

Article

Deposition Kinetics and Structural Transformations in WC–12Co and Cr₃C₂–NiCr HVOF Coatings Depending on Powder Dispersion

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Abstract

HVOF coatings based on tungsten and chromium carbides are widely used in aerospace, energy, and oil and gas industries. However, the selection between the wear resistance of WC–Co and the corrosion resistance of Cr₃C₂–NiCr is often hindered by a lack of systematic data on the effect of powder particle size. In this study, WC–12Co and Cr₃C₂–NiCr coatings were deposited onto 12Kh18N10T stainless steel substrates by HVOF spraying using three particle size fractions: <20, 20–32, and 32–40 µm. Individual spray parameters were selected for each material to ensure high-quality deposition (standoff distance 350 mm, one pass for WC–12Co; 250 mm, two passes for Cr₃C₂–NiCr). The influence of powder particle size distribution on coating properties was investigated using a comprehensive set of methods, including scanning electron microscopy, X-ray diffraction with Rietveld quantitative phase analysis, microhardness testing, tribological testing, electrochemical measurements, and numerical modeling of particle in-flight motion. It was found that the 20–32 µm fraction is optimal for both materials. Different degradation mechanisms were identified: for WC–Co, decarburization of WC with the formation of W₂C and η-phases dominates (maximum for the <20 µm fraction); for Cr₃C₂–NiCr, oxidation and carbide dissociation prevail (in the <20 µm fraction—13.7% Cr₂O₃ and 38.6% Cr₇C₃), leading to low coating thickness (~16 µm) due to loss of ductility and wettability. Numerical modeling confirmed that the high velocity of fine Cr₃C₂–NiCr particles (~680–720 m/s) does not compensate for their overheating, whereas for WC–12Co all fractions have velocities above the critical threshold, but coarse particles (32–40 µm) give porosity up to 3.15% due to insufficient deformation. Corrosion tests showed that under spraying conditions optimized for each material, the Cr₃C₂–NiCr coatings (corrosion rate 0.066–0.102 mm/year) are an order of magnitude superior in corrosion resistance to WC–12Co coatings (corrosion rate 0.353–0.651 mm/year), owing to the passivation of the γ-Ni(Cr) matrix; for WC–Co, the main protective barrier is provided by the structural density.

Keywords: HVOF; WC–12Co; Cr₃C₂–NiCr; particle size distribution; porosity; microhardness; corrosion resistance; numerical modeling; oxidation; Lagrangian particle model



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1. Introduction

High-velocity oxygen-fuel (HVOF) thermal spraying is one of the most effective and technologically flexible methods for producing protective coatings designed for service under conditions of intense abrasive wear, high-temperature oxidation, and corrosive attack. This process enables the formation of dense, low-porosity layers with high adhesion to metallic substrates due to the combination of high particle velocities (up to 800–1200 m/s) and moderate temperatures, which minimizes undesirable phase transformations and preserves the original properties of the sprayed materials.

Among the wide range of carbide-based composites used in aircraft engine construction, power engineering, oil and gas equipment, and the defense industry, two systems have gained the greatest acceptance for HVOF spraying: WC–Co (tungsten carbide in a cobalt matrix) and Cr₃C₂–NiCr (chromium carbide in a nickel-chromium binder). These coatings are also considered as a promising alternative to environmentally hazardous hard chromium electroplating and as an effective means of increasing the service life of components operating under high contact loads and in aggressive environments [1,2]. Each of these materials possesses a unique combination of properties, making them attractive for various service scenarios. WC–Co coatings are characterized by exceptional hardness (up to 1300–1500 HV), high abrasive wear resistance, and the ability to withstand significant specific loads, which is due to the presence of the superhard WC phase (microhardness ~2200 HV) and a ductile cobalt binder that provides fracture toughness [3–5]. However, cobalt, being anodic with respect to the carbide, is susceptible to selective dissolution in chloride-containing media, leading to galvanic corrosion, loss of interparticle cohesion, and premature coating failure [6]. Furthermore, at elevated temperatures (above 500 °C), WC–Co actively oxidizes with the formation of brittle tungsten oxides, which reduces wear resistance and limits its application in high-temperature assemblies.

Cr₃C₂–NiCr coatings, in contrast, demonstrate high corrosion resistance in aggressive environments due to the formation of a dense passivating Cr₂O₃ film on the surface of the nickel-chromium matrix, and also retain mechanical property stability at temperatures up to 800–900 °C [7,8]. Chromium carbide possesses sufficiently high hardness (1300–1800 HV) and oxidation resistance, but is inferior to WC in absolute hardness and resistance to abrasive wear at room temperature. Thus, in practice, engineers often face a dilemma: whether to prioritize high wear resistance or corrosion resistance and thermal stability.

A key parameter linking the technological process to the final coating characteristics is the particle size distribution (fractional composition) of the initial powder. Particle size determines their thermal inertia, the intensity of heating and melting in the high-velocity gas jet, the trajectory of motion, the degree of deformation upon impact with the substrate, and consequently, the porosity, adhesion, level of residual stresses, and phase composition of the formed layer [9]. Fine particles, with sizes of less than 20 µm, heat up and accelerate rapidly, but are susceptible to overheating, oxidation, and even evaporation, and also lose velocity over long distances due to high aerodynamic drag. Coarse particles (more than 40 µm), on the contrary, possess high inertia, accelerate slowly, and may not reach a temperature sufficient for plastic deformation, leading to increased porosity and reduced bonding strength [10–12]. Therefore, the choice of the optimal fraction requires coordination with other technological parameters, primarily the spray distance, which determines the moment of particle impact with the substrate and their kinetic energy. The distance from the nozzle to the substrate must provide a balance between sufficient particle velocity and temperature, while avoiding overheating of the substrate and excessive oxidation.

Despite the obvious importance of particle size distribution, the literature lacks systematic comparative studies in which the influence of particle size would be investigated simultaneously for two major carbide systems (WC–Co and Cr₃C₂–NiCr) within a unified

experimental methodology and with the involvement of mathematical modeling. Most studies focus on a single material type or vary the composition while keeping the particle size distribution fixed. For example, Celik and Benli [1] conducted a comparative study of WC–12Co and Cr₃C₂–NiCr coatings under identical HVOF conditions, but used only one powder size range (15–45 µm), which did not allow the influence of particle size distribution to be assessed. Chandramouli and co-authors [2] studied the behavior at elevated temperatures of coatings with additions of 30% WC or Cr₃C₂, but the initial powders had a fixed granulometry. Espallargas et al. [3] varied numerous HVOF parameters, but the particle size remained unchanged for each powder type. Wang and colleagues [4] developed a novel WC–40WB–12Co composition with an ultrafine structure, but did not investigate the effect of particle size on deposition kinetics.

On the other hand, studies devoted to the effect of particle size distribution are limited to a single material. In the work of Mruthunjaya and Parashivamurthy [13] on WC–12Co, it was shown that the fine fraction 10–40 µm provides better erosion resistance at 800 °C, despite lower hardness, which is attributed to a more homogeneous structure. Melnyk and co-authors [14] compared micron and nanoscale WC–Co powders, noting an improvement in mechanical properties with decreasing particle size, but also reported increased oxidation and decarburization. In our previous works [5–7], the influence of narrow fractions (15–20, 20–30, 30–40, 40–45 µm) and individual parameters such as spray distance and oxygen flow rate on the structure and properties of the 86WC–10Co–4Cr system was systematically studied. It was established that the 20–30 µm fraction is optimal, providing minimum porosity and maximum hardness. Furthermore, CFD modeling [8] demonstrated that the 21–35 µm fraction provides the most stable in-flight particle velocities and temperatures, which correlates with minimum porosity. However, these results cannot be directly extrapolated to Cr₃C₂–NiCr due to significant differences in density, heat capacity, thermal conductivity, and melting temperature of the materials.

To fill these gaps and to assess the influence of particle size distribution on kinetic energy and particle trajectories, refined mathematical modeling is required. As a foundation, approaches developed in the literature can be considered. Thus, Li and Christofides [15] developed a fundamental model of the HVOF process accounting for particle size distribution; it was shown that impact velocity is determined by the combustion chamber pressure and particle size, while temperature is determined by the fuel-to-oxygen ratio. However, these models employed a simplified description of aerodynamic drag without accounting for particle non-sphericity and individual thermophysical properties. Ganser [16] proposed a universal correlation for the drag coefficient applicable to particles of arbitrary shape over a wide range of Reynolds numbers, which significantly improves prediction accuracy. In the work of Yu and co-authors [17], using three-dimensional CFD, it was shown that non-spherical particles have higher velocity but lower temperature due to increased drag. Kamnis et al. [18] investigated the effect of particle porosity on their dynamics, establishing that porosity up to 6% has an insignificant effect on velocity but increases surface temperature, promoting deposition. Jalali Azizpour and co-authors [19] developed a finite-element model of WC–12Co particle impact with a substrate, determining the critical deposition velocity to be approximately 150 m/s and the optimal velocity to be approximately 400 m/s. Nevertheless, all of the aforementioned modeling studies were performed for a single material type and do not contain a comparative analysis of the two carbide systems taking into account their individual properties.

