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SOME WAYS TO ENSURE RELIABLE OPERATION OF OIL AND GAS EQUIPMENT IN HYDROGEN SULFIDE ENVIRONMENT**.**

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ABSTRACT

Gas fields may contain hydrogen sulfide, mercaptan compounds, carbon dioxide, which activates corrosion, causes corrosion - hydrogen and corrosion-mechanical fracture of the metal. These gas fields should be equip by resistant to hydrogen sulfide equipment. Especially important is the reliability of body parts of Christmas tree wells such as crosses, fountains columns, stop valves that must have high resistance to corrosion, hydrogen induced cracking, sulfide stress corrosion cracking.

Serviceability of the domestic 40XH (40CrNi) and 30XMA (30CrMn improved) and foreign AISI 4130 hull steels of Christmas tree wells in a NACE hydrogen sulfide solution and in stratal water have been investigated and analyzed. The conditions under which steel of the domestic production will become hydrogen sulfide resistance have been determined. The effect of heat treatment of metal on the structure, mechanical properties and resistance to hydrogen sulfide stress corrosion cracking had been shown. To ensure reliable operation and extending the life of equipment oil-and-gas field, where hydrogen sulfide is present, recommended apply means of corrosion protection, among which the most reliable and available is inhibitory protection. The possibility of using an electrometallization aluminum coating for the protection of equipment has been investigated too.

KEY WORDS: steel, hydrogen sulfide, heat treatment, sulfide stress corrosion cracking, inhibitor, aluminum coating

INTRODUCTION

Hydrogen sulfide (H_2S) is one of the dangerous component of gas fields that causes blistering, hydrogen induced cracking (HIC), sulfide stress corrosion cracking (SSCC), and intensive total corrosion of metal. In these cases, in the production of equipment one needs materials resistant to the mentioned types of fracture and efficient methods of their anticorrosive protection. This is especially important for the gas industries of countries of Middle Asia, Canada and the USA, Kazakhstan and others, whose oil and gas deposits contain high concentrations (up to 30 vol. %) of hydrogen sulfide. In Ukraine, where about 400 gas deposits have been opened, one – third of which contains relatively small concentrations of hydrogen sulfide (up to 1.0 vol. %). These gas fields should be equipped by resistant to hydrogen sulfide equipment. Especially important is the reliability of body parts of Christmas tree wells such as crosses, fountains columns, stop valves that must have high resistance to corrosion, hydrogen induced cracking, sulfide stress corrosion cracking. To ensure reliable operation and extending the life of equipment oil-and-gas field, where hydrogen sulfide is present, recommended apply means of corrosion protection, among which the most reliable and available is inhibitory protection and use of protective coatings on the metal.

The aim of the present work is to estimate the workability of domestic steels in comparison with foreign steels, the possibility of application of inhibitory protection and using an electrometallization aluminum coating.

MATERIALS AND METHODS OF INVESTIGATION

The body steels of Christmas tree wells have been investigated (Table1).

Table 1. Chemical composition and mechanical properties of steels

Steel	Alloying element, %									Mechanical properties			
	C	Si	Mn	P*	S*	Cu*	Ni	Cr	Mo	σ_u**, MPa	$\sigma_{0,2}$**, MPa	δ**, %	Ψ**, %
40CrNi (40XH)	0,36-0,44	0,17-0,37	0,50-0,80	0,035	0,035	0,30	1,00-1,40	0,45-0,75	–	635	440	14	40
30CrMo improved	0,26-0,33	0,17-0,37	0,40-0,70	0,025	0,025	0,30	0,30*	0,80-1,10	0,15-0,25	536	414	18	35
AISI 4130	0,27-0,30	0,15-0,30	0,40-1,00	0,025	0,025	0,35	0,50*	0,80-1,15	0,15-0,50	621	414	18	35

* – the maximum allowed values

** – the minimum allowed values

The steel susceptibility to SSCC has been studied on cylindrical specimens according to the NACE Standard [1] in a NACE solution (5% aqueous solution of NaCl + 0.5% CH,COOH and saturation with hydrogen sulfide; pH = 4; t=20°C) The duration of test was 720 h.

