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Strain-induced nucleation at a dislocation pile-up: a nanoscale model for high pressure mechanochemistry

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Abstract

A simple continuum thermodynamic model of strain-induced nucleation at the tip of a dislocation pile-up is developed. This model is applied to explain various mechanochemical phenomena. In particular, it explains why and how the superposition of plastic shear on high pressure leads to: a significant (by a factor of 3–5) reduction of phase transition's and chemical reaction's pressure and pressure hysteresis, the appearance of new phases which were not obtained without shear, strain-controlled (rather than time-controlled) kinetics, or the acceleration of kinetics without changes in the transformation pressure.
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Mechanochemical phenomena under high pressure

Plastic strain-induced structural changes (SCs), which include phase transitions (PTs) and chemical reactions (CRs) under high pressure, are widespread in nature, physical experiments, and modern technologies. One of the mechanisms of deep earthquakes is related to the instability caused by shear strain-induced PT [1]. Shear ignition of energetic materials [2,3] is subject to intensive study with the goal to assess safety

issues. Mechanosynthesis is another example. In this Letter, we will concentrate on the numerous experimental results obtained in rotating Bridgman or diamond anvils [4–12]. They show that the addition of plastic shear, due to the rotation of an anvil, leads to findings that have both fundamental and applied importance.

(1) The volume fraction of the new phase or the reaction product is an increasing function of the plastic shear strain. When rotation stops, SC stops as well [6,8]. Therefore, strain-controlled (rather than time-controlled) kinetics is considered.

(2) The rotation of an anvil leads to a significant (in some cases by factor 3–5) reduction of PT [7,8,11] and

CR [6] pressure. For some PTs (e.g., in InSb, InTe, Ge and Si [8]), direct PT pressure under shear is lower than the equilibrium pressure and even lower than the reverse PT pressure under hydrostatic conditions. At the same time, it was found in [4] that for some PTs (PbO$_2$I $\leftrightarrow$ PbO$_2$II, calcite $\leftrightarrow$ aragonite, quartz $\leftrightarrow$ coesit) additional shear does not change the PT pressure at any temperature; however, it significantly accelerates PT kinetics.

(3) Plastic shear reduces pressure hysteresis, i.e., the difference between the start pressure of direct and reverse PT [7,8].

(4) Rotation of an anvil leads to the formation of new phases which were not produced without rotation [6,9], in particular, phase V of fullerene C$_{60}$ [10,11] which is harder than diamond.

Despite the fundamental and applied significance of the effect of plastic shear on SCs, there have only been our attempts to develop the corresponding theory at the macroscale [12]. Despite the interesting results (PT is induced by rotational plastic instability; and pressure for an irreversible PT from rhombohedral to superhard cubic phase of BN reduces from 55 GPa under hydrostatic conditions to 5.6 GPa under plastic straining), macroscale theory is not sufficient for quantitative analysis.

It is well-studied that strain-induced nucleation, e.g., in TRIP steels at normal pressure, occurs at new defects generated during plastic flow. However, we are not aware of any experimental or theoretical work for materials compressed and sheared in diamond anvils which

(a) determines the nucleating defects;
(b) describes theoretically its effect on nucleation; and
(c) tries to describe phenomena 1–4 in the introduction.

In this Letter, we consider one possible mechanism of intensification of SCs in crystalline materials by the stress concentration created by the dislocation pile-up. Dislocation pile-up is the strongest defect used to model slip transfer from grain to grain [13], temperature induced martensitic PT [14], and deformation twinning [15]. Our model has some distinctions and will allow us to explain the above (and some other) phenomena and find controlling parameters. For an ex-

planation of the reduction of CR pressure by a factor of 3–5, the strongest defect is required like pile-up consisting of $\sim$ 20 dislocations (see estimate after Eq. (6)). If the dislocation pile-up would not be able to explain such an effect, none of the other defects could help and new physics would be required. However, we do not exclude that for some materials with the weaker effect of shear stress on SC pressure, other defects (grain and subgrain boundaries, twins and stacking faults) may be more important. For these defects, some points in the approach of this Letter can be applied as well. Note that under high pressure, even brittle materials can undergo large plastic deformations by dislocation mechanism, so our model is applicable for them as well. We hope that this first conceptual paper in the field will lead to future systematic experimental and theoretical studies.

