Vol. 42 No 1 2019



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Vol. 42 (1), 2019

ISSN 0209-4541

Composite materials - coatings

COMPARATIVE STUDIES OF TRIBOLOGICAL CHARACTERISTICS OF CARBON STEELS WITH GAS FLAME COATINGS FROM NEW MULTI-COMPONENT CARBIDE COMPOSITE MATERIALS

T. PENYASHKI^{a*}, G. KOSTADINOV^a, D. RADEV^b, M. KANDEVA^{c,d}

"Institute of Soil Sciences, Agro-technologies and Plant Protection 'N. Pushkarov'

3 Shose Bankya Street, Sofia, Bulgaria

E-mail: tpeniashki@abv.bg

Ill3 Sofia, Bulgaria Inorganic Chemistry, 'Acad. G. Bontchev' Street, Bl. 11

*Faculty of Industrial Engineering, Tribology Centre, Technical University – Sofia, 8 Kl. Ohridski Blvd., 1000 Sofia, Bulgaria

E-mail: kandevam@gmail.com

South Ural State University, 76 Prospekt Lenina, Chelyabinsk, Russia

BSTRACT

ultra-hard phases - WC, TiB2, B4C and others both individually and in combinations order to maximise the adhesion and wear resistance of the resulting coatings, and hence and tungsten carbide WC on the rate of wear and on wear resistance, as well as the with each other in different ratios. The wear of the coatings under conditions of dry this purpose, are selected conventional composite powders - semi-self-fluxing alloys the operating lifetime of the contact surfaces in terms of resistance to abrasion. For by gas-fuel spraying on carbon steels. The choice of powder compositions is made in ture and different phase composition has been obtained and studied in the present work A new type of wear-resistant and high-hard composite coatings with a complex strucproperties have been defined. analysis, appropriate materials for deposition of coatings with optimum tribologica tions, has been determined. On the basis of the experimental data and comparative relation of abrasive wear with the proportions of components in the powder composireduced the wear of the coated surfaces. The influence of the additions of B₄C, TiB₂ friction is investigated. It has been found that new composite coatings have repeatedly based on Ni-Cr-Co-B-Si to which tungsten carbide alloys BK8 have been added, and

Keywords: Gas flame spraying, WC, B₄C, TiB₂, wear resistance coatings, microstructure, microhardness, self-fluxing alloys.

AIMS AND BACKGROUND

The diversity and complexity of the processes and operating conditions and friction in which wear takes place have led to the creation of numerous methods and means of coatings, on the basis of which various apparatus and equipment were developed. Each of the presently known methods has its advantages, suitable applications and disadvantages that limit the scope of its application.

Gas flame spraying (GFS) (Refs 1–7) is one of the most versatile, lightweight and affordable methods for applying wear-resistant coatings. Through this method can be applied coatings from any materials onto non-metallic and metal surfaces with a thickness up to several millimetres on most diverse in size and shape details, on large and limited areas^{1,2,5–7}. The essence of the method consists in a shock reaction between particulate driven at a high speed in the flame jet and the surface of the material (substrate) on which is deposited the coating^{1,2,5,7}. Fuel (kerosene, acetylene, propylene and hydrogen) and oxygen are fed into a combustion chamber where the hot flame with a temperature > 3000°C flows under high pressure through the nozzle^{1,5,7}.

The powder particles are fed from the nozzle into the flame jet, pass into a plastic and/or semi-plastic state and after contact with the substrate due to the high kinetic energy, they form the coating with adhesion and cohesive contact bonds with the base surface⁸⁻¹¹. Bonding is achieved by diffusion of the alloys into the base metal. Bonding of the coating alloy and base metal is similar to that obtained in brasing: a liquid phase is linked with a solid phase, by diffusion^{9,11}.

