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B. D. SUMM, Yu. V. GORYUNOV, N. V. PERTSOV, E. D. SHCHUKIN

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Abstract**Full Text**

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PHYSICAL CHEMISTRY

B. D. SUMM, Yu. V. GORYUNOV, N. V. PERTSOV, E. D. SHCHUKIN
and Academician **P. A. REBINDER**

DEVELOPMENT OF CRACKS IN A BENT ZINC PLATE UPON LOCAL APPLICATION OF A LIQUID SURFACE-ACTIVE METAL (MERCURY)

We have previously studied in detail the regularities of the action of low-melting metallic coatings on the deformation and strength properties of single-crystal specimens of certain more refractory metals; in these experiments the coating was a thin, several-micron-order liquid film applied over the entire surface of the specimen. It was shown that the presence of a film of a liquid surface-active metal can lead to a qualitative change in the mechanical properties of the tested single crystal: from highly plastic it can become very brittle and weak (¹⁻⁴). This effect is explained in light of the concepts we have developed concerning the influence of adsorption from the surrounding medium on the mechanical properties of solids: the loss of strength in the presence of a strongly surface-active medium—a metallic melt—is caused by a sharp decrease in the free energy of new surfaces developing in the specimen during its deformation and fracture. Atoms of the melt thereby penetrate into the volume of the specimen, to the microcracks developing within it, by irregular diffusion (two-dimensional migration) along various defects of the crystal structure.

In the present work we have for the first time studied the development of fracture cracks under local application to a specimen of a small drop of an adsorption-active melt (mercury). Plates of technical zinc (98.7% Zn) of thickness δ from 0.8 to 3 mm and width a up to 50 cm were used as specimens. The plates were subjected to bending according to the scheme of Fig. 1 under the action of a force F , the tensile stresses p_m on the surface of the plate at the place where the drop was applied being comparatively small: $\sim 7-8$ kg/mm² (the tensile strength of zinc is ≈ 18 kg/mm²). In this case, in the absence of mercury, the plates, during the time usual for an experiment (~ 10 min), still do not undergo large residual deformations, and with an increase in stress the plates can be bent to a right angle without the appearance of visible cracks. Mercury was

applied to the zinc on the upper (stretched) side of the plate, at a distance of 15–30 mm from the line of fastening of the specimen, in the form of a single drop of mass m from 0.2 to 40 mg; to ensure contact (i.e., wetting) of the zinc with mercury at the point of its application, a small fresh scratch was sufficient (or slight etching with alkali).

When $p_m \approx 7 \text{ kg/mm}^2$ is reached at the point of contact with mercury, a crack appears in the specimen which immediately—within 1–2 sec. or fractions of a second—absorbs all the mercury lying on the surface and rapidly grows in the direction perpendicular to p_m . Subsequently the rate of crack propagation decreases and after 5–10 min. becomes already very small. Over most of its length the crack at this time penetrates into the depth of the plate almost through its entire thickness δ . The practically final crack length L is determined by the amount of mercury applied m (Fig. 2). The process of devel-

tion of the crack can be represented by means of the following scheme, developed by one of the authors (E. D. Shchukin) and constituting a first approximation. A crack can grow only as mercury atoms penetrate into the prefracture zone at the crack tip. Mercury reaches this region by two-dimensional migration along the crack walls.

At the same time, as a result of volume diffusion, mercury is absorbed by the crack walls along its entire length. Therefore, the faster the migration proceeds and the more slowly volume diffusion takes place, the more “productively” mercury will be used in the sense of facilitating the development of new surface regions at the crack tip. Thus, the kinetics of crack propagation is determined by competition between two processes: (1) two-dimensional migration of adsorption-active atoms along the crack walls and (2) their diffusion into the bulk, normal to the crack walls.

Fig. 1. Scheme of crack development during local application of a drop of mercury to a bent zinc plate

Let us assume, for simplicity, that crack development (in each direction from the drop) proceeds with a constant velocity equal to the migration velocity v . Then a surface element of the crack dx is opened after a time $t_1 = x/v$ following the nucleation of the crack (see Fig. 1). To some approximation it may be assumed that the penetration of mercury from the crack surface into the bulk of zinc is described by the usual diffusion equation (one-dimensional case) with a constant coefficient D . (It should be expected that in the present case this coefficient may be considerably higher than under normal diffusion of mercury into an undistorted zinc lattice, owing to the looseness of the walls of the newly formed crack, densely penetrated by all kinds of defects, pores, and ultramicrocracks; therefore the process under consideration is more properly called “quasi-volume diffusion.”) In this case, from 1 cm² of crack surface, during the time t after the opening of the given element, an amount

$$(2/\pi)C_0(Dt)^{1/2} = kt^{1/2}$$

Figure 3 and Figure 4: graphs of crack growth over time

Figure 1: Figure 3 and Figure 4: graphs of crack growth over time

grams of surface-active substance enters the bulk (C_0 is the concentration in the surface layer).