Net thermodynamic driving force for structural changes

For a solid–solid SC, the transformation strain, $\boldsymbol{\varepsilon}_t$, transforms a unit cell of the stress-free parent phase into a unit cell of the stress-free product phase. In the simplest case, when the temperature θ is fixed and homogeneous in a transforming volume and the change in the elastic moduli is neglected, the net thermodynamic driving force for SC, F, in the volume V_n bounded by surface Σ is [16]:

$$F = (X - K)V_n$$
$$= \int_{V_n} \int_0^{\boldsymbol{\varepsilon}_{t2}} \boldsymbol{T} : d\boldsymbol{\varepsilon}_t \, dV_n - (\Delta\psi(\theta) + K)V_n - \Gamma\Sigma. \quad (1)$$

Here X is the driving force for SC, which represents the dissipation increment due to SC only (i.e., excluding plastic dissipation) during the entire transformation process, averaged over the transforming region; K is the athermal dissipation due to SC related mostly to interface friction; $\boldsymbol{T}$ is the stress tensor; $\Delta\psi$ is the jump in the thermal part of the free energy; Γ is the surface energy, and the indices 1 and 2 denote the values before and after SC; $\boldsymbol{A}:\boldsymbol{B} = A_{ij}B_{ji}$ is the contraction of tensors over two indices.

The key point of Eq. (1) is that it takes into account the whole history of stress tensor variation during the
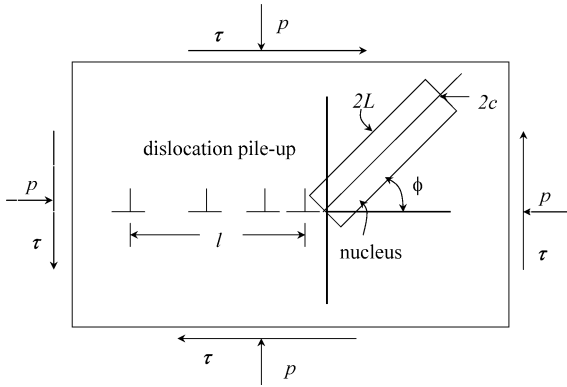
Fig. 1. The nucleation scheme at the tip of dislocation pile-up.

transformation process, which depends, in particular, on the interaction of the transforming region with the surrounding material. For elastic materials, the expression for XV_n coincides with the change in Gibbs free energy of the whole system [16].

Assume that plastic flow occurs by the activation of Frank–Read or Köehler sources and motion of generated edge dislocations to a barrier (e.g., grain, twin or subgrain boundary). Dislocation pile-up of length l assists in nucleating of the second phase region. A nucleus will be considered as a pill-box with sizes $2L \times 2c \times b$, with $n = c/L \ll 1$ (Fig. 1), inclined under angle ϕ in the pile-up direction. Plane stress and small strain formulations are used. Transformation strain $\boldsymbol{\varepsilon}_t$ in the nucleus is an invariant plane strain consisting of shears, 0.5γ, along the sides L and c, and the normal strain, ε, along side c. External stresses have normal p and shear τ components, where τ is the resolved shear stress for the dislocation motion.

