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Environmentally enhanced instability of stressed solids

B. I. YAKOBSON
Department of Physics, North Carolina State University, Raleigh, NC 27695, USA
E. D. SHCHUKIN
Materials Science and Engineering Department, Johns Hopkins University, Baltimore, MD 21218, USA

Environment-sensitive mechanical behaviour of solids is considered as a loss of surface stability, which is enhanced by simultaneous action of mechanical stresses, surface flaws and active media. A model is proposed based on mass transport during the surface roughness development, involving competition between two driving forces: chemical potential excess in the regions of stress concentration near the bottom of a concavity and surface tension. The excess of chemical potential may lead to the fracture crack formation, while the surface tension tends to heal it. A preliminary discussion shows the applicability of the model to the variety of effects (strength and durability reduction or treatment facilitation due to adsorption, contact with akin liquids, including embrittlement by liquid metals, heterogeneous catalysis, etc.)

1. Introduction

The strength of solids and materials is invariably important in two formally opposite but closely related aspects: as reliability, durability of material in service, and as pliability during treatment, i.e. both as a maximum and as a minimum resistance to external effects. In both cases, the strength is a complicated function of chemical composition, real (defect) structure of a solid, deformation and fracture conditions (stressed state, time, temperature, etc.), and physico-chemical processes on the surface interacting with a medium. These factors are visibly represented in the classical Griffith equation, $\sigma_c \sim (Y\gamma/c)^{1/2}$, where Y is the elasticity modulus, c the crack length, and γ the surface energy. This equation, being a particular case of description of a new phase nucleation (after Gibbs–Volmer), is essentially thermodynamic and, consequently, has a rather universal character. These correspond, respectively, to the "ideal strength" or cohesion energy density, Y, given defect structure (linear parameter, c), and specific work of the new surface formation ("effective" γ^*, depending upon concrete conditions but always in accordance with "thermodynamic" γ).

Fracture (including wear, dispersion during machining, etc.) is a process of new surface formation, and it begins as a rule (in glasses, always) on a surface of a body. Thus surface properties and interactions with a media are significant and even decisive in strength control. Various aspects of environment-sensitive mechanical behaviour have been described in the abundant literature [1–4]. Below we mention briefly some typical data obtained by one of the authors.

(i) Strong embrittlement of rock-salt crystals by $AlCl_3$ melt has been observed at temperatures when clean NaCl samples are ductile.

(ii) Adsorption of water vapour results in a decrease in strength of $Mg(OH)_2$ fine porous samples by a factor of two. Independent measurements of the strength, σ_c, and of the surface energy decrease (Fig. 1), $\Delta\gamma = RT\int\Gamma \, d\ln p_w$, confirm the validity of the Griffith approach (Γ is the water adsorption at vapour pressure, p_w). In a similar manner, water diminishes the strength of glasses and quartz; the effects depend essentially upon pH value.

(iii) On the contrary, non-polar organic solids, e.g. mono- and polycrystalline naphthalene, demonstrate a corresponding decrease in surface energy and in strength in contact with non-polar media, particularly benzene (both in liquid and in vapour). This allowed discussion of a specific, selective surface activity of liquid media with respect to a certain solids, akin in their chemical nature.

(iv) The embrittlement of solid metals by the action of liquid ones [1, 5, 6] is very well known; for example, zinc in contact with mercury, copper with bismuth, aluminium with gallium, iron and steels with zinc, titanium and its alloys in contact with cadmium, etc. Recently, such effects have been studied on refractory transition metals also, e.g. on molybdenum in contact with liquid gold [7], in agreement with estimation of their interaction energy (Table I).

(v) Liquid indium lowers the strength of InSb crystals; gallium, copper and especially gold embrittle germanium; the strength of graphite diminishes when in contact with liquid aluminium.

