

PHYSICS OF STRENGTH AND PLASTICITY

On an Excited State of Grain Boundary in Nano- and Submicrocrystals

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Based on the analysis of experimental data concerning the structure and physical and mechanical properties of nano- and submicrocrystals, the authors arrived at the conclusion that the anomalies of these properties are caused by the excitation of grain boundaries which is accompanied by the appearance of a long-range elastic field. With these conditions, it is profitable from the thermodynamic point of view for the system investigated to turn to the heterogeneous state, in which the field of grain boundaries is screened by the interlayer with a lower viscosity. Having the same structure as the rest of a grain, this interlayer possesses a whole set of attributes of a thermodynamic phase. This fact enables us to carry out the standard analysis of the phase equilibrium between this interlayer and a grain core. The results obtained explain the experimental dependence of the volume part of such interlayer on the grain size. From the microscopic point of view, the screening properties of the interlayer are caused by the diffusion of atomic potential relief which results in a decrease of shear viscosity. On the mesoscopic level this system is similar to a mixed state of a superconductor of the second type.

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1. INTRODUCTION

A new class of metal materials with submicrocrystalline (SMC) structure was recently produced and is widely investigated now (see [1]). Unlike nanocrystals (NC) they do not have porosity and a size of their grain is ~ 0.1 micron. As a rule, such a small size is achieved as a result of a big plastic deformation with the subsequent fixing of the initial states of recrystallization. In comparison with usual polycrystals both NC and SMC are characterized by lower values of the Debye temperature and elastic constants, anomalous high values of diffusivity,

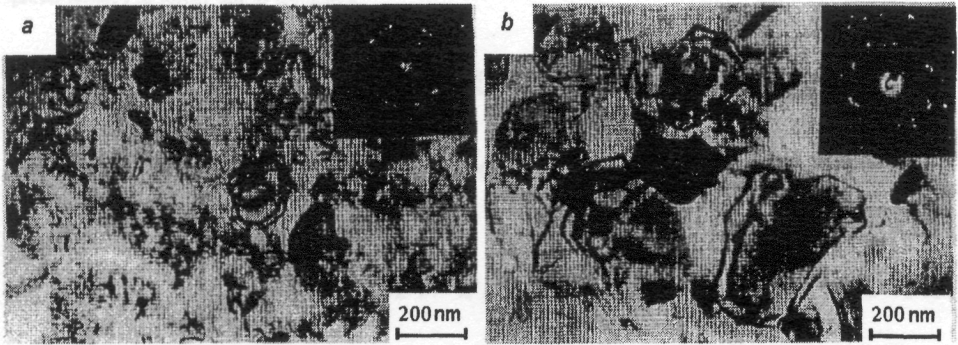


Figure 1. The microstructure observed in DFEM and diffraction patterns of the alloy Al-4% Cu-0.5% Zr: *a*—after deformation $\epsilon = 6$ at room temperature; *b*—after the same deformation and annealing at 413 K for 2 hours [1].

low-temperature superplasticity, *etc.* The fundamental feature of these systems consists in the presence of an anomalous boundary zone which encloses intercrystalline boundaries [2]. When these boundaries have a usual thickness of about interatomic distance, the said zone spans by some tens angstrom, and in this sense it is possible to speak about a grain boundary phase (GBP) [1, 2]. Though its crystalline structure does not differ from a usual one, the atoms of GBP have 'a higher dynamic activity' (see [1] and below), and the anomalous properties of NC and SMC are due to this fact.

The nature of these properties still remains not clear. In this connection in Section 2 the analysis of experimental data is performed which enables us to arrive at the conclusion that the anomalous behaviour of NC and SMC is bound to a growth of mean square displacement of the GBP atoms, which, in turn, is caused by the softening of interatomic bonds. On this basis the thermodynamic stability analysis is performed of the stability of the elastic-stress heterogeneous mixture consisting of GBP and a usual crystalline phase (distribution of elastic fields of such a mixture is discussed in Section 2 and in Appendix). Microscopic nature of GBP is discussed in Section 4 using a concept of a tuneable potential relief [3]. It is shown that similarly to a mixed state of the second type superconductor, the excitation of the grain boundary (GB) in NC and SMC results in formation of the GBP interlayer which screens a long-range field of stresses of the excited GB.

2. ANALYSIS OF EXPERIMENTAL DATA

In Fig. 1, a microstructure and diffraction patterns are shown of the alloy Al-4% Cu-0.5% Zr with a grain size of ~ 0.2 microns. In initial highly deformed state (degree of logarithmic deformation $\epsilon = 6$) con-

TABLE 1.

Average grain size $2R$, μm	Sub-spectrum	Relative integrated intensity (volume fraction of GBP, ρ , corresponds to subspectrum 2)	Effective magnetic field, kOe	Half-width of external spectrum peaks, mm/s
0.12	1	0.78 ± 0.02	331 ± 5	0.32 ± 0.05
	2	0.22 ± 0.02	301 ± 5	0.32 ± 0.05
0.23	1	0.91 ± 0.02	331 ± 5	0.33 ± 0.05
	2	0.09 ± 0.02	301 ± 5	0.54 ± 0.05
0.23	1	0.87 ± 0.02	329 ± 5	0.33 ± 0.05
	2	0.13 ± 0.02	299 ± 5	0.35 ± 0.05
0.26	1	0.93 ± 0.02	331 ± 5	0.34 ± 0.05
	2	0.07 ± 0.02	299 ± 5	0.38 ± 0.05
0.65	1	0.95 ± 0.02	330 ± 5	0.30 ± 0.05
	2	0.05 ± 0.02	302 ± 5	0.40 ± 0.05

tours of an extinction inside grains are clearly seen which indicate considerable elastic stresses near the GB (Fig. 1a). In addition, in the initial state a strip contrast is not present in electron-microscopic photos in a dark field (DFEM). It appears if a sample is subjected to two-hour annealing at 413 K (see Fig. 1b). Extinction contours also disappear and clear kikuchi-lines appear on the diffraction pattern obtained from a separate grain.

The absence of a typical strip contrast in a microphotograph of a deformed sample (see Fig. 1a) proves that its initial state differs from an annealed one in principle. The presence of elastic stresses in the deformed state and appearance of the kikuchi-lines in annealed state denote a strong nonequilibrium character of the deformed state. As in the sample under investigation dislocations and other defects are absent, one can arrive at the conclusion that the nonequilibrium of the system is caused by a state of the GB itself. This conclusion is proved by the data on the investigation of the Debye temperature Θ obtained from a temperature dependence of Mössbauer spectra [1]. It appeared that in an initial state the value of Θ is by $\sim 10\%$ lower than that in the equilibrium state. Taking into account the correlation $u \propto \Theta^{-1}$ of the Debye temperature Θ and a mean square displacement of atoms u [4], we arrive at the conclusion that the atoms have a higher vibration amplitude in the deformed state. Apparently, such an increase of the dynamic activ-

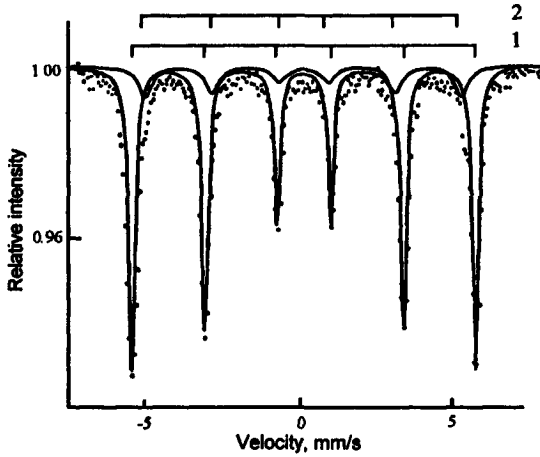


Figure 2. Mössbauer spectrum (isotope ^{57}Co in Cr) of SMC-iron (grain size is 0.22 microns) at room temperature. The points correspond to experimental data, the lines correspond to resolution in components [2].

ity of atoms is caused by a strong non-equilibrium of the system.

