Influence of diffusion alloying of structural steels by nickel and copper in the medium of low-melting liquid-metal solutions on their corrosion resistance

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The paper considered the effect of Ni-Cu-based coatings obtained by diffusion metallization from a medium of low-melting liquid metal solutions on corrosion resistance of structural steels. It was revealed that diffusion saturation of Ni-Cu steels U8, Kh12MF, 40Kh, steel 20 formed diffusion coatings with a thickness of 10-42 μm on their surface. Thickness of the coatings depended on the modes of diffusion saturation and the coated material. It was found out that corrosion resistance of the coated materials increases in the environment of 30 % aqueous HCl and 3 % NaCl solutions with rise of the diffusion saturation temperature. The maximum corrosion resistance was obtained after diffusion saturation at the temperature of 1070 °C. Ni-Cu-based coatings allow to reduce the corrosion rate of steels in the NaCl environment: for the steel U8 by 26.21 times, for the steel Kh12MF by 21.48 times, for the steel 40Kh by 18.46 times, for the steel steel 20 by 13.9 times. Corrosion rate of steels in HCl environment is also reduced: for the steel U8 by 20.23 times, for the steel Kh12MF by 20.06 times, for the steel 40Kh by 17.35 times, for the steel 20 by 11.45 times. It was revealed that chromium-alloyed steels are undergone additional alloying coating with chromium, diffusing from the coated sample, which allows to obtain a minimal corrosion rate in both HCl and NaCl environments. Thus, the corrosion rate of steel Kh12MF after Ni-Cu coating in NaCl was 0.025 $g/(m^2 \cdot h)$, in HCl – 0.289 $g/(m^2 \cdot h)$. The highest corrosion rate was detected on the samples made of U8 steel: in NaCl 0.032 $g/(m^2 \cdot h)$, in HCl – 0.039 $g/(m^2 \cdot h)$.
Keywords: thermal chemical treatment, diffusion, coatings, diffusion metallization, nickel, copper, corrosion resistance.
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Introduction

Increase of corrosion resistance of machine components, which are operated in aggressive environment, is one of the actual problems for modern industry [1-5]. Application of the functional coatings on the surface of such components is considered as an up-to-date approach for increase of their corrosion resistance [6-8]. Thermal chemical treatment (TCT) is one of the most various groups of technological methods for application of coatings. The following TCT methods are used: cementation, nitriding, boriding, aluminizing, galvanizing etc. [9-12]. However, at present time use of these technologies is restricted, except of cementation and nitriding. It is connected with incomplete mastering of such technologies and insufficient conducted experiments for studying the properties of diffusion coatings.

Diffusion alloying in the medium of low-melting liquid-metal solutions (DALLS) is considered as the most prospective TCT technology [13, 14]. This technology allows to obtain defect-free coatings with homogeneous structure on the components with complicated shape, which are fabricated from structural steels, cast irons, hard alloys. It is based on the appearance of isothermal selective mass transfer of coating components, which are solved in liquid-metal solutions (being a transportation medium), and on consequent diffusion of these elements in the coating material with forming of solid solutions or chemical compounds [10].

Nickel-base coatings are interesting from the point of view of increase of corrosion resistance of structural materials. In this case, introduction of such elements as chromium and copper in a coating promotes increase of corrosion resistance of nickel coatings. In this connection, application of multi-component coatings of Ni-Cu system can make positive effect on corrosion resistance of structural materials. However, it is not examined sufficiently for this type of coatings.

Analysis of corrosion resistance of structural materials with application of Ni-Cu coating on the surface of these steels using DALLS technology is the aim of this research.

Technique of the research

Experimental investigations were carried out on cylinder samples with diameter 20 mm and height 30 mm. These samples were fabricated from the following steels: steel 20, 40Kh, U8, Kh12MF.