One of the main problems of gas thermal spray coatings is their porosity, lack of homogeneity on account of poor agglomeration of powder particles, high roughness of surface and low adhesion to substrate. These result in insufficient corrosion and wear resistance of such coatings^{3,4,8–11}. Increasing the wear resistance of the gas flame coatings is related to the development of new materials and technologies to increase adhesion and uniformity, as well as the hardness of the contact surfaces.

The purpose of the present work is to obtain new coatings with improved hardness, wear resistance and triboefficiency from composite materials based on hardalloy compounds, metals and additives from super-hard materials by gas thermal spray deposition.

To obtain a higher wear resistance, was carried out investigation and establishing of suitable powder compositions for gas flame spraying (GFS) and a comparative study of the quality characteristics and the tribological properties of the resulting coatings.

The main issues of this task are the selection of components of the layering material and their quantitative ratio. In the selection of the composition of the material was also taken into account the change of its properties in the process of gas thermal spraying.

^{*} For correspondence.

EXPERIMENTAL

thermal spray torch (Fig. 1). Application of coatings was carried out using a 'SuperJet-S-Eutalloy' oxy-acetylene

Substrate. The coatings were applied on square plates measuring $10 \times 10 \times 4$ and 15×10 application includes mechanical treatment, cleaning, and blasting (erosion). substrate hardness range is 190-210 HV. Preparation of the substrate prior to coating 15×5 and $\times 6$ mm from steel 45 with a chemical composition given in Table 1. The



Fig. 1. Device for manual gas fuel deposition (reproduced by permission of Castolin Eutectic?)

Table 1. Chemical composition (wt.%) of the coated material (medium-carbon steel substrate)

balance	< 0.25	<0.04	< 0.04	< 0.30	0.5-0.8	0.17-0.37	0.42-0.50	Percentage
Fe	Cr	S	P	Z	Mn	Si	С	Element

obtained dense and uniform coatings. coatings, were selected conditions suitable for gas flame spraying in which solid are evaluation of the uniformity, density, roughness, grain size of porosity of the resulting tested materials were applied coatings on steel substrates. After visual comparative Initially, in a wide range of values of technological parameters with each of the

Parameters of application modes:

Combustion gases: acetylene, oxygen;

Pressure of $O_2 - 4$ bars;

Acetylene pressure – 0.7 bars;

Spray distance $\approx 120-130$ mm;

Angle of impact – 90 degree;

Powder flow rate – 20–25 g/min;

Flame temperature ≈ 3000°C Preheating – to 350–400°C;

Methodology of measurements:

the mass loss of tested samples. - Balance WPS 180/C/2, which has 0.0001 g sensitivity, was used to determine

- a VT-300 digital microscope (Fig. 4). were measured by using a Profilometer - AR-132B and Pocket Leptoskop 2021 Fe (Figs 2 and 3). Density, uniformity and morphology of coatings were monitored by - The surface roughness R_a , μ m, and thickness B, μ m, of the resulting contingu
- a Hardometer Al 150A (Fig. 5). The determination of the surface hardness of the coatings was performed with



Fig. 2. Profilometer - AR-132B



Fig. 3. Pocket Leptoskop 2021 Fe



Fig. 4. VT-300 digital microscope

sectional sections by metallographic microscope 'Neophot 22' (Germany) - The microstructure of the coatings was studied by optical microscopy on cross-

- The distribution of elements in the surface layer and microstructural analysis of the coatings along with the interface region were performed with the support of electron microscope 'Bruker' by scanning and transmission electron microscopy (SEM and TEM).
- The tribological properties and wear resistance of the coatings were investigated by comparative tests of friction with tribotester type 'Thumb-disk' under dry surface friction with hard-fixed abrasive particles (Fig. 6). The wear characteristics test method consists in measuring the mass wear *m* of the samples for a specific friction path *L* (friction cycles) under constant conditions—load *P* and glide speed *V* (Refs 8 and 12).



