CHEMICAL CORROSION AND FRACTURE OF A "HOT" PIPELINE OF AN AMMONIA-SYNTHESIS COLUMN

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We investigate the character of fracture of welded joints of a gas pipeline made of 18Kh3MV steel after passing the ammonia synthesis column. Hydrogen corrosion of welded joints and nitration that proceed under the action of high temperatures (up to 350°C) and pressures (up to 32 MPa) in mixtures of nitrogen with hydrogen and ammonia are important for fracture.

Import installations for large-capacity production of ammonia have been operating at Ukrainian plants for about 20 years or even more and are subjected to considerable corrosion [1, 2]. The equipment of a unit of synthesis is one of the most dangerous as for fracture. Synthesis of ammonia is performed on a catalyst in a column at a pressure of 24–32 MPa and at a temperature of 400–420°C. After passing the synthesis column, gases (hydrogen, nitrogen, and ammonia — 15%) come into a heat exchanger through the pipeline at the same pressure and a temperature of up to 350°C. At a pressure higher than 10 MPa and at a temperature higher than 200°C, hydrogen can lead to hydrogen corrosion [3]. For this reason, a pipeline is made of hydrogen-resistant pipes of ∅ 400 × 69 mm, ∅ 410 × 42 mm, and ∅ 419 × 42 mm and medium-alloyed 17CrMoV10 (of the type 18Kh3MV) and STPA-24 (of the type 10Kh2M1) steels. The length of the pipeline is equal to 40 m. The pipeline has 12–16 welds. Moreover, it is bent in the form of a "welded bend" from the synthesis column, which is connected with the other sections of the pipeline and column by flange joints.

A "hot" pipeline is the most vulnerable section of the unit of synthesis. Elements of the pipeline are welded at the plant-manufacturer and, under assembly conditions, by hand by using electric-arc welding with preliminary heating to a temperature of 300–500°C with a TG-3SM welding wire 2.4 mm in diameter and SM-3 electrodes (of the 06Kh3M1 type) with a diameter from 3.2 to 5.0 mm. Welded joints of 18Kh3MV and 10Kh2M1 steels are susceptible to the appearance of cold welding cracks due to the possibility of the formation of hardened bainite structures of increased hardness and low plasticity. For this reason, welded joints are tempered at 680°C for 4 h to remove residual stresses.

Mechanical characteristics of steels of a pipeline after 14–20 years of service change so much that, at certain welded joints, hardness increases and plasticity decreases (see Table 1).

We examined five pipelines at various enterprises for a long period (about 20 years) and found that through cracks appeared in the welded joints of two pipelines (the first crack appeared in the 12th year of service). After 10 years, we observed cracks on the internal surface and, sometimes, on the external surface of all pipelines. One of the pipelines that had served for 25 years was replaced with a new one and sent off for investigation. We also cut out several sections containing through cracks of a pipeline produced by another enterprise that had served for 14 years.

We established that all welded joints of the cut pipeline contain cracks of various depths on the internal surface. A through crack appeared in an assembly welded joint after 12 years of service. A year before the appearance of symptoms of leak, the hardness of this weld reached 310 HB, with a hardness of the parent metal of 190 HB. The crack is situated transverse to the weld (along the axis of the pipe). For this reason, ultrasonic control did not reveal its presence. Electron fractography established the zones of plastic and brittle fracture, i.e., the crack propagated with time. Metallographic investigations showed that a great number of microcracks branch off from the main crack and the metal adjacent to it is decarbonized to a small depth due to hydrogen corrosion followed by the formation of methane in the reaction $C + 4H \rightarrow CH_4$. However, a microhardness of the decarbonized layer equal to 5.1 GPa at

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a microhardness of the matrix of 3.4 GPa means that this layer (ferrite saturated with nitrogen) is rather brittle and easily cracked. Decarbonization of steel became possible due to a decrease in the amount of alloying elements, chromium and molybdenum, in the matrix. These elements form carbides in the course of time, which is confirmed by the analysis of carbides. In the original state, molybdenum in carbides accounts for 20.9% and, after 20 years of service, reaches as high as 43.3%. A certain amount of carbon is also bound in carbides. For this reason, the decarbonized layer is very small. Hydrogen corrosion proceeds according to the mechanism of penetration of atomic hydrogen into a metal, as demonstrated by a decrease in the amount of hydrogen with removal from the internal surface to the external one. For example, for a welded joint and the pipe, it decreases from 210 to 30–90 cm^3/kg (see Fig. 1). We observed splashes of the concentration of hydrogen in the defects of welded joints. In pipes and flanges, where defects occur more rarely, the amount of hydrogen smoothly decreases from the internal surface to the external one.

