Physics

1958

SovietRxiv

Abstract

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Physics

E. D. Shchukin

A Criterion of Crystal Deformability and Adsorption Effects

(Presented by Academician P. A. Rebinder on 2 X 1957)

It is known that adsorption from the surrounding medium can strongly affect the strength and deformation properties of a solid. This phenomenon, which is very general in character, was discovered and comprehensively investigated in the works of P. A. Rebinder and his school (1–6). It has been established, in particular, that adsorption of various organic surface-active substances plasticizes metallic crystals and lowers their yield point, with certain temperatures and rates of deformation corresponding to the maximum manifestation of the effect (4). Strong adsorption-active media—low-melting metals in the form of a thin film or impurities at temperatures above their melting point—can cause the appearance of catastrophic brittleness of a crystal with a manyfold decrease in strength (5,6). These effects are due to the facilitated formation and development in the crystal of microcracks and other structural defects, as well as nuclei of slips, as a result of the decrease in the free energy of the new surfaces formed in the process of deformation. It is of interest to establish the connection between these propositions and the dislocation theory of plastic flow and brittle fracture (7–18).

According to Mott's theory, local stress concentrations in a crystal are caused by dislocation pile-ups formed before various obstacles in the slip plane (8). Under a shear stress τ and with n dislocations in the pile-up, the force per unit length of the leading dislocation reaches the value $n\tau b$, where b is the unit translation (Burgers vector) (9). Apparently, even at small τ, the leading dislocations are capable of coalescing with the formation of a hollow core—a microcrack nucleus; as $n\tau$ increases, the microcrack develops, maintaining equilibrium, which will be lost only if, at the given τ, the number of dislocations reaches the critical value N. Analysis of Stroh' s approximate and internally consistent scheme (10), in comparison with Griffith' s criterion (11), leads to the following estimate: $N \simeq 12\sigma/\tau b$, where σ is the specific free energy of the surface of the developing microcrack.

In reality n is limited by two factors. 1) If the leading dislocation is pinned completely firmly, then at a distance L before the obstacle

Fig. 1

Figure 1: Fig. 1

$$n_1 \simeq \pi(1-\mu)L\tau/Gb$$

dislocations can accumulate $^{(12)}$; here μ is Poisson' s coefficient, G is the shear modulus, and L has the meaning of the diameter for non-thick ($\lesssim 1$ mm) single crystals and of the grain size for polycrystals. 2) The obstacle is characterized by a potential barrier $U(x)$; its height $U_{\max}$ determines the activation energy for overcoming the obstacle at $\tau = 0$, while the quantity $|\,\mathrm{grad}\, U(x)|_{\max}/b^2 = \tau_1(0)$ is the local stress necessary for breakthrough at $T = 0^\circ$K $^{(13)}$. In the general case, the activation energy

$$U_A(n\tau) = U_{\max}\eta(\varphi),$$

where $\varphi = n\tau/\tau_1(0)$; the function $\eta(\varphi)$ is determined by the form of the barrier $U(x)$. Let v dislocations arrive at the obstacle each second; then the rate of their accumulation $\dot{n} = v-$

$-\nu\lambda\exp[-U_A(n\tau)/kT]$; here ν is the frequency of lattice vibrations, and λ is the number of points where rupture may occur. Dynamic equilibrium corresponds to $\dot{n} = 0$, i.e. $n_2 = \tau_1/\tau$, where the local stress is $\tau_1 = \tau_1(0)\varphi(\eta)$ and $\eta = kT\ln(\nu\lambda/v)/U_{\max}$.

Putting $n = \min\{n_1; n_2\}$, we introduce the quantity $S = N/n$; $S > 1$ corresponds to the overcoming of the barrier by dislocations at $n < N$, i.e. to plastic deformation; for $S \leqslant 1$ a nonequilibrium crack develops—brittle fracture occurs. Consequently, S has the meaning of a criterion of the deformability of a crystal. Under extension at a rate $\dot{\varepsilon}$ of a single crystal whose slip plane makes an angle χ with the axis of the specimen, and with mean spacing between slip lines h, the parameter v may be estimated as follows: $v \simeq \dot{\varepsilon}hu/b\cos\chi$, where u is a factor of microinhomogeneity of deformation, taking into account localization of shear and determined by the ratio of the total number of slip lines to the number active at each given instant.