The aim of the present work is a comparative investigation of the influence of particle size distribution (<20, 20–32, and 32–40 µm) on the structure, phase composition, mechanical, tribological, and corrosion properties of HVOF-sprayed Cr₃C₂–NiCr and WC–12Co coatings deposited onto 12Kh18N10T stainless steel, with the application of numerical mod-

eling of particle motion that accounts for non-sphericity and the individual thermophysical properties of the materials. To achieve this goal, the following tasks were formulated:

- Experimental deposition of coatings using individually selected parameters for each material (standoff distance, number of passes) that ensure high-quality deposition for most of the fractions.
- Investigation of the microstructure, porosity, phase composition (by the Rietveld method), microhardness, wear resistance, and corrosion resistance of the obtained coatings.
- Development of a one-dimensional Lagrangian model of particle motion using the Ganser correlation for the drag coefficient, accounting for sphericity and intra-fractional size distribution.
- Comparison of the calculated particle velocities at the working standoff distances with the experimental data on deposition efficiency and mechanical properties.

The scientific novelty of this work lies in the first direct comparative study of the influence of narrow particle size fractions on the structure and properties of two carbide systems (WC–12Co and Cr₃C₂–NiCr) under HVOF spraying conditions individually optimized for each material, using an advanced Lagrangian particle motion model.

2. Materials and Methods

2.1. Substrate Material and Initial Powders

12Kh18N10T stainless steel (AISI 321 analogue) with dimensions of 40 × 40 × 5 mm was used as the substrate. The choice of this steel is due to its wide application in the aviation, chemical, and power engineering industries, as well as its high corrosion resistance combined with satisfactory strength, which allows for a correct assessment of the protective properties of the deposited coatings. The chemical composition of the steel (Table 1) complies with the requirements of GOST 5632–72 and is confirmed by the manufacturer’s certificate.

Table 1. Chemical composition of 12Kh18N10T steel (wt.%).

Element	C	Si	Mn	P	S	Cr	Ni	Ti	Fe
Content (wt.%)	≤0.12	≤0.8	≤2.0	≤0.035	≤0.02	17–19	9–11	0.4–1.0	balance

Before spraying, the substrate surfaces were ground with P600 emery paper to remove the oxide film and level the surface relief. Subsequently, sandblasting was carried out with F36 electrocorundum at a pressure of 0.8 MPa, which made it possible to create a uniform roughness of $R_a \approx 5\text{--}6\text{ }\mu\text{m}$, necessary for mechanical interlocking of particles with the substrate. After treatment, the samples were ultrasonically cleaned in acetone for 10 min to remove abrasive residues and organic contaminants.

For spraying, commercial WC–12Co powders (agglomerated and sintered spherical particles, density 14,280 kg/m³) and Cr₃C₂–NiCr powders (sintered spherical particles, density 7200 kg/m³) were used.

Each initial powder was subjected to air classification into narrow fractions using a vibrating screen with a set of sieves. The following fractions were obtained: <20, 20–32, and 32–40 μm . The sample designations used further in the text are given in Table 2.

2.2. Equipment and HVOF Spraying Parameters

Spraying was carried out using an industrial HVOF system with a propane-oxygen 2700DJM torch (Oerlikon Metco, Pfäffikon, Switzerland), equipped with a water cooling system and a gas flow control unit.

Table 2. Designation of the investigated samples.

Designation	Fraction, μm	Material
CrC-1	up to 20	$\text{Cr}_3\text{C}_2\text{-NiCr}$
CrC-2	20–32	
CrC-3	32–40	
WC-1	up to 20	WC-12Co
WC-2	20–32	
WC-3	32–40	

Due to the significant difference in density and thermophysical properties of the materials (Table 3), the spraying parameters were individually selected for each powder type to ensure high-quality deposition for all fractions (with the exception of the technologically extreme case of CrC-1, which will be discussed further). The main difference consisted in the standoff distance and the number of passes: for WC-12Co (a denser and more inertial material)—standoff distance of 350 mm, one pass; for $\text{Cr}_3\text{C}_2\text{-NiCr}$ (less dense, decelerating faster in the flow)—standoff distance of 250 mm, two passes. All other parameters—gas pressures, powder feed rate, torch traverse speed—were fixed at a constant level to ensure comparability of the results (Table 3). This approach replicates the real conditions for producing composite coatings from powder mixtures, where it is impossible to independently adjust the parameters for each component.

Table 3. HVOF spraying parameters.

Parameter	Value for $\text{Cr}_3\text{C}_2\text{-NiCr}$	Value for WC-12Co
Standoff distance, mm	250	350
Propane pressure, bar	0.6	0.6
Oxygen pressure, bar	1.2	1.2
Nitrogen (carrier gas) pressure, bar	1.1	1.1
Air pressure, bar	0.8	0.8
Nitrogen flow rate, l/h	400	400
Powder feed rate, g/min	25	25
Spraying time, s	20	20
Powder consumption per cycle, g	8.3	8.3
Torch traverse speed, mm/s	13	13
Number of passes	2	1

Before spraying, the substrates were fixed in a special fixture, and the torch was moved along a predetermined trajectory using a robotic manipulator to ensure thickness uniformity (Figure 1).

2.3. Metallographic Preparation and Microstructural Analysis

To study the microstructure and elemental composition, the samples were cut and mounted in epoxy resin (Struers EpoFix) and subjected to grinding on a sequence of abrasive papers (P120–P2500) with water cooling. Final polishing was performed on cloth wheels using diamond pastes with a grain size of 1 μm until a defect-free mirror finish was obtained (the absence of scratches and pull-outs was assessed using an optical microscope at $\times 200$ magnification).

The microstructure of cross-sections was investigated by scanning electron microscopy (SEM) using a Tescan VEGA 3 LMH instrument (Tescan, Brno, Czech Republic). Imaging was performed in backscattered electron (BSE) mode at an accelerating voltage of 30 kV and a working distance of 15 mm, which provides sufficient contrast between phases with different atomic numbers. Coating thickness was measured on SEM images at $\times 100$ magni-

fication as the arithmetic mean of vertical profiles uniformly distributed across the width of the specimen.

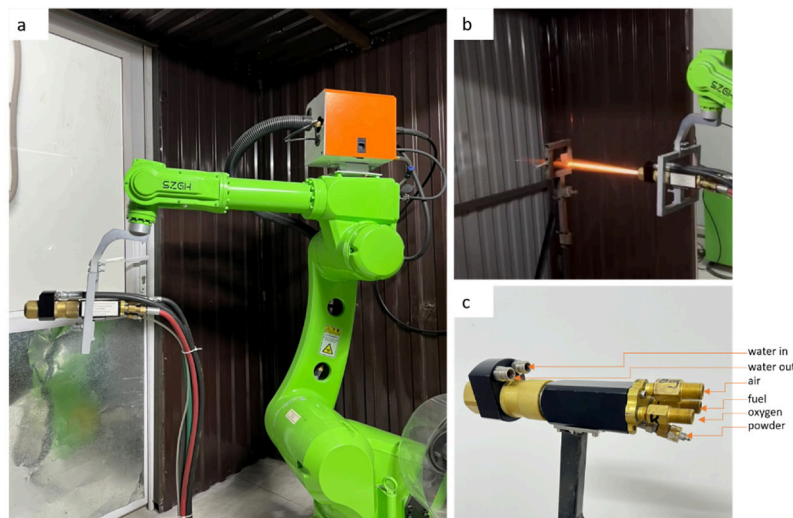


Figure 1. HVOF spraying system with a Diamond Jet 2700 torch: (a) robotic manipulator with mounting fixture and torch; (b) HVOF spraying process of coating deposition onto samples; (c) design of the Diamond Jet 2700 torch.

2.4. Quantitative Porosity Assessment

Porosity was evaluated by computer-aided analysis of SEM images of cross-sections obtained at $\times 100$ magnification using ImageJ 1.54 g software. This magnification was chosen to cover a representative area of the coating with sufficient resolution to identify pores down to $0.5\ \mu\text{m}$ in size. Pre-processing of the images included:

- Manual removal of epoxy mounting and substrate areas;
- Conversion to 8-bit format and brightness/contrast adjustment for uniform thresholding;
- Binarization using the Otsu algorithm followed by manual threshold adjustment to exclude artifacts.

