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IMPACT OF Co–Cr, Ni, AND NiCr BINDER SYSTEMS ON THE MICROSTRUCTURE AND FUNCTIONAL PROPERTIES OF WC COATINGS PRODUCED BY DETONATION SPRAYING

This study investigates the influence of metallic binder composition (Co–Cr, Ni, and NiCr) on the microstructure and performance characteristics of tungsten carbide-based coatings deposited by detonation spraying. A comprehensive characterization was carried out using scanning electron microscopy, EDS elemental mapping, microhardness testing, tribological evaluation, scratch testing, and electrochemical corrosion analysis. The results demonstrate that binder type significantly affects coating porosity, WC phase distribution, hardness, and tribological behavior. The WC–Co-Cr coating exhibited the most favorable combination of properties: the lowest coefficient of friction (0.515), the highest microhardness (1232.55 HV), the best scratch resistance, and superior corrosion resistance in 3.5 wt.% NaCl solution. The WC–Ni coating showed the lowest porosity (0.40%) due to the high fluidity of the nickel binder, while WC–NiCr demonstrated the highest porosity (2.78%) and the most pronounced susceptibility to cracking under progressive loading. The findings confirm the strong potential of detonation-sprayed WC–Co-Cr coatings for extending the service life of pipeline valves and other components operating under wear and corrosion conditions in the oil and gas industry.

Keywords: detonation spraying, tungsten carbide, WC–Co-Cr, microstructure, porosity, microhardness, tribological properties, corrosion resistance.

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Детонациялық шашырату арқылы алынған WC жабындарының микроқұрылымы мен функционалдық қасиеттеріне Co–Cr, Ni және NiCr байланыстырғыш жүйелерінің әсері

Бұл зерттеу детонациялық шашырату әдісімен жағылған вольфрам карбиді негізіндегі жабындардың микроқұрылымы мен эксплуатациялық сипаттамаларына металл байланыстырғыш құрамының (Co–Cr, Ni және NiCr) әсерін зерттейді. Кешенді сипаттама сканерлеуші электрондық микроскопия, ЭДС элементтік картографиялау, микрокаттылықты өлшеу, трибологиялық бағалау, сызу сынағы және электрохимиялық коррозия талдауы арқылы жүргізілді. Нәтижелер байланыстырғыш түрінің жабын кеуектілігіне, WC фазасының таралуына, каттылығына және трибологиялық мінез-құлқына айтарлықтай әсер ететінін көрсетеді. WC–Co-Cr жабыны қасиеттердің ең қолайлы үйлесімін көрсетті: ең төменгі үйкеліс коэффициенті (0,515), ең жоғары микрокаттылық (1232,55 HV), ең жақсы сызуға төзімділік және 3,5 мас.% NaCl ерітіндісіндегі жоғары коррозиялық төзімділік. WC–Ni жабыны никель байланыстырғышының жоғары сұйықтығына байланысты ең төменгі кеуектілікті (0,40%) көрсетті, ал WC–NiCr ең жоғары кеуектілікті (2,78%) және прогрессивті жүктеме кезінде жарықшақтануға ең айқын бейімділікті байқатты. Алынған нәтижелер мұнай-газ саласында тозу мен коррозия жағдайында жұмыс істейтін құбыр арматурасы мен басқа компоненттердің қызмет мерзімін ұзарту үшін детонациялық шашырату арқылы алынған WC–Co-Cr жабындарының жоғары әлеуетін растайды.

Түйін сөздер: детонациялық шашырату, вольфрам карбиді, WC–Co-Cr, микроқұрылым, кеуектілік, микрокаттылық, трибологиялық қасиеттер, коррозиялық төзімділік.