The results of Mössbauer studies which have been carried out on pure iron at room temperature are of fundamental importance [2]. As is seen from Fig. 2 and Table 1, Mössbauer spectra represent a superposition of components 1 and 2 which differ significantly in parameters of the electrical and magnetic hyperfine structure. It proves the presence of two different states of iron atoms. The parameters of more intensive component 1 practically coincide with the parameters of coarse-grained $\alpha\text{-Fe}$. The presence of component 2, apparently, is bound to an excited state of atoms near the GB. It is seen from the table that at the grain radius $R \approx 0.06$ micron a fraction of such atoms $p = (22 \pm 2)\%$. Thus, using $p \approx 3d/R$, one can find a half-thickness of the boundary layer $d = (4.4 \pm 0.4)$ nm. So high values of $2d$ in comparison with the atomic scale prove not only the presence of the geometric GB but also the presence of GBP located in the boundary layer of the grain (see Fig. 3). The structural studies do not detect discrepancies in the arrangement of atoms in the initial granular phase (GP) and GBP [1]. However, as it is seen from aforesaid, the atoms of GBP are characterized by increased values of mean square displacement which distinguish GBP from GP.

Thus, the differences of deformed and annealed states of the sample exhibited in Fig. 1, are caused by a non-equilibrium of the grain which is characterized by the presence of GBP. It should be noted that a primary reason for this non-equilibrium is not the massive GBP but geometric GB. It is confirmed by the fact that the excited state of SMC is achieved not at once after cold deformation but only as a result of the subsequent an-

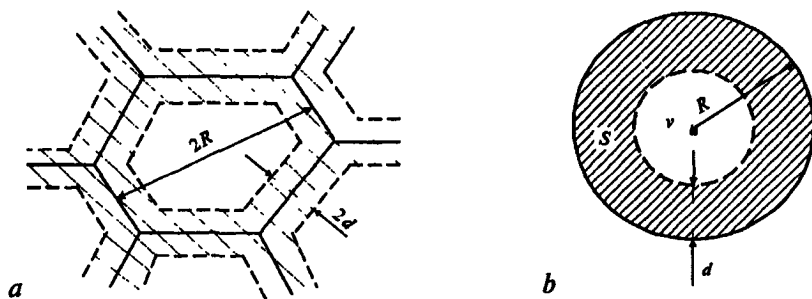


Figure 3. *a*—pattern of phase distribution in NC and SMC (the region of GBP is shaded); *b*—spherical model of phases distribution in a separate grain.

nealing, which, without changing the grain size, results in formation of well-defined GB [1]. In this case such processes as fragmentation, rotation of grains as a whole, dynamic recrystallization, *etc.*, take place. [5]. All of them are caused by an intensive transition of lattice dislocations in the GB. As a result, the GB passes into an excited state. The presence of such state results in formation of a long-range component of the elastic field. According to [6], this component decays with distance x from GB by the law $x^{-1/2}$. As the electron-microscopy studies (see Fig. 1) indicate localisation of the deformation field in a boundary area of the GBP, one can assume that this area causes a screening of the long-range field of the excited GB on distances $d \leq 10$ nm.

It is obvious that such nonequilibrium state should be separated in a phase space from the equilibrium state by a barrier of a finite height Q . There should be the system degradation accompanied by relaxation of elastic stresses at heating to temperature T commensurable with value Q . Really, as it is seen from microphotographs in Fig. 4, the annealing of predeformed SMC-alloy Al-4% Cu-0.5% Zr at 343–353 K results in a slight (20–30%) decrease of the number of extinction contours, and the banding contrast is not revealed at all. It means that in spite of the relaxation of 20–30% of elastic stresses, the GB has remained in the nonequilibrium state. With heating temperature increase to 363 K about a third of grains gets the banding contrast, *i.e.*, they pass into the equilibrium state. Extinction contours due to stresses disappear; however, the growth of grains at this temperature does not occur yet. It begins only at $T = 373$ K when the size of 0.17 microns is attained after 30 min, and 80–90% of grains get the banding contrast after passing into the equilibrium state.

As according to electron-microscopy data the elastic stresses are an essential attribute of the excited state of a grain (see Fig. 1), the data on lattice distortions caused by these stresses are of significant importance. Figure 5 shows the kinetic curves obtained as a result of dilatometric studies of the alloy Al-4% Cu-0.5% Zr. It is seen that in

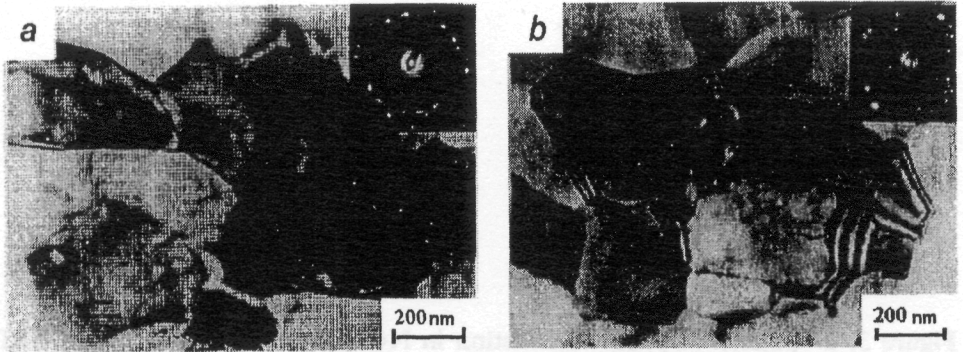


Figure 4. Microstructure and diffraction patterns of the alloy Al-4% Cu-0.5% Zr; *a*—deformation + annealing at 353 K; *b*—deformation + annealing at 363 K.

transition of SMC to the equilibrium state the compression is observed which does not exceed the value $\Delta l/l \sim 2 \cdot 10^{-4}$ (in the case of the constant grain size). As the volume fraction of GBP $p \approx 3d/R$ at a thickness of interlayers $d \leq 10^2 \text{ \AA}$ and radius of grains $R \sim 5 \cdot 10^3 \text{ \AA}$ does not exceed 10%, one can arrive at a conclusion that the strain δ caused by transition of the GBP into the equilibrium state and related to the dilatation by the expression $\Delta l/l = p\delta$ is inappreciable, $\delta \sim 10^{-3}$. Obviously, so small increase of the interatomic distance in GBP can not cause considerable elastic distortions resulting in the strongly developed extinction contour shown in Fig. 1. Indeed, high resolution electron-microscopy studies [7] reveal a lattice deformation in GBP of no less than 3–5% which exceeds the value $\delta \sim 0.1\%$ caused by the lattice expansion by more than one order of magnitude.

Using a time dependence of the dilatation $\Delta l/l$ (see Fig. 5), one can easily estimate the height Q of the barrier which separates equilibrium and nonequilibrium states of the system. To do that, let us approximate the initial section of this dependence by a Debye exponential curve $\exp(-t/\tau)$ where the relaxation time is defined by the Arrhenius relation $\tau \propto \exp(Q/T)$. Using a slope angle of the dependence $\ln \tau(T^{-1})$ obtained, one can find the value of $Q = 4.3 \cdot 10^3 \text{ K}$. It is about half of the activation energy of a boundary self-diffusion process in aluminum [8].

