

Article

Microstructure and Tribological Properties of HVOF-Sprayed Nanostructured WC-12Co/Fe₃O₄ Coatings

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Abstract: Due to wear and improper operation, many machine parts become useless, which is why issues of friction and wear remain constantly relevant across all industrial sectors. This paper presents the results of research on the microstructure and properties of a nanostructural composite coating containing solid lubricant. The coating was deposited from a mixture of nanostructural WC-12Co powder and nanostructural Fe₃O₄ powder using HVOF spraying. Despite significant differences in grain size and density of both powders, the deposited coating consisted of WC-12Co matrix containing evenly distributed Fe₃O₄. The XRD analysis of the coating confirmed the presence of both components and the presence of W₂C, which resulted from the decarburization of WC due to the high temperature during the spraying process. Furthermore, the microstructure analysis of the coatings confirmed that they contained both nanostructural WC and Fe₃O₄ grains that were present in the feedstock. The coefficients of friction, microhardness, and wear of the nanostructured composite coatings were determined using an experimental binomial program. Based on the ANOVA conducted, it was determined that the most significant impact on the friction coefficient is the Fe₃O₄ content in the sprayed mixture, while the oxygen to propane ratio affects the microhardness. For the wear of nanostructural composite coatings, the most important parameter is the spraying distance.

Keywords: nanocomposite; HVOF; WC-12Co; Fe₃O₄; tribology; solid lubricant



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1. Introduction

The problems of friction and wear are constantly essential in all branches of industry because they largely determine efficiency. Properly constructed friction nodes should be characterized by high wear resistance, which allows for significant material savings, and a low friction coefficient, which in turn reduces the amount of energy used to overcome resistance to movement. Meeting these requirements is possible by appropriate selection of materials for the friction pair and the introduction of a lubricant that is delivered to places where friction occurs. The lack of direct contact between the surfaces of the friction pair elements allows for the elimination of pathological wear processes such as adhesive and abrasive wear. The separation of these surfaces can be achieved using liquid lubricants [1–3]. However, this requires introducing an appropriate lubrication system into the structure, often with seals and heat exchangers. Service is also necessary to control the quantity and quality and to replenish the necessary amount of lubricant. If the lubrication system fails, accelerated wear occurs and then the device fails. Another possibility of separating the mating surfaces is to introduce solid lubricant into the friction pair. This refers to solid bodies that have relatively low cohesive forces and can therefore be easily

plastically deformed. They may have a crystalline or amorphous structure. Low cohesion may either characterize the entire body or occur only in certain preferred slip directions, and in terms of cohesion, it has an anisotropic character. Thanks to this property, these materials are resistant to compression and susceptible to shearing, i.e., shifting of sheets [4,5]. The advantages of solid lubricants include much greater mechanical and thermal resistance than liquid and plastic lubricants, which allows them to be used in a much wider range of operating conditions. They are used especially where there are high specific pressures, low or high temperatures, vacuum, and aggressive environments. The use of solid lubricants is also beneficial where the presence of liquid lubricants is undesirable, e.g., in the electronics, food, or printing industries, and in places where access to a working device may be difficult, e.g., orbital stations. Simplifying the structure of the friction pair and reducing its weight is also of great importance. The ecological aspect is also important, because the elimination of the lubricant excludes the possibility of environmental contamination. The advantages of materials with solid lubricant properties requires the development of technologies for their application. Therefore, it is necessary to analyze their properties, working conditions in which we want to use them, and technological possibilities [6,7]. Various types of CVD and PVD methods [8,9], electro-spark [10,11] and laser technology [12,13] offer greater possibilities of applying thin coatings of many materials that are solid lubricants. They allow coatings of precisely defined thickness to be obtained, very well bonded to the substrate, without the need for expensive finishing processing. However, these technologies are expensive and the application possibilities are limited by the size of a given part. A completely different group of methods for introducing solid lubricant into the friction pair is based on the concept of creating composite structures containing solid lubricant using various thermal spraying techniques [14,15]. One of them is HVOF spraying, which has enabled the deposition of composite coatings containing various solid lubricants for many years [16–18]. The next stage is the use of nanostructured materials, which have much better properties [19–21]. In most cases, the share of solid lubricant is set arbitrarily and the coatings are deposited using the same parameters [16,18,22–25]. Therefore, knowledge of the influence of spraying parameters on the properties of coatings is very important. Therefore, the use of statistical methods for optimizing spraying parameters is a very effective solution to this issue [26,27]. This is particularly interesting in the case of composite coatings consisting of both a nanostructured matrix and a nanostructured solid lubricant. In the studies carried out, nanostructured WC-Co with very good mechanical and anti-wear properties [21,26] and nanostructured Fe_3O_4 , which has the properties of a solid lubricant [28,29], were used. In recent years, various forms of nanostructured Fe_3O_4 have been used as nano-lubricant additives in various oils, resulting in significant reductions in friction coefficient and wear [30–33]. Therefore, the next step and novelty is the use of nanostructured Fe_3O_4 as a solid lubricant in a nanostructured matrix under dry friction conditions. The purpose of this study is to investigate the microstructure and tribological properties of nanostructured WC-12Co/ Fe_3O_4 composite coatings deposited by HVOF based on the DOE experiment. The experiment presented in this article includes the following stages: developing a binomial experiment plan, the identification of nanostructures in powder materials, the identification of nanostructures in HVOF-sprayed coatings, the determination of optimal HVOF spraying parameters, a verification experiment, an analysis of the results, and a discussion.

2. Experiment

2.1. Materials and Methods

A coating material made from a composite of nanostructured WC-12Co (Nanox S7412, Inframat Corp., Manchester, CT, USA) with added nanostructured Fe_3O_4 (Nanox 26FE23, Inframat Corp., Manchester, CT, USA) was prepared by mixing measured quantities of the components in a V-type mixer for one hour in reference to the data in Table 1. The particle size distribution was determined by means of a Sympatec GmbH Helios laser analyzer. Coatings were deposited using the Hybrid Diamond Jet (Sulzer Metco) supersonic

spray system with specified parameters (Table 2). Before spraying, samples made of C45 steel were degreased and sandblasted with EB14 electrocorundum under 0.5 MPa air pressure. Samples for metallographic studies were cut using an “ISOMET—low-speed saw” (BUEHLER) equipped with a diamond blade, and microsections of the coatings were prepared on a “LaboPol—5” (STRUERS) polishing machine. Coating examinations were conducted using JSM Jeol 7100F and Jeol JSM 5400 scanning microscopes equipped with an ISIS 300 Oxford (EDS) microprobe for chemical composition analysis. The FEI E-SEM XL 30 (FEI Company, Hillsboro, OR, USA) and TEM: FEI Tecnai G2 SuperTWIN 200 kV (FEI Company, Hillsboro, OR, USA) equipped with an SIS MegaView III CCD camera were applied for microstructure analysis. The chemical composition investigation was performed using an energy-dispersive X-ray spectrometer produced by EDAX. An FIB: ThermoFisher Scios 2 Dual Beam microscope (Thermo Fisher Scientific Inc., Waltham, MA, USA) and EasyLift lift-out system were applied to cut out the thin foils using the focused ion beam (FIB) technique. Phase composition was analyzed using a Bruker D8 Discover X-ray diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) with CoK α radiation (wavelength of 1.7903 Å). The phase composition was analyzed using Diffraction EVA V3.0 and HighScore Plus 4.8 software with the ICDD PDF-4+ crystallographic database. Measurements were performed on the coating surface area for each sample without prior preparation. Samples were weighed on a Denver Instrument Company scale with an accuracy of 0.0001 g. HV0.1 microhardness tests of coatings were conducted using an MMT-X3 hardness tester (Matuzawa Co., Ltd., Akita, Japan) with automatic microhardness reading, averaged from 10 measurements. Tests of the friction coefficient and the wear of HVOF-sprayed coatings were carried out with the use of a ball-on-disk T-01 tribotester (The Institute for Sustainable Technologies, Radom, Poland). The counter body was a ¼” diameter ball made of 100Cr6 steel. The ring’s rotational speed and mass were set before testing. Continuous friction force measurement was collected by a computer during the one-hour test. The investigations were performed under 4.9 N load and at a linear speed of 0.5 m/s and temperature of 25 °C. Each coating was tested three times. The surface of the coatings was ground and polished on diamond polishing suspensions with a finishing gradation of 1 µm. After polishing, all samples had a rough surface roughness (Ra) equal to 0.012 ÷ 0.016 µm.