Fig. 5. Micro hardometer Al 150A

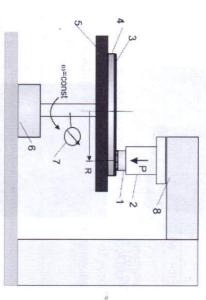


Fig. 6. Tribotester type 'Thumb-disk'

The following wear characteristics were calculated:

– Mass wear:

$$m = m_0 - m_p \text{ mg} \tag{1}$$

where m_0 is the mass of the sample before friction; m_i – the mass of the sample after friction.

– Specific wear (i_s): the ruptured mass of friction from the surface layer for normal load P = 1 N per friction path L = 1 m and nominal contact area $A_a = 1$ mm²:

$$i_5 = m/(PL), \, \text{mg/N m}$$
 (2)

Wear intensity – the amount of wear per unit of friction work:

$$I = m/(PL)$$

where m is the wear of the solid for the test time; P – the normal load, and L – the friction path passed;

— Wear resistance (I_s) : Reciprocal value of the wear intensity.

The experimental conditions for testing the wear of the test coatings are given in Table 2.

Table 2. Parameters of the experiment in studying the wear of the tested coatings

10	9	8	7	6	S	4	w	2	<u>, </u>	No	
10 abrasive surface	ambient temperature	sliding speed of the contact centre site	friction time	the friction path of the centre of the contact site	distance between the axis of rotation and the centre of the contact site	speed of rotation	nominal contact pressure	nominal contact area	normal load	Parameter	**
Corund P 120	T₀ = 20°C	$V_{\rm c} = 0.8 {\rm m/s}$	$t = 5 \min$	$S_c = 238.64 \text{ m}$	$R_c = 80 \text{ mm}$	$n = 95 \text{ min}^{-1}$	$P_{\rm a} = 44.4 \rm N/cm^2$	$A_{\rm a} = 2.25 {\rm cm}^2$	P = 100 N	Value	C

RESULTS AND DISCUSSION

RESEARCH AND SELECTION OF MATERIALS FOR GAS FLAME SPRAYING

One of the main factors determining the efficiency of the process is the choice of the coating material, which must have sufficient flexural and destructive strength, and to contain the necessary components in order to obtain an adhesive layer with predetermined chemical and physical-mechanical properties.

To coating materials most often a complex of properties is required, such as: high wear resistance; high rigidity; strength and toughness; strong connection with the substrate; heat resistance; chemical resistance at high temperatures and low chemical affinity to the other friction material; corrosion resistance; high quality features; low friction coefficient; good thermal conductivity; low coefficient of thermal expansion; technological and economic requirements.

A necessary and important condition for creating a good coating is the formation of a strong bond between the substrate and the covering materials. In this case the nature of the materials of the substrate and the powder particles and their energy state during the connection are determining factors for the formation of a strong bond^{8,9,11,12}.

How more the components of the coating material in size and structure of the crystal lattice are more similar to the substrate material and the greater their solubility in the substrate material, the more compounds and solid solutions will be obtained which provide a strong metallurgical bond with the substrate^{13–16}.

Gas flame spraying is accompanied by rapid specific chemical-thermal phenomena, occurring at high temperatures and pressures. These conditions require preventing the formation of oxide and nitrite phases which cause brittleness of the applied layer, which can be accomplished by using self-fluxing additives^{17–20}.

The requirements of high wear resistance, hardness, corrosion and chemical resistance, good tensile strength and conductivity correspond to carbides, borides and nitrides of the metals from IV–VI group, and metals from group VIII (Fe, Co, Cr, Ni) of the Periodic Table of Mendeleev.

Therefore, taking into account the specific features of the gas-fuel spraying, it is necessary to use such a material, from which it is possible for the optimum process time to obtain a higher quantity of better quality metal on the coated surface. It is required micro-alloying and stabilising additives in order to increase the transfer from liquid phase.

