Corrosion protection of steel 30KhGSN2A in hydrogen sulphide-containing media using diffusion nickel coatings

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This paper investigates the effect of diffusion alloying from a medium of low melting liquid metal solutions (DALMMS) of 30KhGSN2A steel with Ni–Cu and Ni–Cr elemental compositions on the structure, elemental composition of surface layers and corrosion resistance in hydrogen sulphide containing media. When DALMMS of 30KhGSN2A steel with Ni–Cu is used, coatings consisting of 3 layers are formed on the surface of the steel: a surface layer, a transition layer saturated with copper, a transition layer of a base layer. The coatings have a low microhardness (133 HV), the maximum concentration of nickel is 44 %, of copper – 80 %. The total thickness of the coatings is up to 30 μm. When DALMMS of 30KhGSN2A steel with Ni–Cr is used, coatings consisting of 2 layers are formed on the steel surface: a surface carbide layer, a transition layer of a base coating. The coatings are characterized by high surface microhardness (2000 HV). The total thickness of the coatings is up to 20 μm. The maximum concentration of chromium was 75 %, of nickel – 20 %. When tested for hydrogen cracking resistance, samples with both types of coatings showed no corrosion. The average value of total (continuous) corrosion for the Ni–Cu coating was 0.031 mm/year and for the Ni–Cr coating 0.048 mm/year. When tested for stress-sulfide cracking test, the maximum time to fracture for a Ni–Cr coated sample was 313 hours, while the Ni–Cu coated samples withstood the test completely (720 hours) without destruction or coating failure. It was revealed that diffusion Ni–Cu coatings were found to be effective in protecting the base metal from general hydrogen sulphide corrosion at the temperatures up to 150 °C, with a protection rate of over 98 % (tested according to the standard NACE MR0175/ISO 15156).

Key words: chemical and thermal treatment, diffusion, coatings, diffusion metallization, nickel, copper, chromium, corrosion resistance, hydrogen sulphide.
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Abstract

Hydrogen sulfide corrosion is one of the most often noted negative appearances during operating of oil and gas equipment. Its origination is connected with large amount of hydrogen sulfide in processed raw materials (hydrogen sulfide content in watered oil can reach 500 mg/l for several oil wells) or with high operating temperature, which lead to splitting of substances with hydrogen sulfide content and hydrogen sulfide extraction [1, 2]. So, the number of rejects for downhole equipment, caused by hydrogen sulfide corrosion, reaches 20 % of total number of rejects [1].

Steel 30KhGSN2A is considered as one of the widely distributed materials for fabrication of components of oil and gas equipment. This steel is used for manufacture of heavy-loaded components, because it is characterized by high corrosion resistance and workability. However, application of this steel in hydrogen sulfide media requires use of the technologies decreasing its corrosion rate.

To provide protection, two approaches are used: development of corrosion inhibitors and development of materials which are resistant to hydrogen sulfide action [3–7]. Creation of corrosion-resistant protective layers (coatings) on the surface of equipment is a technology with high scientific and practical interest [8–12]. As a rule, application of coatings is more efficient in comparison with component manufacture completely of material, which is resistant to hydrogen sulfide corrosion, due to high cost of such materials.

Chemical-thermal treatment of components, and particularly diffusion alloying from a medium of low melting liquid metal solutions (DALMMS) is one of the prospective methods for hydrogen sulfide corrosion protection. This technology allows to create coatings on the base of such elements as Ni, Cr, Cu, Al, Ti, Mo etc. and their compositions. Forming of coatings occurs via diffusive mass transfer of diffusants. which were diluted in melt, to the surface of coated product, owing to presence of concentration gradient [13, 14].

Based of the previously conducted investigations, dual-component coatings of Ni–Cr and Ni–Cu systems are characterized with high general corrosion resistance in the medium with 3 % NaCl and 30 % HCl content [15]. In this connection, examination of influence of these coatings on steel corrosion in hydrogen sulfide media is rather actual.

The aim of this research is analysis of influence of application of diffusion Ni–Cr and Ni–Cu coatings on steel corrosion resistance in hydrogen sulfide media.

Methods

The research was carried out for steels 30KhGSN2A. Flat samples 50 × 30 × 5 mm were used, as well as rollers for perforation of downholes. Three batches of samples were prepared for each testing series. Chemical composition of coated steel is presented in the **Table 1**.