Table 1. Parameters for HVOF spraying.

Level	Parameter			
	η , wt.% Fe ₃ O ₄	λ , O ₂ /C ₃ H ₈	d, mm	Q, L/min
Lower	5	4.4	180	336
Upper	15	5.0	230	414

Table 2. Binomial plan for HVOF experiment.

Experiment	η wt.% Fe ₃ O ₄	λ O ₂ /C ₃ H ₈	d mm	Q L/min	CoF, μ	Microhardness HV0.1	Coating Wear, g
1	5	4.7	180	336	0.2642	867.4	0.00089
2	5	4.7	200	375	0.3133	993.5	0.00143
3	5	5.0	180	375	0.3934	845.9	0.00061
4	5	5.0	200	336	0.3057	873.2	0.00071
5	15	4.7	180	375	0.2143	907.4	0.00131
6	15	4.7	200	336	0.1966	899.9	0.00161
7	15	5.0	180	336	0.2162	874.2	0.00157
8	15	5.0	200	375	0.2096	864.2	0.00199

2.2. Design of Experiment

In the experiment, the spraying parameters were changed on two levels (upper and lower), where η —percentage weight of Fe₃O₄ Nanox in the mixture with WC-12Co Nanox;

λ —the ratio of oxygen to propane in the flammable mixture; d —spraying distance; Q —air flow (Table 1).

In the conducted research, a binomial distribution was utilized, and measurements were carried out according to the binomial plan shown in Table 2 to determine the effect of spraying parameters on the coefficient of friction (CoF), microhardness, and coating wear.

The collected results from Table 2 were analyzed statistically using ANOVA and $2^{(k-p)}$. In HVOF spraying processes, it is assumed that the coating property (output parameter) is related to the input factors of the spraying process by a mathematical relationship (1) [34,35]:

$$y = f(x_n) \quad (1)$$

where x_n refers to the input factors. It is important to plan the experiment with a minimum number of input factors so that the process of selecting the best output value is not complicated. It seems that the following linear function meets our expectations (2) [36]:

$$y = a_0 + a_1x_1 + \dots + a_nx_n \quad (2)$$

where a_0 is the mean value, a_1, a_n is the linear regression coefficient, and n is the number of input parameters.

In the first-order two-level programs, the input factors are normalized to two levels, upper (1) and lower (−1), and the central values are calculated as the arithmetic mean of the input factor. The significance of the coefficients was assessed with the use of ANOVA, F and p tests. The quality of the obtained results is presented in Pareto diagrams or profiles of approximated values and utility.

The new values of the input factors were estimated in proportion to coefficients of the linear Equation (2), determined for the output parameters of friction, HV0.1 microhardness, and coating wear. On the basis of the coefficients of Equation (2), new input parameter values were estimated. For instance, the new value of Q was calculated based on the weight proportion expressed in Equation (3).

$$Q_N = Q_D + (Q_U + Q_D) * a_{kN} \quad (3)$$

$$a_{kN} = (a_{kh} + a_{kF} + a_{kW}) / \Sigma i(a_{iH} + a_{iF} + a_{iW}) \quad (4)$$

where Q_N —the new value estimated based on the carried out research; Q_N and Q_N —lower and upper values of the input parameter. Coefficient a_{kN} determines the influence of the estimated coefficient on the value of the examined output parameters, which are friction, HV0.1 microhardness, and coating wear. In the applied statistical optimization analysis, an important part is the analysis of variance and the study of the utility function, the geometric equivalent of which is called profiles of approximated values. The analysis of the graphical presentation itself shows the average value for the examined output quantity along with the effect (influence) of the input values. For the selected analyzed input value, its influence on the output value is determined by the slope of the line. If the slope of the line is negative, an increase in the value of the input parameter reduces the analyzed output value. And of course, when the coefficient is positive, the input parameter associated with the line affects the input value proportionally. If the slope coefficient is close to zero, it means that the impact of the input value (or rather its change) is insignificant. The Pareto diagram systematically reflects the contribution of individual input quantities to the value of the output quantity. The parameter $p = 0.05$ is marked on the charts, indicating the statistical significance of the selected parameter [36,37].

3. Results and Discussion

3.1. Microstructure of Nanostructured WC-12Co Nanox Powder

Figure 1a presents the shape of the grains of WC-12Co Nanox. The grains are of irregular shape but some of them are spherical. This grain structure is usually created in the agglomeration and sintering process. This method of producing powder is usually

associated with significant porosity which is visible in the microsection of powder grains (Figure 1b). The manufacturer of the powder declares that a single grain of the powder consists of tungsten carbide sized 100 to 500 nm. The analysis of grain surface makes it possible to confirm this declaration (Figure 1c). Tungsten carbide particles in this size range can be specified on the powder grain surface, at very high magnification (Figure 1d). The measurement of the powder grain size distribution (Figure 2a) showed a fairly wide range of their diameters, reaching an almost three-fold difference in value ($d_{10} = 22.72 \mu\text{m}$, $d_{50} = 34.50 \mu\text{m}$, $d_{90} = 51.72 \mu\text{m}$). The X-ray diffraction pattern of the powder confirmed the phase composition declared by the manufacturer, a clearly visible WC phase and much smaller peaks of cobalt, the share of which is only 12 wt.% (Figure 3a).

