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Modeling of the kinetics of laser hardening of a titanium alloy

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One of the key mechanisms resulting in the hardening of titanium alloy products subjected to compression by a shock wave resulting from the action of a short and powerful laser pulse is considered. It was shown that the induced jump in the dislocation density at the grain boundary temporarily shifts the equilibrium towards grains of smaller radius. The grain kinetics model is studied in the dimensional space using the famous Lifshitz–Slezov method plus a small generalization of it. The dynamics of the average grain size was calculated and an asymptotic grain size distribution function was obtained as a result. The dynamic equations take into account the entropy of dislocations. The results of processing of experimental data on residual stresses on the sample surface after its processing by a single pulse are also presented. Based on the residual stresses it is possible to estimate the maximum temperature that was reached during plastic deformations.

Keywords: one-dimensional defects, dislocations, entropy, laser peening.

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Introduction

Laser peening is currently one of the most promising and widely used methods of hardening products made of steel, aluminum and titanium alloys abroad. Hardening of materials by peening with a shock wave initiated by laser radiation (LSP, Laser Shock Peening) [1–3] is a complex surface treatment process that allows creating compressive stresses in various materials not only on the surface (several microns), but also at depths up to 1–2 mm.

The laser hardening process has been used in the aerospace industry to increase the fatigue strength of compressor blades made of titanium alloys [4–6]. An increase in the fatigue strength threshold of the product is associated with the induction of compressive residual stresses. Grain grinding also results in hardening. Pulse duration, spot diameter on the sample, laser beam energy, and mechanical properties of the material undergoing LSP are the most important factors determining the magnitude of residual stresses on the surface, as well as the stress distribution over the sample depth.

The description of the LSP surface treatment technology for various products contains some details specific to the laser hardening process (Fig. 1): the treated surface of the product is covered with a layer that is opaque to laser radiation with a low evaporation temperature, for example, black paint, aluminum foil or sticky vinyl tape; a wide transparent water jet with a thickness of 2–3 mm is formed on top of this layer.

The energy of the laser pulse is absorbed by the opaque layer, which results in its heating, evaporation, and ionization of „sacrificial“ layer, which is bounded on one side by the surface of the product, and by a water flow prevents plasma expansion on the other side (Fig. 1).

The limiting medium is one of the key factors in the hardening process, since most of the energy of the formed plasma is released into the free space around the target without limiting medium. The retaining medium contributes to the formation of a powerful shock wave, which ensures the strengthening of the material. Incident laser radiation does not result in heating of the metal surface, since it does not completely destroy the absorbing layer, which has low thermal conductivity, and energy from the plasma is not transferred to the metal surface, which could lead to surface damage.

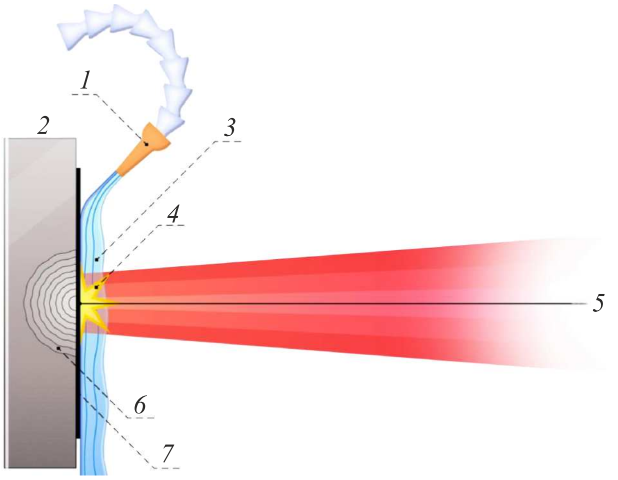

Figure 1. Laser hardening operation diagram: *1* — water nozzle, *2* — sample, *3* — laminar flow, *4* — plasma, *5* — laser radiation, *6* — shock wave, *7* — absorbing layer.

1. Measurement of stresses in the near-surface layer before and after laser treatment

Parameters of the neodymium-activated phosphate glass laser system Nd^{3+}: pulse duration from 10 to 25 ns, laser pulse energy up to 50 J with a nominally rectangular spatial profile of laser radiation, the spot size on the sample varies from 5 to 10 mm depending on the experimental task. The power density of the laser beam on the surface to be treated can be varied in the range of $3-10\,\mathrm{GW/cm^2}$. So, high-pressure plasma is the shock wave source, water is the inertial retaining layer, adhesive PVC tape is the ablation layer. The shock wave (SW) creates a high-pressure zone of the order of $3-10$ GPa, which implements the regime of plastic deformations with the increase of temperature primarily along grain boundaries. Thermal expansion followed by cooling results in residual stresses, which are detected by X-ray diffraction analysis and electron spectroscopy in the metal surface layer before and after laser treatment.

We worked with samples made of titanium alloy, in which black vinyl tape with a rubber adhesive layer was used as an absorbing coating. The thickness of the adhesive tape was $150\,\mu$m. Experiments were conducted that showed that the use of vinyl black tape is the most technologically suitable option.