Forming of diffusion coatings on the surface of samples was realized by their dipping and holding during preset time in the bath with low-melting melt. The samples were held in eutectic Pb–Li melts with addition of the following powders: Ni 10 % + Cr 5 %; Ni 10 % + Cu 10 %. Saturation was carried out at the temperatures 1000 °C, 1025 °C, 1050 °C during 5 hours. As a result, coating elements diffuse in the surface layer of product and provide alloying with forming of diffusion coating.

Examination of corrosion resistance of coatings was conducted within several stages: (1) determination of total (continuous) corrosion; (2) testing for hydrogen cracking resistance; (3) testing for sulfide corrosion cracking under stress; (4) testing of rollers for perforation of downholes according to the standard NACE MR0175/ISO 15156.

The experiment was implemented in accordance to the following standards: GOST 9.908-85; NACE TM0284-2016; NACE TM0177-2016; NACE MR0175/ISO 15156. Based on the requirements of the standard NACE TM0177-2016, the samples were loaded during testing for sulfide corrosion cracking under stress to 72 % from the yield strength, what was equal to 380 N/mm^2. Structure and mechanical properties of the samples after DALMMS correspond to these parameters of steel after normalization. Corrosion rate was determined via mass decrease of the samples. The testing was conducted in solutions with the following composition: 5 % NaCl + 0.02 % $NaHCO_3$, saturated CO_2; solution A (corresponding to NACE TM0284-2016); 50 g/l NaCl + 5 g/l $C_2H_4O_2$.

The pickling method (in correspondence with the GOST R 9.907-2007 / ISO 8407:1991 – Methods for removal of corrosion products after corrosion testing) was used for removal of corrosion products from the control samples after finishing the experiment. Water solution, containing 500 g/l of hydrochloric acid (ρ = 1.19 g/l) and 3.5 g/l of hexamine, was used as solution for pickling.

Corrosion protection degree (%) of the coating was calculated in the following way:

$$C = 100\frac{V_0 - V_1}{V_0},$$

where V_0 – corrosion rate in a blank experiment; V_1 – corrosion rate of the samples with protective coating.

To analyze the obtained data about DALMMS influence on composition, physical-chemical and mechanical properties of the surface layers (coatings), the following procedures were carried out:

– metallographic examinations on polished sections, which were prepared via standard technique;

– studies for thickness determination of coatings and for examination of their structure were conducted using universal optical microscope NU-2E (Carl Zeiss Jena), while microhardness determination was carried out by microhardness meter Dura Scan Falcon 500.

– determination of elementary composition of coatings was implemented via the method of micro-X-ray spectral analysis using scanning electron microscope Tescan Lyra 3 with the system PCMA Oxford Ultim MAX.

Results and discussion

Structure and composition of coatings

The conducted studies displayed that diffusion coating were formed on the surface of examined materials as a results of DALMMS. Micro-pictures of these coatings are presented in the **Fig. 1**.

It can be seen from the Fig. 1 that Ni–Cu and Ni–Cr coatings after DALMMS have different thickness and structure. So, the surface carbide layer with microhardness 2000 HV and thickness 5 μm is forming on the surface of samples after application of Ni–Cr coatings (see Fig. 1*a*, 1). The transition solid solution layer (2) is forming between the surface and base layers. Then material acquires initial elementary composition and structure. Building of Ni–Cu coatings is more complicated (see Fig. 1*b*), it is characterized by presence of three diffusion layers: the surface layer 1 (with increased Fe and Ni content), the first layer 2 (with increased Cu content) and the transition layer 3 (with lowered Cu and Ni concentration down to base concentration). Ni–Cu coatings are characterized by low microhardness (133 HV), however, thickness of both surface and transition layers is larger than that for Ni–Cr coating and makes 30 μm in comparison with 20 μm. Micro-X-ray analysis of the coatings is showed in the **Fig. 2**.

It can be seen from the results of micro-X-ray spectral analysis, that the coatings have high concentration of alloying elements. So, chromium content for the Ni–Cr coatings was equal to 75 %, while nickel content is small and makes 1.5 %. Maximal nickel concentration was revealed in the layer under the carbide layer, it substantiated 20 % (maximal chromium content in the transition layer was 8 %). As for Ni–Cu coatings, maximal nickel concentration was observed in the first layer of coating, it was equal to 44 %, while copper concentration was 13 %. Maximal copper concentration was revealed in the layer No. 1 (see Fig. 1), with copper and nickel concentration 80 % and 14 % respectively. Copper concentration in the transition layer was 10 % and nickel concentration – 40 %, then smooth lowering of concentration values for the alloying elements to base concentration is observed.