The level of loading of the specimens was chosen relative to the minimum admissible value of the yield strength of steel: 0.8, 0.7, 0.6, etc. Steel considered suitable for use in technological environments with hydrogen sulfide admixture if $\sigma_{tsscc} \geq 0,8\times\sigma_{0,2min}$ [2]. The susceptibility of steels to HIC has been studied according to the NACE Standard TM-02-84 [3].

The corrosion resistance of steels was determined by gravimetric method on the specimen-plates (30x20x3mm) in a NACE solution (5% solution NaCl + 0.5% CH_3COOH, saturated H_2S, pH = 3, 20 ° C) and in stratal water. The type of stratal water is chloride-calcium, its mineralization is 500 mg/l, and pH is 6.8-7.2.

Efficiency of domestic inhibitors (Naftokhim-3 and Naftokhim-8) in comparison with a foreign inhibitor Dodicor have been studied too. Efficiency is determined by the protection degree Z (%) $Z=\{K_{no} - K_{ni} / K_{no}\}\times 100\%$, and retardation factor (b) of corrosion rate $\gamma = K_{no} / K_{ni}$.

K_{no} and K_{ni} are the corrosion rates of the metal in a medium without inhibitors and with it.

Electrometallization aluminum coating on the 20 steel was applied by electro-arc spraying (U = 30V; I = 150 A; air pressure 6 atm; distance to sample 150 mm). Degreasing, drying and jet processing with corundum of samples from 20 steel were performed before spraying. Corrosion resistance and SSCC resistance of samples with coating have been investigated.

RESULTS AND DISCUSSION

The body parts for Christmas tree are make from 40Cr, 40CrNi, 25CrMnSi steels. It should be noted that 40Cr and 25CrMnS steel have low resistance to SSCC and to hydrogen embrittlemen, while 40 CrNi steel, which contains 1.0 ... 1.4% Ni, can not be used in hydrogen sulfide media, since the NACE MR0175-96 standard [4] prohibits the use of low alloy steels with a nickel content of ≥1%.

Leading firms such as Cameron, Shaffer, the body parts of shut-off valves resistant to hydrogen sulfide make from steels like AISI 4130 with Cr-Mo alloying system. The casing and tubing pipes of high strength are also made from this brand of steel. Domestic analogue of this steel is 30CrMo improved steel (Table 1).

Corrosion and corrosion – mechanical properties of domestic 40CrNi, $30CrMo_{impr.}$ steels and foreign AISI 4130 steel have been investigated.

The corrosion resistance point was determined on a 10-point scale in accordance with GOST 13819-68. It should be noted that the metal of the body, the flange and the bushing, made of steel 40CrNi, were investigated separately (Fig.1, Table 2).

Table 2. Corrosion rate of low alloy steels

Steel	Stratal water		NACE solution	
	K_n mm/year	Corrosion resistance point	K_n mm/year	Corrosion resistance point
40CrNi (flange)	0,041	4	0,19	6

30CrMo impr.	0,031	4	0,15	6
AISI 4130	0,024	4	0,12	6

It was established that the corrosion rate of the investigated steels in the stratal water corresponds to the 4th point, and in the NACE solution (5% aqueous NaCl solution + 0.5% CH_3COOH, saturated with H_2S, pH 3 · 20 ° C) - to the 6 point on a 10-point scale. The values of the corrosion rates of steels in the NACE solution are 4.6 ... 5 times higher than in stratal water (pH 7,6…8). So, the stratal waters of gas fields of the Western region of Ukraine are less aggressive than the NACE solution, therefore it is advisable to make hull details of the Christmas tree from 30CrMo improved steel, which meets the requirements of the international NACE MR0175-96 Standard.

