On the nature of crystal plasticity under compression

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Abstract. The nanostructuring of crystals into domains under uniform compression, the plasticity of a solid nanostructure under pressure, and the bimodal distribution of domains size are explained based on the dependence of the surface energy and surface pressure from the shape, size, and density of nanocrystals.

It is known that as the uniform (hydrostatic) compression grows, fluctuations in a thermodynamically equilibrium single crystal of an elementary (singlecomponent) substance are decreased. Based on these considerations, it seems that upon compression of the crystal its structure must become more homogeneous. However, experiments show that this is true only if the uniform compression is low ($v/v_0 > 0.85$), whereas at a high level of compression ($v/v_0 < 0.6$), a single crystal of an elementary substance acquires a nanocrystalline domain structure. A domain is a region of a crystal that differs from neighboring ones by the direction of the displacement vector of crystal lattice and has an intercrystalline surface. Here, $v/v_0$ is the ratio of the specific volume (per atom: $v = V/N$) of the crystal at pressure $P$ and temperature $T$ and volume when $P = 0$ and $T = 0$ K.

It was noted [1] that the distribution histograms for the number of megaplastic-deformation-induced domains plotted against their characteristic linear size have two maxima, $d_{s1}$ and $d_{s2}$ with $d_{s1} < d_{s2}$. Here, $d_{s} = \Sigma_{s}/1/2$, where $\Sigma_{s}$ is the area of the electron-microscopic image of the domain. That is, domains resulting from nanostructuring have a bimodal size distribution.

Theoretical methods that studying the influence of nanostructuring on the strength and plasticity of materials assume that the intercrystalline surface in a crystal exists a priori. But the question why the crystal, starting from a certain pressure, experiences fragmentation (nanostructuring) and acquires a domain structure with a clear-cut interdomain surface remains unclear. When a crystal becomes nanostructured, the appearance of an interdomain surface ($\Sigma$) seems to make the system less stable because of the contribution of surface energy: $\Sigma \cdot \sigma$, where $\sigma$ is the specific surface energy (energy per unit area). Then, why does the baric nanostructuring of the crystal take place? Why does a nanostructured solid substance under compression become plastic? Why do the distribution histograms of the number of domains resulted from nanofragmentation have a bimodal form? To answer these questions, one should know how the surface energy and surface pressure depend on the shape and size of the nanocrystal at different densities and temperatures.

It is shown (Fig. 1 top graph) that the nature of the baric structuring of the crystal is that the surface energy of the crystal becomes negative ($\sigma < 0$) at $P > P_{pr}$ [2, 3]. At this, as was shown in [4], the intercrystalline surface energy of domain ($\sigma_{d}$) in structured solid is related to the surface energy of freestanding nanocrystal by formula: $\sigma_{d} = \chi \cdot \sigma$, where the coefficient $\chi$ depends on the crystallographic indices of the contacting faces of the domains: $1 > \chi > 0$. 

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Therefore, if performed $\sigma < 0$, then we have $\sigma_d < 0$ too.

![Graphs](image)

**Figure 1.** Pressure dependences of the specific surface energy for the (100) face (upper panel), $\Delta_p(P)$ (middle panel), and $\sigma(1 - \Delta_p)$ (lower panel) for BCC iron. Continuous lines, $T = 300$ K; dashed line, $T = 1500$ K.

In addition, it is shown (Fig. 1 bottom graph), that the structured at compression solid substance becomes plastical due to the growth of surface pressure $P_{sf}$ in the nanocrystal. For
the surface pressure was obtained the following expression [5]:

\[ P_{sf} = \left[ \frac{\partial (\sigma \Sigma / N)}{\partial V} \right]_{T,N} = P_{ls} \cdot (1 - \Delta_p), \]

(1)

where \( P_{ls} \) is the Laplace pressure, which is determined by the change of surface area at the change of volume of nanosystem:

\[ P_{ls} = \sigma \cdot \left[ \frac{\partial (\Sigma / N)}{\partial V} \right]_{T,N}, \]

(2)

the expression for the function \( \Delta_p \) is given by: \( \Delta_p = - \frac{\partial \ln(\sigma)}{\partial \ln(N)} \).

In Fig. 1 are shown the calculated by method from [5] for the macrocrystalline body-centered cubic (BCC) iron the isothermal dependencies from pressure (in GPa) of the next functions: \( \sigma(100) \) is the specific surface energy (in \( 10^{-3} \) J/m\(^2\)) for (100) face – top graph, \( \Delta_p(P) \) – the middle graph, \( \sigma(1 - \Delta_p) \) – the lower graph.

It was assumed that the atoms interact via the pairwise potential of the Mie-Lennard-Jones:

\[ \varphi(r) = \frac{D}{(b - a)} \left[ a \left( \frac{r_0}{r} \right)^b - b \left( \frac{r_0}{r} \right)^a \right]. \]

(3)

Here, \( D \) and \( r_0 \) are the depth and the coordinate of the potential minimum, \( b > a > 1 \) are the numerical parameters. Parameters of the Mie-Lennard-Jones potential (3) for BCC-Fe defined in [3] are: \( r_0 = 2.4775 \times 10^{-10} \) m, \( D/k_B = 12576.7 \) K, \( a = 2.95 \), \( b = 8.26 \).

