Journal of Applied Mechanics and Technical Physics, Vol. 39, No. 3, 1998

STRENGTH REDUCTION OF METALS UPON HYDROGEN CHEMISORPTION AT THE TIP OF A CRACK

V. M. Kornev

UDC 539.375

When hydrogen interacts with the freshly formed surface, the interatomic bonds at the tip of a crack in the single crystal of a metal are known to break. The decrease in the brittle strength of the single crystals of metals in the presence of hydrogen in the crack compared with the strength of the same metal in the absence of hydrogen is estimated quantitatively using comparative criteria of brittle strength.

Introduction. "Adsorption of surfactants from the surroundings by a deformable solid has been found long ago to affect markedly the deformation and strength properties of a body" [1, p. 645] (see also [2]). "... Chemically assisted fracture is ubiquitous, but there are no systems understood so well that the preceding ideas have been applied in a quantitative way" [3, p. 117].

In the present paper, we study the process of brittle fracture of the single crystals of cracked metals in which either a surfactant is absent or there is hydrogen which reacts with the freshly formed surface at the crack tip. To estimate the strength of single crystals, Novozhilov's modified discrete criterion of brittle strength is used in the first case (interatomic forces, which are described using the Morse potential, act in the vicinity of the crack tip), and a modified criterion of brittle strength in the second. To do this, chemical transformations occurring at the crack tip are taken into consideration: the freshly formed surface of a deformable solid adsorbs a surfactant (hydrogen).

The values of the critical lengths of bond-failure cracks were obtained on the basis of the two criteria at a given level of loading, and they usually differ by an order of magnitude. If the critical lengths of bond-failure cracks obtained according to the sufficient criterion are regarded as a basis of calculations, the critical load of crack initiation decreases severalfold in the presence of hydrogen. Thus, chemically enhanced brittle fracture of the cracked single crystals of metals is described quantitatively in the form of comparative brittle-strength criteria.

1. Mechanical Models that Take into Account Physicochemical Transformations at the Tip of a Crack. There are many papers dealing with the effect of hydrogen on brittle fracture of metals (e.g., [4–9]). Attention has been given mainly to hydrogen embrittlement when the crack growth is controlled by the adsorption of atomic hydrogen. The existing theories are mainly descriptive. To estimate quantitatively the effect of hydrogen on brittle fracture, the ideas developed at Rebinder's school seem to us most appropriate [1, 2, 9]. Hydrogen adsorption on a metal, hydrogen diffusion in a metal (reversible embrittlement), and the formation of hydrides affect markedly the strength properties of metals [9]. We note that "in a deformable metal, the number of active centers that are capable of interacting increases; the activated chemisorption of hydrogen occurs in this case. ... In a hydrogen-enriched metal, the crack growth is promoted by hydrogen chemisorption at the crack tips rather than by hydrogen diffused in the metal matrix" (see [9, p. 9]).

We shall pass from the description of the physicochemical process of fracture to the construction of mechanical models. We consider single crystals of metals with planar cracks. Let tensile forces σ_∞ acting along the normal to the crack plane be applied to a solid. We consider two cases:

(1) any surfactant is absent in the crack (model No. 1);

Lavrent'ev Institute of Hydrodynamics, Siberian Division, Russian Academy of Sciences, Novosibirsk 630090. Translated from Prikladnaya Mekhanika i Tekhnicheskaya Fizika, Vol. 39, No. 3, pp. 173–178, May–June, 1998. Original article submitted September 18, 1996.

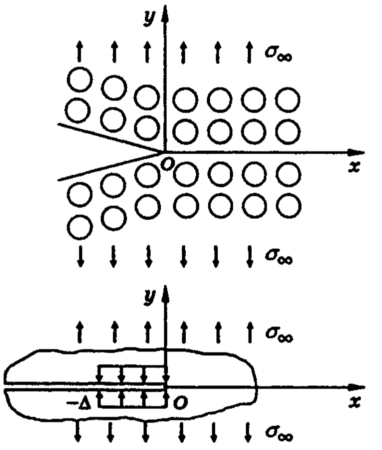

Fig. 1

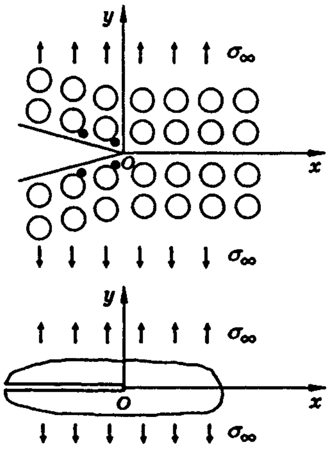

Fig. 2

(2) the hydrogen in the crack reacts with the freshly formed surface of a metal at the crack tip (model No. 2).