Diffusion coating was applied on the samples via DALLS technology, which includes dipping of the samples in low-melting solution with consequent isothermal holding. During this process the elements, which are the base for forming of the coating, are diffusing to the sample surface and provide

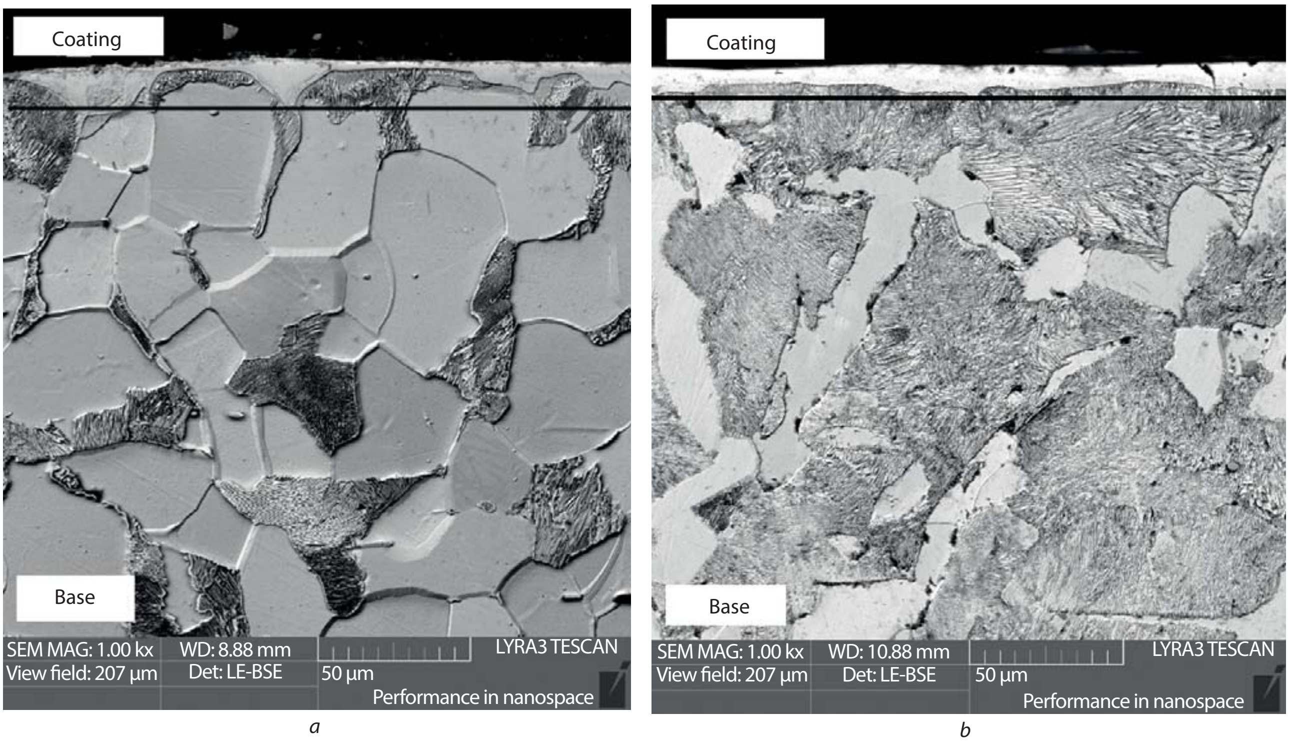


Fig. 1. Pictures of the surface layers of steels after DALLS: *a* – 40Kh, *b* – U8

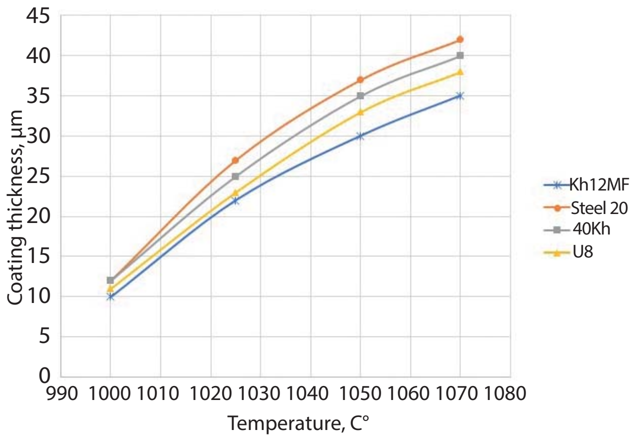


Fig. 2. Coating thickness dependence on DALLS temperature and coating steel grade

alloying of its surface layer. Pb-Bi-Li melt with eutectic composition was used as low-melting solution; Ni (2.5 %) and Cu (5.0 %) were introduced in this melt as diffusion elements.

DALLS was conducted in the developed and patented unit for diffusion metallization in the medium of low-melting liquid-metal solutions, which allows to combine DALLS processes and consequent heat treatment [15].