Thus, as a result of developed plastic deformation and preliminary annealing, the lattice dislocations are absorbed by GB which passes into the nonequilibrium state characterized by the presence of a long-range elastic field. In order to prevent the macroscopic contribution to the thermodynamic potential, the interlayer of GBP screening this field is formed near GB. The stability of the elastic-strain heterogeneous structure is caused by the presence of the barrier Q which separates the excited SMC-state from the equilibrium one. The validity of such pattern is confirmed by the following experiment. If we anneal a deformed

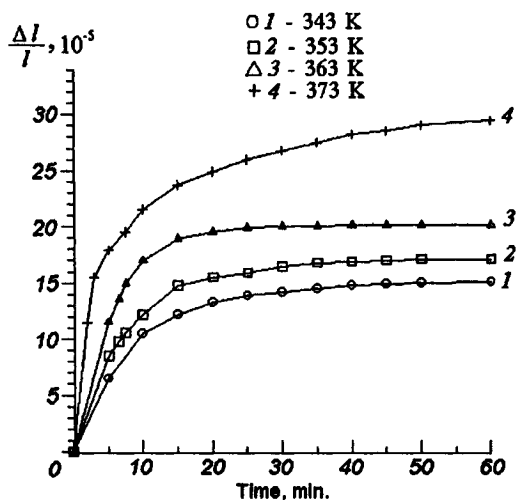


Figure 5. Time dependence of relative compression of an SMC-sample of Al-4% Cu-0.5% Zr during annealing at different temperatures.

sample at 373 K for 30 min and cool it to room temperature, then at repeated heating to 363 K it does not exhibit a typical dilatometric behaviour (see Fig. 5). Apparently, this is due to the fact that during preliminary annealing at 373 K the system overcame the barrier Q and passed into the irreversible equilibrium state.

Existence of GBP is also confirmed by the anomalous behaviour of such physical properties as Curie temperature T_c , saturation magnetization I_s , hysteresis properties of magnetics, heat capacity, *etc.* [1]. In pure Ni, transition to the SMC excited state results in reduction of T_c by 30–40 K, the value of I_s decreases by $\sim 10\%$. As both quantities T_c and I_s are structurally insensitive characteristics, such a behaviour indicates microscopy changes in the case of GBP. Indeed, as it is seen from dilatometric measurements, the formation of GBP results in the growth of interatomic distances which causes a decrease of the overlapping integral and, as a consequence, drop of T_c and I_s .

The softening of SMC elasticity modulus with the decrease of the grain size is of great importance (see Fig. 6) [1]. It can be understood if we consider an elastic medium as a heterogeneous mixture of GP and GBP the former of which has usual elasticity modulus λ_v , and the latter has a reduced value of λ_s . Then in an additive approach which corresponds to summation of the contributions of strain fields, the medium containing the volume fraction p of GBP and the rest $1-p$ of usual GP is characterized by the effective elasticity modulus

$$\lambda^{-1} = (1 - p)\lambda_v^{-1} + p\lambda_s^{-1} \quad \lambda_s < \lambda_v. \quad (1)$$

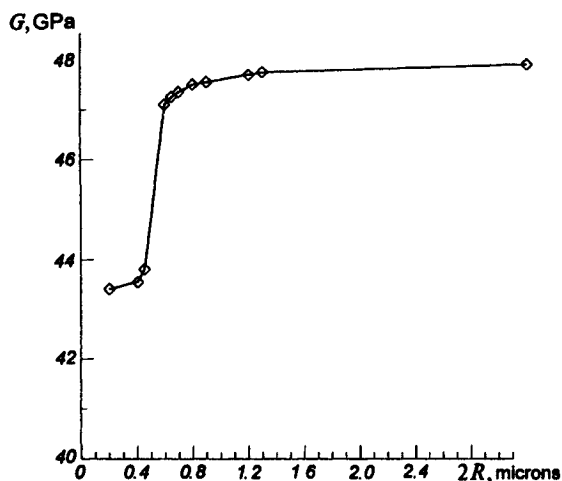


Figure 6. Dependence of SMC-copper shear modulus on the grain size [1].

The estimations of experimental data based on this approach give values of λ_s , which are tens percent of the usual λ_v [1]. For example, in NC palladium $\lambda_s/\lambda_v \approx 0.34$ [1]. Study of SMC-samples of nickel in excited and normal states has shown [9] that the magnetization I_s behaves similarly to λ^{-1} in (1).

Let us present in conclusion other data confirming the presence of GBP in the nonequilibrium state [1]. Figure 7 shows the curves of the strain of a magnesium alloy possessing SMC-structure. In the excited (deformed) state the critical yield stress σ_c is approximately 10% higher than that in the equilibrium state (in steels the increase of σ_c caused by GB excitation reached 50%). Depending on the grain radius R , the value of this stress is approximated by the known Hall-Petch dependence [10]

$$\sigma_c = \sigma_0 + KR^{-1/2}, \quad \sigma_0, K = \text{const.} \quad (2)$$

As it is seen from Fig. 8, this dependence sharply changes its slope K at the characteristic grain size $2R_c \approx 0.5 \mu\text{m}$. Just at this size the softening of the elastic modulus of SMC also takes place (Fig. 6).

To a greater extent the effects described above are displayed in transition from SMC to NC in which case the decrease of the grain size results in the increase of the volume fraction of GBP to $p \leq 100\%$. According to the results of [11], in this case the Mössbauer spectrum split increases, the Debye temperature significantly decreases, softening of the elasticity modulus is revealed stronger. The nonequilibrium character of the system is the reason for an about hundredfold increase of the grain boundary diffusion coefficient D of NC [11] (in SMC its multiplicity is reduced to several tens of times [1]). Using Einstein relations $D \propto \eta^{-1}$, one

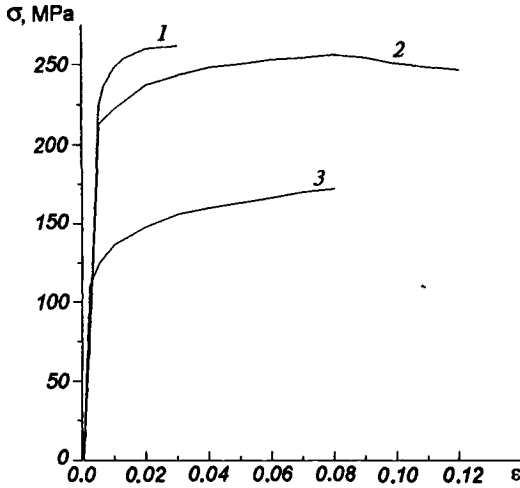


Figure 7. Dependence of elastic stress σ on strain ϵ of SMC magnesium alloy MA8 at room temperature and strain rate $\dot{\epsilon} = 5 \cdot 10^{-4} \text{ s}^{-1}$ (1—excited SMC-structure with the grain size $0.3 \text{ }\mu\text{m}$; 2—annealed SMC-structure with the same grain size; 3—alloy with a grain size of $10 \text{ }\mu\text{m}$) [1].

can conclude that GBP represents a liquid-like interlayer (with a crystalline structure!) which possesses a decreased value of the shift toughness coefficient η . It causes superplastic properties of SMC and NC at lower temperatures and high damping properties and toughness [1, 11].

3. DISTRIBUTION OF ELASTIC FIELDS

Experimental data presented in section 2 show that the elastic stresses contribute significantly to thermodynamics of NC and SMC. However, according to dilatometric data, the static change of interatomic distance averaged by a grain is $\delta a \leq 10^{-3} a$, and thus can not provide a sufficient level of these stresses. However, at more detailed consideration the situation appears not so simple and requires an additional analysis.

