CMDWC 2021

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Ni-based coatings for oil and gas industry fabricated by cold gas spraying

Ekaterina Alekseeva[1], *, Margarita Shishkova[1], *, Darya Strekalovskaya[1], Dmitry Gerashchenkov[2] and Pavel Glukhov[3]

[1] Scientific and Technological Complex "New technologies and materials", Institute of Advanced Engineering Technologies, Peter the Great Saint-Petersburg Polytechnic University, Polytechnicheskaya 29, 194064 St. Petersburg, Russia;
[2] NRC "Kurchatov Institute" - CRISM "Prometey", 49 Shpalernaya str., St. Petersburg, Russia, 191015;
[3] PAO "Severstal", Directorate of Technical Development and Quality, 30 Mira str., 162608 Cherepovets, Russia
* Correspondence: alekseeva_el@spbstu.ru;

Abstract: This paper presents the results of the study of nickel-based coatings fabricated by cold gas spraying. In this study compositions based on Ni, Ni-Cu, Ni-Zn, Ni-Al_2O_3/TiC coatings applied to low alloyed steel bases were investigated. The composition, type of powder (mechanical mix or mechanically alloying) and thickness varied to choose the optimal characteristics for recovery, repair procedures, and specific applications in the oil and gas industry media. The second phase was added to Ni-base coatings to increase corrosion and wear resistance. Pure nickel coatings were also studied as a benchmark. Corrosion resistance was studied by means of electrochemical testing, autoclave testing in simulated oilfield conditions. Hydroabrasive resistance was studied using the unique testing bench. Scanning electron microscopy mappings, microhardness testing, and adhesion testing were used to correlate the results of the tests with the structure, continuity, and porosity of the studied coatings. It was shown that applying mechanical alloying of the powder did not lead to an effective increase of corrosion and hydroabrasive resistance. All the studied coating specimens have a sufficiently high adhesion. Ni-Zn coating has the lowest corrosion resistance and high hydroabrasive resistance. Ni-Cu coatings have high corrosion and the lowest hydroabrasive resistance. Al_2O_3/TiC additives give ambiguous results in the studied properties. Thickness of 40 – 60 microns provides sufficient performance of the studied coatings. Thus, varying chemical composition, thickness of coatings allows obtaining optimal qualities of Ni-based coatings made by cold gas spraying for use in the oil and gas industry.

Keywords: Ni-coatings, composite coating; cold gas spraying, oil and gas industry, corrosion, coatings, cold spray coatings; protective coating; hydroabrasive resistance

1. Introduction

The aggressive conditions of the oil and gas industry require the use of corrosion-resistant materials for service in chloride-containing media, saturated with hydrogen sulfide and carbon dioxide aqueous solutions, containing abrasive particles [1, 2]. However, the use of corrosion-resistant steels and alloys is associated with significant capital costs and technical drawbacks, therefore the use of various types of coatings is becoming increasingly important for the oil and gas industry [2]. At the moment nonmetallic polymer epoxy coatings are widely used for oilfield pipelines, and tubing, aluminum, zinc metallization, nickel coatings used for tubing and for more expensive downhole equipment, etc.

Highly aggressive operating conditions require the use of nickel coatings since nickel provides corrosion resistance in wide range of conditions, wear resistance, heat resistance [4]. Nickel-based coatings of various compositions can be applied by various methods: the widespread methods of electrochemical and chemical deposition [5, 6], cladding [7, 8] thermal spray methods [9-11], CVD [12] and PVD [13] methods.

Thermal spray methods allow obtaining coatings with various compositions controlled over the thickness of the coating. The method of cold gas-dynamic spraying or cold spraying, based on the effect of the formation of a strong metal layer when a two-phase supersonic flow hits a normally located surface is relatively economical, technological, and ecological compared above mentioned methods, and therefore was used in this work [14]. The limitation of this method is the use of mainly ductile materials for spraying and the fractional composition of no more than 60 microns and a relatively low coefficient of use of powders [15]. The technology finds its application for repair and restoration work, for the protection of welding seams the restoration of worn surfaces and cracks.

