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## STRENGTH AND PLASTICITY

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# Elastic Properties, Internal Stresses, and Excess Volume of Nanomaterials

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**Abstract**—The analytical dependences of the stress-state characteristics of the single-component nanocrystalline materials on the magnitude of the excess volume have been determined. It has been shown that local fluctuations in the internal stresses of these materials can significantly exceed the values of the macroscopic ultimate strength.

**Keywords:** nanocrystalline materials, intercrystalline boundaries, excess volume, internal stresses

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## INTRODUCTION

The volume per mass unit of the nanocrystalline materials (nanomaterials) produced by the extreme mechanical treatments (mechanical alloying, equal-channel angular pressing, etc.) increases slightly compared with that of single crystals of the same chemical composition [1, 2]. The measured volume increment  $\delta V$  is called the *excess volume* [1] or *free volume* [2], and its value depends on the average size of the nanocrystallites. The free volume can significantly affect the kinetic and thermodynamic properties of the nanomaterials. For example, in nanomaterials, the rate of mass transfer [3], as well as the solubility of the impurities and alloying elements [4], is significantly enhanced; the formation of metastable phases and chemical compounds, which do not exist in single crystals, becomes possible [5]; and anomalies of some physicomaterial properties are observed [1, 6].

The reason for these significant changes in the properties of the nanomaterials becomes clear if we note that many of these properties are structure-dependent. The only significant difference in the nanomaterials from single crystals is the presence of a dense system of intercrystallite boundaries. Thus, the majority of the nanomaterial properties should be related to the properties of their system of boundaries. Moreover, the effect of the intercrystallite boundaries can manifest most clearly in the change of the properties of single-component materials.

From the thermodynamic point of view, the appearance of free volume in nanomaterials occurs by no means accidentally, since the thermodynamic theory of surface phenomena suggests that the interface boundaries can have their own excess volume [7].

Hence, the free volume of the nanomaterials must be proportional to the total number of the intercrystallite boundaries. Taking this fact into account, using the available experimental data on the measurements of the free volume in metallic nanomaterials with an average size of nanocrystals of about  $D \approx 200$  nm (see, e.g., [1, 6]), it can be shown that the value of the free volume in the nanocrystalline materials with  $D \leq 10$  nm can reach  $\delta V \sim (1-3)\%$ . These estimates are in good agreement with the calculated values given in [2].

The intercrystallite boundaries substantially change the local atomic density of materials [7, 8] and, thus, introduce irreversible volumetric deformations into the crystal lattice. In nanomaterials, these deformations can cause significant internal stresses [1, 6]. If the volume fraction of the intercrystallite boundaries is large, the change in the atomic density and the internal stresses will contribute significantly to the thermodynamic potentials [7], which provides the difference between the properties of the nanomaterials and single crystals.

The irreversible changes in the atomic density that are introduced by the system of the intercrystallite boundaries cannot be measured experimentally. However, they must contribute to the value of the free volume of the nanomaterials, since it characterizes the irreversible volume changes that occur upon the severe plastic deformation. This means that there can be a correlation between the values of the internal stresses and free volume. Such a correlation would be convenient for experimental investigations of the nanomaterials in the stressed state.

The aim of this work is to determine the analytical dependence of the stress-state characteristics of the

single-component nanocrystalline materials on the value of the free volume.

## THEORETICAL MODELS

### *Statistical Determination of the Fields of Internal Stresses and Free Volume of Nanomaterials*

The structure of a single-component nanomaterial can be characterized by a set of macroscopic parameters, i.e., the number of atoms  $n_a$ , the average size of the crystallites  $D$ , a set of values  $\chi$  that define the texture parameters, etc. The application of this definition allows one to obtain an almost infinite number of samples that vary in shape, dimension, and nanocrystallite orientation. One of the possible ways to produce these samples is shown below.

The volume of any single crystal can be divided in mind into smaller nanovolumes, e.g., Bernal polyhedra or Voronoi–Delaunay polyhedra [9], which correspond to the macroscopic parameters of the nanomaterial. After this division is made, we can arbitrarily change the crystallographic orientation of the crystallites with the continuity of the material being preserved. As a result, we obtain a sample with one of the possible realizations of the required nanocrystalline structure.

We can count the total number of the samples  $N_C$ , which represent the macroscopically isotropic nanomaterial. To this end, we should note that using  $n_a$  sites of the crystal lattice we can construct  $N_{Gb} \sim n_a^2$  intercrystallite boundaries of various types. The amount of the faces in the faceting of the nanomaterial can be calculated as follows:

$$N_b \approx 3V/D^3 \approx 3n_a a^3/D^3. \quad (1)$$

Here,  $V$  is the nanomaterial volume; and  $a$  is the lattice parameter. The majority of the nanomaterials have  $D \leq 100$  nm; therefore, at  $V = 10^{-6}$  m<sup>3</sup> we have  $N_b \geq 10^{15}$ . Since  $N_{Gb} \gg N_b$ , the magnitude of  $N_C$  is of the same order of magnitude as the total number of the various sets of the intercrystallite boundaries, each of which completely covers all the faces of the nanostructure as follows:

$$N_C \sim \frac{N_{Gb}!}{(N_{Gb} - N_b)! N_b!} \gg N_{Gb}. \quad (2)$$

The choice of these sets of boundaries is almost arbitrary and is only restricted by the conditions of mechanical equilibrium of the facets at the junctions of the nanocrystallites. It follows from the obtained estimates that an investigation of the relationship between the internal stresses and the free volume in nanomaterials requires a statistical description.

