by a laser beam to a certain temperature within 10^{-6} seconds.

Fig. 2 shows the results of calculating the temperature dependences of the total volume part of the crystalline phase $X(t)$ and the volumetric parts of the crystalline phases $X_i(t)$ formed during the heating of the amorphous $Fe_{90}Zr_{10}$ alloy carried out according to the equations (1)-(8).

Calculations have shown that the crystallization process of the $Fe_{90}Zr_{10}$ alloy takes place in two stages in accordance with the state diagram of the binary Fe-Zr system [6]. At a temperature of 600 K, solid solution of zirconium in the α-Fe crystallizes, while the concen-

tration of zirconium in the amorphous matrix increases. With further heating at 650 K, crystallization of a solid solution of zirconium and iron begins in the chemical compound Fe_3Zr.

The integral curve of the temperature dependence of the volumetric part of the crystalline phase is characterized by the presence of a «shelf», which indicates the two-stage crystallization process. The temperature range of crystallization at slow heating (0.16 K/s) is 90 K. We analyze the peculiarities of the crystallization process of amorphous alloys under the influence of laser treatment. Fig. 3 shows the calculated temperature dependence of the volume fraction of the crystalline phase under pulsed laser heating.

The high heating rates, achieved by laser treatment of amorphous alloys, create a number of differences in the course of crystallization process compared with crystallization during slow isothermal annealing. According to the calculations, impulse heating to temperatures below 550 K does not cause crystallization.

After 551 K, there are significant changes in the crystallization kinetics. At 552 K, the crystalline phase part has reached the value of 8 %. In the interval from 552 K to 553 K, there is a sharp jump in the value of the crystal phase proportion from 8 % to 99 %, that is a complete crystallization of the amorphous alloy occurs.
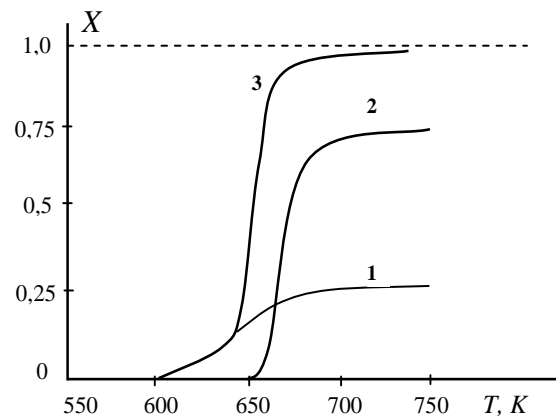

Fig. 2 – Temperature dependence of the volume part of phases that appear in the process of continuous heating of the amorphous $Fe_{90}Zr_{10}$ alloy: curve 1 is the part of the crystalline β-phase, curve 2 is the part of the crystalline γ-phase, curve 3 is the total volume part of the crystalline phase $X(T)$

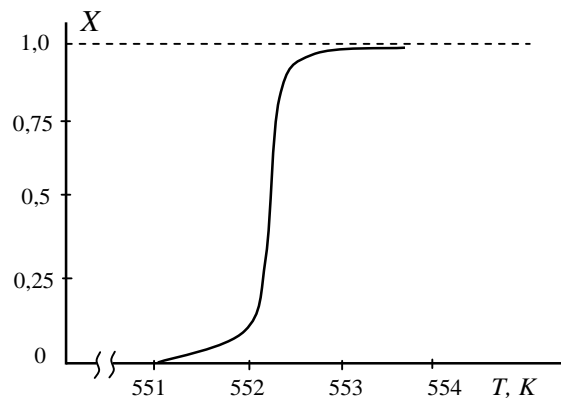**Fig. 3** – Temperature dependence of the volume part of the crystalline phase under pulsed laser heating of the amorphous $Fe_{90}Zr_{10}$ alloy

The calculations carried out have shown that explosive crystallization may occur in the pulsed laser annealing in binary amorphous alloys of the Fe-Zr system. The temperature at which explosive crystallization is possible due to the laser pulse was less by 60 K than the temperature of the beginning of intensive crystallization at slow heating.

4. CONCLUSIONS

The calculations carried out within the framework of the modified theory of homogeneous nucleation for

binary systems have shown that the crystallization process of alloys of the Fe-Zr system with slow heating is two-stage: initially the solid solution of Zr in the α-Fe crystallizes, then crystallization starts in the chemical compound Fe₃Zr. Complete crystallization occurs in the temperature range of 90 K. It is shown that during pulsed laser annealing in binary amorphous alloy Fe₉₀Zr₁₀ there can be a phenomenon of explosive crystallization at a temperature lower by 60 K than the temperature of the beginning of intensive crystallization at slow heating.

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Ініціювання процесу вибухової кристалізації в аморфних сплавах системи Fe-Zr імпульсною лазерною обробкою

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Для аналізу можливості протікання процесу вибухової кристалізації при лазерній обробці бінарних аморфних сплавів системи Fe-Zr в роботі було проведено ряд теоретичних розрахунків. Розрахунки проводились в рамках модифікованої теорії гомогенної кристалізації для бінарних сплавів, в якій врахована робота, пов'язана із флуктуацією концентрації. Розрахунки характеристик процесу кристалізації розраховувались для двох режимів: повільне нагрівання зі швидкістю 0.16 К/с та миттєвий лазерний імпульс, при цьому вважалось, що аморфна стрічка нагрівалась лазерним променем до певної температури за час 10^{-6} с. Інтегральна крива температурної залежності об'ємної частки кристалічної фази під час повільних ізотермічних відпалів характеризується наявністю "полички", яка свідчить про двостадійність процесу кристалізації. Температурний інтервал кристалізації при повільному нагріванні складав 90 К. Високі швидкості нагрівання, що досягаються при лазерній обробці аморфних сплавів, створюють ряд відмінностей в протіканні процесів кристалізації у порівнянні з кристалізацією під час повільних ізотермічних відпалів. Згідно проведених розрахунків, імпульсне нагрівання до температур менших за 550 К кристалізацію не викликає. Після 551 К відбуваються істотні зміни в кінетиці кристалізації. При 552 К частка кристалічної фази складе 8 %. В інтервалі від 552 К до 553 К спостерігається різкий стрибок значення частки кристалічної фази від 8 % до 99 %, тобто відбувається повна кристалізація аморфного сплаву. Проведені теоретичні розрахунки показали, що при імпульсному лазерному відпалі в бінарних аморфних сплавах системи Fe-Zr може відбуватися явище вибухової кристалізації. Температура, при якій можлива вибухова кристалізація за рахунок лазерного імпульсу виявилась меншою на 60 К за температуру початку інтенсивної кристалізації при повільному нагріванні.

Ключові слова: Вибухова кристалізація, Імпульсний лазерний відпал, Аморфний сплав, Процес кристалізації, Відносна інтегральна вільна енергія Гіббса, Об'ємна частка кристалічної фази.