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Research article

PROPERTIES OF 13% CHROMIUM WIRE ELECTRIC ARC SPRAYING COATINGS

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Abstract. The article considers the nature and some mechanical properties of corrosion-resistant metallizing steel coatings produced out of 13% chromium wires. The carbon is confirmed to influence on the phase composition, hardness, adhesion strength of the coating to the substrate, elasticity module and bending strength of the coating material. The authors estimated a relative wear resistance of sprayed coatings under abrasive friction. They showed the data on the adhesion strength and elasticity module of the coating depending on the carbon content in the 13% Chr wires. The difference in the adhesion strength of the coatings can be explained by quenching processes during spraying and the variability of the elastic module of the applied material.

Keywords: electric arc spraying, phase composition, wear resistance, microhardness, porosity, adhesion, spraying

1. Introduction

As a rule, operation of oilfield well equipment and pipelines is connected with interaction with corrosive media containing mechanical impurities. This leads to the intensive corrosion-mechanical wear of the contacting surfaces [1,2]. To reduce the intensity of surface destruction and reduce the number of failures in production of pipes and parts of oil submersible equipment high-alloy steels are used. So, in particular, steels containing up to 12 to 14% chromium are widely used in oilwell and oilfield environments containing a significant amount of CO2. To ensure the required level of corrosion resistance in steels used for the equipment operating under carbon dioxide corrosion conditions, the carbon content is limited. So, according to Gazprom industry standard STO 2-4.1-228-2008 in the metal of casing and tubing with such an alloying system, the carbon content should not exceed 0.22%. A higher carbon content leads to chromium carbides precipitation and causes a decrease in the corrosion resistance of the solid solution. At the same time, the mechanical impurities in the well cause an intense wear effect and require an increase in the hardness of the surface layer due to the use of higher carbon steel grades.

The production of bimetallic items and systems is one of the actively developing trends in mechanic engineering in recent decades. A widely used group of technologies that allow us to create such products are methods of thermal spraying, in particular, electric arc spraying. This and other related coating technologies let us use high-alloy steels and alloys cost-effectively, both at the stage of production and during its maintenance.

A promising trend of creating coatings with high corrosion and wear resistance is the use of corrosion-resistant steels coatings with a higher content of chromium and carbon.

The coatings applied by thermal spraying have a complex structure of heavily deformed metal particles, oxides and pores. The performance properties of coatings depend on their

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mechanical properties (ultimate strength, elasticity module, the value and distribution of stresses, hardness, etc.).

Residual and phase transformations in the material are inherent in thermal gas coatings [3]. Stresses in coatings affect their strength, adhesion to the substrate, deformation [4]. So, if we define the mechanical properties and stresses in the coating, it will be possible to evaluate its performance properties.

Internal stresses in thermal gas coatings are defined by the methods of drilling holes [5,6], thermography methods [7], the method of continuous measurement of hardness [8], etc.

Due to the high cooling rate the use of electric arc spraying methods of coatings allows to prevent the transition of chromium to the carbide phase and maintain the required level of corrosion resistance and at the same time increase the hardness and wear resistance of the surface layer.

The aim of this work was to study the properties of coatings by electric arc spraying with 13% chromium wires and different carbon content under different spraying modes.

2. Methods

For the research the authors used solid wires with a diameter of 1.2 mm, the chemical composition of which is presented in Table 1.

Table 1. Chemical composition of welding materials for electric arc spraying (GOST 2246-70, GOST 10543-98)

Grade	C	Si	Mn	Cr	Ni	S	P
Sv-12Kh13	0.09-0.14	0.3-0.7	0.3-0.7	12-14	≤ 0.6	≤ 0.025	≤ 0.03
Np-20Kh14	0.16-0.25	≤ 0.8	≤ 0.8	13-15	≤ 0.60	≤ 0.025	≤ 0.03
Np-30Kh13	0.25-0.35	≤ 0.8	≤ 0.8	12.0-14.0	-	≤ 0.025	≤ 0.03
Np-40Kh13	0.35-0.45	≤ 0.8	≤ 0.8	12.0-14.0	-	≤ 0.025	≤ 0.03

For the research samples were sprayed at a 2250-2275 J/s thermal power of the arc at a voltage from 28V to 35V and a spray distance of 100 mm.

