

## SPONTANEOUS FRACTURE OF SOLIDS AS AFFECTED BY SURFACTANTS

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*Fracture of solids under the action of surfactants is studied. The limiting case of manifestation of chemisorption effects without significant effect of mechanical stresses is considered. The growth of plane cracks in solids with a regular structure upon contact with surfactants is described for the case where the model of the process is molecular wedge-assisted crack wedging. The critical stress-intensity factors are estimated in terms of the critical crack opening in wedging by a semi-infinite wedge of constant thickness. An anomalously low resistance to breaking of a solid into parts is observed under certain conditions (spontaneous fracture).*

**Introduction.** The refinement of Novozhilov's necessary and sufficient criteria of brittle strength [1] for crystalline solids has allowed a quantitative description of the Rehbinder effect [2–4].

In the review by Rehbinder and Shkutin [5], both spontaneous dispersion of solids and the facilitation of mechanical dispersion are discussed; however, attention is paid mainly to physicochemical processes. Below, these phenomena are analyzed from the viewpoint of physicochemical mechanics and it is noteworthy that "... in principle, refine dispersion cannot be a completely mechanical process: connected with development of a new huge surface, it necessarily requires the interference of physicochemical factors to control phenomena that occur at the interface boundaries ..." [5, p. 36].

It is natural to use the Neuber–Novozhilov approach [1, 6, 7] in formulating the strength criteria for sharp cracks in structured continuous solids.

**1. Stress States in the Vicinity of Crack Tips.** *Physicochemical Description of Fracture.* The single crystals of solids with plane cracks having a rectilinear front are considered. For simplicity, the plane problems of a crack are analyzed for a square Bravais lattice. Let the tensile stresses applied to a solid at infinity be equal to zero:  $\sigma_\infty = 0$ . The crack propagation for  $\sigma_\infty = 0$  corresponds to spontaneous fracture of a solid as affected by surfactants. Let there be hydrogen (surfactant) in a crack which reacts with the freshly formed solid surface at the crack tip, and the formed hydrides accumulate at the surface of the crack in the vicinity of its tip. This case under the action of tensile stresses ( $\sigma_\infty \neq 0$ ) is analyzed thoroughly in [3]; for normal-rupture cracks, the assumptions that the interatomic-interaction forces are absent in the vicinity of the crack tip and that the volume change in the formation of hydrides and their strength at the crack tip can be ignored were made. We discard the latter assumption; then, the hydrides formed in the neighborhood of the crack tip can be modelled by a molecular wedge. The stress-strained state in the neighborhood of the crack tip is determined by this wedge in the absence of loading ( $\sigma_\infty = 0$ ).

A similar formulation is expedient when spontaneous fracture of solids is studied (see [5, p. 33–36]). In particular, the problem of the choice of construction materials for the chamber shells subjected to radiation exists [8]. The effect of surface deformation and the formation of blisters is called radiation blistering [8]. In the absence of external loading, shelling of the surface occurs after the formation of blisters. Spontaneous fracture is possible upon hydrogenation of metal titanium: dissolution of hydrogen in the depth of the metal is accompanied by the increase in the volume of the formed solid product compared to the initial volume of a pure metal [9, pp. 31–37].

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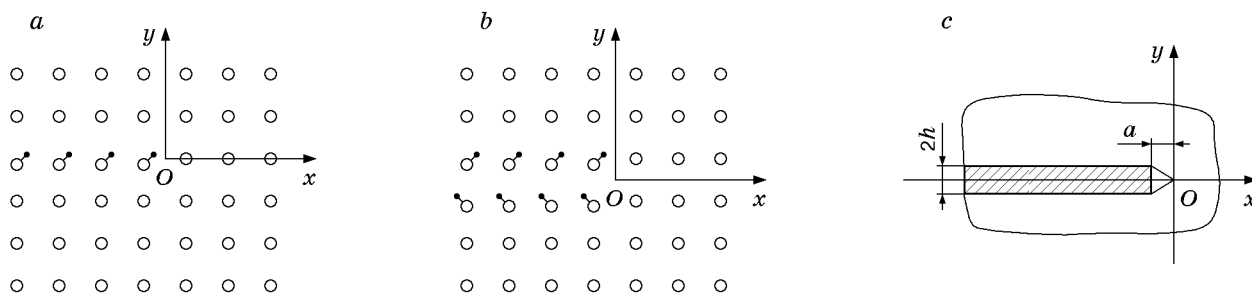


