Physical Chemistry

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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ON THE ROLE OF KINETIC FACTORS IN THE PROCESS OF ADSORPTIONAL LOWERING OF THE STRENGTH OF METALS

It is known that, in the presence of small amounts of adsorption-active metallic melts, many metals and alloys undergo brittle fracture under small tensile stresses as a result of a strong lowering of the free surface energy of the solid metal ([1,2]). On the microscale, the effect of adsorptional lowering of strength consists in facilitating the rearrangement and rupture of interatomic bonds in the solid body. The elementary act of growth of a microcrack is the rupture of the bond I—I between atoms located directly at the crack tip (Fig. 1). The influence of an atom A of an adsorption-active melt on this process can manifest itself only on the condition that the given atom is within the range of action of the interatomic forces I—I. Further advance of the crack front at the same low level of tensile stresses requires the presence of an adsorption-active atom already in the zone of atoms II—II, and so on. Thus, the manifestation of adsorptional lowering of strength is closely connected with the kinetics of propagation of the liquid metal. It is precisely the rate at which the melt enters the crack tip that determines the average rate of its growth under the given conditions ([3]).

Fig. 1

Let, in the absence of an adsorption-active melt, under tension at a constant rate $\dot{\varepsilon} = d\varepsilon/dt$, fracture of the specimen occur at a deformation ε_0; the time to fracture is $t_0 \approx \varepsilon_0/\dot{\varepsilon}$. Let the average rate of propagation of melt atoms along the crack walls be equal to v_1; in this case the time of propagation of the melt over the entire cross section of a specimen of diameter L is, in order of magnitude, $t_1 \approx L/v_1$. For fracture of the specimen at a low level of tensile stresses, it is necessary that, in the presence of the melt, the fracture crack develop over the entire cross section faster than the stress sufficient for fracture of the given solid metal in the absence of adsorption-active atoms is reached. It may therefore be considered that the inequality $t_1 < t_0$, or, equivalently, $\dot{\varepsilon} < v_1\varepsilon_0/L$, will be the “kinetic” condition for the manifestation of adsorptional lowering of strength (it is obvious that it must be fulfilled together with the “thermodynamic” condition —a strong lowering of the free surface energy)*. In other words, the average rate of entry of the adsorption-active melt into the zone before— failure must satisfy the inequality

$$v_1 > L\dot{\varepsilon}/\varepsilon_0. \tag{1}$$

This condition, however, requires clarification. We have shown that at very low deformation rates (and a sufficiently high temperature T) the effect of adsorption-induced lowering of the strength of metals disappears: brittle fracture gives way to plastic flow, despite the lowering of the free surface energy (^{5}). If the corresponding minimum rate is $\dot{\varepsilon}_{\text{min}} = \dot{\varepsilon}_{\text{min}}(T)$, then the manifestation of adsorption-induced lowering of strength is possible only under the condition

$$\dot{\varepsilon} > \dot{\varepsilon}_{\text{min}}. \tag{2}$$

Comparing inequalities (1) and (2), we arrive at the following conclusion: if $v_1 < L\dot{\varepsilon}_{\text{min}}/\varepsilon_0$, then adsorption-induced lowering of strength cannot appear at all; but if $v_1 > L\dot{\varepsilon}_{\text{min}}/\varepsilon_0$, then adsorption-induced lowering of strength should be observed in a limited interval of deformation rates

$$\dot{\varepsilon}_{\text{min}} < \dot{\varepsilon} < \dot{\varepsilon}_{\text{max}}, \quad \text{where } \dot{\varepsilon}_{\text{max}} \simeq v_1\varepsilon_0/L. \tag{3}$$

Condition (3) determines the upper limiting value of the deformation rate at which manifestation of adsorption-induced lowering of strength is still possible. At $\dot{\varepsilon} > \dot{\varepsilon}_{\text{max}}$ the strength limit of the solid metal will be reached so rapidly that the facilitation of fracture caused by the presence of an adsorption-active melt will practically not have time to make itself felt. Such disappearance of adsorption-induced lowering of strength was observed, for example, in tensile testing of steel specimens at high speed (^{6}).

