Mechanical strain and structural phase transition in small particles

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LETTER TO THE EDITOR

MECHANICAL STRAIN AND STRUCTURAL PHASE TRANSITION IN SMALL PARTICLES[1]

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Dedicated to Professor Mladen Paić on the occasion of his 90$^{\mathbf{th}}$ birthday

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Strain energy as a part of the Gibbs free-energy change during the structural phase transition in small particles has been analysed. A special attention has been paid to the transitions that are characterized by small latent heats and large volume changes (large strains in the crystal lattice). Under the assumption that the dilatation of the nucleus of the phase just in formation causes plastic deformation of the particle, a new expression for the strain energy has been formulated. It shows that this energy may be greatly reduced if particles are sufficiently small.

[1] A part of this work was presented on the "Second Croatian–Slovenian Crystallographic Meeting" held in Stubičke toplice, September, 1993.

The general expression for the Gibbs free-energy change, ΔG, associated with the formation of a small region of a new solid phase (embryo) inside a piece of the parent solid phase (matrix), is composed of three terms. According to the classical theory of nucleation [1], the first term, ΔG_v , represents the bulk free-energy difference between the two phases. It is negative if the new phase has lower free-energy. The second and third term, ΔG_I and ΔG_s, describe the interfacial and strain energy, respectively. These terms are evidently positive. Assuming that the embryo is shaped spherically, the Gibbs free-energy ΔG is a function of the embryo's radius r only. The phase transition cannot begin until the sum of all three terms becomes negative. However, when this condition is satisfied, the curve of ΔG versus r passes through the maximum, ΔG^*, at the critical radius, r^*, and then decreases. If the radius of an embryo becomes bigger than r^*, the embryo turns into a nucleus of a new phase which can grow further without limitations.

Let us concentrate on the main problem of this work, the strain energy. Generally, its magnitude can be deduced from the theory of Eshelby [2] who has treated the formation of embryos in an infinite and elastic continuum. Eshelby's equations show that the strain energy depends on the mechanical properties of the two phases and on the volume change during the transition. For example, in white–to–gray tin transition, in which the volume change is very large, by about 22%, the strain energy considerably exceeds the bulk free-energy. As a consequence, the formation of nuclei of gray tin inside an infinite matrix of white tin is simply impossible [3]. For reasons which will be clear later, we have to mention again that Eshelby's equations have been derived for infinite matrices. This means that the strain energy should be treated as a size-independent quantity.

In this note we show that the problem of strain energy can be treated in a different manner for small particles. Our treatment is based on three suppositions that are realistic at least for metallic systems. The first and the most important is that a sufficiently small particle is not an infinite but a finite matrix. The second is that the material of the particle possesses a yield point below which it behaves as an elastic body, but above which it is deformed plastically at a constant stress (it flows). The third supposition is that the matrix strain at the yield point is very small, i.e., much smaller than the strain that would have been caused by the embryo growth. Following Eshelby, we now consider several imaginary operations leading to the appearance of a new phase inside a particle with properties just defined.

First, we remove a small volume of material from the center of the particle (with radius R) and allow it to undergo an unconstrained transformation. Then, we compress it to its original size and shape, insert it into the hole in the particle again and weld the two regions over their surface of contact. Now, we have an assembly of a particle with an embryo which is in the state of self-stress. Its amount is given by

$$\Sigma_0 = 3K \left(\frac{\Delta r}{r}\right)_0 , \tag{1}$$

and the strain energy of the assembly per unit volume is given by

$$\Delta g_s = \frac{9K}{2}\left(\frac{\Delta r}{r}\right)_0^2 . \qquad (2)$$

K is the bulk modulus of the embrio and $(\Delta r/r)_0$ is the relative change of its radius at the end of unconstrained transformation.

Then we let the embryo expand. The change in its radius is Δr and the new particle width (compared to the old one: $D = R - r$) is equal $D' = R + \Delta R - (r + \Delta r)$. The expansion of the embryo, evidently, causes the stress in the particle and, according to its presumed stress-strain diagram, causes the plastic deformation of the whole particle. We intend now to find relation between $(\Delta r/r)$ and the size of a particle appropriately expressed as the ratio R/r.