The literature data show that the composition of coatings, presence of additives, application modes significantly affect the properties of coatings. So, there is evidence of increased wear resistance and corrosion resistance when copper is added to a nickel matrix [16, 17]. Zinc additive provides a high level of adhesion and increased corrosion resistance [18, 19]. In [19–23] it was shown that the use of modifiers or composite coatings can improve the characteristics of the nickel-based coatings. Nickel matrix reinforced with particles such as Al_2O_3, SiC, ZrO_2, SiO_2, etc. of nanoscale or micron size improves the corrosion resistance, wear-resistance, and microhardness of steel.

Therefore, the purpose of this work is to study the effect of the chemical composition (Ni, Ni-Cu, Ni-Zn, Ni-Al_2O_3, Ni-TiC) on the corrosion and wear-resistance of nickel coatings obtained by the cold gas dynamic spraying (CS) method to assess their applicability in the oil and gas industry.

2. Materials and Methods

The deposition of nickel coatings was carried out using the method of cold gas-dynamic spraying on a commercially "Dimet-403" installation. To obtain a uniform thickness of the coating on the surface of the substrate, a Kawasaki-FS 003 robot is used, on which the sputtering unit of the Dimet-403 installation is fixed. The robotic arm also provides a predetermined movement speed in the required interval.

The process of CS includes the following procedures: control of commercially produced gas-atomized powders for chemical and fractional composition by means of a laser diffraction particle size analyzer Malvern Zetasizer Nano-ZS and Malvern Mastersizer 2000; preparation of two types of composite powders - mechanical mixture and mechanically alloyed powder on an IVCh-3 type attritor installation; heat treatment of powder materials by means of SNOL–30/1100 Muffle Furnace; sandblasting the surface of the substrate; applying a powder mixture to a substrate.

The coating was carried out on low carbon steel plates. Mechanical mixtures and mechanically alloyed pure nickel and nickel powders with the addition of copper and zinc of various concentrations were used as powders for coating; Al_2O_3 and TiC powder was used to modify the coatings. The compositions and thicknesses of the applied coatings are given in Table 1.

Table 1. Composition and thickness of the applied coatings

Sample	**Chemical composition, wt.%**	**Thickness, ±5 μm**
Ni90-Cu10/150	Ni - 90%, Cu - 10%	150
Ni90-Cu10/40	Ni – 90%, Cu – 10%	40

Ni60-Cu40/120	Ni – 60%, Cu – 40%	120
Ni60-Cu40/50	Ni – 60%, Cu – 40%	50
Ni60-Zn40/100	Ni – 60%, Zn – 40 %	100
Ni60-Zn40/200	Ni – 60%, Zn – 40%	200
Ni90-Zn10/150	Ni – 90 %, Zn – 10 %	150
Ni90-Zn10/50	Ni – 90%, Zn – 10%	50
Ni60-$Al_2O_3$40/130	Ni –60%, Al_2O_3 – 40%	130
Ni60-$Al_2O_3$40/60	Ni – 60%, Al_2O_3 – 40%	60
Ni100/30	Ni – 100%	30
Ni90-TiC10	Ni – 90%, TiC – 10%	70
Ni60-TiC40	Ni – 60%, TiC – 40%	70
Ni50-Cu50-TiC40 (MA) Mechanically Alloyed	Ni – 50%, Cu – 50%	30

Corrosion tests

Electrochemical corrosion tests were conducted in a three-electrode cell using a Versa stat potentiostat/ galvanostat device in NaCl 3.0 wt.% 2,5 pH solution. The platinum electrode and the saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode. Potentiodynamic polarization test was carried out with a scan rate of 0,16 mV s^{-1}. The essence of the methodology for calculating the theoretical corrosion rates is based on measuring the polarization resistance of the investigated coatings (working electrode), which makes it possible to calculate the corrosion rates of the test material. Theoretical corrosion rates were calculated using Tafel curves according to [24].

