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B.K. Rakhadilov[1,3], N. Muktanova[2,3*], D.N. Kakimzhanov[2,3], P. Kowalewski[4]

[1]Sarsen Amanzholov East Kazakhstan University, Ust-Kamenogorsk 070000, Kazakhstan;
[2]Daulet Serikbaev East Kazakhstan Technical University, Ust-Kamenogorsk 070002, Kazakhstan;
[3]PlasmaScience LLP, Ust-Kamenogorsk 070010, Kazakhstan;
[4]Wrocław University of Science and Technology, Wrocław, Poland
[*]Corresponding author's e-mail: muktanovan@gmail.com

Effect of HVOF method spraying parameters on phase composition and mechanical and tribological properties of 86WC-10Co-4Cr coating

Valve components used in the petroleum industry are subjected to intense wear during operation, which leads to a sharp decrease in their durability. Usually, the often subjected to the wear process surface of the valves is treated by tungsten carbide cladding to improve its durability. Because of the difficulty in applying tungsten carbide using conventional surfacing techniques, high velocity oxyfuel (HVOF) spraying technology is recommended. In this work, the mechanical, tribological properties and phase composition of 86WC-10Co-4Cr composition coatings obtained by HVOF Termika-3 high-velocity gas-fuel spraying were investigated. Varying the technological parameters of spraying was carried out by changing the spraying distance, which led to differences in the thickness of the coatings. The phase composition, microstructure and distribution of elements were analyzed using X-ray diffraction (XRD), scanning electron microscopy (SEM) methods. The hardness of the samples was measured on a microhardness tester using the Vickers method, the friction coefficient and the wear rate were investigated using a friction and wear tester. It was determined that the surface of the coatings had developed character and high roughness. The results of X-ray phase analysis showed the predominance of hexagonal WC as the major phase, with a small amount of hexagonal tungsten carbide W2C as the minor phase, and the minor presence of cobalt oxide CoO. It was found that the increased wear resistance and low friction coefficient of 86WC-10Co-4Cr coatings are explained by the high volume fraction of hard and stable WC grains with high resistance to wear.

Keywords: wear resistance, ceramic-metal coatings, high-velocity gas-flame spraying, gate valve, carbides, decarburization, friction coefficient, microstructure.

Introduction

Any significant annual demand of oil and gas production and refining industry for shut-off valves, as well as the high cost of repair and preventive maintenance work determines the need to increase the actual service life of gate valves and the duration of the overhaul period. Gate valves are one of the important elements in the transportation of oil and gas, in the process of production from the well and through a complex network of pipelines, determining safe operating conditions and environmental protection. Gate valves used in the oil industry cause complex problems, one of which is their tightness. The main component affecting the tightness of the gate valve and its good performance is the gate-seat assembly. The durability of the gate assembly is ensured by using high strength, hard materials in all wear processes (adhesion, abrasion, erosion, cavitation and corrosion), especially tungsten carbide sprayed using the high velocity gas flame spraying (HVOF) process [1]. Over the last decade, a significant number of studies have been published on various HVOF gun designs such as JP5000 [2, 3], warm spray [4, 5], DJ2700/2600 [6], Jetkote II [7, 8], CJS [6] and K2 [8]. These studies have mainly focused on obtaining WC-Co-Cg coatings, which are widely used under high tribological loading conditions for wear protection such as abrasion, contact fatigue, erosion and sliding. An additional advantage of high velocity gas flame spraying is that it can replace electrolytic hard chrome plating (EHC). The EHC process uses toxic chromium compounds, especially hexavalent chromium [Cr(VI)], which is a carcinogen and poses a serious threat to the environment and human health. In addition, the application of EHC on an industrial scale requires high requirements for industrial ventilation, electrolyte disposal and water treatment systems, which increases safety and environmental costs [9–11]. Therefore, the HVOF process is much more efficient than EHC. HVOF high velocity gas flame spraying method is most often used to deposit carbide-based materials, including 86WC-10Co-4Cr, which have high performance characteristics and are the most suitable materials to increase the service life of shut-off valve parts. High wear resistance of gas-thermal WC-Co coatings is provided by the combination of WC as a solid component and cobalt as a plastic binder [12–14]. To improve the corrosion resistance of WC-Co coatings, WC-Co powders are alloyed with chromium, as the Co-Cr matrix provides higher corrosion resistance than WC-Co materials. 86WC-10Co-4Cr- coatings have high hardness, low coefficient of friction, and their wear resistance is 3...5 times higher compared to hard chromium [4, 15, 16]. On obtaining a good coating, it also requires tuning the appropriate process parameters. Among the many parameters that strongly influence the quality and properties of the produced coatings is the spraying distance, which is one of the key parameters.

Therefore, the present work describes the mechanical and tribological properties of 86WC-10Co-4Cr coatings obtained at different spraying distances using the HVOF Termika-3 process.

Materials and methods

In the present work, to provide improvement of tribological properties of the “gate-seat” assembly of the valve of pipeline fittings, sintered metal-ceramic powder of tungsten carbide in cobalt-chromium matrix 86WC-10Co-4Cr (JSC “Polema”, Tula, Russia) with particle size 15÷50 microns was used. Samples from high-alloyed, corrosion-resistant steel 30X13 were used as a substrate. Before spraying, the substrate surface was sandblasted under pressure of 0.6 MPa using electrocorundum.

