Laser and Particle Beams (2010), *28*, 437–442.
© Cambridge University Press, 2010 0263-0346/10 $20.00
doi:10.1017/S0263034610000443

Laser-assisted metal surface micro- and nanostructurization

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(Received 13 July 2009; Accepted 1 June 2010)

Abstract

The kinetics of the crystallization of metals from the melt under superfast cooling velocities realized in the treatment of the materials by ultrashort laser pulses is investigated. The size distribution function for crystalline phase nuclei is analytically found within the framework of the classical kinetic equation in case of superfast temperature changing. The average number of particles in the crystalline nuclei and relative volume of the crystalline phase are determined as functions of thermodynamic and laser treatment regime parameters. Good agreement is observed with experimental results for ultrashort laser pulses induced micro- and nanostructures production.

Keywords: Kinetic equation; Kinetics of the crystallization; Micro- and nanostructures; Ultrashort laser pulses

INTRODUCTION

Modification of the structure and phase properties of metal and alloy surface layers under superfast cooling velocities are widely used to produce superfine crystalline and amorphous structures with an application of laser pulses of different duration (Breinan *et al.*, 1976; Bacci *et al.*, 1980; Firsov & Golub, 1988; Kanavin *et al.*, 2008; Kokora *et al.*, 1988). Rapid development of ultrashort lasers opens up possibilities for new applications of material precision treatment as compared to conventional lasers (Basov *et al.*, 1999; Bauer *et al.*, 2005; Guo & Vorobyev, 2006; Kanavin *et al.*, 2008). Nanostructuring of metal surface layers makes use of femtosecond laser pulses with the intensities close to the threshold ones, where one observes metal melting in a small volume without any significant ablation.

After the end of the laser pulse, the melt is rapidly crystallized due to the heat propagation into the specimen depth. Due to superfast cooling (10^9 K/s and higher), the size of the produced crystallites may be compared with an interatomic spacing. In this case, an amorphous layer may be formed, if the cooling velocity exceeds the freezing rate. The formation of a superfine crystalline or amorphous surface structures under the action of the laser pulses are called in the literature "laser glazing" (Bacci *et al.*, 1980; Breinan *et al.*, 1976; Firsov & Golub, 1988; Kanavin *et al.*, 2008; Kokora *et al.*, 1988).

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The dynamics of the melt under the action of a femtosecond laser pulse on the metal has yet to be adequately studied (Bauer *et al.*, 2005; Guo & Vorobyev, 2006). A detailed description of surface nano-modification morphology for the use of femtosecond laser pulses is given in Guo and Vorobyev (2006). It is shown that at laser pulse duration, ~ 65 fs, and low laser intensity, $\sim 5 \times 10^{12}$ W/cm^2, one can produce different structures (pores, rings, convexities) of the size $\sim 40-100$ nm. The morphology of nanostructures formed at the metal surface under the action of a laser pulse depends on both the laser intensity and the number of irradiating pulses, and needs further investigation.

In case of a femtosecond pulse, the material heating and melting processes take place under essentially nonlinear and non-equilibrium conditions. However, the kinetics of the melt cooling after the action of a supershort laser pulse is defined, finally, by the velocity of heat propagation into the material depth, and for the metals this velocity ranges around $10^{13}-10^{15}$ K/s. So, the time of cooling is larger than 10^{-12} s. This means that one can make use of a heat model applied to a classical description of the crystallization kinetics.

The most universal approach to the description of the kinetics of the cooling process under the laser action is based on the investigation of the distribution function $Z(n, t)$ for the numbers of the crystalline phase nuclei contained n atoms at the given time moment t (Christian, 1978; Kanavin *et al.*, 2008). The distribution function $Z(n, t)$ being known, one can define the average size of crystallites formed under the cooling, and the relative volume of a crystalline phase.

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In this paper, an analytical solution of a kinetic equation for the distribution function $Z(n, t)$ is considered specific features of metal crystallization in the alloys under superfast cooling velocity. The problem of growth of a superfine crystal phase of micro- and nanosize under superfast cooling is analyzed analytically and numerically.

THEORETICAL MODEL

Formulation of the Problem

The thermodynamic condition of the phase transition of the first kind for crystallization process is (Christian, 1978):

$$\Phi_S(T_0) < \Phi_l(T),\ T < T_0, \tag{1}$$

where Φ_s and Φ_l are specific free energies for solid (s) and liquid (l) phases, respectively, and T_0 is the threshold temperature of the crystallization.