The initial level of residual stresses in the near-surface layer of the working sample was preliminarily measured. Reference zones with size of 15×15 mm were cut out by electric discharge machining after processing the samples with laser radiation in various modes and then these references zones were studied using X-ray diffractometer. Macrostresses were measured using Dron-8 X-ray diffractometer produced by NPP „Burevestnik“. The value of residual macrostresses was determined using the X-ray line of Ti (10.4), for which the Wolf–Bragg angle is equal to 130.88. The Poisson ratio of 0.32 and the Young's modulus of 112 GPa, were used in the calculation. The measurements showed that the internal stresses in the near-surface layer for the initial sample are 273 MPa. The induced residual stresses are 376 MPa when the sample is treated with a pulse with a power density of $4.9\,\mathrm{GW/cm^2}$. The induced residual stresses reached 436 MPa in a sample processed by a single laser pulse with a power density of $5.2\,\mathrm{GW/cm^2}$.

Since the induced residual stresses were of the order of 400 MPa, and the coefficient of thermal expansion of titanium is $9 \cdot 10^{-6}\,\mathrm{K}^{-1}$, these data can be used to estimate the heating of the sample to $\Delta T = 400\,\mathrm{K}$ from the room temperature. Information about the temperature of the grain shell of the order of 700 K is used for calculation of the intergranular diffusion coefficient.

Since laser hardening is accompanied by a change of the grain size, we will analyze the causes and consequences of grain size dynamics in the main part of this paper. We will first point out that physical processes occur on completely different time scales: laser pulses — tens of nanoseconds, pressure pulses behind the SW front — microseconds, and diffusion processes along grain boundaries — seconds. Therefore, the grain size kinetics is a process „spreaded“ over time, which does not end after the attenuation of SW. The dynamics of grain sizes is associated with the entropy in a number of studies [7].

2. Dislocations as a source of residual entropy that does not disappear at zero temperature

Entropy is an important concept that follows energy in importance. Entropy is a measure of disorder. Disorder, like the internal energy of atoms, increases with temperature because of the increase of thermal vibrations of lattice atoms; the spectrum of such phonon vibrations is limited by the Debye temperature Θ. The entropy in the case of $T \gg \Theta$ in terms of one atom is $s = k[4 + 3\ln\frac{T}{\Theta}]$, where k is the Boltzmann constant. The entropy of thermal vibrations generally inherits the properties of entropy in the gas aggregate state, except for the introduction of an upper bound on the spectrum of thermal vibrations in accordance with $3N\nu$ vibrational degrees of freedom. Many metals in reality are polycrystals. And each single crystal (or grain) can have a structure that is far from ideal. New aspects of disorder arise from lattice defects. Zero-dimensional defects of the crystal lattice are the most common. Their density increases with the increase of temperature. The most important ones for further analysis are one-dimensional defects called dislocations. In this case, the ideal order is distorted either along the edge dislocation due to an extra atomic half-plane, or along the centerline of the screw dislocation, when a virtual cut is made along it and one side of the crystal is shifted by a lattice step. The occurrence of such defects results in additional lattice stresses, and they cannot be eliminated by moving a single atom. Since the case of such defects is a property of the crystal geometry, let us agree to call such defects topological for convenience, since their formation and disappearance are associated with the movement of a large group of atoms. The dimension of dislocation defects is equal to one, since the properties of crystal ordering and lattice periodicity are broken at the core line. The dislocation deformation of a crystal has the following property from the point of view of elasticity theory: the elastic displacement vector receives a finite increment equal to the Burgers vector when traversing any closed contour spanning the dislocation line. The main property of dislocations is that their stress field affects neighboring dislocations. As a consequence, the stress value for the plasticity threshold on the surface of a single crystal exceeds the plasticity threshold inside the crystal structure [8]. The interaction of dislocations reduces the shear stress inside the crystal by several times the value of the stress at the boundary. And it becomes stronger as the radius of the single crystal decreases! The effect of grain size on the strength of polycrystalline metals is given by the well-known Hall–Petch ratio [9.10]:

$$\sigma_A = \sigma_0 + k_{HP} D^{-1/2}. \tag{1}$$

Here σ_A — yield stress (plastic yield stress), σ_0 — stress to overcome friction to dislocation motion in the absence of obstacles, k_{HP} — slope of the Hall and Petch curve (H–P), D — grain size. These values are $\sigma_0 = 78.45\,\text{MPa}$, $k = 0.40\,\text{MN/m}^{3/2}$ for titanium in a hexagonal package. This behavior is bounded from below by the grain size $d_c = 10 - 50\,\text{nm}$.

According to Lie's theory [11], the yield strength is the stress required to overcome an obstacle in the form of forests of dislocations near grain boundaries. In this case, the yield stress is the collective effect of a set of dislocations that creates a threshold stress preventing the movement of dislocations. For metals

$$\tau = \tau_0 + \alpha G b \sqrt{\rho}, \tag{2}$$

τ_0 — initial friction stress, ρ — dislocation density, α of the order of 0.4, G — shear modulus, b — Burgers vector($2.57 \cdot 10^{-10}\,\text{m}$). It follows from experimental observations that the dislocation density is inversely proportional to the grain diameter D. The number of dislocations during deformation is proportional to the number of protrusions at the grain boundary or the area of grain boundaries per unit volume (we assume that the density of protrusions per unit area weakly depends on the grain dimeter). Then $\rho \propto S_v$, but S_v is inversely proportional to the grain diameter ($S_v = 3/D$). If the grain is considered round and large enough, then the angle ϑ between dislocations at the boundary is $\vartheta = d/D$ (d — distance between dislocations). On the other hand, the angle of rotation of the grain boundary surface at a step of one dislocation is given by the ratio between the lattice pitch b (the Burgers vector and the actual height of the protrusion) and the distance between dislocations $\vartheta = b/d$ and the dislocation density is inversely proportional to the average square of the distances between them $\rho d^2 = 1$:

$$\rho \propto \frac{1}{bD}. \tag{3}$$

Substituting (3) in (2) results in Hall–Petch formula, where the constant k_{HP} is of the order $\alpha G\sqrt{b}$. It should be noted that $G\sqrt{b} = 0.6\,\text{MN/m}^{3/2}$. The value $Gb\sqrt{\rho} = Gb/d = 2G\frac{1}{2}\frac{\partial u_y}{\partial x} = 2Gu_{xy} = \sigma_{xy}$ defines the off-diagonal terms of the strain tensor. The relation $bD = d^2 = \rho^{-1}$, which follows from two definitions of grain surface curvature, sets the condition for the equilibrium of grain size and dislocation density. If it is distorted, the system evolves to meet this condition, for example, if the dislocation density has changed due to external interference.