Metalloceramic coatings 86WC-10Co-4Cr with different spraying distances were obtained on HVOF Termika-3 (PlasmaScience LLP, Ust-Kamenogorsk). Table shows the parameters of coating spraying, spraying distance values and an example code. The dwell time of all three samples during spraying was 10 s.

Table

Spray coating regimes 86WC-10Co-4Cr

Example code	A1	A2	A3
Spraying distance, mm	200	300	400
Parameter regimes on the gas control panel	Optimal values		
Propane-butane mixture	2.9 Bar		
Oxygen	5 Bar		
Compressed air	3.2 Bar		

The morphology and cross-section of the initial powder are presented in Figure 1 (SEM Phenom XL, Wroclaw University of Science and Technology, Wroclaw, Poland). The powder particles were sintered according to the manufacturer and their size ranged from 15 to 50 μm. Porosity of coatings was evaluated by SEM images using image analysis software Altami Studio 4.0 of optical microscope Altami MET 5S (Altami LLC, St. Petersburg, Russia). From the figure it can be seen that the powder particles are predominantly spherical in shape (Fig. 1*a*). This is important from the technological point of view, as it provides a suitable bulkiness of the powder particles during spraying. According to the SEM analysis of the powder cross-sectional image (Fig. 1*b*), it is found that morphologically the structure consists of two phases with different colors, where, polygonal WC particles have a light color and the metallic phase of cobalt-chromium (matrix) is represented in dark gray color. The tungsten carbide particles are well distributed and embedded in the cobalt-chromium matrix, which is in agreement with many studies in the reported literatures [17–19]. It can also be observed that pores are present, which may facilitate heat distribution and promote better melting or semi-melting of the particles.

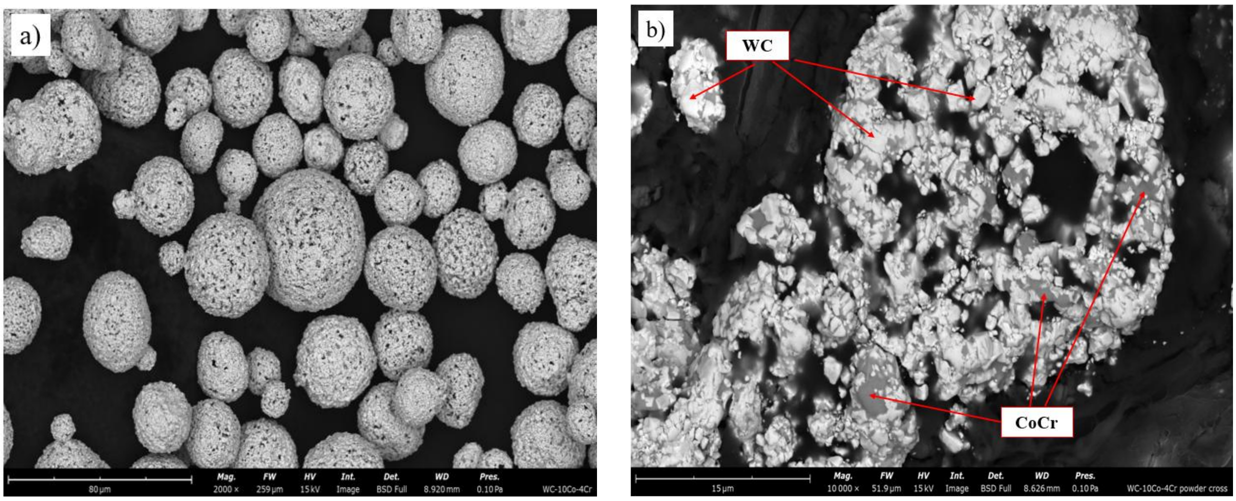


Figure 1. Morphology of the initial (*a*) and cross section (*b*) powder agglomerate86WC-10Co-4Cr

X-ray diffraction analysis (XRD) of the powders and coatings was performed on a Cu-Kα-emitting X'PertPRO diffractometer (Philips Corporation, Amsterdam, Netherlands) (λ = 0.154 nm) operated at a voltage and current of 40 kV and 30 mA, respectively. Measurements were performed over a 2θ range from 10° to 80°, and for the experiments the step width and exposure time were set to 0.05° and 0.5 s for each step. The roughness of the coatings Ra after spraying was determined using a Leica DCM8 3D profilometer (Wroclaw University of Science and Technology, Wroclaw, Poland). The microstructure of the fabricated coatings was analyzed using a Phenom XL scanning electron microscope. For each sample 20–25 images were taken at different magnifications. The microhardness of the samples was measured along the cross section of the coatings (10 measurements for each type of coating) on a microtweedometer MMT-X7B (Wroclaw University of Science and Technology, Wroclaw, Poland) at indenter loads m = 200 g and dwell time 10 s. Tribological wear tests were carried out on a friction machine using the standard technique “reciprocating motion” (Wroclaw University of Science and Technology, Wroclaw, Poland), where as a counterbody used SiC ball with a diameter of 3.969 mm and hardness HV = 2800 mm was pressed by weights (with a force Fn) to the surface of the sample, at a load of 20 N and linear velocity of 5 mm s-1, the length of the wear track 3 mm. The system moving the plate consisted of two bearing bodies moving in the same direction, allowing the friction force to be shared. The actuator was an electric drive consisting of a stepper motor and helical gear. The motion force was transferred from the larger bogie to the smaller bogie using a strain gauge load cell. The system allowed a fixed motion of the steel plate relative to the ball with a defined velocity Vs and displacement S. The force causing the motion FT was recorded at a frequency of 10 Hz. The kinematic diagram of the friction pair used during the tests is shown in Figure 2.