First, let us consider the field of strain $\epsilon_i(\mathbf{r})$, created by an excited GB [6]. For the usual boundary simulated by an equidistant distribution of dislocations the elastic stresses decay with distance x from it according to the exponential law $\sigma_0(x) \propto \exp(-x/w)$, where w is the microscopy scale determined by the distance between grain boundary dislocations [12]. In the case of GB excitation due to absorption of lattice dislocations, the dispersion of distances between grain boundary dislocations takes place, and the stochastic component $\sigma(\mathbf{r})$ is superimposed on the exponential component $\sigma_0(\mathbf{r})$ [6]. It is alternating in the direction parallel to GB, so average by volume $\bar{\sigma}(\mathbf{r}) = 0$. The dispersion

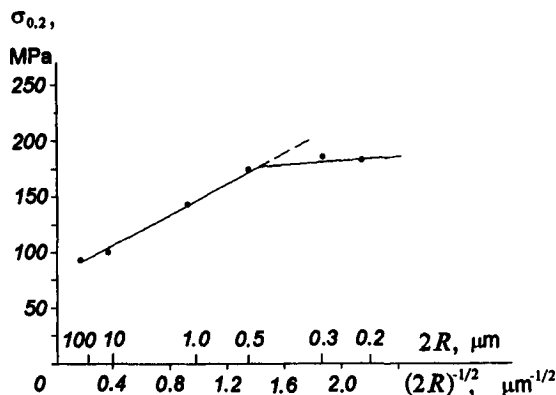


Figure 8. Dependence of yield stress $\sigma_{0.2}$ on the grain size of the magnesium alloy MA8 at room temperature [1].

of the field $\sigma(r)$ decays with distance x from GB as $\delta/x^{1/2}$, where δ is the dispersion of distances between boundary dislocations. Thus, taking into account the fact that the formation of the liquid-like interlayer of GBP screens an elastic field of GB across the thickness d , one can arrive at the conclusion that the excitation of GB results in the occurrence of the alternating (in the directions parallel to GB) field of strain $\varepsilon_d(r)$, slightly varying by the thickness of GBP. The average value of this field $\overline{\varepsilon_d(r)} \approx 0$ for distances $x > w$.

Except for the indicated component caused by the excitation of GB, two others are present which are connected with the occurrence of GBP (according to the data of section 2, this is revealed in a softening of elastic modulus and the Debye temperature decrease). From the microscopy point of view such a behaviour is explained by the change of the atomic potential relief $U(r)$ (see Fig. 9). Indeed, as the elastic modulus λ and curvature of the parabola $U = cr^2/2$ which can be reduced to the stiffness of a spring c which simulates the interatomic bond, are related by the equality $c = \lambda a$, where a is an interatomic distance, the softening of the elastic modulus λ means the decrease of the curvature of $U(r)$ dependence. As is seen from Fig. 9, at this level of excitation (temperature T) it results in the growth of the displacement from the value u_0 which is typical for GP, to the value u , in GBP. Within the framework of the Debye theory such increase follows from the formula of [4]:

$$u^2 = 9\hbar T / (m\Theta^2) \quad (3)$$

Due to the decrease of Debye temperature Θ (here temperatures T and Θ are expressed in energy unites, m is the atom mass, \hbar is the Planck constant). As is known [4], at the melting temperature T_m an effective strain $\varepsilon_d = u/a$ is estimated by Lindemann value $\varepsilon_m \approx 0.2$, and at me-

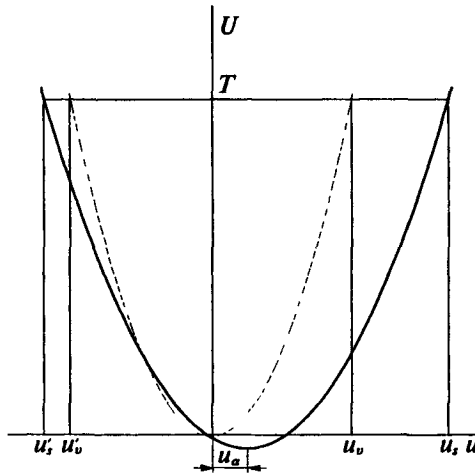


Figure 9. View of the dependence of the potential relief in GP (dotted line) and GBP (solid line). The displacement by the abscissa axis determines the static strain (10), and by the axis of ordinates—the change of the potential energy of the atom at the transfer into the excited state.

dium temperatures $T \approx 0.1 T_m$ formula (3) gives $\epsilon_v \geq 5\%$. It characterizes the initial GP. To determine the effective strain ϵ_s appropriate to GBP, let us use condition $(c_v/2)u_v^2 = (c_s/2)u_s^2 = T$, whence follows $\epsilon_s = u_s/a = (c_v/c_s)^{1/2}(u_v/a) = (\lambda_v/\lambda_s)^{1/2}\epsilon_v$ (see Fig. 9). The maximal ratio of the elastic modules $\lambda_v/\lambda_s \approx 3$, so the difference strains $\tilde{\epsilon} \equiv \epsilon_s - \epsilon_v \sim 5\%$ according to [1]. Just such a value was observed in a high resolution electron-microscopy experiment [7]. As a result, we arrive at an important conclusion: the elastic stresses in heterogeneous SMC-structure are caused not only by static distortions of the lattice $\epsilon_s(\mathbf{r})$ connected with the GB excitation, but also by a difference of vibration amplitudes of atoms in GBP and GP.

Let us estimate the level of these stresses using the given softening $\Delta\lambda$ of GBP elasticity modulus. According to [4], $\Delta\lambda$ results in the rise of the number of ultrasonic phonons \bar{n}_k in the state specified by the wave vector \mathbf{k} by

$$|\Delta \bar{n}_k| \approx |\Delta(T/s\hbar k)| \approx (T/\hbar s^2 k)\Delta s \propto (\Delta\lambda)^{1/2}, \tag{4}$$

where $s = (\lambda/\rho)^{1/2}$ is sound velocity, ρ is the density of the medium. As a result, a phonon density gradient $|\nabla_{\mathbf{k}}| \sim \Delta \bar{n}_k/VR$, where V is volume, appears between GBP and GP fields which results in the diffusion flow

$$j_k = D|\nabla_{\mathbf{k}}| \sim (D/R)(\Delta \bar{n}_k/V). \tag{5}$$

This flow is directed from the grain periphery where GBP is localised

to the central part ($D \sim sl$ is diffusivity which is determined by the phonon free length l). As the components of the elastic stress tensor σ_k represent a flow of a phonon momentum flow $\hbar \mathbf{k}$ [13], one can arrive at a conclusion that the setting of the stationary flow (5) means the occurrence of an elastic field component

$$\sigma_k = \hbar \mathbf{k} \cdot \vec{j}_k \sim \frac{\hbar s k}{V} \frac{l}{R} \Delta \bar{n}_k. \quad (6)$$

As a result, total (by the wave vector \mathbf{k}) elastic field is determined by an estimate

$$\sigma_d \sim \frac{T}{\Omega} \frac{l}{R} \frac{\Delta s}{s} \leq \frac{T}{\Omega} \left(\frac{\Delta \lambda}{\lambda} \right)^{1/2}, \quad (7)$$

where Ω is the atomic volume. It is accepted in (7) that the phonon free length l is restricted by the grain size R . Thus, σ_d increases as a square root of the softening of the elastic stress modulus $\Delta \lambda$.

Equation (7) can be formed as a standard dependence $\sigma_d(\varepsilon_d)$ of the elastic field on an effective strain $\varepsilon_d = u/a$ caused by a mean square displacement u of an atom during its oscillations. To do that let us write the relations [4],

$$u^2 = \sum |U_{\mathbf{k}}|^2, \quad |U_{\mathbf{k}}|^2 \cong \frac{\hbar \bar{n}_{\mathbf{k}}}{N m s k}, \quad \bar{n}_{\mathbf{k}} \gg 1, \quad (8)$$

between the mean square displacement u , the Fourier image of the displacements field $U_{\mathbf{k}}$, and the number of phonons $\bar{n}_{\mathbf{k}}$ in the state with the wave vector \mathbf{k} (N is the number of atoms). After determination of the number of phonons \mathbf{k} from here, let us find from formula (6)

$$\sigma_d \sim \lambda (l/R) (\varepsilon_s^2 - \varepsilon_v^2) \sim \lambda \bar{\varepsilon}_d \tilde{\varepsilon}_d, \quad \varepsilon_d^2 = \sum_{\mathbf{k}} \mathbf{k}^2 |U_{\mathbf{k}}|^2, \quad (9)$$

where it is accepted that $l \sim R$ and the relation $s^2 = \lambda \Omega / m$ of sound speed s and elastic modulus λ , atomic volume Ω and mass m is taken into account. The local value of the dynamic strain ε_d is assigned by the formula similar to formula (8), the quantity $\bar{\varepsilon}_d = (\varepsilon_v + \varepsilon_s) / 2$ determines the grain-average level of strain, $\tilde{\varepsilon}_d = \varepsilon_s - \varepsilon_v$ determines its dispersion.