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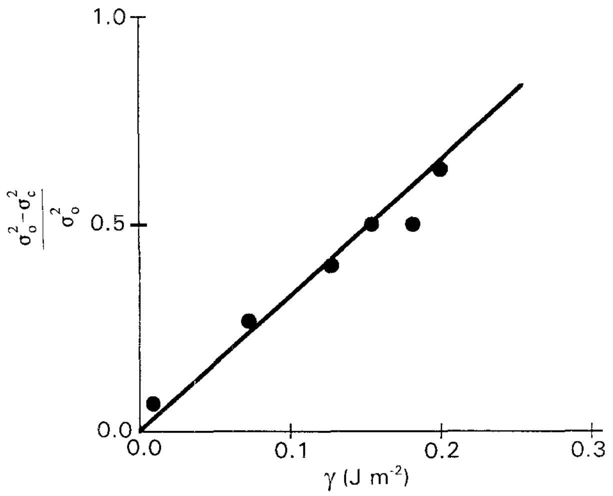

Figure 1 Comparison of independently found values of reduction in strength and free surface energy of magnesium hydroxide in presence of water vapour [1].

TABLE I Embrittlement of refractory metals (sol.) by liquid ones (liq.): (+) experimentally observed, (−) absent, in comparison with evaluation of the energy of mixing, ΔH_m, and interfacial energy, γ_{s-l} [7].

Sol.–liq.	ΔH_m (eV at^{-1})	γ_{s-l} (mJ m^{-2})	Effect
Mo–Au	0.74	580	+
Mo–Hg	3.14	1980	−
Nb–Sn	0.22	240	+
Nb–Cd	2.57	1470	−
Ti–Cd	0.28	260	+
Ti–Pb	− 2.73	?	−
Ti–Hg	0.06	140	+
Ti–Ga	− 1.79	?	−
W–Pb	0.39	420	
W–Hg	3.75	2380	
Zr–Bi	0.94	500	+

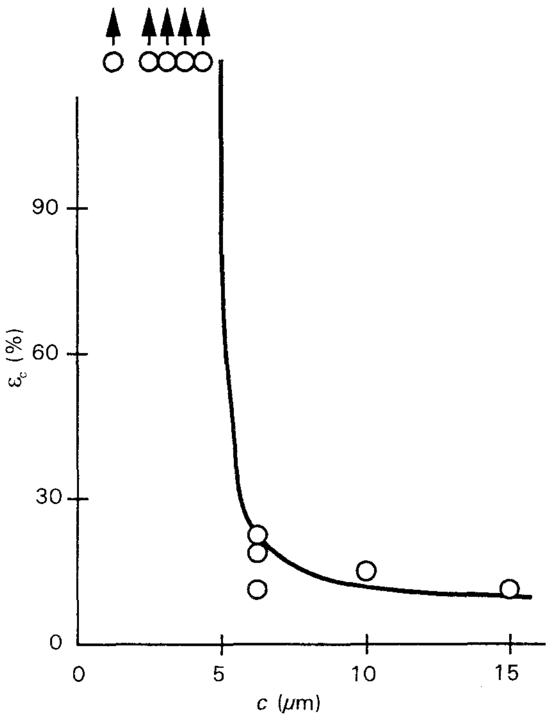

Figure 2 Effect of defector-pricks by indentor of different depth, c, applied to the undamaged monocrystals of zinc on reduction in limiting deformation, ε_c, in the presence of a mercury film [1].

In the experiments mentioned above, the dissolution of a solid was prevented by the previous saturation of a liquid phase with the substance of the solid at a given temperature. However, local dissolution could take place in zones of increased chemical potential due to stress concentration. An important role is played here by defects in samples, especially at their surfaces. As a rule, perfect single crystals with an "ideal" surface do not reveal such a strong environmental influence. On the contrary, a characteristic brittle–ductile transition is observed on samples with previously introduced surface microdefects, when such defects reach some critical size (e.g. on zinc single crystals covered with the thinnest mercury film, Fig. 2).

In addition to these reversible physico-chemical phenomena caused by wetting and adsorption, there is another broad spectrum of fracture processes enhanced by the ambient media. These involve explicitly heterogeneous chemical reactions. It was shown that catalytic reactions, e.g. alcohol conversion on MgO, hydrocarbon cracking on alumosilicate systems, etc., results in a considerable decrease in strength and durability of the catalyst. Therefore, catalytic reactions may lead to a dramatic increase in the surface self-diffusion coefficient up to several orders of magnitude. For example, on the nickel surface during benzene hydrogenation, on iron during CO oxidation [8, 9]. Recently, it was shown that reduction of Zn^{2+} ions in a ground tempered steel sample (used as a cathode in a corresponding electrochemical cell) results in a two-fold increase in the machining effectiveness.