The classic theory assumes that phase transition of the first kind is realized by way of thermofluctuational formation of new location of atoms (Christian, 1978). Nuclei can only grow if there is a thermodynamic stimulus of the transformation defined by the sum of energy variations caused by the appearance of the new phase nuclei. The specific free energy change caused by the new phase nuclei generation for the cooling process can be written as follows:

$$\Delta\Phi = \Delta\Phi^{\upsilon} + \Delta\Phi^{S},$$
$$\Delta\Phi^{S} = \chi\sigma n^{2/3},\ \Delta\Phi^{\upsilon} = \Delta f n,\ \Delta f = \Delta h\frac{T_0 - T(t)}{T(t)}, \tag{2}$$

where indexes υ and s denotes the volume and surface terms, respectively, Δh is the latent heat of the phase transition, σ is the phase boundary surface energy, and χ is the form-factor of the nuclei.

The nuclei distribution function $Z(n, t)$ satisfies the normalizing condition

$$\int_0^{\infty} Z(n,t)dn = N, \tag{3}$$

N is the complete number of the atoms in the volume. The kinetic equation for $Z(n, t)$ takes into account both their fluctuations and the decrease or increase in the dimension of new phase nuclei determined by thermodynamics, and can be written as follows (Christian, 1978):

$$\frac{\partial Z(n,t)}{\partial t} = \nu n^{2/3}\exp\left(-\frac{U}{kT(t)}\right) \times \left\{\frac{\partial^2 Z}{\partial n^2} + \frac{1}{kT(t)}\frac{\partial}{\partial n}\left[\frac{\partial\Delta\Phi(n)}{\partial n}Z(n,t)\right]\right\}, \tag{4}$$

where U is an activation energy of the phase transition, i.e., the electron energy difference due to crossing of the phase boundary, ν — Debye frequency, k — Boltzmann constant. The first term on the right-hand side of Eq. (4) describes the diffusion of the initial nuclei distribution and the second one describes the migration of this distribution in the particle number space (Breinan *et al.*, 1976). Both processes are of the thermofluctuational origin and are droved by the overcooling at the melt-solid boundary. Taking into account the volume term one can obtain the following relationship

$$\frac{\partial\Delta\Phi^{\upsilon}}{\partial n} = -\Delta h\frac{T_0 - T(t)}{T_0}. \tag{5}$$

As initial condition to Eq. (4) we use the system completeness, i.e., the condition of particle conservation:

$$Z(n, 0) = 2N\delta(n-1),\ \int_1^{\infty}\delta(n-1)dn = \frac{1}{2}. \tag{6}$$

The boundary conditions are as follows:

$$Z(n,t)|_{n=1} = N,\ Z(n\to\infty, t) = 0. \tag{7}$$

The second equation in (7) excludes from the consideration the case of very large nuclei of the new phase (boundary condition of the Bekker-Doering's theory). This statement is especially valid for short duration of the cooling taking place during the laser action where large nuclei have no time to grow.

A superfast cooling also implies that from the very beginning a sufficient amount of crystalline nuclei of the over-critical size are available, i.e., all the over-critical nuclei are automatically included into the system. Indeed, in the analysis of the crystallization, the attention is given to the volume and surface terms in Eq. (2), which determine the radius r_c (or the number of particles n_c) of critical nucleous corresponding to the maximum of free energy variation. In case of spherical nucleous formation.

$$r_c(t) = \frac{2\sigma}{\Delta h}\frac{T_0}{T_0 - T(t)}. \tag{8}$$

It follows from (8) that in the case of superfast cooling (taking into account that a decrease in the laser pulse duration increases the temperature change rate) subcritical nuclei become over-critical in a short period of time. Hence, the superfast cooling kinetics is determined not so much by nucleation process as by the growth of the existing nuclei.

The metallographic investigations (Kokora *et al.*, 1988) shows that crystalline nuclei produced after superfast cooling of metal melt have a nidle-dendrite form. Therefore, we consider the existence of nuclei of a plate form as primary. Then the pre-exponential factor in (4) is proportional to n, and not to the value $n^{2/3}$. The latter gives a possibility to obtain the solution to Eq. (4) in explicit form (Kanavin *et al.*, 2008).

