FRACTURE OF METALS UNDER THE ACTION OF HYDROGEN-CONTAINING MEDIA

A. L. Bichuya

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It is known that hydrogen in contact with metallic constructional materials reduces their strength properties [1-10]. It should be noted that the role of hydrogen in the change in the physicomechanical properties of metals is revealed when the direct action of hydrogen (gaseous or electrolytic) on the metal is absent and tests are made in media such as water, ammonia, hydrogen sulfide, etc., which may be only a supplier of hydrogen liberated in contact of these media with metal during deformation and causing hydrogen embrittlement [11, 12]. For example, in tests in water its molecules are normally in contact with a passivated surface. The chemistry of the surface of oxides in contact with water is quite complex. It has been assumed [13] that the same reactions are inherent to surface hydroxyl and aquo-groups of oxides as for hydroaquo cations. The hydroxyaquo cation \([\text{M(OH)}_x(\text{H}_2\text{O})_y]^{(n-x)+}\) (here \(n\) is the degree of oxidation of the metal) is amphoteric and may donate or acquire a proton according to the reaction:

\[
[M(\text{OH})_x(\text{H}_2\text{O})_y]^{(n-x)-} = [M(\text{HO})_{x-1}(\text{H}_2\text{O})]^{(n-x-1)+} + \text{H}^+ \]

which is true for surface ions of metals in oxides. It is also not impossible that the surface hydroxyl ion itself donates a proton:

\[
S^+ \text{OH}^- = S^+ \text{O}_2^- + \text{H}^+_\text{ads},
\]

where \(S\) is a surface center with a total positive charge. Consequently, in the interaction of water with an oxidized metallic surface the formation of hydrogen ions, which are adsorbed on the surface of the metal and with a certain activation may diffuse inward, is completely probable. In addition the fresh surface of the metal occurring as the result of chemical failure of the oxide films is, as the result of catalytic activity, capable of intensifying dissociation of the water with the formation of hydrogen ions. In particular, the wear resistance of friction units is related to the formation of hydrogen at the point of contact of the rubbing pair and with further hydrogen absorption [11]. A tremendous influence on these processes is exerted by the catalytic properties of the rubbing surfaces, which are sharply strengthened in view of the continuous renewal of the surfaces, with the rate of the reaction increasing by several orders of magnitude. Cases are known of the formation of hydrogen during friction in the presence of the metal of free carbon according to the reaction \(\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2\); \(\text{C} + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}_2\) or as the result of reduction from water of iron oxide by iron or by other active metals: \(3\text{Fe} + 4\text{H}_2\text{O} \rightarrow 4\text{H}_2 + \text{Fe}_3\text{O}_4\). In addition the mechanical activation and catalytic properties of the rubbing surfaces promote chemical transformations accompanied by the liberation of hydrogen. Traditionally relatively inactive corrosive media such as water or even moist air on samples with artificially applied cracks may have a significant influence on the crack resistance of metals and alloys [14]. The acceleration of a crack is related to the action of hydrogen formed as the result of dissociation of water at the crack tip [15]. Entry of hydrogen into the prefailure zone is also apparently responsible for acceleration of crack development in cyclic loading.

It must be taken into consideration that adsorption of a hydrogen-containing product in the first stage occurs on oxide films which are capable of changing the character of the adsorption [16], as the result of which the catalytic activity in the process of dissociation of the product may not be revealed and hydrogen absorption will not be so intense. If metals fail under those conditions when the formation of oxides is more suitable energywise, the role of oxygen in the change in strength properties amounts to the action of it only as a surface active medium interacting with the oxide of the metal. The picture may change if the hydrogen reduces the oxides: \(\text{MO}_x \rightarrow \text{H}_2\text{gas} + \text{H}_2\text{Ogas}\).

