Elastic Instability of Grain Boundaries and the Physical Origin of Superplasticity

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Matter between contiguous crystallites is assimilated to a thin elastic plate immersed in a different elastic medium. It is shown that a shear stress exceeding a critical value should corrugate the boundary and induce periodic normal stress fields in the two adjacent crystal surfaces, which cause motion of vacancies in closed loops between the two crystals. The consequent cyclic transport of atoms in the opposite sense determines crystal sliding at a temperature dependent relative speed. Most of the phenomenology of superplastic allows follows in a quantitative manner.

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Superplasticity constitutes a fascinating subject and a challenge for condensed matter theorists because the precise microscopic mechanism that makes solid materials behave in many respects as fluids, without leaving the solid structure, is still under discussion.

The most salient feature of superplastic solids is the ability to undergo extensive, neck-free, tensile deformation prior to fracture. Instead of failing after a plastic deformation of a few percent, the sample subjected to a tensile stress beyond the elastic limit enters the superplastic regime characterized by uniform strains of thousands of percent. Elongations of 10–20 times are not infrequent in superplastic alloys and a record strain of 80 times has been reported for an aluminum bronze [1]. The phenomenon is realized in a range of temperatures close to half the melting point in kelvins for strain rates in a range that starts at about 10^{-4}–10^{-2} s^{-1}, depending on the material.

Most theoretical studies give a power law for the relation between the strain rate and the applied stress. However, this disagrees with experiments if the exponent is assumed constant. The variation of the exponent is ascribed to changes in the accommodation mechanism of grain misfits [2,3]. Although superplastic materials may be very different, they all exhibit a common deformation phenomenology. This suggests that superplasticity is caused by a very basic physical mechanism which yet remains unknown.

Although based on the same general principles, the explanation of the superplastic flow put forward here is rather different from the traditional approaches. It is consistent with a theory published recently by Lagos and Duque that produces excellent agreement with experiments over the whole range of strain rates [4–6]. However, the present approach provides deeper insight into the phenomenon.

Superplastic grain boundary sliding seems connected with a recent study of interfaces in solids [7]. By Monte Carlo simulation and analytical treatment it is shown that, in general, ideally planar structures in bulk crystalline materials become rough when subjected to in-plane shear forces [7]. The system undergoes an elastic instability followed by atomic transport driven by the induced stress fields. This effect is closely related to Asaro-Tiller-Grinfeld instability, i.e., stress induced buckling of solid surfaces into trenches or islands [8–10], and with the spontaneous roughening of thin films produced by strong in-plane stresses arising from lattice mismatch with the substrate [11–16].

Roughening of stressed surfaces has become a very active field of physical research. This phenomenon is well established by theory, computer simulation, and experiment. Experimental observations of the surface instabilities [13,16,17] provide indirect experimental support to the predicted stress induced roughening of bulk interfaces and grain boundaries [7], which has the same physical origin but is of more difficult experimental detection.

The structure of the derivation is as follows: (i) First, it is shown that the boundary separating two crystallites may become elastically unstable and undergo a periodic deformation when subjected to an overcritical shear stress. The main consequence of boundary corrugation is the rise of periodic normal stress fields in the two crystal surfaces. (ii) Second, the effect of this periodic stress field on the thermodynamic equilibrium of vacancies in the interfaces between the two crystals and intergranular matter is examined. It is well known that grain boundaries are efficient sources, or sinks, for vacancies [18]. It will be shown that the induced stresses cause loop motion of vacancies across the grain boundaries, which provides not only an accommodation mechanism, but also, and primarily, the driving force for crystal sliding.

We now examine the first point of the derivation in detail. Adjacent crystallites are separated by the grain boundary, which is a layer of several atomic distances thick that smoothly matches the two crystal structures. When the system is subjected to external forces its mechanical analysis must distinguish intergranular and crystalline matter as separate units because they have slightly different mechanical properties [19,20]. Intergrain matter will be assimilated into a thin elastic plate immersed in a different elastic medium representing the crystals.