The total stress $\boldsymbol{T} = \boldsymbol{\sigma} + \boldsymbol{\sigma}_{es} + \boldsymbol{\sigma}_d$, where $\boldsymbol{\sigma}$, $\boldsymbol{\sigma}_{es}$, and $\boldsymbol{\sigma}_d$ are the contributions from external stress, internal stresses due to transformation strain (Eshelby inclusion stress), and dislocation pile-up, respectively. The work of $\boldsymbol{\sigma}_{es}$ is estimated for an ellipsoidal cylinder of infinite length with semiaxes L and c, and it is equal to the energy of such an inclusion, i.e., [17] $-4bn^2L^2s(\varepsilon^2 + \gamma^2)$. Here $s = \mu\pi/(8(1-\nu))$, μ and ν are the shear modulus and Poisson ratio, respectively. The stress field of the pile-up will be approximated by the stress field of the superdislocation [13]

$$\sigma = \frac{l\tau}{2}\frac{\sin\phi}{r}, \qquad \tau_l = \frac{l\tau}{2}\frac{\cos\phi}{r}, \tag{2}$$

where r is the current radius of the points of nucleus and σ is the normal stresses along sides L and c. This will give us the lower bound since, for small distances, the stress for pile-up varies as $r^{-1/2}$; however the analytical expression is too complex for close-form integration. Note that stresses through the factor

$$l\tau = \frac{\mu N|\boldsymbol{b}|}{\pi(1-\nu)} \tag{3}$$

are proportional to the number N of dislocations in a pile-up, i.e., they can be extremely high [13]. Here $\boldsymbol{b}$ is the Burgers vector. Calculating the transformation work and maximizing it with respect to angle ϕ, one obtains

$$\tan\phi = \frac{\varepsilon}{\gamma}, \qquad F = AL^2 + BL,$$

$$B := l\tau b\sqrt{\varepsilon^2 + \gamma^2}\, n \ln\frac{2}{n} - 4\Gamma b,$$

$$A = ab - 8\Gamma n,$$

$$a = (p\varepsilon + \tau\gamma - \Delta\psi - K)4n - n^2 4s(\varepsilon^2 + \gamma^2).$$

The cut off radius of dislocation is taken as c, which underestimates the transformation work.

Thermally activated nucleation

If $B < 0$, which is the case for the weak or no dislocation pile-up and low τ, then SC is possible for $A > 0$ only and requires thermal fluctuations. Designating $\bar{B} = B/(4b)$, substituting critical nucleus length $L_c = -B/(2A)$ in the equation for the activation energy $Q = -F$, and minimizing Q with respect to b, one obtains $b = 16\Gamma n/a$, $A = 8\Gamma n$, $Q = 128\Gamma n\bar{B}^2/a^2$. For an observable nucleation rate it is usually assumed $Q = 40k\theta$, where $k = 1.38 \times 10^{-23}$ N m/K is the Boltzmann constant. Solving this equation for p, one obtains

$$p = \frac{\Delta\psi + K + ns(\varepsilon^2 + \gamma^2)}{\varepsilon} + \frac{\Gamma}{\varepsilon}\sqrt{\frac{\Gamma}{5k\theta n}}$$

$$- \tau\left(\frac{\gamma}{\varepsilon} + \frac{l}{4}\sqrt{\frac{\Gamma n}{5k\theta}\left(1 + \left(\frac{\gamma}{\varepsilon}\right)^2\right)}\ln\frac{2}{n}\right). \tag{4}$$

Substituting $\Delta\psi = 1$ GPa, $K = 0.5$ GPa, $\varepsilon = 0.1$, $\gamma = 0.2$, $\mu = 80$ GPa, $\nu = 0.3$, $\Gamma = 0.1$ N/m, $l = 2 \times 10^{-7}$ m and $n = 0.1$, one obtains the relationship $p(\tau)$ (p and τ in GPa) for various temperatures (Fig. 2). All
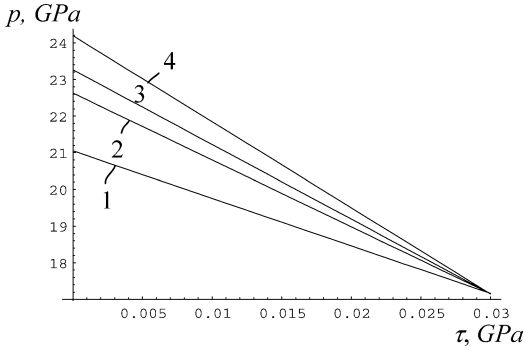
Fig. 2. Dependence of SC pressure on shear stress for the pile-up length $l = 2 \times 10^{-7}$ m and various temperatures (K): (1) 1000; (2) 500; (3) 400; (4) 300.