The analysis of the scientific and technical information^{3,4,8,10–13} showed that for high-wear-resistance coatings should be used mainly difficult-melting metals and their compounds. In the fullest extent, to the above requirements correspond the high-wear-resistance and high-strength compounds, such as hard alloys based on tungsten and titanium carbides, titanium carbon nitrides, nitrides and borides with a single or multi-metal bond and various technological additives^{13–20}. The development of chemistry and technologies allows us to accept the particularly high efficiency of complex coatings from composite materials that have unique properties. The main task in creating powder compositions is to increase the amount of liquid phase. In the transferred in solid phase products are practically not so firmly fixed to the surface of the substrate as the products in liquid phase. This can be achieved by the introduction of plasticising phases. The plasticiser phase material also must to well wet the wear-resistant carbide and boride phases, and to ensures their robust bond to the coating and to the substrate.

One way to maximally preserve the beneficial properties of the individual components of the coating material is to introduce self-fluxing additives (B, Si, C, etc.) into the composition of the material^{20–24}.

The problem of adhesion of deposits and wear in the present work is solved by using of new composite materials with bonding components forming unlimited solutions in iron (Co, Ni, Cr), securing the necessary performance characteristics of the surface layer. Two types of metal compositions: Co-Cr-Ni-B-Si-C and Ni-Cr-B-Si-Fe-C are defined as bonding phases of the powder compositions based on the above. As the basis for their preparation, were used powders with trademarks 10612 – based on Ni.

According to the data for the mutual solubility of the metals and the compounds^{13,16,17,19,21,24}, taking into account the principles established for the selection of the bonding and wear-resistant components^{9,11,15,16,19-24} and using the wettability data of the difficult compounds and alloys^{15–17,19–21}, the following compositions of powder mixtures were selected and formulated to provide the effective forming wear-resistant layers on the steel surfaces:

- (1) NWT10B10 80% (55% (0.6% C, 2.86% Si, 12% Cr, 3.94% Fe, 77% Ni 3.6% B) + 45% WC) + 10% B₄C + 10%TiB₂.
- (2) NWW10T10B10 70% (55% (0.6% C, 2.86% Si, 12% Cr, 3.94% Fe, 0% Co, 77% Ni, 3.6% B) + 45% WC) +10% WK8 + 10% B_4 C + 10% TiB₂ (WK8 is hard alloy with 92% WC and % Co).
- (3) NWW10T20B20 50% (55% (0.6% C, 2.86% Si, 12% Cr, 3.94% Fe, 77% Ni, 3.6% B) + 45% WC) + 10% WK8 + 20% B₄C + 20%TiB₂.
- (4) NWT20B20 60% (55% (0.6% C, 2.86% Si, 12% Cr, 3.94% Fe, 77% Ni, 3.6% B) + 45% WC) + 20% B₄C + 20% TiB₂.
- (5) KWB10 90% (45% (1.5% C, 1.5% Si, 23% Cr, 0.5% Fe, 42% Co, 30% Ni, 1.5% B) + 55% WC) + 10% B₄C.
- (6) KWT10B10 80% (45% (1.5% C, 1.5% Si, 23% Cr, 0.5% Fe, 42% Co, 30% Ni, 1.5% B) + 55% WC) + 10% B₄C + 10% TiB₂.

The powdered compositions obtained in percent by weight were milled and homogenised in a mill 'Planet Fritsch'. The average particle size of the plasticised metal composition range is 45 ± 5 µm, and of additives B_4C , TiB_2 and WK8 – the grain size is 20 ± 5 µm.

Special attention in the selection of the bonding metals in the composition of the casting powders is given to Co, Ni and Cr. Iron and chromium have unlimited solubility in solid and liquid state, regardless of temperature. Chromium has a higher wear resistance than iron and particularly high wear resistance in various aggressive environments.