Thus, the general problem of resistance to deformation and fracture, presents the problem of stability of a surface. In this connection, micro- and "nano-" methods of mechanical testing of near-surface layers and thin films [10–12] are particularly valuable as most sensitive to the role of surface and media, besides studying samples with deliberately introduced surface defects [1, 10]. It is of special interest to consider the principal possibility and statistical regularities of an instability and spontaneous development of fracture even in the absence of obvious defects (or information about them).

2. Kinetic equations for the interface geometry

2.1. Feedback loop, qualitative description

In general terms, one can say that the surface provides additional degrees of freedom (atomic mobility along the surface or via normal-to-the-surface exchange with the environment), which always increases the overall compliance to external effects. The possibility of any mass transfer added to the inhomogeneous mechanical stress makes the solid body leave its original (formally stable from the point of view of elastic mechanics) configuration, and this process (though slow) may play a determining role in material durability. An obvious extreme is a viscous flow in a glassy material, resulting in a rupture [13]. We consider, below, an option presented by simple dissolution or evaporation, when the role of the surface and environment is more distinct, while other mass-transfer processes, enhanced by mechanical stress distribution, may be treated in a similar manner.

Consider a surface of a stressed solid material exposed to a fluid ambiance of any nature (Fig. 3). Principally, there is always an exchange of constituent atoms of the solid and the environment. The dissolution/accretion of solid phase is governed by the chemical potential gap between solute and solid, affected by the stress field, which simply adds certain local deformation energy to the chemical potential. Any concavity (dent) on the surface serves as a stress-concentrator, thus resulting in a greater chemical potential at the bottom of the concavity (tip of the dent). This leads to an enhanced dissolution at such a local area, subsequent growth of a dent and further change in the local stress and chemical potential. This feedback (stress field–dissolution–stress), complemented by the stabilizing surface tension, may result in an instability of the surface and delayed fracture. There is an analogy with another feedback loop situation (stress–*fracture*–diffusion–stress . . .), in which case the self-fracture front propagation was considered [14], but the initiation of the front was not addressed.

2.2. Kinetics of the boundary-line propagation

Quantitatively, the linear contribution of stress in the chemical potential can only arise from the normal component, because any forces perpendicular to the direction of the boundary displacement produce no work. However, normal component contribution still vanishes because of mechanical equilibrium between phases. A quadratic term allows for material compressibility and contains only forces parallel to the surface, because normal stress is invariant across the boundary. These arguments do not substitute, of course, a rigorous derivation (see [15] and references therein). Assume that in a two-dimensional x–y projection (Fig. 3) the instantaneous interface profile is represented by some "shape" function $y(x, t)$. The chemical potential with respect to that on flat stressed surface is

$$\Delta\mu(x) = a^3\left\{\frac{1}{2Y}[\sigma(x)^2 - \sigma_0^2] - \gamma\frac{y_{xx}}{(1 + y_x^2)^{3/2}}\right\} \quad (1)$$

where the first term represents excess of the elastic energy per atom (a^3 is atomic volume), while the second allows for the local surface energy and is proportional to the curvature. Consider mass transfer in a direction normal to the surface, which can be dissolution–accretion in the case of solid–liquid interface or evaporation–condensation in the case of solid–gas surface. To eliminate the trivial process of dissolution all along the surface, we assume here that solute is in equilibrium with homogeneously stressed flat interface, which simply means that the number of atoms leaving the solid phase equals the number of atoms returning from the solute, $v_{\rightarrow} = v_{\leftarrow} = v_0$. Note that very far from equilibrium, this type of dissolution *en mass* prevails upon any local inhomogeneities and results in simple rounding of all flaws (as in the well-known Yoffe effect, taking place in unsaturated media). It remains beyond the scope of our consideration. Both curvature and excessive stress in solid phase affect its (local) free energy (Equation 1). This changes activation barrier and the (forward) rate of the dissolution, leaving in most cases backward rate $v_{\leftarrow}$ with no changes. Thus

