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Abstract

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INVESTIGATION OF THE MECHANISM OF HYDROGEN BRITTLENESS OF STEEL

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To solve the problem posed, it is useful to consider separately the influence of large and small hydrogen contents on the properties of the metal.

At high concentrations, measured in tens of cubic centimeters of hydrogen per 100 g of metal, hydrogen brittleness, as a rule, is intergranular in character and is often accompanied by the formation of cracks along grain boundaries even before the specimens are tested for strength (1). The cause of intergranular brittleness and of crack formation during hydrogen charging at elevated temperatures from an atmosphere of gaseous hydrogen under high pressure is the creation of a high hydrogen pressure in pores along the grain boundaries (1,2). This explanation is unambiguous, since there is no other source of tensile stresses in the specimen. During hydrogen charging, only compressive stresses are applied to the specimen, set by the pressure of the gaseous hydrogen surrounding the specimen. It has been established that crack formation during hydrogen charging is facilitated by the pressure, additional to the action of hydrogen, of gaseous hydrocarbons formed as a result of the interaction of hydrogen with the carbon of the steel at elevated temperatures (1,3). Thus, the mechanism of hydrogen brittleness at high hydrogen contents lends itself to a satisfactory explanation.

It is considerably more difficult to explain the causes of hydrogen brittleness of steel at low hydrogen contents, less than 10 cm^3 per 100 g of metal. An important distinguishing feature of the hydrogen brittleness of steel at low contents is its dependence on the rate of deformation. Hydrogen brittleness manifests itself to the greatest extent at low deformation rates and under conditions of delayed fracture of specimens under the action of a constant load. Manifestations of hydrogen brittleness are suppressed with increasing deformation rate (4,5).

To explain this regularity, a hypothesis was put forward according to which, with a "uniform" distribution of hydrogen in the metal, brittleness does not arise; for embrittlement, its localization in microscopic regions is necessary. Such localization is produced by directed diffusion of hydrogen, caused by the nonuniform stress field that arises during deformation (4–7). It is assumed that hydrogen diffuses to sites and regions of the lattice that are in a state of volumetric tension (7).

Fig. 1

Figure 1: Fig. 1

A consequence of the indicated mechanism is the dependence of the manifestation of hydrogen brittleness on the ratio between the diffusional mobility of hydrogen in the crystal lattice and the rate of deformation of the specimens. At low deformation rates, diffusion and localization of hydrogen have time to take place, which provides the conditions for the occurrence of brittleness. At high deformation rates, diffusion and localization of hydrogen do not have time to occur, and brittleness does not arise (4,5,7).

It follows from the hypothesis that the limiting process in hydrogen embrittlement is the process of hydrogen diffusion. To check whether this is indeed the case, one can determine the activation energy of delayed fracture of steel caused by hydrogen and compare it with the magni-

activation energy of hydrogen diffusion. Agreement of the quantities being compared will indicate the correctness of the proposed mechanism of hydrogen embrittlement, and vice versa.

The aim of the present investigation is thus to determine experimentally the activation energy of the process of delayed fracture caused by hydrogen, and to compare the values obtained with the activation energy of the process of hydrogen diffusion in steel.

Fig. 1. Change in the potential energy of hydrogen atoms during diffusion in the crystal lattice of steel. ΔH_D is the activation energy of diffusion in a regular lattice; ΔH_{D_1} is the activation energy of diffusion in a lattice with traps (a and b are traps)

On the basis of a number of experiments (8, 9), it is now assumed that at normal temperature there are two different types of diffusional mobility of hydrogen in steel.

The first type of diffusion is associated with the ordinary diffusion process, consisting of transitions of hydrogen dissolved in the crystal lattice of iron from one elementary cell to another. The activation energy of this process coincides with the activation energy of hydrogen diffusion at high temperatures and, according to various sources, is equal to 2900 (10); 3050 (11); 3200 cal/mole (9). This type of diffusion at normal temperature appears in the first moments after hydrogen enters the steel.