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Влияние связующих систем Co–Cr, Ni и NiCr на микроструктуру и функциональные свойства WC-покрытий, полученных методом детонационного напыления

В настоящей работе исследуется влияние состава металлической связки (Co–Cr, Ni и NiCr) на микроструктуру и эксплуатационные характеристики покрытий на основе карбида вольфрама, нанесённых методом детонационного напыления. Комплексная характеризация проводилась с использованием сканирующей электронной микроскопии, ЭДС-картирования элементов, измерения микротвёрдости, трибологических испытаний, скретч-теста и электрохимического коррозионного анализа. Результаты показывают, что тип связующего существенно влияет на пористость покрытия, распределение фазы WC, твёрдость и трибологическое поведение. Покрытие WC–Co-Cr продемонстрировало наиболее благоприятное сочетание свойств: наименьший коэффициент трения (0,515), наибольшую микротвёрдость (1232,55 HV), наилучшую стойкость к царапанию и высокую коррозионную стойкость в 3,5 мас.% растворе NaCl. Покрытие WC–Ni показало наименьшую пористость (0,40%) благодаря высокой текучести никелевой связки, тогда как WC–NiCr отличалось наибольшей пористостью (2,78%) и наиболее выраженной склонностью к растрескиванию при прогрессивном нагружении. Полученные результаты подтверждают высокий потенциал покрытий WC–Co-Cr, нанесённых детонационным напылением, для продления ресурса трубопроводной арматуры и других компонентов, работающих в условиях износа и коррозии в нефтегазовой отрасли.

Ключевые слова: детонационное напыление, карбид вольфрама, WC–Co-Cr, микроструктура, пористость, микротвёрдость, трибологические свойства, коррозионная стойкость.

Introduction

Ensuring reliable and environmentally safe transportation of oil and petroleum products remains one of the most critical engineering challenges in the modern energy sector. Addressing this issue requires a comprehensive approach that encompasses both the design and manufacture of high-quality pipeline fittings and the use of materials with superior mechanical strength and wear resistance. Of particular importance is extending the service life of key components such as gate valves and control elements, which operate under conditions of intense mechanical and chemical exposure. Thermal spray coating technologies have proven to be among the most effective methods for surface protection of such components [1, 2].

Among the most promising thermal spray techniques are high-velocity oxygen–fuel spraying (HVOF), plasma spraying, and detonation spraying [3]. HVOF is distinguished by its ability to produce dense, well-adhered coatings with excellent wear and corrosion resistance, making it widely used in industrial applications [4, 5]. Plasma spraying, in turn, offers exceptional versatility, enabling the deposition of a broad range of materials — from ceramics to metals — and allowing the formation of high-quality, durable coatings suitable for demanding service environments [6, 7]. Detonation spraying is a more advanced technology that harnesses the energy of a controlled detonation wave to accelerate powder particles to extremely high velocities. This process provides coatings with outstanding adhesion strength and minimal oxidation, which makes it particularly well-suited for the deposition of wear-resistant coatings in high-performance applications [8–10].

Tungsten carbide (WC)-based powders are widely employed in applications requiring high abrasion and erosion resistance, hardness, and thermal stability. Composite powders, in which WC acts as the hard phase and a metallic component serves as the binder, are the most common formulation, since pure tungsten carbide — despite its exceptional hardness — is inherently brittle and prone to fracture under impact loading [11–13]. To improve toughness and mechanical integrity, alloying elements such as nickel (Ni), cobalt (Co), and chromium (Cr) are introduced as binders. Nickel, being more ductile than WC, enhances the fracture resistance of the WC–Ni composite; although the

overall hardness is somewhat reduced, the material becomes significantly more suitable for operation in corrosive and chemically aggressive environments [14]. The addition of chromium to the nickel binder markedly improves corrosion resistance and high-temperature oxidation stability. The Co–Cr binder system, in which cobalt serves as the primary matrix phase, provides an outstanding combination of mechanical strength, toughness, and wear resistance, and is widely applied in cutting tools, hard-facing components, and wear-resistant parts across various industries [15, 16].

Although the properties of WC–Co-Cr, WC–Ni, and WC–NiCr coatings deposited by HVOF and plasma spraying have been studied fairly extensively, comparative data on analogous systems produced specifically by detonation spraying remain scarce. In particular, there is a lack of systematic information on the influence of binder type on the mechanisms of microstructure formation, phase composition, and operational performance of coatings at the extremely high particle velocities characteristic of detonation technology. This knowledge gap underscores the relevance and novelty of the present study.

The objective of this work is to conduct a comparative analysis of the microstructure, phase composition, mechanical, tribological, and corrosion properties of WC-based coatings with Co–Cr, Ni, and NiCr binders deposited by detonation spraying, and to establish the relationships between binder composition and coating performance.