To this end, let us choose a sample of the nanomaterial and enumerate all the faces of its faceting of its nanocrystallites in a definite order. Each part of the

intercrystallite boundary (facet), which is located at a face  $j$  ( $j = 1, 2, \dots, N_b$ ), creates in its vicinity a nonuniform distribution of the atomic density  $n_j(\mathbf{r} - \mathbf{r}_j, \mathbf{p}_j)$ . Here,  $\mathbf{r}$  is the radius vector of the points inside the volume of the nanomaterial;  $\mathbf{r}_j$  is the radius vector of a geometrical position of a facet center;  $\mathbf{p}_j$  is the set of parameters that characterize the macroscopic and microscopic properties of the facet [7, 8]. The distribution  $n_j(\mathbf{r} - \mathbf{r}_j, \mathbf{p}_j)$  differs from the atomic-density distribution of a single crystal  $n_M(\mathbf{r})$  as follows:

$$\Delta_j n(\mathbf{r} - \mathbf{r}_j, \mathbf{p}_j) = n_j(\mathbf{r} - \mathbf{r}_j, \mathbf{p}_j) - n_M(\mathbf{r}). \quad (3)$$

In the model of unrelaxed boundaries [7, 8], any changes in the atomic density are completely localized in the thin layer with a thickness on the order of the crystal-lattice parameter (we assume that the volume of the  $j$ th face is equal to the volume of the  $j$ th facet). These changes are determined by inelastic displacements of atoms. The changes in the atomic density introduced by these displacements are designated by  $\Delta_j^{nl} n(\mathbf{r} - \mathbf{r}_j, \mathbf{p}_j)$ . The function  $\Delta_j^{nl} n(\mathbf{r} - \mathbf{r}_j, \mathbf{p}_j)$  is defined by an atomic model of the corresponding facet and is assumed to be known for each facet. We determine the distribution of irreversible changes in the atomic density over the volume of the entire nanomaterial by the summation over all faces of the nanostructure:

$$\Delta^{nl} n(\mathbf{r}) = \sum_j \Delta_j^{nl} n(\mathbf{r} - \mathbf{r}_j, \mathbf{p}_j). \quad (4)$$

Inhomogeneous changes in the density  $\Delta^{nl} n(\mathbf{r})$  create a field of internal pressure  $p(\mathbf{r})$  in the material, which causes additional elastic deformations. The tensors of elastic stresses  $\boldsymbol{\sigma}(\mathbf{r})$  and the total deformations  $\boldsymbol{\varepsilon}(\mathbf{r})$  in the bulk of the nanomaterial can be determined by solving the corresponding boundary problem [10, 11]. The set of equations for this problem includes the equation of the mechanical equilibrium

$$\text{div} \boldsymbol{\sigma}(\mathbf{r}) = -\text{grad} p(\mathbf{r}), \quad (5a)$$

the constitutive equations of the medium

$$\boldsymbol{\sigma}(\mathbf{r}) = \boldsymbol{\varphi}(\boldsymbol{\varepsilon}), \quad (5b)$$

compatibility equations for the  $\boldsymbol{\varepsilon}(\mathbf{r})$  tensor [10, 11], and the conditions of equilibrium for the internal  $A$  and external  $A_{ex}$  boundaries of the material

$$(\boldsymbol{\sigma} \cdot \mathbf{n}) = \mathbf{f}_A, \quad (\boldsymbol{\sigma} \cdot \mathbf{n}) = \mathbf{f}_{ex}, \quad (5c)$$

where  $\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}^{nl} + \boldsymbol{\varepsilon}^{el}$ ,  $\boldsymbol{\varepsilon}^{el}$  and  $\boldsymbol{\varepsilon}^{nl}$  are the tensors of the elastic and inelastic deformations, respectively;  $\mathbf{n}$  is the vector normal to the considered surfaces; and  $\mathbf{f}_A$  and  $\mathbf{f}_{ex}$  are the density vectors of the corresponding surface forces.

Given the stress tensor  $\boldsymbol{\sigma}(\mathbf{r})$ , using the constitutive equations, we can determine the tensor of elastic

deformations  $\boldsymbol{\varepsilon}^{\text{el}}(\mathbf{r})$  and the corresponding additional changes in the atomic density  $\Delta n^{\text{el}}(\mathbf{r})$  in the bulk of the material, including the volume of the system of boundaries. Then, the total distribution of the changes in the atomic density of the bulk of the nanomaterial is given by the following expression:

$$\Delta n(\mathbf{r}) = \Delta^{\text{nl}} n(\mathbf{r}) + \Delta^{\text{el}} n(\mathbf{r}). \quad (6)$$