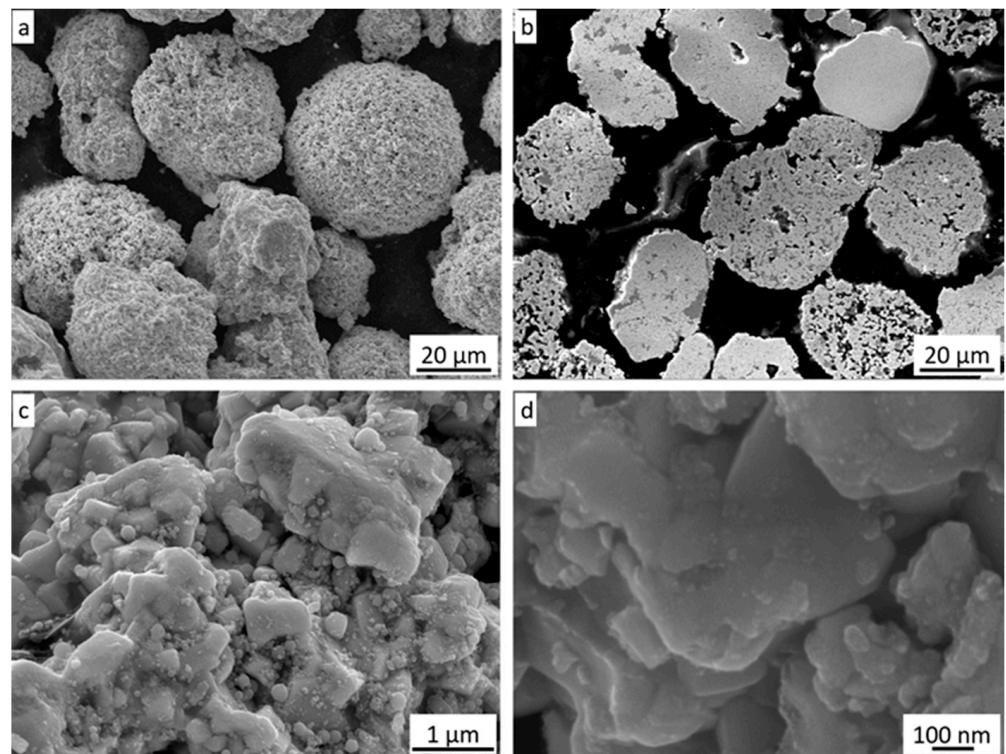


Figure 1. WC-12Co Nanox powder: (a) grain morphology, (b) grain cross-section, (c) grain surface morphology, and (d) nanograins at grain surface.

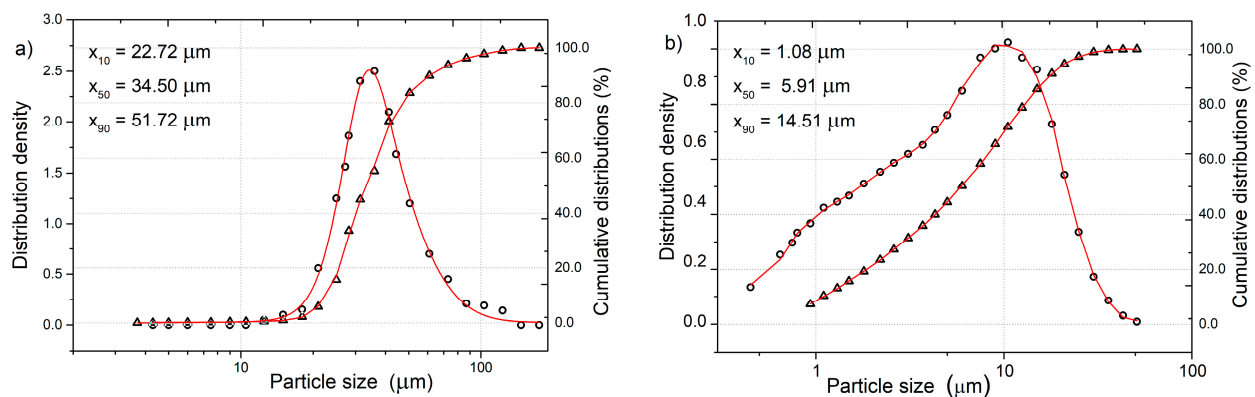


Figure 2. Particle size distribution of powder, showing (o) distribution density and (Δ) cumulative distribution (%): (a) WC-12Co Nanox; (b) Fe_3O_4 Nanox.

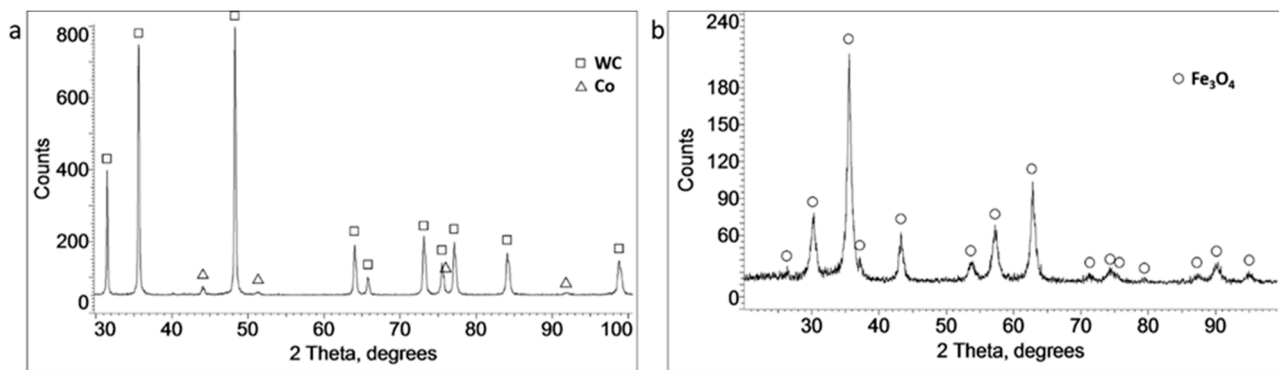


Figure 3. X-ray diffraction pattern of powder: (a) WC-12Co Nanox; (b) Fe₃O₄ Nanox.

3.2. Microstructure of Nanostructured Fe₃O₄ Nanox Powder

The morphology of Fe₃O₄ Nanox grains is shown in Figure 4a. A very large difference in grain size is visible, which was confirmed by the analysis of the grain size distribution (Figure 2b). Analysis of the obtained powder parameters ($d_{10} = 1.08 \mu\text{m}$, $d_{50} = 5.95 \mu\text{m}$, $d_{90} = 17.41 \mu\text{m}$) indicates that it consists of very fine grains compared to WC-12Co Nanox powder. Moreover, powder grains are characterized by an irregular and spherical shape resulting from the agglomeration and sintering process. Analysis of the grain cross-section revealed their significant porosity (Figure 4b). Additionally, each grain consists of smaller particles of very different size, from submicrons to several microns (Figure 4c). Further analysis of these small particles showed that they all have a very homogenous structure and consist of Fe₃O₄ nanograins of a very similar size (Figure 4d). Microstructure images in bright field, dark field, and corresponding electron diffraction highlight the crystallite structure, estimating the crystallite size to be around $13 \text{ nm} \pm 3 \text{ nm}$ (Figure 5). The XRD analysis confirmed that this nanostructured powder does not contain any impurities and consists only of pure magnetite (Figure 3b).

