

3. V. G. Fokin and S. I. Ivanov, "The method of strips for investigation of the residual stresses in multilayer plates," in: Proceedings of Kuibyshev Aviation Institute [in Russian], No. 53 (1971), pp. 16-23.
4. I. A. Birger and M. L. Kozlov, "Determination of the residual stresses in a plate with elastic parameters varying across the thickness," *Zavod. Lab.*, No. 2, 239-241 (1975).
5. D. A. Ignat'kov, "Determination of the residual stresses in piecewise nonuniform rods and cylindrical parts," *Probl. Prochn.*, No. 2, 68-72 (1980).
6. M. L. Kozlov, "Approximate closed solutions of the axially symmetric problem of deformation of a nonuniform cylinder," *Izv. Vyssh. Uchebn. Zaved., Mashinostr.*, No. 11, 5-11 (1977).
7. M. L. Kozlov, "Approximate closed solutions of the axially symmetric problem of deformation of a nonuniform disk of arbitrary profile," *Probl. Prochn.*, No. 8, 110-114 (1982).
8. M. L. Kozlov, "Determination of the residual stresses in the coating of a nonuniform disk of variable cross section," in: Summaries of Papers for the Scientific and Technical Conference on the Strength of Turbine Rotor Elements [in Russian], Zhitomir (1981), pp. 18-19.
9. M. L. Kozlov, "The general principle of nondestructive mechanical methods of investigation of the residual stressed condition of coatings," *Probl. Prochn.*, No. 3, 82-86 (1982).
10. M. L. Kozlov, "Residual stresses in coatings: nondestructive mechanical methods of determination and control," in: Proceedings of the All-Union Symposium on Residual Stresses and Methods of Control [in Russian], *Inst. Prikl. Mat. Akad. Nauk SSSR*, Moscow (1982), pp. 53-58.
11. M. L. Kozlov, *Residual Stresses in Multilayer Anisotropic Coatings* [in Russian], Lvov (1983), Deposited in the All-Union Institute for Scientific and Technical Information Nov. 17, 1983, No. 6156.

CATALYTIC DECOMPOSITION OF HYDROGEN SULFIDE ON THE SURFACE OF A SULFIDE FILM IN HYDROGEN SULFIDE-CONTAINING MEDIA

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Intense hydrogen absorption and embrittlement of steels in hydrogen sulfide-containing electrolytes occurs as the result of penetration into them of atomic hydrogen formed according to an electrochemical mechanism. Such a mechanism is inapplicable for explaining the observed [1] intense embrittlement of steels under the action of dissolved hydrogen sulfide in benzine and other organic media in which dissociation of hydrogen sulfide has not been recorded experimentally. At the same time in hydrogen sulfide-containing organic media a sulfide film is formed on the surface of the steels as the result of chemical interaction of the H_2S molecules with the metal. The atomic hydrogen formed penetrates into the metal and causes embrittlement of it. If hydrogen impregnation occurs only according to such a mechanism then it must weaken with an increase in film thickness and completely stop with stoppage of its growth (the sulfide film is insoluble in the medium). If hydrogen impregnation continues after stoppage of growth of the sulfide film, then in this case it occurs according to a different mechanism such as the result of catalytic decomposition of the hydrogen sulfide on the sulfide film.

To clarify this question the interrelationship between penetrability of hydrogen into the metal and the growth of the sulfide film on its surface was studied.

The penetrability of hydrogen through an 0.5 mm thick Armco iron sheet membrane was investigated using an earlier introduced method [2]. A saturated solution of potassium

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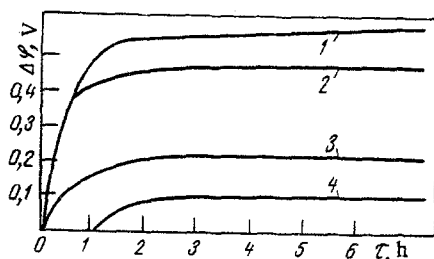


Fig. 1

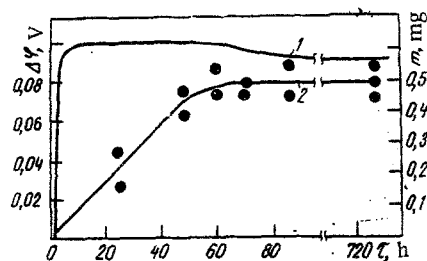


Fig. 2

Fig. 1. Influence of the type of medium on hydrogen penetrability: 1) 10% H_2SO_4 solution; 2) NACE (5% NaCl + 0.5% CH_3COOH + H_2S); 3) 5% NaCl + 0.5% CH_3COOH ; 4) benzine + H_2S .

Fig. 2. Relationship of hydrogen penetrability (1) and weight of the sulfide film (2) in hydrogen sulfide-saturated benzene to time.

bichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) at 17°C was used for passivation.