The difference  $\Delta n(\mathbf{r})$  can be correlated with the volume deformation at any point described by  $\mathbf{r}$ . To this end, in the small vicinity of this point, we fix a certain number of the nearest-neighbor atoms,  $N_0$ . In the case of the single crystal, they would occupy the volume  $V_0$ , but in the case of the nanomaterial, the local volume is

$$V(\mathbf{r}) = V_0 + \Delta V(\mathbf{r}), \quad (7)$$

where  $\Delta V(\mathbf{r})$  is the change in the volume at point  $\mathbf{r}$  due to the displacement of atoms. Hence, the following relationships appear:

$$n(\mathbf{r}) = n_0[1 - \varepsilon_V(\mathbf{r})]; \quad (8)$$

$$\Delta n(\mathbf{r}) = -n_0 \varepsilon_V(\mathbf{r}); \quad (9)$$

$$\varepsilon_V(\mathbf{r}) = \Delta V(\mathbf{r})/V(\mathbf{r}). \quad (10)$$

Here,  $\varepsilon_V(\mathbf{r})$  is the total local volume deformation at the point  $\mathbf{r}$  of the nanomaterial and  $n(\mathbf{r}) = N_0/V(\mathbf{r})$  and  $n_0 = N_0/V_0$  are the local and macroscopic atomic densities of the nanomaterial and of the single crystal, respectively. The volume deformation  $\varepsilon_V(\mathbf{r})$  is related to the invariants of the total deformation tensor  $\boldsymbol{\varepsilon}(\mathbf{r})$  as follows [11]:

$$\varepsilon_V(\mathbf{r}) = \varepsilon_{ii} + \varepsilon_{ijk}\varepsilon_{kl} + \frac{1}{6}e_{ikl}e_{jnm}\varepsilon_{ij}\varepsilon_{kn}\varepsilon_{lm}, \quad (11)$$

where  $\varepsilon_{ij}$  ( $i, j = 1, 2, 3$ ) are the components of the tensor  $\boldsymbol{\varepsilon}(\mathbf{r})$  and  $e_{ikl}$  are the components of the unit anti-symmetric tensor of the third order. The repetition of symbols implies summation over them.

It follows from Eqs. (3) and (5)–(9) that the tensor of  $\varepsilon_V(\mathbf{r})$  can be expanded into the elastic  $\varepsilon_V^{\text{el}}(\mathbf{r})$  and inelastic  $\varepsilon_V^{\text{nl}}(\mathbf{r})$  components:

$$\varepsilon_V(\mathbf{r}) = \varepsilon_V^{\text{nl}}(\mathbf{r}) + \varepsilon_V^{\text{el}}(\mathbf{r}), \quad (12)$$

$$\varepsilon_V^{\text{nl}}(\mathbf{r}) = \sum_j \varepsilon_{j,V}^{\text{nl}}(\mathbf{r} - \mathbf{r}_j, \boldsymbol{\rho}_j), \quad (13)$$

where  $\varepsilon_{j,V}^{\text{nl}}(\mathbf{r} - \mathbf{r}_j, \boldsymbol{\rho}_j)$  is the distribution of the irreversible volume deformation, which is determined by the  $j$ th face.

For different samples of the nanomaterial, the set of parameters  $\mathbf{r}_j$  and  $\boldsymbol{\rho}_j$  can have arbitrary values. This means that the functions  $\boldsymbol{\sigma}(\mathbf{r})$ ,  $\boldsymbol{\varepsilon}(\mathbf{r})$ ,  $\varepsilon_V^{\text{el}}(\mathbf{r})$ , and  $\varepsilon_V^{\text{nl}}(\mathbf{r})$  should be considered as functionals of a random array

of the parameters  $\mathbf{r}_j$  and  $\boldsymbol{\rho}_j$ . Therefore, only their average values over the statistical ensemble, i.e.,  $\langle \boldsymbol{\sigma}(\mathbf{r}) \rangle_s$ ,  $\langle \boldsymbol{\varepsilon}(\mathbf{r}) \rangle_s$ ,  $\langle \varepsilon_V^{\text{el}}(\mathbf{r}) \rangle_s$ , and  $\langle \varepsilon_V^{\text{nl}}(\mathbf{r}) \rangle_s$ , which take into account an array of all arbitrary realizations of the samples that represent the structure of the nanomaterial, can be useful for investigations. The angular brackets  $\langle \dots \rangle_s$  designate averaging over the statistical ensemble.

The systems of boundaries can introduce a free volume into the nanomaterial, which is determined by the following expression:

$$V_f = \left\langle \int dV \varepsilon_V(\mathbf{r}) \right\rangle_s = \langle V \langle \varepsilon_V(\mathbf{r}) \rangle_V \rangle_s. \quad (14)$$

Angular brackets  $\langle \dots \rangle_V$  designate averaging over the entire volume of the nanomaterial. Therefore, to calculate internal stresses in the nanomaterials, it is sufficient to solve the boundary problem (5a)–(5c) for the stochastic field of the volume deformation  $\varepsilon_V^{\text{nl}}(\mathbf{r})$ , which is associated with the system of intercrystallite boundaries.

The solution of this problem for even one randomly chosen sample encounters significant difficulties of both calculational and physical character. The calculation difficulties are due to the fact that the number of faces in each sample is too large, i.e.,  $N_b \gg 1$ , and the number of samples required to construct the statistical ensemble is still greater, i.e.,  $N_c \gg N_b$ . Difficulties of a physical character emerge in an attempt to establish the constitutive equations (5b).