Fig. 1. Criterion of deformability S for pure and amalgamated zinc single crystals at $A = B = C = 1$, $\lambda \sim 10^3$ (10); in this case the logarithmic term in (2) is ~ 30. In the first case (Zn) it is assumed that $\sigma \sim 10^3$ erg/cm^2, $U(x) \sim \exp(-x/a)$, $U_{\max} \sim 0.9$ eV and $\tau_1(0) \sim 7 \cdot 10^{10}$ dyn/cm^2; the model used is the interaction of intersecting dislocations ($^{14-16}$). In the second case (Zn–Hg) $\sigma \sim 250$ erg/cm^2, $U(x) \sim [1 + (x/a)^2]^{-1}$, $U_{\max} \sim 1.2$ eV and $\tau_1(0) \sim 10^{11}$ dyn/cm^2; the model is the interaction of dislocations with a condensed atmosphere of interstitial atoms (^{13,14}).

Thus, the criterion S takes the following form:

$$S = \begin{cases} S_1 = A\dfrac{\sigma G}{L}\dfrac{1}{\tau^2}, & \text{for } \tau < \tau^*, \\ S_2 = B\dfrac{\sigma}{b\tau_1}, & \text{for } \tau > \tau^*; \end{cases} \qquad \tau^* = C\sqrt{\frac{Gb\tau_1}{L}}, \tag{1}$$

$$\tau_1 = \tau_1(0)\varphi(\eta) = \tau_1(0)\varphi\left(\frac{kT}{U_{\max}}\ln\frac{\nu\lambda b\cos\chi}{\dot{\varepsilon}hu}\right), \tag{2}$$

where A, B, and C are dimensionless coefficients, of order of magnitude close to 1, since, owing to the use of the linear approximation of the theory of elasticity of isotropic media, the numerical coefficient in the expression for N is somewhat overestimated, while in the expression for n_1 it is underestimated; in a qualitative discussion they may be omitted.

If $S_2 < 1$, then brittle fracture occurs at $S_1 = 1$, i.e. at a strength $\tau_c \simeq \sqrt{\sigma G/L}$; if $S_2 > 1$, then τ^* has the meaning of a yield limit. As an example, in Fig. 1 the lines of S are plotted for zinc single crystals of diameter $\sim$ 1 mm at $\dot{\varepsilon} \sim 10\%$ min^{-1}, $\chi \sim 45^\circ$, and under corresponding assumptions regarding the value of $U_{\max}$ and the form of $U(x)$ of those energy barriers which play the principal role in the temperature intervals under consideration. Crystals of pure zinc exhibit low-temperature brittleness; at ordinary temperatures they are highly plastic, and the yield limit is small. In crystals coated with the thinnest film of mercury, the value of σ decreases sharply—and not only

not only on the surface of the crystal, but also on internal microsurfaces—owing to the rapid two-dimensional migration of mercury atoms along hollow dislocation cores and along the microcracks developing on their basis. The line S_1 shifts to the left, and the lines S_2 downward; the additional lowering of S_2 in the region of intermediate temperatures is due to the greater value of $U_{\max}$ for amalgamated crystals. In agreement with experiment (^{6}), the criterion S indicates catastrophic brittleness with a considerable decrease in strength up to $T_c \sim 420^\circ$K; at $T \gg T_c$ high plasticity is restored. Below $T_m = 234^\circ$K mercury ceases to migrate and, consequently, also ceases to lower σ, so that the usual strength is restored. S_1 coincides abruptly with the line S_1 for pure crystals; only the difference in the temperature dependence of S_2 remains, which corresponds to the higher rate of hardening of crystals with interstitial atoms.

According to relations (1) and (2), the critical temperature T_c of the transition from brittleness to plasticity is equal to

$$T_c = \frac{U_{\max}\eta(S_0)}{k\ln(\gamma\lambda b\cos\chi/\varepsilon hu)}, \quad \text{where} \quad S_0 = \frac{\sigma}{b\tau_1(0)}. \tag{3}$$

If the melting point of the base metal is T_M, and that of a certain low-melting additive capable of producing a significant decrease in σ is T_m, then the following cases are possible:

a) $T_m < T_c < T_M$—brittleness at reduced strength in a limited temperature interval $T_m \div T_c$ (for example, Zn—Hg);

b) $T_m < T_M < T_c$—brittleness at reduced strength from T_m up to T_M (for example, Zn—Sn (^{5}));

c) $T_c < T_m$—absence of the effect, i.e. the condition for suitability of the given additive.

To estimate the width of the transition interval near T_c, it is convenient to consider the "measure of plasticity"

$$M = \exp\left[-\frac{U_{\max}\eta(S_0)}{k}\left(\frac{1}{T} - \frac{1}{T_c}\right)\right]$$

or the "probability of plastic flow" $W = 1 - \exp(-M)$. In the case mentioned, Zn—Hg, the function $W(T)$ gives a sharp transition from 0 to 1 in a 40–50-degree interval near $T_c \sim 420$°K, and agrees well with the experimental dependence $\varepsilon_{\max}(T)$ (^{6}).

