Technical Physics, 2022, Vol. 67, No. 14

05

On the possible mechanism of external infrasonic mechanical stimulating the process of formation of nanocrystals in an amorphous metal film

© E.E. Slyadnikov,[1,2,3] I.Y. Turchanovsky[2]

[1] Institute of Strength Physics and Materials Science, Siberian Branch, Russian Academy of Sciences,
634055 Tomsk, Russia
[2] Federal Research Center for Information and Computational Technologies,
630090 Novosibirsk, Russia
[3] Tomsk State University of Control Systems and Radioelectronics,
634050 Tomsk, Russia
e-mail: eeslyadnikov@gmail.com

Received February 13, 2021
Revised April 24, 2021
Accepted May 28, 2021

A kinetic model, a physical reason and a condition for stimulated by external infrasonic mechanical vibrations of the formation of nanocrystals in an amorphous metal film. The nanostructural elements of the amorphous medium are responsible for these processes: locally ordered nanoclusters and nanoregions containing free volume, which contain two-level systems. When glass is deformed, two-level systems are excited, due to which they make a significant contribution to inelastic deformation, structural relaxation, formation of nanoclusters and nanocrystals. The physical mechanism of nanocrystallization of metallic glass during mechanical exposure includes, in addition to the mechanism of local thermal fluctuations, also athermal mechanism of quantum tunneling of atoms or atomic groups stimulated by inelastic deformation.

Keywords: Kinetic model, amorphous metal film, nanocrystals, infrasonic mechanical vibrations.

DOI: 10.21883/TP.2022.14.55219.35-21

Introduction

Amorphous metal alloys became widely used in electrical engineering, radio and space engineering [1]. Amorphous metal alloys with a nanostructure appearing as randomly oriented nanocrystals in an amorphous matrix [2,3] have unique mechanical properties. For nanostructuring of liquid-hardened amorphous film, low-frequency mechanical vibrations are used at a temperature well below the glass transition temperature, while the deformation of the sample remains within the elastic region [4]. TiNi-based amorphous thin tape samples, $40\,\mu$m thick, 1.6 mm wide and $10\,\mu$m long were exposed for 10 minutes to 20 Hz infrasound with displacement amplitudes of $1\,\mu$m and $4\,\mu$m at the temperature of $T_0 = 25^\circ$C. The structure of the amorphous alloy was tested by X-ray diffraction (XRD) technique and high resolution transmission electron microscopy (HRTEM) before and after low-frequency treatment. XRD and HRTEM data testify that the initial alloy is completely amorphous; the structure of the sample exposed to mechanical oscillations with an amplitude of $1\,\mu$m is close to that of the initially untreated sample(the short-range order changes and the free volume decreases); nonspherical clusters with regular atomic positions and sizes of 3–5 nm arise in the amorphous matrix in the structure of the sample exposed to mechanical oscillations with an amplitude of $4\,\mu$m.

It was established [4] that the mechanical action slightly reduces the latent crystallization heat, i.e. the free energy of state with nanocrystals slightly decreases compared to the free energy of the amorphous state. The chemical and phase compositions of alloys with and without nanocrystals are the same, so the reason behind infrasound stimulation of nanocrystallization is not related to diffusion, being caused by collective atomic rearrangements during structural relaxation.

Further experimental studies showed [5] that the increase of oscillations duration to 2 h enhances the size of clusters, and their growth can be different in different directions. After mechanical oscillations within 4 h the film acquires a crystalline structure consisting of irregularly shaped grains of different crystal-lattice orientations, with amorphous islands embedded in them.

The influence mechanism of mechanical oscillations on the nanocrystallization of amorphous material remains unclear.

According to classical ideas [2,3,6], crystal nucleation in amorphous alloys can take place following the homogeneous or heterogeneous mechanism. In the vicinity of glass transition temperature, homogeneous nucleation takes place through fluctuational (spontaneous) nucleation with a radius greater than the critical one [2,3,6]. Below the glass transition temperature, heterogeneous nucleation (on the defects, boundaries, etc.) [2,3,6,7] and the nucleation driven by „frozen-in“ crystallization centers play a significant role in the crystallization process.

However, typical densities of heterogeneous nuclei in metallic melts make $10^{14}-10^{12}\,\mathrm{m}^{-3}$. Even in amorphous alloys with no nanoscale crystallites, the crystallite density visibly exceeds those values (for example, in the $Fe_{80}B_{20}$ alloy the crystallite density makes $10^{18}\,m^{-3}$ [9]). In nanostructured systems (e.g., in Cu−Ti [10]) alloys) the crystallite density can reach $10^{25}\,m^{-3}$, so the major part of crystal nuclei are most likely to be formed by homogenous nucleation during annealing.

The analysis of physical conditions of nanocrystallization by stationary annealing and mechanical action [2–5] shows that the mechanisms of amorphous film nanocrystallization in those impacts differ significantly. In thermal annealing, the sample temperature is much higher than the room temperature, the nanocrystallization proceeds slowly and is largely homogeneous, and nanocrystals are formed throughout the volume, by way of thermofluctuation.

In mechanical action, the temperature of the medium equals room temperature, so the probability of nanocrystal formation by ordinary thermofluctuation is much lower than at annealing temperature, due to the high activation energy of nanocrystal formation process. However, mechanical oscillations with an amplitude of $4\,\mu$m produce significant shear stresses in the film. At a critical value of shear stress, the medium loses its shear stability, and inelastic irreversible deformation occurs. Therefore, the mechanism of metallic glass nanocrystallization in mechanical action should include, apart from the local thermal fluctuations, athermal quantum tunneling of atoms or atomic groups [11–13], stimulated by inelastic irreversible deformation. Inelastic deformability of amorphous metallic alloys, their ability to structural relaxation and formation of nanocrystals are associated with the collective interatomic metallic bonding in which collective atomic displacements [2,3] can be accomplished much easier. Therefore, in constructing the mechanism of inelastic deformation, of structural relaxation and nanocrystallization of metallic glass, the influence of the electronic subsystem [14–16] should be taken into account, and specifically for metallic glass, the localization of the conduction electron in the nanometer potential well and phason [16] formation.

The aim of this paper is to describe a potential physical mechanism, kinetic model, physical cause and condition of the first order infrasound-stimulated non-equilibrium transition in a metal film from the amorphous state to a nanostructure. This approach should take into account both thermal and athermal mechanisms of inelastic deformation, structural relaxation, and nanocrystallization, and also, the localization of the conduction electron in the potential well of the emerged nanocrystal, and phason formation.

1. Physical mechanism of inelastic deformation of metallic glasses

Inelastic deformation is explained by local static atom/atomic group displacements from their initial equilibrium positions to new equilibrium positions located at a less than an interatomic distance away from their initial positions, in response to an applied shear stress σ [17–21]. The probability of such atomic rearrangement through thermal fluctuation is proportional to $\exp\left(-\frac{(E_a-\sigma a_0^3)}{kT}\right)$, where E_a is the energy activation barrier of rearrangement, and a_0 is the interatomic distance. In plastic deformation it is assumed that $(E_a-\sigma a_0^3)\le 0$, while in inelastic deformation $(E_a-\sigma a_0^3)>0$, therefore inelastic deformation is thermoactivated. However, the inelastic deformation effect is observed experimentally at cryogenic temperature (77 K) [22], where the thermal fluctuation energy is low (0.007 eV), and at lower temperatures [23]. Therefore, it is important to establish the physical mechanism of inelastic deformation of metallic glasses within the room temperatures range and below.