#### *Constitutive Equations of Elasticity of Isotropic Nanocrystalline Materials*

The main problem of formulating constitutive equations (5b) lies in taking into account the effect of the total deformation  $\boldsymbol{\varepsilon}(\mathbf{r})$  on the elastic properties of the nanomaterials. In this case, the methods of the nonlinear theory of elasticity are inapplicable, since the total deformations include irreversible inelastic deformations. This means that the study of deformation fields in the bulk of the nanomaterials requires implementing completely different methods of investigation. The multiparameter approximation of Grüneisen [12] can become the possible base for these methods.

In this approximation, a differential correlation is established between the phonon frequencies  $\omega_s(\mathbf{k})$  of the isotropic material and its volume  $V$  as follows:

$$\partial(\ln \omega_s(\mathbf{k})) = -\gamma_{ks} \partial(\ln V), \quad (15)$$

where  $s$  is the index that indicates the polarization of the normal oscillation,  $\mathbf{k}$  is the wave vector, and  $\gamma_{ks}$  is the constant of the normal oscillation  $(\mathbf{k}, s)$ . The existence of a correlation between the phonon frequencies and the volume is characteristic of the nonlinear deformation theory in which the deformations can be

irreversible. That is why the relationship (15) is fully applicable to the description of the intercrystallite-boundary systems.

The values of the frequency of the long-wave oscillations are determined by the macroscopic properties of the elastic body. For this range of the spectrum, the integration of Eq. (15) with a fixed wave vector results in the following expression:

$$c_s(\varepsilon) = c_s(0)(1 - \varepsilon)^{\gamma_s}. \quad (16)$$

Here,  $\varepsilon$  is an arbitrary volume deformation of a medium;  $c_s(\varepsilon)$  and  $c_s(0)$  are the velocities of an acoustic mode with  $s$  polarization in deformed and undeformed media, respectively;  $\gamma_s$  represents two constants that are independent of  $\mathbf{k}$ ; and  $s = (l, t)$ , where indices  $l$  and  $t$  represent longitudinal and transverse polarization, respectively.

Formula (16) can be used to determine the dependences of the elastic moduli of the medium on the volume deformation  $\varepsilon$ . To this end, we consider the  $c_s(\varepsilon)$  dependence on the elastic moduli and the mass density of the isotropic material [13]:

$$\begin{aligned} c_l^2(\varepsilon) &= \frac{3K(\varepsilon)(1 - \sigma(\varepsilon))}{\rho(\varepsilon)(1 + \sigma(\varepsilon))}, \\ c_t^2(\varepsilon) &= \frac{3K(\varepsilon)(1 - 2\sigma(\varepsilon))}{2\rho(\varepsilon)(1 + \sigma(\varepsilon))}. \end{aligned} \quad (17)$$

Here,  $K(\varepsilon)$  is the modulus of isothermal compression of the deformed material;  $\sigma(\varepsilon)$  is the Poisson coefficient;  $\rho(\varepsilon) = \rho_0(1 - \varepsilon)$  is the local mass density of the nanomaterial; and  $\rho_0$  is the macroscopic mass density of the undeformed material.

From relationships (16) and (17), we have

$$\sigma(\varepsilon) = \frac{(1 - \sigma_0)(1 - \varepsilon)^{2\Delta\gamma} + 2\sigma_0 - 1}{2(1 - \sigma_0)(1 - \varepsilon)^{2\Delta\gamma} + 2\sigma_0 - 1}; \quad (18)$$

$$\begin{aligned} K(\varepsilon) &= K_0(1 - \varepsilon)^{2(\gamma_l - \Delta\gamma) - 1} \frac{(1 + \sigma(\varepsilon))}{1 + \sigma_0} \\ &\times \{2(1 - \sigma_0)(1 - \varepsilon)^{\Delta\gamma} - 1 + 2\sigma_0\}; \end{aligned} \quad (19)$$

$$\frac{c_l(\varepsilon)}{c_t(\varepsilon)} = \frac{c_l(0)}{c_t(0)}(1 - \varepsilon)^{\Delta\gamma}, \quad \Delta\gamma = \gamma_l - \gamma_t. \quad (20)$$

Here,  $K_0$  and  $\sigma_0$  are the modulus of isothermal compression and the Poisson coefficient of the single crystal, respectively.

The presented data can be used to determine the free volume of the nanocrystalline materials.

#### *Free Volume and Fluctuations of Atomic Density in Intercrystallite Boundaries*

The boundary problem (5a)–(5c) for nanomaterials can be significantly simplified. The simplification can be carried out using available experimental data on

the defect structure and on the level of internal deformations in nanomaterials. To this end, we divide the volume of the nanomaterial into two parts, i.e., the volume occupied by the system of intercrystallite boundaries  $V_{Gb}$  and the total volume of the internal parts of the crystallites  $V_{Cr}$ .