According to the analysis carried out, the decrease of the Debye temperature Θ in the region of GBP causes a growth of displacements (3) and, hence, results in elastic stresses (7) and (9). It is characteristic that unlike the standard Hooke law they are proportional not to the first degree of specific strains ε_v and ε_s but to a difference of their squares. However, as the strain dispersion $\tilde{\varepsilon}_d$ is, in fact, a source of the field, one can consider that the linear relation $\sigma_d = \lambda_{\text{ef}} \tilde{\varepsilon}_d$ still remains valid, though the effective elasticity modulus $\lambda_{\text{ef}} \sim \lambda \bar{\varepsilon}_d$ decreases in comparison with the initial modulus λ due to the presence of average strain $\varepsilon_d \leq 10\%$.

Comparing the static field $\varepsilon_b(\mathbf{r})$ caused by GB excitation and the dynamic component $\tilde{\varepsilon}_d(\mathbf{r})$ connected with the increase of the vibration amplitude of the atoms in the region of GBP, one can notice that both these components represent the dispersion of a random field of displacements. However, if in the first case the stochastic character is revealed in the alternate change of the sign of the dependence $\varepsilon_b(\mathbf{r})$ on mesoscale distances $\sim w$, in the second case this character is revealed in the change of displacements of atoms at their oscillations in a varying potential relief $U(\mathbf{r})$ within the time interval $\sim (m/c)^{1/2}$. If this change is symmetric with reference to lattice points, the components $\varepsilon_b(\mathbf{r})$, $\tilde{\varepsilon}_d(\mathbf{r})$ represent a complete set of strain field components. However, one can assume that at a reconstruction of the contour $U(\mathbf{r})$ the important effects of an anharmonicity will appear which are characterized by Grüneisen constant γ [4]. Then, in addition to the dynamic component $\tilde{\varepsilon}_d(\mathbf{r})$, the formation of GBP will result in static distortions (see Fig. 9)

$$\varepsilon_a = -\Delta\gamma \frac{\Delta\Theta}{\Theta}, \quad (10)$$

which are caused by changes of the Debye temperature Θ and Grüneisen parameter $\Delta\gamma$. According to the data presented in Section 2, a typical value $|\Delta\Theta/\Theta| \sim 0.1$. As to the quantity $\Delta\gamma$, one should take into account that it determines not anharmonicity itself which is characterized by value $\Delta\gamma = 2$ [4], but the degree of its change at the relief $U(\mathbf{r})$ reconstruction. Therefore, one can expect that $\Delta\gamma \ll \gamma \sim 1$ and use the estimate $\varepsilon_a \ll 10^{-1}$. It is attested by the results of dilatometric studies presented in Section 2.

Thus, the total distortion field of the nonequilibrium heterogeneous grain structure with the excited GB is determined by the equation

$$\varepsilon^2 = (\varepsilon_b + \varepsilon_a)^2 + (\varepsilon_s^2 - \varepsilon_v^2). \quad (11)$$

The structure of this equation is specified by a stochastic character of the components of the total field $\varepsilon(\mathbf{r})$ discussed above. Due to a static character of the contribution of the excited GB $\varepsilon_b(\mathbf{r})$ and anharmonic component $\varepsilon_a(\mathbf{r})$ of the field connected with the reconstruction of the atomic relief of GBP their values are added; as to the dynamic components $\varepsilon_d(\mathbf{r})$ determined by values ε_s in GBP and ε_v in GP, only its moments of the second order are additive. The component $\varepsilon_b \propto \delta$ increases with the rise of the non-equilibrium degree of GB which is determined by the dispersion of distances between grain boundary dislocations. On the other hand, to provide the screening of the increased stresses $\sigma(\mathbf{r})$, the diffusion of the potential relief $U(\mathbf{r})$ in the GBP region should increase [3], resulting in an increase of the difference of displacements $u_s - u_v$, and consequently, in the increase of the difference of the squares effective strains, $\varepsilon_s^2 - \varepsilon_v^2$. For the same reason the anharmonic contribution ε_a can

also increase. As a result, an increase of the total strain ϵ takes place. The elastic energy of a heterogeneous structure of a grain which corresponds to this strain is determined within the framework of the approximation of elastic-isotropic continuum in Appendix.

4. THERMODYNAMICS OF GBP AND GP PHASE EQUILIBRIUM

Let us consider all grains as identical spheres of radius R . GBP is assumed to be a spherical layer located on a periphery of a grain and having the half-thickness d (see Fig. 3b). Then the volume fraction of GBP p is determined by the expression

$$p = 1 - (1 - d/R)^3. \quad (12)$$

The condition of a thermodynamic phase equilibrium (see [14])

$$\mu_v(P_v, T) = \mu_s(P_s, T) + E \quad (13)$$

is determined by the contribution of the elastic field E (see equation A14 in Appendix) and the dependence of chemical potentials μ_s , μ_v on pressures P_s , P_v in volumes of GP and GBP, respectively (temperatures T of different phases are, naturally, identical). As GP is confined to two surfaces (see Fig. 3b), pressure P_v differs from external pressure P by Laplace pressure $P_{L0} = 2\sigma_0/R$ caused by a surface-tension of GB σ_0 and similar component $P_L = 2\sigma/(R - d)$, caused by the presence of a phase boundary with a surface tension σ . As a result, one can obtain for GP using the method described in [14]:

$$\mu_v(P_v) = \mu_{v0} + 2\sigma_0\Omega/R + 2\sigma\Omega/(R - d), \quad (14)$$

where Ω is atomic volume, $\mu_{v0} = \mu_v(P)$.

As the Laplace pressure P_{L0} caused by GB influences GBP, the second summand of the right-hand side of (14) appears in the expression for the chemical potential $\mu_s(P_s)$. Here we have, instead of (14)

$$\mu_s(P_s) = \mu_{s0} + 2\sigma_0\Omega/R, \quad (15)$$

where $\mu_{s0} = \mu_s(P)$, and the phase equilibrium condition (13) takes on the following form

$$\mu_{v0} + 2\sigma\Omega/(R - d) = \mu_{s0} + E. \quad (16)$$

A nonequilibrium character of GBP is expressed by the condition $\mu_{v0} < \mu_{s0}$.

To analyse Eq. (16), let us introduce a dimensionless parameter

$$\alpha = \frac{\mu_{s0} - \mu_{v0}}{(\Lambda/2)\epsilon^2\Omega}, \quad (17)$$

which determines the ratio between GP advantages in comparison with GBP from the thermodynamic point of view and elastic energy which is determined by the elastic modulus Λ and strain ϵ (see A12, (11)). Let us also introduce a typical size

$$\rho = \frac{2\sigma}{(\Lambda/2)\epsilon^2}, \quad (18)$$

which is determined by the ratio between surface and elastic components. With provision for (A14), (17), and (18), condition (16) takes the form

$$p = \rho/(R - d) - \alpha. \quad (19)$$

Hence, it follows that GBP formation begins when the grain size becomes less than a critical one:

$$R_c \equiv \rho/\alpha = 2\sigma\Omega/(\mu_{s0} - \mu_{v0}). \quad (20)$$

As one should expect, thermodynamically stable GBP is realized in materials with high values of the surface-tension coefficient of the phase boundary σ (do not confuse to a grain boundary tension σ_0), and also with small values of elastic strain (11) and difference $\mu_{s0} - \mu_{v0}$ of the chemical potentials of phases (slightly nonequilibrium GBP). Apparently, these conditions are easily realized in metal materials.