According to the theory of welding processes [9], an increase in arc voltage leads to burnout of alloying elements and carbon. Therefore, at the first stage of research, the losses of carbon and chromium during electric arc spraying with a 30Kh13 wire were determined depending on the operating voltage with an optical emission analyzer of chemical composition FOUNDRY-MASTERLAB. The thickness of the metallizing coating of the samples for evaluating the chemical composition was 0.30 mm.

The adhesion of the coatings was defined by the pull-off method with a universal tensile testing machine SHIMADZU (ENF 200K2) in accordance with GOST 9.304-87.

The same setup was used to estimate the tensile strength and elastic module of sprayed coatings at three-point bending according to the GOST 20019-74 method. The tests were carried out on samples 35±1 mm long, 5.0±0.25 мм width and height.

Samples of the coating material were received by spraying into a groove of specified dimensions before filling it. Then the samples were removed and ground in order to get items with specified dimensions. The module of elasticity and ultimate strength was defined by the three-point bending method with a loading rate of the samples of 1 mm/min.

The elastic module of the metallizing coating materials was evaluated at stresses in the range of 0.1-0.2 of the ultimate strength.

The microstructure of the coatings was evaluated in cross-section by inverted metallographic microscope Nikon ECLIPSEMA200, X-ray diffraction analysis was carried out on a DRON-3M diffractometer, and the microhardness was measured on a DuraScan-20 hardness tester.

The assessment of the coatings wear resistance was carried out on a Khrushchev-Babichev stand when the sprayed material was rubbed against the S2G 24A 40-NMA cleaning pad. When testing for wear resistance 20HGSNM steel with a hardness of 450-480 HV was used as a standard. Testing samples were cylindrical steel items with a diameter of 25 mm and a height of 15 mm, on the end surface of which coatings with a thickness of 0.35±0.1 mm were sprayed. To prevent overheating of the items and to ensure the similar cooling conditions, the items were fixed in holes along the perimeter of the technological disk with a diameter of 50 mm before spraying. During spraying the disk rotated at a speed of 60 rpm. After spraying, the coating surfaces were ground to a thickness of 0.30±0.05mm.

3. Discussion

In the electric arc spraying (EAS) method coatings are produced from liquid metal particles sized from 20 to 200 microns. When a part hits the surface, it deforms and simultaneously cools at a rate of several hundred degrees per second. It is not yet possible to theoretically evaluate the expected structure and properties of coatings in such complicated and fast processes; therefore it is necessary to carry out a large amount of experimental research. [10,11]. Evaluation of metallization modes influence on the degree of burnout of chromium was carried out using an electric arc with the same thermal power, but operating at different voltage and current (Table 2).

A chemical composition analysis of the sprayed layer showed that the arc voltage increase above 30V leads to a more intense burnout of alloying elements and a decrease in adhesion during pull-off. So, in further research, the spraying of coatings was carried out at an arc voltage of 30V.