We have shown that, in analyzing the conditions of fracture of a solid body, wedge-shaped cracks are of greatest interest; in their blunt-ended portions they are characterized by a free surface that is not yet fully developed (^{7}). The displacement of adsorption-active atoms in this region, i.e., in the immediate vicinity of the prefracture zone, can occur only by migration (^{3,8}). This process can proceed sufficiently rapidly only when there is a significant concentration gradient along the entire path of migration (surface diffusion). In turn, a high

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* A strong lowering of surface energy (and the corresponding substantial lowering of strength and plasticity) usually occurs in those cases where the molten metal has a narrow but finite region of solubility in the solid state in the more refractory metal. Such cases correspond, as a rule, to a simple binary phase diagram of the eutectic type without intermetallic compounds (^{4}).

concentration gradient can be ensured only in the presence of liquid metal in the form of an independent phase ([9,10]).

Thus, for the kinetic condition of adsorption-induced lowering of strength to be fulfilled, a phase of adsorption-active melt must exist on the surface of the specimen being deformed throughout the entire period of growth of the fracture crack.

Immediately after being applied to the solid metal, the liquid metal begins to diffuse into the bulk of the specimen, and as a result the amount of the initial melt (in the form of a phase) gradually decreases. In connection with this, it is necessary to estimate the minimum amount of melt required for the manifestation of adsorption-induced lowering of strength when the contact time of the liquid metal with the solid before the onset of deformation is unlimited. Let M be the mass of the specimen (for definiteness, a single crystal), and m the mass of the liquid metallic coating applied to the specimen. Let the solubility of the coating metal in the given solid metal at the experimental temperature T be c. If $c > m/M$, then after a certain time, depending on the diffusion coefficient and the contact area, the liquid phase on the specimen surface disappears. Under these conditions, adsorption-active atoms will no longer be able to enter the embryonic microcracks at a sufficient rate, and adsorption-induced lowering of strength will not be able to appear. Consequently, if $c > m/M$, then adsorption-induced lowering of strength is observed only for a limited time from the beginning of mutual contact between the liquid and solid metals up to the moment of application of the load.

loading. On the contrary, if $c > m/M$, then the liquid phase on the surface of the single crystal will persist indefinitely (evaporation can usually be neglected), and the adsorption-induced reduction of strength will appear at any time of preliminary contact of the melt with the specimen.

These conclusions are confirmed by data obtained in tensile tests of zinc single crystals which, for a long time before the onset of tension, were in contact with a known amount of mercury ([11]). With an initial amount of mercury less than 0.1% of the mass of the specimen, the single crystals are ductile—they fracture at large elongations and stresses. At concentrations greater than 0.1%, with the same long holding time, a sharp, almost discontinuous drop in strength is observed, and ductile fracture gives way to brittle fracture, i.e., an adsorption-induced reduction of strength appears. A similar result is also observed on polycrystalline zinc plates held for different times in contact with a mercury film: at $m/M > 0.3\%$ the adsorption-induced reduction of strength appeared indefinitely long, whereas at lower mercury concentrations the effect gradually disappeared.*

Since the rate of diffusional dissolution of a liquid metal in a solid is proportional to the contact area, the time of manifestation of the adsorption-induced strength-reduction effect (for $c > m/M$) depends on the method by which the liquid metal is applied. In particular, when the melt is applied locally in the form of a drop, the effect persists longer than when the same mass of liquid metal is applied continuously (as a film).

Kinetic conditions impose definite limitations on the character of the growth of an incipient, "equilibrium" microcrack into a fracture crack.