The penetrability of hydrogen from purified benzine saturated with hydrogen sulfide into a hollow cylinder of 20 steel filled with glycerine was also determined. The cylinder wall thickness was 0.5 mm, the outer diameter 16 mm, and the height 60 mm. The increase in internal pressure was recorded from the change in the height of the column of glycerine in a tube (inner diameter 1.8 mm) tightly connected to the end of the cylinder.

Before conducting the experiment all of the specimens were cleaned with grinding paper and degreased.

The weight of the sulfide film formed on the surface of the Armco iron specimens in hydrogen sulfide-saturated benzene was measured by the gravimetric method. The weight of sulfur precipitated on the surface of the iron sulfide in H_2S saturated distilled water was determined after evaporation of the water and baking of the contents of the flask for 2 h at 180°C . Lumps of iron sulfide from 4.5 to 5 g with an average area of outer surface of 5 cm^2 were placed in flasks containing 50 ml each of distilled water.

All of the experiments were conducted with constant bubbling of hydrogen sulfide to maintain a constant content of it in the solution.

As the result of measurement of the hydrogen penetrability from the electrolytes and nonelectrolytes it was established that the flow of hydrogen from the iron-hydrogen sulfide-saturated benzene system changes insignificantly with time and is equal to 0.2 of the flow from the Fe-NACE (5% NaCl + 0.5% CH_3COOH + H_2S) system (Fig. 1). Since during growth of the sulfide film in interaction of the hydrogen sulfide in the iron- H_2S saturated benzene system according to the chemical mechanism the hydrogen penetrability must decrease to zero a hypothesis of a catalytic mechanism of decomposition of hydrogen sulfide on the surface of the sulfide film has been advanced.

The following were determined for confirmation of it:

- a) the increase in weight of specimens exposed in H_2S saturated benzene;
- b) the hydrogen penetrability from H_2S saturated benzene;
- c) the presence of iron ions in the hydrogen sulfide-containing benzene (with the use of bathophenanthroline [3]).

It was established that growth of the sulfide film stops after 60-70 h of exposure and after 60 h of exposure the hydrogen penetrability drops by 10% (Fig. 2). During the whole experiment Fe^{2+} ions did not appear in the investigated media.

In order to verify this data (Fig. 2) an experiment was made on the penetrability of hydrogen into a hollow cylinder from hydrogen sulfide-saturated benzene. An increase in the absolute height of the glycerine column indicates hydrogen penetration (Fig. 3).

Let us consider the mechanism of interaction of hydrogen sulfide with the surface of the iron in hydrogen sulfide-saturated benzene. In this system hydrogen sulfide is in molecular form since benzene is a dielectric and we did not detect dissociation of H_2S in benzene. Let us separate the time of interaction of hydrogen sulfide with the surface of the iron into

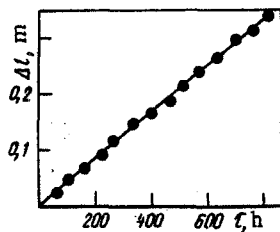


Fig. 3

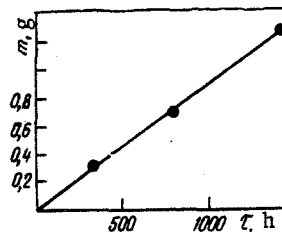


Fig. 4

Fig. 3. Relationship of the internal pressure in the hollow cylinder to hold time in hydrogen sulfide-saturated benzene.

Fig. 4. Relationship of the weight of sulfur precipitated on the surface of the iron sulfide in hydrogen sulfide-saturated distilled water to time.

three stages, I up to 10 h, II from 10 to 60 h, and III after 60 h of exposure in H_2S saturated benzene (Fig. 2).

In stage I an intense increase in hydrogen penetration and intense growth of the sulfide film occur as the result of interaction of the hydrogen sulfide with the surface of the iron according to a chemical mechanism:

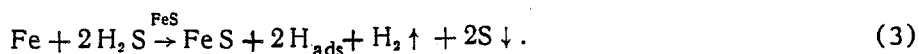


In stage II the process of hydrogen penetration stabilizes and the weight of the sulfide film continues to increase. Probably interaction according to reaction (1) prevails.

In stage III the increase in weight of the sulfide film stops, which indicates a decrease to zero in the contribution of the chemical mechanism to the process of penetration of hydrogen into the metal (the sulfide film is insoluble in the medium). There is an increase in the weight of the sulfur at the bottom of the flask used for determination of the weight of sulfide film in the hydrogen sulfide-containing benzene. Since the hydrogen penetration decreases insignificantly and dissociation of H_2S and the presence of Fe^{2+} ions were not detected in the investigated medium, it may be concluded that in this stage interaction of the hydrogen sulfide according to the catalytic mechanism prevails:



Therefore it may be concluded that the sulfide film is the catalyst for decomposition of hydrogen sulfide. Then the total reaction of interaction of hydrogen sulfide with the surface of the iron and the sulfide film in H_2S saturated benzene is written in the form



It may be assumed that the same mechanism appears in electrolytes saturated with H_2S . In order to be convinced of this the interaction in the iron sulfide- H_2S saturated distilled water system was investigated. An increase in the weight of sulfur on the surface of the iron sulfide (Fig. 4) and continuous liberation of hydrogen from this surface were observed. Obviously catalytic decomposition of H_2S on the surface of the sulfide film occurs in media of electrolytes.

