Investigation of the Effect of Sulfide Inclusions on the Hydrogen Separation of Metal

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Abstract. In the presence of an increased concentration of hydrogen, premature destruction of the metal occurs. Hydrogen brittleness is caused by imperfection of the crystal lattice of metals. Distinguish between hydrogen corrosion caused by molecular hydrogen and hydrogen corrosion caused by atomic hydrogen. The presence of hydrogen in a metal increases the fragility of all metals, without exception. Hydrogen accumulates in traps (vacancies, dislocations). The segregations of carbon and other impurity atoms at grain boundaries enhance the ability of iron to capture hydrogen. Atomic hydrogen resulting from electrochemical reactions penetrates steel at normal temperature, causing it to stratify. Molecular hydrogen generated during the processing of hydrocarbons, electrolysis of water, violation of welding technology, penetrates into steel only at temperatures above 200 °С. The aim of the work was to determine non-metallic inclusions using the metallographic method. The authors also determined the presence of sulfide accumulation in the studied metal of the pipe. It is noted that the amount of sulfide inclusions is approximately the same, both near the metal stratification and on the base metal of the sample.

1.Introduction
Various kinds of defects may appear on the pipeline during operation, such as cracks [1–2], ulcers [3–8], scratches, etc. It is known that in the presence of an increased concentration of hydrogen, premature destruction of the metal occurs, regardless of temperature, but fracture is distinguished at high and low temperatures and pressures. At high temperatures, hydrogen corrosion occurs, which takes carbon atoms from the metal, thereby changing the mechanical properties. At low temperatures, only hydrogen embrittlement occurs [2, 3], in which hydrogen penetrates into the metal in a confined space, in a tank, in a vessel or in a cylinder, etc. Hydrogen penetrates into the metal by the diffusion mechanism, and the more intensively, the stronger the stretched zone, then it accumulates in the metal and when a certain concentration is reached, the mechanical properties of the metal change.

Hydrogen brittleness is caused by imperfection of the crystal lattice of metals [8–20]. The presence of hydrogen in a metal increases the fragility of all metals, without exception.

2. Experimental procedures
The paper presents the results of a study on samples of steel grade 09G2S, selected from the focal zone of destruction of the gas pipeline. There were bundles on the pipe. The defect is believed to have arisen due to hydrogen separation within the metal. To identify the causes of stratification of the metal, the metal was cut with defects, size 40x13x5 mm. The steel 09G2S under study is low-alloyed silica-manganese structural. The mechanical properties of steel, according to GOST 19282-73, are presented in table 1.
Table 1. Mechanical properties of steel 09G2S at room temperature.

| Impact strength  | Strength limit $\sigma_y$, MPa | Elongation at break $\delta$, % | Yield strength, $\sigma_t$, MPa |
|------------------|--------------------------------|-------------------------------|-------------------------------|
| KC$_U$, J/$\text{cm}^2$ | 64 | 490 | 17 |

In the presence of defects, hydrogen is retained in the metal with the formation of a brittle solid solution (strength increases, fracture toughness decreases), metal stratification along the segregation floor, blistering (hydrogen or etching bubbles). Proton capture sites are called hydrogen traps (concentrators). They can be point (vacancies) or linear (dislocations). In the latter case, during plastic deformation, the movement of dislocations will slow down, which leads to an increase in strength and embrittlement. Hydrogen traps are also non-metallic and intermetallic inclusions, grain boundaries. Hydrogen is located in the tetra- and octahedral position in figure 1.

![Figure 1](image1.png)

Figure 1. The location of hydrogen in the metal; a – tetrahedron; b – octahedron; ⬤ – metal atoms, ○ – hydrogen atoms.

The diagram of the formation of the cavity inside the steel is shown in figure 1. Protonated hydrogen encounters in its path an inclusion that does not have a metal bond, i.e. generalized electrons are missing. He takes his electron from the electron gas and enters the inclusion crystal lattice, where molecular hydrogen is formed. The hydrogen pressure in the metal reaches tens, and according to other sources, hundreds of MPa. The resulting mechanical stresses lead to the formation of cracks.

The results of measuring the parameters of atomic hydrogen penetration into iron and steel by the Devanathan-Stachursky method (visible diffusion coefficients $D_0$ $[\text{m}^2/\text{s}]$, activation energy $Q$ $[\text{kJ/mol}]$) are given in Table 2.

Table 2. Diffusion characteristics of hydrogen penetration into iron and steel.

| Material      | Temperature          | $D_0$            | $Q$  |
|---------------|----------------------|------------------|------|
| Pure iron     | 350 K                | $1 - 2.5 \times 10^{-7}$ | $7.6$ |
|               | Ambient temperature  | $0.5 - 1.2 \times 10^{-7}$ | $4 - 7$ |
|               | 298 K                | $7 \times 10^{-9}$ | $10^{11}$ |
| Real steel    |                      |                  |      |

As follows from the table, the apparent diffusion coefficients $D_0$ of pure iron with a low density of dislocations and real steels differ by several orders of magnitude due to the presence of more traps.
Some metals in the presence of hydrogen corrode by the mechanism of chemical corrosion. In this case, weight loss due to the formation of hydrides is observed. Moreover, hydrides are formed at elevated temperatures.

A number of authors hypothesize that the hydrogen separation of the metal is confined to the sites of segregation of sulfide inclusions. To clarify the validity of this hypothesis, the distribution of sulfide inclusions was determined. They were detected by the Baumann method. The sulfide inclusions were detected by the Bumann method. An etchant is required for this method [5 ml H2SO4; 100 ml of H2O]. This method was proposed by Baumann in 1906. It is the simplest imprinting method for detecting sulfur distribution and is therefore widely used.