Porosity was calculated as the ratio of the total area of dark regions (pores) to the total area of the analyzed coating region.

2.5. XRD and Quantitative Phase Analysis

The phase composition of the initial powders and as-sprayed coatings was determined by X-ray diffraction using a D6 PHASER diffractometer (Bruker AXS, Germany, Karlsruhe) with Cu-K α radiation (wavelength $\lambda = 1.5406\ \text{\AA}$, voltage 40 kV, current 30 mA). Scans were performed in the 2θ range from 20 to 90° with a step size of 0.02° and a counting time of 0.5 s per step.

Phase identification and preliminary processing were carried out using the HighScore Plus 3.0 software package with the PDF-2 database (ICDD). Quantitative phase analysis was performed using the Rietveld full-profile refinement method. Crystallographic information files CIF downloaded from the open crystallographic database were used for the calculations.

2.6. Microhardness Measurement

The microhardness of the coatings was measured by the Vickers method in accordance with ISO 6507-1 [20] using a digital HV-1 DT microhardness tester (Shanghai HLV, Shanghai, China). A load of 0.1 kgf (HV0.1) was applied with a dwell time of 10 s. This load provides an indentation size comparable to the scale of microstructural inhomogeneities

and minimizes the influence of the substrate (the thickness of all coatings, with the exception of CrC-1, exceeded 200 μm , which is more than 10 times the depth of the deformation zone at HV0.1).

Measurements were performed on transverse metallographic sections in the central part of the coating. For each sample, 15 indentations were made, uniformly distributed across the width of the section.

2.7. Dry Sliding Tribological Tests

The tribological characteristics of the coatings were evaluated using an Anton Paar TRB3 tribometer (Anton Paar GmbH, Graz, Austria) in a ball-on-disk configuration. The counterbody was a steel ball with a diameter of 6 mm made of 100Cr6 steel (hardness ~ 850 HV), fixed in a holder. The choice of this counterbody is based on modeling the “coating–steel” friction pair, which is typical for machine-building tribological assemblies.

Test conditions:

- Normal load: 10 N;
- Sliding speed: 5 cm/s;
- Wear track radius: 3 mm;
- Total sliding distance: 100 m;
- Ambient temperature: 22 $^{\circ}\text{C}$.

During the test, the friction coefficient was automatically recorded. After the test, the wear track profile was measured using an HY2300 profilometer (Anytester (Hefei) Co., Ltd., Hefei, China). The wear volume V (mm^3) was calculated as the product of the cross-sectional area of the groove and its length, and the specific wear rate k ($\text{mm}^3/(\text{N}\cdot\text{m})$) was calculated using the formula:

$$k = \frac{V}{F \times L} \quad (1)$$

where $F = 10$ N is the applied normal load, and $L = 100$ m is the total sliding distance.

2.8. Electrochemical Corrosion Resistance Testing

The corrosion behavior of the coatings was investigated by potentiodynamic polarization using a CS300M potentiostat–galvanostat (Corrtest Instruments, Wuhan, China) equipped with a flat CS936 three-electrode cell.

Electrode configuration: Working electrode—the test sample, isolated from the remaining surface, with a contact area with the electrolyte of 1 cm^2 ; reference electrode—saturated silver chloride electrode (Ag/AgCl, 3 M KCl); auxiliary electrode—a platinum grid. The electrolyte was a 3.5% aqueous NaCl solution prepared from distilled water.

Before each measurement, the sample was kept in the electrolyte for 30 min to stabilize the open circuit potential (OCP). Polarization was started from a potential 0.5 V more negative than OCP and swept in the anodic direction up to +1.5 V vs. OCP at a scan rate of 1 mV/s (which corresponds to a quasi-stationary polarization regime). The corrosion current was determined by extrapolation of the Tafel regions of the cathodic and anodic branches. The corrosion rate v_{corr} in mm/year was calculated according to Faraday’s law:

$$v_{\text{corr}} = \frac{3.27 \cdot 10^{-3} \cdot i_{\text{corr}} \cdot M}{n \cdot \rho} \quad (2)$$

where M is the average molar mass of the material (g/mol), n is the number of electrons involved in the reaction, and ρ is the density of the coating (g/cm^3).

2.9. Numerical Modeling of Particle Motion in the Gas-Flame Flow

To quantitatively assess the influence of particle size and material properties on their kinetic energy at the moment of impact with the substrate, a one-dimensional Lagrangian model of powder particle motion in a high-velocity gas-flame flow was employed. The model allows the calculation of the axial particle velocity. The gas velocity at a distance L from the nozzle exit is approximated by an exponential function [17,21]:

$$V_g(L) = V_0 e^{-\alpha L}, \quad (3)$$

where V_0 is the initial gas velocity at the nozzle exit (for the 2700DJM torch with propane fuel), equal to 1680 m/s, and α is an empirical attenuation coefficient that accounts for the loss of gas velocity due to turbulent mixing with the surrounding air. For WC-12Co particles, $\alpha = 2.0 \text{ m}^{-1}$ was adopted; for $\text{Cr}_3\text{C}_2\text{-NiCr}$, $\alpha = 3.5 \text{ m}^{-1}$, which reflects the difference in material density (14,280 and 7200 kg/m³, respectively) and, consequently, the different inertia of the particles, affecting their interaction with the turbulent flow.

The motion of a spherical particle under the action of aerodynamic drag force is described by the equation:

$$\frac{dV_p}{dt} = \frac{3\rho_g C_D}{4\rho_p d_p} (V_g - V_p)^2, \quad (4)$$

where V_p is the particle velocity, $\rho_g = 0.3 \text{ kg/m}^3$ is the gas density, ρ_p is the particle material density, d_p is the particle diameter, C_D is the drag coefficient.

To calculate C_D , the universal correlation proposed by Ganser (1993) [16] was used, which accounts for particle non-sphericity through the sphericity parameter ϕ . Unlike empirical formulas limited to specific Reynolds number ranges, the Ganser model is applicable over a wide range of Re and allows for correct description of the aerodynamics of both spherical and agglomerated particles.

The Ganser model introduces two shape factors, which are defined through the sphericity ϕ . The Stokes shape factor (affects drag in the laminar regime):

$$K_1 = \left(\frac{1}{3} + \frac{2}{3}\phi^{-1/2} \right)^{-1}, \quad (5)$$

and the Newton shape factor (affects drag in the turbulent regime):

$$\lg K_2 = 1.8148(-\lg \phi)^{0.5743}. \quad (6)$$

The value $\phi = 1$ corresponds to an ideal sphere; for real $\text{Cr}_3\text{C}_2\text{-NiCr}$ and WC-12Co powders, the values $\phi = 0.85$ and $\phi = 0.9$, respectively, were adopted, which is consistent with the manufacturers' data and the results of morphological analysis. The generalized Reynolds number is defined as:

$$Re_{gen} = Re \cdot K_1 \cdot K_2, \quad (7)$$

where $Re = \rho_g |V_g - V_p| d_p / \mu_g$ is the standard Reynolds number, $\mu_g = 5.0 \times 10^{-5} \text{ Pa}\cdot\text{s}$ is the dynamic viscosity of the gas, K_1 is the Stokes shape factor, and K_2 is the Newton shape factor.

The drag coefficient is calculated using the empirical formula:

$$\frac{C_D}{K_2} = \frac{24}{Re_{gen}} \left(1 + 0.1118 Re_{gen}^{0.6567} \right) + \frac{0.4305}{1 + 3305/Re_{gen}} \quad (8)$$

This correlation provides a smooth transition from the Stokes regime ($C_D \approx \frac{1}{Re}$) to the Newton regime ($C_D \approx 0.44$) with increasing Re .

Numerical integration of the equation of motion was performed using the 4th-order Runge–Kutta method with a step size of 5 mm over the interval from 0 to 500 mm from the nozzle exit. The calculations were implemented as a custom script in the Python 3.13 programming language within the PyCharm 2024.3 integrated development environment.

3. Results

3.1. Coating Thickness and Structure

All coatings exhibit a lamellar structure characteristic of HVOF spraying, with no large cracks or delamination at the coating–substrate interface (Figures 2 and 3). The thickness and porosity depend systematically on the particle size distribution (Table 4).