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Solution to Kinetic Equation

Eq. (4) can be written after the assumptions mentioned above as follows:

$$\frac{\partial Z}{\partial t} = n\nu \exp\left(-\frac{U}{kT(t)}\right)\left[\frac{\partial^2 Z}{\partial n^2} - \frac{\Delta h}{kT(t)}\frac{T_0 - T(t)}{T_0}\frac{\partial Z}{\partial n}\right]. \quad (9)$$

Let us make a change of variables

$$\vartheta(t) = \frac{\Delta h}{kT_0}\frac{T_0 - T(t)}{T(t)}, \upsilon(t) = \frac{\partial T}{\partial t}, \frac{\partial Z}{\partial t} = \frac{\partial Z}{\partial \vartheta}\frac{\partial \vartheta}{\partial t}, \quad (10)$$

where υ is the cooling rate. Then (9) can be presented in the form:

$$\frac{\partial Z}{\partial \vartheta} = nD_0(\vartheta)\exp\left(-\frac{U}{\Delta h}\vartheta\right)\left[\frac{\partial^2 Z(\vartheta, n)}{\partial n^2} - \vartheta\frac{\partial Z}{\partial n}\right]$$

$$D_0(\vartheta) = \frac{\Delta h\nu}{\upsilon(\vartheta)k}\left[\vartheta + \frac{\Delta h}{kT_0}\right]^2 \exp\left(-\frac{U}{kT_0}\right). \quad (11)$$

We will solve Eq. (11) using operator method applied to Schrödinger equation (Kanavin *et al.*, 2008). It is necessary to find an evolution operator of the system $\hat{S}$:

$$Z_f = \hat{S}Z_{in}, Z_{in} = Z(n,\vartheta = 0), Z_f = Z(n, \vartheta \to \infty), \quad (12)$$

where Z_{in} and Z_f are the initial and final distribution functions. The estimation of the evolution operator is reduced to the solution to a set of differential equations relative to the parameters α и β (Kanavin *et al.*, 2008):

$$\alpha(t) = \nu \exp[-\beta(t)]\int_0^t \exp\left[\beta(t) - \frac{U}{kT(\tau)}\right]d\tau$$

$$\beta(t) = -\frac{\Delta h\nu}{kT_0}\int_0^t \frac{T_0 - T(\tau)}{T(\tau)}\exp\left(-\frac{U}{kT(\tau)}\right)d\tau. \quad (13)$$

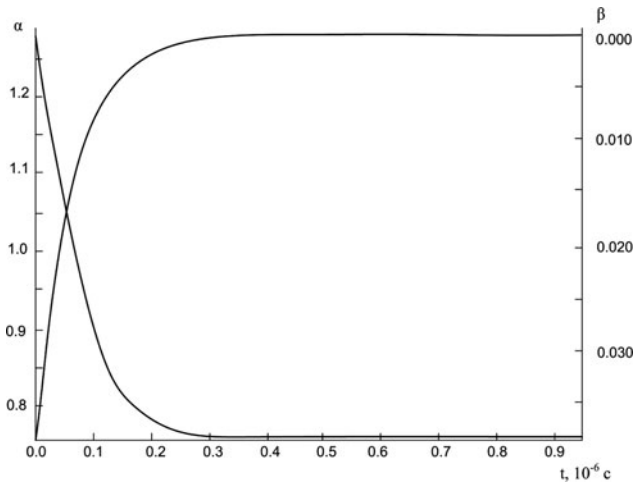


Fig. 1. Time dependences of parameters $\alpha(t)$ and $\beta(t)$ for Fe at a linear fashion of cooling ($\tau = 5$ μs, $U/kT_0 = 17.1$).

The final form of alpha and beta can be found knowing the mode of the temperature variation during cooling. It is determined by the regime of laser treatment and by the thermodynamic properties of the material.

RESULTS AND DISCUSSION

Distribution Function

To determine $\alpha(t)$ and $\beta(t)$ we consider the most widespread time dependences of the temperature:

$$T(t) = \begin{cases} T_0 - \varepsilon t, 0 \le t \le T_0/\varepsilon \\ T_0\left(\frac{\tau}{t}\right)^m, \tau < t < \infty \\ T_0 \exp(-pt), 0 \le t < \infty \end{cases}, \quad (14)$$

where ε, m, and p are the functions of the laser beam parameters. The parameters $\alpha(t)$ and $\beta(t)$ for the linear mode of cooling are presented in Figure 1. It is clear that α and β reach their stationary values within the linear mode of cooling. The explicit form of the evolution operator allows one to analyze its action onto the initial distribution function. If we restrict to the initial designation function of the crystalline phase particle numbers can be written in the following integral form:

$$Z_f(\alpha, \beta, n) = \frac{\sqrt{n}}{\alpha}\int_0^\infty d\xi Z_{in}\left(\frac{1}{4}\xi^2 e^\beta\right)\exp\left(-\frac{4n + \xi^2}{4\alpha}\right) \times I_1\left(\xi\frac{\sqrt{n}}{\alpha}\right), \quad (15)$$

I_1 is the modified Bessel function of the first kind.