The first microscopic model of elementary cooperative inelastic rearrangements in metallic glasses based on the concept of homogeneously distributed free volume was proposed by Argon [17]. The model [18] assumes that due to the glass structure heterogeneity, regions arise in it with a free volume excessive with respect to the „ideal structure“— the„relaxation centers“. An activation energy spectrum model [19], and also, a directed structural relaxation model oriented by an external force [20] are commonly used nowadays. The model [21] proposes a method to describe the local structure of amorphous alloys based on the concept of *n*-, *p*- and τ-defects.

The [24] paper proposes a polycluster model of amorphous state structure in which elementary rearrangements of atomic configurations take place at intercluster boundaries, through exposure to external forces, this happening through thermal fluctuations at high temperatures, and through quantum tunneling at low temperatures. It is also worth mentioning earlier works [25,26] that had a significant impact on the modern concepts of inelastic deformation in solids. It was shown [25] that if impurity atoms have high mobility, e.g. as hydrogen in metals, then diffusion relaxation occurs under strain gradient conditions. The non-diffusive mechanism of martensitic phase transformation is proposed in [26], according to which the lattice cell of a new phase is formed as a result of spontaneous distortion (inelastic rearrangement) of the old phase cell.

Comparing the polycluster model [24] and the free volume model [17–21] note that in the latter, the stress-induced inelastic atomic rearrangements occur in the regions of empty cavities localization, the availability and local structure of those not being associated with the existence of local ordering. Therefore, regardless of the free volume nature, origin and distribution it plays a crucial role in inelastic deformation and structural relaxation in liquid-hardened metallic glasses.

The mechanical properties of metallic glasses are structurally sensitive, so they depend on the method of amorphous state preparation [2–5]. During liquid „hardening“ dislocations, disclinations and other defects are unlikely to appear in the system, so in order to create a mechanism of inelastic deformation, structural relaxation in hardened metallic glass, it is most adequate to use a free (excess) volume model [17–21] and a polycluster model [24].

Of particular interest are the structural elements of the amorphous medium („relaxation centers“) that contain free volume and can be rearranged not only through thermal fluctuations, but also through quantum tunneling. An atom moving in the double-well potential created by the surrounding atoms, or a group of atoms that can form two or more configurations with slightly different energies with all other atoms in the structure remaining essentially the same, is a two-level system [11–13,24]. The transition of an atom from one well to another, or the transition of one atomic arrangement to another, meaning the transition from one energy level to another can occur through quantum tunneling at room and lower temperatures. This occurs when the two-level system is about to degenerate, i.e., the levels of zero atom oscillations in each of the neighboring wells, without regard to tunneling, should have little difference. The initial resonance detuning of $\Delta_0 \ll 1$ eV, and the initial tunneling frequency of $\omega_K^0 = \omega_0 \exp\left(-\frac{a}{a_{dB}}\right)$, on the one hand, should be much lower than Δ_0, for the initial level splitting $E_0 = \sqrt{\Delta_0^2 + \hbar^2(\omega_K^2)^2}$ to be small ($\sim \Delta$), and on the other hand, not too small to allow tunneling to be manifested during the experiment.

Here a_{dB} is the de Breuil wavelength, a is the width of the potential barrier in the double-well potential $\omega_0 \approx 10^{13}$ Hz.

In order to estimate the atom tunneling significant parameters, let us make a model calculation. Let us assume that an atom in a free-volume nanodomain finds itself in a binary potential, or a group of atoms exists capable of forming two configurations with slightly different energies [11–13,24]. The potential energy of the system can be represented as the total of two single-well potentials, U_L and U_R. At the reference time, in the absence of mechanical load, the left (L) and the right (R) potential wells have different depths, the left well being deeper than the right one. The impact of an external mechanical force on the system results in a change of the distance between the atoms in the medium (deformation), which, in turn, changes the shape of the double-well potential.

Let us assume that the wave functions Ψ_L, Ψ_R and energy eigenvalue E_L, E_R for the Schrödinger equation with single-well potentials U_L, U_R are known. The complete Hamiltonian of a one-dimensional system with a double-well potential $U_L + U_R$ is written as [27]:

$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U_L + U_R,$$

$$\Psi = a_L\Psi_L + a_R\Psi_R, \quad \Delta = E_L - E_R. \tag{1}$$

Assuming a weak overlapping of the wave functions Ψ_L and Ψ_R ($S = \int dx \Psi_L \Psi_R \ll 1$), let us find the stationary level energy $E_\pm$

$$E_\pm = \frac{1}{2}\,[E_L + E_R \pm \sqrt{D}], \quad D = \Delta^2 + 4U_{LR}^L U_{LR}^R,$$

$$U_{LR}^L = \int dx \Psi_L U_L \Psi_R \tag{2}$$

and stationary states $\Psi_\pm$ in which the atom is delocalized between the two wells. A linear combination of stationary wave functions $\Psi(x,t)$ satisfying the Schrödinger time equation with the Hamiltonian (1) and the initial condition $\Psi(t=0) = \Psi_L$, allows identifying the probability of finding the atom in the left well

$$W(t) = a(t)^2 = 1 - \frac{16(\Delta + \sqrt{D})^2 U_{LR}^L U_{LR}^R}{\left[(\Delta + \sqrt{D})^2 + 4U_{LR}^L U_{LR}^R\right]^2}\sin^2\left(\frac{\sqrt{D}}{2\hbar}t\right),$$

$$a(t) = \int dx\, \Psi(x,t)\Psi_L(x). \tag{3}$$

$W(t)$ is a periodic time function oscillating from one to a certain minimum value to be determined by the resonance detuning Δ and by the value of the product $U_{LR}^L U_{LR}^R$.

If $\Delta = 0$, then

$$W(t) = 1 - \sin^2\left(\frac{\sqrt{U_{LR}^L U_{LR}^R}}{\hbar}t\right).$$

The probability of finding an atom in the left well varies from one to zero with the period of

$$\tau = \frac{\pi\hbar}{\sqrt{U_{LR}^L U_{LR}^R}},$$

and the atom spends the same amount of time in both wells. If $\Delta^2 \gg 4U_{LR}^L U_{LR}^R$, then

$$W(t) = 1 - \frac{4U_{LR}^L U_{LR}^R}{\Delta^2}\sin^2\left(\frac{\Delta}{2\hbar}t\right).$$

The atom stays in the left potential well almost all the time. When the external mechanical force is equal to zero, the $\Delta < 0$, $\Delta^2 \gg 4U_{LR}^L U_{LR}^R$ scenario is implemented and the atom only stays in the left well. With the critical deformation value, the $\Delta = 0$ situation is reached, and the atom tunnels into the right well. Further increase of the strain leads to $\Delta > 0$, $\Delta^2 \gg 4U_{LR}^L U_{LR}^R$ case, and the atom is only found in the right well. Since inelastic displacement of an atom is an elementary act of structural relaxation of the medium under load and is accompanied by stress relaxation, it leads to a change in the atom positions from the immediate surroundings and „freezing“ of the modified form of the double-well potential. As a result, the atom does not return to the left well but remains in the right well after the load is removed. This is how elementary inelastic deformation occurs in metallic glass at $T = 0$.