The polycrystalline structure is a significant factor for the properties of titanium alloys considered in this problem statement. The properties of a single crystal have been studied for a long time. Data of the equation of state [12] are known (for the spherical part of the stress tensor), and in the case of the use of off-diagonal part of the stress tensor, the peculiarities of sliding of single crystals along the sliding planes of are known [13]. The required threshold stresses depend on the choice of plane and diameter of the single crystal. There are many degrees of freedom associated with the packing of grains and their size in the case of a polycrystalline structure. Therefore, the equation of state alone is not sufficient, since it corresponds only to volumetric compression. Off-diagonal elements of the stress tensor have a threshold above which plastic deformations begin, and the Young's modulus works below. Here, the choice of parameters of the Johnson–Cook model, which describes strain hardening as a function of plastic strain and plastic strain rate, comes to the fore. The stress of plastic deformation (flow or extrusion) increases as the strain rate increases

$$Y = \sigma_y \left(1 + C \ln\left|\frac{\dot{\varepsilon}}{\dot{\varepsilon}_0}\right|\right), \quad \sigma_y = A + B\varepsilon^{0.5}. \tag{4}$$

The value σ_y for titanium alloy VT6 is determined by the constant [14] $A = 900\,\text{MPa}$, $B = 509\,\text{MPa}$, $C = 0.03$. The dependence of the constant A on the dislocation density in the sample at a given phase state of matter is given by the formula (2). $A = 300\,\text{MPa}$ for pure titanium.

The superposition of deformation on the crystal structure of the grain leads to a shift of dislocations along it by a certain distance. The equation relating the relative amount of strain and dislocation shear distance is known as „Taylor–Orowan's equation". The plastic shear strain ε is proportional to the dislocation density ρ and the Burgers vector b:

$$\varepsilon = k\rho b\bar{l}. \tag{5}$$

Here $\bar{l}$ — the average dislocation path. It should be borne in mind that the strain does not coincide with the direction of motion of dislocations, which introduces a correction factor k of the order of one into the formula. Obviously, the average displacement of $\bar{l}$ is limited by the distance between the dislocations of $1/\sqrt{\rho}$ and the grain size. A formula describing the increase of dislocation density under rapid deformations can be obtained by differentiating the Taylor–Orowan's equation (υ — dislocation rate):

$$\dot{\rho} = \frac{\dot{\varepsilon}}{bl} - \frac{\rho\upsilon}{l}. \tag{6}$$

The density of dislocations increases from the center of the grain to its boundaries, and dislocations on the grain surface can disappear, annihilate with porosity or other dislocations with the release of stored energy, stall at the energy barrier, or gradually collapse through the diffusion of surface atoms along the grain boundaries. The dislocation should overcome the Peierls–Nabarro potential barrier for movement [15]. Its shape is close to sinusoidal. It is possible to show using a dimensionless model of a physical pendulum with the Hamiltonian $H = \frac{1}{2}\dot{x}^2 - \omega_0^2 \cos x$ that the separatrix of the finite motion corresponds to the energy of the system $H/\omega_0^2 = 1$. The motion is finite in the case of lower energies, otherwise it is infinite. Analysis in elliptic functions shows that the complexity of the dislocation oscillation spectrum increases as $\ln\sqrt{\frac{32}{|H/\omega_0^2-1|}}$ in the neighborhood of the separatriss. An increase of the number of excited harmonic oscillations changes the entropy of dislocations, which is directly related to the temperature of the dislocation subsystem. The nonlinear dependence of entropy, and hence free energy, on proximity to the separatriss makes dislocation dynamics a complex function of stored energy, and interaction with phonons complements it with the viscous friction effect [16]. In view of the fact that the entropy of moving dislocations requires a strict definition, which is currently absent, we will limit ourselves in this paper to the influence of the geometric entropy of topological defects on the grain size kinetics. Analysis of kinetics taking into account the entropy of dislocations as a function of the temperature of the dislocation subsystem — a topic for future research. The field of deformations of a moving dislocation was considered earlier in the paper in Ref. [17] and the review in Ref. [18], in which the field nature of the equations of motion of dislocations was substantiated and the effective mass of dislocations was introduced.

The effect of the rate of plastic deformations on the free energy value was considered earlier in Ref. [19]. The point of slope change corresponds to the plastic deformation threshold when the slope of the stress curve changes on the graph of stress values due to deformation. The activation energy of plastic deformation turned out to be proportional to the natural logarithm of the strain rate $\dot{\varepsilon}$ in units of the characteristic scale $\dot{\varepsilon}_0 = 10^7\,\mathrm{s}^{-1}$. The stress value oscillates as a function of increasing plastic deformation at low strain rates $\dot{\varepsilon} = 10^{-2}{-}10^{-3}\,\mathrm{s}^{-1}$ [20]. The oscillation period is related to grain size. Plastic deformations occur in the form of sliding along grain boundaries or sliding dislocations along sliding planes. The accumulation of dislocations at grain boundaries affects the strength of grains and the sliding of grains along their boundaries. The dislocation energy is about $Ub = 2\,\mathrm{eV}$ per one link of the dislocation core.