Consider now two contiguous crystallites exerting shear forces on the grain boundary between them. The shear forces are parallel to the interfaces. One can model the system as an elastic plate of thickness d_1, width b, and

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length L, subjected to a shear stress τ and, for the sake of generality, axial compressive forces of strength F applied to the edges of size b. Both the compressing and shear forces are parallel to the main direction, associated with the length L. Only the main dimension and transversal deformations, normal to the plane of the plate, will be considered. The magnitudes b and L will cancel in the final solution.

The plate modeling the grain boundary is immersed in an elastic medium that represents crystalline matter. This way, if a section δx of the plate, at distance x from the left end along the main dimension, undergoes a transversal shift $y(x)$, then the elastic medium will exert on it a restitutive force $-2\alpha y(x) b\,\delta x$, where 2α is a constant proportional to the Young modulus of the crystals. If $F = \tau = 0$, the plate remains plane.

This is a problem of material mechanics that can be solved using the general equation originally attributed to Euler, commonly used by engineers to calculate shapes of loaded beams,

$$\frac{y''}{(1 - y'^2)^{3/2}} = -\frac{M(x)}{EI}, \tag{1}$$

where E denotes Young's elasticity modulus of the plate and I is the moment of inertia of the transversal section. The function $M(x)$ stands for the moment of the forces applied in the interval $[0, x]$ with respect to the point x of the plate. The left-hand side of Eq. (1) is the curvature at x. To be more specific with regard to our problem,

$$\frac{y''}{(1 + y'^2)^{3/2}} = \frac{\tau b d_1}{EI} x - \frac{F}{EI}(y - y_0) - \frac{2\alpha b}{EI}\int_0^x y(x')(x - x')\,dx' - \frac{M_0}{EI}, \tag{2}$$

where $y_0 = y(0)$ and M_0 is an external moment applied at $x = 0$.

Assume that $y'(x) \ll 1$ for any x in $[0, L]$. Equation (2) then admits the solution

$$y(x) = \delta \sin(kx). \tag{3}$$

By replacing in Eq. (2) it is found that $M_0 = y_0 = 0$,

$$k^4 - \frac{F}{EI}k^2 + \frac{2\alpha b}{EI} = 0, \tag{4}$$

and

$$\tau d_1 = \frac{2\alpha\delta}{k}. \tag{5}$$

Equations (4) and (5) determine the periodicity $2\ell = 2\pi/k$ and amplitude δ of the solution.

However, Eq. (4) gives real solutions for k only if $F \geq 2\sqrt{2\alpha b EI} \equiv F_c$. Hence the existence of periodic solutions demands a compressing force F parallel to the boundary and greater than the critical value F_c. As discussed below in the paragraph after Eq. (7), such force is highly expected in stressed real systems. The constant k also has a minimal value, given by

$$k_{\min}^2 = \sqrt{\frac{2\alpha b}{EI}}, \tag{6}$$

which determines a maximum for the semiperiod ℓ. The two cases $\tau = 0$ and $\alpha = F = 0$ can be solved in general and are useful to gain insight into the behavior of the system.

Replacing [in Eq. (6)] $\alpha = E'/d$ and the explicit expression for the moment of inertia $I = b d_1^3/12$, where E' is the Young modulus of the crystal and d is the grain size, one finds that the semiperiod $\ell = \pi/k$ of the periodic overcritical solution is bounded by

$$\ell(\max) = \pi\left(\frac{d d_1^3 E}{24E'}\right)^{1/4}. \tag{7}$$

Considering $E' \approx E$, $d = 10^{-3}$ cm, and estimating the grain boundary thickness as ten atomic distances, $d_1 \approx 3 \times 10^{-7}$ cm, and Eq. (7) gives $\ell(\max) \approx 10^{-6}$ [cm] $= 10^{-2}$ [μm].