The energy level splitting corresponding to two atomic arrangements between which the transitions occur is expressed through Δ and $\hbar\omega_K = \sqrt{4U_{LR}^L U_{LR}^R}$ by the following relation: $E = \sqrt{\hbar^2\omega_K^2 + \Delta^2}$. There are many such two-level systems (relaxation centers) in glass that are characterized by the difference between the energies (resonance detuning) Δ in the two states and the tunnel transition frequency $\omega_K = \omega_0 \exp\left(-\frac{a}{a_{dB}}\right)$. Both those values are statistically distributed within certain intervals. A study of the distribution of double-well potentials parameters testifies of the potential availability of two groups of such potentials — soft (with the inter-well barrier $V \sim 10^{-4}{-}10^{-3}\,\mathrm{eV}$), and hard ones ($V \sim 10^{-1}{-}1\,\mathrm{eV}$) [11–13,24] ones. In the temperature domain $T \approx 1{-}300\,\mathrm{K}$, thermal hoppings are activated between the states whose barrier value makes $V \le 10^{-4}{-}2.4 \cdot 10^{-2}\,\mathrm{eV}$, so a hard potential quantum tunneling mechanism is more likely for a two-level system.

In one-particle model of phonon interaction with two-level systems [11–13,24], the seed energy difference Δ, also called the asymmetry parameter, is renormalized, and the distance between the two levels of the two-level system becomes equal to $E = \sqrt{\hbar^2\omega_K^2 + \Delta^2}$. In real systems, transitions are possible between those diagonal states. They are conditioned by the connection of the two-level system with oscillations of the environment atoms and are accompanied by the emission or absorption of phonons. In transition of the phonon wave the atoms forming the potential curve of the two-level system are displaced. This distorts the individual wells of the curve thus leading to a shift in $\delta\Delta$ seed levels. The shape of the potential barrier also changes causing a change in the seed tunneling frequency $\delta\omega_K$:

$$\delta\Delta = B_{ij}\varepsilon_{ij},\ \delta\omega_K = D_{ij}\varepsilon_{ij},\ \varepsilon_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} - \frac{\partial u_j}{\partial x_i}\right). \tag{4}$$

Here B_{ij}, D_{ij} are the tensors of deformation potentials depending on the local structure of the glass in the point of two-level system location, ε_{ij} is the strain tensor expressed through the displacement vector components u_i. The energy per atom over a deformation cycle $\varepsilon = 4 \cdot 10^{-4}$ is equal to $e_a \approx 1 \cdot 10^{-6}\,\mathrm{eV}$, so $\delta\Delta \approx e_a \approx 1 \cdot 10^{-6}\,\mathrm{eV}$. As $\Delta_0 < 0$, we can estimate the $|\Delta_0| \approx \delta\Delta \approx 1 \cdot 10^{-6}\,\mathrm{eV}$ and the maximum value of $\omega_K \approx 10^9\,\mathrm{s}^{-1}$.

In glass deformation two-level systems are excited, so that they make a significant contribution to inelastic deformation, structural relaxation and the formation of nanoclusters and nanocrystals. (4) demonstrates that the morphology (shape) of nanoclusters and nanocrystals formed during inelastic deformation is anisotropic being determined by the tensor of strain potentials which depend on the local structure of glass in the place where the two-level system is located.

Let us investigate the tunneling transition of an atom from one potential well to another at a finite temperature using the density operator formalism ρ [28]. In this case the atom tunneling between the wells interacts with the thermostat (the solid-phase environment maintaining its temperature during transitions). Using Ψ_L, Ψ_R eigenvectors as basis vectors, we obtain differential equations for the matrix elements of the density operator ρ, to the S accuracy.

$$i\hbar\frac{\partial\rho_{LL}}{\partial t} = U(\rho_{RL} - \rho_{LR}) - \frac{i\hbar}{\tau_{LL}}(\rho_{LL} - \rho_{LL}^0),$$

$$U \equiv U_{LR}^L = U_{LR}^R, \quad \tau_{ij} = \tau_{ji}, \quad i, j = L, R, \tag{5}$$

$$i\hbar\frac{\partial\rho_{RR}}{\partial t} = U(\rho_{LR} - \rho_{RL}) - \frac{i\hbar}{\tau_{LL}}(\rho_{RR} - \rho_{RR}^0),$$

$$\rho_{jj}^0 = \frac{e^{-\frac{E_j}{kT}}}{\sum\limits_i e^{-\frac{E_i}{kT}}}, \quad \rho_{j\neq j}^0 = 0, \tag{6}$$

$$i\hbar\frac{\partial\rho_{LR}}{\partial t} = \left(\Delta - \frac{i\hbar}{\tau_{LR}}\right)\rho_{LR} - U(\rho_{LL} - \rho_{RR}), \quad \rho_{LR} = \rho_{RL}^*, \tag{7}$$

The diagonal matrix element ρ_{LL} means that it is probabilistically possible to find an atom in the left well. For the sake of simplicity, the system under study is characterized by two relaxation times: the longitudinal relaxation time of the system $\tau_{LL} = \tau_R$ with an atom in the left (right) potential well, and $\tau_{LR} = \tau_{RL}$ — the transverse relaxation time of non-diagonal matrix elements. If the period of quantum oscillations is much shorter than the time of longitudinal and transverse relaxation, the process is coherent; and the probability of tunneling is an oscillatory function of time, i.e it is described by quantum kinetics. When the atom tunneling time significantly exceeds the longitudinal or transverse relaxation time, coherence is disturbed, and the probability of finding a particle in a certain state can be derived from the solution of classical kinetic equations.

Let us estimate the T_* temperature at which the quantum sub-barrier tunneling frequency of the atom ω_K becomes equal to the frequency of the over-barrier fluctuation hopping ω_T. Using Gamow formula and Arrhenius law and setting the exponents equal, we obtain

$$\omega_K = \omega_0 e^{-\frac{a}{a_{dB}}}, \quad \omega_T = \omega_0 e^{-\frac{V}{kT}},$$

$$a_{dB} = \frac{\hbar}{\sqrt{2mV}}, \quad T_* = \sqrt{\frac{V}{2m}}\frac{\hbar}{ak}, \tag{8}$$

where a_{dB} is the de Breuil wavelength, V, a is the height and width of the potential barrier in the double-well potential. (8) demonstrates that T_* increases in proportion to $\sqrt{V}$ and with m growing, and decreases proportionally to $\frac{1}{\sqrt{m}}$, $\frac{1}{a}$.

