INFLUENCE OF CHROMIUM CONCENTRATION ON THE ABRASIVE WEAR OF Ni-Cr-B-Si COATINGS APPLIED BY HIGH VELOCITY OXYGEN FUEL

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Abstract: This research work studies the characteristics of wear and wear resistance of composite powder coatings, deposited by high velocity oxygen fuel, which contain composite mixtures Ni-Cr-B-Si having different chromium concentrations – 9.9%; 13.2%; 14%; 16% and 20%, at one and the same size of the particles and the same content of the remaining elements. The coating of 20% Cr does not contain B and Si. Out of each powder composite coatings have been prepared without any preliminary thermal treatment of the substrate and with preliminary thermal treatment of the substrate up to 650°C. The coatings have been tested under identical conditions of dry friction over a surface of solid firmly attached abrasive particles using tribological testing device „Pin-on-disk“. Results have been obtained and the dependences of the hardness, mass wear, intensity of the wearing process, absolute and relative wear resistance on the Cr concentration under identical conditions of friction. It has been found out that for all the coatings the preliminary thermal treatment of the substrate leads to a decrease in the wear intensity. Upon increasing Cr concentration the wear intensity diminishes and it reaches minimal values at 16% Cr. In the case of coatings having 20% Cr concentration the wear intensity is increased, which is due to the absence of the components B and Si in the composite mixture, whereupon no inter-metallic structures are formed having high hardness and wear resistance. The obtained results have no analogues in the current literature and they have not been published by the authors.

Key words: HVOF coatings, chromium, tribology, abrasion wear,

1. Introduction

The basic priorities of contemporary engineering science and practice refer to enhancement of energy effectiveness and functionality of the industrial systems in harmonic coexistence with clean environment, preservation of natural resources and improving of the quality of life. These priorities are connected with the genesis of tribology as contemporary science and technology for contact processes of friction, wear and greasing in the technical systems [1-3]. The lowering of the wear intensity in the machines appears to be the central task of tribology tribological technologies. It is the reason for more than 85% of the machine failures, huge expenses of materials and human resources for spare parts, consumables and expenses for maintenance in the process of operation. The decrease in the wear intensity results not only in...
lower financial expenses, but also decrease in extraction of raw materials from the natural environment, which is directly connected with the equilibrium in eco-systems [4÷10].

The abrasive and erosive wear are the most dangerous types of wear in the machines for ore mining, road construction, agricultural technique, energy production, transportation, air craft building and space technology [1]. They are the reason for more than 50% of all the technical failures due to wear of machine components and the expenses due to it in the world reach 1-4% of the gross domestic product GDP of the developed industrial countries in the world. The problem of abrasive and erosive wear resistance of tribological materials is of exceptional importance and actuality, which is evidenced by the fact that there exist 17 active standards ASTM, concerning the abrasive wear and at least 4 standards connected with the erosion wear.

It is of special importance for the high wear resistance of tribology materials to combine high hardness and plasticity, which are mutually self-excluding aspects and they cannot be achieved by most of the conventional tribology technologies [11÷24].

The composite powder coatings, deposited by means of high velocity oxygen fuel (HVOF) are a new generation of tribo-materials, allowing to achieve a wide range of combining mechanical and tribological characteristics – high adhesion strength, density, hardness, wear resistance, corrosion stability. The powder particles obtain high kinetic and thermal energy in the flame jet, passing over into semi-plastic and/or plastic state in the form of droplets or particles and they interact with the substrate being deformed, whereupon they form thin lamellas. Upon their collision with roughness of the substrate the particles- droplets are being cooled down, forming adhesion bonds with the surface and cohesion bonds between each other leading to generation of the laminar structure of the composite coating. Due to the high velocity and low contact time of the particles with oxygen under definite conditions they do not form oxides, which fact is a prerequisite for good tribological properties of the coatings [25÷26]. HVOF-coatings are the object of intensive investigations and they are continuously being improved [27÷35]. The results of studies of the authors and those of other researchers show that the mechanical and tribological characteristics of the HVOF-coatings, depend not only on the parameters of the technological regime of deposition, but also to a great extent they depend on the chemical composition and on the concentrations of the chemical elements in the powder composite material, the size of the particles and on the temperature of the substrate [29, 31, 35].

According to the specialized literature the most widely used in the practice high quality powder metal composites, known as „super alloys“, can be divided into two large groups: powder composites based on nickel: nickel – chromium – boron - silicon (Ni-Cr-B-Si) and powder composites based on cobalt: tungsten – cobalt – chromium alloys. The chromium at high temperatures is involved into contact interactions with the carbon, silicon and boron, whereupon it forms new inter-metallic structures. It forms with the carbon solid high-melting structure (Cr3C2) having a green colour, which is not dissolved in acids and which attributes to the coating high corrosion stability. Chromium forms with the oxygen some oxides (CrO3, Cr2O3), which are characterized by high hardness and fragility [33, 34].