In the  $V_{Cr}$  volume of the mechanically equilibrium nanomaterials, single dislocations or their groups are experimentally observed [1]. This means that the elastic deformations in this volume should not exceed the macroscopic elastic strength of the material. Hence, the average values of the tensor components  $\varepsilon^{el}(\mathbf{r})$  in the  $V_{Cr}$  volume should satisfy the following inequality:

$$\left\langle |\varepsilon_{ij}^{el} \varepsilon_{ij}^{el}|^{1/2} \right\rangle_V \leq 10^{-3}, \quad (i, j = 1, 2, 3).$$

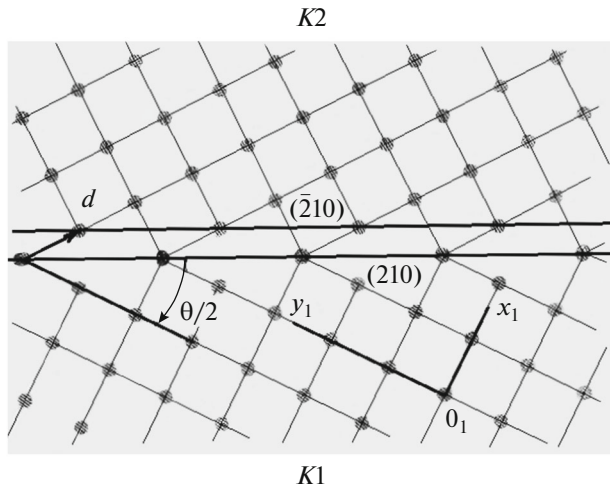
In the  $V_{Gb}$  volume, the values of the components of the tensor of the total deformation  $\varepsilon(\mathbf{r})$  are large, i.e.,  $|\varepsilon_{ij} \varepsilon_{ij}|^{1/2} \sim 1$ , [7, 8]. Therefore, their average value over the material bulk  $\left\langle |\varepsilon_{ij} \varepsilon_{ij}|^{1/2} \right\rangle_V \sim v_{Gb}$ ;  $v_{Gb} \approx H_{Gb} A_{Gb}$  is the volume fraction of the boundaries in the material;  $H_{Gb} \sim a$ , the average thickness of the boundary; and  $A_{Gb} \approx 3/D$ , the total area of all faces per unit volume [7]. These estimates agree with the experimental data on X-ray diffraction in nanomaterials [1, 6]. Now, we can find the average size of the nanocrystallites at which we can neglect the elastic deformations in the  $V_{Cr}$  volume. To this end, it is sufficient for the following inequality be satisfied:  $\left\langle |\varepsilon_{ij} \varepsilon_{ij}|^{1/2} \right\rangle_V \geq 10 \left\langle |\varepsilon_{ij}^{el} \varepsilon_{ij}^{el}|^{1/2} \right\rangle_V$ . As a result, we

have  $v_{Gb} \geq 10^{-2}$  and  $D \leq 3 \times 10^2 a$ . Assuming that  $3a \approx 1$  nm, we obtain  $D \leq 100$  nm. This is valid for almost any nanocrystalline material in use.

The solution to the boundary problem (5a)–(5c) in the  $V_{Gb}$  volume can be also simplified by considering it separately for each facet. This approximation is convenient, since it allows one to arbitrary set the shape of a facet and its position in the coordinate system. However, this approximation neglects the contribution from the junctions of the crystallites into the excess volume. In this approximation, the relative accuracy of the calculation results is close to the ratio of the volume of all junctions to the volume of the boundary system of the nanomaterial, which is considered satisfactory at the magnitudes of  $H_{Gb} \sim a$  and  $D \geq 3$  nm.

Therefore, when analyzing the internal stresses and excess volume of the majority of practically important nanocrystalline materials, it is sufficient to take into account only total deformations that are only distributed over the volume of separate facets covering the nanocrystallites.

In connection with this, we will consider the peculiarities of the volume deformation distribution over a separate intercrystallite boundary. An example of this



Atomic structure of tilt boundary of the simple cubic lattice that separates  $K1$  and  $K2$  crystallites rotated by an angle of  $\theta = 36.87^\circ$  relative to each other.

boundary in a simple cubic lattice is shown in the figure. This is a symmetric tilt boundary that separates the  $K1$  and  $K2$  crystallites which are turned by an angle of  $\theta = 36.87^\circ$  relative to each other about the axis  $[001]$  orthogonal to the plane of the figure [7, 8]. The boundary is characterized by the reciprocal density of the coinciding sites  $\Sigma = 5$  and a set of microscopic parameters which are defined by the vector  $\mathbf{d}$ . This vector describes the shift of the atomic plane  $(\bar{2}10)$  of the crystallite  $K2$  relative to the atomic plane  $(210)$  of the crystallite  $K1$ . The planes are specified in the crystallographic coordinate system  $(x_1, y_1, z_1)$  of the  $K1$  crystallite. For convenience, we assume that the area of the boundary is not limited, and the distribution of the volume deformation  $\varepsilon_V(\mathbf{r})$  is averaged over the thickness of the boundary.