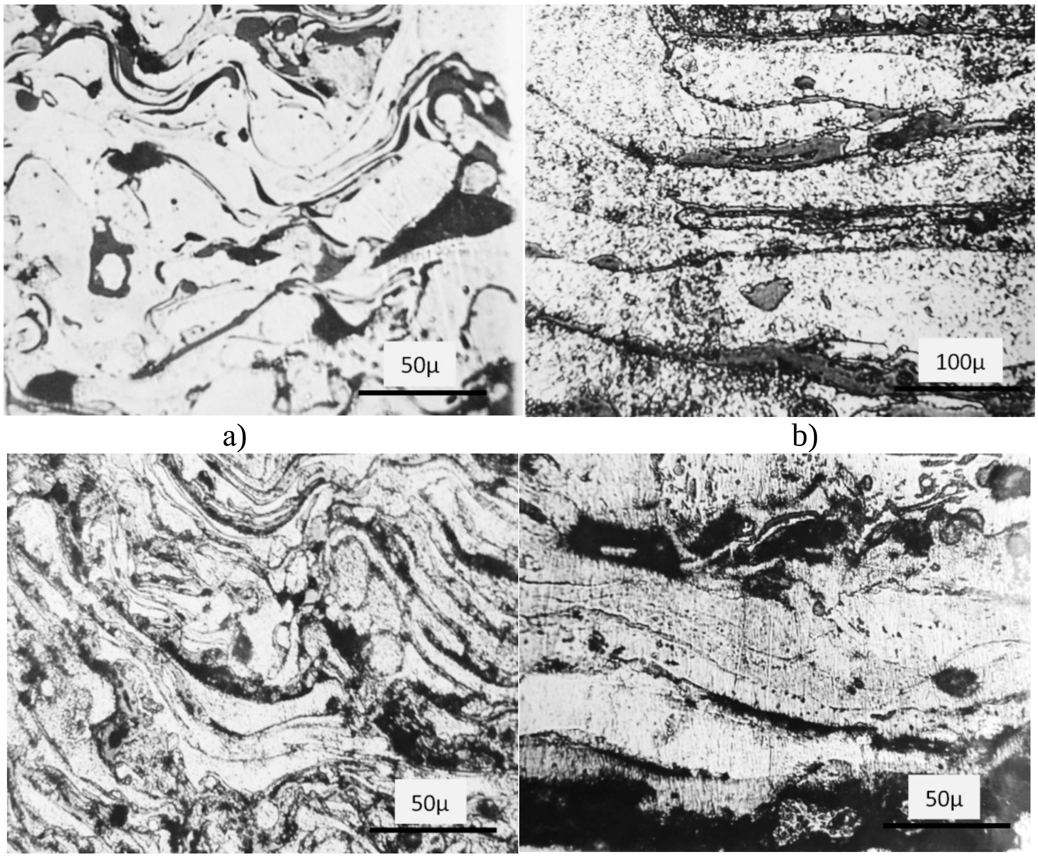
The structure of the sprayed coatings is shown in Fig. 1.

Table 2. Carbon and chromium content change in wire coatings 30Kh13 (C=0.31%, Chr=13.2%)

Electric arc parameters			Alloying elements,% weight.		Coating adhesion strength $\sigma_{pull\text{-}off}$, MPa
Power, kW	Curre nt, A	Voltage, V	Carbon	Chromium	
2.25	90	25	0.25	12.8	30.6
2.25	75	30	0.26	12.8	30.7
2.28	65	35	0.19	11.2	23.5

Spayed coatings are characterized by layered structure and porosity, which is 10-14% for Sv-12Kh13 wire coating, 14-16% for Np-20Kh13 and Np-30Kh13 wire coating and 8-14% for Np-40Kh13 wire coating. This corresponds to the data [13].

X-ray diffraction analysis of coatings showed that the metal sprayed by Sv-12Kh13 wire has mostly Fe_{α} (~87%, weight), and also spinel phases $Fe(Cr, Fe)_2O_4$ (13%). Oxide phase has a variable composition from Fe_3O_4 to $FeCr_2O_4$. Carbide phase is not observed, obviously due to its low weight volume (1-3%). According to metallographic study, sprayed layers out of 12Kh13 have impurities with microhardness of 375-420 $HV_{0.1}$.



c) d)

Fig. 1. The structure of the sprayed coatings of different chemical composition: a)12Kh13, b) 20Kh13, c) 30Kh13, d) 40Kh13

A structure of Np-20Kh13 wire coating does not almost differ from a metal structure of Sv-12Kh13 wire. The hardness of coating is ranged between 412-448 HV. The structure of surface is martensite-ferrite. Carbide impurities, the microhardness of which has to be higher than 1000-1100 HV, are not detected.

X-ray diffraction analysis of Np-30Kh13 wire coatings showed that oxygen and nitrogen exist in molecular entities Fe_3O_4 and Fe_2N. The distribution of chromium between the phase components slightly varies from 15-16.2% in dark impurities to 10.5% in light ones. Microhardness ranges from 470HV to 550 HV, but there are impurities with hardness up to 640 HV.

The study of Np-40Kh13 wire coating did not detect carbide phases, as well as in coatings sprayed from wires with lower carbon content. This is probably due to the very high cooling rates. A similar conclusion was made in the research[13]. Coating hardness was 507-562 HV.

Comparison of the fixed level of hardness of metallized coatings with the characteristics of steels of similar composition showed that the metal of the sprayed layer is close in this indicator to the heat treated monolithic metal. An increase of hardness during spraying is observed only in low-carbon compositions and is not connected with the carbide phases. (Table 3).