The metal grain boundary is a collection of a large number of dislocations covering the grain surface. The metal phase is the same on both sides of the interface, but the orientation of the crystallographic axes is different. This orientation defect can serve as a source of new dislocations during rapid compression. Any impurity inside the grain can also result in the generation of dislocations under heavy load. The energy of the grain boundary is assumed to be equal to the total energy of all dislocations per unit surface. A single area of the grain surface has the following energy [15]:

$$E_{gb}(\vartheta) = E_0\vartheta(A - \ln\vartheta),$$
$$E_0 = \frac{Gb}{4\pi(1-\nu)}. \qquad (7)$$

Here we introduce the angle $\vartheta = \frac{b}{d}$, which is equal to the ratio of the length of the Burgers vector b to the distance between dislocations d on the grain surface of a given size D. The surface energy sums up the contribution of stresses generated by dislocations. Grain boundary energy measurements for titanium [21] at 1100°C give a value of $1\,\mathrm{J/m^2}$ (this is 0.4 eV/atom), while the formation of a single vacancy in α-titanium requires $U = 1.27\,\mathrm{eV}$ [22]. We emphasize that we are talking about the surface at the grain interface, and not at the open boundary. It is necessary to overcome the activation energy associated with the periodic potential along the interface for the occurrence of diffusion along grain boundaries. As the grain boundary temperature increases from room temperature to 720 K, the activation energy decreases due to an increase of the entropy of atoms $\Delta G = U - sT$ in the heated lattice. Measurements of the activation energy also showed its dependence on the grain size. For instance, the change of the typical grain size in titanium from coarse-grained to submicron size ($\oslash = 0.8\,\mu\mathrm{m}$) [23] reduces the activation energy of self-diffusion along grain boundaries from 140 to 74 kJ/mol. The dependence of the activation energy on the grain size emphasizes the fact that the Gibbs free energy is also affected by the entropy of topological defects, i.e., there is also a contribution of the energy of defects forming the grain boundary in addition to the action of heated atoms. Since this surface energy depends on the dislocation density and increases with the decrease of the grain size, the Gibbs free energy (in terms of one atom) also contains a term tied to the entropy of dislocations $\Delta G = U - sT - b^2E_{gb}(\vartheta)$. Rapid deformations caused by the SW result in plastic deformations, where the lattice layers shift instead of a real change in volume, giving rise to dislocations. Using the variable ϑ, the free energy can be represented as the differential of two variables $dF(T,\vartheta) = -s(T)dT - s(\vartheta)d\vartheta$, the first term is the thermal entropy of atoms $s(T)$, the second term by analogy is the entropy of dislocations $s(\vartheta) = -\left(\frac{\partial F_{gb}}{\partial\vartheta}\right)_T = E_0b^2(A - 1 - \ln\vartheta) > 0$. Entropy is positive, so $\vartheta < \vartheta_{\max} \approx 1/3$. Here $b^2E_{gb}(\vartheta)$ is the sum of the surface energy of one-dimensional defects in terms of an atom (7).

For further analysis, it is necessary to estimate the temperature at the grain boundary. The heating of the metal during compression as well as the residual heating is small because the SW in our case is weak, on the order of 1−10 GPa. The estimate obtained by Zeldovich in [24] for SW heating at 25 GPa for aluminum gives the heating value relative to room temperature at $\Delta T = 331\,\mathrm{K}$, and for isentropic discharge, the residual heating is $\Delta T = 134\,\mathrm{K}$. Estimates for titanium in the case of SW of $p = 10\,\mathrm{GPa}$ can be obtained from the equation

$$p = K(1-x) + p_{T0}\left(\frac{1}{x}\right)^{\Gamma_0+1},$$
$$x = \frac{V}{V_0} = 0.909,\ p_{T0} = \frac{\Gamma_0 c_V T_0}{V_0} = 0.77\,\mathrm{GPa},\ K = 100\,\mathrm{GPa}. \qquad (8)$$

The heating by SW in titanium is equal to $\Delta T = 33\,\mathrm{K}$; it is related to taking into account the pressure of thermal vibrations of lattice atoms. The residual heating for isentropic unloading, excluding plastic deformations, is equal to $\Delta T = 0.02\,\mathrm{K}$.

The deviator of the stress tensor results in plastic deformations inside and along grain boundaries at pressures above the threshold. Fast loads cause the creation of dislocations and their movement along the grain. A potential barrier at the grain boundary results in a release of the kinetic energy of dislocations near the grain surface. Also, a certain number of dislocations when reaching the grain boundaries annihilate with dislocations that came to the boundaries from the other side of the adjacent grain. This energy is the source of heat. Also, the heat source is the friction of the grains with each other. As shown above, the heating of the metal due to spherical compressive stresses is small, while the heating of the grain surface due to plastic deformations will be more significant.