It was established that $30CrMo_{impr}$. steel and 40CrNi steel are not susceptible to HIC. The 30Cr and AISI 4130 steel have high threshold values: $\geq 0,8\times\sigma_{0,2min}$ (Fig. 1). But the SSCC resistance of the of 40CrNi steel is smaller and different for the individual parts of the valve body. The highest values $\sigma_{tsscc} = 0,6\times\sigma_{0,2min}$ for sections of the main body and bushing, and the smallest $\sigma_{tsscc} = 0,5\times\sigma_{0,2min}$ for the flange. Therefore, in order to assess the performance of case details of complex configuration in hydrogen sulfide media, it is necessary to determine the SSCC resistance of the metal for separate elements.

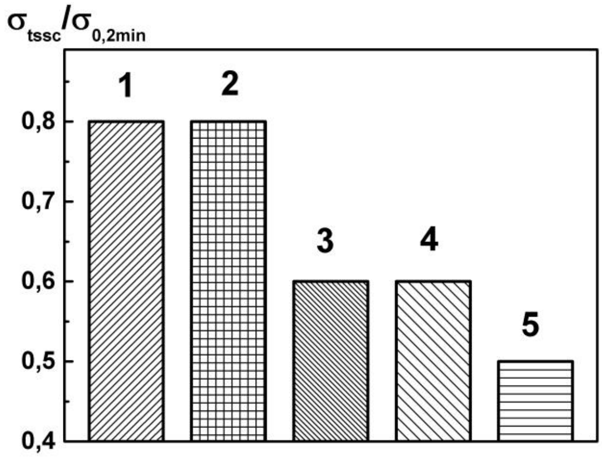


Fig.1. Thresholds resistance to SSCC of steels:
1 – $30CrMo_{impr}$;
2 – AISI 4130;
3 – 40XH(body);
4 – 40XH(bushing));
5 – 40XH(flange)

It is possible to increase the efficiency of domestic 30XMA steel in the hydrogen sulfide environment by improving its microstructure. Thermal treatment substantially affects the structure (Fig. 2), mechanical and other properties of steels, including SSCC resistance .

For the possibility of using structural materials for the production of parts of oil and gas equipment, their SSCC resistance was investigated after heat treatment. In particular, samples from 30CrMo improved steel after quenching at 890 ° C in oil were investigated, followed by tempering at temperatures of 570 ° C, 600 ° C, and 650 °C (2 hours exposure, air cooling) for the predisposition to the SSCC in the NACE solution.

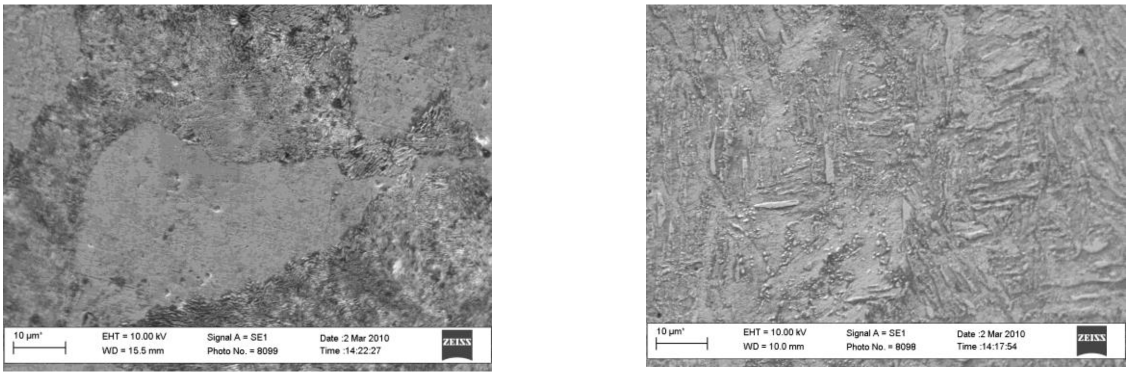
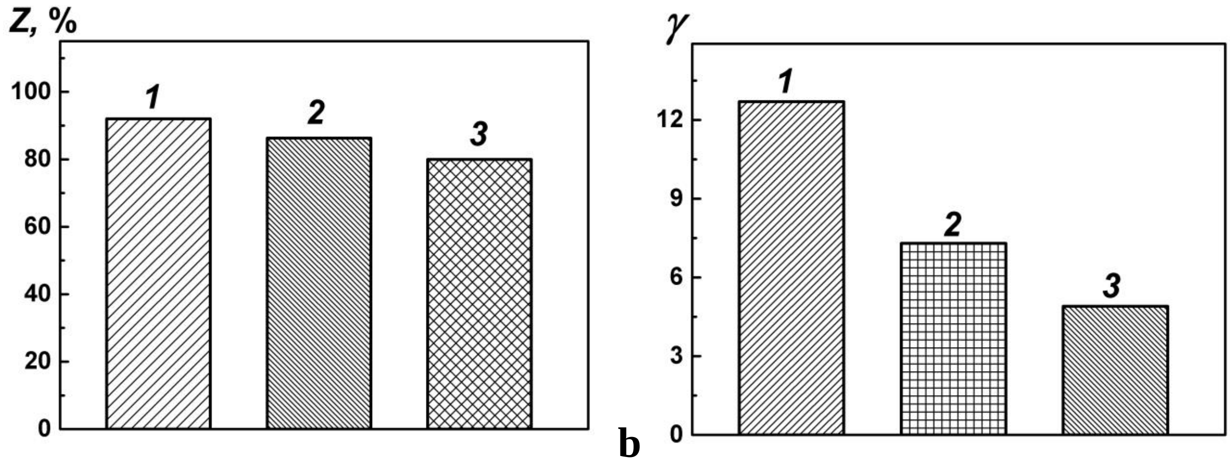