Table 1. Mechanical Characteristics of the Metal of a Pipeline

Name	σ_u, MPa	$\sigma_{0.2}$, MPa	ψ, %	δ, %	HB
Steel SMV-5					
Parent metal	497–763	472–657	—	16–29.2	153–212
Welded joints	393–733	—	—	—	140–290
According to standard	650–850	≥ 450	—	≥ 16.0	201–221
Steel 17CrMoV10					
Weld 1	735–790	594–686	67–71	16.5–19.8	217–246
Weld 2	1065–1070	928–947	21–51	10–19	308–345
According to standard	650–850	≥ 450	—	≥ 16.0	—

In two welded joints (one of them contains seven through cracks) of the pipeline that served for 14 years, in addition to through cracks, we revealed cracks reaching the external surface. The welded joints have the following mechanical characteristics: σ_u = 791 MPa, σ_y = 624 MPa, ψ = 67.7%, δ = 16.7%, a_k = 148.4 J/cm^2, and HB 308–345 at a hardness of the parent metal of 179–191 HB. The plasticity and, especially, the impact toughness and relative elongation of the metal drop. A great number of cracks near the main crack reaching the internal surface are situated in a decarbonized metal. In this weld, the amount of hydrogen varies from 351 on the external surface to 382 cm^3/kg inside the weld. Hydrogen is distributed nonuniformly across the thickness. Smaller fluctuations of the concentration of hydrogen are observed in welded joints of the cut pipeline where cracks are formed mainly on the internal surface and the maximum hydrogenation (up to 209 cm^3/kg) also occurs closer to the internal surface. Metallographic investigations of these welded joints show the decomposition of pearlite, its spheroidization, and the formation of voids and microcracks along grain surfaces.

A number of factors influence the fracture of welded joints of pipelines containing mixtures of nitrogen with hydrogen and ammonia after passing the synthesis column. In the first place, due to a faulty thermal treatment, welding cold cracks appear in welded joints. Atomic hydrogen penetrating into a metal, a small amount of which is formed due to the cathodic decomposition of hydrogen molecules into atoms on the steel surface under the action of high pressure and temperature, is converted to molecular form and promotes the propagation of the emerging cracks. Residual welding stresses also increase the growth of some cracks. In the case where a crack reaches the internal surface or is initiated on this surface, a weak decarbonization of metal along the crack followed by the subsequent nitration and formation of a brittle structure is also possible. The oscillations of a pipeline and creep have a certain effect on the formation of cracks and their propagation in welds.

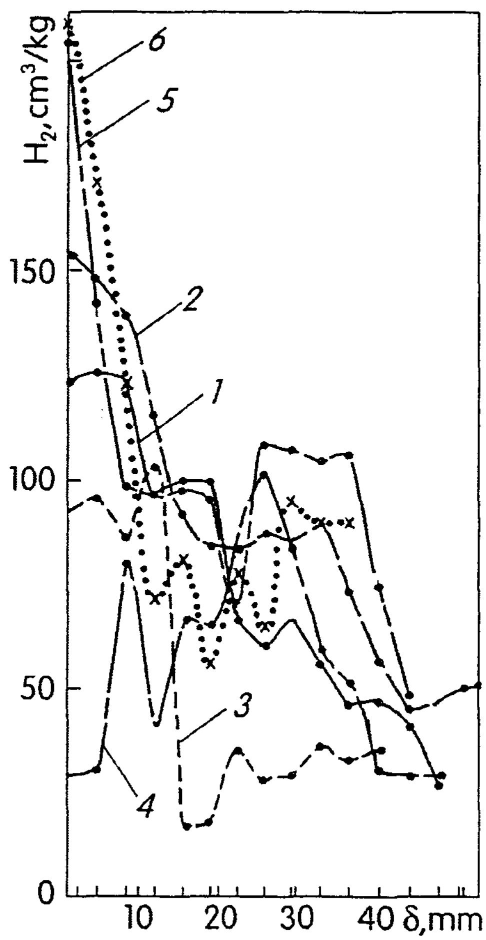

Fig. 1. Distribution of hydrogen in a welded joint across the thickness of the pipe from the internal surface in the flange (1), transition (2), welds (3–5), and pipe of ∅ 419 × 42 mm (6).

The experience in service of pipelines shows that, after 10 years of service, the appearance of through cracks that can lead to serious accidents is possible. In order to avoid this, it is necessary to carry out a timely complex inspection of pipelines from the ammonia synthesis column to a heat exchanger in the course of a scheduled suspension of production.

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