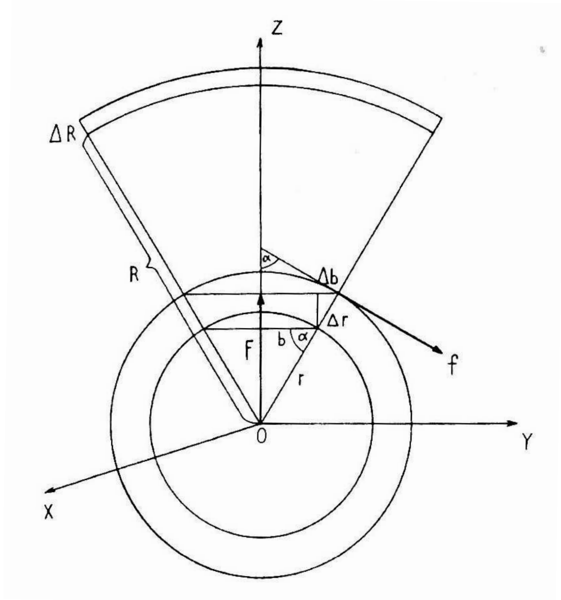

Fig. 1. A sphere of a radius r, representing an expanding embryo in a matrix with the radius R.

Imagine a small calotte of a sphere representing an embryo. This sphere of radius r is in the centre of the particle of radius R, as is shown in Fig. 1. Since the area of the sphere is large in comparison to the area of the calotte, we assume that the area of the calotte is approximately equal to the area of its base (represented by a circle of radius b). If the embryo is partly expanded, the circumference of the base, $o = 2\pi b$, is increased by the amount $\Delta o = 2\pi\Delta b$. A force is acting on the base of the calotte from the interior of the sphere. Its origin is the difference ΔP between the pressures in the sphere and in the surrounding medium. This force is parallel to the axis Oz through the centre of the sphere, and its amount, $F = \pi(b + \Delta b)^2\Delta P$, must be in equilibrium with the forces from the exterior of the sphere. They are distributed around the base of the calotte and point tangentially to the sphere. Evidently, these forces are caused by the stress p in the particle (which is caused by the embryo expansion) and their sum is equal to $f = 2\pi p(b + \Delta b)D'$. The value of p should correspond to the stress under which, according to the presumed stress-strain diagram, the matrix flows. In equilibrium, the force F is equal to the sum of all forces f projected onto the radius of the sphere ($F = f \cos\alpha$). Since $\Delta b/b = \Delta r/r$ and $\cos\alpha = b/r$, the pressure difference is

$$\Delta P = \frac{2pD'/r}{1 + \Delta r/r}. \tag{3}$$

It corresponds to the stress in a partly relaxed embryo which, in accordance with Eq. (1), is given by

$$\Sigma = 3K \left[\left(\frac{\Delta r}{r} \right)_0 - \frac{\Delta r}{r} \right]. \tag{4}$$

The corresponding strain energy is

$$g_s = \frac{9K}{2} \left[\left(\frac{\Delta r}{r} \right)_0^2 - \left(\frac{\Delta r}{r} \right)^2 \right]. \tag{5}$$

Equating (3) and (4), we have

$$\frac{D'}{r} = \frac{3K}{2p} \left[\left(\frac{\Delta r}{r} \right)_0 - \frac{\Delta r}{r} \right] \left(1 + \frac{\Delta r}{r} \right). \tag{6}$$

We assume that the volume of the particle is constant:

$$\mathrm{d}V = \mathrm{d} \left[\frac{4\pi}{3} (R + \Delta R)^3 - \frac{4\pi}{3} (r + \Delta r)^3 \right] = 0. \tag{7}$$

Combining Eqs. (6) and (7), we finally obtain the equation relating $\Delta r/r$ and R/r:

$$\left(\frac{R}{r} \right)^3 - \left\{ 1 + \frac{\Delta r}{r} + C \left[\left(\frac{\Delta r}{r} \right)_0 - \frac{\Delta r}{r} \right] \left(1 + \frac{\Delta r}{r} \right) \right\} \left(\frac{R}{r} \right)^2 + \frac{\Delta r}{r} = 0 \tag{8}$$

The quantity $C = 3K/2p$ is compounded of the two above–mentioned constants, K and p, which describe the mechanical properties of the embryo and particle, respectively.