Diffusion saturation was carried out within the temperature range 1000-1070 °C with 5 hours holding. The samples were cleaned with removal of liquid-metal melt traces via their pickling in the mixture of vinegar acid and hydrogen peroxide.

Corrosion tests were conducted in the 30 % HCl aqueous solution and 3 % NaCl. The tests were carried out at the room temperature during 720 hours. Resistance of coatings was evaluated by their external appearance and mass varying of the samples.

In this case calculation of corrosion rate was conducted via the formula:

$$V = \frac{\Delta m}{s \cdot t}$$

where V – corrosion rate, (g/m^2·h); Δm – sample mass variation, g; s – surface square, m^2; t – testing time, hour.

In order to analyze the obtained data about influence of complex thermal chemical treatment (CTCT) on composition, the following researches were carried out to examine physical-chemical and mechanical properties of the surface layers (coatings), which are formed on carbon, alloyed low carbon and medium carbon steels:

- metallographic examinations on polished micro-samples, which were prepared according to the standard technique;
- pickling of micro-samples in 3 % HNO_3 alcohol solution, to reveal the structure of base metal and coating;
- studies for determination of coatings thickness and their structure, using universal optical microscope NU-2E (Carl Zeiss Jena), and determination of microhardness – using microhardness tester Dura Scan Falcon 500;
- weighing the samples using labor scales Radwag WAS 160/C/2;
- determination of elementary composition of coatings via the method of X-ray microprobe spectral analysis

(MPSA), using scanning electron microscope Tescan Lyra 3 with the system PCMA Oxford Ultim MAX.

Results and discussion

The studies displayed that diffusion coating is formed on the surface of samples during CTCT. Ni-Cu coatings on the samples of 40Kh and U8 steels after pickling are shown on the **Fig. 1**.

It was revealed that diffusion coatings are forming within the examined temperature range with DALLS duration 5 hours. At the same time, thickness of coatings depended on saturation temperature and material grade. So, the coating thickness for steel St3 was 42 μm and 12 μm at the temperatures 1070 °C and 1000 °C respectively. The minimal values of coating thickness were obtained for the steel Kh12MF (**Fig. 2**).

Increase of the coating thickness with saturation temperature rise is connected with more active passing of diffusion processes with temperature rise both in liquid phase (input of a diffusant to the surface of coated sample) and in solid phase (removal of diffusant inside the sample); it explains forming of more thick coatings. The mechanism of forming of Ni-Cu coatings is considered in details in previous researches [10].

It can be noted as a result of analysis of distribution charts for the elements that the coatings contain such elements as Ni, Cu, Fe, Cr. The surface layer of coatings is characterized by high content of elemental diffusants (Ni, Cu); it can be mentioned also that chromium diffusion occurs during DALLS in the surface layers from the base metal, what provides additional alloying of the coating. Distribution charts for the elements after coating of 40Kh steel are presented on the **Fig. 3**.

To reveal the influence of application of Ni-Cu coating on corrosion resistance, the samples without coating were compared with the samples having maximal coating thickness. Conduction of the tests displayed that steel without coating have lower corrosion resistance in comparison with the materials subjected to DALLS (**Fig. 4**).

Based on the analysis of the presented data, DALLS allows to decrease corrosion rate of the examined steels. Visual observation of the samples displayed that corrosion damage was homogeneous along the whole surface of samples, both in 3 % NaCl, and in 30 % HCl solutions (**Fig. 5**).

It was revealed that the examined materials are characterized by different corrosion rate. So, corrosion rate of U8 tool steel without coating makes 0.839 g/(m²·h), while corrosion rate of steel 20 was 0.39 g/(m²·h). Thus, corrosion rate increased with rise of carbon content. In this case the examined sample should be considered as a galvanic microcell, where anode is presented by ferrite and cathode – be cementite; it provides more intensive conduction of corrosion processes in steels with high carbon content.