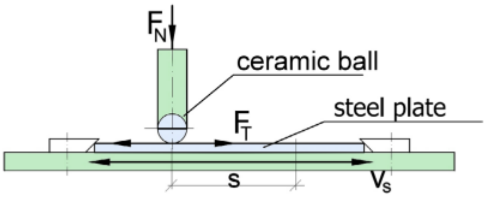


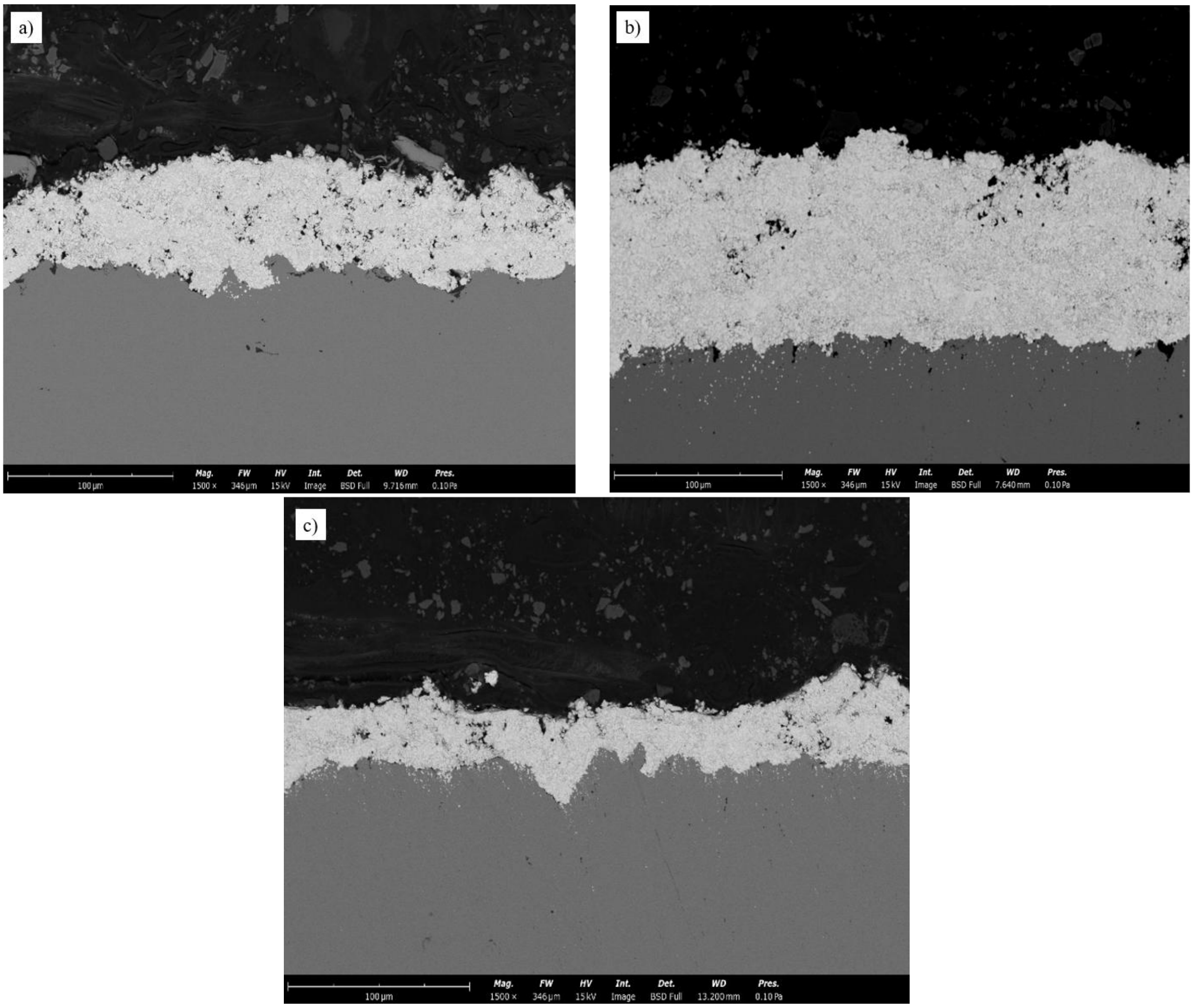
Figure 2. Structural diagram of the system used for friction and wear of coatings in the plate-ball system [20]

At each stage of the series of three measurements, the steel plate (on a moving carriage) performed a series of 500 motion cycles. The motion cycle consisted of two displacements (Vs_{max} = 5 mm s^{-1}) in both directions. The movement time in each direction was 0.4 s and the load on the friction node was FN=2N. The tests were carried out under technically dry friction conditions. The friction coefficient μ was calculated based on the average friction force FT. The average width of the wear track measured with a LEICA DCM8 microscope (Wroclaw University of Science and Technology, Wroclaw, Poland) after the test was taken as the wear value.