The present publication represents the results from an investigation about the influence of chromium concentration on the abrasion wear of Ni-Cr-B-Si coatings, deposited by means of supersonic flame jet on a substrate with and without thermal treatment of the substrate.
2. Materials and technology

Ten types of HVOF-coatings have been prepared, combined in five groups of chromium concentration in the powder mixture - 9.9%, 13.2%, 14%, 16%, 20% and approximately the same composition with respect to the other chemical elements. Two types of coatings with definite Cr concentration have been obtained for each group – without thermal treatment of the substrate (cold HVOF process) and with preliminary calcination of the substrate in a thermal chamber at temperature 650° C in the course of 60 minutes. The coatings having thermal treatment of the substrate are denoted by PHS. The group of coatings №9 and №10 contain in their composition 20% Cr and 80% Ni without inclusion of other elements, which are present in the other coatings.

Table 1 represents the designation, description, chemical composition, hardness and thickness of the studied coatings.

Table 1. Description, chemical composition, hardness and thickness of the tested coatings

| Sample | Coating designation | Description | Chemical composition, wt. % | Hardness HRC | Thickness µm |
|--------|---------------------|-------------|----------------------------|--------------|--------------|
| 1      | 72M40               | Coatings without heat treatment of the substrate | Cr: 9.9; Si: 3.1; B: 1.7; Fe: 3.2; C: 0.35; Mo: 3; Cu: 3; Ni Balance | 55±56 HRC | 410±415 |
| 2      | 72M40:PHS           | Coatings with heat treatment of the substrate | Cr: 13.2; Si: 3.98; B: 2.79; Fe: 4.6; Co: 0.03; C: 0.63; Ni Balance | 58±59 HRC | 400±412 |
| 3      | 602P                | Coatings without heat treatment of the substrate | Cr: 14; Si: 4.2; B: 2.9; Fe: 4.6; C: 0.6; Mo: 2.5; Cu: 2.4; Ni Balance | 57±58 HRC | 395±400 |
| 4      | 602P:PHS            | Coatings with heat treatment of the substrate | Cr: 16; Si: 4.4; B: 3.4; Fe: 2.7; C: 0.6; Mo: 3; Cu: 3; Ni Balance | 59±60 HRC | 408±414 |
| 5      | 80M60               | Coatings without heat treatment of the substrate | Cr: 20; Ni: 80 | 57±60 HRC | 395±406 |
| 6      | 80M60:PHS           | Coatings with heat treatment of the substrate | Cr: 20; Ni: 80 | 59±60 HRC | 400±405 |
| 7      | 1355                | Coatings without heat treatment of the substrate | Cr: 16; Si: 4.4; B: 3.4; Fe: 2.7; C: 0.6; Mo: 3; Cu: 3; Ni Balance | 58±59 HRC | 394±405 |
| 8      | 1355:PHS            | Coatings with heat treatment of the substrate | Cr: 20; Ni: 80 | 61±62 HRC | 404±410 |
| 9      | HN40                | Coatings without heat treatment of the substrate | Cr: 20; Ni: 80 | 54±55 HRC | 400±408 |
| 10     | HN40:PHS            | Coatings with heat treatment of the substrate | Cr: 20; Ni: 80 | 57±60 HRC | 393±403 |

All the coatings have been deposited on a substrate of one and the same material – steel of chemical composition: C – 0.15%; S - 0.025%; Mn – 0.8%; P – 0.011%; Si – 0.21%; Cr – 0.3%; Ni – 0.3% and hardness 193.6 ± 219.5 HV.

The particles in all the powder composites have one and the same size - 45±2.5 µm. Before placing of the powder composite inside the system for thermal spraying, it is heated for 30
minutes at temperature 150°C in thermal chamber for removing the moisture and the other adsorbed organic molecules.

In order to increase the adhesion strength of the coatings the substrate is heated preliminarily in three stages: cleaning, erosion with abrasive particles (blasting) and mechanical treatment. The cleaning is aimed at the removal of mechanical contaminants, adsorbed organic molecules, moisture and other components, and it is carried out using a solvent. The extraction of the adsorbed gas molecules and elements in the depth of the surface layer is achieved by burning of the surface of the substrate with a flame to reach 100°C at a distance of the nozzle 40 mm and at an angle of 45° or with vapour spraying device. After this operation again the surface is cleaned with a solvent.

Upon erosion of the surface of the substrate (blasting) one can achieve a definite level of roughness of the substrate, which is of essential importance for the level of the adhesion strength of the coating. We used abrasive material „Grit”, in accordance with the requirements of the standard ISO 11126, having granular composition of the abrasive material in the following percentage ratio: 3.15 ÷ 1.4 mm – 9.32%; 1.63 ÷ 0.5 mm – 16.4%; 1.4 ÷ 1.0 mm – 15.8%; 1.0 ÷ 0.63 mm – 39.6%; 0.5 ÷ 0.315 mm – 9.32%; 0.315 ÷ 0.16 mm – 9.32%; particles having sizes below 0.15 mm of the various fractions – up to 100% of the following chemical compounds: SiO$_2$ – 41%, combined in the form of silicates; AlO – 8.3%, MgO – 6.6%, CaO – 5.5% and MnO – 0.4%.

The system for blasting has the following technical parameters: input pressure 8 atm; operating pressure in the nozzle – 4 atm; diameter of the nozzle 7 mm; distance between the nozzle and the surface – 30 mm; angle of interaction of the jet with the surface – 90°.