In summary, an ideal grain boundary subjected to shear stress and a concurrent compressing force F, parallel to the plane of the boundary and greater than the critical value F_c, should periodically distort the boundary with semiperiod ℓ. A compressing in-plane force F is expected to occur in any real grain boundary under shearing, as a consequence of geometric imperfections in the crystallite surfaces. In effect, a pure shear exerted by the two crystallites on the intergrain region is partially transformed into in-plane compression by interface steps, small second phase inclusions, or triple junctions.

The most important result for what follows is that the periodic distortion of the boundary induces a periodic normal stress field

$$\sigma_1(x) = \pm\alpha\delta \sin\left(\frac{\pi}{\ell}x\right) \tag{8}$$

in the surfaces of the two adjacent crystallites. The positive sign applies to one of the crystal surfaces and the minus sign applies to the other one. In effect, for each value of x the stresses in the two crystal surfaces have opposite signs. If one of the crystals is compressed by the transversal displacement of the grain boundary then the other one is tractioned. This point is mentioned because it has important consequences.

Let us now discuss point (ii), stated previously. It is well known that grain boundaries may trap or release lattice vacancies very efficiently. This can be understood from the widely accepted idea that intergranular regions essentially consist of ordered crystalline matter with a high density of dislocations [18]. Assimilating a dislocation to a plane array of vacancies, one can think of the grain boundary as a particular phase of condensed vacancies in thermodynamic equilibrium with the vacancies diffusing through the crystallites, which constitute the free phase. The equilibrium equation is [4]

$$\eta(1 - \eta)^{\gamma-1} = \tfrac{1}{2}\exp[-\beta\epsilon_B(\sigma)], \qquad (9)$$

where η is the atomic concentration of vacancies diffusing freely in the crystallites, γ is the number of atomic sites per vacancy in the grain boundary, $\epsilon_B(\sigma)$ is the binding energy of a vacancy in the grain boundary relative to the energy of a free defect, $\beta = 1/(k_B T)$, k_B is the Boltzmann constant, and T is the absolute temperature. Equation (9) simply expresses the detailed balance of vacancy transfers.

The equilibrium concentration η of crystal vacancies depends on the stresses through the dependence of the condensation energy ϵ_B on them. In general, the energy associated with a vacancy depends on the positions of the surrounding atoms. It is reasonable to assume that if the crystal is strained ϵ_B will vary mostly with the volume dilation, and angular changes will have a minor effect. In an isotropic solid the elastic dilation is connected by Hooke's law with the hydrostatic pressure $\sigma = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3$, where σ_{ij} are the components of the stress tensor, hence $\epsilon_B = \epsilon_B(\sigma)$.

With Eq. (9) in mind, consider what happens when the stress fields of Eq. (8) are exerted on the crystal surfaces adjacent to the grain boundary. By Eq. (9) the equilibrium concentration $\eta = \eta[\sigma + \sigma_1(x)]$ varies periodically in each crystal surface and hence the intergranular region will release and capture vacancies in alternate sectors of length ℓ. On the other hand, the equilibrium concentration in the two sides of the corrugated grain boundary are $\eta(\sigma + \sigma_1)$ and $\eta(\sigma - \sigma_1)$. The consequent transversal concentration gradient determines a transversal flow of vacancies across the grain boundary. Vacancies evaporate from one side while condensing at the other side of the boundary. As σ_1, the transversal flux density vector varies periodically with x and changes sign each semiperiod ℓ.

Contiguous opposite currents across the boundary close by diffusional flow through the crystallites. The stress variation along the x direction induces a periodic concentration gradient in the longitudinal direction and, consequently, diffusive flow parallel to the boundary. The drift velocities in the two crystals have opposite senses, and the stream lines are essentially closed loops crossing the grain boundary and involving both crystals. In this manner, the periodic normal stresses given by Eq. (8) determine the transport of vacancies in a succession of closed paths between the two crystals. Focusing now on just the crystal surfaces, vacancies flow continuously along them, and the resulting lattice diffusion in the two surfaces has opposite senses. This involves a relative motion, or sliding, of the two adjacent crystals.