The evaluation of the relative wear resistance of metallized coatings during friction against abrasives expectedly showed an increase of this indicator depending on the carbon content in the coating metal due to martensite (Fig. 2).

Table 3. Chemical composition and some properties of 13% chromium alloys

Grade	12Kh13	20Kh13	30Kh13	40Kh13
Heat treatment of steel	N*	N*	Q+T**	Q+T**
Steel hardness, HV	191-229	290-342	235-280	504-650
Coating hardness, HV	375-420	412-448	470-550	507-562

*Normalization; **Hardening and tempering

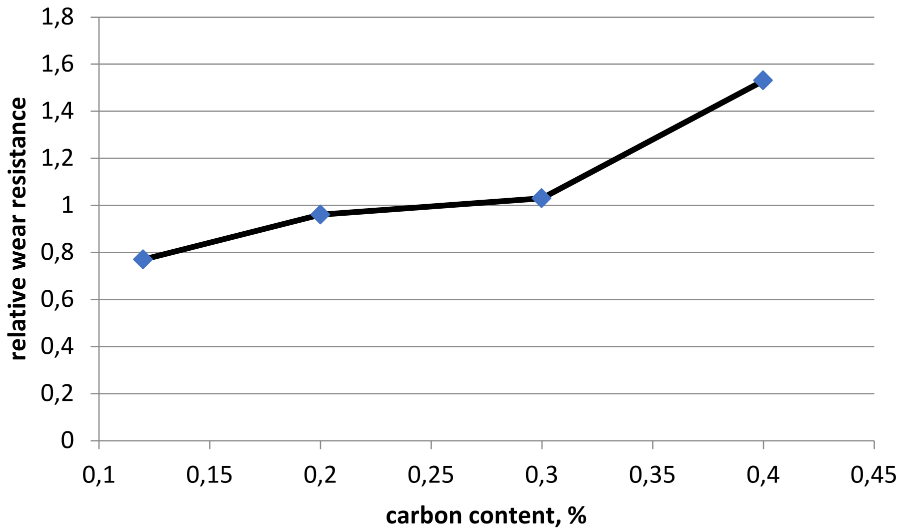


Fig. 2. Relative wear resistance change of metallized coatings depending on the carbon content in 13% Chr steel

Adhesion tests at pull-off showed that the adhesion strength of the sprayed metal to the surface of the steel sample tends to decrease as the carbon content increases from 30 MPa to 20 MPa (Table 4).

The flex module appeared to be most sensitive to the carbon content in the sprayed metal among the established mechanical properties which with an increase of carbon to 0.40% decreases by 60% in relation to the value of this indicator for the Sv-12Kh13 wire metal. The bending strength changes significantly less and is in the range of 306-348 MPa for all investigated compositions (Table 4).

Table 4. Some characteristics of coatings sprayed by the electric arc spraying method

Coating material	Adhesion by pull-off, MPa	Bending strength, MPa	Flex module, MPa
12Kh13	-	348	97950
20Kh13	30.7	318	80740
30Kh13	23.8	306	59228
40Kh13	20.1	325	39440

A decrease in the adhesion of coatings and the elastic module of the sprayed metal is connected with an increase of internal stresses in the coatings due to an increase in the size of crystal grids with the large volumes of martensitic structures.

Probably, a decrease in adhesion may be connected with an increase in the difference in the values of the elastic module of the coating material and the steel base. A negative influence of a discontinuous change in the elastic module on the adhesive and cohesive strength of the coating material is mentioned in [12,14].

4. Conclusion

Based on the data received, the following conclusions can be made:

1. The results received during our research confirm that it is reasonable to use 20Kh13 and 30Kh13 materials when restoring parts with high wear. When strengthening new products by applying coatings of relatively small thickness, it is better to use 40Kh13.
2. 30Kh13 and 40Kh13 coatings can be recommended for application to the surface of oil-submersible equipment made of less carbon high-chromium steels to increase wear resistance in contact with abrasive and mechanical impurities of the oilfield environment.
3. The transition of chromium to carbides in medium-carbon high-chromium steels depletes the matrix, which leads to a decrease in the corrosion resistance of steels of the Kh13 type. In sprayed materials these processes are suppressed, which allows us to maintain corrosion resistance when spraying higher carbon coatings that provide an increased level of hardness.

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