The dependence (19) is in a qualitative agreement with the results of Mössbauer spectroscopy presented in Table 1 where the value of p is given as a relative intensity of the area of subspectrum 2 in Fig. 2. If the last point $2R = 0.65$ microns is not taken into account for which the experimental error is of about a quantity measured, the dependence of GBP volume fraction p on the grain radius R is of the form of the continuous curve in Fig. 10. In this case the parameters (18), (20) possess the values

$$\rho \approx 16 \text{ nm}, \quad R_c \approx 0.4 \text{ } \mu\text{m}, \quad (21)$$

and the value of a relative dispersion of experimental and fitting data is of about 6%. The parameter ρ determines a typical thickness of GBP, R_c determines a critical grain size starting from which nonequilibrium GBP becomes stable.

Thus, the thermodynamic analysis performed shows that in SMC and NC the formation of stable GBP is possible. The thickness d of this phase grows with the decrease of the grain size R . The solution of combined equations (12), (19) results in dependence $d_p(R)$. A view of this dependence is presented in Fig. 11. Its feature consists in the fact that with the decrease of the grain radius the volume fraction achieves its maximal value

$$p_{\max} = (3 - \alpha)/4, \quad (22)$$

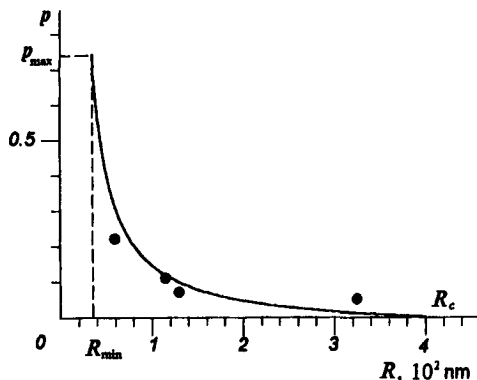


Figure 10. Dependence of GBP volume fraction on the grain radius at $\alpha = 0.04$, $d = 14.5$ nm (the points correspond to the experimental data presented in Table 1).

which is always less than unity. It indicates that even in NC not a whole grain transforms into the excited state. For SMC within the region of experimental observation always $r \ll R$, and the linearly falling dependence of the following kind is realized:

$$d \approx (\rho/3)(1 - R/R_c). \quad (23)$$

For NC, where $d \sim R \sim \rho$, the dependence $d(R)$ is non-linear, and the thickness of GBP increases with the decrease of R much faster, reaching the point in which the minimum grain radius is $R_{\min} = 3^{-1}4^{4/3}(1 + \alpha)^{4/3}\rho \approx 2.20\rho$, and the maximal GBP thickness $d_{\max} = \{1 - (1 + \alpha)/4^{1/3}\}R_{\min} \approx 0.37R_{\min} \approx 0.78\rho$.

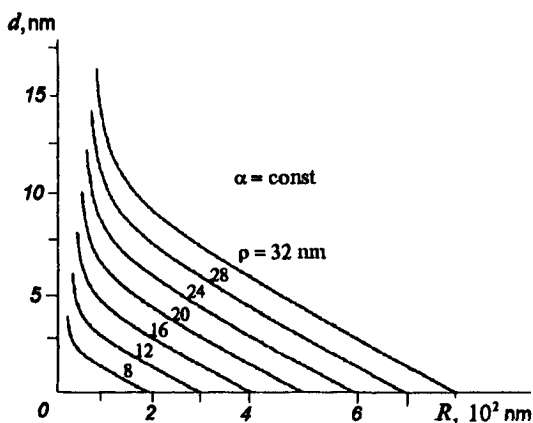


Figure 11. Dependence of GBP interlayer thickness on the radius of the grain at $\alpha = 0.04$.

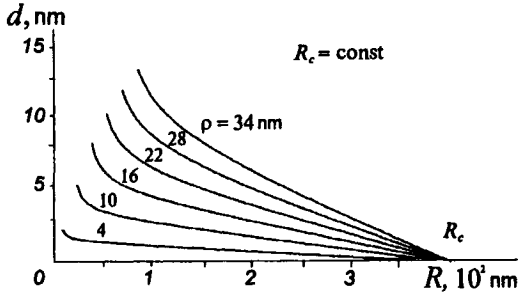


Figure 12. Dependence of GBP interlayer thickness on the radius of the grain at $R_c = 4 \cdot 10^2$ nm.

With the growth of the degree of non-equilibrium of the system all three parameters ϵ , $\mu_{s0} - \mu_{v0}$, σ increase, and the behaviour of quantities ρ , α , R_c which determine the kind of dependences $p(R)$, $d(R)$ becomes undetermined. However, as is seen from Fig. 11 and limit dependences (23), the parameter ρ can only grow with excitation of the system parameter as it promotes an increase of GBP thickness d . If parameter α also increases with the same intensity, the critical radius R_c does not vary, and the dependence $d_p(R)$ has a view presented in Fig. 12. In the opposite case, when the parameter α insignificantly varies, excitation of GB promotes a simultaneous increase of quantities ρ and R_c , and the dependence $d_p(R)$ is realized similar to that shown on Fig. 11. Actually, the first of the specified situations ($R_c \approx \text{const}$) takes place. In this case the excitation of the system has an insignificant effect on the value of elastic energy $\sim \Lambda \epsilon^2$ and results in the identical rise of the degree of GBP non-equilibrium $\mu_{s0} - \mu_{v0}$ and surface tension σ on the phase boundary. This statement is testified to by the fact that consideration of the phase equilibrium conditions within the framework of Ginzburg-Landau scheme (see, for example, Section 8.2 in [15]), results in the relationship $\sigma \propto \mu_{s0} - \mu_{v0}$.

5. DISCUSSION

The described thermodynamic analysis is based on the assumption according to which the anomalous region of the crystal forming around GB is considered as a thermodynamic phase, which is non-equilibrium but can be in a metastable state. To substantiate such an assumption, one should answer the question: what is the microscopic nature of the difference of the excited GBP from usual GP? In other words, it is necessary to clarify the physical sense of the 'order' parameter η distinguishing these phases. According to the analysis of experimental data (see Section 2) the specified difference consists only in the degree of

excitation (dynamic activity) of atoms, in this connection it is more suitable to name value η as the excitation parameter (EP)¹.

At first sight, it may appear that the value of the difference $u_s - u_0$ between the typical values of mean square displacements of atoms in GBP and GP plays the role of EP. However, it is seen from Fig. 9 that this difference is caused by the change of the potential relief of atoms $U(\mathbf{r})$, in this connection the value $u_s - u_0$ represents only the secondary EP (such as distortions of a lattice of solid solution at its ordering [15]). The change of coordinate dependence $U(\mathbf{r})$ of the potential energy of atoms with respect to the initial dependence $U_0(\mathbf{r})$ which corresponds to equilibrium GP should be considered as the initial reason for excitation of GBP atoms.²

Let us present a scheme [16, 3] which enables us to determine EP η using the change of the atomic potential relief $U(\mathbf{r})$. If the set of fields $\{U(\mathbf{r})\}$ is not stochastic which is realized at different degrees of action Θ as a result of which the excited GB is formed, we can write

$$\eta = \frac{\overline{|\Delta U(\mathbf{r})|^2}}{|\Delta U(\mathbf{r})|^2_{\max}}, \quad \Delta U(\mathbf{r}) = U(\mathbf{r}) - U_0(\mathbf{r}), \quad (24)$$

where the overline means GBP volume averaging. It is obvious that such definition means that the ensemble of potential relief $\{U(\mathbf{r})\}$ has a distribution of probability $P\{U(\mathbf{r})\} = \delta\{U(\mathbf{r}) - U(\mathbf{r})\}$ of the microcanonical type.