Next the mechanism described above is examined in a quantitative way to determine the relative speed between adjacent crystallites. By taking the gradient of Eq. (9) and inserting the same equation into the resulting expression, one obtains

$$\frac{1 - \gamma\eta}{\eta(1 - \eta)}\,\Delta\eta = -\beta\nabla\epsilon_B(\sigma). \qquad (10)$$

By replacing $d\epsilon_B/d\sigma \equiv -\Omega^*$ and $\vec{J}_v = -(D/\Omega_0)\nabla\eta$, where $\vec{J}_v$ is the vacancy density of flux, D is the diffusion coefficient, and Ω_0 is the atomic volume, Eq. (10) becomes

$$\vec{J}_v = -\frac{D}{k_B T}\,\frac{\Omega^*}{\Omega_0}\,\frac{\eta(1 - \eta)}{1 - \gamma\eta}\,\nabla\sigma. \qquad (11)$$

Identifying $-\vec{J}_v$ with the density of flux for lattice diffusion $\vec{J}_{\mathrm{lattice}} = \vec{v}/\Omega_0$, where $1/\Omega_0$ represents the atomic density and $\vec{v}$ is the mean atomic drift velocity, it is found that

$$\vec{v} = \frac{D}{k_B T}\,\frac{\eta(1 - \eta)}{1 - \gamma\eta}\,\Omega^*\nabla\sigma. \qquad (12)$$

The derivative of the normal stress σ_1 induced in the surface of contiguous crystals is periodic with amplitude

$$\left(\frac{d\sigma_1}{dx}\right)_{\max} = \frac{\pi\alpha\delta}{\ell} = \frac{\pi^2 d_1}{2\ell^2}\,\tau. \qquad (13)$$

Replacing in Eq. (12), and multiplying by 2 to account for the opposite motion of the surfaces with respect to the grain boundary, one obtains the relative speed of the sliding surfaces

$$\begin{aligned} \Delta v_{i'} &= \frac{\pi^2 d_1}{\ell^2}\,\frac{D}{k_B T}\,\frac{\eta(1 - \eta)}{1 - \gamma\eta}\,\Omega^*\tau_{i'z'}, \\ \Delta v_{z'} &= 0 \qquad (i' = x', y'), \end{aligned} \qquad (14)$$

where $\tau_{i'z'}$, $i' = x', y'$, are the components of the shear stress expressed in a frame of reference that has the $x'y'$ plane in the boundary surface.

The task is now to transform this result into a practical equation relating the flow stresses with the strain rates. The procedure will be described in general because it is rather technical. The only physical input is the equation $\dot{\varepsilon}_{iz} = \langle\Delta v_i\rangle_z/d$, $i = x, y, z$, which relates the strain rates $\dot{\varepsilon}_{ij}$ with the components of the relative sliding velocities of the crystallites. Here d represents the grain size and the frame of reference xyz is unique for all of the crystallites. Δv_i represents the projection of the relative velocity given by Eq. (14) on the i axis of the main frame of reference xyz. The symbol $\langle\cdots\rangle_z$ means the average over all orientations of the boundary plane that keep the normal vector in the subspace $z > 0$.

By choosing the axes of xyz parallel to the principal directions of the stress tensor, the projections and average are accomplished with the help of rotation matrices. Although fairly laborious, the procedure is straightforward and yields the simple result

$$(\dot{\varepsilon}_{ij}) = \frac{\pi d_1}{3d\ell^2}\frac{D_0}{k_B T}\exp\left(-\frac{\epsilon_a + \epsilon_B}{k_B T}\right)\exp\left(\frac{\Omega^*}{k_B T}\sigma\right)\Omega^*\begin{pmatrix} 2\sigma_x - \sigma_y - \sigma_z & 0 & 0 \\ 0 & -\sigma_x + 2\sigma_y - \sigma_z & 0 \\ 0 & 0 & -\sigma_x - \sigma_y + 2\sigma_z \end{pmatrix}, \quad (15)$$