Consideration of the sample with coating (Fig. 1, 3) revealed that coating structure differs essentially from coated material by larger homogeneity, absence of coarse grains with distinctly expressed interphase boundaries, absence of defects providing the contact between corrosion active medium and coating material. Thereby we can emphasize the

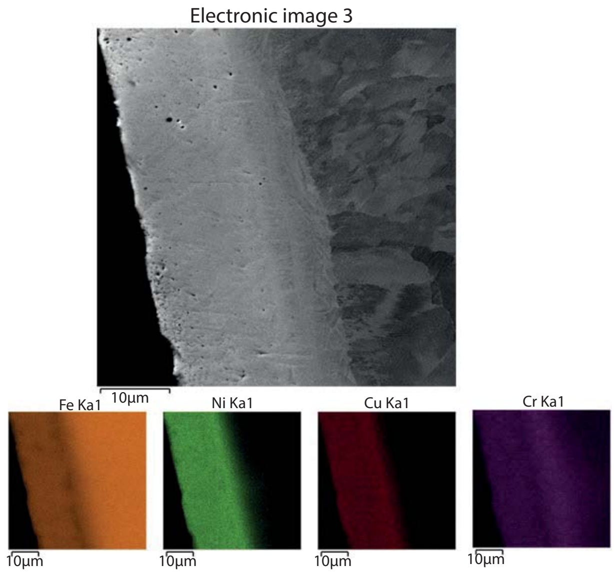


Fig. 3. Distribution charts for the elements in a diffusion coating

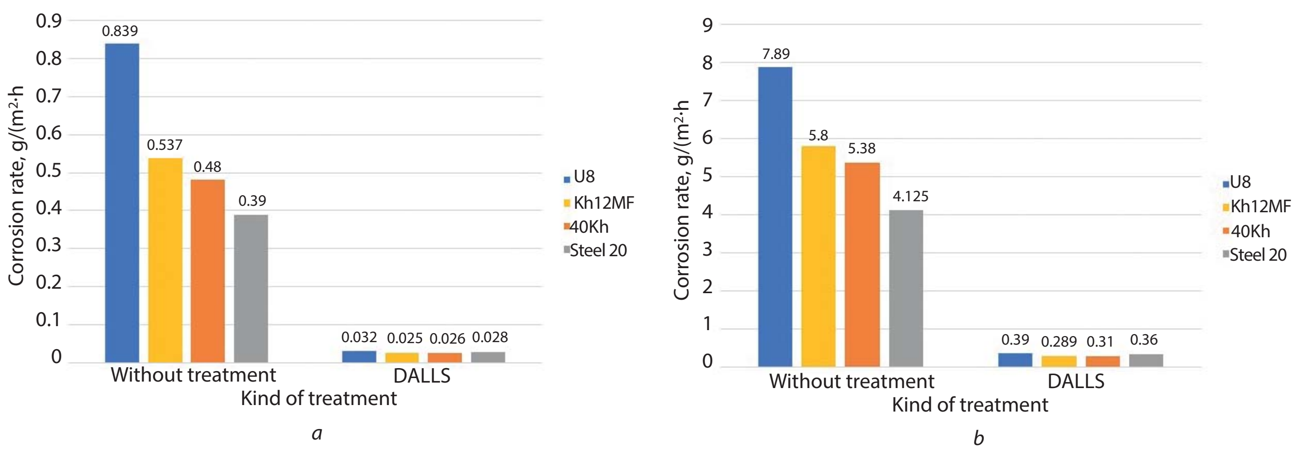


Fig. 4. Relationship between corrosion rate of the steels and corrosion active medium:
a – 3 % NaCl; *b* – 30 % HCl

structural aspect which stipulates increase of steel corrosion resistance after application of coating. In addition to this structural aspect, the influence of elementary composition of coating on corrosion resistance should be underlined. It was found out in the previously conducted researches, that during DALLS the coating contains from solid solution Fe-Ni-Cu [12]. Presence of alloying elements in steel, e.g. chromium (Fig. 3), leads to diffusion of these elements to the sample surface. Thus, the elements, which make the base for forming the coating (Cu, Ni, Cr), can influence on corrosion rate via shift of the chemical potential on samples surface to its more positive values in comparison with the sample surface without coating; it provides their more easy passivation.