The second type of diffusion has an activation energy $2\text{-}2^{1/2}$ times greater and usually appears after a sufficiently long residence of hydrogen in steel (8, 9). It is assumed that, during prolonged residence of hydrogen in steel, it enters "traps," in which the hydrogen atoms have lower energy than in ordinary interstices, as shown, for example, in the scheme in Fig. 1. The traps may possibly be

Fig. 2

Figure 2: Fig. 2

dislocations, which retain hydrogen. In the second case the rate of diffusion may be controlled by the rate at which hydrogen atoms leave the traps ([8], [9], [12]).

Fig. 2. Dependence of the longevity of quenched plates of 5KhNM steel on temperature and load in bending tests in the first $(1, 2, 3)$ and second (4) series of experiments. Breaking load: 1—30 kgf; 2 and 4—60 kgf; 3—80 kgf

Taking into account the dual character of hydrogen diffusion at normal temperature, experiments on delayed fracture should be carried out under different conditions: the kinetics of fracture should be studied in the first case at the moment hydrogen enters the steel and in the second case under conditions of prolonged residence of hydrogen in the steel. In accordance with this, two series of experiments were performed.

Plates measuring $3 \times 10 \times 80$ mm were made from 5KhNM steel. The plates were quenched in oil from 830° and tempered for one hour at 150°. In this condition the plates had a hardness of 60-63 Rockwell units and a strength of 350-400 kgf in bending tests (distance between supports 40 mm).

In the first series of experiments the plates, in a special fixture, were given elastic bending by a constant concentrated force. The load on the plates was 30, 60, and 80 kgf. The plates in the bent state were subjected to···

were subjected to electrolytic hydrogen charging on the tensile side at temperatures of 5, 20, and 40°. In each separate experiment the time was measured from the beginning of hydrogen charging to the moment of fracture of the plate. Observations showed that fracture of the specimens always coincided in time with the moment of formation of the first crack.

In the second series of experiments the plates were first hydrogen-charged for 2 hours, held for another 2 hours at room temperature, and then tested in the same device for long-term strength in bending under the action of a constant load of 60 kG at temperatures of 5 and 40°. The results obtained are presented in Table 1 and in Fig. 2.

Table 1

Arithmetic mean values of the time (in sec) to fracture of plates as a function of load and experimental temperature. Each time value is the mean of 20.

Load, kG	5° C	20° C	40° C
First series of experiments*	**First series of experiments***	**First series of experiments***	**First series of experiments***
30	1558	1116	745
60	190	148	114

Load, kG	5° C	20° C	40° C
80	66	50	–
Second series of experiments**	**Second series of experiments****	**Second series of experiments****	**Second series of experiments****
60	143	–	25

* Time from the beginning of electrolytic hydrogen charging to fracture of the previously bent plates.
** Time from loading of the previously hydrogen-charged plates to fracture.

From the data presented in Fig. 2 it follows that the activation energy of the process of delayed fracture of hardened plates of 5KhNM steel in the first series of experiments was found to be 3536 cal/mole at a load of 30 kG; 2536 cal/mole at a load of 60 kG, and 2903 cal/mole at a load of 80 kG. From these data it follows that it is not possible to establish a dependence of the activation energy on stress, since it is obscured by the scatter of the data. The mean value of the activation energy obtained is close to 3000 cal/mole, i.e., to the value of the activation energy of hydrogen diffusion at elevated temperatures or at normal temperature, when hydrogen is located in the interstices of the crystal lattice. The first series of experiments corresponds precisely to such conditions, since the hydrogen atoms, at the very moment of entering the crystal lattice of the steel, came under the action of the nonuniform field of elastic stresses imposed by bending and could diffuse under the action of this field.

The activation energy of the process of delayed fracture in the second series of experiments was found to be 8638 cal/mole, i.e., almost 3 times greater than in the first series (Fig. 2). This could have occurred only as a result of hydrogen entering "traps" of the type shown in Fig. 1.

The results obtained confirm the hypothesis set forth above. The limiting process in the delayed fracture of steel is indeed hydrogen diffusion, and the two different kinetics of delayed fracture in the two series of experiments carried out testify to the correctness of the concepts being developed concerning two different characters of hydrogen diffusion in the crystal lattice of iron at low temperatures and concerning the real existence of hydrogen "traps" in steel.

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