For simplicity, planar problems of a crack are analyzed for a simple square Bravais lattice.

Figures 1 and 2 show both cases [the atoms of metal single crystals are indicated by open circles, and hydrogen atoms by filled circles; physical models of a cracked single crystal are shown at the top, and mechanical models at the bottom (only the right tip of the crack in the crystalline lattice is given)]. The Cartesian coordinate system is located according to the position of the right crack tip in physical models or the position of the right tip of a cut in mechanical models (the crack in mechanical models is simulated by a bilateral cut). The loaded section of the cut, which simulates the forces of interatomic interaction at the crack tip (Δ is the length of the section), is shown at the bottom of Fig. 1; thus, the mechanical problem is partially linearized.

Physical formulations of the problem are distinguished by the absence or presence of a surfactant (hydrogen) in the crack, and mechanical formulations are distinguished by the presence or absence of the loaded section of the cut in the vicinity of the crack tip.

The atomic radii of metals and the parameters of the crystal lattices of metals are considerably larger (by one or two orders of magnitude) than the size of atomic hydrogen or a proton (see [10, Table 3.1, Appendix 5]). The proton radius can be estimated to be $r_{\mathrm{H}^+} \ll 0.53 \cdot 10^{-10}$ m, since the size of the hydrogen atom is $r_{\mathrm{H}} = 0.53 \cdot 10^{-10}$ m, which facilitates the penetration of hydrogen into the crack tip. Hydrogen is adsorbed by the formed surface of a metal.

Let metal hydrides of a uniform or variable molecular composition be formed at the crack tip because of chemisorption [4, 7]. The hydrides formed break completely or partially the forces of interatomic interaction of a metal single crystal at the crack tip only for superstressed interatomic bonds. The forces of interatomic interaction are assumed to be absent at the crack tip. We ignore the change in the volume during the formation of hydrides and the strength of a hydride at the crack tip. In this case, any forces associated with wedging and intermolecular interaction are absent at the crack tip and a mechanical model is obtained (Fig. 2). Hydrogen supply into the crack tip is limited by diffusion and, hence, the above consideration is true only for quasistatic loading. It is noteworthy that the weak effect of hydrogen on the strength characteristics of metals was shown in high-speed deformation in experiments.

A comparison of mechanical model Nos. 1 and 2 makes it possible to conclude that metal deformation (Fig. 2) is facilitated by stresses σ_∞ applied at infinity owing to a decrease in rigidity compared with metal deformation shown in Fig. 1. For $\Delta \to 0$, model No. 1 is continuously transformed into model No. 2.

2. Brittle-Fracture Criteria That Take into Account the Effect of a Surfactant at the Tip of a Crack. We shall consider cracked metal single crystals with vacancies. As Novozhilov in [11], we introduce the discrete-integral criteria of brittle strength (the two-dimensional case) for the weakest monolayer of atoms in the case of sharp bond-failure cracks [12–14]:

$$\frac{1}{kr_e}\int\limits_0^{nr_e} \sigma_y(x,0)\,dx \leqslant \delta\sigma_m. \tag{2.1}$$

Here σ_y are the normal stresses at the crack tip (these stresses act deep in the metal single crystal with a crack of length $2l$), Oxy is a rectangular coordinate system (Figs. 1 and 2), r_e is the spacing between the atomic centers, n and k are numbers and moreover $n \geqslant k \geqslant 1$ (k is the number of acting interatomic bonds), nr_e is the averaging interval, σ_m and $\delta\sigma_m$ are the theoretical strengths in the absence [15] and in the presence of a surfactant in the crack, respectively, and δ is a parameter; note that $\delta = 1$ for the first mechanical model and $\delta \leqslant 1$ for the second mechanical model. The parameter δ describes chemically enhanced fracture: the theoretical strength of a metal can decrease in the presence of a surfactant. "It is known that the bonding forces of the superficial metal atoms are changed and redistributed owing to chemisorption; moreover, the lattice parameter increases. Hence, the chemisorbed hydrogen at the crack tip will facilitate the rearrangement and break of the interatomic bonds of a metal. Since the influence of a chemisorbed atom is long-term, ... this can change significantly the strength of interatomic bonds" [9, p. 10]. However, the author is not aware of concrete numerical results on the decrease in the theoretical strength of a metal in contact with a surfactant.