According to some researchers^{13,15,16,19,21,22}, the combination of Cr with Ni helps to increase the wear resistance. The thermal action of the gas stream on the substrate in the presence of nickel can lead both to solid Ni solutions in Fe and to the formution of additional FeNi₃-type compounds and, in the presence of B, Fe₃Ni₄B (Refs.1, 5, 10, 19 and 23).

Cobalt is a major component of the 'super alloys', which are mainly used in high temperature alloys, and of wear-resistant alloys, also used in tools steels and high speed steels. The presence of Co in steels and alloys leads to high hardness, corrosion resistance and high resistance to wear.

Taking into account the available literature^{12,13,15,17,19,24} and the results of the current preliminary measurements of the composition of our chosen bonding metals, Cr and Co are always present in compositions.

The purpose of the self-fluxing additives in the compositions created is to reduce the formation of oxide films on the deposited surfaces to improve the process and obtain dense and uniform coatings with higher thickness and wear resistance^{19–24}.

Silicon is widely used as a deoxidiser in steel. Carbon as a supplement is necessary to compensate for the possible de-carbonation of the surface layer of the material in heating caused by the high temperature in the jet, especially in the presence of Co. In addition, to compensate de-carbonation, boron is chosen to serve as a donor for the formation of wear-resistant borides in the coating.

Titanium diboride is distinguished by its very high hardness, wear resistance and chemical resistance. Boron carbide B_4C is a super-hard material with extremely high wear resistance and abrasion resistance^{13–16,18,20}. The WK8 alloy – WC + 8% Co was added to increase the amount of WC and cobalt. WC and TiB₂, in addition to abrasive wear, are also resistant to impact loads.

Coating characterisation. The results of the study showed that the surface layers are inhomogeneous, non-uniformal, similar in form and structure with acceptable repeatability of the qualitative characteristics. All layers are to some extent porous. The reason for this is the presence of non-melted particles of the hard phases in the composition of the powders remaining in the lamellae of the coating obtained, as well as of the unfilled spaces between the lamellae due to their incomplete bonding to each other in the heat-sealing process.

Flame coatings applied with the above materials are characterised by low porosity (Fig. 7). Their thickness is in the range 150–350 μ m, roughness R_a – 10–18 μ m, and the hardness HRC of the various laminating powder materials varies within the range 63–72. Due to the presence of pores and inhomogeneity in the structure and the presence of a matrix of lower hardness and high hard carbide phase, the hardness of the surface layers varies widely. Due to the higher content of carbide phases, the values obtained are higher than those at GFS with conventional commercial powders^{5,7,8,10,13}. Maximum hardness is achieved with the KWT10B10 and NWW10T10B10 compositions – to 72 HRC coating in the operating mode of the thickness change area from 250 to 300 μ m.

Figures 7 and 8 show the topography and microstructure of the coatings from KWT10B10 and NWT10B10 compositions on steel 45, and in Fig. 9 is shown the distribution of the elemental composition of the coating from powder composition NWW10B10T10.



Fig. 7. Microrelief of the coating of NWT10B10 - applied on steel 45

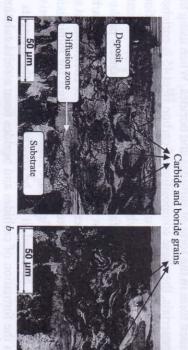


Fig. 8. Cross-section microphotographs of microstructure of coatings applied on steel 45: coating material KWT10B10 -a, and coating material NWT10B10 -b

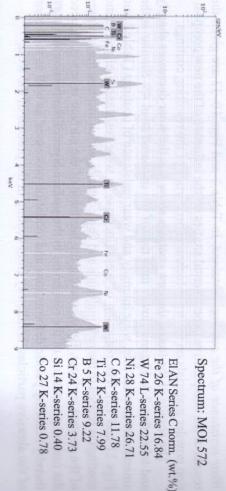


Fig. 9. Elemental composition of NWW10B10T10 material coating on steel 45 obtained by TEM analysis

The microstructure study shows that all layers are made of lamellar polycrystalline grains. Between the sections are observed a porous portion, as well as grains with a rounded shape. The observed microstructure can be characterised as follows: grains

with rod and point shapes and grains with complex asymmetric shape, a complex substructure resembling the corresponding image of a rocky area. Obviously is the inhomogeneous distribution of the elements in the coatings produced by the investigated powder mixtures.