For a two-level system with a hard potential, the values $V \approx 1\,\mathrm{eV}$, $m \approx 10^{-25}\,\mathrm{kg}$, $a_{dB} \approx 0.56 \cdot 10^{-12}\,\mathrm{m}$ are characteristic. At the barrier width of $a = 3 \cdot 10^{-11}$; $1.5 \cdot 10^{-11}$; $0.9 \cdot 10^{-11}\,\mathrm{m}$ (0.1;0.05;0.03 of interatomic distance) we get $T_* \approx 65$; 216; 721 K and quantum tunneling frequency $\omega_K \approx 10^{-10}$; 20; 10^5 Hz, respectively. For a structural transformation with local atoms displacements much smaller than the interatomic distance, the tunneling effect is significant for room temperatures, being a core effect for lower temperatures. Therefore, a possible physical mechanism of inelastic deformation at room temperature is quantum tunneling of certain atoms in the double-well potential, or of atomic groups. The ability of amorphous alloys to inelastic irreversible deformation, to structural relaxation, and to formation of nanoclusters and nanocrystals is associated with the collective interatomic metallic bonding with which collective atomic displacement processes can be much more easily accomplished.

2. Localized electron states in the potential nanometer well, and phason formation

Let us assume that the electron moves in a three-dimensional potential well, spherically symmetric with respect to the center of force. In this case, the potential energy only depends on the distance from the electron to the center of force — $U(r)$. Let us assume that the three-dimensional potential well has the following form: $U(r) = -U_0$ at $r < a$, and is equal to zero at $r > a$. In the spherical coordinate system, the Schrödinger equation for stationary states has the following form [27]:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\Psi\right) + \frac{2m}{\hbar^2}\big(E - U(r)\big)\Psi = 0. \tag{9}$$

Let us introduce a new function $\Phi = r\Psi$. Then the equation (9) can easily be reduced to the form

$$\frac{d^2}{dr^2}\Phi + \frac{2m}{\hbar^2}\big(E - U(r)\big)\Phi = 0. \tag{10}$$

This equation is mathematically identical to the Schrödinger equation for the one-dimensional case [27]. However, a boundary condition should be taken into account that at $r = 0$ the function Φ should go to zero, because otherwise the wave function $\Psi = \frac{\Phi}{r}$ would become infinite. Then, to solve the equations (10) finite at $r = 0$ and converting to zero at $r \to \infty$ we can take

$$\Phi = B\sin(kr)\text{at} \quad r \le a,$$

$$\Phi = C\exp(-\alpha r) \quad \text{at} \quad r > a,$$

$$k = \sqrt{\frac{2m(E+U_0)}{\hbar^2}}, \quad \alpha = \sqrt{-\frac{2mE}{\hbar^2}} \tag{11}$$

(as we are considering a particle inside a potential well, we should assume $E < 0$). Thus, the problem was reduced to a problem of electron motion in a one-dimensional potential well, so the energy levels are defined in the same way. The only difference is that now it is necessary to discard the states with even wave functions only leaving the states with odd wave functions.

The fundamental difference between a one-dimensional potential well and a three-dimensional potential wells is that for a one-dimensional well, there always exists at least one eigenvalue of energy with an even wave function. In the case of a spherically symmetric rectangular well, this may not be the case. From the equation $k^2 + \alpha^2 = \frac{2m}{\hbar^2}U_0$ it is clear that if

$$\frac{2mU_0a^2}{\hbar^2} < \left(\frac{\pi}{2}\right)^2, \quad \text{i.e.} \quad U_0 < \frac{\pi^2\hbar^2}{8ma^2}, \tag{12}$$

then the curve set by the equation $\operatorname{tg}\left(\frac{ka}{2}\right) = -\frac{k}{\alpha}$ will never intersect the circle set by the equation $k^2 + \alpha^2 = \frac{2m}{\hbar^2}U_0$. This means that if condition (12) is satisfied, no discrete energy spectrum level will appear in the potential well because the well power is too low.

Substituting the values of the fundamental constants — $\hbar \cong 1 \cdot 10^{-34}$ J, the electron mass $m = 9 \cdot 10^{-31}$ kg, for the radii of the first, second, third coordination sphere $a_1 = 0.35 \cdot 10^{-9}$ m, $a_2 = 0.7 \cdot 10^{-9}$ m, $a_3 = 1.05 \cdot 10^{-9}$ m, we obtain $U_0(a_1) = 0.7$ eV,respectively $U_0(a_2) = 0.18$ eV, $U_0(a_3) = 0.08$ eV. From physical grounds it follows that a perfect local order can propagate starting from the first coordination sphere, and the minimum radius of the potential well is equal to the interatomic distance $a_1 = 0.35 \cdot 10^{-9}$ m. For an electron localized state to occur in a potential well with a minimum radius, the depth of the potential well of the produced nanocrystal should be approximately equal to 1 eV.

The principal condition for the production of fluctuons [16] is the mobility of the atomic system ensuring its potential rapid rearrangement and production of fluctuations with a minor change of the thermodynamic potential. Such situation is implemented near the first kind phase-transition point from amorphous to crystalline state, where the densities of thermodynamic potentials of both structures become close. With high interphase surface energy inherent to the solid-phase transformation, the fluctuating formation of the crystalline phase region leads to a significant change in the thermodynamic potential and can be unstable (non-equilibrium). However, in case of an attraction of the conduction electron to the crystal phase region, the electron can be localized in it. If the related decrease in electron energy exceeds the increase in thermodynamic potential energy during the formation of the crystalline phase region, then the fluctuation stabilizes. The resulting thermodynamically stable formation of a region of a new phase with an electron localized in it (non-equilibrium if an electron is not available) is called a phason [16]. As shown in Sect. 1, the formation of the nanodomain of the crystal phase can also occur through quantum tunneling stimulated by inelastic deformation, so under such conditions localization is also possible of the conduction electron and phason production in the crystal phase nanodomain.

In the simplest case, the phason can be described as a spherical nanoparticle of the crystalline phase of R radius, with a potential well corresponding to it, $-U$ in depth, relative to the average potential energy of the amorphous state. The change in the thermodynamic potential $\Delta\Phi$ is expressed by the formula

$$\Delta\Phi(R) = \frac{4}{3}\pi R^3\varphi' + 4\pi R^2\sigma_s + E_e(R),$$

$$E_e(R) = -U + \frac{\hbar^2k^2}{2m_*}, \tag{13}$$

where $E_e(R)$ is the electron energy in a potential well, $-U$ in depth, and m_* is the effective mass of the electron. Here $\varphi' < 0$ is the difference of thermodynamic potentials densities of crystalline and amorphous states, σ_s is the interphase surface energy. The first term in (13) takes into account the decrease of potential Φ of the amorphous state during the phason formation, the second term is the increase of Φ due to the formation of the phase boundary with the additional surface energy σ_s, the third term describes the negative contribution to $\Delta\Phi$ of the energy of localized conduction electron.