Fig. 2. Microstructure of $30CrMo_{impr.}$ steel before (a) and after heat treatment (б): oil hardening under 890 ºC and following tempering under 650 ºC.

It was established that all samples (5 samples per experiment) survived the test base (720 hours) at stresses of 80% from the yield strength of the 30CrMo impr steel after leaving at 650 ºC, 600 ºC and 570 ºC. This indicates the high resistance of the structural material to the SSCC and confirms the possibility of using $30CrMo_{impr}$.steel for the manufacture of parts of the oil and gas equipment, which works in contact with technological environments containing high concentrations of hydrogen sulfide. It should be noted that samples that were not subjected to heat treatment survived only 192 hours of testing under the same conditions.

For safe operation of equipment in gas fields, technological product of which contains hydrogen sulfide (H_2S), it is necessary to use means of anticorrosion protection. Inhibitor protection is the most available [5]. Actual problem of present day is – investigation of high effective, competitive domestic inhibitors and estimation of their protective action.

The influence of Naftokhim-8, Naftohim-3 and Dodikor inhibitors on inhibition of total corrosion of 20 pipe steel was studied gravimetrically by the degree of protection Z and retardation factor γ of the corrosion rate. It was established that the degree of protection Z of domestic inhibitors Naftokhim-8, Naftohim-3 and Foreign Dodikor make up 92%, 86.3% and 80%, and the retardation factor γ of the corrosion rate are respectively 12.7; 7.3 and 4.9 (Fig 3).



b

a

Fig.3. Degree of protection Z(*a*) and retardation factor γ (*b*) of hydrogen sulfide corrosion rate of inhibitors for the 20 steel : 1 - Naftokhim-8; 2 - Naftohim-3; 3 - Dodikor

The visual inspection of samples after testing in the hydrogen sulfide environment with the inhibitor Naftokhim-8 confirms its effectiveness even after three months of exposure. The surface of the samples is clean and without pitting (Fig.4).