From Figs 7–9, it can be seen that the microrelief of the obtained coatings is uneven and heterogeneous both in structure as well as in composition. There is a diffusion of particulate of coated material in the substrate but it was monitored a reverse diffusion – of the iron in the direction of the coating. The quantitative microanalysis of the coatings detects the presence of Fe, Cr, Co, Si, Ti and W. The light elements C and B partially burn or form new compounds with the elements from the substrate. The distribution of Ti and W repeats that of C and B, which confirms that Ti and W are present in a bonded form in the form of carbides and borides. When using the new multi-component materials, the phase composition of carbon steel 45 is enriched with more carbides and borides than at using of conventional powdered compositions and approaches to that of high-speed steels, which implies a significant improvement in the exploitation properties of the coated surfaces. The coatings with densely packed hard carbides and borides in a matrix form an impenetrable barrier to abrasive particles.

The short contact time of the particles with oxygen from the environment and the presence of self-flushing additives create favourable conditions for minimising the oxides in the coating, which in turn is of immense importance for the wear resistance.

On the basis of the data obtained, it can be concluded that the elements which are not involved in the formation of carbides and borides form a solid solution with the iron. The formation of a metal matrix in the form of a solid solution is confirmed by their distribution in coating surface and from cross-section microphotographs.

Wear resistance of the coatings obtained. In Table 3 and Figs 10–13 are given the results of the comparative experimental studies on the influence of the new composition powder materials on the tribo-technical properties of the resulting coatings.

The results of the test of the new coatings show that the wear decreases sharply and takes that 2.5–12 times lower than that of the uncoated steel 45. Similar is the amendment in wear rate, wear intensity and wear resistance of coatings (Table 3 and Figs 11 and 12). The reduction of wear (increase in wear resistance) of gas flame coatings is related to the new materials and new coatings, which increase the hardness of the contact surfaces. By increasing the hardness of the surface layers is reduced the mutual penetration of the roughness in the surface layer of the friction surfaces, thereby reducing plastic deformations and oxidation processes, as well as the action of the abrasive particles, breakaway from coating in the process of the wear.

Table 3. Parameters of wear of test samples

6 KWIIOBIO	CHILITA	5 KWB10	4 NWT20B20	3 NWW10T20B20	2 NWW10T10B1	1 NWT10B10	CONSTRUCT STATES AND	No Coating designation
Substrat steel 45	B10	10	B20	20B20	10B10	B10		Ignation
1089.5	90.8	91.2	398.3	142.5	105.3	158.2	(mg)	Mass loss
217.90	18.20	18.20	79.70	28.50	21.10	1.60	(mg/min)	Wear rate
456×10^{-2}	38.0×10^{-2}	38.2×10^{-2}	167×10^{-2}	59.7×10^{-2}	44.4×10^{-2}	66.3×10^{-2}	(mg/m)	Intensity
0.22	2.60	2.60	0.60	1.70	2.30	1.50	(m/mg)	Wear resistan