To assess the corrosion resistance of nickel coatings under simulated operational conditions the samples were tested in an autoclave in 5.0 wt.% NaCl solution saturated of hydrogen sulfide (P_{H2S}=1 MPa) and nitrogen (P_{N2}= 5MPa) at temperature +80℃ for 240 hours. The autoclave test method in simulated conditions of oil wells is described in detail in [25]. A gravimetric method was used to assess the corrosion rates. Before testing, the samples were weighed with an accuracy up to 0.0001 g, and the edges of the samples were insulated with an epoxy compound. To assess the degradation of coatings measurement of the adhesion value before and after tests by the pull-off strength method according to ASTM D4541 was used.

Hydroabrasive testing

Evaluation of hydroabrasive wear was carried out on a laboratory test bench installation. Wear assessment was conducted using the gravimetric method. The tests were carried out in water solution with the addition of 0.5% wt. quartz sand fraction 0.4 – 0.8 mm. The testing process consists of the following processes: the weighting of the test sample, preparation of the test solution by introducing abrasive particles into it, the supply of this solution to the surface of the sample in the submerged jet mode from a distance of 50 mm and at the angle of 90° to a sample under a constant circulation of the solution, weighing the sample after testing and evaluating the results. The method is described in detail in [26].

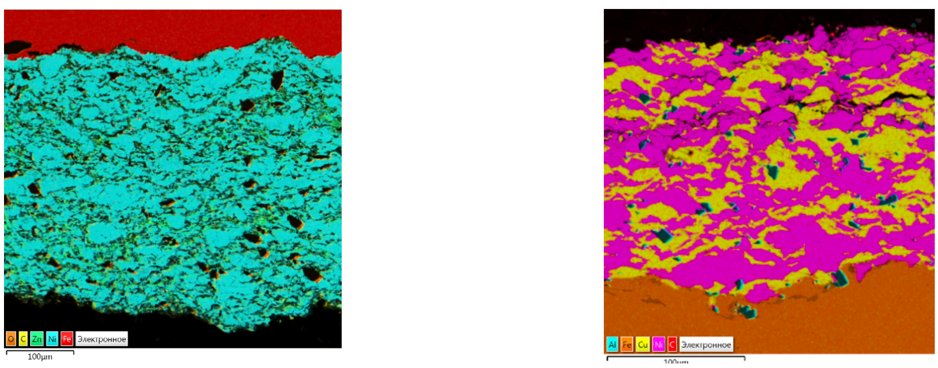
Microstructure and microhardness investigation

Scanning electron microscopy Tescan VEGA 3 equipped with Inca X-Max EDS analyzer were used for microstructure and chemical analysis of the studied coatings and powders. The microhardness was measured using a Vickers microhardness tester (Reichert-Jung Micro-Durmat 4000) with a load of 50 g applied for 15 s and reported as the average of five different readings. Porosity was defined in accordance ASTM STP947: the sample is immersed in a solution of potassium ferricyanide and sodium chloride, kept for 5 minutes at a temperature of 18-30 ° C. On the controlled surface, the number of blue dots corresponding to the number of pores is counted. Then the average number of pores is calculated as the ratio of the number of pores to the area of the controlled surface.

3. Results and discussion

3.1. *Characterization of Microstructure of coatings*

Figure 1,a illustrates the structure of Ni-Zn coatings with the various ratios of elements. As it is shown in the image, the coatings have an even distribution of zinc in the nickel matrix, there are some micro-discontinuities and, no cracks in the structures. Dark "islands" of Al_2O_3 with an average size of 2-5 microns are clearly visible in the structures. This can be seen in the shades of the spectrum (aluminum and oxygen are indicated on the energy dispersive spectrum map together); by size (size of the fraction of aluminum oxide) and shape (aluminum oxide has a fragmented form; pores, on the contrary, are usually round).