Fig. 3. SC pressure versus temperature for several values of $\tau_i l = \tau l$ (10^{-9} GPa m) (number of dislocations): (1) the equilibrium PT line; (2) 5.6; (3) 5.2; (4) 4.0; (5) 2.0.

plots intersect at the point corresponding to $B = 0$ and barrierless nucleation. The smaller the temperature is, the stronger the effect of shear stress is. If the term with γ/ε is negligible, p depends on the combination τl. For $\theta = 300$ K, one gets $p = 24.2 - 233.2\tau$. The effect of shear stresses is much more pronounced for a thermally activated than for barrierless nucleation. However, because shear stress is limited by the condition $B \leqslant 0$, i.e., $\tau \leqslant 0.030$ GPa, the minimal pressure for thermally activated nucleation is 17.24.

For relatively weak defects, one has to take into account preexisting defects because they can produce a comparable stress concentration. Dislocation pile-ups observed at zero external stresses are equilibrated by internal stresses τ_i, e.g., due to friction, misfit strain or other defects.

By utilizing Eq. (3), the internal shear stress τ_i in the absence of external stresses can be estimated, which are caused by a preexisting (subscript p) dislocation pile-up of length l_p consisting of N_p dislocations. Then at zero external shear stress, $\tau = 0$, Eq. (2) is valid with τ_i and l_p substituted for τ and l, and Eq. (4) can be transformed to

$$p = f(\theta) + \frac{\Gamma}{\varepsilon} \sqrt{\frac{\Gamma}{5k\theta n}}$$
$$- 0.25\tau_i l_p \sqrt{\frac{\Gamma n}{5k\theta} \left(1 + \left(\frac{\gamma}{\varepsilon}\right)^2\right)} \ln \frac{2}{n}. \qquad (5)$$

The first term in Eq. (4) is designated as $f(\theta)$, where $p = f(\theta)$ represents the equation of the SC line for an infinitely long waiting time in the absence of external and internal shear stresses and defects. If K
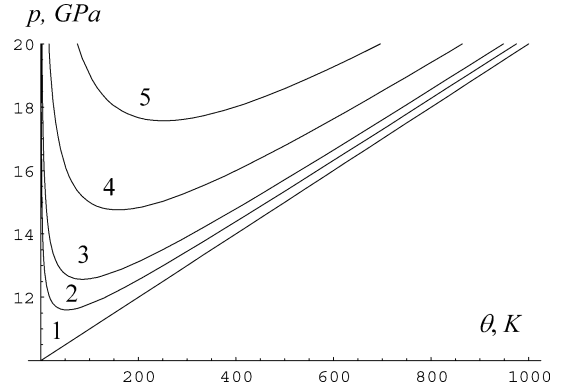
and Eshelby energy are negligible, $f(\theta)$ represents an equilibrium line between phases. Since the term $\tau\gamma/\varepsilon$ in Eq. (4) is negligible, the effect of both external and internal shear stresses can be expressed in terms of the number of dislocations in pile-up (see Eq. (3)).

Let us begin with the case, when $N = N_p$ (i.e., $\tau l = \tau_i l_p$), then Eqs. (4) and (5) give practically the same result. In Fig. 3, relationships $p(\theta)$ are plotted for the equilibrium PT line $p = f(\theta) = 10 + \theta/100$, and for lines described by Eq. (5) (or Eq. (4)) for several values of $\tau_i l_p = \tau l$. Deviation from the equilibrium line is a kinetic effect which decreases with temperature growth. Let, e.g., $\tau_i l_p = 5.2 \times 10^{-9}$ GPa m with no external stresses. Above some temperature, say $\theta \simeq 500$ K, deviation of Eq. (5) from the equilibrium line is within the experimental error, and the experimental kinetic curve can be used to determine the 'equilibrium' phase diagram.