Results and discussion

Figure 3 shows the cross-sectional morphology of the coatings obtained at different spraying distances: A1 — 200 mm, A2 — 300 mm, A3 — 400 mm. All coatings are tightly adhered to the substrate without any cracks and failures and no signs of delamination were observed. The thicknesses of the coatings were h = 60 µm, h = 97 µm and h = 35 µm for samples A1, A2 and A3, respectively. According to the variation of the spraying distance, a variety in the thickness of the coatings was observed. In all coatings, the relative porosity did not exceed 1.6 %, but the lowest porosity with a value of 0.5 % was shown by the coating obtained at a spraying distance of 300 mm (Fig. 3b). Hence, the porosity is 1.6 %, 0.5 % and 1.3 % for samples A1, A2 and A3, respectively.

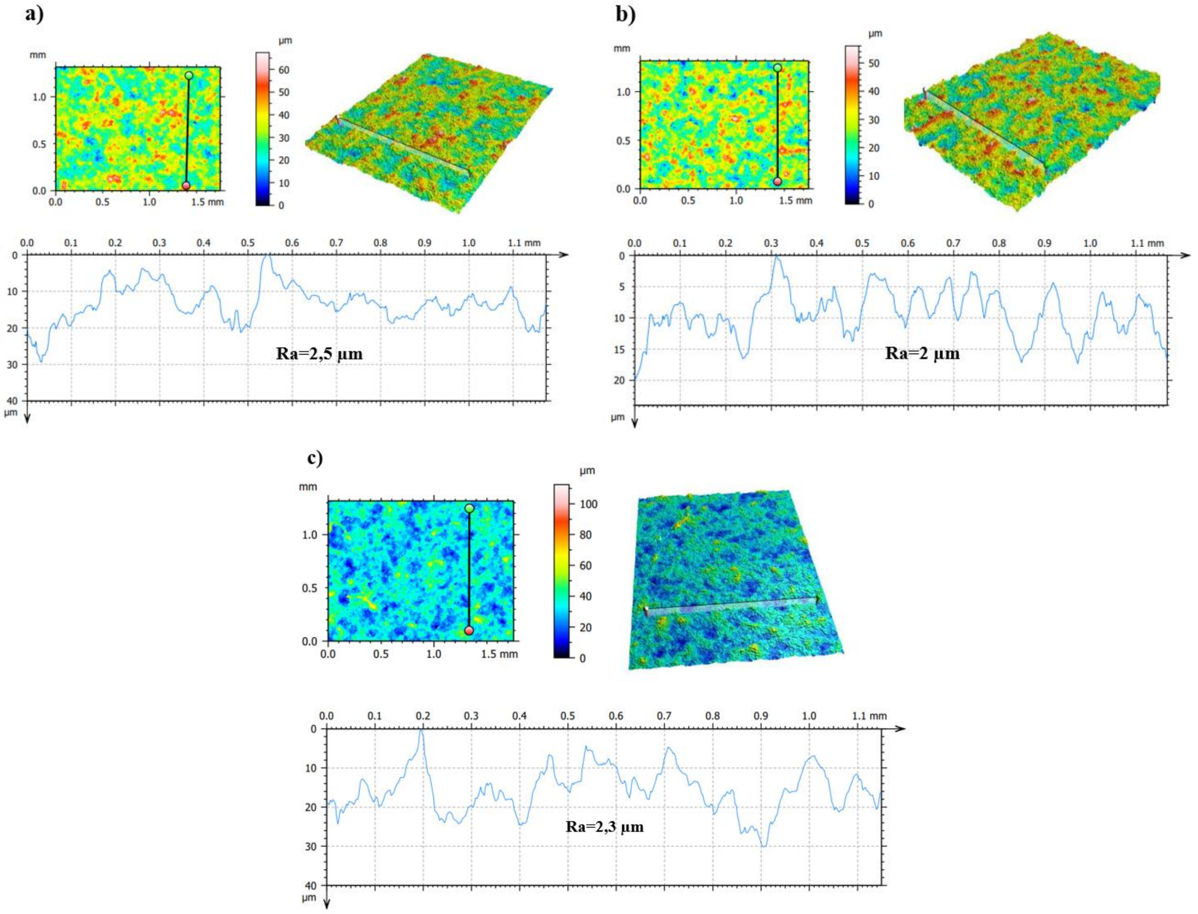
When the spraying distance is increased to 200 mm, the powder particles experience prolonged exposure to heat, which may cause them to overheat and result in the formation of microporous structure in the coating. Further, when the spraying distance is increased up to 300 mm, there is a gradual decrease in the heat effect and more intensive material deposition, which contributes to the formation of a more homogeneous and low-porosity coating. When further increasing the spraying distance up to 400 mm, leads to uneven application of the material, which is probably caused by the non-dissolution of WC in the spraying process and rapid cooling of the particles when reaching the substrate.



a — 200 mm; *b* — 300 mm; *c* — 400 mm

Figure 3. SEM images of the cross-sectional morphology of 86WC-10Co-4Cr coatings obtained by varying the spraying distance