In the case of a flat SW, the spherical part of the stress tensor is equal to 2/3 of the pressure amplitude, and the third part falls on the deviator part of the stresses, which is responsible for shear deformations and plastic deformations. The rate of plastic deformations is of the order $\dot{\varepsilon}_0 = 10^7\,\mathrm{s}^{-1}$ under the impact of SW. The antiphase wave dampens the pressure wave after 3μ s after reflection from the back wall of the sample. $\dot{\varepsilon}_0 \Delta t = 0.3$ is much larger than the elastic strain — $6\,\mathrm{GPa}/K = 0.06$. The estimate of the energy accumulated in a grain of $100\,\mu\mathrm{m}$ $(V = 10^{-6}\,\mathrm{cm}^3)$ is $E = (3\,\mathrm{GPa} \cdot 10^{-12}\,\mathrm{m}^3) \cdot 0.3 = 10^{-3}\mathrm{J}$. This energy reserve leads to heating by $E/(c_V V) = 420\,\mathrm{K}$. The specific (volume) heat capacity of titanium of $c_V = 2.36\,\mathrm{J/(cm^3{\cdot}K)}$ and the grain volume are taken into account here.

If the dislocation density is $\rho = 10^{11}/\mathrm{cm}^2$, then a grain with a diameter of $D = 100\,\mu\mathrm{m}$ will store energy of the order $2.2\,\mathrm{eV}{\cdot}10^{11+4} \cdot 10^{-12}/b = 1.4 \cdot 10^{-6}\,\mathrm{J}$. Heating due to plastic deformations occurs from the grain energy boundary. Dislocation energy is brought here and heat is released during grain-boundary friction (and viscous friction against dislocation motion gives a relatively small volume heat capacity per grain): $W = \alpha b D^2 \rho \upsilon^2 = 0.1\,\mathrm{W}$, $\alpha = 10^{-5}\,\mathrm{Pa{\cdot}s}$, $\upsilon = 10^3\,\mathrm{m/s}$. The temperature along a grain of 100 microns (μm) practically equalizes (Fig. 2, 3) after a time on the order of $100\,\mu\mathrm{s}$, the temperature at the grain boundary will be about $700\,\mathrm{K}$. The estimation of the heating of the grain shell, given in Sec. 1, based on data on induced residual stresses and the coefficient of thermal expansion of titanium. The heating reaches $\Delta T = 400\,\mathrm{K}$ from the initial room temperature according to the estimation.

We do not take into account the contribution of vacancies to the total entropy here. This choice is due to the fact that the number of vacancies is determined by the ratio of the vacancy birth energy to temperature. In turn, the intense generation of dislocations is caused by rapid deformation at the SW front. A whole group of atoms should be shifted to permit the formation of a dislocation, so the number of dislocations depends not so much on temperature as on the shape and size of grains and the rate of plastic deformation. The energy stored in dislocations in terms of one atomic plane is of the order of $2.2\,\mathrm{eV}$. This energy is stored in the stresses of the crystal lattice, i.e., in disturbances of the lattice order of the structure, not only locally in the core of the dislocation, but also distributed over space. The energy dependence has a logarithmic singularity cut off by the distance to neighboring dislocations. This type of non-local order disturbance is weakly sensitive to temperature variations, but it is sensitive to the density of such one-dimensional defects. Since the dislocation density determines the curvature of the surface at the boundary, the modification of the free energy along the grain boundary is tied to a new order parameter — the angle of curvature ϑ. The variation of the free energy of the grain boundary at a constant temperature as a function of the surface curvature determines the entropy value in the Gibbs free energy $-\frac{\Delta G}{T} = \frac{-U(T)+s(T)T+E_{gb}(\vartheta)}{T}$ in terms of one atom of the surface. Let the grain diameter be a. On its surface with the lattice step b equal to the Burgers vector will be of the order of $n = a^2/b^2$ atoms. A change of the number of atoms by one unit causes a change of size by $da = \frac{b^2}{2a}$. The characteristic time and probability of activation of the process is determined by the Debye frequency $\upsilon_D = 7.9 \cdot 10^{+12}\,\mathrm{s}^{-1}$ and the activation energy ΔG in accordance with the logic of papers [25,26]. The value $D_s^{gb} = b^2 \upsilon_D \exp(-\Delta G/T)$ is associated with the self-diffusion coefficient over grain boundaries. The pre-exponential multiplier is defined with an accuracy of a constant of the order of one. Since there are two flows: to and from the grain, and the difference in flows is attributable to the difference in entropy between the actual grain size a and the effective size calculated from the dislocation density $a_d(t) = \frac{1}{b\rho(t)}$, the dynamics of the grain size will be determined by an equation of the form $(\vartheta = b/d = d/a = \sqrt{b/a})$:

$$\dot{a} = -\frac{b^2 \upsilon_D}{a}\left\{\exp\left(-\frac{U_0}{kT} + \frac{E_0 b^2}{kT}\sqrt{\frac{b}{a_d}}\ln\sqrt{\frac{a_d c}{b}}\right)\right.$$
$$\left. - \exp\left(-\frac{U_0}{kT} + \frac{E_0 b^2}{kT}\sqrt{\frac{b}{a}}\ln\sqrt{\frac{a c}{b}}\right)\right\}. \tag{9}$$

Here $U_0 = U - sT$, and the constant A from (7) is redefined as $A = \ln\sqrt{c}$; also, it should be noted that $\vartheta = b/d = d/a = \sqrt{b/a}$. Let us introduce the self-diffusion coefficient $D_0 = b^2 \upsilon_D \exp(-U_0/kT)$ and the dimensionless modulation constant $\varepsilon = E_0 b^2/kT$. Then

$$\dot{a} = -\frac{D_0}{a}\left\{\exp\left(\varepsilon\sqrt{\frac{b}{a_d}}\ln\sqrt{\frac{a_d c}{b}}\right) - \exp\left(\varepsilon\sqrt{\frac{b}{a}}\ln\sqrt{\frac{a c}{b}}\right)\right\}. \tag{10}$$

The form of the equation (10) is quite similar to the equation of coalescence kinetics [27]. We neglect dislocation losses at the boundary here for simplification.