By applying an external stress, we do not change the local stresses τ_l and σ_l due to preexisting pile-up and the 'equilibrium' phase diagram (as is observed in experiments [4]), if the number of dislocations N_p in pile-up does not change. In fact, for any given N_p, the local stresses are independent of applied stress (external plus internal), see Eqs. (2) and (3).

However, an external stress produces new dislocation pile-ups. After exhausting all preexisting defects, kinetics of pressure-induced PT is saturated. For strain-induced nucleation, many more defects can be generated and more product phase can appear. This was observed in experiments [4] for $PbO_2I \rightarrow PbO_2II$

PT: kinetics with shear is much more intensive. If $N > N_p$ ($\tau l > \tau_i l_p$), in particular when new dislocations are generated in preexisting pile-ups, e.g., $\tau l = 5.6 \times 10^{-9}$ GPa m, then external shear again does not change 'phase equilibrium' conditions (Fig. 3), but reduces the temperature at which PT occurs at 'phase equilibrium' conditions, as it occurs in experiments [4].

Barrierless nucleation

If $B > 0$, which is true for the strong dislocation pile-up and large τ, even for $A < 0$ for a relatively small L, one has $F > 0$. That shows that barrierless nucleation occurs independent of the magnitude of A and pressure. However, the equilibrium value of $L_e = -B/A$, determined from the condition $F = 0$, depends on A. If we take $\Gamma = 0.1$ N/m (typical value for semicoherent interface for steels), $n = 0.1$, $\varepsilon = 0.1$ and $\gamma = 0.2$, then the criterion $B > 0$ results in $l\tau > 5.97$ N/m. This condition can be easily satisfied for reasonable values of τ and l, e.g., $\tau = 0.1$, $l = 60$ nm or $l = 1$ μm and $\tau = 0.006$. For a coherent nucleus for ferrous and nonferrous alloys, $\Gamma = 0.01$ N/m which makes barrierless nucleation even easier. Let us define the effect of shear stress on SC pressure for a detectable size of nucleus, using condition $L = -B/A$, i.e.,

$$p = \frac{\Gamma}{\varepsilon}\left(\frac{2}{b} + \frac{1}{nL}\right) + \frac{\Delta\psi + K + ns(\varepsilon^2 + \gamma^2)}{\varepsilon}$$
$$- \tau\left(\frac{\gamma}{\varepsilon} + \frac{1}{4}\sqrt{1 + \left(\frac{\gamma}{\varepsilon}\right)^2}\frac{l}{L}\ln\frac{2}{n}\right). \qquad (6)$$

The main parameter which determines the reduction of SC pressure due to shear stresses is l/L. The characteristic size of the strain-induced unit in steel is 100 nm, so $L = 50$ nm. Parameter l depends significantly on microstructure and is limited, approximately, by a quarter of the grain size. If we take $l = 1$–10 μm, then $l/L = 20$–200. In this case, the effect of macroscopic shear stress is negligible in comparison with the effect of dislocation pile-up, and the SC pressure can be reduced significantly. Substituting the same numbers as before and $b = 10^{-6}$ m, $|\boldsymbol{b}| = 3 \times 10^{-10}$ m, neglecting the term $10^{-8}/L$ and using Eq. (3), one obtains $p = 17.24 - (2 + 1.675l/L)\tau =$ $17.64 - 2\tau - 1.828 \times 10^{-8}N/L$, where L is in m. The larger the nucleus is, the smaller the effect of pile-up and shear stresses. For an infinite nucleus, which corresponds to $A = 0$, we have $p = 17.24 - 2\tau$. For $2L = 50$ nm and $l = 10^3$ nm, Eq. (6) simplifies to $p = 17.64 - 68.99\tau \simeq 17.64 - 0.731N$. For a minimal value $\tau = 5.97 \times 10^{-3}$, determined from the condition $B = 0$, one has $p = 17.23$. For $\tau = 0.2$ ($N \simeq 19$), $p = 3.84$, i.e., the reduction of SC pressure by a factor of 3–5 and higher can be justified using the above model. For $\tau = 0.256$ ($N \simeq 24$), $p = 0$, which is essentially lower than the SC equilibrium pressure, $p_e = 10$, and even the reverse SC pressure of 2.6 under hydrostatic conditions.

