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Structure and properties of WC-10Co4Cr coatings obtained with high velocity atmospheric plasma spraying

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ABSTRACT

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Introduction. Carbon steel is often used for the manufacture of various machine parts, but its operation in aggressive conditions (operation of steel parts under conditions of wear, high temperatures and aggressive corrosive environments) contributes to an extreme decline in properties, up to failure. To solve this problem the modification of the working surfaces of steel parts can be used. It increases its wear resistance, corrosion resistance, and service life. Metal-ceramic coatings based on WC are often used to improve the hardness, wear resistance and corrosion resistance of steel parts. The work purpose is to study the effect of high velocity atmospheric plasma spraying (HV-APS) modes on the structure, phase composition and properties of WC-Co coatings. Materials and methods. 86% WC-10% Co-4% Cr coatings were deposited on a mild steel substrate with help of the HV-APS method. The structure and phase composition of the coatings were analyzed using optical microscopy, scanning electron microscopy, and X-ray phase analysis. In addition, the results of measurements of porosity, microhardness, wear resistance, as well as a qualitative assessment of the adhesion are shown in this paper. Results and discussion. It is shown that all coatings are characterized by high density, absence of cracks and oxide films. Using the SEM and XRD methods, it is found that the coatings contain WC and $W_{2}C$ particles uniformly distributed in the metal matrix. The matrix is an amorphous or nanocrystalline supersaturated Co(W,C) solid solution. The maximum amount of carbides (49%) is observed in coatings obtained by deposition from a distance of 170 mm, arc current - 140 A; the minimum (25 %) is observed in coatings obtained by deposition from a distance of 250 mm, arc current - 200 A. The coatings with the maximum amount of carbides have the maximum values of microhardness $(1,284 \text{ HV}_{0.1})$ and wear resistance. It is established that all coatings are characterized by high adhesion.

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Introduction

Various machine components are often made of steel. This is because steel has the complex of high mechanical, technological and physical-chemical properties. Despite these advantages, the operation of steel components in aggressive conditions – operation of steel parts under conditions of wear, high temperatures and aggressive corrosive environments – contributes to a rapid decrease in its properties, up to failure. The

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solution to this problem is the modification of the working surfaces of steel parts can be used to increase its wear resistance and corrosion resistance, which will increase its service life [1, 2]. In addition, the formation of thin coatings saves a permissible level of ductility of the components.

Steel components with cermet coatings based on tungsten carbide (WC) are often used in industries such as oil, aerospace, metallurgical, chemical, and machine building due to its high hardness, wear resistance, and corrosion resistance [3–6]. The main technologies for these materials' production are HVOF and APS [7–11]. Due to its high hardness and brittleness, WC particles are usually deposited together with a metal binder to form composite coatings. Such coatings combine high ductility, impact strength, and technological effectiveness of the binder (Co, Ni, Ti, Fe, Cu, and others) and high wear and corrosion resistance of ceramics [12, 13].

The change the spraying modes or the characteristics of the sprayed powder allows control the structure, phase composition, and also the properties of the coatings. The authors of [14] established the dependence of the porosity and corrosion resistance of 88% WC-12% Co HVOF coatings on the heating temperature of particles in a carrier gas jet. A higher heating temperature contributed to the formation of an amorphous structure in the coatings and an increase in corrosion resistance. The authors of [15] showed that the change of HVOF modes affect the phase composition, porosity, and hardness of 88% WC-12% Co coatings and allow controlling its tribological characteristics. It is stated in [16–18] that the use of nanostructured WC-Co powder makes it possible to significantly increase the hardness, wear resistance, and corrosion resistance compared to coatings obtained from micron-sized WC-Co powders. The paper [7] shows that the use of pore-free ultrafine-grained WC-Co powder made it possible to obtain coatings consisting only of WC and an amorphous and nanocrystalline Co matrix. Its wear resistance was 4 times higher than that of coatings obtained from a coarser powder. On the other hand, the authors of [19, 20] demonstrated that when deposited by gas-thermal methods, most of the nanosized WC powder has time to decompose in the spray jet, which, in turn, leads to a decrease in the wear resistance of the formed coatings. The paper [5] shows that the composition of the Ar/He or Ar/H, plasma-forming gas has an influence on wear resistance more than the size of the sprayed particles. For example, the Ar/He plasma jet (with a lower operating temperature) reduced the degree of decarburization of the WC particles and thus increases its volume fraction in the coating. Since the coatings sprayed with Ar/He jet had a higher volume fraction of WC particles, it was characterized by higher values of hardness, wear resistance, and also toughness. The authors also reported that during Ar/He plasma spraying with a jet, coatings made of nanosized powder, rather than made of micron powder, had greater wear resistance.