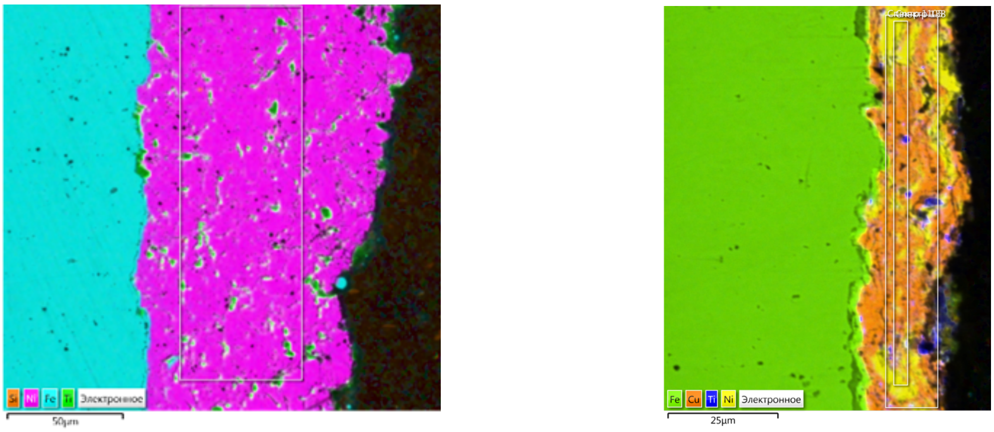


a) **b)**

Figure 1. Ni-Zn coatings (a) Ni60-Zn40/200 (b) Ni60-Cu40/120

Microstructures of the Ni-Cu coatings show cracks in the form of bundles, fig. 1,b. EDS analysis of the Ni-Cu coatings shows the uneven distribution of Cu in the nickel matrix. There are randomly distributed dark islands of Al_2O_3 in the matrix as well as in the Ni-Zn coatings and the pure Ni samples.

It can be seen from Fig. 2 (a, b) that the TiC reinforcing particles in the Ni matrix are evenly distributed as a separated particle and the groups of several particles in the size up to 5 microns. It was found that mechanically alloyed powders (Fig.2, b) is difficult to apply, which appears in the structure as a separate layer with pores. This may be due to the fact that as a result of the powder particles processing a significant work hardening is happened, in addition, a large amount of oxygen is absorbed by the powder surface.



a) **b)**

Figure 2. Nickel coatings with reinforcing particles: (a) Ni60-TiC40 (b) Ni50-Cu50-TiC40 (MA)

Porosity and microhardness for types of nickel-based coatings, depending on the chemical composition of these coatings (nickel-copper, nickel-zinc, nickel- reinforcing particles, pure nickel) are shown in Table 2.

Table 2. The average values of porosity and microhardness of the studied types of coatings

Nickel coating type	Porosity, unit / cm²	Microhardness, HV
Ni-Cu	*0.6*	*90*
Ni-Zn	*2.1*	*170*
Ni-Al_2O_3	*0.5*	*130*
Ni	*1.1*	*185*
Ni-TiC	*1.1*	90
Ni-Cu-TiC (MA)	*1.2*	100

3.2. *Characterization of corrosion properties*

Corrosion rates obtained from the polarization curves are given in Figure 3. The samples of Ni-Zn coating have the lowest resistance to corrosion, the corrosion rate under test conditions is 2.5 - 2.6 mm / year, which is explained by the low corrosion resistance of zinc and its active dissolution under the test conditions and also a high porosity of the samples. However, in real conditions, zinc has a protective effect of nickel matrix, which allows these types of coatings to be successfully used. The samples of Ni-Cu and Ni-Al_2O_3 coatings have the higher corrosion resistance, corrosion rates are 0.8 – 0.9 mm/year and 0.5 – 0.6 mm/year, respectively that could be associated with high corrosion resistance of Cu and low porosity of the samples. The corrosion resistance of pure Ni-coating (Ni100/30) is lower than that of the coatings with the addition of Al_2O_3, so the presence of these particles enhances corrosion resistance that could be explained by low porosity of the samples of Ni-Al_2O_3. It is important to note that the addition of TiC particles and mechanical alloying powder mixture does not increase the corrosion resistance of the coatings.

