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Abstract

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On the Influence of Oxide Films and an Adsorption-Active Medium on the Creep of Copper Wire

(Presented by Academician P. A. Rehbinder on 30 V 1958)

The adsorption influence of the external medium on the mechanical properties of deformable solids was established in the works of P. A. Rehbinder’ s school (1).

The action of surface-active substances during deformation of metals has been studied in nonpolar hydrocarbon liquids, which themselves, as was shown (2), do not affect the mechanical properties of a metal in the process of creep. Polar media, in particular water, are surface-active on some metals, and when evaluating the effect of the influence of substances dissolved in them, the action of the solvent must be taken into account. In addition, if the medium interacts chemically with the metal, forming, for example, an oxide film on its surface, then these new formations may exert a noticeable influence on the mechanical properties of the metal.

In the works of Roscoe and Andrade (3) it was noted that oxide films on single crystals can substantially strengthen the latter, increasing the yield point and impeding further deformation in the main plastic region under tension at a constant rate, or reducing the rate of plastic flow under tension at a constant load.

Rozhanskii and Rehbinder (4) studied the role of oxide films in the adsorption effect of facilitating the deformation of metals. Lichtman and Ostrovskii (5), in investigating this phenomenon on cadmium single crystals, established that the influence of an oxide film increases with decreasing specimen diameter and increasing oxide-film thickness, and depends on the orientation of the single crystal, the maximum of the effect lying in the region of initial-orientation angles χ_0 close to 45°. They proposed an explanation of this effect based on the so-called size factor. Apparently, the possibility is not excluded, as confirmed by some works (6), that oxide films with thicknesses on the order of thousands of angstroms possess increased tensile strength, close to the theoretical value. The presence of such a film delays plastic deformation of a single crystal until the load on the specimen reaches a value sufficient to rupture the brittle oxide film; after this, only slip along the slip planes of the single crystal is possible. Calculation of the stress in the oxide film at which its rupture occurs gives values

Fig. 1

Figure 1: Fig. 1

agreeing, in order of magnitude, with the theoretical values of the strength of ionic crystals.

The influence of oxide films on polycrystalline metals has been studied only for films with thicknesses from several microns to tens of microns (7). Of particular interest is the elucidation of the action of thin oxide films on the mechanical properties of polycrystals. We found that deformation of polycrystalline copper wire is hindered if it is carried out in water. Specimens in the form of wire made of electrolytic copper, 0.5 mm in diameter, were annealed to obtain a grain size necessary for the optimal manifestation of the adsorption effect (on the order of 0.1 mm) and were etched in ammonium persulfate.

Stretching was carried out under a constant load below the yield point, on a special apparatus. The procedure is described in more detail in work (8).

It was established that, during deformation in distilled water, the initial creep rate, as well as the strain accumulated by a given time, decreases sharply in comparison with the changes in these quantities during tests in air. In Fig. 1 the creep curves of copper in air (1) and in water (2) are given. As can be seen from the figure, curve 2 lies considerably below curve 1.

Fig. 1

When the specimens are immersed in water, they become covered with a reddish oxide film, the thickness of which amounts to hundreds of angstroms (9). The formation of an oxide film on the surface of copper is apparently caused by the oxygen of the air dissolved in the water. Indeed, purging the cuvette with water with hydrogen removes the hardening effect—the curves in air and in water treated in this way coincide; conversely, purging with air increases the effect, the hardening increasing with increasing purging time and reaching a limiting value when purged for approximately 60 min.

Rebinder and Wenström established the phenomenon of electrocapillary lowering of the strength of solid metals, analogous to the electrocapillary lowering of surface tension at the metal—electrolyte boundary (11).

In our laboratory V. A. Krongauz showed that the application of cathodic polarization during the deformation of copper, removing the oxide film and preventing its formation, eliminates the hardening effect. Thus, the hardening effect arises only in the presence of oxide films, while the creation of conditions under which they do not arise or are removed leads to the disappearance of the effect. Hydrogen peroxide, as a more active agent, should have acted more strongly, since catalytic decomposition of H_2O_2 occurs on copper with the liberation of active atomic oxygen. However, precisely because of the active action of H_2O_2 on the metal, a continuous oxide film is not formed; instead, corrosive destruction occurs, as a result of which some facilitation of the flow of the metal is observed already in a 3% H_2O_2 solution as compared with flow in water (Fig. 1, 3). At a concentration of 10% H_2O_2, the curve lies even higher than in tests in air (Fig. 1, 4).

Surface-active substances (for example, butyl alcohol), adsorbed on the metal from an aqueous medium, also increase the creep rate of copper specimens in comparison with creep not only in water, but also in air.

Table 1

Medium	v_0	ε_{15}, %	$\frac{v_a - v_{H_2O}}{v_{H_2O}}$, %	$\frac{\varepsilon_a - \varepsilon_{H_2O}}{\varepsilon_{H_2O}}$, %	$\frac{v_a - v_{air}}{v_{air}}$, %	$\frac{\varepsilon_a - \varepsilon_{air}}{\varepsilon_{air}}$, %
Air	3.1	0.240			−39.5	−35.5
Water	2.0	0.145			−30.4	−25.8
3% H_2O_2 solution	2.3	0.167	15	15	+19.5	+16.1
10% H_2O_2 solution	3.6	0.287	80	98	+50.0	+77.4
1% C_4H_9OH solution	5.5	0.360	175	148		

(Figs. 1, 5). Table 1 gives: the initial flow rates v_0, the values of the deformation (in percent) accumulated in 15 min, ε_{15}, the magnitude of the relative increase (decrease) in the initial flow rate, and the relative increase (decrease) in deformation under tension in active and inactive media, both relative to water and to air.

From the data presented it follows that thin oxide films can exert a substantial influence on the mechanical properties not only of single crystals but also of polycrystalline specimens. In the present case, however, this phenomenon cannot be explained by the increased strength of an oxide film of small thickness, since one would then have to assume that the oxide film is subjected to loads necessary for its rupture that considerably exceed the theoretical strength.

The reduction in the creep rate under the influence of thin oxide films on the metal surface can be explained on the basis of dislocation concepts. During deformation of a specimen, the dislocations that are formed tend to emerge at the surface. The oxide film on the metal surface prevents this because of an increase in the potential barrier of short-range forces, which repel dislocations from the surface and hinder their emergence under the action of the applied shear stresses and image forces. Therefore dislocation emergence can occur only at stresses greater than those required for a metal with a surface free of oxide films (^{10}). A similar barrier may be provided not only by an oxide film but, in general, by a surface with altered properties, for example one subjected to work hardening. Apparently, the oxide film primarily affects dislocations generated by a source with one fixed end; such sources are located near the surface and have a lower "starting stress" than a source with two fixed ends. Blocking of sources with one fixed end leads to deformation beginning at appreciably higher source starting stresses. Under creep conditions, a delay in the emergence of some dislocations per unit time means a reduction in the flow rate and a decrease in deformation over the given time.

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