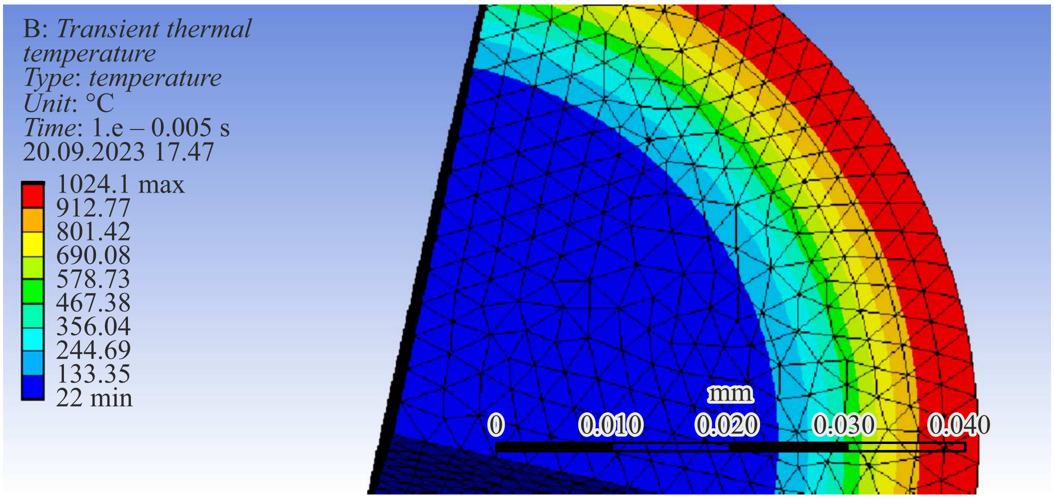

Figure 2. Grain heating by heat flow from plastic deformations after 10 μs.

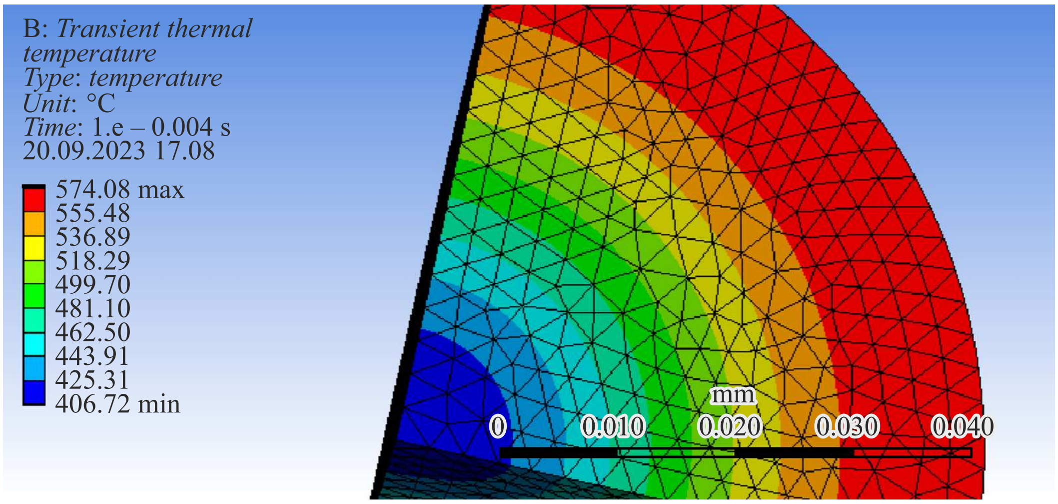

Figure 3. Grain heating by heat flow from plastic deformations after 100 μs.

3. Grain size distribution function

The theory presented here is based on the paper [27,28]. Considering $\upsilon(a) = \frac{da}{dt}$ as the speed of grain movement in the dimensional space, it is possible to introduce the grain size distribution function $f(t, a)$, normalized to the number of particles in unit volume

$$N(t) = \int_0^\infty da\, f(t, a). \tag{11}$$

The distribution function is given by the continuity equation in this space:

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial a}(f\upsilon) = 0. \tag{12}$$

Finally, we note the law of complete conservation of matter, which is expressed by the integral

$$Q = \frac{4\pi}{3}\int_0^\infty a^3 f(t, a)da. \tag{13}$$

Let us introduce a dimensionless quantity through the ratio of a certain characteristic size associated with the dynamics of grain size

$$x(t) = \frac{a_k(t)}{a_k(0)}. \tag{14}$$

Let us assume that in the characteristic size decreases in time, so that and the value of

$$\tau = -3\ln x(t) \tag{15}$$

monotonically increases and can be considered as a new time variable. Let us introduce the following variable as a new dimensionless function for the grain size

$$u = \frac{a}{a_k(t)}. \tag{16}$$

The continuity equation follows from the relation $\varphi(\tau, u)du = f(t, a)da$ in new variables, so that

$$\frac{\partial \varphi}{\partial \tau} + \frac{\partial}{\partial u}(\upsilon\varphi) = 0. \tag{17}$$