There are two possible ways in which adsorption-active atoms may penetrate from the specimen surface into an incipient microcrack: 1) capillary spreading of the liquid-metal phase, when, in the process of deformation, the micropore reaches the surface in the form of a very fine capillary ("funnel"). Only in the immediate vicinity of the boundary of the prefracture zone, where the crack narrows to dimensions of atomic order, does capillary suction give way to migration. In this case, however, the diffusion path is very short and is traversed comparatively rapidly; therefore the crack-growth rate is limited by the rate of capillary flow. 2) The micropore (fracture nucleus) has no capillary outlet, and the penetration of adsorption-active atoms into this micropore occurs only along defects of the crystal structure (along hollow dislocation cores, individual dislocations, etc.) by the mechanism of irregular diffusion (migration).

Each of these processes corresponds to a different average velocity v_1 of propagation of melt atoms along the crack walls; consequently, two upper limits of the deformation rate may exist—$\dot{\varepsilon}_{\max k}$ and $\dot{\varepsilon}_{\max d}$. Since, in capillary propagation, v_1 is considerably greater than in diffusion propagation, $\dot{\varepsilon}_{\max k}$ may exceed $\dot{\varepsilon}_{\max d}$ by several orders of magnitude.

We have shown that, for many solid-metal/liquid-metal pairs, in the absence of external forces the propagation of adsorption-active atoms over a solid metallic surface usually proceeds only by diffusion; at the same time, in some cases, along with diffusion propagation, phase spreading of the liquid metal is also possible ([13]). Evidently, in the first case $\dot{\varepsilon}_{\max d}$ is the upper limit of the deformation rate. For example, in tensile tests of zinc single crystals in the presence of liquid gallium, $v_1 \simeq L/t_1 \simeq L/(L^2/D_p) \simeq D_p/L$, where D_p is the coefficient of surface diffusion of gallium on zinc (at 30°, $D_p \simeq 10^{-4}$ cm^2/sec (14)). For zinc single crystals, ε_0 amounts to several hundred percent. It follows from relation (3) that, for a specimen diameter of 1 mm, $\dot{\varepsilon}_{\max d} \simeq 10^2$—$10^3$% min^{-1}.

In those cases where, depending on the microrelief of the solid surface, both forms of spreading of the liquid metal are possible (phase spreading and surface diffusion (13, 15)), it is possible, generally speaking, for two upper limits of the rate of deformation to exist (for example, for the pair Zn—Hg). For such pairs, at low rates of deformation, diffusive penetration already provides a sufficient

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* It is precisely the disappearance of the liquid-metal phase (as a result of diffusional absorption) that is the principal cause of the cessation of growth of macroscopic cracks formed during deformation of large specimens in the presence of a drop of an adsorption-active melt ([3, 12]).

rate of feeding of the crack tip. Under such a loading regime, numerous cracks, clearly visible in microsections (16), may develop inside a single crystal even before final fracture occurs. At the same time, for the Zn–Hg pair, adsorption-induced reduction of strength is also possible at larger rates $\dot{\varepsilon}_{\max d} < \dot{\varepsilon} < \dot{\varepsilon}_{\max k}$, but in this case phase penetration of the melt into the crack is already necessary, i.e., the nucleus must emerge at the surface. For polycrystals such a possibility is always realized, since under these conditions cracks develop, as a rule, along grain boundaries (17). For single crystals, the required capillary emergence of a nucleus at the surface cannot always occur at the initial stages of deformation. As a result, experiments with single crystals at high tensile rates give poorer reproducibility of the adsorption-induced reduction of strength. To estimate the value of v_1 in the case of "phase" feeding (for the Zn–Hg pair), we use the equation of capillary flow $L^2 \simeq [(\sigma \cos\theta) r/2\eta]\, t$, where σ is the surface tension of the liquid, η its viscosity, r the capillary radius, and θ the contact angle. Taking $r \simeq 10^{-4}$ cm, $\sigma \simeq 470$ erg/cm^2, $\eta \simeq 0.01$ poise, and $\theta \simeq 0$, we find $\dot{\varepsilon}_{\max k} \simeq 10^6$—$10^7$% min^{-1} (for specimens 1 mm in diameter).

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