$$\begin{aligned}\frac{v}{v_0} &= \frac{v_{\rightarrow} - v_{\leftarrow}}{v_0} \\ &= \exp\left[\frac{\Delta\mu(x)}{kT}\right] - 1 \\ &\approx \frac{\Delta\mu(x)}{kT}\end{aligned} \quad (2)$$

where the last approximate linearization is not necessary but simplifies further steps. A non-zero dissolution rate, v, gives a displacement of the boundary line in a direction normal to the interface, thus time evolution can be described by the equation

$$\frac{\partial}{\partial t}y(x, t) = -v(1 + y_x^2)^{1/2} \quad (3)$$

Here, we neglect the difference between the actual and reference systems, which may result in minor corrections. Equations 1–3 principally describe the evolution of the interface due to its stress-enhanced dissolution, provided one can relate local stress distribution, $\sigma(x)$, with a free boundary shape, $y(x)$. This problem of the linear elasticity theory deserves special attention.

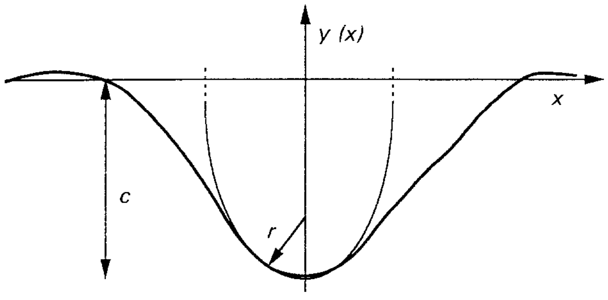

Figure 3 Two-dimensional interface profile represented by a "shape" function $y(x, t)$ with the two principal parameters, depth, c, and radius of curvature, r.

3. Dimensionless form and reduced description

3.1. Geometry–stress mapping

Loading of the body far away from the region of interest results, for a perfectly flat surface, in certain tangential stress, σ_0. In the case of an uneven boundary, the resulting tangential stress is not constant but is changing along the interface, although it is still proportional to the external load. It is noteworthy, that distribution of stress is the same for a plane stress or plane strain of an isotropic material and does not depend upon its elastic constants [16]. This means that the ratio $\sigma(x)/\sigma_0$ depends upon geometry only, and corresponding single-valued mapping can be described by some operator $\hat{O}$: $\sigma(x)/\sigma_0 = \hat{O}y(x)$. In other words, whenever an external tangential stress is applied, the tangential component of magnitude $\sigma_0\hat{O}y(x)$ occurs at every point $\{x, y(x)\}$ of the boundary. Finding $\hat{O}$ is a task of elasticity theory, generally tractable by numerical methods only (note that operator $\hat{O}$ is non-linear even in case of linear elasticity). What is important for us now is the fact that this operator is dimensionless and contains no parameters specific for the particular materia' This property makes it possible to collect Equations 1–3 and present resulting kinetic equation in the form [17]

$$\frac{\partial y}{\partial t} = \frac{y_{xx}}{1 + y_x^2} + \frac{1}{4}\left(1 + y_x^2\right)^{1/2}\left(1 - [\hat{O}y(x)]^2\right) \tag{4}$$

with all physical parameters "buried" in dimensionless time and length units

$$\Delta t = \left(\frac{\gamma Y^2}{2\sigma_0^4}\right)\left(\frac{kT}{a^3 v_0}\right) \tag{5a}$$

and

$$\Delta l = \frac{\gamma Y}{2\sigma_0^2} \tag{5b}$$

The first term in Equation 4 corresponds to the surface energy, flattening surface at positions of large curvature, while the second term allows for the "ejection" of atoms from highly stressed positions. Thus, without any specific calculations, one gets an idea about scale (both in time and space) of possible instability from Equations 5a and b. However, any further analysis should involve some information about the relation between the shape-function $y(x)$ and stress $\sigma(x)$; in other words the operator $\hat{O}$ in Equation 4 must be specified.