Materials and Methods

WC–Co-Cr, WC–Ni, and WC–NiCr powders with a particle size fraction of 15–45 μm were used as the spray materials. The chemical compositions of the powders and substrate are presented in Tables 1–2. Steel 45 was used as the substrate material. Prior to spraying, the substrate surfaces were grit-blasted with electrocorundum (fraction 0.4–0.6 mm) to achieve the required surface roughness, followed by ultrasonic cleaning in acetone.

Table 1. Chemical composition of the WC-based powders (wt.%)

Material	W	C	Co	Cr	Ni
WC–Co-Cr	Base	5.3	10.0	4.0	—
WC–Ni	Base	5.0	—	—	10.0
WC–NiCr	Base	5.0	—	8.0	6.0

Table 2. Chemical composition of Steel 45 substrate (%)

Fe	C	Si	Mn	P	S	Cr	Ni	Cu
Base	0.42–0.5	0.17–0.37	0.5–0.8	≤0.030	≤0.035	≤0.25	≤0.30	≤0.30

The coatings were deposited using a CCDS2000 detonation spraying system (LIH SB RAS, Novosibirsk, Russia) equipped with a computer-controlled unit enabling precise regulation of process parameters, including the oxygen-to-acetylene ratio and the volume of the explosive charge. The spraying distance was set to 300 mm, with a barrel gas filling level of 78% ($C_2H_2/C_3H_8/N_2/O_2$).

The morphological characteristics of the powder particles, as well as the surface and cross-sections of the coatings, were examined by scanning electron microscopy (SEM) using a TESCAN VEGA4 LMH instrument (TESCAN, Brno, Czech Republic); energy-dispersive spectroscopy (EDS) analysis was performed using an Xplore 30 system (Oxford Instruments, Oxford, UK).

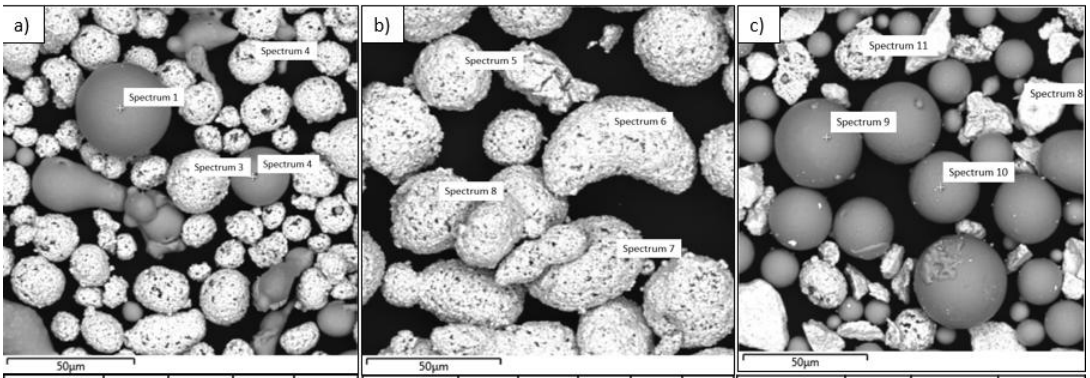
Porosity was evaluated from cross-sectional SEM images in accordance with ASTM E2109 using ImageJ software version 1.54g. Microhardness and elastic modulus of the coatings were measured using a FISCHERSCOPE HM 2000 system (Helmut Fischer GmbH, Sindelfingen, Germany) with WIN-HCU software version 7.1, in compliance with ISO 14577. A total of nine indentations were performed at a load of 300 mN with a dwell time of 10 s. Tribological testing was carried out on an Anton Paar TRb3 tribometer using the ball-on-disc configuration in accordance with ASTM G133-95 and ASTM G99 standards. Tests were performed at room temperature under dry sliding conditions, with a 6 mm diameter ball of 100Cr6 steel serving as the counterbody. The applied load was 6 N, the linear sliding speed was 3 cm/s, the wear track radius was 3 mm, and the total sliding distance was 60 m. Surface roughness of the coatings was measured using an SSR300+ contact profilometer (China). Electrochemical testing for corrosion resistance evaluation was conducted using a CS300 potentiostat-galvanostat in a 3.5 wt.% aqueous NaCl solution at room temperature (25 °C). Measurements were performed in a standard three-electrode cell, where the coating sample with a working area of 1 cm² served as the working