Table 1. Chemical composition of 30KhGSN2A steel

C	Si	Mn	Ni	S	P	Cr	Cu
0.27–0.34	0.9–1.2	1–1.3	1.4–1.8	up to 0.025	up to 0.025	0.9–1.2	up to 0.3

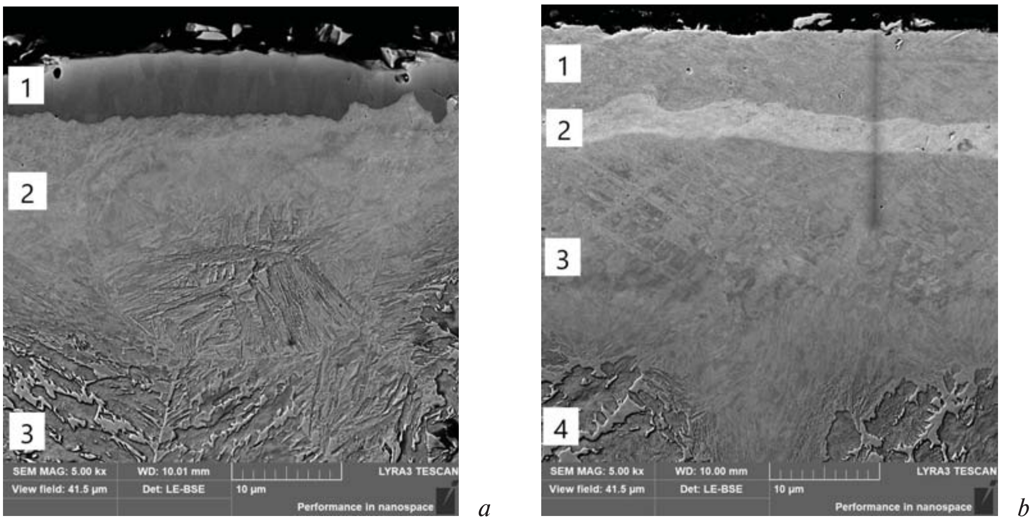
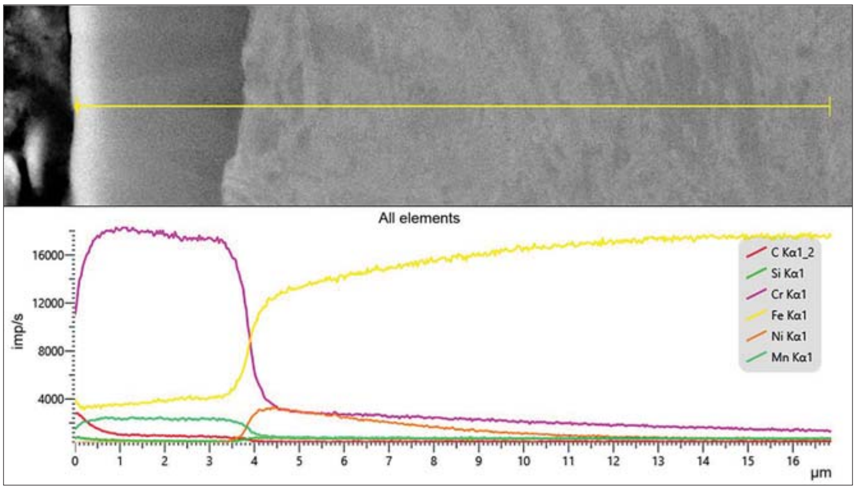
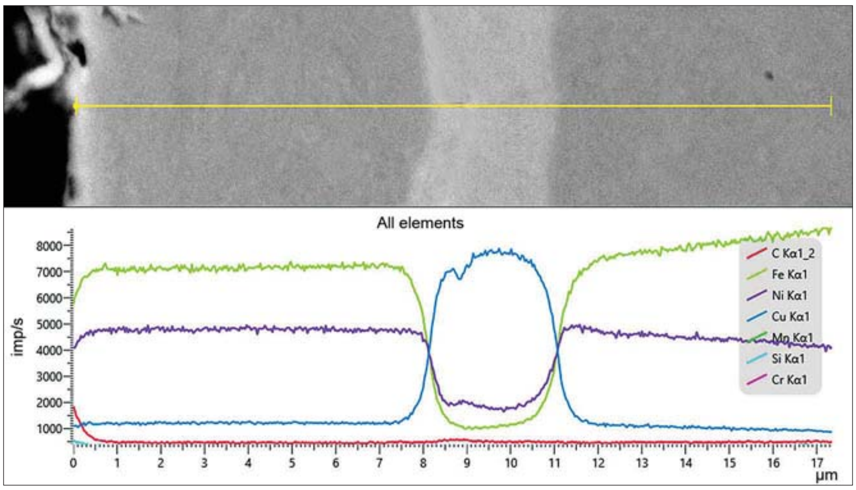