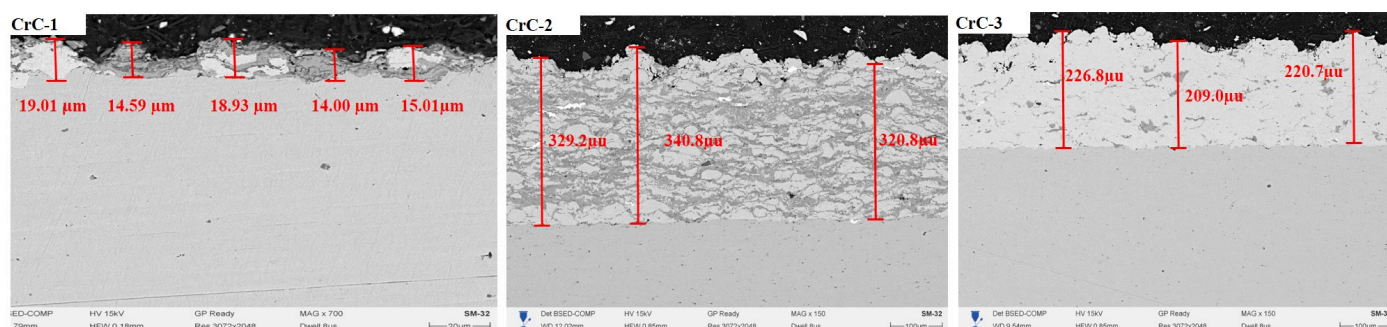


Figure 2. SEM images of cross-sections of samples sprayed with Cr_3C_2 –NiCr powder: CrC-1, CrC-2, CrC-3 at $\times 100$ magnification.

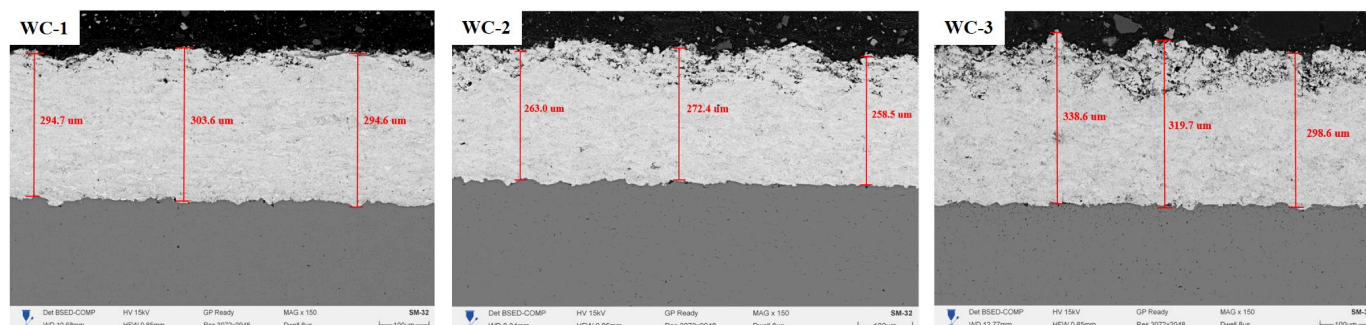


Figure 3. SEM images of cross-sections of samples sprayed with WC-12Co powder: WC-1, WC-2, WC-3 at $\times 100$ magnification.

Table 4. Thickness and porosity of the coatings.

Sample	Thickness, μm	Porosity, %
CrC-1	15.8 ± 2.9	— *
CrC-2	330.3 ± 10.0	0.20
CrC-3	216.9 ± 12.5	0.29
WC-1	297.6 ± 4.5	0.45
WC-2	264.0 ± 7.8	1.37
WC-3	319.0 ± 12.3	3.15

* For the CrC-1 sample, porosity was not calculated due to the anomalously low coating thickness.

For the Cr_3C_2 –NiCr system, sample CrC-1 ($<20 \mu\text{m}$) showed an anomalously low thickness of only $15.8 \pm 2.9 \mu\text{m}$, which is almost an order of magnitude less than that of CrC-2 (20 – $32 \mu\text{m}$, $330.3 \pm 10.0 \mu\text{m}$) and CrC-3 (32 – $40 \mu\text{m}$, $216.9 \pm 12.5 \mu\text{m}$). The reason is

the overheating and oxidation of fine particles in the high-temperature zone of the flame, as well as their low kinetic energy at the working standoff distance [22–26]. Porosity is minimal for CrC-2 (0.20%), which confirms the optimality of this fraction.

For WC–12Co, all three fractions form coatings with a thickness of 264–319 μm (Table 4). The lowest porosity is observed for WC-1 (0.45%), and the highest for WC-3 (3.15%).

3.2. Microhardness of Coatings

Microhardness is an integral characteristic reflecting the structural density, the degree of retention of strengthening phases, and the defectiveness level of the coating. The Vickers microhardness measurement results are presented in Figure 4. The substrate (12Kh18N10T steel) had a hardness of 180.6 ± 10.0 HV.

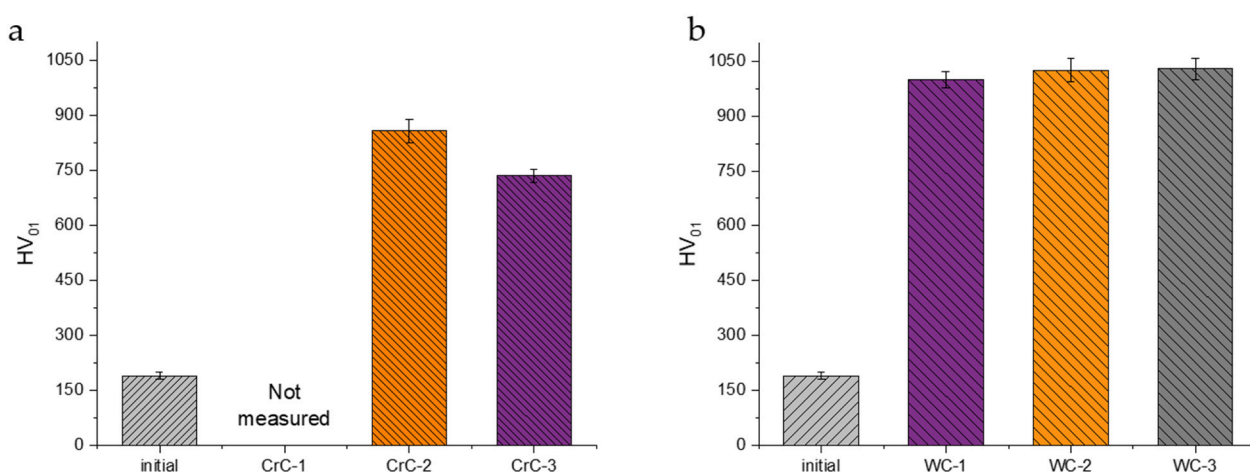


Figure 4. Microhardness (HV_{0.1}) of the substrate material and HVOF-sprayed coatings: (a) Cr₃C₂-NiCr powder coatings (samples CrC-1, CrC-2, CrC-3); (b) WC-12Co powder coatings (samples WC-1, WC-2, WC-3).

For Cr₃C₂-NiCr, the maximum value was recorded for sample CrC-2 (20–32 μm fraction)— 856.9 ± 31.2 HV. Sample CrC-3 (32–40 μm) shows a hardness of 735.0 ± 18.2 HV—the reduction is due to increased porosity and insufficient deformation of coarse particles. For CrC-1 (<20 μm), measurement was impossible due to the small thickness (~15.8 μm).

For WC-12Co, all samples demonstrate hardness more than 5 times higher than that of the substrate. The highest values were achieved for WC-2 (20–32 μm)— 1024.8 ± 32.0 HV and WC-3 (32–40 μm)— 1029.3 ± 29.1 HV. Sample WC-1 (<20 μm) has the lowest hardness among the WC coatings— 999.3 ± 22.3 HV.

3.3. Tribological Properties

Dry sliding friction tests (Figure 5, Table 5) revealed a clear dependence of wear resistance on particle size distribution for both materials.

Table 5. Wear track parameters and specific wear rate of the coatings.