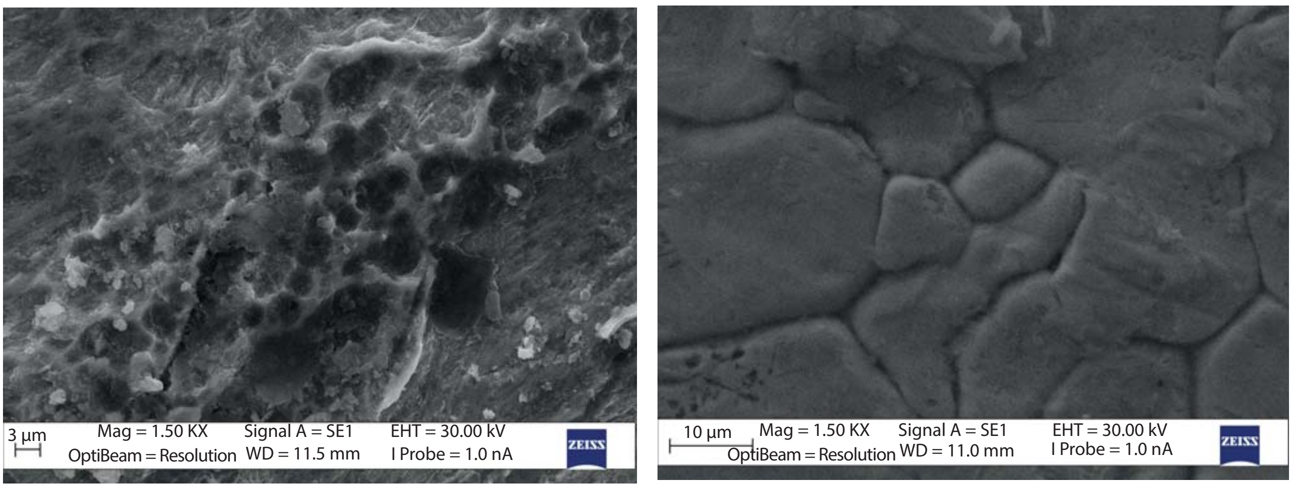
It is necessary to note that corrosion rate of materials is various after coating application. The minimal corrosion rate was registered for chromium-alloyed steels, and it rises with increase of chromium content. This feature is connected with chromium diffusion from material core to its surface during diffusion saturation, and thereby the coating is additionally alloyed (Fig. 3). So, in NaCl solution, corrosion rate for U8 steel made 0.032 g/(m^2·h), while for Kh12MF steel this parameter was equal to 0.025 g/(m^2·h). Maximal decrease of corrosion rate (by 26 times) was observed for U8 steel (Fig. 4*a*).

a *b*

Fig. 5. The samples from Kh12MF steel after testing in HCl medium during 720 hours:
a – without coating; *b* - Ni-Cu coating

The examined coatings also allowed to decrease corrosion rate in solution of hydrochloric acid. HCl medium is more aggressive relating to the considering materials, what is manifested in increase of corrosion rate in comparison with the samples which were tested in NaCl medium. E.g., corrosion rate of steel 20 in 3 % solution of NaCl made 0.39 g/(m^2·h), while in HCl medium this parameter was equal to 4.125 g/(m^2·h). In this connection, corrosion resistance of the samples with coatings also decreases slightly (in comparison with the samples without coatings). So, corrosion rate of U8 steel in HCl solution decreased by 20 times, while in NaCl solution it decreased by 26 times. Fig. 5 displays the pictures of the samples from steel Kh12MF after 720 hours of testing in HCl medium. Essential corrosion damage can be seen on the sample without coating, while the coated sample demonstrates absence of serious corrosion defects. The pictures of the samples surface of 40Kh steel after 720 hours of testing in NaCl solution are presented on the **Fig. 6**. The sample without coating demonstrates cracks and presence of corrosion products, while no significant defects caused by corrosion damage were revealed on the coated sample.

It should be mentioned that procedures of diffusion saturation have influence on corrosion rate. This dependence is practically linear: the higher is saturation temperature, the larger is corrosion resistance. It is connected with increase of intensity of diffusion processes with rise of DALLS temperature, what leads to enlargement both of the coating thickness (Fig. 2) and of concentration of elemental diffusants in the coating. The results of investigations of corrosion resistance of different materials, with application of coatings on their surface under various technological conditions, are presented in the **Tables 1** and **2**.



a *b*

Fig. 6. Surface of U8 steel samples after 720 hour testing in HCl medium:
a – without coating; *b* – after DALLS