The method is based on the following reactions: sulfuric acid reacts with iron and manganese sulfides in steel to form hydrogen sulfide by reaction:

\[(\text{Fe, Mn})S + H_2SO_4 \rightarrow (\text{Fe, Mn})SO_4 + H_2S↑\]  
(1)

the hydrogen sulfide formed interacts with silver halides AgHal (Hal - Br, I), which is in the emulsion of photo paper with the formation of brown silver sulfide by the reaction:

\[H_2S + 2\text{AgHal} \rightarrow \text{Ag}_2S + 2\text{HHal}.\]  
(2)

The method is implemented as follows: Conventional non-fixed photo paper in daylight is impregnated with dilute sulfuric acid and then excess acid is removed. Then the paper is pressed with an emulsion layer for approximately 2 minutes to a previously sanded and degreased sample, and a thin press is used to avoid slipping when using glossy paper. The paper is thoroughly washed, fixed, washed again with water and dried. From the freshly prepared surface of the sample, you can get 2 to 3 prints, which even with a longer one will still be less intense than the first.

Photo paper should be as thin as possible. This rule applies to all fingerprinting methods. Photo paper, especially bromine silver with a clear gradation of shades, is best suited. Immersion in dilute sulfuric acid lasts about 2 minutes; if the duration of the paper is too short, it absorbs an insufficient amount of liquid; if it is too long, gelatin swells very much, which leads to an unsharp picture due to increased diffusion of the reagents.

The clarity of the print depends on the degree of roughness of the surface of the sample and the print media [14]. Even if you manage to get good prints using the Baumann method of rather rough surfaces (filed or pre-sanded), you should avoid too much surface deformation during sample preparation. On prints obtained from surfaces treated by cutting, on dark areas, traces of processing can be detected.

Defects of the investigated surface, such as cracks, pores, and others, due to their increased corrosion by acid due to the large surface, often lead to an incorrect interpretation of the print. It is necessary to maintain the optimal sulfuric acid content in the solution - about 5%.

3. Results and discussion
To determine the amount of sulfide inclusions in the test sample, “Photocont” photo paper was impregnated with a solution of 5 ml of H2SO4; 100 ml of H2O. After impregnation, excess acid was removed with a cotton swab. The impregnated photo paper was rolled onto the sample using a photographic roller, kept on the surface of the sample for 10 minutes, washed under a stream of cold water and dried. The obtained sulfur imprint was examined using a stereoscopic microscope MBS 10 at a magnification of 100x. The number of inclusions was calculated using an ocular mesh. Photographs of prints are shown in figures 2–3.
4. Conclusion

Studies of the distribution of sulfide inclusions were carried out according to the Bauman method, which is the simplest method for obtaining fingerprints to detect the distribution of sulfur and is therefore widely used. It was established that the number of sulfide inclusions does not exceed the first point according to GOST 1778-70 (ISO 4967-79). It was noted that the number of sulfide inclusions is approximately the same, both near the metal stratification and on the base metal of the sample, this fact proves that sulfide inclusions do not affect the process of metal stratification process.

References

[1] Nasibullina O A, Gareev A G and Rizvanov R G 2018 Solid State Phenomena 284 1302–1306
[2] Gaysin E Sh, Frolov Y A and Nasibullina O A 2020 IOP Conf. Ser.: Earth and Environ. Sci. 459 032055
[3] Nasibullina O A and Tyusenkov A S 2019 IOP Conf. Ser.: Mater. Sci. Eng. 537 022018
[4] Abdullin I G and Gareev A G 1993 Physico-chemical mechanics of materials 29(5) 97–98
[5] Yakhin A V, Karetnikov D V, Rizvanov R G, Abakacheva E M and Gareev A G 2019 Chemical and Petroleum Engineering 54(11–12) 801–805
[6] Zaripov M Z, Fairushin A M and Karetnikov D V 2019 Materials Science Forum 946 883–888
[7] Faritov A T, Rozhdestvenskii Yu G, Yamshchikova S A, Minnikhanova E R and Tyusenkov A S 2016 Russian Metallurgy (Metally) 11 1035–1041
[8] Kuzeev I R, Ibragimov I G, Bayazitov M I, Davydov S N and Khairudinov I R 1985 Chem. and Technology of Fuels and Oils 22(3) 111–113
[9] Tyusenkov A S, Rubtsov A V and Tlyasheva R R 2017 Solid State Phenomena 265 868–872
[10] Vakulenko M V and Zharinova N V 2020 IOP Conf. Ser.: Mater. Sci. Eng. 862 062022
[11] Nasibullina O A and Gareev A G 2019 Materials Science Forum 946 20–24
[12] Abdullin I G and Gareev A G 1994 Materials Science 29(5) 539–541
[13] Zharinova N V and Vakulenko M V 2020 IOP Conf. Ser.: Mater. Sci. Eng. 862 032014
[14] Abdulganiev M R, Khasanov R N and Gafarova V A 2019 Materials Science Forum 945 569–573
[15] Krioni N K, Mingazheva A A, Kononova A Yu, Mingazhev A D and Gafarova V A 2017 Solid State Phenomena 265 215–220
[16] Mingazhev A D, Kuzeev I R and Gafarova V A 2020 J. Phys.: Conf. Ser. 1515 042074
[17] Tyusenkov A S and Nasibullina O A 2019 IOP Conf. Ser.: Mater. Sci. Eng. 687 066016
[18] Latypov O R, Bugai D E and Boev E V 2015 Chemical and Petrol. Eng. 51 283–285
[19] Nasibullina O A and Tyusenkov A S 2019 IOP Conf. Ser.: Mater. Sci. Eng. 537 022023

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