where σ_x, σ_y, and σ_z are the principal stresses, $\sigma \equiv \sigma_x + \sigma_y + \sigma_z$, and use was made of the activated expression $D(T) = D_0 \exp[-\epsilon_a/(k_B T)]$ for the diffusion coefficient. Also it was assumed a linear dependence $\epsilon_B(\sigma) = \epsilon_B - \Omega^*\sigma$ of the condensation energy with the normal stresses. As expected, $\dot{\varepsilon}_{xx} + \dot{\varepsilon}_{yy} + \dot{\varepsilon}_{zz} = 0$, which means that volume remains unchanged in the deformation. For uniaxial tensile stresses $\sigma = \sigma_z, \sigma_x = \sigma_y = 0$, Eq. (15) reduces to

$$\dot{\varepsilon} = C_0 \frac{\Omega^*\sigma}{k_B T}\exp\left(-\frac{\epsilon_0 - \Omega^*\sigma}{k_B T}\right), \quad (16)$$

where $\epsilon_0 = \epsilon_a + \epsilon_B$ and C_0 is the preexponential factor in Eq. (15).

Figure 1 shows the uniaxial tensile stresses $\sigma = \sigma_z$ applied to samples of the particularly stable alloy Al-7475, deformed at constant stress rates $\dot{\varepsilon} = \dot{\varepsilon}_{zz}$ at four temperatures [21]. The solid curves illustrate the results given by Eq. (16) with C_0, ϵ_0, and Ω^* chosen to fit the data. The force F grows at the expense of the shear force exerted on the grain boundary. Thus, the critical value F_c determines a threshold stress σ_c. In Fig. 1, $\sigma_c = 0$.

From the value $C_0 = 1.1 \times 10^9$ s^{-1} given by the fit shown in Fig. 1, one can estimate the semiperiod ℓ of the grain boundary corrugation. It is found that $\ell \approx 10^{-6}$ [cm], which agrees well with the estimate obtained previously from Eq. (7).

The dependence of $\dot{\varepsilon}$ on grain size also agrees with experimental results. For $F \gg F_c \approx 0.1$ [MPa] $\times\, d^2$, Eq. (4) yields ℓ proportional to d. Thus, from Eqs. (15) and (16), C_0 is proportional to d^{-3}. On the other hand, adjusting Eq. (16) to the data of Ref. [21] for $T = 789$ K and different grain sizes, one obtains the same dependence of C_0 on d.

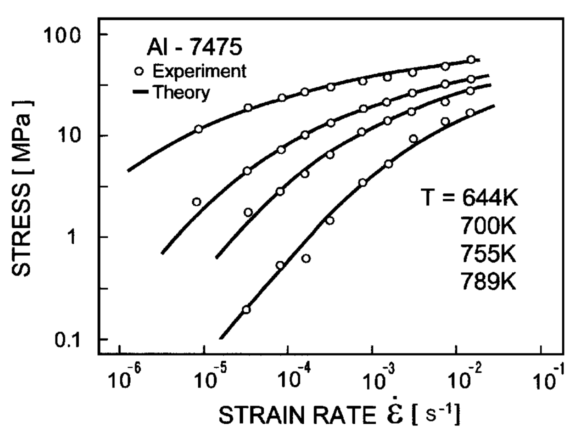

FIG. 1. Plot of the experimental results of Ref. [21] for the alloy Al-7475 at four temperatures. The continuous lines represent Eq. (16) with $C_0 = 1.1 \times 10^9$ s^{-1}, $\Omega^* = 1.23 \times 10^{-21}$ cm^3, and $\epsilon_0 = 1.9$ eV.

In conclusion, superplastic flow depends on the efficiency of grain boundaries for capturing and releasing vacancies. However, it depends mostly on the sensitivity of this ability on the local normal stress, which is governed by $\Omega^* = |d\epsilon_B/d\sigma|$. Computer simulations show that vacancies have a significant effect on quasistatic grain boundary sliding, even without a morphological instability [22].

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