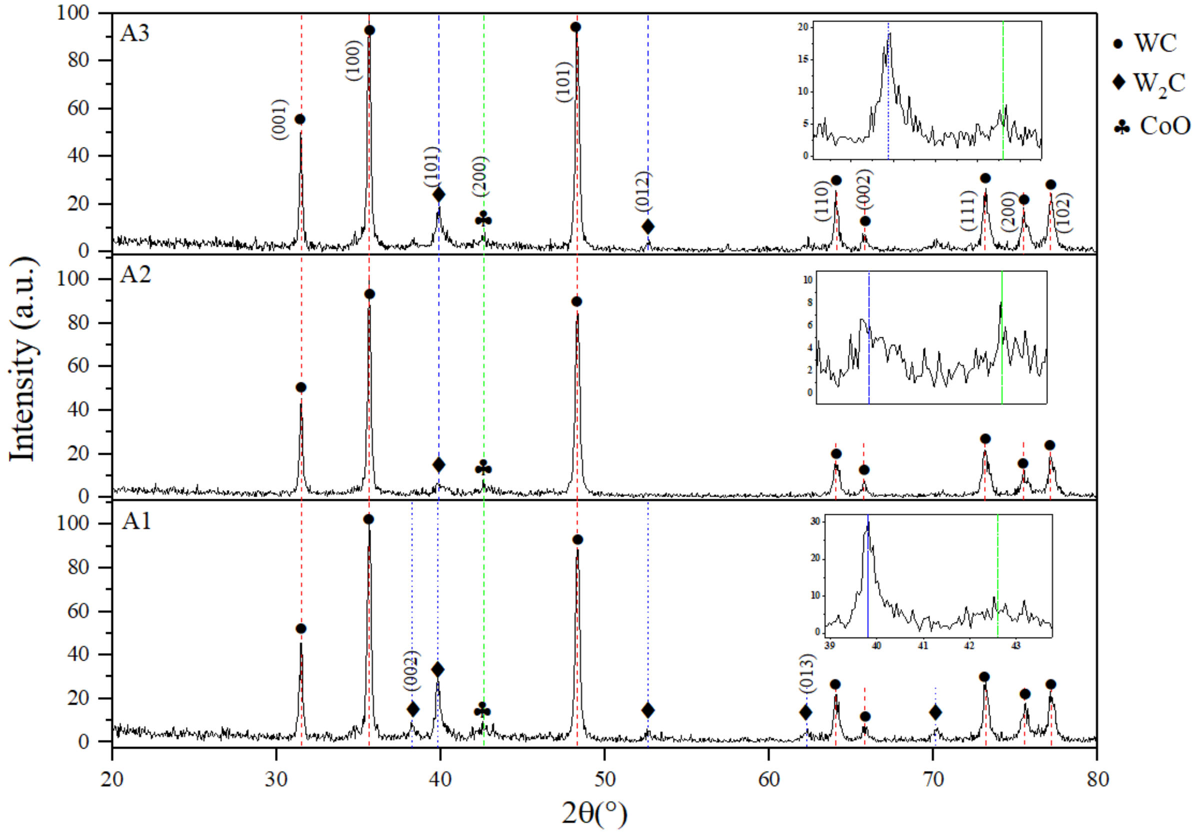
Figure 4 displays the surface roughness measurements of the coatings obtained using a Leica DCM8 3D profilometer. Images at different depths of the focal plane were acquired and a three-dimensional image and a plot of the distribution of the arithmetic mean profile deviation over the surface of 86WC-10Co-4Cr coatings were created from these images (Fig. 4). In the analyzed samples there is a slight change in the surface roughness, which is characterized by a regular fine microrelief. The roughness values are 2.5 μm, 2 μm and 2.3 μm for samples A1, A2 and A3, respectively.



a — A1 — 200 mm; *b* — A2 — 300 mm and *c* — A3 — 400 mm

Figure 4. Topographic images and surface roughnesses of Ra coatings obtained with varying the spraying distance

Figure 5 shows the diffractograms of 86WC-10Co-4Cr based coatings obtained with different spraying distances. The results of XRD analysis showed that the phase composition of the coatings consists of hexagonal higher tungsten carbide WC as the major phase and a relatively small fraction of hexagonal lower tungsten carbide W_2C as the minor phase, and there are also cobalt oxide CoO peaks present, the latter two of which were obtained as a result of thermal decomposition of the powder during spraying, which is in agreement with the author's study [21]. Based on the diagram of state of the W-C double system, it can be assumed that in the temperature range of 2400–2800 °C there is a loss of carbon from the WC phase, which leads to the formation of the brittle phase W2C [22–24]. At a spraying distance of 200 mm, the particles can have a higher temperature and velocity, which promotes a more intense decomposition of WC to W_2C. This resulted in high intensity of W_2C phase in A1 coating compared to other coatings. At a spraying distance of 300 mm, the particle and surface temperature, may be lower compared to the distance of 200 mm, which resulted in less intensive decomposition of WC to W_2C and hence lower intensity of the W_2C phase in the A2 coating. At a spraying distance of 400 mm, the particle and surface temperatures may not be as high as at closer distances. However, due to the increased residence time of the particles in the flame, they have more time to cool down and interact with the substrate. This may favor a more intense decomposition of WC to W_2C, which in turn may lead to an increase in the intensity of the W_2C phase in the A3 coating, as can be seen in Figure 5. The formation of the CoO oxide phase is explained by the fact that the high-speed gas flame spraying used an oxygen-propane mixture as the oxidizing gas flame medium, which leads to a more intense interaction between WC and oxygen. As a result, there is a partial loss of carbon, consequently, the excess carbon formed as a result of WC dissolution diffuses into the metal matrix and forms another carbide W_2C and oxide CoO phase. Thus, the appearance of the W_2C phase in the coatings can be attributed to the partial decarburization of WC during the deposition process. This mechanism is well known for coatings containing tungsten carbide, as confirmed by literature sources [25, 26].