We shall consider the stress-strain state in the two cases: σ_y has already been obtained in the fist case (see relation (2.6) in [12]) and, in the second case, σ_y is used as the classical representation of the solution with a singularity in the Griffith problem $\sigma_y(x,0) = \sigma_\infty + K_I/(2\pi x)^{1/2}$, where K_I is the stress-intensity factor.

Despite the fact that the stress-strain state of the systems, which correspond to both mechanical models, differs considerably in the vicinity of the crack tip, the brittle-strength criteria (2.1) have been formulated in a uniform manner. For model No. 1, the brittle-strength criterion coincides completely with Novozhilov's sufficient brittle-strength criterion with allowance for necessary improvements [11–14]: the forces of interatomic bonding that actually act in a metal single crystal are modeled by a loaded segment of a cut, its length Δ is obtained from an energetic point of view, and it is related to the radius of separation of the forces of interatomic bonding. For model No. 2, a brittle-strength criterion proposed in a particular case for $n = k = 1$ and $\delta = 1$ coincides with Novozhilov's necessary brittle-strength criterion [11], but it has a different physical meaning.

After appropriate manipulations and transformations [12], if one assumes that $\Delta/l \ll 1$ and $r_e/l \ll 1$, for the first case we obtain an equation for determination of the dimensionless parameter $a = \Delta/r_e$:

$$a + a^{1/2}(1+a)\arcsin(1/(1+a)^{1/2}) = (\pi/4)(1-\nu^2)^{-1}\beta. \tag{2.2}$$

Here ν is the Poisson ratio and β is a constant that depends on the potential of interatomic interaction. The choice of any potential determines the surface-energy density $\gamma = \beta r_e \sigma_m^2 E^{-1}$ in the Griffith problem, where E is the modulus of elasticity of a metal single crystal (see relations (2.4) and (2.5) in [12]). Andreev et al. [12] gave values of the parameter β for the Morse, Lennard-Jones, and Mie potentials and also for Morse's generalized potential. We shall discuss the effect of the parameter β in relation (2.2). This parameter is the characteristic constant for the chosen potential of interatomic interaction [12], and one can estimate it roughly as $2 < \beta < 10$. For $\nu = 1/3$, solutions of Eqs. (2.2) were obtained for the Morse and Lennard-Jones potentials: $a \approx 1.04$ and $a \approx 1.43$, respectively. Thus, the Lennard-Jones potential exerts a more prolonged effect compared to the Morse potential. It is worth noting that, for $\beta \to \infty$, the solution of Eq. (2.2) is $a = 0$ and, consequently, mechanical model No. 1 is continuously transformed into model No. 2 for $\Delta \to 0$ (we note that stress-strain states that correspond to these models differ significantly). For the first case, computation results concerning the determination of the critical crack lengths $2l_{nk}^{*(1)}/r_e$ at a prescribed level of loading σ_∞/σ_m were taken from [12, 13].

We pass to the second case. After appropriate manipulations for a sharp-tipped bond-failure crack in the presence of vacancies at the tip, we estimate the critical coefficient of the stress-intensity factor $K_I^{*(2)}$:

$$K_I^{*(2)}/\sigma_\infty \leqslant (k\delta\sigma_m/n\sigma_\infty - 1)(\pi n r_e/2)^{1/2}. \tag{2.3}$$

If one takes account of the known equality $K_I = \sigma_\infty(\pi l_{nk})^{1/2}$ for the Griffith problem (model No. 2), the critical crack length $2l_{nk}^{*(2)}/r_e$, obtained according to the discrete-integral criterion, is related to the relative

TABLE 1

σ_m/σ_∞	$2l_{11}^{*(1)}/r_e$		$2l_{11}^{*(2)}/r_e$	$\sigma_\infty^{*(1)}/\sigma_\infty^{*(2)}$	
1	2	3	4	5	6
10	530	680	81	2.40	2.70
20	2120	2700	361	2.35	2.65
100	53110	67600	9801	2.31	2.61