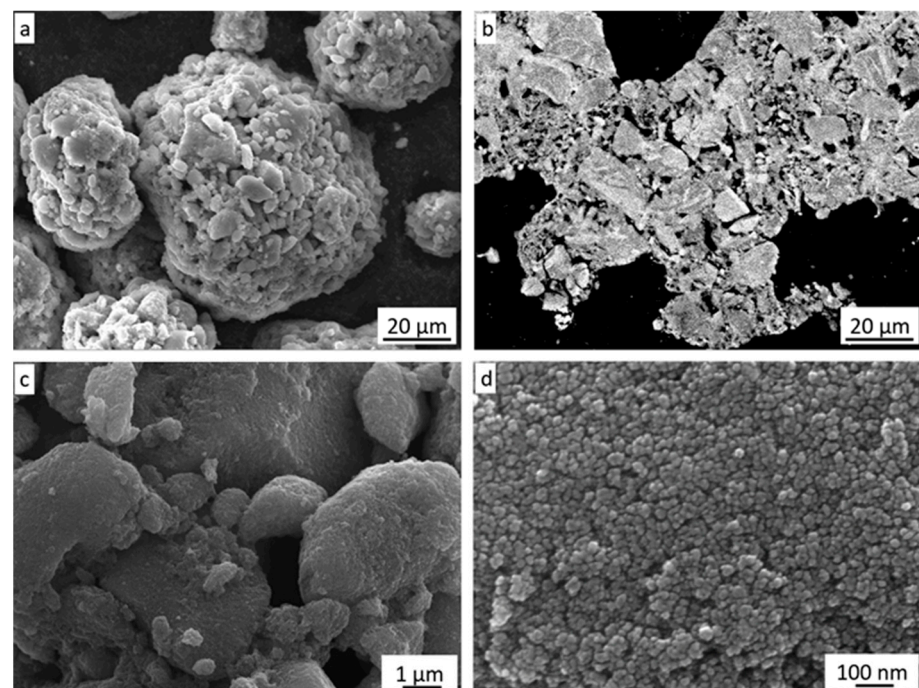


Figure 4. Fe₃O₄ Nanox powder: (a) grain morphology, (b) grain cross-section, (c) grain surface morphology, and (d) nanograins at grain surface.

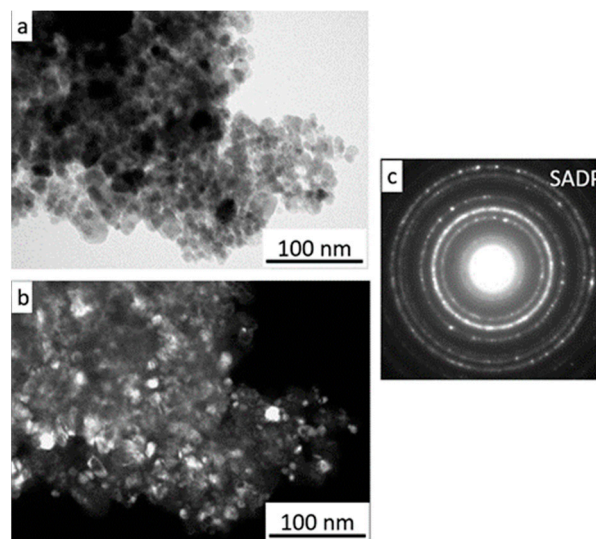


Figure 5. Nanostructure of Fe_3O_4 Nanox powder: (a) in the bright field (BF), (b) in the dark field (DF), and (c) electron diffraction (SADP).

3.3. Microstructure of Nanostructured WC-12Co/ Fe_3O_4 Coating

Figure 6a presents the microstructure of the deposited WC-12Co Nanox powder mixture with 15 wt.% Fe_3O_4 Nanox powder. A uniform distribution of the Fe_3O_4 phase in the form of thin bands that are several micrometers thick in the WC-Co matrix is visible. At higher magnification, the presence of pores is noticeable, which are the result of the significant porosity of the sprayed powders (Figures 6b and 7a). Deformed WC-12Co grains (light phase) together with deformed Fe_3O_4 grains (dark phase) are visible on the coating surface (Figure 6c). As in the case of the cross-section of the coating, at high magnification, the pores between the lamellas are visible (6d).

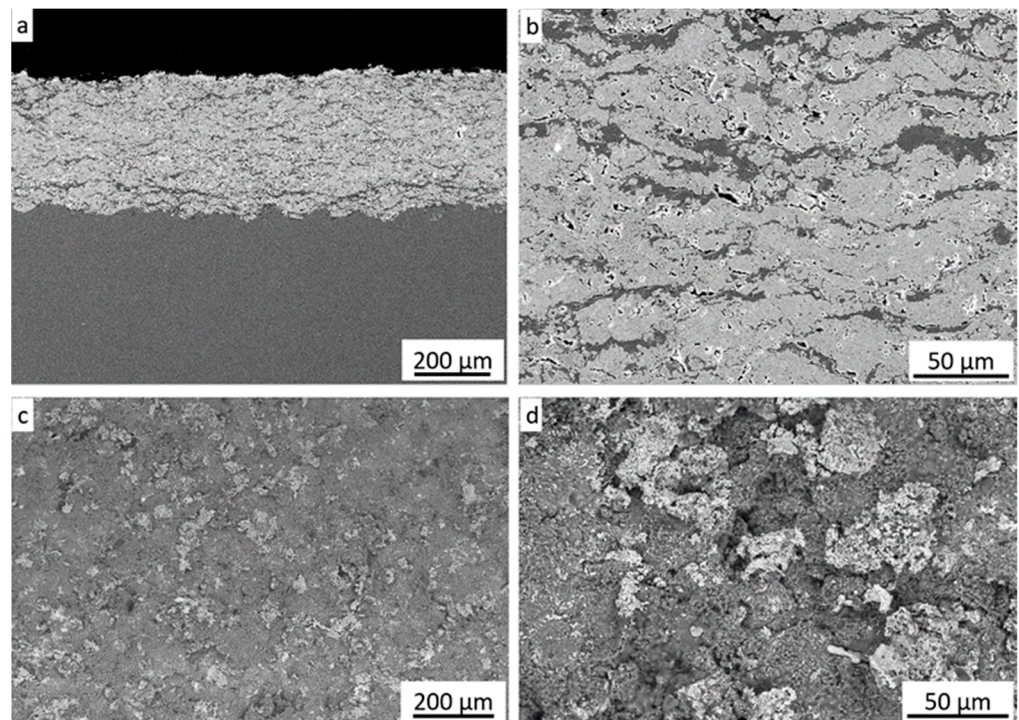


Figure 6. Microstructure of nanostructured WC-12Co/ Fe_3O_4 coating: (a) mag. 100 $\times$ and (b) mag. 500 $\times$; (c) morphology of surface: mag. 100 $\times$ and (d) mag. 500 $\times$.