Barrierless nucleation, which does not require thermal fluctuations, explains the strain-controlled rather than time-controlled kinetics. Indeed, the prescribed strain increment generates dislocation pile-ups with barrierless, i.e., very fast nucleation and growth of the new phase up to the length L_e. For the observation time of 1 s, this looks like instantaneous SC. As straining stops, no new defects and nuclei appear and the growth of the existing nuclei is thermodynamically impossible.

Pure hydrostatic pressure in homogeneous systems does not cause plastic flow and the appearance of strong stress concentrators, which explains the unique role of shear stress and strains on SC. Even for $\gamma = 0$ (e.g., for isostructural, electronic PTs in Ce and its alloys), i.e., when τ does not contribute to transformation work, Eq. (6) exhibits a significant effect of τ on p because of the pressure concentration at the tip of the pile-up (see Eq. (2)).

One of the conditions of applicability of the above model is that the dislocation pile-up does not activate alternative mechanisms of stress relaxation like dislocation slip, twinning, or fracture. This limits maximum τ by τ_r, necessary for the activation of alternative relaxation mechanisms, as well as l. Stress τ_r is not smaller than the macroscopic yield stress in shear, which was taken into account in the range of τ in the above estimates. If only SC and dislocation slip compete, then any increase in the strain rate has to promote the SC, similar to competition between slip and twinning [15]. For slip, higher shear stress is necessary for higher strain-rate, which increases τ in Eq. (6). Indeed, some experiments show significant reduction in PT and CR pressure under increased strain rate [5,8].

Because length l is limited by the grain size, which significantly reduces during large plastic deformation, one way to intensify SC is related to the increase in grain size and l. This can be done by annealing and re-crystallization. On the other hand, reduction in grain size has to suppress strain-induced SC, which is the case for explosives [2] (the importance of dislocation mechanisms for CRs in molecular energetic crystals is discussed in [2], for some other CRs see [18]). As the yield stress in shear τ is limited, there exists a lowest possible pressure, p_ε^d, below which strain-induced SC is impossible. An increase in the yield stress (by increasing strain, strain-rate and pressure) leads to a decrease in p_ε^d which is observed experimentally [5,8].

Dislocation pile-up generates both compressive and tensile pressure of the same magnitude. Consequently, it simultaneously promotes both direct and reverse SC in different regions, which explains the reduction in pressure hysteresis. The same equations with tensile ε can be applied to the reverse SC.

Even without plastic shear, the nonhydrostatic stress state contributes differently to the driving force X for SC to two alternative phases if they have a different transformation strain deviator. Consequently, the non-hydrostatic stress state can lead to phases which are hidden at the hydrostatic experiment. Stress concentration due to strain-induced defects and consequently the driving force for SC, are greater in the stronger of the two alternative phases. This demonstrates the importance of plastic straining for the search of new strong phases. The Landau theory for elastic materials suggests that defects can induce phases which are unstable in bulk [19]. Plastic straining, increasing K for reverse SC [12,16], can stabilize them. More detailed numerical treatment of nucleation at dislocation pile-up and other defects can be completed in the framework of Landau–Ginzburg theory of PT [20,21]. The use of Landau potential [21] which takes into account most of the specific features of strong stress-induced martensitic PT observed in experiments will yield more precise results.

Acknowledgements

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