Sum up, the following conclusion can be drawn: nowadays, *HVOF* and *APS* methods for obtaining cermet coatings have been investigated in sufficient detail. It is shown that after the development of the technology of deposition of a particular powder, it is possible to clearly control the properties of the resulting coatings. This paper presents the results of studying the effect of *HV-APS* modes using air as a plasma-forming gas on the structure, phase composition, and properties of *WC-Co* coatings.

Method of experiment

A commercial granulated 86% WC-10% Co-4% Cr powder with a dispersion of 15–38 μ m was used for the coatings spraying. HV-APS was performed using an electric arc plasma torch PNK-50 developed by the Institute of Theoretical and Applied Mechanics of the Siberian Branch of the Russian Academy of Sciences. Cylindrical substrates for spraying with a diameter of 20 mm and a height of 7.5 mm were prepared from a commercial low carbon Steel 20 (0.2% C). The cermet coatings were sprayed to the frontal surface of the cylindrical substrates, which was precleared by sandblasting. Table 1 shows HV-APS modes. The variable parameter was the spraying distance – 170 and 250 mm and the arc current – 140, 170 and 200 A. Air with the addition of 4 vol.% methane was used as the plasma-forming, transporting, and focusing gas.

Samples for structural studies, as well as measurements of microhardness and porosity, were transverse microsections prepared according to the standard method: mechanical grinding using suspensions containing Al_2O_3 particles of various grain sizes (9, 6, 3 and 1 µm) and finishing polishing on cloth using colloidal

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Spraying distance, mm	Arc current, A	Spraying modes
	140	170/140
170	170	170/170
	200	170/200
	140	250/140
250	170	250/170
	200	250/200

The modes of HV-APS

a solution of silicon oxide with a grain size of 0.04 µm. The microstructure of the samples was studied using an *Olympus GX-51* optical microscope (*Olympus*, Japan) equipped with the *OLYMPUS Stream Image Analysis Stream Essentials 1.9.1* software for measuring the porosity of materials, as well as a *Carl Zeiss EVO50 XVP* scanning electron microscope with an *EDS X-Act* microanalyzer. The phase composition was studied using an *ARL X'TRA* X-ray diffractometer in *CuKa* radiation. The diffraction patterns were recorded at the time t = 3 s with a step $\Delta 2\theta = 0.05^{\circ}$. To reveal the phase composition, a layer about 50 µm thick was removed from each sample from the side of the coating. The microhardness of the structural components of the coatings was evaluated on a *Wolpert Group 402MVD* microhardness tester at a load of 100 g [21].

Wear tests were carried out in accordance with *ASTM G65*. The cermet coatings were spraying on steel plates with the size of $25 \times 75 \times 3$ mm. The coatings thickness was $300-350 \mu$ m. During the test, the abrasive material (electrocorundum) was fed into the friction zone and pressed against the sample by a rotating rubber roller. The sample was pressed against the roller with a lever (a force of 44 N). The rotational speed of the roller was 60 rpm. Based on the results of weighing, the arithmetic mean value of the weight loss was determined.

To assess the adhesion of the coatings, the samples were bent with 180° around a guide roll with a diameter of 10 mm according to *ASTM E-290*.

Results and discussion

Coatings microstructure

Fig. 1 shows *XRD* spectra of the initial powder and coatings formed by different spraying modes. The main phases of the powder are tungsten carbide WC (51-939) and cobalt *Co* (15-806) (Fig. 1, *a*).