The explicit form of the initial distribution function is determined along with other factors by the cooling rate, for example, if

$$Z_{in} = Z_0\delta(n - n_0), \quad (16)$$

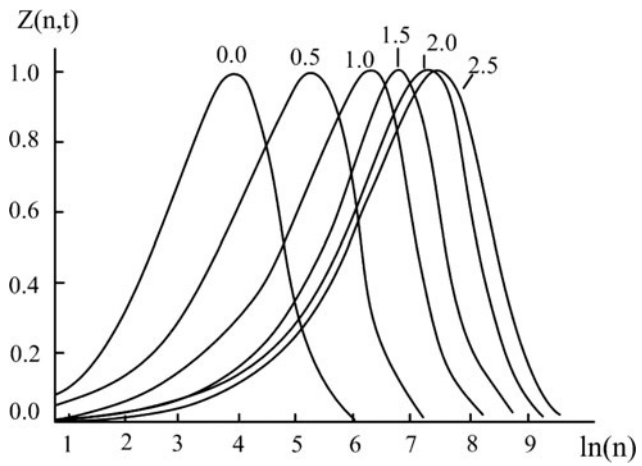


Fig. 2. Dependence of the distribution function $Z(n,t)$ on the particle number n at different instants of time ($U/kT_0 = 15$).

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then for the linear and power mode of the cooling rate the following expression is valid

$$Z_f = \left(\frac{n}{\alpha^2}e^{-\beta}\right)^{3/4}\exp\left[-\frac{\left(\sqrt{n}-\sqrt{n_0}e^{-\beta/2}\right)}{\alpha}\right]. \quad (17)$$

Figure 2 shows the calculation results for the time evolution of the distribution function $Z(n, t)$. It is evident that this function drifts significantly at the initial period of cooling and does not vary practically until the end of cooling.

Determination of the average Number of Particles and Volume of the Crystallized Phase

Expression (15) can be shown to satisfy the conservation condition (6). As a matter of fact,

$$\int_0^\infty Z_f(\alpha, \beta, n)dn = \int_0^\infty \frac{\sqrt{n}}{\alpha}dn \int_0^\infty d\xi Z_{in}\left(\frac{1}{4}\xi^2 e^{\beta}\right) \times \exp\left(-\frac{4n+\xi^2}{4\alpha}\right)I_1\left(\xi\frac{\sqrt{n}}{\alpha}\right) = Ne^{\beta}. \quad (18)$$

Actually, this is the number of new phase particles at $t \to \infty$. If $t \to 0$ parameter $\beta \to 0$ and, hence, relationship (3) is valid. Then, the relative variation of the crystalline phase volume can be found explicitly:

$$\frac{\Delta V}{V} = \frac{V_{in}-V_f}{V_{in}} = \frac{N\Delta V - Ne^{\beta}\Delta V}{N\Delta V} = 1 - e^{\beta}. \quad (19)$$

Formula (19) corresponds to phenomenological Kolmogorov-Avraamy equation, which describes the crystallization kinetics in the approximation of the constant nucleation velocities (Christian, 1978):

$$\frac{\Delta V}{V} = 1 - \exp(-Kt). \quad (20)$$

In (20), the crystalline volume fraction is developed at time t and constant temperature. K and n are suitable parameters: n is determined by the nucleation process and should be an integer from 1 to 4, K is defined by the nuclei growth and is time dependent. The explicit form of alpha and beta as functions of the thermodynamic parameters of the substance allows one to determine $\Delta V/V$.

Table 1. *Characteristics of metals*

Metals	T_0, K	U, eV	Δh,kJ/mole
Fe	1812	7.87	13.8
Al	933.5	5.98	10.75
Ni	1726	7.63	17.6

The average size of nuclei crystallized or average number of atoms in new formations is another important feature. Using the definition

$$\langle n\rangle = \frac{1}{N}\int_0^{\bar{n}} Z(n, t)ndn, \quad (21)$$

where $\langle n\rangle$ is a sufficiently large (but limited) number of particles. Taking into account that the transition in the integration limits from $\bar{n}$ to ∞ it is possible at high cooling rates to estimate the average number of particles in the crystallite in the explicit form:

$$\langle n\rangle = \frac{3\alpha}{2}\left[\alpha - 1 - \frac{1}{\alpha}\ln\left(1-\frac{\alpha}{3}\right)\right]. \quad (22)$$