electrode, a platinum plate as the counter electrode, and a silver/silver chloride electrode as the reference electrode. Prior to recording the polarization curves, the samples were immersed in the electrolyte for 60 minutes to stabilize the open-circuit potential, after which potentiodynamic polarization was carried out by scanning the potential from −0.1 V to +0.1 V relative to the reference electrode at a scan rate of 0.5 mV/s. The key corrosion parameters — corrosion potential E_{corr} and corrosion current density i_{corr} - were determined from the polarization curves by Tafel extrapolation using CS Studio6 software, based on the results of three replicate measurements.

Results and discussion

The starting powders consist predominantly of spherical particles. The WC–Co-Cr powder is composed of fully fused particles, whereas WC–Ni and WC–NiCr represent mechanical mixtures of tungsten carbide with nickel or nichrome, respectively.

Microstructural analysis of the deposited coatings revealed the formation of a dense lamellar structure with strong adhesion to the substrate. The coating thickness, determined from cross-sectional examination, was 55 μm for WC–Co-Cr, 171 μm for WC–Ni, and 175 μm for WC–NiCr. Unlike the homogeneous WC–Co-Cr powder, the WC–Ni and WC–NiCr powders are composite in nature. Under the short-duration, high-velocity thermal exposure conditions of detonation spraying, the available time is insufficient for complete mutual melting and diffusion between the refractory WC phase and the metallic binder.



	W	C	Ni	Cr
Spectrum 1			77.60	22.40
Spectrum 2			78.63	21.37
Spectrum 3	79.20	18.80	2.00	
Spectrum 4	83.58	16.42		

	W	C	Co	Cr	O
Spectrum 5	78.20	8.81	8.59	2.81	1.59
Spectrum 6	78.86	13.58	2.37	0.85	4.34
Spectrum 7	66.91	18.67	6.91	4.10	3.41
Spectrum 8	79.91	11.65	5.57	1.50	1.38

	W	C	Ni
Spectrum 9			100.00
Spectrum 10			100.00
Spectrum 11	76.07	23.93	
Spectrum 12	90.59	9.41	

Figure 1 – SEM images of (A) WC-Co-Cr, (B) WC-Ni, and (C) WC-NiCr.

As a result, a characteristic layered composite structure is formed, in which the more ductile nickel or nichrome particles, upon impact deformation, wrap around and lock the hard, virtually non-deformable WC particles, retaining them as a reinforcing phase within the coating. The character of this layered composite structure formation directly governs the porosity of the resulting coatings. Since WC–Ni and WC–NiCr powders are mechanical mixtures, the degree of interaction between the metallic binder and WC particles is determined not only by temperature, but also by the plasticity of the binder and its ability to flow and fill interlamellar gaps during impact compaction [18]. For nickel-based binders, which possess a lower melting point and higher fluidity, the most effective filling of interparticle voids is observed, resulting in the minimum porosity of the WC–Ni coating (0.40%).

In the WC–Co-Cr system, despite the homogeneity of the starting powder, the higher melting point and lower plasticity of the Co–Cr binder compared to Ni restrict the degree of binder spreading. Consequently, some interlamellar regions remain incompletely filled, leading to a porosity level of 1.23%.

The highest porosity is observed in the WC–NiCr coating (2.78%). This is attributed to the fact that the addition of chromium increases the viscosity of the metallic phase and reduces its capacity for plastic deformation upon impact with the surface. Furthermore, Cr promotes partial segregation and

deterioration of WC particle wettability, which leads to the formation of micropores within the coating structure. Thus, the differences in porosity are governed by the combined influence of binder melting point, fluidity, WC particle wettability, and the specific features of phase interaction during detonation spraying [17, 19].