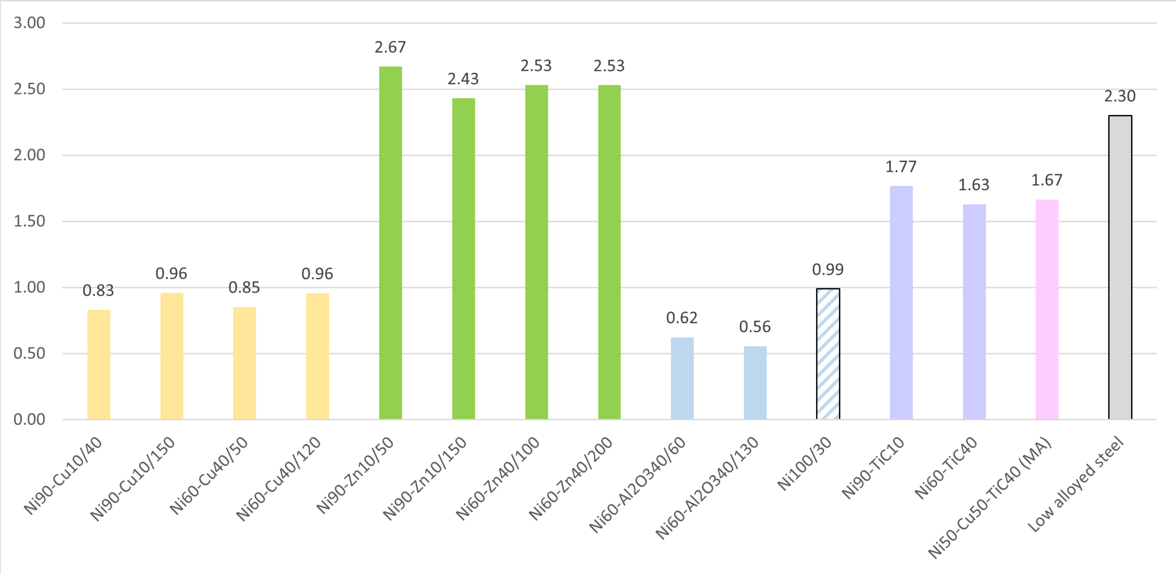


Figure 3. Corrosion rate (in mm per year) of nickel coatings. calculated using electrochemical tests in a 3% NaCl solution with pH = 2.5

Results of corrosion testing in the simulated oil and gas media in the autoclave are given in Fig.4.