It should be noted that $\langle n\rangle$ is completely determined by the value α, i.e., by the diffusion mode of the initial distribution of the particle numbers, and $\Delta V/V$ depends on β only, i.e., on the distribution function drift in the space of particle numbers. The values of $\langle n\rangle$ and $\Delta V/V$ depend on the metal thermodynamic parameters (Eq. (13)). In Table 1, are listed important thermodynamic parameters of metals (Fe, Al, Ni). The results of calculation of the values $\Delta V/V$ and $\langle n\rangle$ for exponential fashion of cooling are presented in Figures 3 and 4. Figure 3 shows the volume e^{β} *versus* the cooling rate (Kanavin *et al.*, 2008). The function $\exp(\beta) \to 0$ and the melt crystallizes practically completely ($\Delta V/V \to 1$) at small υ. For example, it is $\upsilon \sim 1.8 \times 10^6$ K/s for Fe, $\upsilon \sim 2.8 \times 10^5$ K/s for Al, $\upsilon \sim 1.73 \times 10^5$ K/s for Ni. Increase in υ leads to partial crystallization of the melt volume ($\exp(\beta) \to 1$ at $\Delta V/V \to 0$ in asymptotic limit $t \to \infty$). In this case, we may assume that a residual fraction of the melt tends to amorphization (solidified liquid). So, in case of Fe at $\upsilon \sim 1.8 \times 10^9$ K/s approximately 0.996 of the

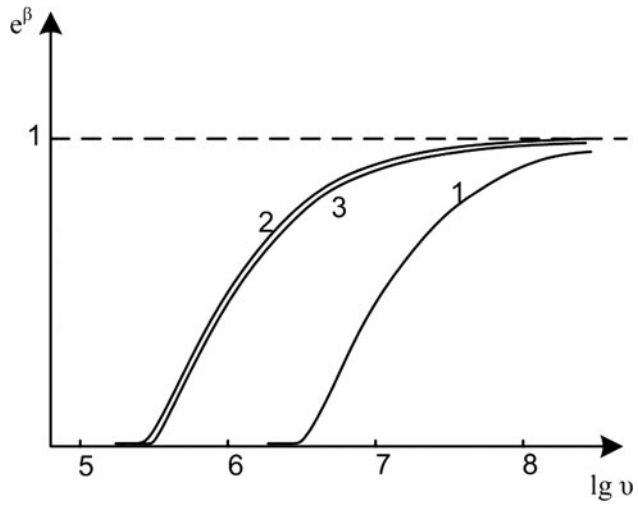


Fig. 3. Calculated dependence of the relative portion of the new phase volume on the cooling rate: **1** – Fe, **2** – Ni, **3** – Al.

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melt volume have to be amorphous. For Al and Ni, the same amorphization fraction must be reached at $\upsilon \sim 9.3 \times 10^8$ K/s and $\upsilon \sim 7.3 \times 10^7$ K/s, respectively.

At the same time, $\langle n \rangle$ varies rather substantially up to two orders of magnitude at small increase of the cooling rate (Kanavin *et al.*, 2008). So, $\langle n \rangle$ varies within the interval from 537 to 14 particles in Fe nucleous at the variation of υ from 4.6×10^6 K/s to 4.7×10^6 K/s; $\langle n \rangle$ varies from 1243 to 3 for Al at $\upsilon = (4.58–4.7) \times 10^5$ K/s; $\langle n \rangle$ varies from 462 to 2 for Ni at $\upsilon = (4.34–4.43) \times 10^5$ K/s. In rapid quenching structure for rapid cool steels has been produced by melt sputtering technique (Firsov & Golub, 1988). It has been shown that the mean nucleous particle number in a structure (called η-phase) was about 80 (the crystallite size about 40–100 nm). Such sizes of nanostructures were observed in Guo and Vorobyev (2006) under the metal treatment by femtosecond laser pulses.

It should be pointed out that a detailed calculation and comparison of the results with experimental data are difficult because of the absence of the precise values of thermodynamic parameters. Moreover, under the action of the laser femtosecond pulses the cooling rate make come up to 10^{15} K/s, and the structure of the frozen melt, the presence and the sizes of the corresponding nanostructures will be defined by the dynamics of the processes taking place in the melt under cooling (Kanavin *et al.*, 2008).