The coatings have been deposited using the device MICROJET+Hybrid, which makes use of fuel mixture of acetylene and oxygen. The parameters of the technological regime of deposition of the coatings are listed in Table 2.

**Table 2. Technological regime parameters for HVOF coating deposition**

| Parameter                              | Technological regime |
|----------------------------------------|----------------------|
| Propylene/oxygen ratio                 | 55/100, %            |
| Jet velocity                           | 1000 m/s             |
| Distance „nozzle-coating”              | 100 mm               |
| Angle between nozzle and coating       | 90°                  |
| Air pressure from compressor           | 5 bar                |
| N$_2$ pressure in the proportioning device | 4 bar             |
| Velocity of powder material feeding    | 1.5 min$^{-1}$       |
| Mass flowrate of the powder material   | 22 g/min             |

In case of deposition of coatings without thermal treatment (cold HVOF process) the surface of the substrate is heated using flame having temperature up to 200°C, which is measured by Laser infrared thermometer INFRARED.

The coating is deposited in several layers. In the case of the first layer the nozzle is situated at an angle of 45° and at a distance from the substrate 10 mm, while in the consecutive layers – at
a distance of 25 mm. Coatings have been prepared having thickness within the range from 393 µm up to 415 µm. The thickness of the coatings is measured by a portable device Pocket Leptoskop 2021 Fe in 10 points on the surface and the mean arithmetic value is taken (Table 1).

After polishing all surfaces of the coatings have the same roughness Ra=0.450 ÷0.455 µm, which is measured by recording the profile diagram using profile metering device „TESA Rugosurf 10-10G”. Samples of the same sizes have been prepared, which for the purpose of testing the abrasive wear represent plates of dimensions 25mm x 25mm x 6mm, while for testing the erosive wear the samples represent plates of dimensions 30mm x 20 mm x 6 mm.

The hardness of the coatings is measured by hardness-metering device “Bambino” based on the scale of Rockwell (HRC) taking the mean arithmetic value out of three measurements for each sample in order to eliminate some possible effects of segregation.

3. Experimental procedures

The abrasive wear of the coatings is studied under conditions of dry friction during sliding along the surface with firmly attached abrasive particles.

The methodology consists in measurement of the mass wear of the coatings after a definite pathway of friction (number of cycles) under set permanent conditions – loading, sliding velocity, kinds of the abrasive, temperature of the environment. The mass of the samples before and after after a definite pathway of friction is measured by electric balance WPS 180/C/2 with an accuracy of 0.1 mg. In each experiment with each sample the abrasive surface is replaced and prior to each measurement the sample is cleaned removing mechanical and organic particles, thereafter it is dried up using ethyl alcohol in order to prevent the electrostatic effect.

After measuring of the mass wear the wear process characteristics are calculated – reduced intensity of the wear process, the absolute or the relative wear resistance.

The mass wear in [mg] is obtained as the difference between the initial mass of the sample \( m_o \) and its mass \( m_i \) after a definite number of cycles of friction:

\[
m = m_o - m_i
\]

The reduced intensity of the wear process \( i_r \) represents the mass wear \( m \) of the coating per unit of loading \( P \) and per unit of path length \( L \) of friction. It is measured in \( mg/Nm \) and it is estimated by the formula:

\[
i_r = \frac{m}{P \cdot L}
\]

The absolute abrasive wear resistance \( I_r \) is represented as the reciprocal value of the reduced intensity and it has dimension \( Nm/mg \), i.e.

\[
I_r = \frac{1}{i_r} = \frac{P \cdot L}{m}
\]
The relative wear resistance $R_{i,j}$ is a dimensionless quantity and it represents the ratio between the wear resistance of the tested sample $I^i_r$ and the wear resistance of a sample, taken as a standard $I^j_r$, determined during identical regimes of friction, i.e.

$$R_{i,j} = \frac{I^i_r}{I^j_r} \quad (4)$$

The abrasive wear is studied using tribological tester „Pin-on-disc” in case of plane-like contact using the functional scheme, shown in Fig.1. The studied sample with coating 1 (pin) is firmly attached in the holder 2 of the loading head 8, in such a way that the frontal surface of the sample is in contact with the abrasive surface 3, fixed to a horizontal disc 4. The disc 4 is driven by the electric motor 6 and it is rotating around its central vertical axis at constant angle velocity. The normal loading pressure $P$ is adjusted by means of the lever system in the center of the contact plate between the sample and the abrasive surface. The pathway length of friction as a number of cycles ($N$) is selected and then measured by the turnover number metering device 7. The abrasive surface 3 is modeled by impregnated corundum P 320 of hardness 9.0 on the scale of Moos, whereupon the requirement of the standard for minimum 60% higher hardness of the abrasive is observed with respect to that of the surface layer of the tested materials.

![Fig. 1. Schematic diagram of abrasive wear testing on pin-disc tribometer](image)

The investigation of all the coatings has been carried out using a set of the following parameters of the regime of friction: loading 4.5 N, nominal contact surface area $2.25 \times 10^{-6}$ m$^2$; nominal contact pressure 2.0 N/cm$^2$, sliding velocity of 0.155 m/s; type of the abrasive surface - Corundum P 320, temperature of the environment $21^\circ$C.