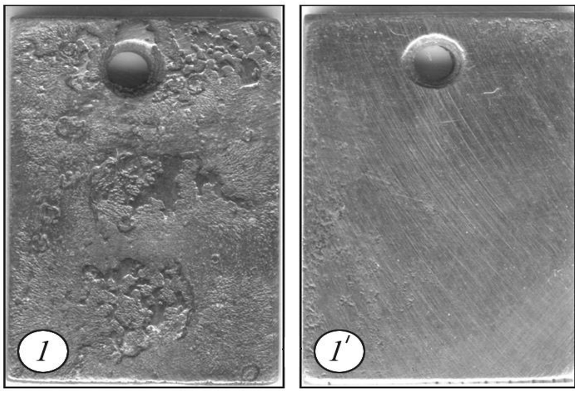


Fig. 4. The surface of 20 steel (1, 1 ') after three months of testing in the NACE solution: 1 - without inhibitor;1' with the inhibitor Naftokhim-8.

Thus, the Naftokhim-8 inhibitor can be successfully used to protect equipment that works in hydrogen sulfide environments.

Much attention is paid to investigation of aluminum protective coatings [6]. The influence of hydrogen sulfide environments on the protective properties of electrometallization aluminum coating on the 20 steel have been investigated.

Aluminum coating was applied by electro-arc spraying. Corrosion rate and SSCC resistance of samples from 20 steel without coating and with coating have been investigated in different media (Fig.5, 6).

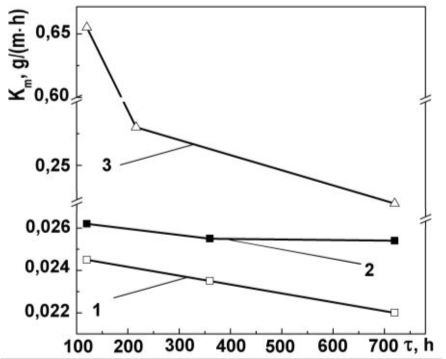


Fig. 5. Corrosion rate of samples with aluminum coating: 1- model sea water; 2- model sea water saturated with hydrogen sulfide; 3 - NACE solution.

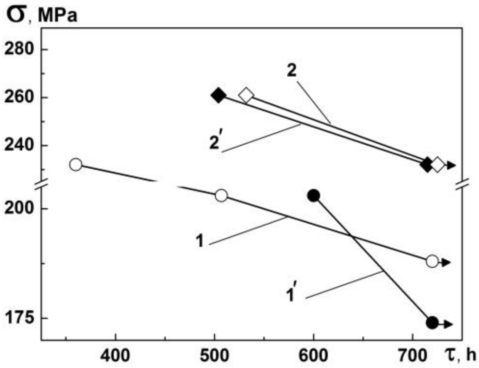


Fig.6. SSCC resistance of samples from steel 20 (1, 1 ') and electrometallization aluminum coating (2, 2'): 1, 2 - model sea water saturated with hydrogen sulfide; 1', 2' - NACE solution.

It was established that electro metallization aluminum coating has a high corrosion resistance in all test media, and hydrogen sulfide practically does not influence on the corrosion rate (Fig.5). We note that the corrosion rate of 20 steel without coating is 0.2g/(m^2h) in hydrogen sulfide, and 0.5 g/(m^2h) in NACE solution (previous research).

It has been established that in the model sea water saturated with hydrogen sulfide and in the NACE solution, the threshold stresses of 20 steel are: $\sigma_{th}= 0.65\sigma_{0.2}$ = 188MPa and $\sigma_{th} = 0.6\sigma_{0.2}$ = 174 MPa, respectively. The samples with coatings showed increased threshold stresses in both solutions: $\sigma_{th}= 0.8\ \sigma_{0.2}$ =232 MPa. Consequently, electrometallization aluminum coatings are advisable to be used to protect equipment that works in hydrogen sulfide media.

CONCLUSIONS

For safe operation of equipment in gas fields, technological product of which contains hydrogen sulfide (H_2S), it is necessary to use inhibitor protection.

Electro metallization aluminum coatings are advisable to be used to protect equipment that works in hydrogen sulfide media.

Body details of the Christmas tree are expediently make of 30 CrMo $_{impr}$ steel. which has passed the appropriate heat treatment and satisfies the requirements of the international standard NACE MR0175-96.

It was shown the significant influence of thermal treatment on the structure and on the SSCC resistance for 30CrMo$_{impr}$ steel.

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