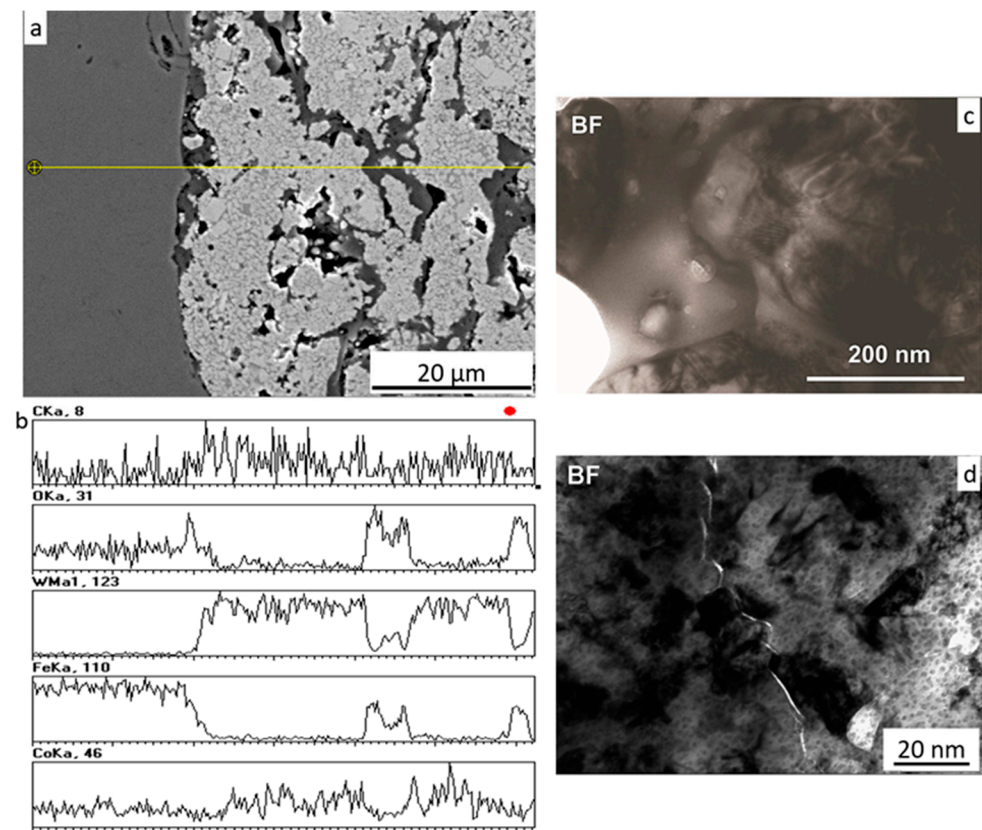


Figure 7. Nanostructured WC-12Co/Fe₃O₄ coating; (a) microstructure, (b) linear analysis, (c) nanograins of WC, and (d) nanograins of Fe₃O₄.

The linear analysis of the microstructure of the nanocomposite coating confirmed the presence of ingredients contained in the feedstock (Figure 7a,b). The high iron content of the substrate drops sharply in the coating where an increase in tungsten and cobalt is seen. The increase in iron presence in the coating coincides with increased oxygen counts, confirming the presence of Fe₃O₄ in this area. Figure 7c shows the nanostructured WC grains in the deposited nanocomposite coating. The nanostructured Fe₃O₄ was also preserved during HVOF process. The very small spherical Fe₃O₄ nanograins present in the starting powder were also retained in the deposited coating (Figure 7d). The analysis of phase composition of the nanostructured composite coating confirmed the presence of all components in the sprayed mixture (Figure 8).

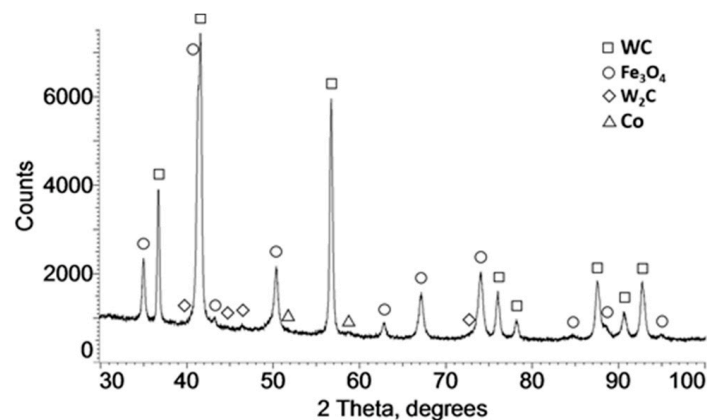


Figure 8. X-ray diffraction pattern of nanostructured WC-12Co/Fe₃O₄ coating.

Small ditungsten carbide (W_2C) peaks are also visible. This is the result of decarburization of monotungsten carbide (WC) under the influence of high temperature of the combustible mixture during the HVOF spraying process.

During flight towards the substrate, these grains are subjected to heating and then, after impact onto the substrate, undergo solidification and cooling. The decarburization process is the result of the thermal history of the particles in flight, because powder consists of smaller and larger grains that can be found in the core of the spray jet as well as on its edges. The high temperature of the process causes the decarburization of tungsten carbide grains to tungsten dicarbide and the appearance of metallic tungsten. These phenomena can be described by the following reactions: $2WC \rightarrow W_2C + C$, $W_2C \rightarrow 2W + C$. Additionally, the significant decrease in the amount of carbon as a result of flame oxidation of the coating can be illustrated by the reaction $2C + O_2 \rightarrow 2CO$ (gas). Other phases can also be created, e.g., Co_3W_3C and Co_6W_6C , which occurred when the WC-Co powder was exposed to high temperatures exceeding its melting point, causing decomposition of WC and its reaction with cobalt. The final phase composition of the coating depends on the spraying technique and operating parameters [38,39]. The HVOF process should be carried out in a such a way as to minimize the presence of the hard and brittle W_2C phase which reduces the tribological properties of the coating [40]. Taking into account the trace amount of this phase in the obtained nanocomposite WC-12Co/Fe₃O₄ coating, it can be assumed that its impact on the wear process was negligible.

3.4. Analysis of Binomial Experiment for CoF of Nanostructured WC-12Co/Fe₃O₄ Coatings

The first parameter subjected to the study is friction. The obtained results were subjected to ANOVA, indicating the input parameter with the highest significance. The analysis showed a statistically significant effect of η on the friction value. The function F took the value of 61.8, with a p -value of 0.004. Other input parameters do not have such an influence, as the function F takes values below 1 and the p -value is significantly greater than 0.05. It was found that the remaining parameters do not have a statistically significant impact on the measured property. The actual impact of these parameters requires further investigation under different experimental conditions. Standardized results were depicted on the Pareto diagram (Figure 9) and profiles of approximated values (Figure 10).

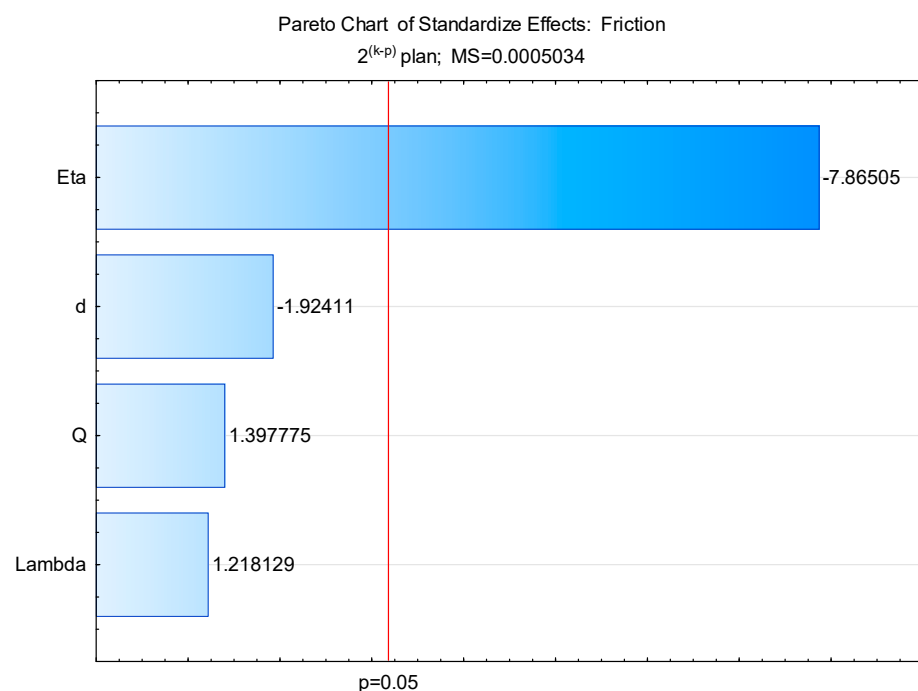


Figure 9. Influence of input parameters on the value of the CoF.