And the speed expression in the new variables has the form

$$\upsilon(u) = \frac{du}{d\tau} = -\frac{x}{3\dot{x}}\frac{du}{dt}$$
$$= -\frac{\Delta[\exp(\frac{\hat{\varepsilon}}{\sqrt{xu}}\ln\sqrt{xu\hat{c}}) - \exp(\frac{\hat{\varepsilon}}{\sqrt{z}}\ln\sqrt{z\hat{c}})] - u^2}{3u}, \tag{18}$$

where the following notation for dimensionless quantities is introduced:

$$z = \frac{a_d}{a_k(0)}, \quad \Delta = \frac{D_0}{x\dot{x}a_k^2(0)},$$
$$\hat{\varepsilon} = \varepsilon\sqrt{\frac{b}{a_k(0)}}, \quad \hat{c} = c\frac{a_k(0)}{b}. \tag{19}$$

The main feature of the case under consideration is that the velocity function has two roots in the domain of definition, and they do not constitute a single multiple root, as in the theory of [27]. In the case of a multiple root, the velocity in the entire domain of definition preserves the sign, and the neighborhood of the multiple root sets the rapid decline of the distribution function when approaching a singular point on the left in the form $\exp(-1/(u_0 - u))$. It can be shown in the case of separate roots that one of the first-order poles is integrable in the vicinity of the point where the velocity vanishes. This is the basis of the theoretical construction developed here. The appendix shows how to obtain a general solution of the equation (17) in terms of the integral (A4). The evolution of the solution over time is given in the general form (A7) from application.

$$\varphi(\tau, u) = \frac{\hat{\chi}_0(\tau - g(u))}{|\upsilon(u)|} \tag{20}$$

Since $a^3 = u^3x^3\overline{a}^3(0) = u^3e^{-\tau}\overline{a}^3(0)$, the function $\hat{\chi}_0$ is found from the condition (13) so that the integral over the total amount of matter is preserved. So this is the exponent:

$$\varphi(\tau, u) = \frac{\exp(\tau - g(u))}{|\upsilon(u)|}. \tag{21}$$

Let us consider as an example the velocity function as a square polynomial $\upsilon(u) = -(u - a)(b - u), \quad b > a$. The function $g(u)$ from (A4) is equal to

$$g(u) = -\frac{1}{b-a}\ln\left|\frac{b}{a}\frac{u-a}{b-u}\right|, \ \exp(-g(u)) = \left|\frac{b}{a}\frac{u-a}{b-u}\right|^{\frac{1}{b-a}}. \tag{22}$$

Therefore, the distribution function (21) in the vicinity of the point a has an integrable singularity, since the degree of the bracket $(u - a)^p$ in the denominator is less than one. The point a is an attractor. Another pole is at the point b and this is a singularity. The scope of the definition cannot include it due to divergence. A characteristic that originates from the boundary of the definition area on the side of $b$moves away from it with time. The time τ starts at zero in physics. The coordinate u belongs to the dimension space, so the domain of its definition is one continuous set, including the point of attraction.

The results of calculations are shown in Fig. 4, 5. We monitor the position of the roots of the function on the right side of the formula(18) using the parameter (19) when solving the time problem. The equality $\overline{u} = 1$ is preserved by controlling the position of the right root. Characteristic time required to change the grain size, order of magnitude 10^3 s.

Qualitative confirmation of the results obtained can be found in a number of papers [29–31]. A coarse-grained

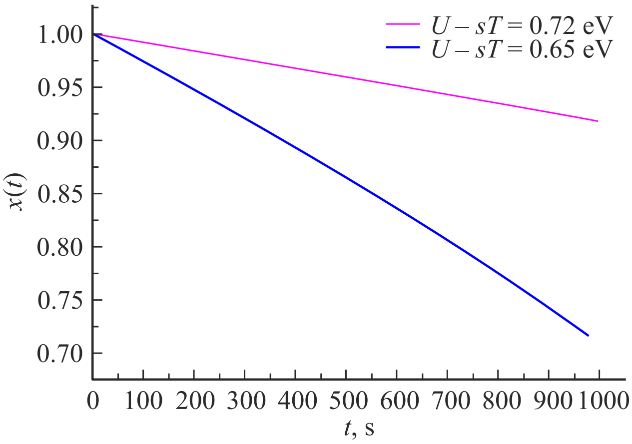

Figure 4. Change in the characteristic grain size for two diffusion activation thresholds.

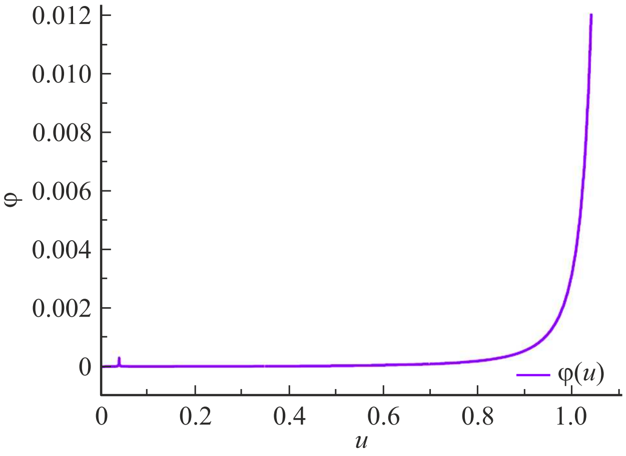

Figure 5. Distribution function in the dimension space $\varphi(u)$, where u - - - normalized size, according to (16), for the case when $U - sT = 0.72$ eV and when $t = 800$ s.