A1 — 200 mm; A2 — 300 mm; A3 — 400 mm

Figure 5. Coating diagrams of 86WC-10Co-4Cr at different spraying distances

The results of measurements of average values of microhardness of coatings depending on the regime of spraying are presented in Figure 6. The results agree with the author's studies [27, 28], i.e., the higher the degree of decarburization (transformation of WC into W_2C), the lower the hardness.

These results also correlate with the XRD data (Fig. 5), where partial decarburization is observed in A1 and A3 coatings, while less pronounced decarburization is observed in A2 coating. This is confirmed by the disappearance of the phase in some angles (52.6 and 62.3°), which, in turn, contributed to the hardness of the coating.

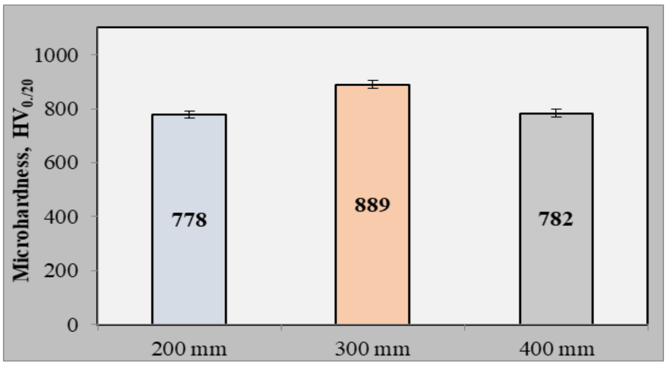
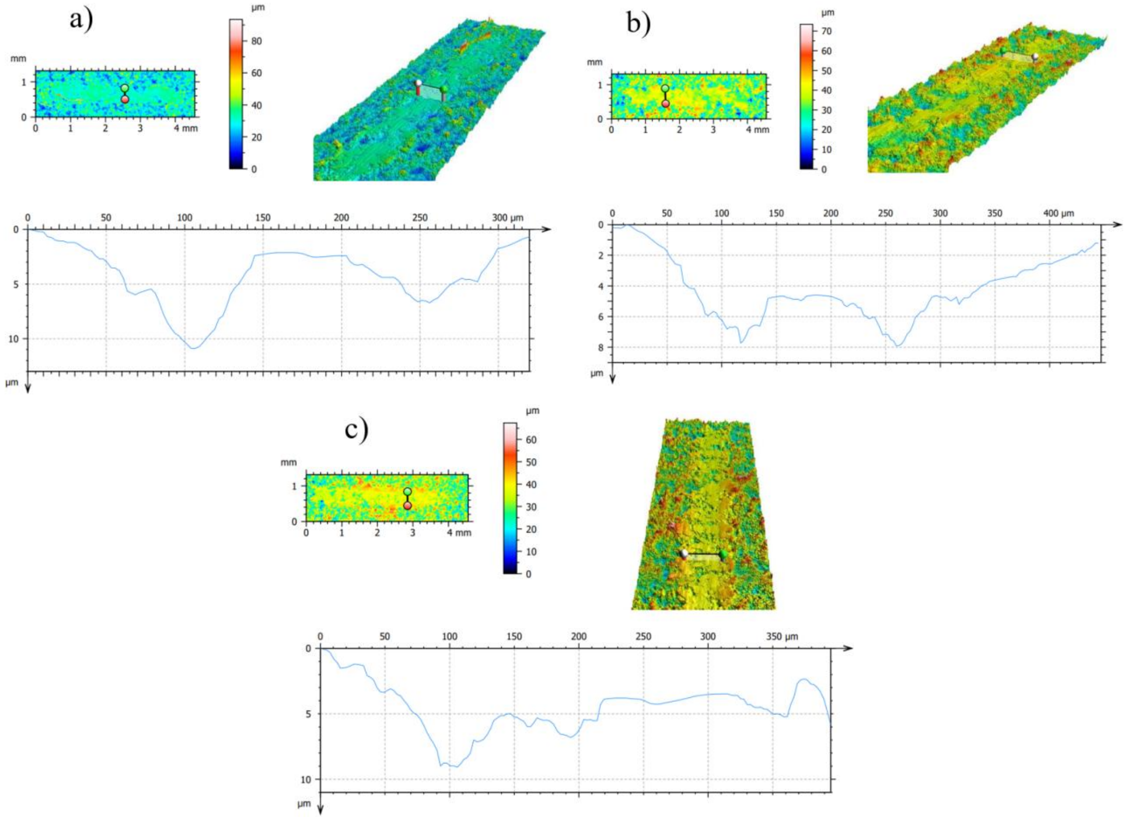


