Research of the occurrence and development of metal defects in sulfide stress cracking inducing environment

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Abstract. Comparative studies of the metal of equipment after long-term operation in high hydrogen sulfide environment are carried out. To compare their resistance to sulfide stress cracking, the samples were hydrogenated under a stress of 0.6-0.9 of yield stress in a hydrogen sulfide environment. Characteristic of surface defects (blisters and bubbles) were identified, their size and time of occurrence were determined. To study the further development of the process, the samples were subjected to intense hydrogenation for 6 hours at maximum tensile stresses of 0.95 of the yield stress. Then they were cut across for conducting a metallographic study in order to identify the initiation and development of cracks in the metal. It is shown that steel containing cerium, which promoted the formation of relatively small globular sulfides, has the highest resistance to sulfide stress cracking. Such inclusions, in contrast to sulfide stringers of the FeS and MnS type, were not sources of crack initiation. Another source of crack initiation was the boundaries of pearlite and ferrite grains contaminated with microimpurities.

1. Introduction
Reliable operation of petrochemical equipment is a complex multifactorial task that requires solving a set of issues for its implementation (choice of material, operating regimes, manufacturing technology, control regulations, preventive measures, etc.). This problem has acquired particular importance in connection with an increase in the share of raw materials containing in their composition an increased amount of hydrogen sulfide in the total volume of extracted and processed oil products. Under such conditions, it is possible to saturate the metal of the equipment with diffusion-mobile hydrogen, which can lead to its embrittlement and destruction. The change in the initial properties of steel during operation can also be associated with temperature parameters, or with the simultaneous effect of the environment and temperature. Therefore, for reliable operation it is necessary to use metal that is resistant to stress corrosion cracking and achieve a homogeneous structure during manufacturing [1].

Currently, the most applicable method for controlling metal operating in hydrogen sulfide environments is the NACE TM0177 2005 method [2], which is effective for comparative testing of materials. For research purposes, other methods are also used, but all of them are based on the NACE method, with modified parameters of either the hydrogen-rich environment, or the loading scheme of the samples.

This paper considers the main changes in the metal surface and its microstructure after hydrogenation in a hydrogen sulfide environment under the tensile stresses in laboratory conditions.
2. Materials and methods

On the basis of the NACE stress corrosion cracking test data, flat samples of studied steels were prepared. Then, tensile stresses were created in the samples on the working side of the metal. A sample placed in a four-point bending frame is shown in figure 1.

![Frame with the fixed sample](image)

**Figure 1.** Frame with the fixed sample for immersion in the installation.

Then the frame with the sample was placed in a vessel with hydrogen sulfide solution. Hydrogenation was carried out in a standard NACE solution under a stress of 0.6-0.95 $\sigma_y$, while determining the time until the appearance of the first defects $t_0$, the number of defects during the basic hydrogenation time of 2 hours and calculating the average diameter of the formed bubbles $D_{av}$.

For research, a metal of approximately equal strength used for extraction and processing of petroleum products containing sulfur compounds in their composition was chosen. Samples were cut from the body and lid of a US-made apparatus and similar metal of Russian production – steel 20 and resistant to corrosion cracking steel grade 20YuCh (analog of AISI 1020 with additional doping with aluminum and rare earth metals), which are currently widely used in industry. The chemical composition of steels and their yield strength are given in table 1.

**Table 1.** Chemical composition and yield strength of the investigated steels.

| Steel grade   | Elements composition, % | Yield strength, $\sigma_y$, MPa |
|---------------|-------------------------|---------------------------------|
|               | C          | Mn        | Si      | Cr     | Cu      | Al     | Ce      | S        | P        |               |
| USA steel     | 0.19       | 0.55      | 0.09    | 0.04   | 0.06    |        | 0.033   | 0.011    |          | 230       |
| Steel 20      | 0.16       | 0.49      | 0.18    | 0.04   | 0.12    |        | 0.031   | 0.019    |          | 230       |
| Steel 20YuCh  | 0.20       | 0.66      | 0.24    | 0.04   | 0.10    | 0.06   | 0.017   | 0.019    |          | 240       |

3. Results and discussion

By analyzing the chemical composition of the three studied steels, taking into account our own research and research by other authors, it is possible to predict its effect on the resistance of steels to sulfide stress cracking [3 – 8].

The carbon content of all tested samples was within the permissible limits, namely 0.15-0.25%, which made it possible to obtain the desired structure.

The manganese content was 0.35-0.66%, which within these limits has a positive effect on the corrosion properties of the steel surface.
In the two investigated samples of steel 20 and steel 20YuCh, the silicon content in the permissible limits of 0.4-0.7%. In the USA steel sample, the silicon content exceeded the permissible limits, which may have led to a deterioration in resistance to corrosion destruction.

Copper in all samples has a positive effect on the strength characteristics of the samples, forming protective films on the metal surface.

Aluminum adversely affects the corrosion properties of the test samples.

The presence of rare earth metals in the composition of alloys used in a hydrogen sulfide environment increases the anticorrosion properties of the samples.

The results obtained after hydrogenation of the samples are shown in table 2 and figures 2-4.