TC17 titanium alloy (Ti-Al-Mo-Cr-Sn-Zr-Fe system) was treated in Ref. [29] under a millimeter layer of water with 15 ns laser pulses with a radiation power density of $F = 9.5\,\mathrm{GW/cm^2}$. The size of initial grains ($43\,\mu$m) was significantly reduced to a submicron size (400 nm) in the near-surface layer of material up to $200\,\mu$m thick. It was found in Ref. [30] that the thickness of the reinforced layer (when measured on a cross-section) reaches 1 mm after treatment with high-power nanosecond laser pulses (15 J per pulse) of Ti-6Al-4V alloy under a thin layer of water ($F = 5\,\mathrm{GW/cm^2}$). Similar size reduction effects are observed for nanometer-sized [31] grains. The initial state of the material studied in this paper is characterized by a submicrocrystalline (SMC) grain structure with an average size of structural elements of 150 nm, and a thin (thickness of the order of $1\,\mu$m) subsurface layer with the initial SMC structure with significantly reduced size to the nanostructured state with the size of the structure elements 75 nm is clearly distinguished after laser treatment of titanium.

Conclusion

The definition of dislocation entropy introduced above corresponds to the classical $s = k\ln\Delta\Gamma$, where $\Delta\Gamma$ is the number of states of the system, and the multiplier k corresponds to the energy capacity of the characteristic state. For instance, in the case of $s(T)$, it is necessary to make the temperature dimensionless dividing it by a given reference T/T_0, then the Boltzmann constant in this temperature scale turns into a constant associated with the energy of the lattice atoms with the reference temperature, $k \to kT_0$. In the case of dislocations, the parameter ϑ is already dimensionless, so the multiplier before the logarithm initially has the energy dimension and is equal to E_0b^2. The density of states depends on the average distance between dislocations. Since the distance between dislocations is bounded from below by the Burgers vector, the entropy at minimal distances vanishes. Since the dislocation density in the grain increases from the middle to the boundary, $\Delta\Gamma$ also changes. Therefore, the movement of dislocations to the grain boundary will be accompanied by the release of thermal energy. If the total energy stored in the dislocation is below the Peierls–Nabarro potential, then there is no translational motion of dislocations, the localized state is transformed into infinite if it is above the Peierls-Nabarro potential. The statistical weight of the state of the system $\Delta\Gamma$ grows near the separatrix according to the Bohr–Sommerfeld rule due to the reduction of the distance between levels in the space of energies. This results in a sharp increase of the entropy near the separatrix. The problem of dislocation entropy as a function of stored energy is solved by calculating the statistical sum of the subsystem state. This is a complex issue that we are putting into a separate study. We plan to study kinetic modeling with these factors in mind in the very near future. In the present paper, we assume that the grain boundary effectively inhibits the flow of dislocations, converting part of the stored energy and entropy into heat. This energy reserve affects the rate of diffusion along grain boundaries in a polycrystalline metal, and a change in the initial density of dislocations at the grain boundary leads to the dynamics of the latter in dimensional space. There is some relation between the grain size and the dislocation density at the boundary in the quasi-equilibrium state. An instantaneous increase of the dislocation density results in a shift of the equilibrium towards grain grinding processes. Characteristic times at which the average grain size in a polycrystalline titanium alloy is transformed were obtained in the paper using the Lifshitz–Slezov method based the theory of phase transitions at the stage of coalescence in the dimensional space, and the form of the distribution function in dimensional space was obtained. The original restriction on multiple roots is removed in the framework of the new analytical construction.

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Conflict of interest

The authors declare that they have no conflict of interest.

Appendix

Let us consider the continuity equation in the dimension space ($\upsilon(u) = \frac{du}{d\tau}$):

$$\frac{\partial\varphi}{\partial\tau} + \frac{\partial}{\partial u}(\upsilon\varphi) = 0, \tag{A1}$$

φ — size distribution function depending on time and coordinate $u = \frac{a}{a_k}$. If we assume that the velocity υ changes very smoothly over time, then it is possible to proceed to the function $\chi = \upsilon\varphi$, whose equation in the adiabatic approximation will be:

$$\frac{\partial\chi}{\partial\tau} + \upsilon\frac{\partial\chi}{\partial u} = 0. \tag{A2}$$

Some features of this equation can be obtained by using the Laplace transform [32]. Let's denote the image of the function $\chi(\tau)$ by the function X (p). It follows from the theory of the Laplace transform that $\chi(\tau - \varsigma) \to e^{-p\varsigma}X(p)$. The equation for images has the form

$$pX + \upsilon\frac{\partial X}{\partial u} = \chi_0(u). \tag{A3}$$

Index zero corresponds to the zero point in time. Let us study the problem on the semi-axis of time $[0, \infty)$. Let us introduce the function

$$g(u) = \int_0^u \frac{dx}{\upsilon(x)}. \tag{A4}$$

A homogeneous equation has a solution of the form

$$X(p, u) = Ce^{-pg(u)}. \tag{A5}$$

Variation of the constant allows finding a complete solution of the equation by substituting

$$C(u) = \int_0^u d\gamma \frac{\chi_0(\gamma)}{\upsilon(\gamma)} e^{pg(\gamma)}. \tag{A6}$$

An inhomogeneous equation is defined by the value of the function at the initial time

$$\chi(\tau, u) = \int_0^u \frac{d\gamma}{\upsilon(\gamma)} \chi_0(\gamma)\delta(\tau + g(\gamma) - g(u)) = \hat{\chi}_0(g(u) - \tau)$$

$$\chi_0(\gamma) = \hat{\chi}_0(g(\gamma)). \tag{A7}$$

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