Fig. 1. Micro-pictures of obtained coatings, DALMMS conditions: 1050 °C, 5 hours; *a* – Ni–Cr coating; *b* – Ni–Cu coating



a



b

Fig. 2. Micro-X-ray analysis of the coatings: *a* – Ni–Cr; *b* – Ni–Cu

Testing of the coatings for corrosion resistance

It was revealed during testing, that both types of coatings promote increase of corrosion resistance for coated samples. They displayed absence of cracks and variation of size of these samples during testing for hydrogen cracking resistance.

However, the examined coatings showed various results during testing for total (continuous) corrosion and for stress-sulfide cracking. The results are displayed in the **Tables 2** and **3**. Considering total corrosion testing, the Ni–Cu coatings demonstrated higher resistance, the average values of total corrosion were 0.031 mm/year for Ni–Cu coatings and 0.048 mm/year for Ni–Cr coatings.

As it was found out during testing (see the Table 3), the samples with Ni–Cr coating did not withstand 720 hours of testing for sulfide stress cracking. Probably it is connected with the features of coating structure. These coatings have the carbide layer (see Fig. 1), which is characterized by high microhardness, but also by high brittleness. So, brittle destruction of sections in the carbide layer can occur as a result of extension stresses, which are acting during testing; it leads to contact between corrosion active medium and the transition layer of the coating. In this case number of alloying elements in this layer is lower than that on the surface by several times, what finalizes in sample destruction. In this connection, Ni–Cu coatings were applied for testing on rollers for perforation of downholes.

The control samples of 30KhGSN2A steel with the following diffusion nickel-copper coatings were used for testing:

No. 1 – without coating;

No. 1 – diffusion metallization t = 1050 °C, τ = 5 hours;

No. 3 – diffusion metallization t = 1025 °C, τ = 5 hours;

No. 4 – diffusion metallization t = 1000 °C, τ = 5 hours;

It was revealed on the base of the testing results, that application of Ni–Cu coatings promotes increase of corrosion resistance in hydrogen sulfide containing medium. It was found out that these coatings are characterized by high protection properties against total hydrogen sulfide corrosion; additionally, no defects in coating and base metal (such as lamination, buckling etc.) were identified for all control samples after finishing the experiment. The results of this experiment are presented in the **Table 4**, and external sight of the samples after testing can be seen in the **Fig. 3**.

We can note moderate decrease of corrosion resistance with lowering of the diffusion saturation temperature. This result is connected with the fact, that the coatings with smaller thickness and concentration of diffusant elements are forming at lower temperatures (**Fig. 4**), what causes

Table 2. The results of testing of the samples in the medium 5 % NaCl + 0.02 % $NaHCO_3$, saturated by CO_2 (Testing duration 96 hours)

No. of sample	Sample mass before testing, g	Sample mass after testing, g	Mass loss, g	Sample square, m^2	Corrosion rate, g/(m^2·hour)	Corrosion rate, mm/year	Average corrosion value, mm/year
Ni–Cu							
1	69.4940	69.4882	0.0058	0.0040	0.0152	0.0170	0.031
2	69.2377	69.2334	0.0043	0.0040	0.0113	0.0126	
3	59.1790	59.1579	0.0211	0.0039	0.0563	0.0629	
Ni–Cr							
1	69.0942	69.0709	0.0233	0.0040	0.0613	0.0684	0.048
2	59.3342	59.3154	0.0188	0.0039	0.0499	0.0557	
3	68.9303	68.9240	0.0063	0.0040	0.0166	0.0185	

Table 3. The results of testing of the samples for sulfide stress cracking (Testing duration 720 hours)

