PHYSICAL CHEMISTRY

1961

SovietRxiv

Fig. 1. Curves of plate deflection under cathodic polarization: 1—iron, 2—rolled nickel, 3—electrolytic nickel (the arrow indicates the moment when the current was switched off)

Figure 1: Fig. 1. Curves of plate deflection under cathodic polarization: 1—iron, 2—rolled nickel, 3—electrolytic nickel (the arrow indicates the moment when the current was switched off)

Abstract

Full Text

PHYSICAL CHEMISTRY

O. S. POPOVA and A. T. SANZHAROVSKII

ON THE QUESTION OF THE EFFECT OF CATHODICALLY REDUCED HYDROGEN ON THE PROPERTIES OF METALS

(Presented by Academician P. A. Rebinder, July 26, 1960)

In order to study the mechanism of the action of hydrogen on the mechanical properties of metals, we investigated the effect of cathodic polarization on changes in certain properties of rolled iron and nickel and of electrodeposited nickel—matte and bright. Cathodic polarization was carried out in 10% H_2SO_4 with the addition of 0.1 g/l Na_2S, at a current density of 100 mA/cm^2 and a temperature of 20-25°C.

Fig. 1. Curves of plate deflection under cathodic polarization: 1—iron, 2—rolled nickel, 3—electrolytic nickel (the arrow indicates the moment when the current was switched off)

In the investigations the following methods were used: 1) diffusion of hydrogen through a diaphragm; 2) bending of mono- and biplates during polarization from one side ([1]) (curves $h = f(\tau)$ obtained by this method are shown in Fig. 1); 3) determination of hydrogen by extraction in vacuum; 4) X-ray analysis; 5) determination of strength before and after cathodic polarization.

In studying the diffusion of hydrogen through rolled nickel it was established that hydrogen penetrates into the metal to a depth not exceeding 30 μ, and creates internal stresses of the order of 10 kg/mm^2. In the process of hydrogen charging, nickel becomes brittle*, and its strength decreases. After the polarization current is switched off, the internal stresses are completely relieved, which indicates the absence of plastic deformation (Fig. 1, 2), but after the stresses have been relieved the metal remains brittle. After exposure in air for 60-70

Figure 2

Figure 2: Figure 2

Figure 3

Figure 3: Figure 3

hours, the brittleness disappears. During the same time all occluded hydrogen leaves the metal.

X-ray investigations revealed dispersion of grains occurring during the process of hydrogen charging (Fig. 2). The strength of nickel after hydrogen charging proved to be 5-6% greater than the initial value.

Investigation of the diffusion of hydrogen through electrodeposited deposits of matte and bright nickel showed that hydrogen diffuses into electrodeposited nickel more rapidly and more deeply than into rolled nickel. In turn, hydrogen penetrates into bright nickel more rapidly than into matte nickel. Occluded hydrogen creates internal stresses in nickel deposits—

* Since nickel becomes embrittled only to the depth of hydrogen penetration, and hydrogen penetrates to a very small depth, when thick nickel plates are used the change in brittleness may remain unnoticed.

Fig. 2. X-ray diffraction patterns of nickel: *a*—before hydrogenation; *b*—after hydrogenation

a *b* *c*

Fig. 3. Electrolytic nickel: *a*—during polarization; *b*—immediately after removal of polarization; *c*—after exposure to air

Fig. 4. Iron: *a*—before hydrogenation; *b*—after hydrogenation. 225×

···stresses are also of the order of 10 kg/mm^2. In the process of hydrogen charging the deposits crack (Fig. 3, *a*). When the polarization current is switched off, intensive evolution of hydrogen from the metal occurs; at the same time the internal stresses are relieved (Figs. 1, 3, segment *ab*), but the deposit still remains brittle*. After holding the deposit in air for 60-70 hours, all occluded hydrogen leaves the metal and the brittleness of the deposit disappears (Fig. 3, *v*).

The strength of electrolytic nickel after removal of the brittleness proved to be 15-20% higher than the initial value. X-ray examination revealed broadening

Figure 4

Figure 4: Figure 4

of the lines on X-ray diffraction patterns from nickel deposits after hydrogen charging.

In studying the diffusion of hydrogen through iron it was established that hydrogen penetrates fairly rapidly to a considerable depth of the metal. Diffusion of hydrogen in iron is accompanied by the creation in it of stresses of the order of 15 kg/mm^2 (2), by an increase in brittleness, and by local fracture (Fig. 4). At the same time a considerable amount of hydrogen is incorporated into the iron. Experiments showed that, when hydrogen-charged iron is held in air, the hydrogen leaves the metal spontaneously in 6–7 days. Measurement of strength showed its decrease after hydrogen charging by 15–20%, which is irreversible in character. Investigation of iron foil in bending (number of bends before fracture) revealed that immediately after hydrogen charging the foil withstands 60–70% fewer bends than before hydrogen charging. After holding in air, despite the complete removal of hydrogen from the metal, the bending strength remains reduced by 50% relative to the initial value, i.e., the decrease in strength is only partly reversible, which agrees with the data on the change in strength. X-ray studies did not reveal any change in the parameter of the crystal lattice of iron.