Table 1. **The results of testing of the samples in 3 % NaCl solution**

Material	Temperature of coating application, °C	Mass per unit of the sample surface square before testing, g/m²	Mass per unit of the sample surface square after 720 hours testing, g/m²	Corrosion rate, g/(m²·h)	Decrease of corrosion rate, times (rounded off to integer values)
U8	Without coating	36825.15	3606.6	0.839	-
	1000	36824.05	3677.835	0.05	17
	1025	36946.55	3690.58	0.045	19
	1050	36955.55	3692.115	0.038	22
	1070	36961.85	3693.29	0.032	26
Kh12MF	Without coating	36562.7	3607.685	0.537	-
	1000	36572.4	3653.895	0.037	14
	1025	36628.2	3659.8	0.033	16
	1050	36846.55	3682.12	0.028	19
	1070	36501	3647.83	0.025	21
40Kh	Without coating	36933.5	3649.925	0.48	-
	1000	37060.6	3702.44	0.04	12
	1025	37478.15	3744.64	0.035	14
	1050	37438.2	3741.105	0.03	16
	1070	37066.35	3704.275	0.026	18
Steel 20	Without coating	37063.05	3671.02	0.39	
	1000	36779	3673.825	0.045	9
	1025	37064.3	3702.9	0.039	10
	1050	37182.25	3715.235	0.033	12
	1070	37283.85	3725.85	0.028	14

Table 2. **The results of testing of the samples in 30 % HCl solution**

Material	Temperature of coating application, °C	Mass per unit of the sample surface square before testing, g/m²	Mass per unit of the sample surface square after 720 hours testing, g/m²	Corrosion rate, g/(m²·h)	Decrease of corrosion rate, times (rounded off to integer values)
U8	Without coating	36945	2980.5	7.89	-
	1000	36950	3647	0.53	15
	1025	36960.05	3652.58	0.48	16
	1050	36949.95	3656.09	0.43	18
	1070	36962.66	3660.98	0.39	20
Kh12MF	Without coating	36285.4	3103..825	5.8	-
	1000	36172.8	3581.095	0.3999	14
	1025	36313.65	3598.795	0.36	16
	1050	36317.25	3602.77	0.32	18
	1070	36357.9	3609.64	0.289	20
40Kh	Without coating	36992.3	3212.51	5.38	-
	1000	36938.05	3653.95	0.44	12
	1025	36956.25	3660.34	0.39	14
	1050	36999.5	3669.193	0.3399	16
	1070	36976.9	3669.6	0.31	17
Steel 20	Without coating	37034.7	3330.25	4.125	-
	1000	37062.5	3661.015	0.5	8
	1025	37184.9	3677.775	0.45	9
	1050	37289.2	3692.735	0.399	10
	1070	37333.35	3700.765	0.36	11

The conducted investigations displayed that Ni-Cu coatings, which were applied via DALLS technology within the temperature range 1000-1070 °C, promote increase of corrosion resistance of the examined materials both in NaCl and HCl media. It should be also noted that corrosion rate of different materials also differs after DALLS treatment. These differences are connected with peculiarities of forming the coatings on steels with various elementary and phase composition. First of all, coatings on various materials have different thickness values. As soon as coating thickness increased, its protection properties improved (see Tables 1 and 2). Additionally, diffusion of alloying elements in a coating takes place in alloy steels (as it was mentioned above); it also promotes corrosion resistance increasing. Thus, Ni-Cu-based coatings can be used efficiently for forming of corrosion-resistant coatings on the surface of structural steels. These coatings provide increase of corrosion resistance in NaCl and HCl media.

Conclusions

1. Diffusion coating with thickness 10-42 µm is forming on the surface Ni-Cu alloyed structural steels during diffusion alloying in the medium of low-melting liquid-metal solutions (DALLS), depending on the coated material and diffusion saturation procedures.

2. Increase of corrosion resistance after DALLS is caused both by varying of the surface layer structure of coating material and by variation of its elementary composition, what contributes surface potential shifting to more positive values.

3. It was established that various materials are characterized by different corrosion resistance after DALLS. It is connected both with different thicknesses of obtained coatings and with additional coating alloying by chromium.

4. Maximal efficiency of application of diffusion Ni-Cu coatings was revealed for the tool steel U8, which has minimal corrosion resistance among the presented materials. Corrosion rate decreased in HCl and NaCl media by 20 and 26 times respectively.

5. Minimal corrosion rate was found out on the samples manufactured from the steel Kh12MF. Corrosion rate for this case made 0.289 g/(m²·h) and 0.025 g/(m²·h) in HCl and NaCl media respectively. It is connected with presence of alloying elements in the coating material, which support additional alloying of the coating.

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