The X-ray patterns of all coatings (Fig. 1, b-g) are almost the same: the main phases are WC (65-4539) and W_2C (35-776). The peak intensity of the WC phase in the coatings is lower than in the powder, which indicates its lower volume fraction. It could indicate its lower volume fraction. The W_2C phase is formed as a result of decarburization of WC according to the reactions [22]:

$$2WC \leftrightarrow W_2C + C;$$
$$2WC + O_2 \leftrightarrow W_2C + CO_2.$$

The shift of the diffraction peak of the W_2C phase could indicate a change in the interatomic distances.

The absence of cobalt in the coatings' X-ray diffraction patterns is explained with the fact that, during spraying part of the WC is dissolved in the cobalt matrix, and then upon rapid cooling an amorphous or nanocrystalline supersaturated Co(W,C) solid solution is formed on a cold substrate or already solidified splats. Its formation is indicated by a wide diffraction halo in the range $2\theta = 37-47^{\circ}$. According to the data of [22–24], the formation of η phases (Co_3W_3C , Co_2W_4C , or Co_6W_6C) is also possible in the matrix, although we did not identify it with X-ray diffraction analysis.

Fig. 2, a-f shows the cross-sectional images of the WC-Co coatings fabricated by different modes. Its average thickness is 150–200 µm. All coatings are characterized with high density and good adhesion



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Fig. 1. X-ray diffraction patterns of powder (*a*) and coatings formed by different modes: *b* - 170/140; *c* - 170/170; *d* - 170/200; *e* - 250/140; *f* - 250/170; *g* - 250/200



Fig. 2. The structure of *HV-APS* coatings. The modes: *a* – 170/140; *b* – 170/170; *c* – 170/200; *d* – 250/140; *e* – 250/170; *f* – 250/200

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bonding to the substrate. The absence of cracks, as well as carbide particles crumbled out during spraying, indicates a high cohesive bonding. All coatings have a layered structure typical for thermal spraying.

It should be noted that the resulting coatings are characterized by a significant difference in the mass fraction of carbides. Fig. 2, a-c (top row) shows coatings obtained at a spraying distance of 170 mm, and Fig. 2, d-f (bottom row) – at a distance of 250 mm. The arc current was also changed during spraying: 140 A (Fig. 2, a, d), 170 A (Fig. 2, b, e) and 200 A (Fig. 2, c, f). It can be seen that the spraying distance, as well as the arc current, have a significant effect on the amount of carbides. The dependence of the mass fraction of carbides on the spraying modes is shown in Fig. 3. The amount of WC and W_2C decreases with increasing arc current and spraying distance. This is because the arc current increases, therefor the plasma flow temperature



Fig. 3. Dependence of the $WC+W_2C$ mass fraction on spraying modes

also increases, which leads to heating of *WC* particles to higher temperatures. The maximum amount of carbides (49 %) is observed in coatings formed using the 170/140 mode, the minimum (25 %) is in the 250/200 mode.

Fig. 4, *a* shows the *SEM* image of the coating obtained by the *BSE* mode. It can be seen that the *WC* particles are located inside the splats and have different size (points 4 and 5 in Fig. 4, *a*). There are also areas without *WC* particles in the coatings (points 1–3 in Fig. 4, *a*). Depending on the time of exposure to high temperatures on the tungsten carbide particles, the degree of its decomposition will be different. It is known that when heated in a plasma jet, *WC* particles begin to melt and tungsten and carbon atoms diffuse into the liquid cobalt matrix. When this molten material is cooled at rates much higher than the critical ones, an amorphous or nanocrystalline supersaturated Co(W,C) solid solution is fixed. The scheme (Fig. 4b) shows that the degree of decarburization of *WC* particles is not the same in different splats. Thus, the particles practically do not melt in splats with a darker matrix (point 5 in Fig. 4, *a*) in contrast to splats with a lighter matrix (point 4 in Fig. 4. *a*). Depending on the amount of tungsten and carbon dissolved in cobalt, the matrix is characterized by different shades of gray. According to the X-ray microanalysis data (Table 2), the lighter areas (point 1 in Fig. 4, *a*) contain more tungsten, while the darker areas (point 3 in Fig. 4, *a*) contain less. The obtained data are in good agreement with the data of [5].