Figure 6. Microhardness of 86WC-10Co-4Cr coatings as a function of spraying distance

Tribological wear tests were performed on a friction machine (Fig. 2) using the standard “reciprocating motion” technique. Figure 7 shows the wear marks observed on the coating surface after the friction machine tests. Also shown is a graph illustrating the dependence of the wear mark width on its depth, which was obtained using a Leica DCM8 3D microscope.



a — 200 mm; *b* — 300 mm; *c* — 400 mm

Figure 7. Wear traces observed on the surface of 86WC-10Co-4Cr coating after reciprocating wear test

As shown in Figure 7*a*, the coating obtained at a spraying distance of 200 mm undergoes wear to a greater depth compared to other coatings (Fig.7*b*, *c*), which show signs of wear to a less significant depth. Figure 8 present graph shows the dependence of the wear volume on the spraying distance.

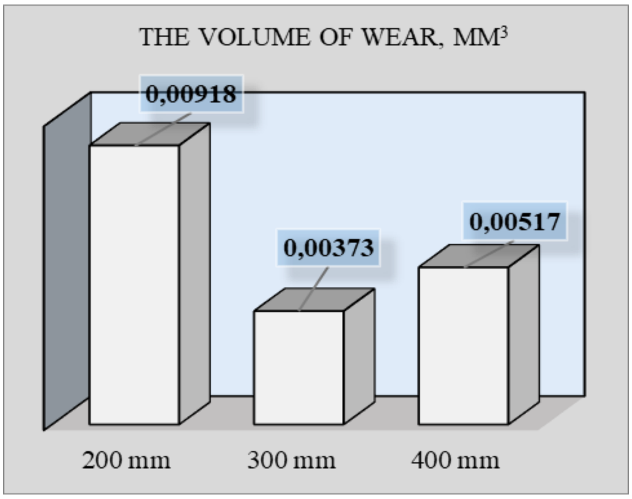


Figure 8. Graph of dependence of wear volume on the spraying distance

It has been established that with the increase of spraying distance the average friction coefficient and wear volume of 86WC-10Co-4Cr metal-ceramic coating change by jumps, taking values $\mu = 0{,}23369$; $\mu = 0{,}0562$; $\mu = 0{,}0566$ and $v = 0{,}00918$ mm³; $v = 0{,}00373$ mm³; $v = 0{,}00517$ mm³ (Fig. 8) for samples A1, A2 and A3. It can be seen from Figure 8 that the maximum wear resistance is characteristic of the coating obtained at a spraying distance of 300 mm, while the minimum is for the sample obtained at a spraying distance of 200 mm. The increase in wear resistance can be explained by the decrease in the content of the lowest carbide phase W_2C, which is in agreement with the results of XRD analysis (Fig. 5 (A2)). The coating obtained at a spraying distance of 300 mm is characterized by a high-volume fraction of hard and stable WC grains with high wear resistance. Thus, the tribological test results show that the A2 coating after high-speed gas-flame spraying has improved wear resistance and low coefficient of friction.

Conclusions

Thus, summarizing the above results, the following main conclusions of this paper can be drawn:

High velocity gas-flame spraying of 86WC-10Co-4Cr powder at different spacing resulted in coatings with dense structure without cracks and fractures, tightly adhering to the base.

The porosity of the coatings did not exceed 1.6 %. The lowest porosity with the index of 0.5 % was the coating obtained at a spraying distance of 300 mm.

X-ray diffraction analysis showed that the phase composition of the metal-ceramic coatings consisted of hexagonal WC, hexagonal W_2C and cubic cobalt oxide (CoO). The average spraying distance (300 mm) resulted in a less intense decomposition of WC to W_2C.

It was found that the maximum microhardness ($889HV_{0.2}$) was observed in A2 coating, which can be attributed to the decrease in the W_2C phase fraction, while the minimum microhardness values were observed in A1 and A3 coatings.

The roughness of the coatings practically does not change with increasing spraying distance: 2.5 μm, 2 μm and 2.3 μm for samples A1 — 200 mm, A2 — 300 mm and A3 — 400 mm, respectively.

The maximum wear resistance is observed for the coating obtained at a spraying distance of 300 mm (wear volume 0.00373 mm^3), while the minimum wear resistance is characteristic of the coating obtained at a distance of 200 mm ($v = 0.00918$ mm^3).

Acknowledgments

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Б.К. Рахадилов, Н. Мұқтанова, Д.Н. Кәкімжанов, П. Ковалевский

86WC-10Co-4Cr жабынының фазалық құрамы мен механикалық-трибологиялық қасиеттеріне HVOF әдісінің бүрку параметрлерінің әсері