Sample	Track Depth, μm	V, mm^3	k, $\times 10^{-6} \text{ mm}^3/(\text{N} \cdot \text{m})$
CrC-1	—	—	—
CrC-2	1.00	5.00×10^{-3}	5.00
CrC-3	1.40	8.37×10^{-3}	8.37
WC-1	1.25	2.67×10^{-3}	2.67
WC-2	1.29	2.13×10^{-3}	2.13
WC-3	1.11	2.00×10^{-3}	2.00

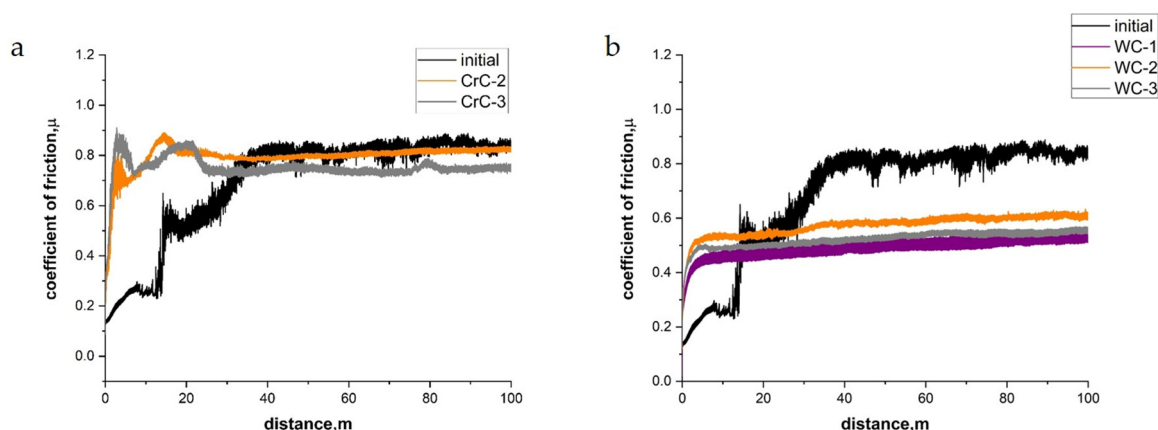


Figure 5. Dependence of the friction coefficient (μ) on sliding distance (m): (a) substrate and Cr_3C_2 -NiCr coatings (CrC-2, CrC-3); (b) substrate and WC-12Co coatings (WC-1, WC-2, WC-3).

The Cr_3C_2 -NiCr coatings showed a relatively high and unstable friction coefficient (0.8–0.9), indicating structural heterogeneity. Among the Cr_3C_2 -NiCr coatings, the lowest specific wear rate was recorded for sample CrC-2 (20–32 μm)— $5.00 \times 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m})$. The highest wear rate was observed for sample CrC-3 (32–40 μm)— $8.37 \times 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m})$. For sample CrC-1 (<20 μm), wear volume measurement was not performed due to insufficient coating thickness. For the Cr_3C_2 -NiCr coatings, a clear dependence of wear resistance on the particle size of the initial powder was established. The optimal fraction providing the minimum specific wear rate is 20–32 μm (sample CrC-2).

The WC-12Co-based coatings (samples WC-1, WC-2, WC-3) demonstrated relatively low and stable friction coefficient values throughout the tests, indicating good wear resistance and structural homogeneity [27–30].

Among the WC-12Co coatings, the lowest specific wear rate was recorded for sample WC-3 (32–40 μm)— $2.00 \times 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m})$. Sample WC-1 (<20 μm) showed a value of $2.67 \times 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m})$, and WC-2 (20–32 μm)— $2.13 \times 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m})$.

3.4. Phase Analysis of Coatings (XRD)

X-ray diffraction analysis made it possible to quantitatively assess the changes in phase composition as a function of particle size distribution (Figures 6 and 7, Tables 6 and 7).

Table 6. Results of quantitative phase analysis of Cr_3C_2 -NiCr coatings.

Sample	$\gamma\text{-Ni}(\text{Cr})$, %	CrNi_3 , %	Cr_7C_3 , %	Cr_2O_3 , %
CrC-1	35.7	12.0	38.6	13.7
CrC-2	80.4	0.9	18.7	0
CrC-3	82.4	0.5	17.1	0

Table 7. Results of quantitative phase analysis of WC-12Co coatings.

Sample	WC, %	W, %	W_2C , %	Co, %
WC-1	86.0	1.3	9.5	3.2
WC-2	93.2	2.7	2.8	1.3
WC-3	92.5	3.0	3.2	1.3

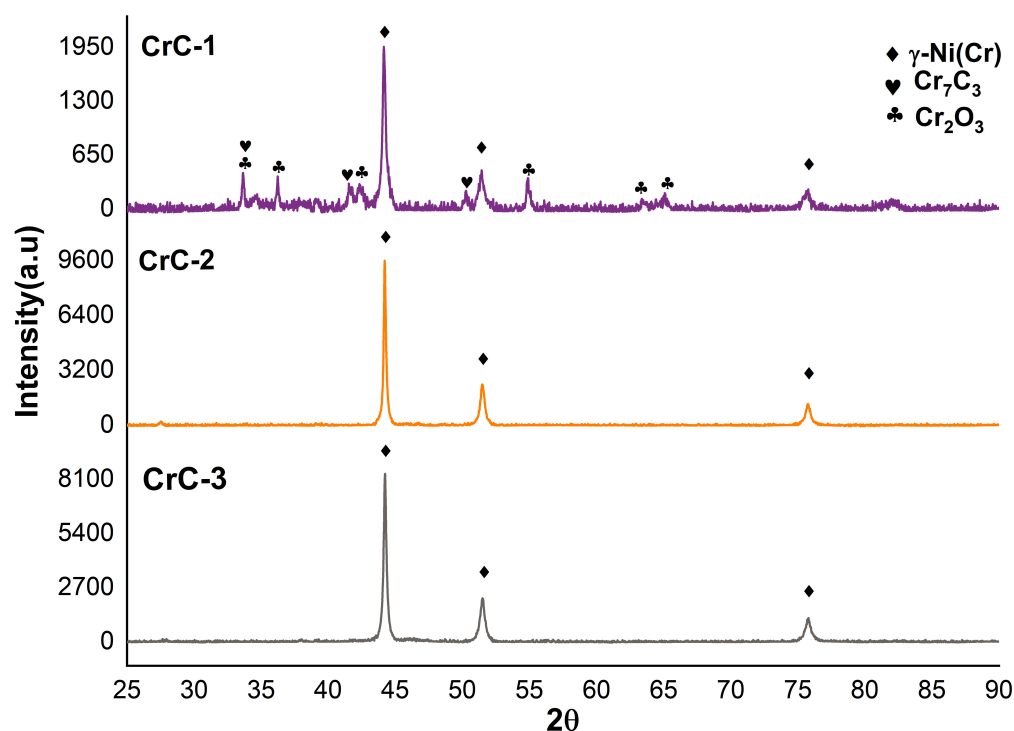


Figure 6. XRD patterns of Cr_3C_2 -NiCr coatings.

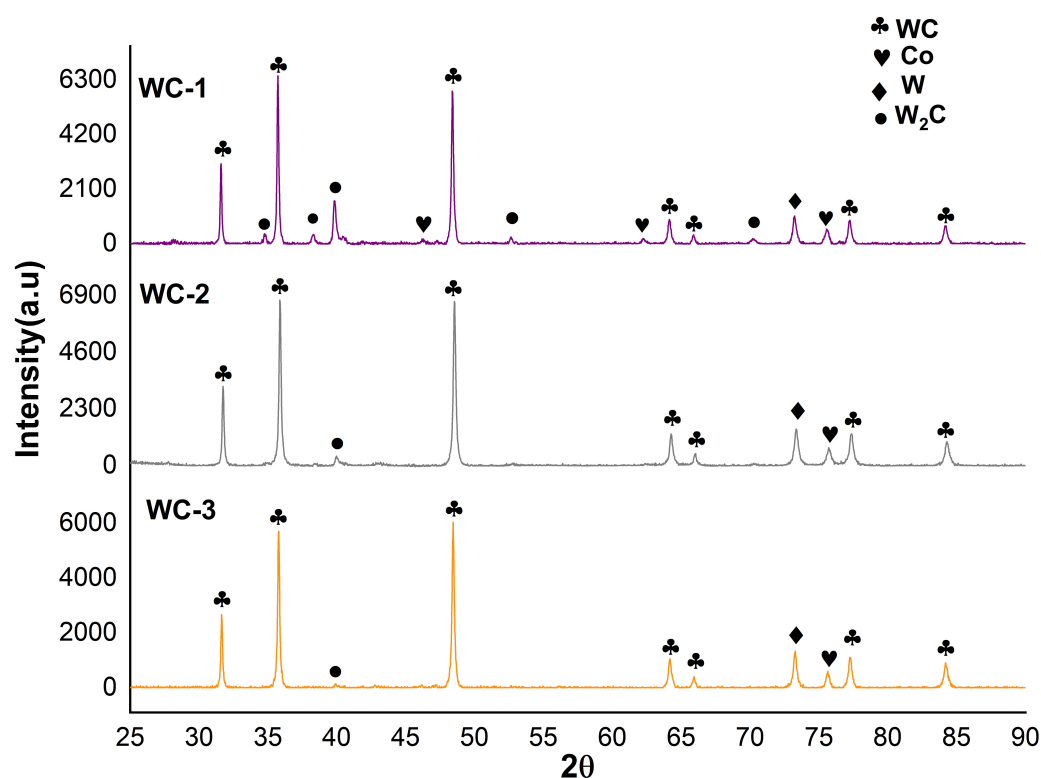


Figure 7. XRD patterns of WC-12Co coatings.