No. of sample	Diameter of sample, mm	Properties of testing sample $\sigma_{0.2}$, N/mm²	Stress value, N/mm²	Force, kgf	pH of solution in the end of testing	H_2S concentration in the end of testing, mg/l	Time until defect appearance /absence of defect, hour
Ni–Cu							
1	6.03	380	273.6	797.29	3.04	2635	720 hours without destruction
2	6.11	380	273.6	818.58	2.844	2585	720 hours without destruction
3	6.17	380	273.6	839.74	2.96	2623	720 hours without destruction
Ni–Cr							
1	6.03	380	273.6	797.29	2.91	2692	313 hours until destruction
2	6.25	380	273.6	856.52	2.97	2657	300 hours until destruction
3	6.16	380	273.6	832.03	2.96	2553	310 hours until destruction

Fig. 3. The samples after testing for total hydrogen sulfide corrosion: *a* – without coating; *b* – with Ni–Cu coating

Table 4. Protection properties of diffusion coatings against total hydrogen sulfide corrosion

No. of sample	Corrosion rate, mm/year	Protection degree, %
1	2.5	–
2	0.07	98.2
3	0.07	98.2
4	0.08	98.0

lowering of protection properties of coatings. Distribution of the elements in the coating for various saturation conditions are also showed in the Fig. 4.

It can be seen that nickel and copper concentration in the coating and in the transition layers depends on DALMMS temperature. So, at the temperature 1050 °Cnickel and copper concentration on the surface makes 44 % and 13 % respectively, while lowering of the temperature down to 1000 °C leads to decrease of concentration of these metals to 40 % and 9.8 % respectively. Thus, lowered concentration of the alloying elements at lower DALMMS temperatures finalizes in decrease of corrosion resistance in coated products.

Thus, it was revealed that it is rational way to use nickel-copper coatings for protection of equipment operating in hydrogen sulfide media. Ni–Cu coatings can be efficiently applied for corrosion protection of rollers for perforation of downholes, components of stop valves, couplings of tubing-string pipes and other products, which are in direct contact with such aggressive media. As for Ni–Cr coatings, it is expedient to use them as wear-resistance coatings or to apply in components, which are not subjected to essential stresses that are able to lead to brittle destruction of the surface layers of coatings. Such coatings can be applied on the components of compressor equipment, pumps or hydraulic systems for supporting of seam pressure. Technological simplicity, possibility of coating application on large-size components and components with complicated shape allow to consider such types of coatings as prospective for use in the oil and gas industry.

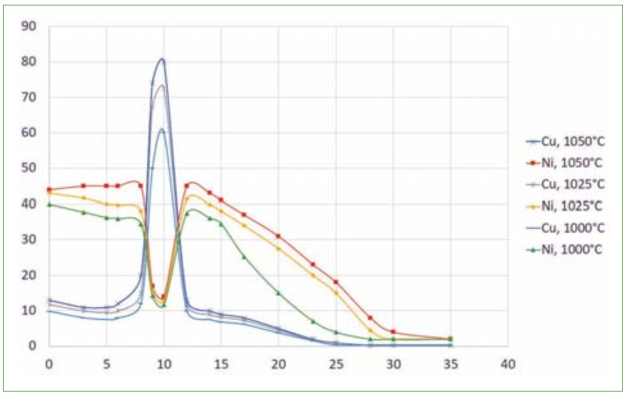


Fig. 4. Nickel and copper distribution at different saturation temperatures, saturation time 5 hours

Conclusions

1. When DALMMS of 30KhGSN2A steel with Ni–Cu is used, coatings consisting of 3 layers are formed on the surface of the steel: a surface layer, a transition layer saturated with copper, a transition layer of a base layer. The coatings have a low microhardness (133 HV). The total thickness of the coatings is up to 30 μm.

2. When DALMMS of 30KhGSN2A steel with Ni–Cr is used, coatings consisting of 2 layers are formed on the steel surface: a surface carbide layer, a transition layer of a base coating. The coatings are characterized by high surface microhardness (2000 HV). The total thickness of the coatings is up to 20 μm.

3. When tested for hydrogen cracking resistance, samples with both types of coatings showed no corrosion.

4. When tested for total (continuous) corrosion resistance, Ni–Cu coatings displayed higher resistance. The average value of total (continuous) corrosion for the Ni–Cu coating was 0.031 mm/year and for the Ni–Cr coating 0.048 mm/year.

5. When tested for hydrogen sulfide cracking under stress, only samples with Ni–Cu coating passed testing successfully.

6. It was revealed that diffusion Ni–Cu coatings were found to be effective in protecting the base metal from general hydrogen sulphide corrosion at the temperatures up to 150 °C, with a protection rate of over 98 % (tested according to the standard NACE MR0175/ISO 15156).

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