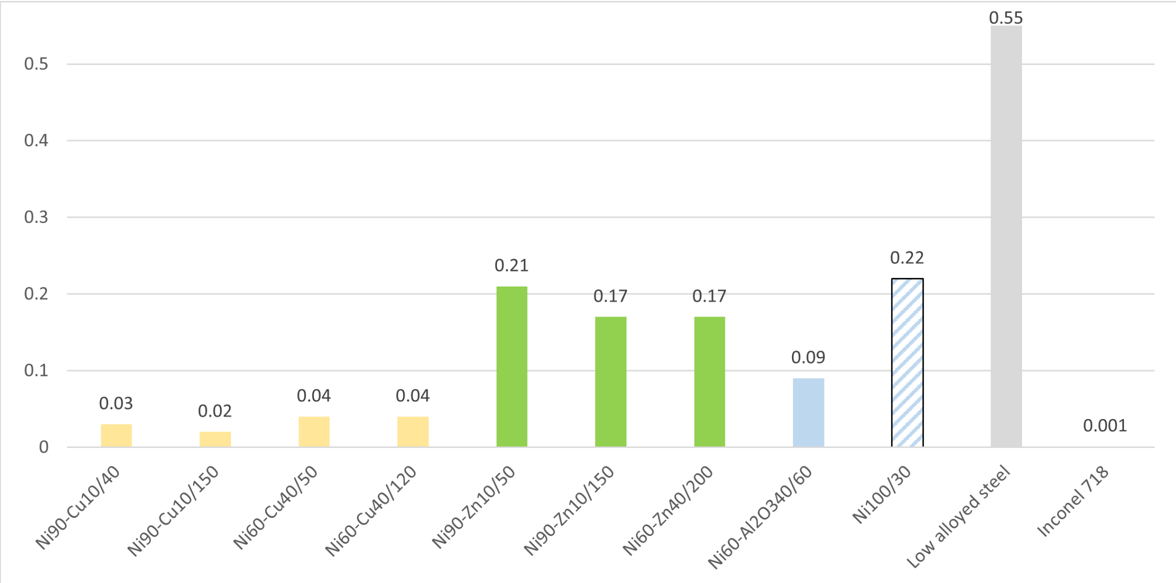


Figure 4. Corrosion rate of nickel coatings in 3% NaCl solution with pH = 2.5

The results of autoclave tests are consistent with the results of electrochemical studies: Ni-Cu samples demonstrate the highest corrosion resistance under the test conditions, corrosion rates are 0.02 – 0.04 mm/year. However, samples of Ni-Al_2O_3, Ni-Zn, have the higher corrosion rates 0.099

mm/year, and 0.2 mm/year, respectively. Pure nickel samples showed a low corrosion resistance due to the low density of the obtained coating.

For comparison, the corrosion rate values for low alloy steel and Inconel 718 nickel-based alloy are given in Fig.4. It can be seen that Ni-Cu samples have an order of magnitude higher corrosion rate compared to Inconel 718. It is also seen that, compared with a low-alloy steel, the studied nickel-based coatings provide the significant corrosion protection: the corrosion rates with the coatings are 3 to 10 times lower.

All the studied coatings have a sufficiently high adhesion before the autoclave corrosion tests (Table 3) except the mechanically alloyed Ni50-Cu50-TiC40 (MA) sample. The adhesion strength of the coating after the autoclave tests shows decrease of adhesion by 20-40% to the initial values.

Table 3. Adhesion strength values before and after the autoclave test

Sample	Adhesion before, MPa	Adhesion after, MPa
Ni60-Cu40/50	6.36	4.04
Ni60-Cu40/120	6.61	4.40
Ni90-Cu10/150	6.82	6.41
Ni90-Cu10/40	4.83	5.87
Ni60-Zn40/100	6.65	4.50
Ni60-Zn40/200	6.24	5.25
Ni90-Zn10/150	5.72	5.36
Ni90-Zn10/50	7.81	7.54
Ni60-Al2O340/130	9.34	8.89
Ni100/30	5.85	7.95
Ni90-TiC10	9.57	4.70
Ni60-TiC40	7.54	5.89
Ni50-Cu50-TiC40 (MA)	4.80	4.00

3.2. *Characterization of wear properties*

Figure 5 shows the results of hydroabrasive testing in an aqueous solution with 0.5 wt. % quartz sand during 0.5 and 1 hour. As it can be seen from the Fig.5, the microhardness (Table 2) values correlate with the wear resistance of the coatings. The highest resistance to hydroabrasive wear has the Ni samples (a microhardness of 185 HV), Ni-Zn (170 HV), Ni-Al_2O_3 coatings (130 HV). The Ni-Cu samples and the Ni-TiC samples have the lowest resistance due to lower hardness and the presence of discontinuities in the structures. The average weight losses for all investigated samples are 0.02 – 0.1 g/h, with the exception of nickel-copper, nickel-corundum coatings.