In this case, each of the facets located at face  $j$  of the system of faceting of the nanocrystallites, where  $j = (1, 2, \dots, N_b)$ , has a two-dimensional periodic or quasiperiodic structure [7, 8]. Therefore, the function  $\varepsilon_{V,j}(\mathbf{r})$  that corresponds to the facets is also periodic or quasiperiodic. It is convenient to write it as follows:

$$\varepsilon_{V,j}(\mathbf{r}) = \varepsilon_{j,0} + \delta\varepsilon_{V,j}(\mathbf{r}). \quad (21)$$

Here,  $\varepsilon_{j,0} = \langle \varepsilon_{V,j}(\mathbf{r}) \rangle_j$  is the value of  $\varepsilon_{V,j}(\mathbf{r})$  averaged over the area of a facet at the  $j$ th face;  $\delta\varepsilon_{V,j}(\mathbf{r})$  is a function that describes the deviation of the atomic density in the plane of the intercrystallite boundary from the average value (fluctuation):  $\langle \delta\varepsilon_{V,j}(\mathbf{r}) \rangle_j = 0$ . The angular brackets  $\langle \dots \rangle_j$  designate averaging over the area of the  $j$ th facet. Since the different types of

boundaries at the nanocrystallite faces are located randomly, the values of  $\varepsilon_{j,0}$  are also random.

The deformation  $\varepsilon_{V,j}(\mathbf{r})$  at each point in the volume of the  $j$ th facet induces an appropriate internal pressure  $p(\mathbf{r})$ . In this case, the condition of the mechanical equilibrium (5c) should be satisfied. The application of this condition to a separate facet means that the average value of the pressure over the area of the facet must be equal to the external pressure  $p_0$  as follows:

$$\langle p(\mathbf{r}) \rangle_j = p_0. \quad (22)$$

Condition (22) allows one to determine the values of  $\varepsilon_{j,0}$  for all facets  $j = (1, 2, \dots, N_b)$ . Indeed, if the temperature is fixed and the macroscopic continuity of the material is retained, the pressure  $p(\mathbf{r})$  correlates with the volume deformation  $\varepsilon$  via the following differential equation:

$$dp = -K(\varepsilon) \frac{d\varepsilon}{1 - \varepsilon}. \quad (23)$$

This equation follows from the thermodynamic relationship  $\frac{1}{K} = -\left(\frac{\partial V}{V \partial p}\right)_T$  and local dependence  $V(\mathbf{r}) = V_0/(1 - \varepsilon)$ , where  $T$  is the absolute temperature. Therefore, at  $\varepsilon = \varepsilon_{j,0}$ , based on condition (22), along with expression (23), the equation for determining the value of  $\varepsilon_{j,0}$  can be derived. The explicit form of this equation is derived by integrating expression (23), taking into account relationships (18) and (19).

The direct substitution of expressions (18) and (19) into formulas (22) and (23) results in the equation that contains the required parameter  $\varepsilon_{j,0}$  in the arguments of the special functions. The solution to such equations is possible only by numerical methods. However, in the majority of practically important cases, the problem can be solved analytically. To this end, we expand expressions (18) and (19) into Taylor series. As a result, limiting the series to the square power of  $\varepsilon$ , we have the following equations:

$$\sigma(\varepsilon) = \sigma_0 + \sigma_1 \varepsilon + \sigma_2 \varepsilon^2, \quad (24)$$

$$K(\varepsilon) = K_0(1 + k_1 \varepsilon + k_2 \varepsilon^2); \quad (25)$$

$$p(\varepsilon) = p_0 - K_0 \{ \varepsilon + (k_1 + 1) \varepsilon^2 / 2 + (k_2 + k_1 + 1) \varepsilon^3 / 3 \}; \quad (26)$$

$$\sigma_1 = -2\Delta\gamma(1 - \sigma_0)(1 - 2\sigma_0); \quad (27)$$

$$\sigma_2 = -\Delta\gamma(1 - \sigma_0)(1 - 2\sigma_0) \times \{ 2\Delta\gamma(3 - 4\sigma_0) + 1 \}; \quad (28)$$

$$k_1 = -(2\gamma_1 + 1) + \sigma_1 / (1 + \sigma_0); \quad (29)$$

$$k_2 = 2\gamma_1(\gamma_1 + 1) + \{ \sigma_2 - (2\gamma_1 + 1) \sigma_1 \} / (1 + \sigma_0). \quad (30)$$

In this case, Eq. (22) has a fairly simple form

$$\begin{aligned} & \epsilon_{j,0} + (k_1 + 1) \left( \epsilon_{j,0}^2 + \langle \delta \epsilon_{V,j}^2(\mathbf{r}) \rangle_j \right) / 2 \\ & + (k_2 + k_1 + 1) \left( \epsilon_{j,0}^3 + 3 \epsilon_{j,0} \langle \delta \epsilon_{V,j}^2(\mathbf{r}) \rangle_j \right) / 3 = 0. \end{aligned} \quad (31)$$

As the first approximation, we assume that  $\epsilon_{j,0} \ll 1$ . Assuming that, in (31)  $\epsilon_{j,0} \sim \langle \delta \epsilon_{V,j}^2(\mathbf{r}) \rangle_j$ , we find

$$\epsilon_{j,0} = -(k_1 + 1) \langle \delta \epsilon_{V,j}^2(\mathbf{r}) \rangle_j / 2. \quad (32)$$

Expression (32) establishes the correlation between the value of the free volume of an individual intercrystallite boundary and fluctuations of the atomic density of its structure.