Fig. 1

Figure 1 shows the simplest scheme of such a wedge for a square Bravais lattice for the plane case. In Fig. 1a and b, the atoms in a single crystal of the substance are shown by circles, and the hydrogen atoms by points. This figure also shows the physical models of single crystals with a molecular wedge consisting of one and two series of hydride molecules, respectively, and Fig. 1c shows the mechanical model of a solid with a crack into which a constant-thickness wedge is inserted (the crack in mechanical models is simulated by a bilateral cut). Here  $2h$  is the thickness of the wedge and  $a$  is the distance from the end of the wedge to the crack tip. Only the right tip of the crack is considered. The position of the Cartesian coordinate system is aligned with the position of the right crack tip in physical models or with the right tip of the cut in mechanical models. The simplest model proposed corresponds to the formation of molecular wedges along the planes of the single-crystal lattice. The general case of an arbitrary position of the wedge relative to the crystal lattice is omitted.

Let the surfactant (hydrogen) be chemically sorbed inside the crack and quite a stable compound be formed. Hydrides can have a constant or variable molecular composition [10–12]. We assume that the minimum diameter of a molecule of this compound exceeds the constant of the crystal lattice of the single crystal of the initial substance  $r_e$ . Then, the quantity  $r_e$  is compared with the crystal-lattice constant of the hydride crystal  $r_e^*$ , and the diameter of the hydride molecule is determined by the chemical formula of the hydride. One or two layers of molecules of the newly formed compound can form a similarity of the molecular wedge (the number of layers of the hydride molecules is determined by the time of a chemical reaction on the freshly formed surface). For  $\sigma_\infty = 0$ , the substance of the molecular wedge is oblate, and, generally speaking, no significant strength restrictions are imposed on this substance.

Depending on the position of the newly formed compound or hydride relative to the crack tip, the diameters of their molecules can act as a force bridge under loading on a cracked solid [4, 13] or a molecular wedge in the absence of loading on the cracked solid.

We estimate the thickness of the molecular wedge formed by the hydrides  $\text{TiH}_2$  in the Ti single crystal. “As titanium is absorbed by hydrogen, the volume of the material increases . . . . This leads to the formation of microcracks in the material; merging in the microcracks, the latter cause fracture of titanium. The cracks pass through a grain and the sites of aggregation of hydrides” [9, p. 18]. For the molecular-wedge thickness  $2h$ , we have the following relations:

$$2h \simeq r_e^* - r_e, \quad 2h/r_e \simeq r_e^*/r_e - 1; \quad (1.1)$$

$$2h \simeq 2r_e^* - 2r_e, \quad 2h/r_e \simeq 2(r_e^*/r_e - 1). \quad (1.2)$$

Here  $r_e = 2.92 \cdot 10^{-10}$  m and  $r_e^* = 4.45 \cdot 10^{-10}$  m are the atomic-lattice constants of the Ti and  $\text{TiH}_2$  single crystals, respectively [11, 14]. Relations (1.1) and (1.2) refer to molecular wedges consisting of one and two series of molecules of the hydride  $\text{TiH}_2$ , respectively, and the distance from the ends of the wedges to the crack tips is estimated to be  $a \approx r_e$  (Fig. 1a and b). For the  $\text{Ti}_2$  single crystals, the molecular-wedge thickness calculated from relations (1.1) and (1.2) is considerable, because the end of the wedge is close to the crack tip ( $a \approx 2.92 \cdot 10^{-10}$  m). In relations (1.1) and (1.2), the sign “ $\simeq$ ” is used, since the atomic distance in a lamina of  $\text{TiH}_2$  can differ from the lattice constant  $r_e^*$  of the  $\text{TiH}_2$  single crystal, and the distances between