In samples CrC-2 and CrC-3, intense reflections of γ -Ni(Cr) ($2\theta \approx 44.2^\circ$) and Cr_3C_2 ($2\theta \approx 51.5^\circ, 75.7^\circ$) are preserved, confirming the high retention of the carbide phase. The intensity of the main (111) γ -Ni(Cr) peak is maximum for CrC-2 (9579.6 counts) and CrC-3 (8368.8 counts), indicating high crystallinity of the binder [31,32].

In sample CrC-1 ($<20 \mu\text{m}$), the intensity of the matrix peak decreases almost 5-fold (to 1896.0 counts), and Cr_2O_3 oxide and higher carbide Cr_7C_3 appear—a consequence of

overheating and oxidation of fine particles. Rietveld quantitative analysis (Table 6) shows: the fraction of the γ -Ni(Cr) matrix in CrC-2 and CrC-3 is 80.4 and 82.4%, respectively, and Cr_2O_3 is absent; in CrC-1—only 35.7% matrix, 13.7% Cr_2O_3 , and 38.6% Cr_7C_3 .

The diffractograms of all WC–12Co-sprayed samples contain the main peaks of hexagonal WC, as well as reflections of W_2C , metallic W, and Co, indicating partial decarburization. Qualitatively, the phase composition is the same for all fractions; the differences are quantitative in nature.

The maximum WC content was recorded for WC-2 (93.2%), and the minimum for WC-1 (86.0%) (Table 7). In WC-1, the content of W_2C (9.5%) and η -phases (reflected in the increased Co content of 3.2%, which indirectly indicates the formation of $\text{Co}_3\text{W}_3\text{C}/\text{Co}_6\text{W}_6\text{C}$) is also increased.

Comparison of XRD data with the results of mechanical and tribological tests reveals a direct correlation between the phase composition and the performance properties of the coatings. For the WC–12Co system, maximum hardness and minimum wear rate are achieved with the highest retention of the original WC carbide phase: in sample WC-2 (20–32 μm fraction), its content is 93.2%, whereas a decrease in the WC fraction to 86.0% in the fine-grained sample WC-1 is accompanied by a decrease in hardness of approximately 3% and an increase in wear rate by 34%. This deterioration is directly due to intensive decarburization, leading to the formation of less hard W_2C and brittle phases ($\text{Co}_3\text{W}_3\text{C}/\text{Co}_6\text{W}_6\text{C}$), which reduce resistance to abrasive action. A similar trend is observed for Cr_3C_2 –NiCr: sample CrC-2, characterized by a high proportion of the γ -Ni(Cr) matrix (80.4%) and the complete absence of oxide phases, demonstrates the best hardness and wear resistance. In contrast, in the fine fraction CrC-1, intensive oxidation (formation of Cr_2O_3) and excessive precipitation of Cr_7C_3 are recorded, which leads to embrittlement of the structure and, as a consequence, makes it impossible to form a high-quality coating with acceptable mechanical properties. Thus, for both materials, it is the 20–32 μm fraction that provides the optimal balance between the retention of strengthening phases and the minimization of degradation products, which determines its advantage in the entire complex of characteristics [14,25,33,34].

3.5. Corrosion Resistance of Coatings

Corrosion resistance is a critical parameter for coatings operating in aggressive environments, especially in the presence of chloride ions. Table 8 presents the main electrochemical parameters: corrosion potential (E_{cor}), corrosion current density (I_{corr}), and corrosion rate.

Table 8. Results of electrochemical tests in 3.5% NaCl.

Sample	E_{cor} , V	I_{corr} , A/cm ²	Corrosion Rate, mm/Year
CrC-1	-	-	-
CrC-2	−0.1294	8.7162×10^{-6}	0.1023
CrC-3	−0.0573	5.6434×10^{-6}	0.0662
WC-1	−0.1097	3.0086×10^{-3}	0.3529
WC-2	−0.0316	4.0241×10^{-5}	0.4721
WC-3	−0.1047	5.5522×10^{-5}	0.6514

The Cr_3C_2 –NiCr-based coatings demonstrate high corrosion resistance: the corrosion current densities for CrC-2 and CrC-3 are 8.7162×10^{-6} A/cm² and 5.6434×10^{-6} A/cm², respectively, and the corrosion rates do not exceed 0.102 mm/year. This is due to the passivation of the γ -Ni(Cr) matrix with the formation of a protective Cr_2O_3 film, which effectively blocks the penetration of aggressive ions [35]. Among the CrC coatings, the best resistance

is demonstrated by CrC-3 (32–40 μm)—the minimum corrosion rate (0.066 mm/year) and the most positive corrosion potential (−0.0573 V).

The WC-12Co-based coatings are characterized by substantially higher corrosion currents—from $3.01 \times 10^{-5} \text{ A/cm}^2$, which is an order of magnitude higher than the values for CrC coatings (Figure 8). The corrosion rates are 0.353–0.651 mm/year. In contrast to $\text{Cr}_3\text{C}_2\text{-NiCr}$, for WC coatings, the best resistance is demonstrated by the fine fraction WC-1, while the coarse fraction WC-3 shows the worst results. This can be explained by the fact that the cobalt binder is anodic with respect to the carbide phase, which leads to selective dissolution of Co and the formation of galvanic microcouples that accelerate corrosion. In this case, porosity becomes the decisive factor. The minimum porosity of WC-1 (0.45%) limits electrolyte penetration, whereas the increase in porosity in the series WC-1 $\rightarrow$ WC-2 $\rightarrow$ WC-3 correlates with an increase in the corrosion rate.

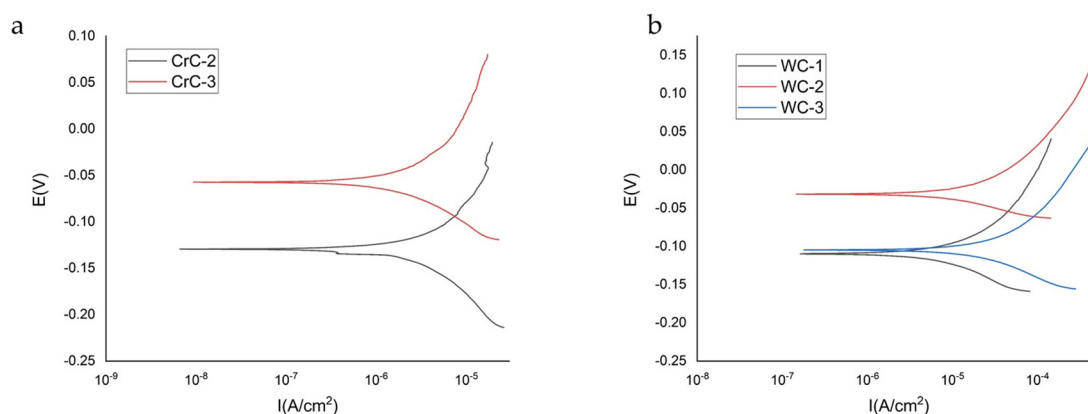


Figure 8. Potentiodynamic polarization curves of corrosion tests of HVOF coatings: (a) $\text{Cr}_3\text{C}_2\text{-NiCr}$ powder coatings (samples CrC-2, CrC-3); (b) WC-12Co powder coatings (samples WC-1, WC-2, WC-3).

3.6. Mathematical Modeling of Particle Motion and Velocity Profile Analysis

Figure 9 shows the calculated axial velocity profiles of particles V_p as a function of the distance from the nozzle exit L for all investigated fractions. The motion dynamics differ significantly depending on the material density and the gas flow attenuation coefficient.