Amorphysation Criterion

A thin amorphous layer (1500 Å) on the pure Al surface has been produced by ruby laser pulse irradiation with the intensity 10^8 W/cm^2 and pulse duration 15 ns (Bacci *et al.*, 1980). The cooling rate was about 10^{10} K/s. In this case, the thickness of the amorphous layer is determined by the melting front velocity (about 10 m/s). A similar regime was used in Breinan *et al.* (1976) for the Fe amorphisation. The cooling rate was about 10^9 K/s above the critical value for Fe (υ_c about 5×10^6 K/s). In case where $\upsilon \sim 5 \times 10^4$ K/s $<< \upsilon_c$ an amorphous layer in Fe was not observed (Breinan *et al.*, 1976).

In other words, there is a critical value of a cooling rate υ_{cr} for each type of metals or alloys, so that we may suppose that $\upsilon \geq \upsilon_{cr}$ is a cooling rate criterion of amorphisation.

Realization of the critical cooling rate is a kinetic condition of amorphisation. On the other hand, the rate of heat removal out of the melt into the bulk of material during the cooling is determined by the thermophysical properties of the melt, and can limit the cooling rate. In case of pulse laser action, the maximum value of the cooling rate is equal to

$$\upsilon_{\max} = \frac{Aq}{\lambda\sqrt{k/\pi\tau}}, \tag{23}$$

where A — is a absorbability, λ — is a heat conductivity of the material, q and τ — intensity and pulse duration of the laser radiation (Kokora *et al.*, 1988).

It was shown in Kanavin *et al.* (2008) that :

$$\upsilon_{cr} = \frac{\nu \Delta h(1 - c_0)}{U \ln P} \exp\left(-\frac{U}{kT_0}\right), \tag{24}$$

where $c_0 \cong 0{,}95$, $U/kT_0 > 5$.

The possibility of amorphisation is determined by laser beam parameters (q and τ), and by thermodynamic material ones (Δh, U, ν, T_0). If we use (23) and (24) we can determine the optimum laser amorphisation regime.

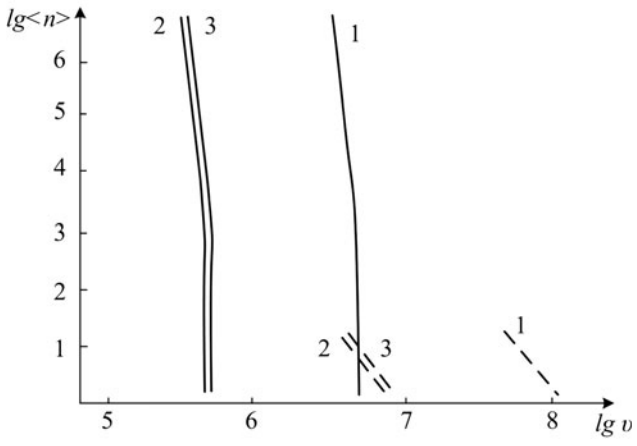


Fig. 4. Calculated dependence of an average number of particles $\langle n \rangle$ in new phase volume on cooling: **1** – Fe, **2** – Ni, **3** – Al. Dash curve is for amorphisation, solid curve is for crystallization.

CONCLUSIONS

The crystallization kinetics of metals from the melt under superfast cooling velocities realized in the treatment of the materials by ultrashort laser pulses has been studied. An explicit solution to kinetic equation for the size distribution function of crystalline phase nuclei at the fast cooling of the melt was analyzed analytically and numerically. Use has been made of physical preconditions for the crystallization process practically realized at superfast cooling: the existence of a sufficiently large number of crystal nuclei of super-critical size and a plate-type shape of the nuclei. An average size of crystallites has been defined, as well as the volume fraction of crystallized phase. The amorphisation criterion for the melt cooling velocity is determined.

The presented expressions for the crystal nuclei size and the new phase volume have been used to describe the experiments on micro- and nanostructuring of the metal surface layers under the action of femtosecond laser pulses. A detailed comparison with the experiment assumes that one should include into consideration the processes describing the dynamics of the melt motion at the beginning of the cooling process.

https://doi.org/10.1017/S0263034610000443 Published online by Cambridge University Press

ACKNOWLEDGMENTS

The work was supported by the RAS Program "Basics of fundamental research of nanotechnologies and nanomaterials," RAS Program "Physical and technological investigation of semiconductor lasers aimed at reaching maximum parameters," and the Russian Foundation for Basic Research, Grant 09-02-00615-a, and RF Ministry of Education and Science Grant 2009-1.1-122-052-025.

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