Let us make sure that $\Delta\Phi$ falls below zero (and phasons are stable) at U above certain value U_0. The minimum value of $\Delta\Phi$ corresponds to the critical value of R_0 determining the radius of the stable phason. Let us determine the value of R_0. Let us consider that a stable phason corresponds to a bound electron state $E_e(R) < 0$. The kinetic energy of the ground state of an electron in a potential well R in radius can be estimated based on $2R = \lambda = \frac{2\pi}{k}$ where λ is the electron wavelength. Substituting k value in the expression for the electron kinetic energy we can find

$$\frac{\hbar^2 k^2}{2m_*} = \frac{\hbar^2 \pi^2}{2m_* R^2}.$$

Then the formula (13) takes the form

$$\Delta\Phi(R) = \frac{4}{3}\pi R^2 \varphi' + 4\pi R^2 \sigma_s - U + \frac{\hbar^2 \pi^2}{2m_* R^2}. \tag{14}$$

By setting $\partial\Delta\Phi(R)/\partial R = 0$, we can find $R_0^4[4\pi\varphi' m_* R_0 + 8\pi\sigma_s m_*] = \hbar^2\pi^2$. With high interphase surface energy of $4\pi|\varphi'|m_* R_0 \ll 8\pi\sigma_s m_*$ or $|\varphi'|R_0 \ll 2\sigma_s$ we obtain

$$R_0 = \left(\frac{\hbar^2 \pi}{8\sigma_s m_*}\right)^{1/4}. \tag{15}$$

The phason radius (15) is determined by the value of interphase surface energy σ_s, and increasing σ_s causes the radius of the phason to decrease. For values of $\sigma_s = 20\,\mathrm{erg/cm^2}$ [16] and $|\varphi'|R_0 \ll 2\sigma_s$ the critical phason radius makes $R_0 \approx 0.5\,\mathrm{nm}$. Based on physical grounds, it is clear that the minimum radius of the phason is equal to the interatomic distance $a_1 = 0.35 \cdot 10^{-9}\,\mathrm{m}$, so the $R_0 \approx 0.5\,\mathrm{nm}$ value of the phason critical radius is quite reasonable.

Let us now consider the conditions for the phason formation. The phason is formed at such values of the system parameters at which the value of $\Delta\Phi(R)$ becomes negative, i.e., at $\Delta\Phi(R_0) = 0$. If condition $\varphi' R_0 \ll 2\sigma_s$ of (14) is satisfied, neglecting the first term in the right-hand side, we obtain

$$4\pi R_0^2 \sigma_s - U_0 + \frac{\hbar^2 \pi^2}{2m_* R_0^2} = 0. \tag{16}$$

The (16) formula determines the critical value U_0 of the potential well depth at which the phason is formed. Using (16), (15), we obtain

$$U_0 = 8\pi\sigma_s R_0^2 = (2\pi)^{3/2}\sqrt{\frac{\hbar^2 \sigma_s}{m_*}}. \tag{17}$$

With the above values of σ_s and $\varphi' R_0 \ll 2\sigma_s$, the value of U_0 makes roughly 1 eV. Since the estimates of the phason radius coincide in terms of the order of magnitude with the experimentally detected values of the nanocrystal radius [2–5], it is reasonable to assume that the nanocrystal formation mechanism in metallic glass is the phason formation mechanism.

3. A non-equilibrium transition model from amorphous structure to nanocrystalline structure

The absence of long-range order in the mutual arrangement of atoms is a defining feature of amorphous bodies [29], so the description of their complex structure based on long-range order parameter only, like for the crystals, is insufficient. The order of body atoms positions regardless of the types of the latter is called topological. The local order of an atom is determined by the configuration of its first coordination sphere, i.e. coordination polyhedron. Experiments prove that in metallic glasses with strong topological disorder, a rather perfect local order is often realized, accurate to elastic distortions, coinciding with the local order in stable or metastable crystalline bodies of the same composition [2,3,30].

The structure of amorphous bodies obtained in works [2,3,30] is well described by the conglomerate model [31]. In this model, the structure of a solid amorphous body consists of atom clusters with a certain short range ordering that are immersed in a medium with a less perfect ordering, such as a system of spheres with random dense packing. Further development of the conglomerate model was a concept of polycluster — a solid consisting of locally regular clusters (LRC) being populations of atoms with a perfect local order [24]. An essential feature of the polycluster is that the cluster boundaries are two-dimensional, of monolayer thickness. Unstable amorphous structures relaxing to the polycluster have regions with imperfect local order that are not two- but three-dimensional. That is, the LRC are separated by three-dimensional regions of local disorder. The structure of the intercluster regions does not allow the atoms in them to possess any perfect types of local order providing maximum values of bonding energy. It is this circumstance that allows concluding that the specific free energy in intercluster regions is higher than in locally regular clusters. Due to that, the relaxation of amorphous structures begins with the rearrangement of intercluster regions, in which process the atoms acquire local ordering. At the same time, both finishing building of regular extensions of existing LRC and forming new LRC is possible.

The latter relaxation option is energetically beneficial when the gain in specific free energy of the new cluster exceeds the new intercluster boundary formation energy. Let us assume that the elastic deformation energy in the cluster grows in proportion to the volume, then, once a certain critical size is achieved, further LRC growth becomes less beneficial than the boundary formation accompanied by stress relaxation. In this case, during relaxation, the amorphous body acquires a nanocluster structure given that the initial structure is not very much different from the nanocluster structure.

In order to describe the relaxation of an amorphous (conglomerate) structure into a nanocluster structure, let us introduce a dimensionless quantity characterizing the structural state of the medium that is called the order parameter η. Physically, the order parameter η is a volume fraction of atoms in the LRC with a perfect local order of a certain type, per unit volume. In a completely amorphous state, the order parameter η is equal to zero, and in a nanocluster structure, the order parameter η is equal to one. The process of structural relaxation is viewed as a temporal sequence of structural states of the medium described by the order parameter variation in time, i.e. $\eta = \eta(t)$. We assume that the amorphous state is unstable in terms of η parameter, i.e. it is not separated from the locally stable nanocluster state by an energy barrier. The structural relaxation of a deformable non-equilibrium homogeneous system to a nanocluster structure is described by the Landau–Khalatnikov equation [32] for the order parameter

$$\frac{\partial \eta}{\partial t} = -\alpha_\eta(T, A)(\eta - 1), \tag{18}$$

$$\alpha_\eta(T, A) = \omega_0\left[e^{-\frac{(E_\alpha - \sigma\nu)}{kT}} + \Theta(A - A_c)e^{-\frac{a}{a_{dB}}}\right], \tag{19}$$

where $\alpha_\eta(T, A)$ is the relaxation rate containing two members of different physical nature. The first of them, a „thermal“one, is associated with local thermal fluctuations of the medium, and the second, an „athermal“one, — with tunneling of an atom or a group of atoms in a double-well potential, stimulated by local inelastic deformation of the medium. E_α is the activation energy of atomic rearrangement, σ is the mechanical stress, and ν is the specific volume per atom. $\Theta(A–A_c)$ is the theta-function which is different from zero when the amplitude of infrasound A causes inelastic irreversible deformation. In cyclic deformation of the medium the order parameter increases in proportion to the number of cycles. With the critical number of deformation cycles $n_c \gg 1$, i.e. over the time $t_c = n_c t_{imp} \gg \alpha_\eta^{-1}$, the medium fully relaxes into a nanocluster structure.

The classical phase transition of the first kind gas–liquid is implemented through the formation of a critical nucleus of a new phase directly in the initial phase [32]. However, the formation of nanocrystals in the amorphous phase volume is greatly hampered by additional factors. For example, the density of the crystalline phase differs from that of the amorphous structure, so in order to form a nanocrystal the elastic stresses should be taken into account occurring in both the nanocrystal and in the amorphous matrix. Another important factor preventing the formation of a nanocrystal are the elastic stresses caused by the coherent coupling of crystal and amorphous lattices. Additionally, low room-temperature mobility of atoms in the amorphous state also inhibits the formation of nanocrystals.