4. Experimental results and discussion

Applying the above described methodology and the device experimental results have been obtained for the mass wear process, the reduced intensity, the absolute and the relative wear resistance for all the studied coatings, listed in Table 1.
The results are represented in the Tables 3, 4 and 5.

In accordance with the data in Table 3 the kinetic curves have been plotted in regard to the mass wear for all coatings with and without thermal treatment of the substrate, represented in the Figures 2, 3, 4, 5 and 6. Each plotted graph represents regression equations of the wearing process as a function of the length of the friction pathway \( m=m(L) \) and the value of the wear intensity \( \dot{i}_r \) at friction pathway length \( L=80 \, m \). It is seen that in the case of dry abrasive friction the dependence of the mass wear as a function of the sliding pathway has linear character for coatings with and without thermal treatment of the substrate.

**Table 3. Abrasive wear of tested coatings**

| Sample | Coating designation | Number of cycles (N) | Sliding distance, m |
|--------|---------------------|----------------------|---------------------|
|        |                     | 100                  | 200 | 300 | 400 |
| 1      | 72M40               | 4.7                  | 8.5 | 12.7| 15.3|
| 2      | 72M40:PHS           | 3.2                  | 5.8 | 11.2| 12.6|
| 3      | 602P                | 4.4                  | 7.9 | 10.6| 12.3|
| 4      | 602P:PHS            | 3.5                  | 7.1 | 9.8 | 10.4|
| 5      | 80M60               | 4.0                  | 6.0 | 7.6 | 10.5|
| 6      | 80M60:PHS           | 3.1                  | 4.2 | 5.8 | 7.6 |
| 7      | 1355                | 1.5                  | 2.2 | 2.8 | 3.3 |
| 8      | 1355:PHS            | 0.9                  | 1.2 | 1.6 | 1.8 |
| 9      | HN40                | 2.9                  | 5.6 | 7.6 | 10.4|
| 10     | HN40:PHS            | 1.8                  | 4.1 | 6.3 | 9.1 |

**Table 4. Wear intensity of the tested coatings**

| Sample | Coating designation | Number of cycles (N) | Sliding distance, m |
|--------|---------------------|----------------------|---------------------|
|        |                     | 100                  | 200 | 300 | 400 |
| 1      | 72M40               | 5.22 x 10^{-2}       | 4.71 x 10^{-2}     | 4.71 x 10^{-2} | 4.24 x 10^{-2}|
| 2      | 72M40:PHS           | 3.56 x 10^{-2}       | 3.22 x 10^{-2}     | 4.15 x 10^{-2} | 3.51 x 10^{-2}|
| 3      | 602P                | 4.89 x 10^{-2}       | 4.4 x 10^{-2}      | 3.93 x 10^{-2} | 3.42 x 10^{-2}|
| 4      | 602P:PHS            | 3.89 x 10^{-2}       | 3.96 x 10^{-2}     | 3.62 x 10^{-2} | 2.89 x 10^{-2}|
| 5      | 80M60               | 4.44 x 10^{-2}       | 3.33 x 10^{-2}     | 2.82 x 10^{-2} | 2.91 x 10^{-2}|
| 6      | 80M60:PHS           | 3.44 x 10^{-2}       | 2.33 x 10^{-2}     | 2.16 x 10^{-2} | 2.11 x 10^{-2}|
| 7      | 1355                | 1.67 x 10^{-2}       | 1.22 x 10^{-2}     | 1.04 x 10^{-2} | 0.91 x 10^{-2}|
| 8      | 1355:PHS            | 1.0 x 10^{-2}        | 0.67 x 10^{-2}     | 0.58 x 10^{-2} | 0.49 x 10^{-2}|
| 9      | HN40                | 3.22 x 10^{-2}       | 3.11 x 10^{-2}     | 2.82 x 10^{-2} | 2.89 x 10^{-2}|
| 10     | HN40:PHS            | 2.0 x 10^{-2}        | 2.22 x 10^{-2}     | 2.33 x 10^{-2} | 2.51 x 10^{-2}|
Table 5. Wear resistance of the tested coatings

| Sample | Coating designation | Number of cycles (N) | Sliding distance, m | Wear resistance, m.N/mg |
|--------|---------------------|----------------------|--------------------|--------------------------|
|        |                     | 100                  | 200                | 300                      | 400                      |
| 1      | 72M40               | 0.19 x 10²            | 0.21 x 10²         | 0.21 x 10²               | 0.24 x 10²               |
| 2      | 72M40:PHS           | 0.28 x 10²            | 0.31 x 10²         | 0.24 x 10²               | 0.28 x 10²               |
| 3      | 602P                | 0.20 x 10²            | 0.23 x 10²         | 0.25 x 10²               | 0.29 x 10²               |
| 4      | 602P:PHS            | 0.26 x 10²            | 0.25 x 10²         | 0.28 x 10²               | 0.35 x 10²               |
| 5      | 80M60               | 0.23 x 10²            | 0.30 x 10²         | 0.35 x 10²               | 0.34 x 10²               |
| 6      | 80M60:PHS           | 0.29 x 10²            | 0.42 x 10²         | 0.46 x 10²               | 0.47 x 10²               |
| 7      | 1355                | 0.60 x 10²            | 0.82 x 10²         | 0.96 x 10²               | 1.10 x 10²               |
| 8      | 1355:PHS            | 1.00 x 10²            | 1.49 x 10²         | 1.72 x 10²               | 2.04 x 10²               |
| 9      | HN40                | 0.31 x 10²            | 0.32 x 10²         | 0.35 x 10²               | 0.35 x 10²               |
| 10     | HN40:PHS            | 0.50 x 10²            | 0.45 x 10²         | 0.43 x 10²               | 0.40 x 10²               |