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Table 2

Area, No.	Chemical element, wt. %				
	W	Со	С	Cr	
1	92.84	2.89	3.52	0.74	
2	87.69	3.28	8.23	0.8	
3	80.59	7.95	7.45	4.0	
4	79.17	9.08	6.83	4.91	
5	77.65	10.52	7.87	3.95	
3 4 5	80.59 79.17 77.65	7.95 9.08 10.52	7.45 6.83 7.87	4.0 4.91 3.95	

Electron	micro	probe	analysis	of	coatings
LICCHON	micro	probe	anary 515	U1	coatings

Mechanical properties and wear resistance of WC-Co coatings

The results of measurements of the coatings microhardness average values depending on the spraying mode are shown in Figs. 5. An increase in the arc current contributes to a decrease in the microhardness values, which can be explained by a decrease in the volume fraction of carbides in the coatings. The influence of the spraying distance is insignificant, while the hardness of the coatings obtained by spraying from a distance of 250 mm is slightly lower. The maximum microhardness (1,284 and 1,287 HV_{0.1}) is typical for coatings obtained using the 170/140 and 250/140 modes. The lowest values of microhardness (1,153 and 1,140 HV_{0.1}) are specific to coatings obtained using 170/200 and 250/200 modes. On the average, the microhardness of carbides is 1,432 ± 107 HV_{0.1}, while that of the cobalt matrix is 772 ± 93 HV_{0.1}. The obtained data are in good agreement with the data of [9, 25].

Fig. 6 shows the results of testing coatings for wear with abrasive particles. According the obtained data, the maximum wear resistance is typical for samples with cermet coatings obtained by 170/140 mode (relative wear resistance – 0.21), the minimum wear resistance is characterized for samples obtained by 250/200 mode (relative wear resistance – 0.14). The decrease in wear resistance can be explained by a decrease in the volume fraction of the carbide phase, which is in a good agreement with the results of microhardness measurements.

To evaluate the adhesion of the coatings, 180° bend tests were carried out in the work. In all cases, the coatings cracked in the bending area, but did not peel off. Fig. 7 shows images of the surface of plates with coatings obtained by modes 170/140 (Fig. 7, *a*) and 250/200 (Fig. 7, *b*) after testing. It can be seen







Fig. 6. Relative wear resistance of coatings formed by different modes



that the cracks in the coatings are almost straight without any branching. The distance between cracks increases with increasing arc current and spraying distance. The obtained data indicate a high adhesion of the coatings.

Conclusions

1. In this paper, a range of high-quality *WC-Co* coatings were formed with using of *HV-APS*. These coatings are characterized by high density, absence of cracks and oxide films.

2. All coatings consist of WC and W_2C particles uniformly distributed in the metal matrix. The matrix is an amorphous or nanocrystalline supersaturated Co(W,C) solid solution.

3. It has been shown that the spraying distance, as well as the arc current, has a significant effect on the volume fraction of carbides. The maximum amount of carbides (49%) is observed in coatings obtained by the 170/140 mode, the minimum ones (25%) — in coatings obtained by the 250/200 mode.

4. The maximum microhardness of coatings is 1,284 and 1,287 HV_{0.1} (modes 170/140 and 250/140), the minimum microhardness is 1,153 and 1,140 HV_{0.1} (modes 170/ 200 and 250/200).

5. The maximum wear resistance is typical for samples with coatings obtained by the 170/140 mode (relative wear resistance 0.21), the minimum value has coatings obtained by the 250/200 mode (relative wear resistance 0.14).

6. All coatings are characterized with high adhesion. It cracked in the bending area, but did not peel off.

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Conflicts of Interest

The authors declare no conflict of interest.

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