So, the elastic energy and other factors significantly increase the energy of nanocrystals formation directly in the amorphous structure, and this heterogeneous state ceases to play the role of the activated complex for the structural transition. Nanocrystals no longer correspond to the lowest energy barrier separating amorphous and crystalline structures. Therefore, in relaxation stimulated by cyclic deformation, to begin with, another homogeneous state is formed from the amorphous state — a nanocluster structure playing the role of a pre-transition state, with nanocrystals to be formed from it afterwards.

To describe the process of non-equilibrium transition of the first kind from amorphous to nanocrystalline structure, let us introduce another dimensionless quantity characterizing the structural state of the medium that is called the order parameter φ. In case of nanostructuring, let us choose as the order parameter the normalized volume fraction of atoms (normalized for the saturation volume fraction) that are located in nanocrystals with perfect local crystal order, per unit volume. In the amorphous state the order parameter is equal to zero, and in the nanocrystalline state the order parameter is equal to one. The structural transformation process is viewed as a temporal sequence of structural states of the medium described by order parameter variation in time, i.e. $\varphi = \varphi(t)$. We assume that in terms of parameter φ the amorphous state is locally stable, being separated by an energy barrier from the locally stable nanocrystalline state located below in terms of free energy. In cyclic deformation, the amorphous structure first relaxes into nanocluster structure in terms of the order parameter η, while the potential energy of local static displacements of atoms (internal energy of inelastic deformation of the medium) is accumulated. Therefore, the energy barrier separating the amorphous and nanocrystalline states by the parameter φ decreases. With critical number of deformation cycles $n_c \gg 1$, the medium goes into a nanocluster state when that energy barrier becomes very small or even equal to zero. The medium becomes unstable with respect to the formation of nanocrystals. The structural relaxation of a deformable non-equilibrium amorphous system to a nanostructured state is described by the Landau–Khalatnikov [32] equation for the order parameter φ

$$\frac{\partial \varphi}{\partial t} = -\alpha_\varphi(T, A)\varphi\left(\varphi - \frac{1}{2}\left[1 - \eta\right]\right)(\varphi - 1), \tag{20}$$

$$\alpha_\varphi(T, A) = \omega_0\left[e^{-\frac{(E_\beta - E_e - \sigma\nu)}{kT}} + \Theta(A - A_c)e^{-\frac{a}{a_{dB}}}\right], \tag{21}$$

where $\alpha_\varphi(T, A)$ is the relaxation rate containing two members of different physical nature. The first of them, a „thermal“one, is associated with local thermal fluctuation of the medium, while the second, an „athermal“one, —

with tunneling of a group of atoms in a double-well potential stimulated by local inelastic deformation of the medium. E_β is activation energy of nanocrystal formation, E_e — the energy of localized conduction electron in local potential well of the nanocrystal. In cyclic deformation of the medium the order parameter η increases in proportion to the number of cycles. With critical number of deformation cycles $n_c \gg 1$, i.e. over the time $t_c = n_c t_{imp}$, the medium fully relaxes into a nanocluster structure $\eta \to 1$, and the energy barrier in terms of parameter φ goes to zero, and nanocrystal formation begins.

As the formation of nanocrystals directly in the amorphous structure is suppressed, the non-equilibrium transition of the first kind has to pass through a pre-transition state — a nanocluster structure, and it is described by two parameters (η, φ) obeying equations (18), (20). From the nanocluster state, the system goes to the nanostructured state through the highest point of the lowest energy barrier in the phase transition coordinate space (η, φ), i.e. the saddle point.

Let us construct a model potential of this phase transition $F(\eta, \varphi)$ in the coordinate space of the phase transition (η, φ). The analysis conducted (18), (20) shows that the transition with two coordinates (η, φ) can be modeled by the following dependence of the model potential

$$F(\eta, \varphi) = \frac{1}{2}\,[\eta - 1]^2 + A(\eta)\varphi^2 + B(\eta)\varphi^3 + \frac{\varphi^4}{4}, \qquad (22)$$

$$A(\eta) = \frac{1}{4}\,[1 + \eta], \quad B(\eta) = -\frac{1}{2}\left[1 + \frac{\eta}{3}\right]. \qquad (23)$$

With $\eta = 0$ factors $A(0) = \frac{1}{4}$, $B(0) = -\frac{1}{2}$, and the simplest potential $F(0, \varphi)$ is double-well and symmetric.

With a fixed parameter $0 \le \eta < 1$, function $F(\eta, \varphi)$ has two minima at $\varphi_1 = 0$, $\varphi_3 = 1$ and one maximum at $\varphi_2 = \frac{1}{2}\,[1-\eta]$. And for

$$\Delta F(\eta, \varphi) = F(\eta, \varphi) - \frac{1}{2}\,[\eta - 1]^2, \quad \Delta F(\eta, \varphi_1) = 0,$$

$$\Delta F(\eta, \varphi_2) = \frac{1}{64}\,[1 - \eta]^3\left[1 + \frac{\eta}{3}\right], \Delta F(\eta, \varphi_3) = -\frac{\eta}{12}. \qquad (24)$$

Thus, with a fixed parameter $0 \le \eta < 1$, function $F(\eta, \varphi)$ can describe the non-equilibrium transition of the first kind from amorphous ($\varphi_1 = 0$) to nanocrystalline state ($\varphi_3 = 1$) through the potential barrier $\Delta F\big(\eta, \varphi_2(\eta)\big)$. Analyzing (22), we can see that function $F(\eta, \varphi)$ in the definition domain of variables $0 \le \eta < 1$, $0 \le \varphi \le 1$ has two minima $(\eta, 0)$, $(\eta, 1)$; one maximum $\big(0, \frac{1}{2}\big)$ and three saddle points (0,0), (0,1), $\big(\eta, \frac{1}{2}\,[1-\eta]\big)$. With $\eta = 1$ the potential barrier $\Delta F\big(\eta, \varphi_2(\eta)\big)$ disappears, point (1,0) becomes an unstable saddle-point, only one minimum (1,1) remains.

From the initial state (0,0), the final state (1,1) can be immediately achieved using, for example, the stoichiometric relation $\eta = \varphi$. But for that, a rather large barrier (almost equal to the maximum) needs to be overcome, as $\Delta F(\eta, \varphi_2)$ can be quite large. This is the classical mechanism of the phase transition of the first kind.

In the transformation amorphous state− nanostructure, the transition barrier is too large due to the elastic energy of nanocrystal formation. But there is another way for that — through the pre-transition state $(\eta \to 1, 0)$. In this state $\varphi_2 = \frac{1}{2}\,[1-\eta]$ tends to zero, so the barrier to be overcome in order to get to the nanostructured state also tends to zero $\Delta F(\eta, \varphi_2) \to 0$. It is much more beneficial to first make a transition along coordinate η from 0 to 1 as this leads to a drastic decrease of barrier $\Delta F(\eta, \varphi_2)$ along coordinate φ. And only afterwards to make the transition along coordinate φ from 0 to 1.