The second observation in the analysis of these curves refers to the fact that the wear of all coatings having thermal treatment of the substrate is less than the wear of the coatings without any thermal treatment of the substrate.

Fig. 2. Mass wear vs. sliding distance for 72M40 and 72M40: PHs coatings
Fig. 3. Mass wear vs. sliding distance for 602P and 602P: PHS coatings

Fig. 4. Mass wear vs. sliding distance for 80M60 and 80M60: PHS coatings
Figure 7 represents graphically the dependence of the wear intensity on the concentration of chromium for coatings without thermal treatment of the substrate and for coatings with thermal treatment of the substrate for one and the same friction pathway length $L = 80\, m$.

The curves have non-linear character with a clearly expressed minimum of the wear intensity at 16% concentration of Cr for coatings with and without thermal treatment. In the first section, in which the chromium concentration is changing within the range from 9.9% to 16% upon increasing of the chromium concentration the wear intensity decreases down to reaching a minimal value at chromium concentration 16% respectively: for coatings without thermal treatment of the substrate $i_r = 0.91 \times 10^{-2}$ mg/Nm and for coatings with thermal treatment of the substrate $i_r = 0.49 \times 10^{-2}$ mg/Nm. In the second section at higher chromium concentration 20% (coatings HN40 and HN40: PHS) the wear intensity is increasing sharply. In spite of the higher chromium concentration the increase in the wear is due to the absence of the elements B, Si, Cu.
and the others, which are contained in the other coatings. These elements in the process of contact interaction of the flame jet with the substrate at the high temperature are forming inter-metallic compounds with the chromium, which lead to decrease in the wear intensity [...].

The curve of the dependence of the wear resistance on the concentration of chromium in coatings without thermal treatment and with thermal treatment of the substrate is reciprocal to the curve of wear intensity (Figure 8).
Figure 9 shows the diagram of the wear resistance of all the tested coatings, which gives clear evidence, that the lowest wear resistance is displayed by coatings having the lowest concentration of chromium without thermal treatment of the substrate - $I_r = 0.24 \times 10^2$ Nm/mg, while the greatest wear resistance is manifested by the coatings having 16% content of chromium with thermal treatment of the substrate - $I_r = 2.04 \times 10^2$ Nm/mg.

Table 6 represents results on the relative wear resistance, calculated by the formula (4). The last two columns reflect the results respectively for the influence of the thermal treatment of the substrate and the effect of chromium concentration in the powder composites. These results are represented in the form of diagrams in Figures 10 and 11.

**Table 6. Relative abrasive wear resistance of the tested coatings**

| Sample | Coating designation | Wear resistance, mN/mg in the sliding distance 80 m | Relative abrasive wear resistance |
|--------|---------------------|---------------------------------------------------|---------------------------------|
| 1      | 72M40               | $0.24 \times 10^2$                                | Influence of heat treatment of the substrate $R_{1,1} = 1$ |
| 2      | 72M40:PHS           | $0.28 \times 10^2$                                | Influence of the concentration of Cr, % $R_{1,1} = 1$ |
| 3      | 602P                | $0.29 \times 10^2$                                | $R_{3,3} = 1$                   |
| 4      | 602P:PHS            | $0.35 \times 10^2$                                | $R_{4,3} = 1.21$                |
| 5      | 80M60               | $0.34 \times 10^2$                                | $R_{5,5} = 1$                   |
| 6      | 80M60:PHS           | $0.47 \times 10^2$                                | $R_{6,5} = 1.38$                |
| 7      | 1355                | $1.10 \times 10^2$                                | $R_{7,7} = 1$                   |
| 8      | 1355:PHS            | $2.04 \times 10^2$                                | $R_{8,5} = 1.84$                |
| 9      | HN40                | $0.35 \times 10^2$                                | $R_{9,9} = 1$                   |
| 10     | HN40:PHS            | $0.40 \times 10^2$                                | $R_{10,9} = 1.14$               |
The strongest influence on the wear resistance is observed for the thermal treatment of the substrate in the case of the coating 1355:PHS having concentration of chromium 16%, for which the wear resistance is 1.84 times higher than that of the same coating without thermal treatment of the support. Next to it follows the coating 80M60:PHS with concentration of chromium 14%. For the remaining coatings the influence of the thermal treatment is almost one and the same ranging from 1,14 to 1,21.