Only the average value of  $\epsilon_{j,0}$  over the statistical ensemble has practical significance. This value is equal to the average density of the distribution of the excess volume over the system of intercrystallite boundaries and can be determined by the following expression:

$$\epsilon_{Gb} = -(k_1 + 1) \langle \langle \delta \epsilon_{V,j}^2(\mathbf{r}) \rangle_j \rangle_s / 2. \quad (33)$$

In the considered approximation, formula (14) defines the value of the excess volume of the nanomaterial as follows:

$$V_f = V_0 \epsilon_{Nm}, \quad (34)$$

where  $V_0$  is the volume of the single crystal, and

$$\epsilon_{Nm} = \epsilon_{Gb} v_{Gb} \quad (35)$$

is the specific value of the excess volume of the nanocrystalline material.

It can be concluded from the above-described estimates that, in the case of the nanomaterials, we have  $\epsilon_{Nm} \sim (1-3) \times 10^{-2}$ . This means that the approximation introduced by formulas (24)–(32) describes the volume changes in the nanomaterials with fairly high accuracy.

#### *Elastic Constants and Internal Stresses in Nanocrystalline Materials*

Let us determine the values of the elastic constants of the nanomaterial. After averaging expressions (24) and (25) over the volume and over the statistical ensemble, we obtain the following linear dependences of the elastic constants on the value of  $\epsilon_{Nm}$ :

$$\langle \sigma(\epsilon) \rangle \approx \sigma_0 + (\sigma_1 - 2\sigma_2 / (k_1 + 1)) \epsilon_{Nm}; \quad (36)$$

$$\langle K(\epsilon) \rangle \approx K_0 \{ 1 + (k_1 - 2k_2 / (k_1 + 1)) \epsilon_{Nm} \}. \quad (37)$$

Using expressions (26) and (33), we find the magnitude of the mean-square fluctuation of the internal pressure  $\delta p = p(\epsilon) - p_0$  in nanocrystalline materials as follows:

$$\langle \delta p^2 \rangle^{1/2} \approx K_0 \{ \epsilon_{Nm} / (\gamma_1 - 0.5\sigma_1 / (1 + \sigma_0)) \}^{1/2}. \quad (38)$$

The pressure is determined as the average value of the diagonal components of the stress tensor [10, 11]. That is why expression (38) provides a convenient estimate of the stressed state of the nanocrystalline materials.

#### DISCUSSION

Expression (38) allows one to estimate the stressed state of the nanomaterials using the known value of  $\epsilon_{Nm}$ , while the formulas (16), (20), (32), (33), and (35)–(37) can be used in the experiments to determine  $\epsilon_{Nm}$ .

In particular, the inhomogeneous deformation of the crystal lattice enables the broadening of X-ray diffraction lines. This effect is used to determine the mean-square deformation  $\epsilon_d = \langle \langle (\Delta d(\mathbf{r})/d)^2 \rangle_s \rangle_v^{1/2}$  in nanomaterials [1, 6]. The angular brackets  $\langle \dots \rangle_v$  designate averaging over the volume, while  $\Delta d(\mathbf{r})/d$  is the local change in the interplanar spacing  $d$  of the lattice. The volume and the linear deformations are connected at point  $\mathbf{r}$  by the relationship  $\epsilon_v(\mathbf{r}) \approx 3\Delta d(\mathbf{r})/d$ . Hence, using (32), (33), and (35), we find

$$\epsilon_d = \{ \epsilon_{Nm} v_{Gb} / (\gamma_1 - 0.5\sigma_1 / (1 + \sigma_0)) \}^{1/2} / 3. \quad (39)$$

This relationship connects the average values of internal deformations in the nanomaterials that are experimentally determined using the excess volume.

Other approaches to the experimental determination of  $\epsilon_{Nm}$ ,  $\gamma_1$ , and  $\gamma_t$  are given by the formulas (16), (20), and (36), (37). For example, the dependences that are specified by expressions (16) and (20) can be measured [14]. This makes it possible to obtain two equations that connect the quantities  $\epsilon_{Nm}$ ,  $\gamma_1$ , and  $\gamma_t$  for a fixed stressed state of the material. On the other hand, the quantity

$$\gamma_G = (\gamma_1 + 2\gamma_t) / 3, \quad (40)$$

which is the average value of the constants  $\gamma_1$  and  $\gamma_t$  over the acoustic spectrum (Grüneisen constant [15]), can also be determined experimentally. Its values for many materials are well known [15]. Thus, the experimental data provide an opportunity to construct a closed system of three equations that define three required values, i.e.,  $\epsilon_{Nm}$ ,  $\gamma_1$ , and  $\gamma_t$ . Measurements of the elastic moduli of the nanomaterials and the application of the expressions (27)–(39), (36), (37), and (40) provide an opportunity of the independent determination of  $\epsilon_{Nm}$ ,  $\gamma_1$ , and  $\gamma_t$ .

For approximate numerical estimates, expressions (36) and (37) can be used in a simpler one-parametric Grüneisen approximation. To this end, it is sufficient to assume that  $\gamma_1 = \gamma_t = \gamma_G$ . Let us estimate the modulus of isothermal compression of nanocrystalline iron in this approximation assuming in formula (37)

that  $\Delta\gamma \approx 0$ ,  $K_0 \approx 1.7 \times 10^{11}$  Pa,  $\gamma_G \approx 2$  [15], and  $\epsilon_{Nm} \sim (1-3) \times 10^{-2}$ . In this case, the relative change in the compression moduli is  $|(K - K_0)/K_0| \sim (5-15) \times 10^{-2}$ . It is an easily measurable quantity.