Based on these parameters, the normal specific volume, the Debye temperature and the first Gruneisen parameter at \( \nu/V_0 = 1 \) are [3]: \( v_0 = \frac{\pi}{6k_B} r_0^3 = 7.0494 \) cm\(^3\)/mole, \( \Theta(1) = 408.073 \) K, \( \gamma(1) = 1.702 \). Here, \( k_B \) is the Boltzmann constant, \( k_p \) is the structure packing coefficient (for BCC structure \( k_p = 0.6802 \)). The state equation for macrocrystalline BCC iron was calculated in [3], where the good agreement with experimental data was obtained.

In Fig. 1 the solid line is the isotherm of 300 K, the dashed line represents the isotherm of 1500 K. The vertical line in the top graph is the area of the scatter of the experimental data for \( \sigma(100) \) at \( P = 0 \) [2, p. 416]: \( \sigma(100)/[10^{-3} \text{ J/m}^2] = 1720 - 2480 \).

Since the inequality \( \sigma \leq 0 \) is fulfilled for \( P \geq P_p \), the Laplace pressure will be negative in accordance with (2) \( (P_{ls} \sim \sigma < 0) \), i.e. \( P_{ls} \) will be tensile. However, when nanocrystals or macrocrystals are compressed, function \( \sigma(1 - \Delta_p) \) varies at the fragmentation point continuously, as it shown in Fig. 1 for BCC-Fe. Therefore, surface pressure according to (1) \( P_{sf} = P_{ls} (1 - \Delta_p) \sim \sigma(1 - \Delta_p) > 0 \) continuously grows with the density of the nanocrystal under compression. A domain resulted from compression will experience elevated surface pressure \( P_{sf} \). The higher the outer pressure, the higher pressure \( P_{sf} \) (Fig. 1). The fragmentation-induced pressure \( P_{sf} \) squeezes the surface bounded domain still greater. As a result, fragmentation-induced domains shrink, leaving a space in between. Therefore, the material nanostructured by baric fragmentation will resemble a fluid material: like any liquid phase, it will take the shape of a vessel containing it.

The nature of the bimodal distribution of domain over sizes, it was felt that the maximum size of the \( d_{1,s} \) corresponds to the domains of deformation origin, and the second maximum size \( d_{1,o} > d_{1,s} \) corresponds to recrystallized domains [1]. However, this bimodality can be explained on the basis of the dependence of energy parameters of a nanocrystal from the shape of its surface. As it shown in [2, 6], using the RP-model of the nanocrystal at high pressures (at \( P \geq P_p \)) formed under of the plastic fragmentation the domain is energetically
advantageous to have a noncubic (i.e. platelike or rodlike) forms. This leads to the bimorphism: within the framework of RP model at constant values of $k_p$, $T$, $v$ and $N$ the noncubic nanocrystal with equal probability can have either platelike or rodlike form. Both these shapes of nanocrystal have equal values $\Sigma$ and $\sigma$, but different values of the diameter (the distance between the most distant atoms): the diameter of platelike shape is less than rodlike. A bimodal distribution of the formed under the “megaplastic” deformation of domains on size, discovered by the authors of [1] can be explained by means of the bimorphism.

At $P > P_f$ the noncubic shapes of the nanocrystal are energetically more favorable than the cubic shape of the same isomers. Therefore, if the pressure is reduced drastically (so that the system would have no time to relax into a single-crystalline state) at $P > P_f$, the compressed nanostructured substance is expected to disintegrate into fragments with a noncubic surface. The dispersion of solids under sudden reset of hydrostatic pressure was discovered in [7]. In that work was shown that, when a compression pressure exceeds some material-specific critical value and at the fast pressure drop (about 2 GPa/ms) not only inorganic materials but also teflone, rubber, paraffin, etc., were dispersed. The substances fragments, which were observed in [7], possess a typical splintery (oblate or prolate) habitus.

Conclusions

Thus, it was found that (i) the baric nanostructuring of a crystal takes place when function $\sigma$ becomes negative, (ii) a nanostructured solid becomes the ductile under compression because of the growth of the surface pressure, which compresses the domains, and (iii) the bimodal distribution for domains which produced by baric nanofragmentation is explained by the fact that under such conditions it is energetically favorable for the domains to have a maximal specific (per atom) surface area.

Therefore, the compression-induced exothermic transition of the crystal to a nanostructural state leads to a sharp rise in the domain density, on the one hand, and to a sharp decrease in the viscosity of the resulting nanostructured medium on the other. Domains produced by such exothermic baric fragmentation exhibit a splintery (platelike or rodlike) habitus. A crystal nanostructured by exothermic baric fragmentation becomes ductile (passes to a fluid state) and takes the shape of a vessel. If the pressure is sharply drop, the nanostructured medium shatters like sprayed liquid.

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