The influence of the concentration of chromium upon the abrasive wear resistance of the coatings is the greatest in the cases of the coatings 1355:PHS and 1355 (16% Cr). For coating with thermal treatment (the coating 1355:PHS) the wear resistance is increased 7,29 times, while for the same coating without thermal treatment (the coating 1355) it is increased 4,58 times,
which is an extraordinary result. Another good result is the increase in the wear resistance of the coatings 80M60:PHS and HN40:PHS, which becomes higher almost to the same degree - respectively 1.68 and 1.67 times. The results on the wear resistance correlate with the hardness of the coatings having different concentrations of Cr (Figure 12).

![Diagram of the influence of Cr concentration on the hardness of the tested coatings](image)

**Fig. 12.** Diagram of the influence of Cr concentration on the hardness of the tested coatings

Figure 13 illustrates the diagram of the interconnection between the abrasive wear resistance and the hardness of the tested coatings.

![Diagram of abrasive wear resistance and hardness of the tested coatings](image)

**Fig. 13.** Diagram of abrasive wear resistance and hardness of the tested coatings
5. Regression models

The experimental curve of the dependence of the wear intensity $i_r$ on the chromium concentration in the range $9.9\% \leq w \leq 16\%$ is considered (fig.14).

The section of the curve where $w > 16\%$ is not considered because it includes coatings №9 and №10 (HN40 and HN40:PHS) with different chemical composition from the other coatings. These coatings contain only nickel (80%) and chromium (20%), which does not give us reason to analyze them in parallel with the other coatings.

Experimental results for the wear intensity at more points on the curve in fig. 7 are presented in Table 7. Graphically, the dependence of the wear intensity on the percentage of chromium is shown in fig. 14.

| $w$, Concentration of Cr, (%) | 9.9  | 11.8 | 13.2 | 14.0 | 15.2 | 16.0 |
|-----------------------------|------|------|------|------|------|------|
| $i_r$, intensity of wear, mg/Nm, without heat treatment of the substrate | 4.24 | 3.82 | 3.42 | 2.91 | 2.1  | 0.91 |
| $i_r$, intensity of wear, mg/Nm, with heat treatment of the substrate | 3.51 | 3.35 | 2.89 | 2.11 | 1.35 | 0.49 |

Based on the regression analysis, analytical dependences of the wear intensity on the chromium concentration were obtained, presented as second- and third-degree polynomials.

For coatings without heat treatment of the substrate the dependence has the following form

$$i_r(w) = a_3w^3 + a_2w^2.$$  \hspace{1cm} (5)

The results are presented on the next figure.
Fig. 13. Analytical dependences of the wear intensity on the chromium concentration for coatings without heat treatment.

The Adjusted R Square is 0.745894827 and shows that 74.58% of the variance of the intensity of wear is predictable from chosen factors \( w^3, w^2 \), i.e. i.e. they are adequately included in the model. The value of the significance F with significance level 0.05 is 0.00012<0.05 (0.012%<5%), i.e. the results are reliable (statistically significant) and the model is adequate. P-values of the coefficients of the regression equations with level of significance 0.05 are smaller than 0.000032, i.e. they are smaller than 0.05, which means that the coefficients are statistically significant, and the adequacy of the model is confirmed.

For coatings without heat treatment of the substrate the dependence has the following form:

\[
 i_r(w) = -0.00599819w^3 + 0.099501902w^2.
\]

The results are presented on the next figure.
The Adjusted $R^2$ is 0.74616892 and shows that 74.62% of the variance of the intensity of wear is predictable from chosen factors ($w^3$, $w^2$), i.e. they are adequately included in the model. The value of the significance $F$ with significance level 0.05 is 0.00011<0.05 (0.011%<5%), i.e. the results are reliable (statistically significant) and the model is adequate. P-values of the coefficients of the regression equations with level of significance 0.05 are smaller than 0.000019, i.e. they are smaller than 0.05, which means that the coefficients are statistically significant, and the adequacy of the model is confirmed.

6. Conclusions

The present research work represents comparison of results for the characteristics of the wear process and the wear resistance of composite powder coatings, deposited by means of high velocity oxygen flame (HVOF), which contain composite mixtures Ni-Cr-B-Si having different concentrations of chromium – 9.9%; 13.2%; 14%; 16% and 20%, at one and the same size of the particles 45 µm and equal content of the other elements boron and silicon. The coating, prepared to have 20% Cr, does not contain the elements B and Si. Each powder composition was applied to obtain coating without preliminary thermal treatment of the substrate and with preliminary thermal treatment of the substrate up to 650°C. The coatings have been tested under identical regimes of dry friction along the surface with firmly attached abrasive particles using a tribotester „Pin-disc“.

Results have been obtained on the dependence of the mass wear as a function of the length of the pathway of friction, the variation of the wear intensity depending on the concentration of chromium for coatings without thermal treatment of the substrate and with thermal treatment of the substrate.

It has been ascertained that for all coatings the preliminary thermal treatment of the substrate leads to a decrease in the wear intensity.

It has been shown that upon increasing the concentration of chromium the wear intensity is decreasing non-linearly, whereupon it reaches minimal values at 16% Cr. In the case of coatings
having 20% concentration of Cr the wear intensity is higher, which is due to the absence of the components B and Si in the composite mixture. In this case no new inter-metallic structures are formed, having high hardness and high wear resistance. A diagram of the interconnection between the hardness of the coatings and their abrasive wear resistance is represented.