The rate of catalytic decomposition of hydrogen sulfide on the surface of the iron sulfide at $20^\circ C$ in hydrogen sulfide-saturated distilled water was calculated based on the experimental data (Fig. 4) using the equation $v_{c.d} = m/(St) = 1.9 \text{ g}/(\text{m}^2 \cdot \text{h})$, where $v_{c.d}$ is the rate of catalytic decomposition of hydrogen sulfide at $20^\circ C$, $m = 3 \text{ g}$ is the weight of H_2S in 1 liter of H_2O , $S = 5 \cdot 10^{-4} \text{ m}^2$ is the area of iron sulfide, and $t = 3120 \text{ h}$ is the time of complete decomposition of the hydrogen sulfide contained in the water with a concentration of 3 g/liter and a temperature of $20^\circ C$.

Therefore, the intense hydrogen absorption by metals in hydrogen sulfide-containing media is the result of two parallel processes interrelated to each other, electrochemical corrosion and catalytic decomposition of H_2S on the surface of the sulfide film.

LITERATURE CITED

1. A. I. Radkevich, I. I. Vasilenko, B. I. Kultan, and M. D. Klapkiv, "The crack resistance of pipe steels in petroleum products and other liquid organic substances saturated with hydrogen sulfide," *Gaz. Promysh., Ser. Kor. i Zashch. Skvazh., Trubopro., Oborud. i Mor. Sooruzh v Gaz. Promysh., Otechest. Proizv. Opyt, Ekspress-Inf.*, No. 1, 15-19 (1986).
2. I. I. Vasilenko and R. K. Melekhov, *Corrosion Cracking of Steels* [in Russian], Naukova Dumka, Kiev (1977).
3. Z. B. Marchenko, *Photometric Determination of Elements* [Russian translation], Mir, Moscow (1972).

HYDROGEN EMBRITTLEMENT OF PEARLITIC STEELS PRONE TO TEMPER BRITTLINESS

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Steels in the condition of temper brittleness are distinguished by an increased tendency toward embrittlement in aggressive hydrogen-containing media [1]. Since during a hot hold the composition of the grains at the boundaries changes, becoming enriched with certain impurity elements, the question arises of the influence of the degree of development of grain boundary impurity segregations on the sensitivity of steels to hydrogen embrittlement.

Type 20Kh3N chrome-nickel steel (0.23 wt.% C, 0.2 Si, 0.53 Mn, 2.93 Cr, 1.58 Ni, 0.01 S, 0.012 P), which possesses a high tendency toward temper brittleness, was selected for the investigations. The specimens, separated into several lots, were aged at 400°C with a hold time (τ) to 1 to 10,000 h. By varying τ different levels of segregation of the impurity elements, primarily phosphorus, at the boundaries of the former austenitic grains were created.

For each lot impact tests were made of standard Charpy specimens and, using the criterion $KCV = 0.6 \text{ MJ/m}^2$, the ductile-to-brittle transition temperature was determined.

The influence of hydrogen on the plastic properties of the steel was investigated on tensile specimens with a gage length of 15 mm and a gage length diam. of 3 mm previously hydrogen impregnated electrolytically for 150 min in 4% H_2SO_4 solution with the addition of 0.25 g/liter of Na_2AsO_3 . The current density (j) was 250 A/m^2 (mild conditions) and 500 A/m^2 (severe conditions) and the opposite electrode platinum. The hydrogen content in the specimens (C_H) before and after hydrogen impregnation was measured by the extraction method with fusion in a Leco instrument. In the unhydrogen impregnated specimens $C_H = 0.7 \cdot 10^{-4}$ at.% and in the hydrogen impregnated $C_H = 3.1 \cdot 10^{-4}$ and $C_H = 3.5 \cdot 10^{-4}$ at.% for the mild and severe conditions, respectively, regardless of the prehistory of the specimens.

The tensile tests before and immediately after hydrogen impregnation were made on an Instron-1195 machine at room temperature with a rate of movement of the crosspiece of 1 mm/min. The reversibility of the plastic properties of the steel was checked on specimens hydrogen impregnated at $j = 500 \text{ A/m}^2$ and then degassed at 150°C for 2 h. The degree of influence of hydrogen was determined from the relative change in the uniform plastic deformation $\lambda = (\epsilon_H - \epsilon)/\epsilon$, where ϵ and ϵ_H are the uniform plastic deformation of the specimens before and after hydrogen impregnation.

The character of fracture was determined on the basis of a fractographic analysis made with the use of a Tesla scanning microscope.

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