In the approximation of  $\Delta\gamma \approx 0$ , the ratio of the values of  $\epsilon_{Nm}$  and  $\epsilon_d$  can be estimated by formula (39); e.g., for nanocrystalline iron at  $\epsilon_{Nm} = (1-3) \times 10^{-2}$ , we obtain  $\epsilon_d \approx (0.7-1.2) \times 10^{-2}$ . These estimates are in good agreement with the known experimental data [1, 6]. Thus, relationship (39) can be used to experimentally estimate the value of the excess volume of the nanomaterials.

In the same approximations, we now calculate the mean-square of the fluctuation of the internal pressure in nanocrystalline iron. To this end, we substitute  $\epsilon_{Nm} \sim 10^{-2}$  into formula (38). As a result, we obtain  $\langle \delta p^2 \rangle^{1/2} \approx 1.2 \times 10^{10}$  Pa. For comparison, here, we provide the magnitudes of the theoretical and macroscopic ultimate strength for iron, i.e.,  $\sigma_{Th} \approx 2 \times 10^{10}$  Pa and  $\sigma_{Fr} \approx 5 \times 10^8$  Pa, respectively [15]. It can be seen from these estimates that the local fluctuations of the internal stresses in the nanomaterials can significantly exceed the value of  $\sigma_{Fr}$ . Since the high internal stresses are found only in small volumes at the intercrystallite boundaries with  $\delta \leq L^2 H_{Gb}/4$ , the material is not destructed on the macroscopic level. Here,  $L \sim (2-5)a$  is the period of the change in the atomic density in the plane of the high-angle boundary [7, 8]. However, it is necessary to take into account such high values of local internal stresses in the analysis of the physical processes that occur in the nanomaterials.

## CONCLUSIONS

(1) Elastic properties and other characteristics of the stressed state of the single-component nanomaterials are defined by the value of the excess volume.

(2) The fluctuations of the internal stresses in the nanomaterials can significantly exceed the value of the macroscopic ultimate strength.

(3) The value of the excess volume in the single-component nanomaterials is characterized by the nonlinear effects caused by the dependence of the elastic moduli on the irreversible volume deformation introduced by intercrystallite boundaries.

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## REFERENCES

1. R. Z. Valiev and I. V. Aleksandrov, *Bulk Nanostructured Metallic Materials: Production, Structure and Properties* (Akademkniga, Moscow, 2007) [in Russian].
2. M. I. Alymov, A. B. Ankudinov, K. N. Agafonov, V. A. Zelenskii, and S. I. Averin, "Effect of the grain size on the density of bulk crystalline materials," *Russ. Metall. (Metally)* **2005**, 273–275 (2005).
3. B. S. Bokstein and A. B. Yaroslavl'tsev, *Diffusion of Atoms and Ions in Solids* (MISIS, Moscow, 2005) [in Russian].
4. L. S. Vasil'ev and S. F. Lomayeva, "On the analysis of mechanism of super saturation of metal powders with interstitial impurities during mechanoactivation," *J. Mater. Sci.* **3**, 5411–5415 (2004).
5. P. E. J. Flewitt and R. K. Wild, *Grain Boundaries. Their Microstructure and Chemistry* (Wiley, Chichester, 2001).
6. A. I. Gusev, *Nanomaterials, Nanostructures, Nanotechnologies* (Fizmatlit, Moscow, 2005) [in Russian].
7. B. S. Bokstein, Ch. V. Kopetskii, and L. S. Shvindlerman, *Thermodynamics and Kinetics of Grain Boundaries in Metals* (Metallurgiya, Moscow, 1986) [in Russian].
8. O. A. Kaibyshev and R. Z. Valiev, *Grain Boundaries and Properties of Metals* (Metallurgiya, Moscow, 1987) [in Russian].
9. N. N. Medvedev, *Voronoi–Delanney Method in Study of Non-Crystalline Systems Structure* (SO RAN, Novosibirsk, 2000) [in Russian].
10. J. D. Eshelby, "The continuum theory of lattice defects," in *Solid State Physics*, **Vol. 3**, Ed. by F. Seitz and D. Turnbull (Academic, New York, 1956), pp. 79–144.
11. G. Ya. Gun, *Theoretical Foundations of Metal Treatment by Pressure* (Metallurgiya, Moscow, 1980) [in Russian].
12. N. W. Nell N. Ashcroft, and N. D. Mermin, *Solid State Physics* (Holt, Rinehart and Winston, New York, 1976).
13. L. D. Landau and E. M. Lifshitz, *Course of Theoretical Physics: Vol. 7, The Theory of Elasticity* (Nauka, Moscow, 1987; Butterworth–Heinemann, 1986, 2012).
14. G. A. Sobolev and A. V. Ponomarev, *Earthquake Physics and Precursors* (Nauka, Moscow, 2003) [in Russian].
15. M. A. Shtremel', *Strength of Alloys. I. Lattice Defects* (Metallurgiya, Moscow, 1982) [in Russian].

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