the atoms in the Ti single crystal in the neighborhood of a damage caused by the molecular wedge can differ from the crystal-lattice constant of the ideal single crystal of Ti. Relations (1.1) and (1.2) are also true for other substances whose hydrides contain two hydrogen atoms.

*Crack Wedging by a Molecular Wedge in a Mechanical Model.* We use the representations of the solutions for stresses at the continuation of a sharp crack  $y = 0$  in the plane problem of the theory of elasticity in terms of the stress-intensity factor  $K_I^0$ . Then, for normal-rupture cracks, at the vicinity of the crack tip, with accuracy to higher-order magnitudes, for the linear problem one can write

$$\sigma_y(x, 0) \simeq \sigma_\infty + K_I^0 / (2\pi x)^{1/2}, \quad (1.3)$$

where  $\sigma_\infty = 0$  are the characteristic stresses specified at infinity. In particular, the stress-strained state of a solid with a semi-infinite crack is determined only by the molecular wedge.

For a sharp crack, in wedging the solid by a semi-infinite wedge of constant thickness, in the absence of friction we write the relation for  $K_I^0$  in the following form [15, pp. 49–50]:

$$K_I^0 = \frac{4Gh}{1 + \varkappa} \sqrt{\frac{2}{\pi a}}. \quad (1.4)$$

Here  $G$  is the modulus of shear,  $\varkappa = 3 - 4\nu$  for the plane-deformed state and  $\varkappa = (3 - \nu)/(1 + \nu)$  for the plane strain state, and  $\nu$  is Poisson's ratio. In relation (1.4), the constants  $G$  and  $\nu$  for the single crystal of the initial substance are used.

**2. Brittle-Fracture Criterion.** Cracked single crystals of metals with vacancies are studied. The discrete-integral criterion of brittle strength (two-dimensional case) is considered for the weakest monolayer of atoms and sharp normal-rupture cracks [3]:

$$\frac{1}{kr_e} \int_0^{nr_e} \sigma_y(x, 0) dx \leq \delta \sigma_m. \quad (2.1)$$

Here  $\sigma_y$  are the normal stresses near the crack tip (these stresses act in the depth of the cracked single crystal),  $Oxy$  is the rectangular coordinate system (Fig. 1),  $r_e$  is the distance between the centers of the atoms in the initial substance,  $n$  and  $k$  are integers ( $n \geq k$ , where  $k$  is the number of interatomic bonds),  $nr_e$  is the averaging interval, and  $\sigma_m$  (or  $\delta \sigma_m$ ) is the theoretical strengths in the absence [16] (or in the presence) of a surfactant in the crack ( $\delta \leq 1$  is the parameter). The parameter  $\delta$  describes chemically intensified fracture: in the presence of a surfactant, the theoretical strength of the initial substance can decrease.

After appropriate transformations [see (2.1) and (1.3)], for a sharp normal-rupture crack, in the presence of vacancies at the crack tip, we obtain an estimate of the critical stress-intensity factor  $K_I^{*0}$ :

$$K_I^{*0} \leq (k\delta\sigma_m/n)(\pi nr_e/2)^{1/2}. \quad (2.2)$$

Submitting expression (1.4) into relation (2.2), we obtain an estimate for the critical thickness of a wedge of constant thickness  $2h^*$ :

$$\frac{2h^*}{r_e} \leq (1 + \varkappa)(1 + \nu) \frac{\pi}{2} \frac{k}{\sqrt{n}} \frac{\delta\sigma_m}{E} \sqrt{\frac{a}{r_e}}. \quad (2.3)$$