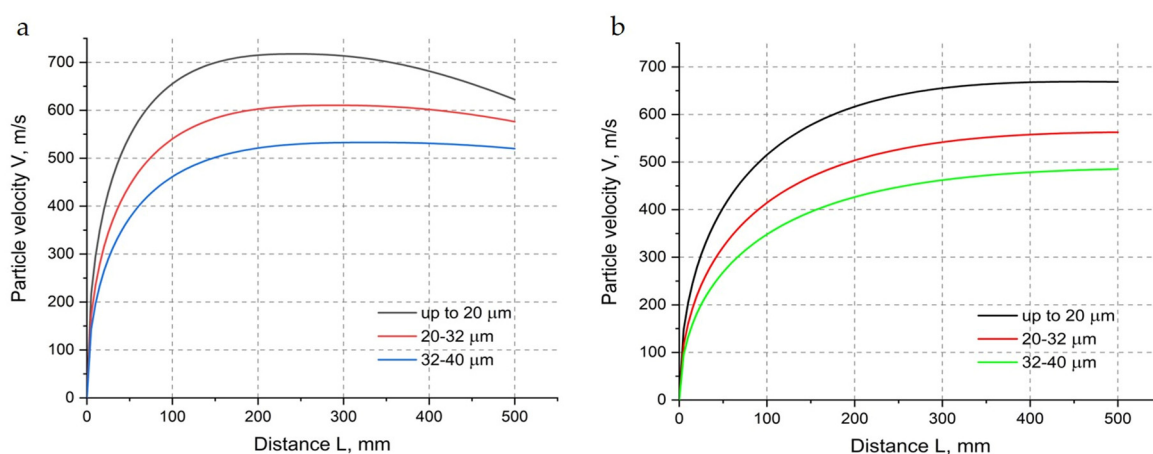


Figure 9. Dependence of particle velocity (V , m/s) on the distance from the nozzle exit (L , mm) for different powder fractions (<20 μm , 20–32 μm , 32–40 μm): (a) $\text{Cr}_3\text{C}_2\text{-NiCr}$; (b) WC-12Co.

For $\text{Cr}_3\text{C}_2\text{-NiCr}$ ($\rho \approx 7.20 \text{ g/cm}^3$, $\alpha = 3.5 \text{ m}^{-1}$, $\varphi = 0.85$), the curves have a pronounced non-monotonic character: after intensive acceleration in the near-nozzle zone, the velocities reach a maximum at distances of 220–350 mm, after which they gradually decrease due to

aerodynamic drag. Due to the lower density, $\text{Cr}_3\text{C}_2\text{-NiCr}$ particles accelerate faster: the peak velocity for the $<20\ \mu\text{m}$ fraction is 720 m/s (at $L \approx 210\ \text{mm}$), whereas for WC–12Co the analogous peak does not exceed 650 m/s. However, due to the larger attenuation coefficient ($\alpha = 3.5\ \text{m}^{-1}$), $\text{Cr}_3\text{C}_2\text{-NiCr}$ particles at distances exceeding 350 mm undergo more intensive deceleration, and by 500 mm their velocity decreases to 520–580 m/s depending on the fraction.

For WC–12Co ($\rho \approx 14.28\ \text{g/cm}^3$, $\alpha = 2.0\ \text{m}^{-1}$, $\varphi = 0.9$), the high density and inertia result in slower acceleration and the preservation of a positive velocity gradient over the entire investigated interval (0–500 mm). At the working standoff distance of 350 mm, the velocities for the <20 , 20–32, and 32–40 μm fractions are 660, 550, and 470 m/s, respectively. At a distance of 500 mm, the fine fraction reaches 670 m/s, while the 20–32 and 32–40 μm fractions reach 560 and 490 m/s, respectively. The absence of a pronounced maximum within 500 mm for the medium and coarse fractions indicates their high inertia and ability to retain kinetic energy over long distances.

4. Discussion

4.1. Influence of Particle Size Distribution on Deposition Kinetics and Structural Density

The conducted study revealed the determining role of the fractional composition of the initial powders in the formation of the structure and properties of HVOF coatings for both the WC–12Co and $\text{Cr}_3\text{C}_2\text{-NiCr}$ systems. The key mechanism linking particle size distribution with deposition quality is the balance between the kinetic energy of particles at the moment of impact and their thermal state, which is confirmed by both experimental data and numerical modeling results [36].

The most revealing result is the anomalously small thickness of the CrC-1 coating ($<20\ \mu\text{m}$ fraction)—only $15.8 \pm 2.9\ \mu\text{m}$, which is almost an order of magnitude less than for CrC-2 and CrC-3. This effect cannot be explained solely by insufficient kinetic energy, since the calculated velocities for fine $\text{Cr}_3\text{C}_2\text{-NiCr}$ particles at a distance of 250 mm are $\sim 650\text{--}700\ \text{m/s}$, which exceeds the critical deposition velocities known from the literature for carbide materials [19]. The reason lies in the combined effect of two factors.

First, fine particles have low thermal inertia and are intensively heated in the high-temperature zone of the gas-flame plume. According to calculations performed in the studies of Kamnis et al. [18], particles smaller than $20\ \mu\text{m}$ can reach temperatures close to the melting point, which leads to their oxidation and even partial evaporation. XRD data for CrC-1 confirm this assumption: the Cr_2O_3 oxide content reaches 13.8%, and the fraction of the original $\gamma\text{-Ni(Cr)}$ matrix decreases to 35.7% compared to 80.4% for CrC-2. The formation of a significant amount of Cr_7C_3 (38.6%) also indicates high-temperature degradation of the original Cr_3C_2 carbide, which is prone to dissociation at temperatures above $1200\ ^\circ\text{C}$ with the formation of carbon-rich carbides [7,8]. Second, due to the small particle size, their trajectory is more susceptible to the influence of turbulent pulsations of the gas flow. As shown in the work of Yu et al. [17], non-spherical particles of small diameter demonstrate higher sensitivity to changes in gas velocity, which can lead to deviation from the optimal trajectory and a decrease in deposition efficiency. In our model, the attenuation coefficient for $\text{Cr}_3\text{C}_2\text{-NiCr}$ ($\alpha = 3.5\ \text{m}^{-1}$) reflects the more intensive deceleration of fine particles due to higher aerodynamic drag; however, at a distance of 250 mm, this effect is not dominant [37].

Thus, for CrC-1, the decisive factor is the thermal degradation of particles in flight, leading to the formation of oxide films on the surface, which prevent high-quality interparticle bonding and adhesion to the substrate. This is consistent with the conclusions of Melnyk et al. [14], who noted an increase in oxidation and decarburization with decreasing particle size of WC–Co. In the case of $\text{Cr}_3\text{C}_2\text{-NiCr}$, where the $\gamma\text{-Ni(Cr)}$ matrix itself is passivating,

the formation of Cr_2O_3 on the particle surface additionally worsens wettability and reduces ductility upon impact, which leads to an almost complete absence of deposition.

The wide thickness range (264–319 μm) for all WC–12Co fractions indicates a broader process window for this material, which is attributed to the high inertia of tungsten carbide particles (density 14.28 g/cm^3), allowing them to retain kinetic energy over long distances. As the calculations show, even for the coarse 32–40 μm fraction, the velocity at a distance of 350 mm is 470 m/s, which exceeds the critical deposition velocity for WC–12Co (~150 m/s according to Jalali Azizpour [19]). However, with increasing particle size, porosity increases (from 0.45% for WC-1 to 3.15% for WC-3), which is explained by insufficient plastic deformation of coarse particles upon impact. This result is fully consistent with our previous works [5–7], where for the 86WC–10Co–4Cr system it was shown that the 20–30 μm fraction provides minimum porosity.

4.2. Phase Transformations and Their Relationship with Mechanical Properties

XRD revealed different degradation mechanisms. For WC–12Co, the main process is decarburization of WC with the formation of W_2C and η -phases ($\text{Co}_3\text{W}_3\text{C}/\text{Co}_6\text{W}_6\text{C}$). The lowest degree of decarburization was recorded for WC-2 (93.2% WC, 2.8% W_2C), and the highest for WC-1 (86.0% WC, 9.5% W_2C). Fine particles heat up faster but spend less time in the high-temperature zone; coarse particles heat up more slowly but remain there longer. The optimal balance is achieved at 20–32 μm . The increased content of η -phases in WC-1 correlates with the minimum hardness among WC coatings (999.3 HV) despite the lowest porosity. For Cr_3C_2 –NiCr in CrC-2 and CrC-3, the fraction of the γ -Ni(Cr) matrix is 80–82%, and oxides are absent. In CrC-1, there is only 35.7% matrix, 13.7% Cr_2O_3 , and 38.6% Cr_7C_3 (a product of Cr_3C_2 dissociation at $T > 1200^\circ\text{C}$). The preservation of the matrix in CrC-2 ensures maximum hardness (856.9 HV) and minimum wear rate ($5.00 \times 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m})$), while the increase in porosity in CrC-3 leads to a decrease in hardness to 735.0 HV. The comparison shows that for WC–Co, the determining factor is the chemical stability of the carbide, while for Cr_3C_2 –NiCr, it is the structural density [38–41].