Based on the regression analysis, analytical dependences of the wear intensity on the chromium concentration for coatings without heat treatment and with heat treatment of the substrate, presented as polynomials of second and third degree, were obtained.

References

[1] Pawlowski L. The Science and Engineering of thermal Spray Coatings (John Wiley & Sons) Chichester (2008).

[2] HOLMBERG K., A. MATTHEWS: Coatings Tribology: Properties, Mechanisms, Techniques and Applications in Surface Engineering. Amsterdam: Elsevier, (2009).

[3] BHUSHAN B., Nanotribology, Nanomechanics and Materials Characterization Studies and Application to Bio/Nanotechnology and Biomimetics, Proceedings, SERBIATRIB’11, Kragujevac, 3 (2011)

[4] Stachowiak G and Batchelor AW Engineering Tribology (Elsevier) (2014).

[5] B. Bhushan: Principles and Applications of Tribology. New York: John Wiley & Sons, (2013).

[6] Kandeva M, Karastoyanov D and Vencl A Advanced Tribological Coatings for Heavy-Duty Applications: Case Studies (Sofia: Prof. Marin Drinov Publishing House of Bulgarian Academy of Sciences) (2016).

[7] Vencl A., Optimization of the deposition parameters of thick atmospheric plasma spray coatings (Journal of the Balkan Tribological Association 18(3), 405 (2012).

[8] Kandeva M., I. Peichev, N. Kostova, K. Stoichkov, Complex Study of Surface layers and Coatings, J Balk Tribol Assoc, 17(3), 387 (2011).

[9] Petrov T., P. Tashev, M. Kandeva, Wear Resistance of Surface Layers Modified with AL₂O₃ and TiCN Nanopowders Weld Overlaid Using TIG and ITIG Methods, Journal of the Balk Tribol Assoc, 22(1), 304 (2016)

[10] Tashev P., R. Lazarova, M. Kandeva, R. Petrov, V. Manolov, Tungsten Inert Gas Weld Overlay Using Nano-Sized Tin Powder, Journal of the Balk Tribol Assoc, 22(3-II), 2916, (2016)

[11] Dimitrova, R, Kandeva M., Kamburov, V., Jordanov, M., Mechanical and Tribological Characteristics of Hardfaced Dispersive Reinforced Aluminium Metal Matrix Layers, Journal of Balk Tribol Assoc, 23(4), 641 (2017)

[12] Kandeva M., Penyashki, T., Kostadinov, G., Kalitchin, Zh., Kaleicheva, J., Wear of Electroless Nickel-Phosphorus Composite Coatings with Nanodiamond Particles, Journal of Environmental Protection and Ecology, 19 (3), 1200 (2018)
[13] Kandeva M., V. Kamburov, Zadorozhnaya, E., Kalitchin, Zh., Abrasion Wear of Electroless Nickel Composite Coatings Modified with Boron Nitride Nanoparticles, Journal of Environmental Protection and Ecology, 19(4), 1690 (2018).

[14] P. Kovac, D. Jesic, S. Sovilj-Nikic, M. Kandeva, Zh. Kalitchin, M. Gostimirovic, B. Savkovic, Energy Aspects of Tribological Behaviour of Nodular Cast Iron, Journal of Environmental Protection and Ecology, 19(1), 163 (2018)

[15] Kandeva M., T. Grozdanova, D. Karastoyanov, E. Assenova, Wear Resistance of WC/Co HVOF-Coatings and Galvanic Cr Coatings Modified by Diamond Nanoparticles, 13th International Conference on Tribology ROTRIB’16, (2016), Galați, Romania, IOP Conf. Series: Materials Science and Engineering, 174, (2017) 012060 doi:10.1088/1757-899X/174 (1) 012060

[16] Kandeva M., V. Balabanov, E. Zadorozhnaya, Zh. Kalitchin, P. Svoboda, Environmental Protection by Self-Organisation of Tribosystems with Self-Lubricating Materials in Dry Friction: Part I. Investigations at different loads, Journal of Environmental Protection and Ecology, 18 (3), 1050, (2017)

[17] Kandeva M., V. Balabanov, E. Zadorozhnaya, Zh. Kalitchin, P. Svoboda, I. Levanov: Environmental Protection by Self-Organisation of Tribosystems with Self-Lubricating Materials in Dry Friction. Part II: Investigations at Different Dry Sliding Rates, Journal of Environmental Protection and Ecology, 18 (4), 1581 (2017)

[18] Kandeva M., P. Svoboda, N. Nikolov, T. Todorov, Y. Sofronov, M. Pokusová, A. Vencl. Effect of Silicon Carbide Nanoparticles Size on Friction Properties of Electroless Nickel Coatings. Journal of Environmental Protection and Ecology, 21(4), 1314 (2020),

[19] Kandeva M., V.Kamburov, K.Nikolov, L. Dimitrov, Abrasive Wear of Ultra-High-Molecular-Weight Polyethylene Modified with Carbon Nanotubes, Journal of the Balkan Tribological Association, 26(2), 272 (2020),

[20] Kandeva M., N. Stoimenov, B. Popov, Zh. Kalitchin, V. Pozhidaeva, Abrasive Wear Resistance of Micro- and Nano-Diamond Particles, Journal of the Balkan Tribological Association, , 26(2), 181 (2020).