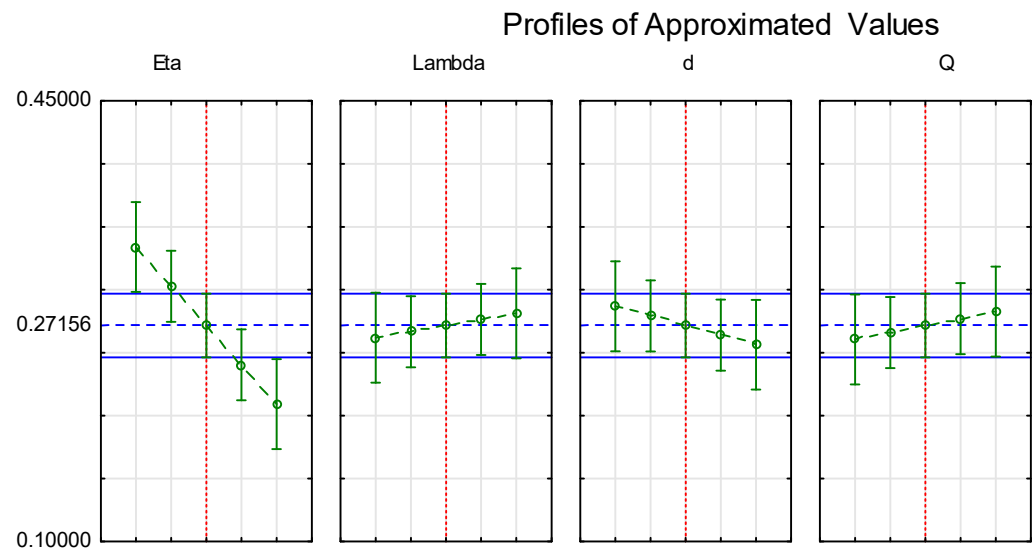


Figure 10. Profiles of approximate values for the CoF.

In the diagram (Figure 10), the range of variability of the utility function (profiles of approximated values) for Eta changes quite dramatically. The slope is negative, so an increase in Eta causes a decrease in the CoF. The remaining parameters do not show significant changes. The influence of the utility function is visible in Equation (5). The assessment of the statistical effect of individual input parameters generated regression coefficients associated with Equation (2), and ultimately, we obtain

$$\text{CoF} = 0.271 - 0.062\eta + 0.009\lambda - 0.016d + 0.011Q \quad (5)$$

3.5. Analysis of Binomial Experiment for Hardness of Nanostructured WC-12Co/Fe₃O₄ Coatings

A statistical test for microhardness, HV_{0.1}, was conducted for two samples, considering 5 wt.% and 15 wt.% of Fe₃O₄ admixture, and the mean values are shown in Table 2. Based on the measurement points, hardness values were compiled to create maps. These maps are presented in Figures 11 and 12.

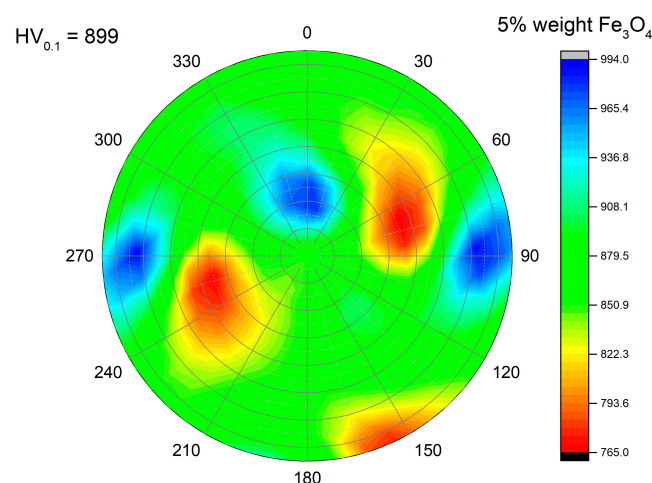


Figure 11. Distribution of microhardness obtained for 5 wt.% Fe₃O₄ content.

In the examined microhardness area, it was 863 ± 21 and 899 ± 25 for samples with Fe₃O₄ admixtures of 5 wt.% and 15 wt.%, respectively. The difference in microhardness values is not statistically significant. Similarly to the friction coefficient, the obtained microhardness results were subjected to ANOVA. The analysis showed no dominant

influence of any input parameter on the examined microhardness. Only the parameter η (Eta) from the group of input parameters has the greatest influence on microhardness. For each investigated input parameter, the function F took values below 1, and the parameter p took values exceeding 0.7, confirming the lack of statistically significant influence of any of the input parameters. A graphical presentation of the contribution of individual factors to the hardness of the coating is presented in a Pareto diagram (Figure 13).

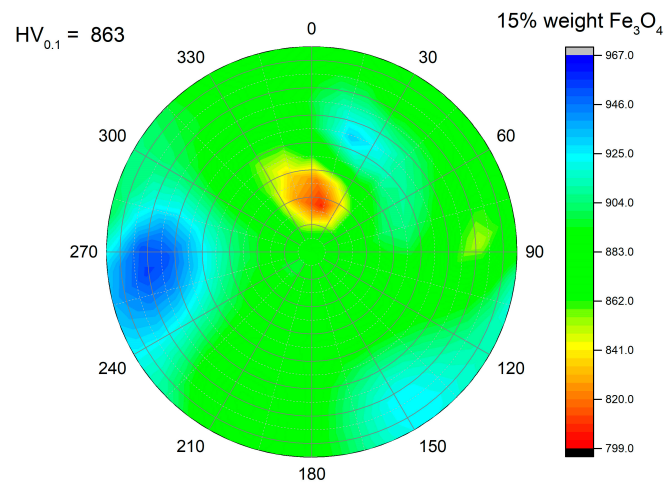


Figure 12. Distribution of microhardness obtained for 15 wt.% Fe_3O_4 content.

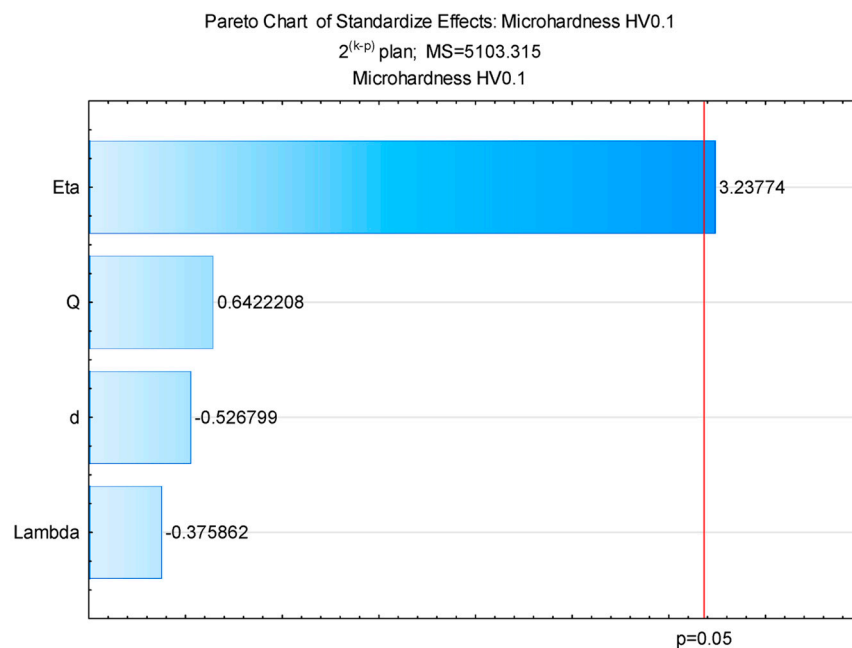


Figure 13. The influence of input parameters on the microhardness value.