4. Assessment of model parameters and conclusions

Let us estimate the density of the stored potential energy of static displacements of the atoms (inelastic deformation) upon infrasonic exposure of the amorphous film. The film size is known from the experiment [4,5]: its length is $l = 1 \cdot 10^{-2}$ m, $r = 1.6 \cdot 10^{-3}$ m, its thickness is $d = 4 \cdot 10^{-5}$ m. Cyclic mechanical exposure time is 10 min, exposure frequency is 20 Hz. The infrasound tensile displacement amplitude is $A = 4 \cdot 10^{-6}$ m, the relative longitudinal elongation of the film making $\varepsilon = \frac{A}{l} = 4 \cdot 10^{-4}$. It is known that the potential energy density of homogeneous longitudinal elastic deformation is $e = \frac{E}{2}\,\varepsilon^2$, where E is the longitudinal elasticity (Young's modulus). The amorphous film is an alloy with nickel (45 percent) and titanium (41 percent) being its main elements. It is known that $E_{textNi} \approx 220$ GPa, $E_{\mathrm{Ti}} \approx 110$ GPa, their average value being $E \approx 165$ GPa. Given the average value of $E \approx 165$ GPa and relative elongation $\varepsilon = \frac{A}{l} = 4 \cdot 10^{-4}$, the potential energy density makes $e \approx 1.3 \cdot 10^4$ J/m^3.

For clarity, let us calculate the potential energy of homogeneous longitudinal elastic deformation per an atom of the medium. As the concentration of atoms in the medium is approximately equals $0.9 \cdot 10^{29}$ atom/m^3, the energy per atom per deformation cycle equals $e_a \approx 1 \cdot 10^{-6}$ eV/atom. Over the time of infrasound exposure, $n = 12\,000$ deformation cycles occur, so the energy input to the system during the entire exposure time makes $ne_a \approx 1.2 \cdot 10^{-2}$ eV/atom. Obviously, only a small fraction (e.g., 10 percent) of this energy can be converted into the potential energy of inelastic deformation. Therefore, the value of the stored potential energy of inelastic strain makes $0.1ne_a \approx 1.2 \cdot 10^{-3}$ eV/atom, which is less than the kinetic energy of an atom at room temperature $kT_0 \approx 0.024$ eV/atom.

The latent heat of amorphous-crystalline transformation, determined through the temperature difference (differential) of the amorphous and crystalline states of the medium $\Delta T \approx 150$ K [33] is known to make $k\Delta T \approx 0.012$ eV/atom. Experiments proved [4] that over 12,000 cycles of infrasound exposure the heat of the amorphous-crystalline transformation slightly decreases. Therefore, the free energy of the amorphous state with nanocrystals gets slightly lower compared with the free energy of the amorphous state. It is reasonable to assume that the latent heat of amorphous state transformation into nanostructured state is much smaller than $k\Delta T \approx 0.012\,\mathrm{eV/atom}$, for example $0.1k\Delta T \approx 0.0012\,\mathrm{eV/atom}$. Thus, the latent heat of transformation of amorphous state into nanostructured state $0.1k\Delta T \approx 0.0012\,\mathrm{eV/atom}$, is equal, in terms of order of magnitude, to the value of stored potential energy of inelastic deformation $0.1ne_a \approx 1.2 \cdot 10^{-3}\,\mathrm{eV/atom}$.

Therefore, we can conclude that the physical cause and condition for the instability onset of the amorphous state relative to the transition to the nanostructured state (formation of nanocrystals) is the accumulation of potential energy of inelastic deformation to a critical value equal to the latent heat of transformation of the amorphous state into nanostructured state.

The estimated stored potential energy density of inelastic deformation, the identified physical reason and condition of the amorphous state instability allows defining the following physical phenomenon of the non-equilibrium transition to the nanostructured state, as well as possible microscopic mechanisms of relaxation into the nanocluster state and the appearance of nanocrystals.

We assume that on weak infrasound exposure with an amplitude of $1\,\mu$m the medium only experiences dynamic displacements of atoms (vibrations of atoms near equilibrium positions), the medium relaxes slowly due to thermal fluctuations, and the amorphous structure changes weakly. External mechanical work turns into elastic oscillation energy of the medium, and then such elastic energy of vibrations (due to phonon-phonon interactions, phonon scattering on a disordered lattice etc.) turns into the thermal energy of the medium.

On high infrasound exposure with an amplitude of $4\,\mu$m, along with dynamic atomic displacements, the medium experiences static atomic displacements to new equilibrium positions (inelastic deformation), and the rate of amorphous medium relaxation into nanocluster state increases significantly. External mechanical work is transformed both into elastic energy of medium oscillations and is stored as potential energy of static atomic displacements (inelastic deformation). With each successive cycle of mechanical loading, the inelastic deformation of the medium grows, and the amorphous structure of the medium changes progressively (the medium rapidly relaxes into nanocluster state). Accordingly, the stored potential energy of inelastic deformation of the medium consistently increases. With a critical number of infrasonic oscillations the stored potential energy of inelastic deformation achieves a critical value (equal to the value of the latent transformation heat), at which the energy barrier separating the amorphous and nanocrystalline states disappears. The amorphous medium becomes absolutely unstable in terms of nanocrystals formation.

The physical mechanisms of medium relaxation into the nanocluster state and infrasound-stimulated nanocrystals formation at room temperature are as follows. At a reference time, the medium is an amorphous matrix with disordered nanodomains containing free volume, and ordered non-crystalline nanoclusters distributed in it. Upon a single infrasound exposure of the medium, an atom with a free volume, at the nanocluster or nanodomain periphery, located in a double-well potential, or a group of atoms capable of forming two configurations with the energies differing insignificantly, can both experience thermal fluctuation (thermal mechanism) and quantum tunneling to new positions (athermal mechanism). For a structural transformation with local static atomic displacements much smaller than the interatomic distance, the tunneling frequency at room temperature is greater than the thermal hopping frequency. This means that at room temperature or below, the athermal (quantum) inelastic deformation mechanism prevails. As a result of inelastic deformation, the size of the cluster with perfect local order increases, and a new nanocluster with perfect local order can arise from the nanodomain with a free volume.

As the temperature dependence of relaxation and tunnel transition times is different, both mechanisms — thermal and athermal — are implemented in the deformation of metallic glasses. As the temperature goes down, the thermal atomic motion freezes thus leading to an exponential decrease in the relaxation rate according to Arrhenius' law. Consequently, at low temperatures the tunnel transition rate exceeds the relaxation one, and coherent tunneling will occur. With the temperature increase, the relaxation rate increases faster than the tunneling one. Those quantities first become equal and afterwards, the relaxation rate can significantly exceed the tunneling rate. The transition process becomes thermofluctuational. Thus, by changing the temperature we can change the inelastic deformation kinetics of metallic glasses from quantum to classical.