The ratio R/r obtained by Eq. (6) (we did not insist on its analytical solution), together with Eq. (5), allows to write a new expression for the strain energy $\Delta g_s(r, R)$. It is R-dependent, what means that it is valid for the particle with the specific radius R. Thus, we obtain an expression which shows what Eshelby's equations do not show the dependence of the strain energy on the size of the matrix. Our expression is valid between two self-evident limits:

$$\Delta g_s = (\Delta g_s)_{max} = \frac{9K}{2}\left(\frac{\Delta r}{r}\right)_0^2 \qquad \text{for} \quad \frac{\Delta r}{r} = 0, \quad \text{or} \quad \frac{R}{r} = \left(\frac{R}{r}\right)_{max}$$

and

$$\Delta g_s = (\Delta g_s)_{min} = 0 \qquad \text{for} \quad \frac{\Delta r}{r} = \left(\frac{\Delta r}{r}\right)_0, \quad \text{or} \quad \frac{R}{r} = 1$$

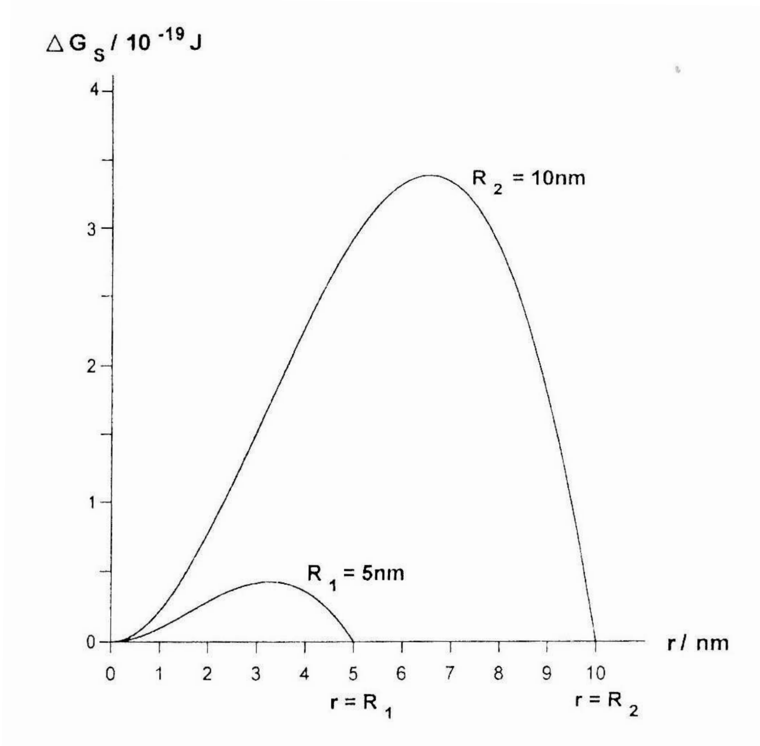

Fig. 2. The dependence of the strain energy ΔG_s on the embryo radius r in small particles of radii R_1 and R_2.

Let us illustrate the results with the calculations for white–to–gray tin transformation. This metal is chosen mainly because its mechanical properties (first of all marked ductility of white tin) and a large volume change during the transformation are in almost ideal accordance with our suppositions. Using the constants for tin [4–6]: $K = 4.33 \cdot 10^{10}$ Pa, $(\Delta r/r)_0 = 0.072$ and $C = 4.42 \cdot 10^4$, and making numerical calculations according to Eqs. (5) and (6), we obtain the results shown in Fig.

2. It shows ΔG_s (not Δg_s) for the particles of two radii: 5 nm and 10 nm. As one can see, smaller particle is characterized by smaller strain energy. This fact is in full accordance with our expectations. Our next note will show the influence that such derived strain energy has on the Gibbs free-energy change during the phase transition of tin. The calculations carried out to estimate the sizes of the particles for which the nucleation process is considerably probable will also be presented as well as our experimental investigations of the phase transition of tin particles of various sizes.

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ENERGIJA NAPREZANJA I STRUKTURNI FAZNI PRIJELAZ U SITNIM ČESTICAMA

Analizirana je energija naprezanja kao dio promjene Gibbsove slobodne energije pri strukturnom faznom prijelazu u sitnim česticama. Posebno su razmatrani oni prijelazi za koje su karakteristične male latentne topline i velike promjene volumena (velika naprezanja u kristalnoj rešetki). Pod pretpostavkom da širenje nukleusa novonastajuće faze uzrokuje plastičnu deformaciju čestice, formuliran je novi izraz za energiju naprezanja. On pokazuje da energija naprezanja može biti jako reducirana ako su čestice dovoljno male.