**Table 2. Results of hydrogenation of the studied steels.**

| Steel grade   | Time before first surface defects appearance, min | Test time, min | Amount of surface defects, mm² | Average diameter of defects, mm |
|--------------|--------------------------------------------------|----------------|---------------------------------|---------------------------------|
| Steel 20     | 10                                               | 120            | 2.16                            | 0.078                           |
| Steel 20 YuCh| 15                                               | 120            | 1.7                             | 0.120                           |
| USA steel    | 5                                                | 60             | 13.9                            | 0.152                           |

These tests show that, in comparison with steel 20 and steel 20YuCh, the time for the appearance of the first surface defects on USA steel is shorter, and the number of bubbles formed is about 10 times is greater, although the chemical composition of steels is approximately the same. Obviously, the deterioration in resistance to stress corrosion cracking of USA metal is associated with its long-term operation. The surface of the samples is shown in figure 2.

![Figure 2](image1.png)  
(a) Bubbles on the surface of hydrogenated samples of steel 20 (a), steel 20YuCh (b), USA steel (c), ×10.

The best result for resistance to sulfide stress cracking was shown by steel 20YuCh (figure 3).
To study the development of stress corrosion cracking, the samples were subjected to intense hydrogenation for 6 hours. Then they were cut across and metallographic studies were carried out in order to identify the initiation and development of cracks in the metal.

The study of the microstructure and process of defects appearance was carried out on microsections of studied steels. It is shown that in steel 20 cracks originate at the interface of pearlite and ferrite grains (figure 4 (a)) and along the sulfide stringers phase of the FeS MnS type (figure 4 (b)). Cracking of pearlite and ferrite grains boundary is due to their surface contamination with microimpurities.

Figure 4. The initiation of microcracks (point 1) in steel 20 at the boundary of pearlite (point 2) and ferrite (point 3) grains (a), along the sulfide stringers phase (point 4) of the FeS·MnS type (b), ×100.
In the USA steel, microcracks (figure 5 (a)) spread along rolling direction and along boundaries of ferrite and pearlite grains, similar to steel 20. The opening of bubbles in the microstructure of USA steel is shown in figure 5 (b).

![Figure 5](image)

**Figure 5.** Crack initiation (a) and bubble opening (b) in USA steel, ×100.

Since the resistance of steel to stress corrosion cracking significantly depends on the quantity and nature of non-metallic inclusions, especially sulfides and oxysulfides [5], the extraction of non-metallic inclusions and its analysis was made for steel 20 and USA steel.

Isolation of nonmetallic inclusions was carried out by electrochemical method in Lukashevich-Duvanova electrolyte: 3% aqueous solution of FeSO₄ (FeSO₄ 7H₂O) + 1% NaCl + 0.25% Rochelle salt (KNaC₄H₄O₆). Electrolysis mode: i ~ 0.025 N cm², t = 24 h, T = 20°C.

The resulting precipitate in addition to slag inclusions contained carbides. In the process of chemical dissolution of carbides, some types of inclusions could be destroyed or changed. Therefore, microscopic examination of inclusions was carried out before dissolving carbides. The inclusions were separated from the carbides and examined under a microscope. The precipitate was subjected to X-ray analysis (URS–70 X-ray machine with “Co” emitter, camera RKV, exposition 10h, U = 30 kV J = 10 mA). The result of X-ray diffraction analysis is: the crystal structure corresponds to compounds of the FeS type, cerium sulfide for steel 20YuCh and Al₂O₃, SiO₂, FeS (quartz) for USA steel. In the study of stable nonmetallic inclusions, the anodic precipitate was subjected to acid-oxidative treatment to dissolve carbides, consisting in the oxidation of carbides with ammonium persulfate and potassium permanganate with simultaneous heating. The released manganese dioxide was treated with a 50% citric acid solution. The precipitate of slag inclusions after the dissolving of carbides was studied again.

According to the results of X-ray structural analysis, the crystal structure corresponds to the following compounds: for steel 20YuCh – Al₂O₃, SiO₂, FeS, cerium sulfide; for USA steel – Al₂O₃, SiO₂, FeS.

### 4. Conclusion

1) The results of X-ray diffraction patterns of non-metallic inclusions of USA steel and steel 20YuCh can be made as follows:

- before the dissolution of carbides, sulfide inclusions in steel 20YuCh are elongated, dark, thin grains up to 0.21×0.017 mm in size. Round matte silicate with size up to 0.0595 mm and irregularly shaped matt translucent silicate with a red-yellow tint with size up to 0.034 mm;
- in USA steel a complex oxysulfide and aluminosilicate inclusions of elongated shape with intracrystalline transparent inclusions up to 0.12×0.051 mm and are dark rounded silicate
inclusions up to 0.085 mm are observed before the dissolution of carbides. Elongated shattered inclusions are also present;

- after dissolution of carbides in steel 20YuCh the aluminosilicate inclusions are transparent or translucent crystals of irregular shape up to 0.0595 mm and some amount of rounded matte and translucent silicate inclusions with rough edges with size up to 0.034 mm. In USA steel after dissolution of carbides the aluminosilicate inclusions are translucent with size up to 0.017 mm for irregular shape inclusions and up to 0.025 mm for rounded one. Also, there was observed a small amount of transparent needle-shaped inclusions (presumably silicon nitride);

- the results of inclusions analysis show that steel 20YuCh contain much fewer inclusions than USA steel, sulfides in it more dispersed and coagulated and significant part of sulfur tied with cerium. This explains the best resistance of 20YuCh steel against sulfide stress cracking.

2) As a result of hydrogenation of three considered steels: steel 20, steel 20YuCh and USA steel the steel 20YuCh showed the best resistance to stress corrosion cracking.

3) The high resistance of 20YuCh steel against sulfide stress cracking is explained by the purity of this steel in terms of inclusions, a much smaller amount and smaller size of sulfide stringers, and the fact that a significant part of the sulfur is tied with cerium.

References
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