[21] Dyakova V., Pl. Tashev, M. Kandeva, Study on the Effect of Nanosized Particles of Tin and SiC on the Wear Resistance, Microstructure and Corrosion Behavior of Overlay Weld Metal, Journal of the Balkan Tribological Association, 26(1), 56 , (2020)

[22] Alaci St., L. Irimescu, F. Ciornei, M. Kandeva, Device and Method for Simultaneous Determination of Rolling and Spinning Friction in a Concentrated Contact, Journal of the Balkan Tribological Association, , 26(1), 1 (2020)

[23] Kandeva M., Yu. Rozhdestvensky, P. Svoboda, Zh. Kalitchin, E. Zadorozhnaya, Influence of the Size of Silicon Carbide Nanoparticles on the Abrasive Wear of Electroless Nickel Coatings. Part 1, Journal of Environmental Protection and Ecology, , 20(4), 1889 (2019)
[23] Kandeva M., Yu. Rozhdestvensky, P. Svoboda, Zh. Kalitchin, E. Zadorozhnaya, Influence of the Size of Silicon Carbide Nanoparticles on the Abrasive Wear of Electroless Nickel Coatings. Part 2, Journal of Environmental Protection and Ecology 21(1), 222 (2020)

[24] Kandeva M., Zh. Kalitchin, P. Svoboda, S. Sovilj-Nikic, General Methodology for Studying the Tribological Processes on the Basis of the Communicative Potential, Journal of the Balkan Tribological Association, 25(2), 432, (2019)

[25] Oksa M, Turunen E, Suhonen T, Varis T and Hannula S 2011 Optimization and characterization of high velocity oxy-fuel sprayed coatings (Techniques, materials and applications Coatings Vol 1 No 1) pp 17-52

[26] Mrdak M R, Vencl A, Nedeljković B D and Stanković M 2013 Influence of plasma spraying parameters on properties of the thermal barrier coatings (Materials Science and Technology Vol 29 No 5) pp 559-567.

[27] Wood R J K and M Roy Tribology of thermal-sprayed coatings (Surface Engineering for Enhanced Performance against Wear) Ed M Roy (Wien: Springer) pp 1, (2013).

[28] Cabral-Miramontes J A, Gaona-Tiburcio C, Almeraya-Calderón F, Estupiñan-Lopez F H, Pedraza-Basulto G K and Poblano-Salas C A Parameter studies on high-velocity oxy-fuel spraying of CoNiCrAlY coatings used in theater on astatic industry (International Journal of Corrosion Article ID 703806) (2014).

[29] Chivavibul P, Watanabe M, Kuroda S, Kawakita J, Komatsu M, Sato K and Kitamura J Effect of powder characteristics on properties of warm-sprayed WC-Co coatings Journal of Thermal Spray Technology 19 (1), 81 (2010).

[30] Liu Y, Fischer T E and Dent A Comparison of HVOF and plasma-sprayed alumina/titania coatings – Microstructure, mechanical properties and abrasion behaviour Surface and Coatings Technology 167(1), 68 (2003)

[31] Kandeva, M., Grozdanova, T., Karastoyanov, D., Ivanov, P., Kalichin, Zh., Tribology Study of High-Technological Composite Coatings Applied Using High Velocity Oxy-Fuel, IOP Conference Series: Materials Science and Engineering, (2018), 295, (1), Art. No 012025, ISSN:1757-8981, 9th International Conference on Tribology, Balkantrib 2017; Cappadocia, Nevsehir; Turkey; 13 September 2017 through 15 September 2017; Code 135934

[32] Kandeva M., B. Ivanova, D. Karastoyanov, T. Grozdanova, E. Assenova, Abrasive Wear of High Velocity Oxygen Fuel (HVOF) Superalloy Coatings under Vibration Load, 13th International Conference on Tribology ROTRIB’16, (2016), Galați, Romania, IOP Conf. Series: Materials Science and Engineering, 174, (2017) 012010 doi:10.1088/1757-899X/174 (1) 012010

[33] Kandeva M., Zadorozhnaya, E., Kalitchin, Zh., Svoboda, P., Tribological Studies Of High Velocity Oxy-Fuel (HVOF) Superalloy Coatings, Journal of the Balkan Tribological Association, 24, (3), 411-428, (2018)
[34] Kandeva M., P. Svoboda, Zh. Kalitchin, T. Penyashki, G. Kostadinov, Wear of Gas-Flame Composite Coatings with Tungsten and Nickel Matrix. Part I. Abrasive Wear, Journal of Environmental Protection and Ecology, 20 (2), 811-822 (2019)

[35] Penyashki T., G. Kostadinov, D. Radev, M. Kandeva, Comparative Studies of Tribological Characteristics of Carbon Steels with Gas Flame Coatings from New Multi-component Carbide Composite Materials, Journal Oxidation Communications, (1), 74-90 (2019).