The difference in the reduction of different oxides is insignificant. The O\(^{2-}\) surface ions of the oxide, interacting with hydrogen, are transformed into OH\(^{-}\) ions [13]. The process develops further if the temperature is sufficiently high for the formation of water from OH groups and its desorption. The trapped centers
Fig. 1. The short-time strength of nitrided Armoc iron: 1) in vacuum; 2) in hydrogen; 3) in ammonia.

Fig. 2. Hydrogen penetrability of Armco iron: 1) in hydrogen; 2) in ammonia; 3) in hydrogen after nitriding in ammonia.

Of the electron immediately convert to cations and the reduced atoms form nuclei of the metallic phase. This stage of reduction depends upon the structure of the oxide, which determines the course of chemisorption of hydrogen. If the metal is capable of chemisorbing hydrogen, as soon as the metallic nucleus occurs the second stage of reduction starts. At the same time, hydrogen is chemisorbed on the metal dissociatively and, migrating along its surface to the metal-oxide interface, causes a reaction close to the interface. Naturally such hydrogen interacts with the oxides more easily than molecular [13]. In the creation of nuclei of the metal by other methods (in the given case by mechanical failure) the incubation period is eliminated and the action of hydrogen appears according to the proposed method. In addition, by the application of stresses it is possible to increase the catalytic activity of the metal as the result of the formation of structural defects.

With time the catalytic activity of metals is capable of changing, and the metal passing into the role of a catalyst is in a condition to suspend the catalytic processes if the strength of its crystalline lattice is insufficient to prevent the transition of the surface intermediate compounds being formed into phase compounds [17].

For a fuller concept of the mechanism of fracture of metals in hydrogen containing media let us consider data on the stress-rupture strength of BrKh-08 and EP-199 alloys and also on the short-time strength in vacuum, hydrogen, and ammonia* (Fig. 1) of previously nitrided Armco iron [12, 18]. In low-cycle fatigue tests of BrKh-08 alloy at 20°C in air and in media of hydrogen and ammonia a reduction in sample life was recorded only in ammonia while gaseous hydrogen did not noticeably influence it [12]. A similar picture was established in investigating the stress-rupture strength of EP-199 alloy [18]. Judging from the tests of nitrided Armco iron (the preliminary nitriding was done for the purpose of eliminating the influence of nitrogen in the experiments in ammonia) under the short-time action of hydrogen and ammonia in the 20-500°C range its strength decreases, especially in ammonia. It would be more logical to expect a very sharp drop in life, particularly in hydrogen, since a very low activation energy is necessary for adsorption of it on metal (heat of chemisorption 137 and 162 kJ/mole for hydrogen and ammonia, respectively [19]) and therefore gaseous hydrogen may be assumed to be a more surface active element in comparison with ammonia. In addition, the data obtained (Fig. 2) makes it possible to conclude that the hydrogen penetrability of Armco iron in hydrogen without the application of a load is more than that in ammonia (as the result of the high heat of adsorption and the low diffusion coefficient at room temperatures the influence of nitrogen may be neglected), that is, the limiting threshold hydrogen concentration in the metal at which there is a marked change in strength properties must occur more quickly in gaseous hydrogen. It has been shown, however, that in ammonia the investigated materials are less strong than in hydrogen. This may be explained by the fact that in ammonia the rate of delivery of hydrogen to the metal is accelerated, particularly as a result of deformation, since the hydrogen penetrability† in the unstressed condition is no greater in ammonia than in hydrogen (Fig. 2). During deformation of a sample the dissociation of ammonia is intensified by the catalytic action of the fresh surfaces. For example, the activation energy for the homogeneous \( \text{NH}_3 \rightarrow \text{NH}_2 + H \) reaction is 326 kJ/mole while in the presence of an Fe or Mo catalyst it drops to 121-176 kJ/mole [20]. Therefore, the energy expenditures on the surface of Armco iron to obtain hydrogen ions in testing in ammonia must be less than in the dissociation of gaseous hydrogen (dissociation energy 432 kJ/mole [21]),

*Yu. D. Nikiforov participated in the work.
†The work was done together with B. V. Kachmar.