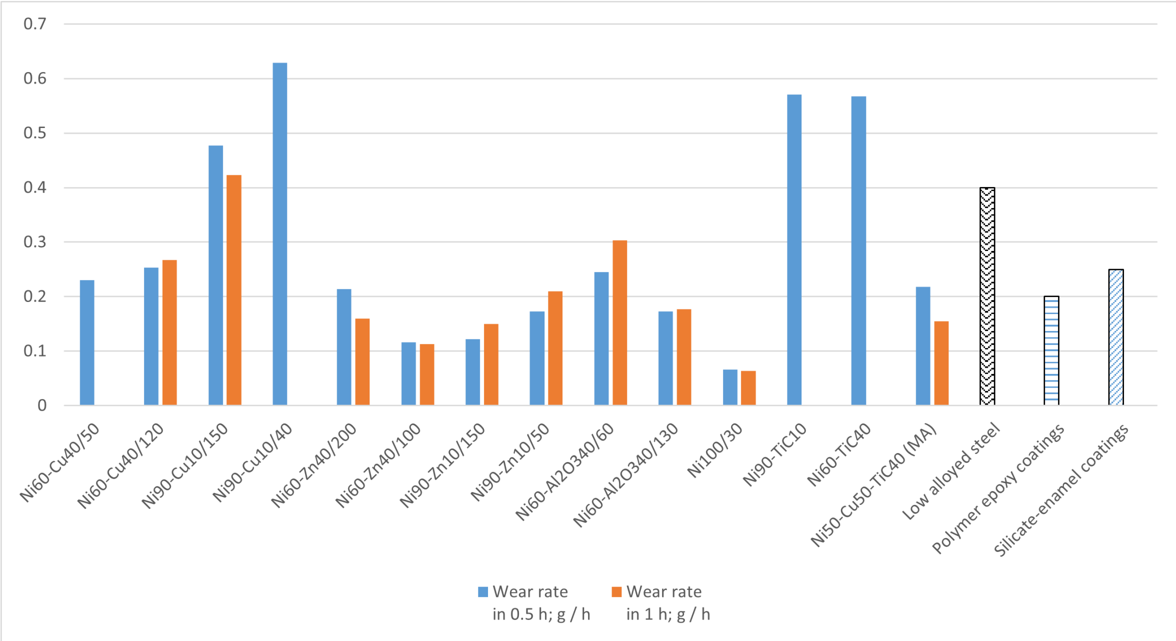


Figure 5. The rate of hydroabrasive wear of coatings for: 0.5 hour; 1 hour

It is worth noting that according to [26] the hydroabrasive wear rates of industrial used coatings for pipelines are 0.15 - 0.25 g/h on the average for coatings on a polymer epoxy base, 0.4 – 0.5 g/h for coatings on a silicate-enamel base, low alloyed steels pipeline steel without any coatings have wear rate 0.4 g/h. Thus, the results of tests for resistance to hydroabrasive wear show that nickel-based coatings are more resistant than industrially used non-metallic coatings.

According to the results of corrosion and hydroabrasive tests, the increase in thickness doesn't give an improvement so the thickness of 40 microns is sufficient to protect against corrosion and wear.

5. Conclusions

In this study, the samples of nickel-based Ni-Zn, Ni-Cu, Ni-Al_2O_3, Ni-TiC, Ni were fabricated by means of cold gas-dynamic spraying. Corrosion and wear resistance of the coatings for use in the oil and gas industry were investigated.

1. It was shown that the coating based on Ni-Zn has the lowest corrosion characteristics (in the simulated oilfield conditions the corrosion rate is 0.17-0.2 mm / year), though, these coatings have the highest wear resistance characteristics. However. the protective effect of zinc allows them to be used as corrosion-resistant. at the same time to be economically attractive.
2. The samples of nickel-copper coatings have high corrosion resistance, but the low wear resistance due to their low hardness. Applying coatings from mechanically alloyed powders of nickel-copper is practically not applied without titanium carbide.
3. The nickel samples have the low resistance to corrosion, but the high resistance to hydro-abrasive wear.
4. Al_2O_3/TiC additives give ambiguous results in the studied properties. Specimens with Al_2O_3 have a low hydroabrasive wear and high corrosion resistance; the introduction of particles TiC was not effective in improving these characteristics.
5. All the studied coating specimens have a sufficiently high adhesion before and after testing in autoclave.
6. Thickness of 40 – 60 microns provides sufficient performance of the studied coatings.

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