TABLE 2

$\frac{\sigma_m}{\sigma_\infty}$	$\frac{2l_{11}^{*(1)}}{2l_{11}^{*(2)}}$	$\frac{\sigma_\infty^{*(1)}}{\sigma_\infty^{*(2)}}$	$\frac{2l_{21}^{*(1)}}{2l_{21}^{*(2)}}$	$\frac{\sigma_\infty^{*(1)}}{\sigma_\infty^{*(2)}}$	$\frac{2l_{31}^{*(1)}}{2l_{31}^{*(2)}}$	$\frac{\sigma_\infty^{*(1)}}{\sigma_\infty^{*(2)}}$	$\frac{2l_{41}^{*(1)}}{2l_{41}^{*(2)}}$	$\frac{\sigma_\infty^{*(1)}}{\sigma_\infty^{*(2)}}$
	$n = 1$		$n = 2$		$n = 3$		$n = 4$	
1	2	3	4	5	6	7	8	9
10	6.54	2.40	14.7	3.27	27.6	3.97	48.9	4.60
20	5.87	2.35	11.6	3.17	18.7	3.82	27.5	4.40
100	5.42	2.31	9.79	3.09	14.3	3.70	19.1	4.23

level of loading $\sigma_m/\sigma_\infty^{*(2)}$ by the relation

$$\frac{2l_{nk}^{*(2)}}{r_e} = \left(\frac{\delta\sigma_m}{\sigma_\infty^{*(2)}} - \frac{n}{k}\right)^2 \frac{k^2}{n}. \tag{2.4}$$

The values of the critical lengths $l_{nk}^{*(1)}$ and $l_{nk}^{*(2)}$ of bond-failure cracks were obtained based on the criteria (2.1) at a given level of loading σ_m/σ_∞ for the first and second cases, respectively. In Table 1, the levels of loading are given in column 1, columns 2 and 3 refer to the critical lengths of cracks (model No. 1) for the Morse and Lennard-Jones potentials [12, 13], column 4 indicates the critical lengths of cracks (model No. 2) for an arbitrary potential of interatomic interaction when $n = k = \delta = 1$ in relation (2.4), and columns 5 and 6 indicate ratios of the critical loads of crack propagation for both models if the critical lengths $l_{11}^{*(1)}$ of bond-failure cracks from columns 2 and 3 are used as the basis of calculations. As usual, the critical lengths of the cracks for the cases considered differ by an order of magnitude, and the critical load of crack initiation in the presence of hydrogen decreases severalfold even in the absence of vacancies.

In compiling Tables 1 and 2, we ignored the possible decrease in the theoretical strength of a metal single crystal in the presence of hydrogen. With the corresponding experimental results on reduction of the theoretical strength, the critical parameters could be readily estimated by means of relation (2.4).

If there are vacancies in front of a crack, the discrepancy between the critical parameters becomes more significant [13, 14]. Computation results in the form of a ratio of critical parameters are given in Table 2, where column 1 refers to the levels of loading, the even columns indicate the $2l_{n1}^{*(1)}$ values calculated for the Morse potential, and the odd columns list the $\sigma_\infty^{*(2)}$ values for cracks of length $2l_{n1}^{*(1)}$ for four values of n and one acting bond $k = 1$.

It follows from the analysis of Tables 1 and 2 that the variation in the level of loading in the averaging interval with one acting bond affects differently the ratios of the critical parameters $2l_{n1}^{*(1)}/2l_{n1}^{*(2)}$ and $\sigma_\infty^{*(1)}/\sigma_\infty^{*(2)}$. The latter ratio depends weakly on these changes.

Thus, chemically enhanced fracture of cracked single crystals of metals has been expressed quantitatively in the form of comparative brittle-strength criteria.

Mechanical model No. 2 agrees well with the conclusions in [9, p. 10]: "...the presence of hydrogen in a metal matrix ... is not predetermining. The presence of chemisorbed hydrogen at the crack tip is the major cause of the decrease in strength properties.... The changes of the strength properties of a metal do not depend on the method of hydrogen supply to the tip of a crack."