Эксплуатация кезінде мұнай өнеркәсібінде қолданылатын клапандардың компоненттері қатты тозуға ұшырайды, бұл олардың беріктігінің күрт төмендеуіне әкеледі. Әдетте, тозу процесіне жиі ұшырайтын ысырмалардың беті, олардың беріктігін арттыру үшін вольфрам карбидін қолдану арқылы балқытумен өңделеді. Дәстүрлі балқыту технологияларын қолдана отырып, вольфрам карбидін қолдану қиын болғандықтан, жоғары жылдамдықты оттегі-отынымен бүрку (HVOF) технологиясын қолдану ұсынылады. Жұмыста HVOF Termika-3 жоғары жылдамдықты газдық жалынды бүрку әдісімен алынған 86WC-10Co-4Cr жабындарының механикалық-трибологиялық қасиеттері мен фазалық құрамы зерттелді. Бүркудің технологиялық параметрлерінің өзгеруі бүрку қашықтығын өзгерту арқылы жүзеге асырылды, бұл жабындардың қалыңдығының өзгеруіне әкелді. Элементтердің таралуы, фазалық құрам, микроқұрылым сканерлеуші электрондық микроскоп (СЭМ) және рентгендік дифракция (РД) әдістерін қолдану арқылы талданды. Сынамалардың қаттылығы Виккерс әдісімен микроқаттылық өлшегіште өлшенді, үйкеліс коэффициенті мен тозу дәрежесі үйкеліс пен тозу өлшегішінің көмегімен зерттелді. Жабындардың беті дамыған сипатқа және жоғары кедір-бұдырға ие екендігі анықталды. Рентгендік фазалық талдау нәтижелері алтыбұрышты WC-нің негізгі фаза ретінде басым болуын, алтыбұрышты вольфрам карбиді W_2C-нің екінші фаза ретінде аз болуын, сондай-ақ CoO кобальт оксидінің шамалы болуын көрсетті. 86WC-10Co-4Cr жабындарының тозуға төзімділігінің жоғары болуы және төмен үйкеліс коэффициентіне ие болуы жоғары қатты және тұрақты WC түйіршіктерніің жоғары көлемді үлесімен түсіндірілетіні анықталды.

Кілт сөздер: тозуға төзімділік, металл-керамикалық жабындар, жоғары жылдамдықты газжалынымен бүрку, ысырма, карбидтер, көміртексіздену, үйкеліс коэффициенті, микроқұрылым.

Б.К. Рахадилов, Н. Муктанова, Д.Н. Какимжанов, П. Ковалевский

Влияние параметров напыления HVOF метода на фазовый состав и механико-трибологические свойства покрытия 86WC-10Co-4Cr

В процессе эксплуатации компоненты клапанов, используемые в нефтяной промышленности, подвергаются интенсивному износу, что приводит к резкому снижению их долговечности. Обычно поверхность затворов, которая часто подвержена процессу износа, обрабатывается наплавкой с применением карбида вольфрама для повышения ее долговечности. В связи с тем, что трудно наносить карбид вольфрама с использованием традиционных технологий наплавки, рекомендуется использовать технологию высокоскоростного кислородно-топливного напыления (HVOF). В данной работе исследованы механико-трибологические свойства и фазовый состав покрытий состава 86WC-10Co-4Cr, полученных методом высокоскоростного газопламенного напыления HVOF Termika–3. Варьирование технологических параметров напыления осуществлялось путем изменения расстояния напыления, что привело к различиям в толщине покрытий. Фазовый состав, микроструктура и распределение элементов проанализированы с использованием методов рентгеновской дифракции (РФА), сканирующей электронной микроскопии (СЭМ). Твердость образцов измерялась на микротвердомере по методу Виккерса, коэффициент трения и степень износа исследовались с применением измерителя трения и износа. Определено, что поверхность покрытий обладает развитым характером и высокой шероховатостью. Результаты рентгенофазового анализа показали преобладание гексагонального WC в качестве основной фазы, с небольшим содержанием гексагонального карбида вольфрама W_2C в качестве второстепенной фазы, а также незначительное присутствие оксида кобальта CoO. Установлено, что повышенная износостойкость и низкий коэффициент трения покрытий 86WC-10Co-4Cr объясняются высокой объемной долей твердых и стабильных зерен WC, обладающих высокой стойкостью к износу.

Ключевые слова: износостойкость, металлокерамические покрытия, высокоскоростное газопламенное напыление, задвижка, карбиды, обезуглероживание, коэффициент трения, микроструктура.

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Information about the authors

Rakhadilov Bauyrzhan Korabaevich — PhD, Senior researcher at Plasma Science LLP, Associate Professor, Sarsen Amanzholov East Kazakhstan University, Ust-Kamenogorsk, Kazakhstan; e-mail: rakhadilovb@mail.ru, https://orcid.org/0000-0001-5990-7123

Muktanova Nazerke — PhD student of 3d years of study in the specialty “Technical Physics” of Daulet Serikbayev East Kazakhstan Technical University, Researcher at Plasma Science LLP, Ust-Kamenogorsk, Kazakhstan; e-mail: muktanovan@gmail.com, https://orcid.org/0000-0002-4823-6640

Kakimzhanov Dauir Nurzhanuly — PhD student of 3d years of study in the specialty “Technical Physics” of Daulet Serikbayev East Kazakhstan Technical University, Researcher at Plasma Science LLP, Ust-Kamenogorsk, Kazakhstan; e-mail: dauir_97@mail.ru, https://orcid.org/0000-0001-9453-0456

Piotr Kowalewski — Doctor of Science, degree: habilitation, Professor, Wroclaw University of Science and Technology, Wroclaw, Poland; e-mail: piotr.kowalewski@pwr.edu.pl, https://orcid.org/0000-0003-2216-5706