3.2. Reduced description of the concavity

To proceed, we resort to a sort of "reduced" description, considering arbitrary surface profile as a sequence of separate concavities of depth c and curvature r^{-1}. Then, we assume that dent geometry can be approximated by an elliptical hole of identical depth and curvature (Fig. 3), which corresponds to the vertical and horizontal axes c and $L = (cr)^{1/2}$, respectively. The clear advantage is that the stress-field distribution around the elliptical hole represents one of the few exactly solvable problems in linear elasticity [16]

$$\frac{\sigma(x)}{\sigma_0} = \hat{O}y(x) = \frac{1 + 2(c/r)^{1/2} - [1 + (c/r)^{1/2}]^2 x^2}{1 + (c/r - 1)x^2} \tag{6}$$

In particular, at the very tip of the concavity ($x = 0$), the local stress attains its maximum value

$$\frac{\sigma(0)}{\sigma_0} = 1 + 2\left(\frac{c}{r}\right)^{1/2} \tag{7}$$

For a sharp dent ($c \gg r$) this is equivalent to the original Griffith description of a narrow crack slit. For the case of very shallow concavity ($c \ll r$) the same result can be easily proved by canonical Fourier analysis: one takes a "perturbed" shape-function as a cosine undulation $y(x) \approx c\cos(x/L)$, so that depth and curvature are the same as for an ellipse, and calculates the Fourier series coefficients for the $\sigma(x)$.

4. Discussion: simple stability criteria and paths to fracture

The simplest way to answer the central question of whether the concavity grows or flattens, is then to determine the sign of the chemical potential deviation at the tip of the concavity. So, we substitute Equation 7 into the dimensionless form of Equation 1 or into Equation 4 to obtain

$$\frac{Y\Delta\mu(0)}{2a^3\sigma_0^2} = \frac{c}{r} + \left(\frac{c}{r}\right)^{1/2} - \frac{1}{r} \tag{8}$$

This gives us stability criteria, which divides the c versus r plane (Fig. 4) into a region of instability ($\Delta\mu > 0$, depth c of the dent increases) and "healing" ($\Delta\mu < 0$, c decreases and concavity flattens). More detailed analysis explicitly includes both $c(t)$ and $r(t)$ and is discussed elsewhere [17]. Here, however, we present (Fig. 4) a few typical trajectories of the evolving surface of a stressed body.

There are two extreme situations, presented by the two regions in Fig. 4. For a small-size unevenness, surface energy plays the dominant role, prevailing upon the stress-related contributions. As a result, the chemical potential at the dent apex is lower than at the flat surface and accretion of the material (from the solution back to the solid phase) leads to the healing of the dent. Therefore, below the line $\Delta\mu(0) = 0$ there is a stability region, when any perturbation of the interface geometry eventually smooths out. Although this process is very slow, it prevents stressed solid from fracturing.

For a relatively extensive undulation ("wavelength" $L = (cr)^{1/2} > 1$, or greater than $0.5\gamma Y/\sigma_0^2$ in real units, according to Equation 5) a stress-concentration effect predominates, increasing the chemical potential and local dissolution rate. This leads, in principle, to the instability of the sample: at the first stage the dent deepens by the stress-enhanced dissolution; eventually it sharpens enough to reach a "tape" of direct brittle fracture at $c/r > \gamma Y/a\sigma_0^2 \gg 1$. This threshold behaviour is in agreement with experimental observations [1], when gently indented samples remain stable, while deeper indentations (i.e. larger c at constant r, determined mainly by the shape of the indentor) bring the sample to the instability region (above the line $\Delta\mu(0) = 0$ in Fig. 4) and therefore leads to fracturing.