The diagrams in Figure 14 emphasize the meaning of the input quantity values. The diagram of the utility of the microhardness differs the most from the level; thus, it provides information about the significant influence on the value of the microhardness. Similarly to the diagram (Figure 10), the range of variability of the utility function for Eta changes quite dramatically. The slope is positive this time, so an increase in Eta causes an increase in the CoF value. The remaining parameters do not show significant changes. The influence of the utility function is visible in Equation (6).

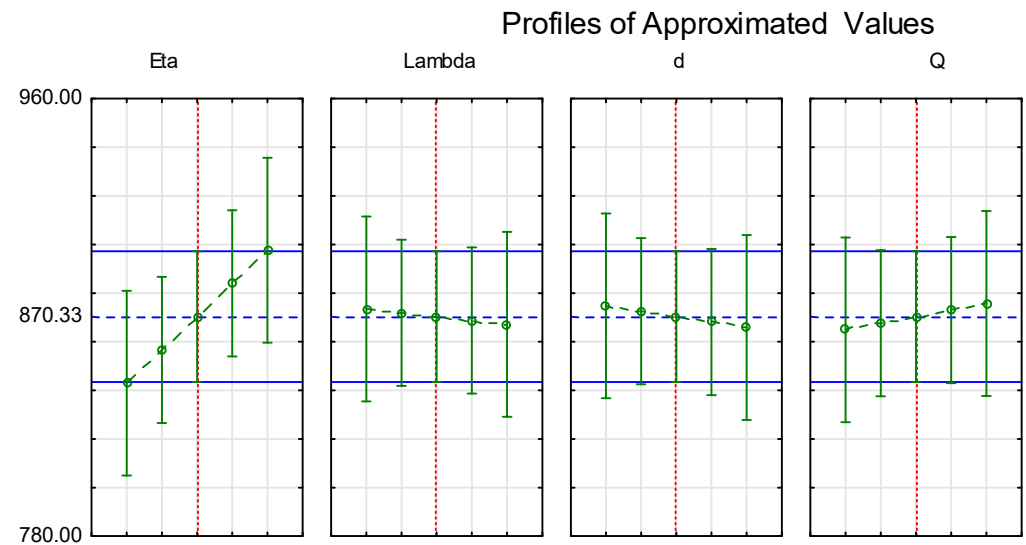


Figure 14. Profiles of approximate values for the microhardness.

The results of the above analysis reflect the coefficients in (6):

$$HV_{0.1} = 870.33 + 27.35\eta - 3.17\lambda + 4.45d + 5.42Q \quad (6)$$

3.6. Analysis of Binomial Experiment for Wear of Nanostructured WC-12Co/Fe₃O₄ Coatings

The next parameter under investigation is coating wear. Similar to previous analyses, the obtained results were subjected to ANOVA to identify the input parameter with the highest significance. The analysis revealed the absence of a dominant input parameter affecting the coating wear value. The remaining input parameters do not have such an influence, as the function F takes values below 1 and the p -value is in the range from 0.2 to 0.7. The standardized results are depicted in a Pareto diagram (Figure 15).

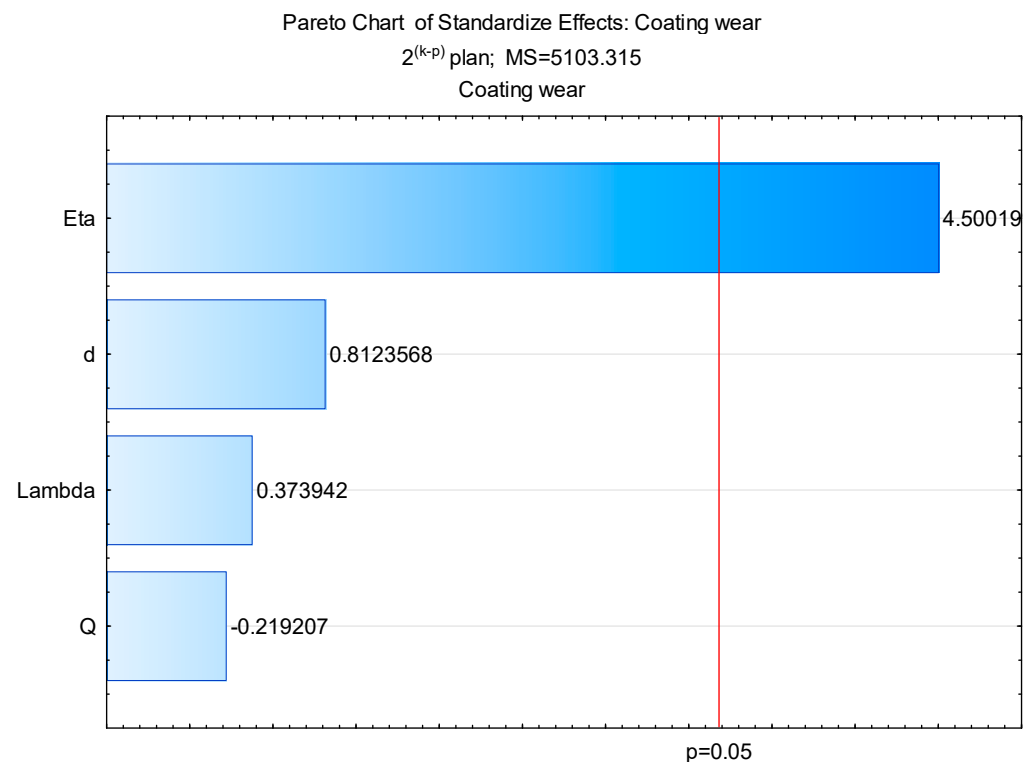


Figure 15. The influence of input parameters on the coating wear value.

The diagram of profiles of approximated values illustrates the distribution of the influence of input parameters on the studied output parameter, which is coating wear (Figure 16). As in the previous diagrams (Figures 10 and 11), the range of variability of the utility function for Eta changes quite dramatically. The slope is positive this time, so Eta causes an increase in the CoF value. The remaining parameters do not show significant changes. The influence of the utility function is visible in Equation (7). The average value of coating wear is equal to 0.00118 g.