Remark. Introduction of the parameter $\delta \leqslant 1$, which characterizes the decrease in the theoretical strength of a metal single crystal because of the presence of chemisorbed impurity (hydrogen) [see relation

(2.1)], has a clear physical meaning. If the hydrogen atom penetrates into a metal, it can be regarded as a foreign atom in the atomic chain at the crack tip. Estimates of the theoretical strengths of ideal atomic chains and atomic chains in the presence of foreign atoms showed [16] that the strengths can differ by one or two orders of magnitude; note that $\delta \ll 1$.

"The analysis performed has shown that hydrogen embrittlement is a particular case of the phenomenon of adsorptive facilitation of the deformation and fracture of solids, which was discovered by Academician P. A. Rebinder ..." [9, p. 11]. Chemically enhanced brittle fracture of the cracked single crystals of metals has been expressed quantitatively in the form of comparable brittle-strength criteria.

This work was supported by the Russian Foundation for Fundamental Research (Grant No. 95-01-00870).

REFERENCES

1. E. D. Shchukin and P. A. Rebinder, "Formation of new surfaces upon deformation and fracture of a solid body in a surfactant," *Colloid J.*, **20**, No. 5, 645–654 (1958).
2. V. I. Likhtman, P. A. Rebinder, and G. V. Karpenko, *Effect of a Surfactant on Metal Deformation* [in Russian], Izd. Akad. Nauk SSSR, Moscow (1954).
3. R. Thompson, "Physics of fracture," in: R. M. Latanision and J. R. Pickens (eds.), *Atomistics of Fracture*, Plenum Press, New York (1983), pp. 167–204.
4. P. Cotterill, *The Hydrogen Embrittlement of Metals*, Pergamon Press, Oxford (1961). P. 100.
5. K. McMagon, K. Braint, and S. Berendgi, "Effect of hydrogen and impurities on brittle fracture of steel," in: D. Taplin (ed.), *Mechanics of Fracture. Fracture of Materials* [Russian translation], Mir, Moscow (1979), pp. 109–133.
6. V. I. Shapovalov, *Effect of Hydrogen on The Structure and Properties of Iron–Carbide Alloys* [in Russian], Metallurgiya, Moscow (1982).
7. P. V. Gel'd, R. A. Ryabov, and L. P. Mokhracheva, *Hydrogen and Physical Properties of Metals and Alloys. Hydrides of Transient Metals* [in Russian], Nauka, Moscow (1985).
8. M. R. Louthan, Jr., "Role of hydrogen in stress corrosion cracking," in: J. Yahalom and A. Aladjem (eds.), *Stress Corrosion Cracking*, Freund, Tel-Aviv (1980), pp. 39–55.
9. G. V. Karpenko, A. K. Litvin, V. I. Tkachev, and V. I. Sushko, "Mechanism of hydrogen brittleness," *Fiz.-Khim. Mekh. Mater.*, **9**, No. 4, 6–12 (1973).
10. G. Schulze, *Metallphysik*, Berlin (1967).
11. V. V. Novozhilov, "On a necessary and sufficient criterion of brittle strength," *Prikl. Mat. Mekh.*, **33**, No. 2, 212–222 (1969).
12. A. V. Andreev, V. M. Kornev, and Yu. V. Tikhomirov, "Breaking of atomic bonds at the apex of a crack. Loss of stability of an atomic-chain section," *Izv. Ross. Akad. Nauk, Mekh. Tverd. Tela*, No. 5, 135–146 (1993).
13. V. M. Kornev and Yu. V. Tikhomirov, "Criterion of brittle fracture of solids with a crack in the presence of a defect in the atomic lattice," *Izv. Ross. Akad. Nauk, Mekh. Tverd. Tela*, No. 2, 185–193 (1994).
14. V. M. Kornev, "Integral criteria for brittle strength of cracked bodies with defects in the presence of vacancies at the tip of a crack. Strength of compacted ceramics-type bodies," *Prikl. Mekh. Tekh. Fiz.*, **37**, No. 5, 168–177 (1996).
15. N. H. Macmillan "The ideal strength of solids," in: *Atomistic of Fracture*, R. Latanision and J. R. Pickens (eds.), Plenum Press, New York (1983), pp. 95–164.
16. V. M. Kornev and Yu. V. Tikhomirov, "Loss of stability of an atomic-chain region in the presence of impurity. Strength reduction of cracked brittle solids," *Prikl. Mekh. Tekh. Fiz.*, **37**, No. 3, 160–173 (1996).