When repeatedly exposed to infrasound, the nanocluster grows and reaches such critical size that its thermal fluctuation — a less likely act of atoms rearrangement into crystalline state — or quantum tunneling — a more likely act of atoms rearrangement — creates a local potential well where the bound conduction electron state occurs. If an electron is attracted to a region of an unstable crystalline phase and localizes in it, an electron energy decrease can compensate for the surface energy of the interphase and a stable formation — a phason — appears. The phason radius is determined by the interphase surface energy σ_s, and the growth of σ_s causes the radius of the phase to decrease. Physically, the phason radius cannot be smaller than the radius of the first coordination sphere. For the values $\sigma_s = 20\,\mathrm{erg/sm^2}$ the critical phason radius is equal to $R_0 \approx 0.5\,\mathrm{nm}$. The critical value of the potential well depth (relative to the average potential energy of the amorphous state), i.e. the condition for phason formation with $R_0 \approx 0.5\,\mathrm{nm}$ makes approximately 1 eV. As the critical phason radius value coincides, in terms of the order of magnitude, with the experimental value of nanocrystal radius [2–5], it is reasonable to assume that the nanocrystal formation mechanism in metallic glass is the phason formation mechanism. When conduction electrons are localized on the resulting nanocrystals, they drive the system energy down, that resulting in stabilization of the state with nanocrystals and formation of locally stable nanostructure (relative to the globally stable crystal structure).

It was proved experimentally [2–5] that the nanocrystals morphology depends on the nanocrystallization method. The difference in the nanocrystals morphology, isotropic when annealed [2,3] and anisotropic in infrasound exposure [4,5] is related to different nanocrystals nucleation and growth mechanisms. In nanocrystallization by high-temperature annealing, nanocrystals nucleation and growth are controlled by thermofluctuational processes. However, at room temperature the contribution of thermofluctuational processes is small, and the inelastic deformation, structural relaxation, and nanocrystallization run by way of quantum transitions in two-level infrared-stimulated nanoscale systems. The anisotropy of the nanocrystal shape is determined by the deformation potential tensor depending on the local structure of the glass in the two-level system site.

Conclusion

Thus, the proposed kinetics model allows formulating the cause, condition and microscopic mechanism of the amorphous-nanostructural transformation in metallic glasses initiated by exposure to infrasound at room temperature and to quantitatively and qualitatively describe the results and regularities proved by experiments.

Funding

The research was performed as part of the state assignment of the Institute of Strength Physics and Materials Science of the Siberian Branch of the Russian Academy of Science (project No.FWRW-2019-0031).

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] M.E. McHenry, M.A. Willard, D.E. Laughlin. Progress in Material Science, **44** (4), 291 (1999).

[2] K. Sudzuki, K. Khudzimori, K. Khasimoto. *Amorfnye Metally* (Metallurgiya, M., 1987) (in Russian)

[3] A.M. Glezer, N.A. Shurygina. *Amorfno-nanokristallicheskiye Splavy* (Fizmatlit, M., 2013) (in Russian)

[4] S. Belyaev, N. Resnina, V. Rubanik, A. Shelyakov, V. Niapomniashchay, E. Ubyivovk, I. Kasatkin. Materi. Lett., **209**, 231 (2017).

[5] S. Belyaev, V. Rubanik jr, N. Resnina, V. Rubanik, E. Ubyivovk, E. Demidova, A. Uzhekina, I. Kasatkin, A. Shelyakov. Mater. Lett., **275**, 128084 (2020).

[6] Y.I. Frenkel. *Vvedeniye v Teoriyu Metallov* (Gos. izd-vo tekhniko-teoret. lit., M.-L., 1950).(in Russian) Y.I. Frenkel. *Kineticheskaya Teoriya Zhidkostey* (Nauka, L., 1975) (in Russian)

[7] W.K. Burton, N. Cabrera, F.C. Frank. Phil. Trans. Roy. Soc., **243**, 299 (1951).

[8] U. Köster, U. Herold. *Crystallization of Metallic Glasses in Topics in Applied Physics: Glassy Metals I,* eds. H.-J. Guntherrodt, H. Beck. (Springer-Verlad, Berlin, 1981), p. 225.

[9] A.L. Greer. Acta Metall., **30**, 171 (1982).

[10] U. Köster, J. Meibhardt, Y. Birol, A. Aronin. Z. Metallkd, **86**, 171 (1995).

[14] P.W. Anderson, B.I. Halperin, C.M. Varma. Philosophical Magazine, **25** (1), 1 (1972).

[12] M.I. Klinger. UFN, **152**, 623 (1987). (in Russian).

[13] Y.Y. Slyadnikov. FTT, **46** (6), 1065 (2004). (in Russian).

[14] R. Pyerls, *Kvantovaya Teoriya Tverdykh Tel* (IIL, M., 1956) (in Russian)

[15] N. Mott, E. Davis. *Elektronnye Protsessy v Nekristallicheskikh Veschestvakh* (Mir, M.,1982) (in Russian)

[16] M.A. Krivoglaz. UFN, **111** (4), 617 (1973). (in Russian).

[17] A.S. Argon. Acta Metall., **27**, 47 (1979).

[18] A.I. Taub, F. Spaepen. Acta Met., **28** (10), 1781 (1980).

[19] M.R.J. Gibbs, J.E. Evetts, J.A. Leake. J. Mater. Sci., **18** (1), 278 (1983).

[20] A.T. Kosilov, V.A. Khonik. Izv. RAN (in Russian) Ser. fizicheskaya, **57** (11), 192 (1993). (in Russian).

[21] T. Egami, V. Vitek. J. Non-Cryst. Sol., **62** (4), 499 (1984).

[22] D.V. Luzgin, V.I. Polkin. Izvestiya Vuzov. (in Russian) Tsvetnaya Metallurgiya, **6**, 71 (2016). (in Russian).

[23] F. Spaepen. Defects in amorphous metals. Les. Houches Lectures XXXV on Physics of Defects, Amsterdam: North Holland Press, 1981, p. 133.

[24] A.S. Bakai. *Poliklasternye amorfnye tela* (Sinteks, Kharkov, 2013)(in Russian)

[25] V.S. Gorskiy. ZTF, **6** (3), 272 (1936).(in Russian)

[26] V.I. Arkharov. *Mezoskopicheskiye Yavleniya v Tverdykh Telakh i ikh Mikrostruktura, v kn. (in Russian) Problemy Sovremennoy Fziki* (Nauka, M., 1980), s. 357, V.I. Arkharov, Izv.(in Russian) AN SSSR, ser. fizicheskaya, **28**, 152 (1964).(in Russian)

[27] L.D. Landau, I.M. Lifshits. *Kvantovaya Mekhanika* (Nauka, M., 1989) (in Russian)

[28] R. Pantel, G. Puthof. *Osnovy Kvantovoy Elektroniki* (Mir, M., 1972) (in Russian)

[29] Dz. Zaiman. *Modeli Besporyadka* (Mir, M., 1982) (in Russian)

[30] J. Hafner. Le Journal de Physique Colloques, **46**, 9 (1985).

[31] A. Ubbelode. *Plavleniye i Kristallicheskaya Struktura* (Mir, M., 1969) (in Russian)

[32] L.D. Landau, I.M. Lifshits. *Fizicheskaya Kinetika* (Nauka, M., 2001) (in Russian)

[33] A.S. Rogachev, S.G Vadchenko, A.S. Schukin, I.D. Kovalev, A.S. Aronin.(in Russian) Pisma v ZTEF, **104**,(10), 740 (2016).(in Russian)