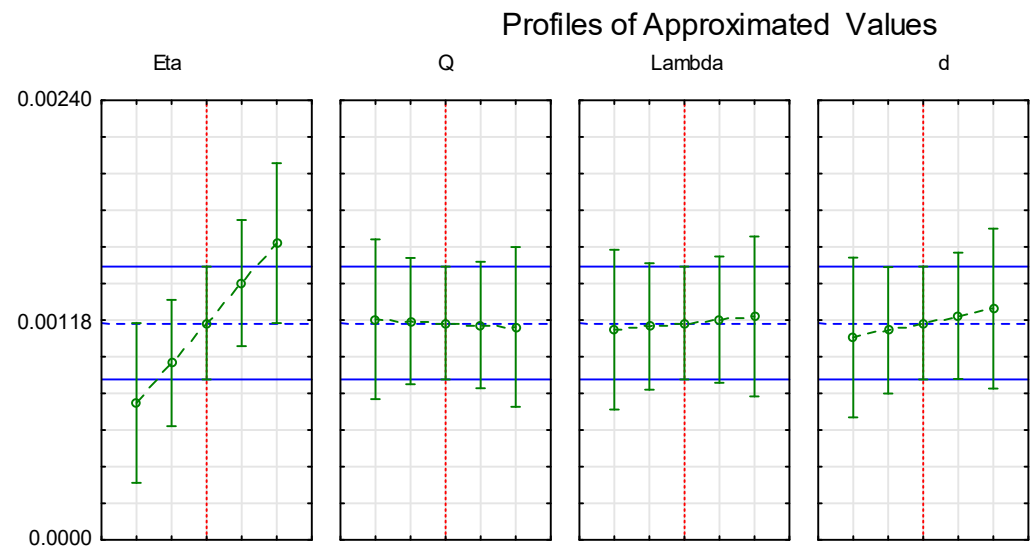


Figure 16. Profiles of approximate values for the coating wear.

As a result of the conducted 2(k-p) binomial analysis, regression coefficients were obtained (7):

$$\text{Coating wear} = 0.00118 + 0.00044\eta - 0.00002 Q + 0.000036\lambda + 0.0000d \quad (7)$$

Based on the obtained results of eight experiments, in accordance with the plan included in Table 2, new values of the input parameters were estimated in accordance with the applied methodology defined by Equations (3) and (4). The bases for calculating the new input values were the coefficients defined in Equations (5)–(7). These parameters were used to spray the verification sample (Table 3). The obtained sample was characterized by the following parameters: CoF—0.1907, hardness—867.4 HV0.1, and coating wear—0.00054.

Table 3. Summary of optimal input values and obtained output values.

Experiment	η wt.% Fe_3O_4	λ $\text{O}_2/\text{C}_3\text{H}_8$	d mm	Q l/min	Coefficient of Friction, μ	Microhardness HV0.1	Coating Wear, g
9	15.9	4.6	175	344.4	0.1907	867.4	0.00054

Friction joints with solid lubricants, especially in nanostructured form, are an interesting subject of research, as it is necessary to explain all the processes that occur between moving elements. Particular attention is paid to the microstructure of the surface, its composition and phase distribution, and the amount of solid lubricant, which have a significant impact on the coefficients of friction and wear. There is an optimal composite composition that ensures minimum values of the coefficients of friction and wear [41]. Analyzing the surface of the HVOF-sprayed coating, it was assumed that the coating consists mainly of WC grains in a cobalt matrix and a solid lubricant (Fe_3O_4). Based on the phase analysis of the composite coating (Figure 8), it can be stated that the W_2C peaks are negligibly small compared to the other components of the coating. Therefore, in this case, the influence

of this component can be neglected in the further analysis of the lubrication process. In the next step, analyzing the surface of the HVOF-sprayed coating, it can be assumed that the coating consisted mainly of WC grains in a cobalt matrix and a solid lubricant in the form of Fe_3O_4 . The processes of sliding friction and wear of the sprayed nanostructured WC-12Co/ Fe_3O_4 HVOF composite coatings were responsible for the formation of grains containing WC and Fe_3O_4 . The particles are fragmented, combined, and distributed in the coating–surface interface. Their dimensions decreased as a result of the development of shear stresses. It can be assumed that the most important aspect in this process seem to be very small, nanostructured WC grains (Figure 7), which contributed to the wear of the coating and the cooperating surface. On the other hand, the presence of nanograins of Fe_3O_4 in them, i.e., Co and especially Fe_3O_4 , caused a decrease in static stresses, and consequently, a decrease in the coefficients of friction and wear. This mechanism also occurs when other solid lubricants are used [16,42–44]. The wear analysis confirmed this lubrication and wear mechanism (Figure 17).

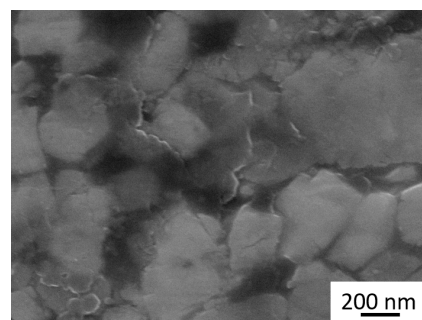


Figure 17. Morphology of the nanostructured Fe_3O_4 films on the nanostructured WC-12Co/ Fe_3O_4 coating.

In this nanostructured composite coating, a low-strength protective film (Fe_3O_4 layer) was formed during the sliding of the ball on the disk. The counter body pressing against the HVOF spray composite coating caused the particles of the solid lubricant, Fe_3O_4 , to fill in the coating pores. The lubricant was spread over the tungsten carbide grains and the cobalt matrix. The smooth surface was able to retain the effectiveness of the lubricating layer (Figure 17). Iron oxide, Fe_3O_4 , is a material with a lamellar structure in the direction (001). At the interface of the coating and the counter body, there were layers varying in thickness. The light WC grains were grey in color varying in intensity. The thin films of nanostructured Fe_3O_4 formed during friction on the surface of tungsten carbides and the cobalt matrix indicated that the HVOF spray nanostructured solid lubricants were characterized by high adhesion. The nanostructured layers of Fe_3O_4 were not regular in shape, which was due to their deformations at the interface in relation to the direction of movement. The nano-lubricating Fe_3O_4 coating formed during collaboration in the friction joint leads to a reduced coefficient of friction and wear.

4. Conclusions

Nanostructured composite WC-12Co/ Fe_3O_4 coatings were deposited by HVOF spraying using a binomial experiment. The microstructure and phase composition of the powders used and sprayed coatings were analyzed by XRD, SEM, and TEM. An analysis of the influence of spraying parameters on the friction coefficient, microhardness, and wear of nanostructured composite coatings was carried out. Based on the research conducted, the following conclusions were drawn:

1. The HVOF-sprayed nanostructured composite coating WC-12Co/ Fe_3O_4 contains nanocrystalline grains, both WC and Fe_3O_4 , which were contained in the nanostructured feedstock.

2. The phase composition of the nanostructured composite coating included the same phases that occurred in the starting powders. However, the high temperature of the HVOF process resulted in the decarburization of WC and the appearance of trace amounts of W_2C .
3. The conducted studies on the influence of input parameters (η , λ , d , Q) on the coefficient of friction, microhardness, and coating wear showed that the greatest influence on the coating properties was the content of Fe_3O_4 . The remaining input parameters did not indicate a significant impact on the tested values.
4. Optimization of the spraying parameters as a result of the binomial experiment allowed for reduction in the friction coefficient by 7% and coating wear by 11%.

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