Fig. 2. Dependence of the total [final] crack length L (mm) on the mass of the mercury drop m (mg) for different plate thicknesses δ : 1 –0.8 mm, 2 –1.85 mm, 3 –3.0 mm. The tangent of the slope angle of the straight lines is exactly $2/3$

By the time t , from the element dx there will have gone into the bulk

$$k(t - t_1)^{1/2} 2\delta dx = 2k\delta(t - x/v)^{1/2} dx,$$

and from the entire surface of one half of the crack

$$2k\delta \int_0^{vt} \sqrt{t - x/v} dx = \frac{4}{3} k\delta vt^{3/2}$$

grams of mercury. If $L = 2vt_k$ is the total final crack length, then by the final time t_k we have

$$\frac{m}{2} = \frac{4}{3} k\delta v \left(\frac{L}{2v} \right)^{3/2},$$

whence

$$L = \frac{1}{2} \left(\frac{3\pi}{2C_0\delta} \right)^{2/3} \left(\frac{v}{D} \right)^{1/3} m^{2/3} = A\delta^{-2/3} m^{2/3},$$

where $A = \text{const.}$

Fig. 2 shows that over a wide interval of values of m the crack length is indeed proportional to the mass of mercury to the power $2/3$; the indicated dependence of L on the plate thickness δ is also well confirmed.

The simple scheme described, however, requires a number of refinements. Thus, experiments have shown that the crack magnitude may depend on the method of loading the specimen. Namely, if during crack development in experiments with a constant load the stress increases appreciably—owing to a decrease in the cross section of the specimen and an increase in the stress concentration at the crack tip—then this leads to a decrease in L . This effect is apparently associated

Fig. 3. Crack growth with time at the initial stages of its development (to one side from the site of initiation) for different masses of mercury m : 1 –40 mg, 2 –10 mg; plate thickness $\delta = 1.85$ mm (according to motion-picture data)

Fig. 4. Crack growth with time at the later stages of its development (to one side from the site of initiation) for different masses of mercury m : 1 –40 mg, 2 –10 mg; plate thickness $\delta = 1.85$ mm

with a sharp loosening of the zinc under considerable overloads in the region of the tip of the main crack, the formation of a multitude of the finest cracks, which intensely absorb mercury and thereby hinder the development of the initial crack. Branching of the crack is often visually observed in this case.

Of particular interest is a detailed study of the kinetics of crack growth. The corresponding data for the very initial stage, obtained by means of motion-picture recording, are presented in Fig. 3; Fig. 4 illustrates the subsequent, slowed crack growth. The curves presented clearly reveal the first, fastest stage of the process, lasting no more than 1 sec, when the crack-growth rate is constant and does not depend on m . During this stage absorption and free spreading of the droplet inside the crack occur. The duration of this stage is naturally greater, the larger the droplet. Subsequently the process apparently develops as follows. As the volume of the crack grows, the mercury is no longer sufficient to fill the whole crack; in this case the mercury is distributed on the crack walls in the form of a more or less thick (phase) layer. This store of mercury is gradually consumed at the next stage, when feeding of the prefracture zone at the crack tip is accomplished by surface migration, by the spreading of thin adsorption layers of mercury. The crack-growth rate decreases. After several minutes there begins the third, slowest and most prolonged stage; at this point there is no longer any visible liquid phase of mercury in the crack, and feeding of the prefracture zone also proceeds by migration only, through redistribution of mercury still preserved in the form of extremely thin layers on the crack walls.

The experiments described thus open up the possibility of a detailed analysis of the role of two-dimensional migration and volume diffusion in connection with the effect of loss of strength of metals under the action of surface-active melts.

We believe that further development of these studies will make it possible to investigate more deeply the kinetics and mechanism of migration of adsorption-active atoms.

Moscow State University
named after M. V. Lomonosov

Institute of Physical Chemistry
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.

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