Another, more interesting aspect of the plot in Fig. 4 is the destabilizing role of the liquid phase. Evidently,

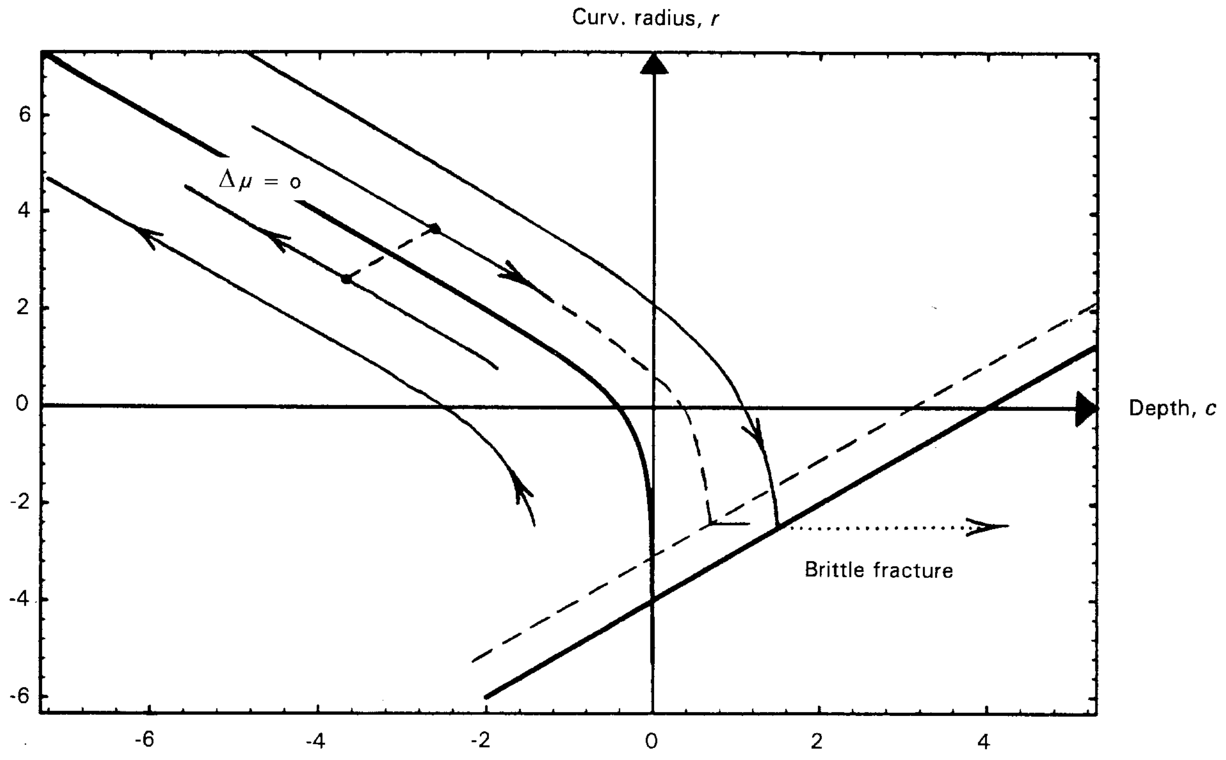

Figure 4 Radius of curvature r versus depth of concavity, c, plane, divided by the curve $\Delta\mu = 0$ into the area of stability (below, left) and instability (above, right). Brittle fracture occurs at parameters to the right of the straight line. Typical trajectories represent possible behaviour: healing or growth of a concavity (pre-fracture). (– – –) Changes associated with a decrease in surface energy, γ.

it changes the kinetic constant v_0, i.e. the time scale of the interface evolution (Equation 5a) may become quite different. Besides that, surface energy, γ, of the liquid changes, which deserves special attention. An effect of a decrease in γ is two-fold. First, it brings the brittle fracture boundary (straight line, intersecting abscissa at point $\gamma Y/a\sigma_0^2$) to the left, closer to the representing point $\{c, r\}$ of the dent. Second, it moves the representing point itself up and to the right, to the greater r and c (let us remember here that both r and c are dimensionless numbers, obtained by relating real dimensions to the unit $\Delta l = 0.5\gamma Y/\sigma_0^2$, Equation 5b). It is then possible, if the boundary line $\Delta\mu(0) = 0$ is crossed, that a reduction in γ leads to destabilization of the surface even during the early stages of the pit growth, as has been observed in experiments described above.

Therefore, this simple model and the plot shown in Fig. 4 present a convenient and useful tool for the analysis of the effects of an active environment on mechanical stability of solids (both in the service of materials and in their treatment). While in qualitative agreement with numerous empirical data, it will require additional details and probably more experimental measurements for a detailed quantitative comparison.

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