A different picture occurs for weak (organic) adsorption-active media, which do not lead to embrittlement of the crystal but are capable, under certain conditions, of plasticizing it. A small change in σ cannot, by itself, noticeably shift the branches of the criterion S. However, if under the given deformation conditions the interaction of dislocations with the free surface of the crystal plays an essential role, then even a small lowering of σ can substantially raise the branch S_2 and thereby shift to the left the point of the yield limit τ^*.

The corresponding energy barrier $U_{\max} = b^2\sigma \simeq 0.5$ eV is caused by the formation of a step when a dislocation emerges at the surface and has considerable steepness—for example,

$$U(x) \sim \frac{-U_{\max}}{1 + (x/a)^3},$$

i.e., in the immediate vicinity of the surface the force determined by it predominates over the slowly varying repulsive "image force" (^{14}). (It is not excluded that an even more important role is played by surface defects blocking individual points on the contour of the slip plane; in this case the barrier may be higher and have another expression, but, as before, it will remain short-range and substantially dependent on σ.) In Fig. 2, $\varphi(\eta)$ is plotted for the indicated form of $U(x)$; $\tau_1(0)$ is $\sim (1 \div 3) \cdot 10^{10}$ dyn/cm^2, and the logarithmic term in (2) is ~ 20 (in this case one should take $\lambda \sim 1$).

According to (2), $\eta = \eta(p_i)$, where the parameters p_i are T, $U_{\max}$, $\dot{\varepsilon}$, etc.

For the change in the yield limit we have $\Delta\tau^*_{p_i} = \dfrac{\partial\tau^*}{\partial p_i}\Delta p_i$, and, in particular,

$$\frac{\Delta\tau_T^*}{\tau^*} = -\frac{1}{2}\frac{\eta}{\varphi}\left|\frac{\partial\varphi}{\partial\eta}\right|\frac{\Delta T}{T}; \qquad \frac{\Delta\tau_\sigma^*}{\tau^*} = \frac{1}{2}\left(1+\frac{\eta}{\varphi}\left|\frac{\partial\varphi}{\partial\eta}\right|\right)\frac{\Delta\sigma}{\sigma}. \tag{4}$$

The last equality means that, for $\eta \sim 0.9$, a decrease of σ by only several tens of erg/cm^2 is capable of reducing the yield limit by a factor of two. The optimum action of an adsorption-active medium corresponds to $\eta \sim 1$. At $\dot{\varepsilon} \sim 10\%$ min^{-1} we have $T_{\text{opt}} \sim 290$°K, and at $\dot{\varepsilon} \sim 500\%$ min^{-1}, $T_{\text{opt}} \sim 370$°K, which agrees well with experiment $^{(4)}$. However, at $\eta \sim 1$ relation (4) cannot give a quantitative estimate of the effect, since in the present case only the surface energy barrier is taken into account. In the general case one should consider the superposition of the strengthening factors $U_j(x)$, i.e., a certain generalized function $\Phi(H)$, including the various $\varphi_j(\eta_j)$. Then the optimum action of the medium is determined by the condition $\frac{\partial^2}{\partial\sigma^2}\tau^*(\Phi) = 0$, and the effects are the more significant, the more noticeable the role of the surface energy barrier is in this region.

Fig. 2. Dependence of $\tau_1/\tau_1(0) = \varphi(U_A/U_{\max}) = \varphi(\eta)$:
a—for $U(x) \sim \exp(-x/a)$;
b—for $U(x) \sim [1+(x/a)^2]^{-1}$;
c—for $U(x) \sim [1+(x/a)^3]^{-1}$.

The generality of the proposed scheme is limited by a number of assumptions which may subsequently be removed: in particular, the exponent of τ in the expression for S_1 may differ from 2, and the branch S_2, generally speaking, is not horizontal; the coefficients A, B, and C require experimental refinement; a more detailed consideration is also necessary of the dependence of S on the crystal orientation. Apparently, this scheme will make it possible to refine quantitatively the criterion of dispersibility $^{(5)}$. Applications of this scheme are closely connected with a careful analysis of the temperature dependence of strengthening factors and of the spectra of their activation energies.

The author expresses gratitude to Acad. P. A. Rebinder and V. N. Rozhanskii for their great assistance and unfailing interest in this work.

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
22 IX 1957

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