4.3. Tribological Behavior

WC–12Co coatings demonstrate a stable friction coefficient (0.4–0.5) due to the formation of a tribo-oxide WO_3 layer [32]. The wear rate for WC-2 (20–32 μm) is $2.13 \times 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m})$, while for WC-3 (32–40 μm) it was slightly lower, at $2.00 \times 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m})$. This may be attributed to the fact that large carbide islands in WC-3 act as abrasion-resistant barriers, and the developed porosity (3.15%) promotes the retention of wear debris in the near-surface layer, thereby reducing the intensity of abrasive action. However, the high porosity of WC-3 significantly reduces the structural integrity and reliability of the coating under cyclic and impact loads, which limits its application in critical tribological components [42]. Therefore, despite the slightly lower wear rate of WC-3, the optimal fraction for WC–12Co in terms of the combination of wear resistance, density, and operational reliability is WC-2 (20–32 μm), which provides a wear rate close to the minimum while having a significantly denser structure (1.37% porosity). For Cr_3C_2 –NiCr, the friction coefficient is higher (0.8–0.9) due to lower hardness and the formation of abrasive Cr_2O_3 . The wear resistance of CrC-2 significantly exceeds that of CrC-3 (5.00 vs. $8.37 \times 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m})$), which correlates with minimum porosity and maximum hardness. In both materials, the 20–32 μm fraction is optimal in terms of wear resistance. Thus, for both materials, the 20–32 μm fraction provides the best balance of wear resistance and structural reliability.

4.4. Corrosion Resistance: Barrier and Passivation Mechanisms

Electrochemical tests showed that Cr_3C_2 –NiCr outperforms WC–12Co by an order of magnitude in corrosion resistance: corrosion current densities— 5.64 – 8.72×10^{-6} vs.

$3.01\text{--}5.55 \times 10^{-5} \text{ A/cm}^2$, corrosion rates— $0.066\text{--}0.102$ vs. $0.353\text{--}0.651 \text{ mm/year}$. The protection of $\text{Cr}_3\text{C}_2\text{--NiCr}$ is provided by passivation of the $\gamma\text{-Ni(Cr)}$ matrix with the formation of a Cr_2O_3 film [35]; galvanic couples between the carbide and the matrix are weakly expressed. For WC–12Co, the cobalt binder is anodic with respect to WC, which causes selective dissolution of Co and galvanic corrosion. The corrosion rate is directly correlated with porosity: WC-1 (0.45%)— 0.353 mm/year , WC-3 (3.15%)— 0.651 mm/year . Consequently, for WC–Co, the protection is predominantly barrier-type, and the fine fraction is preferable, despite the deterioration of mechanical properties.

4.5. Numerical Modeling as a Predictive Tool

The developed one-dimensional Lagrangian model (Ganser correlation [16]) made it possible to interpret the experimental data through impact velocities. For $\text{Cr}_3\text{C}_2\text{--NiCr}$, the calculated velocities at 250 mm are: $<20 \mu\text{m}$ — $680\text{--}720 \text{ m/s}$, $20\text{--}32 \mu\text{m}$ — $600\text{--}650 \text{ m/s}$, $32\text{--}40 \mu\text{m}$ — $540\text{--}580 \text{ m/s}$. The fine fraction should deposit better; however, overheating and oxidation make this impossible—the model requires consideration of the thermal state. For WC–12Co at 350 mm, the velocities are 660, 550, and 470 m/s for the respective fractions. All values are above the critical velocity ($\sim 150 \text{ m/s}$ [19]), but porosity increases with decreasing velocity due to insufficient deformation of coarse particles. The model is qualitatively correct but requires verification with in-flight measurements (PIV, DPV) and supplementation with thermal calculations.

4.6. Prospects for Composite Coatings

The obtained results justify the use of a single $20\text{--}32 \mu\text{m}$ fraction for creating mixed WC–12Co + $\text{Cr}_3\text{C}_2\text{--NiCr}$ coatings combining wear resistance and corrosion resistance. However, the difference in densities (14.28 vs. 7.20 g/cm^3) requires adjustment of the parameters: for example, two-stage spraying with different standoff distances or selection of particle sizes that equalize velocities (finer $\text{Cr}_3\text{C}_2\text{--NiCr}$, coarser WC–12Co). Corrosion tests show that even a small fraction of $\text{Cr}_3\text{C}_2\text{--NiCr}$ can suppress the galvanic corrosion of WC/Co through passivation, which opens the way to gradient structures.

4.7. Limitations and Directions for Future Research

The main limitations include: (1) the one-dimensional nature of the model without accounting for radial distribution and turbulence; (2) the absence of in-flight temperature and velocity measurements; (3) a limited range of fractions; (4) tests only at room temperature and under dry friction conditions. It should be noted that all samples were obtained using a single spraying run for each combination of parameters. This limitation does not affect the main conclusions of the study but should be taken into account when interpreting the absolute values of the properties. Future work should include three-dimensional CFD modeling, verification with experiments, expansion of the fractional composition, as well as investigation of erosion, thermal cycling, and corrosion-mechanical resistance.

5. Conclusions

Based on the conducted experimental and theoretical investigations of the influence of WC–12Co and $\text{Cr}_3\text{C}_2\text{--NiCr}$ powder particle size distribution on the structure and properties of HVOF coatings, the following main conclusions are formulated:

1. Optimal particle size distribution. For both materials, the best combination of density, hardness, and wear resistance is achieved using the $20\text{--}32 \mu\text{m}$ fraction. For $\text{Cr}_3\text{C}_2\text{--NiCr}$, this fraction provides minimum porosity (0.20%), maximum microhardness (856.9 HV), and the lowest specific wear rate ($5.00 \times 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m})$). For WC–12Co, the $20\text{--}32 \mu\text{m}$ fraction is characterized by high hardness (1024.8 HV), low porosity

(1.37%), and a wear rate ($2.13 \times 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m})$) which is only slightly higher than that of the coarse fraction 32–40 μm . However, the 20–32 μm fraction has significantly lower porosity, which improves the structural integrity and reliability of the coating under cyclic loading.

2. Critical role of kinetic and thermal balance. The fine Cr_3C_2 –NiCr fraction (<20 μm) practically does not deposit (thickness $\sim 15.8 \mu\text{m}$) due to overheating and oxidation of particles in flight, which is confirmed by the presence of 13.7% Cr_2O_3 and 38.6% Cr_7C_3 in the composition. Numerical modeling shows that high velocities (680–720 m/s) do not compensate for the loss of ductility. For WC–12Co, the fine fraction, on the contrary, forms a dense coating (porosity 0.45%) but suffers from decarburization (WC content drops to 86.0%), which reduces hardness (999.3 HV) compared to the medium fraction.
3. Different degradation mechanisms. In the WC–12Co system, decarburization of WC with the formation of W_2C and η -phases ($\text{Co}_3\text{W}_3\text{C}/\text{Co}_6\text{W}_6\text{C}$) predominates, with the minimum for the 20–32 μm fraction (93.2% WC, 2.8% W_2C). In the Cr_3C_2 –NiCr system, the main degradation process is oxidation and carbide dissociation; the 20–32 and 32–40 μm fractions retain a high proportion of the γ -Ni(Cr) matrix ($\sim 80\%$) and contain no oxides, whereas the fine fraction completely degrades.
4. Corrosion resistance is determined by different mechanisms. Cr_3C_2 –NiCr coatings outperform WC–12Co by an order of magnitude in 3.5% NaCl due to passivation of the γ -Ni(Cr) matrix (corrosion rate 0.066–0.102 mm/year vs. 0.353–0.651 mm/year). For WC–12Co, the protection is barrier-type, and the fine fraction is preferable (0.353 mm/year at 0.45% porosity), although it is inferior in mechanical properties. Thus, the choice of fraction for WC–Co should be determined by the priority: wear resistance (medium fraction) or corrosion resistance (fine fraction).
5. Applicability of numerical modeling. The developed one-dimensional Lagrangian model, accounting for particle non-sphericity and intra-fractional size distribution (D10, D50, D90), qualitatively describes the experimental trends and allows prediction of impact velocities. For Cr_3C_2 –NiCr, it was revealed that high velocities of fine particles are not a sufficient condition for deposition—consideration of the thermal state is necessary. For WC–12Co, the model correctly reflects the decrease in velocity with increasing particle size, which correlates with increasing porosity.
6. Prospects for composite coatings. The possibility of creating mixed coatings based on WC–12Co and Cr_3C_2 –NiCr using a single optimal 20–32 μm fraction is substantiated. Approaches to equalizing kinetic parameters (adjustment of standoff distance, two-stage spraying, selective size selection) are proposed, and the feasibility of gradient structures is indicated, where inner layers provide corrosion protection and outer layers provide wear resistance.

Limitations and directions for future work. The obtained results are limited to propane fuel and fixed parameters; expansion of the fractional range, experimental verification of in-flight particle velocities and temperatures, as well as tests at elevated temperatures, in aggressive environments with abrasives, and under cyclic loading are required. The priority is experimental investigation of composite and gradient coatings, as well as improvement of the model with the transition to three-dimensional CFD analysis.

6. Patents

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