The nonequilibrium character of the system suggests that in accordance with the rise of the parameter of excitation Θ , the δ -shaped distribution $P\{U(\mathbf{r})\}$ diffuses to take a quasi-Gibbs form [16]

$$P\{U(\mathbf{r})\} \propto \exp\left[-\Theta^{-1} \int V(U(\mathbf{r})) d\mathbf{r}\right], \quad (25)$$

where $V(U(\mathbf{r}))$ is a synergistic potential [17]. In this case the deterministic definition (24) becomes unjustified, and the stochastic one should be used instead [3]:

$$|\eta|^2(\mathbf{r}) = \lim_{|\mathbf{r}-\mathbf{r}'| \rightarrow \infty} \frac{\langle \delta U(\mathbf{r}) \delta U(\mathbf{r}') \rangle}{\langle |\delta U(\mathbf{r})|^2 \rangle}, \quad \delta U(\mathbf{r}) = U(\mathbf{r}) - \langle U(\mathbf{r}) \rangle, \quad (26)$$

¹ One should bear in mind that the initial cause of the non-equilibrium of NC and SMC is GB excitation caused by the absorption of lattice dislocations. Therefore, GBP excitation is, strictly speaking, secondary.

² Whereas the concept of the potential relief of atoms $U(\mathbf{r})$ is widely used and intuitively evident, taking into account its key importance for further discussion, let us note that the dependence $U(\mathbf{r})$ is formally defined as a variation derivative from a thermodynamic potential of the system with respect to the function of the atom spatial distribution [3]. In particular, it follows from this definition that, by analogy with an electrostatics, $U(\mathbf{r})$ can be understood as a potential energy of an 'experimental atom' under the action of potentials of actual and external fields.

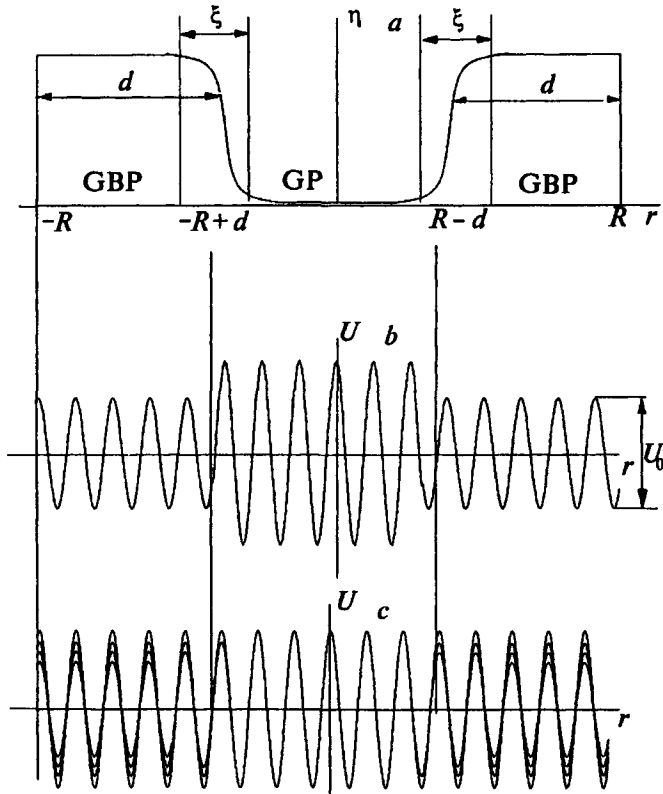


Figure 13. *a*—view of the coordinate dependence of the excitation parameter of the heterogeneous structure of a grain; *b*, *c*—a corresponding potential relief for parameters (24), (26), respectively.

where the angular brackets mean averaging by distribution (25). Within the framework of such an approach a metastable system can be studied by analogy with thermodynamically equilibrium systems, in which the phase transformation takes place in accordance with the change of the excitation parameter Θ [17].

To illustrate definitions (24) and (26), Fig. 13 shows the spatial distribution of EP along the axis r which passes through the centre of grain, and view of the relevant coordinate dependences $U(r)$ of the potential relief.³ The conditions $U(r) = \text{const}$ which correspond to a constant level of reading of dependences $U(r)$ in Figs. 13*b* and 13*c* mean the

³ It should be noted that the function $U(r)$ undergoes prompt changes over interatomic distances and smooth changes over mesoscale distances. The latter stipulate the coarsened coordinate dependence $\eta(r)$ of EP which describes a heterogeneous character of the system.

absence of static strain of the lattice [18]. A deterministic situation which corresponds to Fig. 13*b* is realized in thermally non-excited systems in which the change of the potential relief caused by the softening of interatomic bonds is only of mechanical character. In this case EP (24) is determined by the decrease of the height of the potential relief U_0 , which results in a rise of the coefficient D of grain boundary diffusion (see Section 2).

Actually, the stochastic distribution of reliefs $\{U(\mathbf{r})\}$ is realized which is shown on Fig. 13*c*. Such a system is in a thermally nonequilibrium state which is determined by the parameter Θ , the value of which specifies a level of energy accumulated by GB during the preprocessing of a sample. As well as in the case of mechanical reconstruction of the reliefs (Fig. 13*b*), the decrease of the effective height of the potential relief takes place here which also results in the growth of value D . However, if in the first case the medium is perfectly elastic, *i.e.*, the shear viscosity $\eta = \infty$, the fluctuations of the relief in the second case are caused, apparently, by the processes of viscous flow in medium with $\eta < \infty$ [18]. Just these processes ensure a screening of a long-range field of the excited GB [6] in subsurface volume of GBP. On the other hand, they also cause superplastic properties.

Thus, describing NC and SMC one should prefer the model of a thermally nonequilibrium system for which the fluctuating ensemble of reliefs is realized of the type shown in Fig. 13*c*, and EP is determined by Eq. (26).

The introduction of EP enables one to present a nonequilibrium state of NC and SMC by analogy with a heterogeneous state in semiconductor systems undergoing phase transformation [19, 20]. Here, despite of the loss in surface energy, the nonuniform state is observed due to the fact that in one of the phases the energy of charge carriers is lower than that in the other phase. Therefore, their redistribution takes place, but to prevent the tremendous Coulomb energy, the sizes of the regions of the phases should be restricted to length Λ of the electric field screening. As a result, it is favourable for the system from the energetic point of view to be divided on alternating interlayers of phases with a thickness of $\sim \lambda$ with increased and lowered concentrations of carriers.

As is seen from a pattern represented in Section 3, in our case the role of field carriers is played by phonons, the density of which in GBP region is higher than that in GP region. The grain size R , which naturally restricts the region of elastic field propagation, corresponds to the screening distance λ . These circumstances enable us to present the nonequilibrium system NC and SMC as a heterogeneous state caused by the distribution of the density of phonons. However, there is a number of important distinctions in comparison with semiconductor systems which makes impossible a direct transfer of the formalism described in [19, 20] on our object. First of all, it is due to the geometry of the problem: if in semiconductor systems one-dimensional field distribution

is the distribution with the lowest energy, in our case the symmetry is spherical. It results in the occurrence of Laplace pressure, which, as is seen from Section 4, influences thermodynamics to a greater extent. Besides, if in semiconductor systems the complete number of field carriers is conserved, in our case the number of phonons varies with temperature [4]. Therefore, it is impossible to construct a phase diagram with the indicated region of heterogeneous state existence.⁴

An example of such a state related to an elastic field is the field model of a crystalline structure defect [3] within the framework of which a dislocation and disclination are represented by analogy with Abrikosov vortex in a mixed state of type II superconductor. Typically in this case the core of the defect which corresponds to the excited GBP has the size of about the thickness of the phase boundary. In other words, the defect represents a topological feature (soliton) the size of which practically does not depend on the environmental conditions. Apparently, just such a situation is realized for the heterogeneous state in NC and SMC. Really, it is seen from Table 1 that with change of the grain radius R only a volume fraction p of GBP considerably varies, whereas its thickness d remains practically constant. So one can conclude that the anomalous properties of NC and SMC are caused by the presence of a mixed state of GP and GBP and the latter screens a long-distance elastic field created by the excited GB.