Fig. 10. Mass loss of the tested coatings



Fig. 11. Wear resistance of the tested coatings

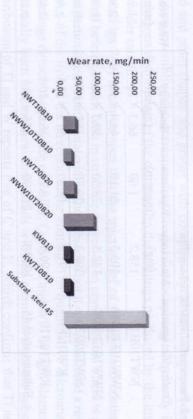


Fig. 12. Wear rate of the tested coatings

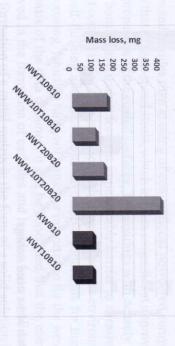


Fig. 13. Comparative mass loss of the tested coatings

The high abrasion resistance of the resulting coatings containing WC – 8% Co, TiB₂, B₄C is due to the combination of very solid carbides and borides and a solid but with a certain plasticity matrix of Co, Cr, Ni. The comparison of the wear of the coated specimens shows that coated with the materials KWB10 and KWT10B10 specimens have 1.2 to 1.75 times lower wear than that of the analogous materials NWT10B10 and NWW10T10B10 with nickel-based bonding metals. The lowest wear and correspondingly highest wear resistance show the coatings of the powder composition KWT10B10. The good wetting of carbide in the cobalt matrix contributes to the high cohesion strength of the resulting metal ceramics.

Wear analysis shows that the presence of B₄C, TiB₂ and WC in the powder compositions is the main reason for the higher wear resistance of these coatings. Apparently, the combination of TiB₂ and B₄C and WC additives in the powder composition allowed to use the full advantages of each of the individual component and to receive higher wear resistance of the layered surfaces compared to that obtained with only WC – TiB₂ or with WC – Co. Over-hard additives in the coating volume form an internal contact mesh with high strength characteristics that provides high resistance against abrasion, the destruction and scratching action from the abrasive particles. The

super-hard B₄C particles, firmly trapped in the metal matrix of the coating, increase its resistance to wear and further contribute to the increased wear resistance of the coating. With the increase of the B₄C and TiB₂ content from 10 to 20%, however, the difference in the wear of the coated and uncoated samples is sharply decreasing. Obviously, the higher concentration of these materials results in a weakening of the connections of the individual grains with the metal matrix in the coating, which results in tear, the more that, the breakaway high hard particles abrasively act on the surface of the coating, further contributing to increased wear.

Powder compositions KWT10B10, KWB10 and NWW10T10B10 are emerging as promising materials for high-performance coatings. Moreover, the proper selection of the bonding metals – Co, Ni and Cr and the presence of the self-fluxing additives B. Si and C in the composition make it possible to form a protective atmosphere which prevents the formation of oxides and allows obtaining of coatings with improved density and strength. The resulting coatings show higher wear-resistance in friction and abrasive conditions many times over than those of substrate, significantly reduce the wear intensity, slow down of wear development over time, and they may be efficiently used to increase the durability of friction of carbon steel surfaces as well as to strengthen rapidly wearing parts of carbon steels and for protection of steel parts for severe wear applications.

CONCLUSIONS

Carbide composite powder multiphase materials have been created on the basis of mixtures of Ni–Cr–B–Si–C and Co–Ni–Cr–B–Si–C with WC, TiB₂ and B₄C additives in varying percentages, and by GFS are received dense coatings with a thickness to 350 µm and wear resistance many times higher than that of non-coated surfaces.

The least wear has the coatings from NWW10T10B10, KWB10 µ KWT10B10 and materials. The high abrasion resistance of the coatings is due to the presence of B₄C and of the combination with TiB₂ and WC in a multi-metal matrix that is the main reason for the higher wear resistance of these coatings. Increasing the content of B₄C and TiB₂ additives to 20% results in a reduction in wear resistance.

The resulting coatings may be efficiently used to strengthen rapidly wearing parts and for protection of steel parts for severe wear applications.

The obtained dependencies and results can be used to control and manage the basic parameters and the tribological properties of the wear-resistant coatings by gas flame sprayed and to develop technologies for the lamination of specific details and parts.

ACKNOWLEDGEMENTS

This study and the results are related to the implementation on tasks: Contract: DN 07/28–15.12.2016 'Research and creation of new wear-resistant coatings using composites and nanomaterials', funded by the National Science Fund at the Ministry of Education and Science, Bulgaria.

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Received 3 February 2019 Revised 26 February 2019