With allowance for the estimate of the theoretical strength of a single crystal [16]  $\sigma_m = \eta E$  ( $0.1 \lesssim \eta \lesssim 0.3$ ), expression (2.3) takes the form  $2h^*/r_e \leq C\eta\sqrt{a/r_e}$ , where  $C = \text{const}$ . For the Ti single crystal, the constant is  $C_{Ti} = 5.71$  for a plane deformed state and  $C_{Ti} = 6.29$  for a plane stress state in the absence of vacancies ( $k = n = 1$ ). Poisson's ratio of the Ti single crystal is taken to be equal to Poisson's ratio for technical Ti alloys, i.e.,  $\nu_{Ti} = 0.3$ .

Figure 2 shows a dependence that characterizes the behavior of the system. Curves 1 and 2 obtained for the equation  $2h/r_e = C\eta\sqrt{a/r_e}$  at  $\eta = 0.1$  and  $0.3$ , respectively, separate the stability (shaded) and instability regions. The points that describe the behavior of the Ti single crystal in the presence of a molecular wedge are shown in Fig. 2. If the point  $(a_0/r_e, 2h_0/r_e)$  on the plane is in the stability region, crack propagation does not occur. If the point  $(a_0/r_e, 2h_0/r_e)$  on the plane is in the instability region, the crack extends a distance equal to one interatomic distance  $r_e$ .

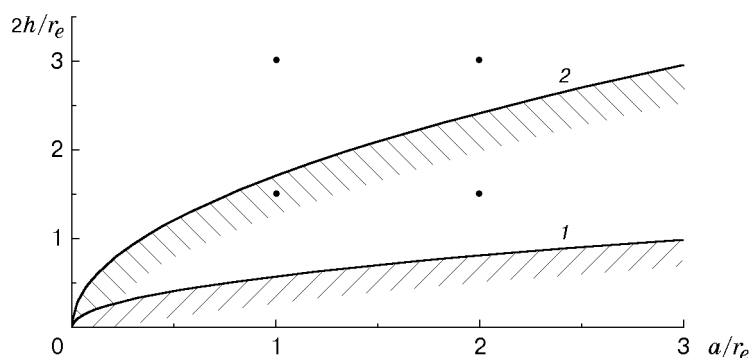


Fig. 2

Let the point  $(a_0/r_e, 2h_0/r_e)$  be in the instability region. After extension of the crack, the value of  $a_0 + r_e$ , which characterizes the distance from the end of the wedge to the new crack tip (the surfactant reacts with the freshly formed surface of the single crystal with delay) changes. The behavior of the system at the point  $[(a_0 + r_e)/r_e, 2h_0/r_e]$  is analyzed, etc.

Let the surfactant coming to a crack reacts with the freshly formed surface of the single crystal. If the chemical reaction of the surfactant with the single-crystal atoms in the vicinity of the crack tip are taken into consideration, the value of  $a_0 + r_e$  decreases, and the end of the wedge moves toward the crack tip.

It is clear that, for quite a thick wedge, crack propagation always occurs at a fixed distance from the wedge end to the crack tip; however, the crack always stops because of an increased distance without making allowance for the chemical reaction of the surfactant with the freshly formed surface.

Calculations for the Ti single crystal show that among the points  $(a_0/r_e, 2h_0/r_e) = (1, 1.52), (2, 1.52), (1, 3.05),$  and  $(2, 3.05)$ , two points  $(1, 1.52)$  and  $(2, 1.52)$  are in the stability region for  $\eta = 0.3$ . Four indicated points are shown in Fig. 2. At small distances from the wedge end to the crack tip ( $a_0/r_e \leq 2$ ), for molecular  $\text{TiH}_2$  wedges consisting of more than two series of molecules, fracture always occurs.

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