The heterogeneous state of SMC and NC presented is investigated in Section 4 within the framework of the simplest macroscopic approach. However, as well as in the case of semiconductor systems [19], it does not allow one to answer the question: what should be the difference of phonon densities in GBP and GP which is necessary to stabilize the heterogeneous state?⁵ Probably, the situation can be clarified further within the framework of the field approach of Ginzburg–Landau type (see study [20]).

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⁴ It should be noted that such a state differs in principle from a usual mixture of phases because in our case the phases cannot be separated as it takes place in a usual multiphase system. The quickly alternating spatial distribution of thermodynamic phases and force fields in a heterogeneous state results in a decrease of its thermodynamic potential in comparison with the values corresponding to separate phases or their usual mixture.

⁵ Obviously, within the framework of the macroscopic approach developed in Section 4, the answer to this question should enable us to establish a relationship between specific scales ρ and R_c , *i.e.*, the value of the parameter α determined by Eq. 17.

APPENDIX. ELASTIC ENERGY OF HETEROGENEOUS GRAIN

Let us proceed from the formula [15]

$$\varepsilon = \frac{1}{2V} \int \int \hat{\mathbf{e}}(\mathbf{r}) : \hat{\hat{\lambda}}(\mathbf{r} - \mathbf{r}') : \hat{\mathbf{e}}(\mathbf{r}') d\mathbf{r} d\mathbf{r}', \quad (\text{A.1})$$

which defines energy $\varepsilon = NE$ per volume of grain $V = (4\pi/3)R^3$ ($N = V/\Omega$ is the number of atoms in this grain, E is energy which falls on each of them, $\hat{\hat{\lambda}}(\mathbf{r} - \mathbf{r}')$ is dispersive elasticity modulus of the medium; a cap denotes a pair of Cartesian indexes, a point denotes convolution by a pair of such indexes. Elastic component $\hat{\mathbf{e}}(\mathbf{r})$ of the total strain tensor

$$\hat{\mathbf{u}} = \frac{1}{2}(\nabla\mathbf{u} + \mathbf{u}\nabla) \quad (\text{A.2})$$

is related to the field of internal strain $\hat{\mathbf{e}}(\mathbf{r})$ by the equation

$$\hat{\mathbf{e}}(\mathbf{r}) = \hat{\mathbf{u}}(\mathbf{r}) - \hat{\mathbf{e}}(\mathbf{r}). \quad (\text{A.3})$$

At a given source $\hat{\mathbf{e}}(\mathbf{r})$ the equilibrium field of displacements $\mathbf{u}(\mathbf{r})$ is determined by the minimum condition

$$\delta\varepsilon/\delta\mathbf{u}(\mathbf{r}) = 0 \quad (\text{A.4})$$

for functional (A.1). Performing Fourier transformations

$$\hat{\hat{\lambda}}_{\mathbf{k}} = \frac{1}{V} \int \hat{\hat{\lambda}}(\mathbf{r}) e^{i\mathbf{k}\mathbf{r}} d\mathbf{r}, \quad \mathbf{u}_{\mathbf{k}} = \frac{1}{V} \int \mathbf{u}(\mathbf{r}) e^{-i\mathbf{k}\mathbf{r}} d\mathbf{r}, \quad \hat{\mathbf{e}}_{\mathbf{k}} = \frac{1}{V} \int \hat{\mathbf{e}}(\mathbf{r}) e^{-i\mathbf{k}\mathbf{r}} d\mathbf{r}, \quad (\text{A.5})$$

one can obtain the equilibrium equation

$$(\mathbf{k} \cdot \hat{\hat{\lambda}}_{\mathbf{k}} \cdot \mathbf{k}) \mathbf{u}_{\mathbf{k}} = -i\mathbf{k} \hat{\hat{\lambda}}_{\mathbf{k}} : \hat{\mathbf{e}}_{\mathbf{k}}. \quad (\text{A.6})$$

The solution can be found using the Green's tensor $\hat{G}_{\mathbf{k}} = k^{-2} \hat{\Omega}_{\mathbf{k}}$, defined by the equation

$$\mathbf{n} \cdot \hat{\hat{\lambda}}_{\mathbf{k}} \cdot \mathbf{n} = \hat{\Omega}_{\mathbf{k}}^{-1}, \quad \mathbf{n} = \mathbf{k}/k. \quad (\text{A.7})$$

Multiplying both members of (A.6) by $\hat{G}_{\mathbf{k}}$, we find the equilibrium strain

$$\hat{\mathbf{u}}_{\mathbf{k}} = \mathbf{n} \hat{\Omega}_{\mathbf{k}} (\mathbf{n} \cdot \hat{\hat{\lambda}}_{\mathbf{k}} : \hat{\mathbf{e}}_{\mathbf{k}}), \quad (\text{A.8})$$

the substitution of which in (A.1) with regard for the transformations inverse to (A.5), results in

$$\varepsilon = \frac{V}{2} \sum_{\mathbf{k}} \hat{\mathbf{e}}_{\mathbf{k}}^* : \hat{\hat{\Lambda}}_{\mathbf{k}} : \hat{\mathbf{e}}_{\mathbf{k}}, \quad (\text{A.9})$$

$$\hat{\Lambda}_{\mathbf{k}} = \hat{\lambda}_{\mathbf{k}} - (\hat{\lambda}_{\mathbf{k}} \cdot \mathbf{n}) \hat{\Omega}_{\mathbf{k}} (\mathbf{n} \cdot \hat{\lambda}_{\mathbf{k}}). \tag{A.10}$$

Formula (A.10) expresses the effective elastic modulus $\hat{\Lambda}_{\mathbf{k}}$ in terms of initial $\hat{\lambda}_{\mathbf{k}}$.

The formulae presented are applicable for the description of an arbitrary elastic medium. To write them in a concrete form, let us use the approximation of an elastic-isotropic continuum for which the tensor of internal strain $\hat{\varepsilon}_{\mathbf{k}} = \varepsilon_{\mathbf{k}} \hat{I}_{\mathbf{k}}$ is proportional to unit \hat{I} , and Eq. (A.7) is solved in a continual limit $\mathbf{k} \rightarrow \mathbf{0}$ where the Cartesian components of the Green's function [21]

$$\Omega_{ij}^0 = \frac{1}{G} \left(\delta_{ij} - \frac{n_i n_j}{2(1 - \nu)} \right), \tag{A.11}$$

G , ν are shear modulus and Poisson's ratio. As a result, the elastic energy (A.9) takes on the form

$$\varepsilon = (V/2) \Lambda \sum_{\mathbf{k}} |\varepsilon_{\mathbf{k}}|^2, \quad \Lambda = 4G(1 + \nu)/(1 - \nu). \tag{A.12}$$

Let us use the result obtained for the heterogeneous model of a grain (see Fig. 3b). Here the spatial dependence of the strain field is stepwise

$$\varepsilon(\mathbf{r}) = \begin{cases} 0 & \text{at } 0 < r < R - d, \\ \varepsilon & \text{at } R - d < r < R, \end{cases} \tag{A.13}$$

where d is the thickness of a spherical interlayer which is occupied by GBP, R is radius of a grain, ε is GBP strain determined by formula (11). Substituting (A.13) into last equation of (A.5), and the result into (A.12), we obtain for elastic energy $E = \varepsilon/N$ per one atom:

$$E = (\Lambda/2) \Omega \varepsilon^2 p, \tag{A.14}$$

where the effective elastic modulus Λ is determined by the second formula of (A.12), Ω is the atomic volume, p is volume fraction of GBP, determined by relation (12).

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