Thus, the investigations carried out revealed that, in a metal, during the diffusion of hydrogen into it, the occurrence of internal stresses and a decrease in its strength take place simultaneously. The mechanism of this process may be represented as follows: hydrogen diffusing into the bulk of the metal accumulates in the cavities of structural defects, creating in them pressures of the order of 10 kg/mm^2. Another part of the hydrogen is adsorbed on the surfaces of these defects, lowering their surface energy. The latter leads to an adsorption-induced reduction in the strength of the metal.

If, owing to adsorption, the strength of the metal is reduced to the magnitude of the internal stresses that have arisen, the metal will begin to fracture (which was in fact observed during polarization of electrolytic nickel). If the magnitude of the internal stresses does not exceed the yield point, fracture of the metal occurs without plastic deformation**. The quantitative relationship between the processes of fracture of the metal under the influence of high pressures and as a result of adsorption-induced lowering of strength may vary greatly from one metal to another (iron, nickel). In addition, in some cases additional processes may appear in some metals that are not observed in others. Thus, for example, diffusion of hydrogen into nickel is accompanied by fragmentation of the grain, whereas in iron no such phenomenon was observed.

Analysis of the experimental results on the diffusion of hydrogen into nickel leads to the conclusion that the determining role in the reduction of the strength of nickel is played by adsorption-induced lowering of strength, while the internal stresses caused by occluded hydrogen play a secondary role***.

---

* The strength of electrolytic nickel is practically equal to zero, and it can be ground into powder (Fig. 3, *b*).

** Thus, for example, nickel fractures without plastic deformation, whereas bending and fracture of iron are accompanied by plastic deformation (Figs. 1, 2 and 1, respectively).

*** The strength of a brilliant nickel deposit before hydrogen charging was 88 kg/mm^2. Cracking occurred at $\sigma_b = 10$ kg/mm^2.

Experiments showed that when the polarization current is switched off, the internal stresses that arose in nickel decrease completely and relatively rapidly, while the metal remains very brittle and has a strength close to zero. This indicates the absence of a connection between the internal stresses, on the one hand, and the decrease in strength and the appearance of brittleness, on the other. Upon exposure to air for 3 days, hydrogen leaves the nickel completely of its own accord, and the brittleness disappears. The strength of the metal, however, not only returns to its initial value but increases by 15-20%. It could be assumed that the disappearance of nickel brittleness and the release of hydrogen are two independent processes occurring simultaneously. In that case, with rapid removal of hydrogen the brittleness should have remained. Experiments showed that rapid removal of hydrogen from the deposit in vacuum without heating over 10-15 min, just like prolonged exposure in air, leads to the disappearance of brittleness.

All the foregoing points to an unambiguous connection between the remaining brittleness and hydrogen (adsorbed hydrogen) that slowly but spontaneously leaves the metal. The observed increase in the strength of nickel after hydrogen charging and removal of the incorporated hydrogen is evidently due to adsorption dispersion of the metal grains. This phenomenon, by its nature, is probably close to the phenomena described in work ([3]).

Analysis of the experimental data on hydrogen charging of iron leads to the conclusion that pressures created by hydrogen in the metal play a major role in the reduction of its strength and in the change of its properties. Thus, irreversible deformation in bending, irreversible reduction of tensile and bending strength, and the presence of local fractures are all the result of pressure rather than of the adsorption action of hydrogen. This is in agreement with the data of ([4]).

Thus, the change in the properties of a metal during hydrogen diffusion occurs both due to stresses created by hydrogen and due to its adsorption. In some cases, the effect of adsorption-induced strength reduction can reach an enormous magnitude; for example, for nickel deposits it amounts to 90% of the initial strength or even more.

The data presented are consistent with the concepts developed by P. A. Rebinder and his co-workers ([5]) concerning the adsorption-induced reduction in the strength of metals under the action of surface-active substances, in the present case gaseous ones.

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
14 VII 1960

REFERENCES CITED

[1] A. T. Sanzharovskii, *ZhFKh*, **34**, No. 9 (1960).
[2] M. Smyalovskii, Z. Shklyarskaya-Smyalovskaya, Bull. Pol. Acad. Sci., Section III, **1**, No. 7 (1953).
[3] E. D. Shchukin, N. V. Pertsov, Yu. V. Goryunov, *Crystallography*, No. 6, 887 (1959).
[4] V. V. Karpenko, R. I. Kripyakevich, *DAN*, **120**, No. 4 (1958).
[5] V. I. Likhtman, P. A. Rebinder, G. V. Karpenko, *The Influence of a Surface-Active Medium on the Processes of Deformation of Metals*, Publishing House of the Academy of Sciences of the USSR, 1954.

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