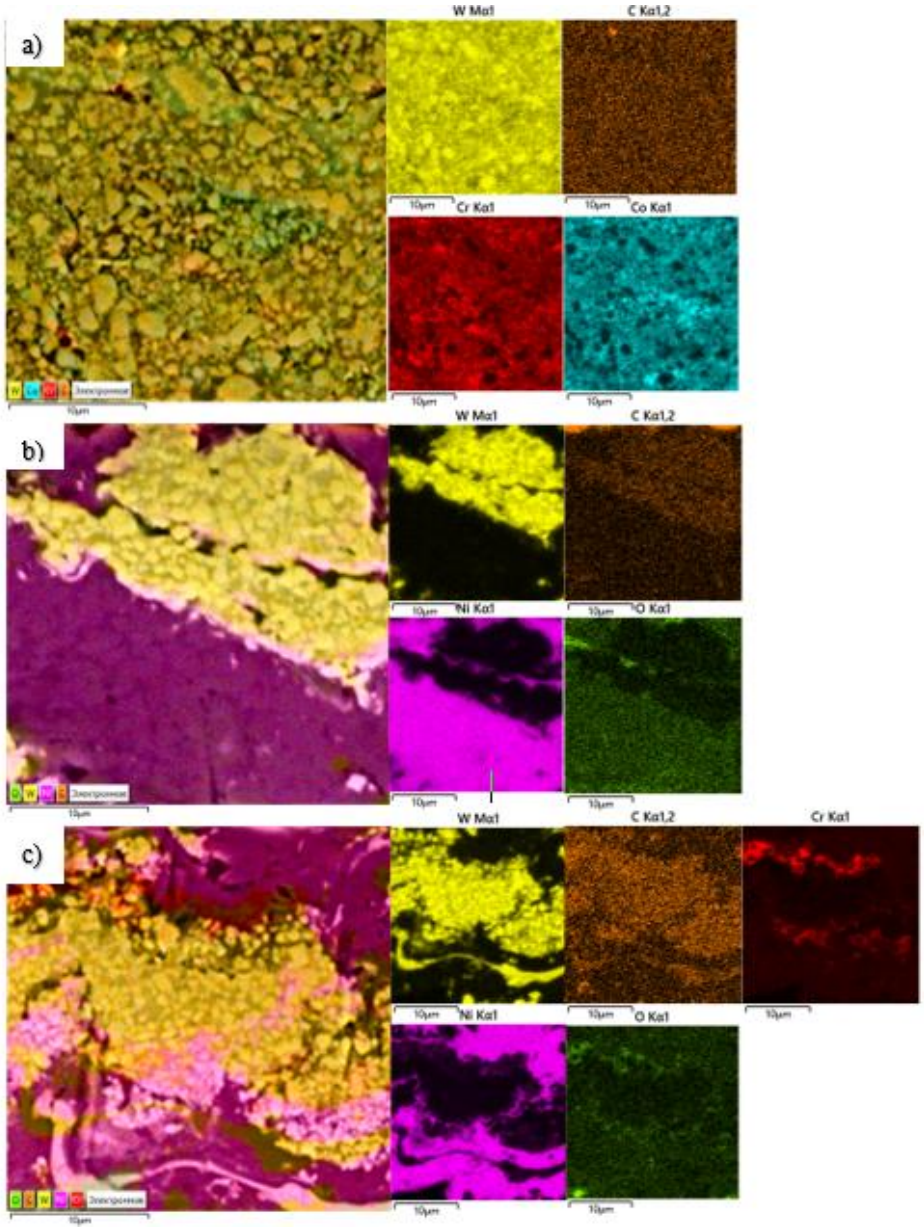


Figure 2 - EDS mapping of elements in detonation-sprayed coatings: (a) WC–Co-Cr, (b) WC–Ni, and (c) WC–NiCr, including element distribution maps and total EDS spectra.

EDS analysis revealed that all three coatings possess a composite structure consisting of a hard WC phase and a metallic binder; however, the chemical composition and elemental distribution differ significantly between the coatings (Figure 2).

The WC–Co-Cr coating contains a high proportion of W (35.90 wt.%), indicating a substantial amount of WC particles. The binder is represented by Co (4.47 wt.%) and Cr (1.59 wt.%), uniformly distributed throughout the coating thickness. Elemental distribution maps confirm the homogeneity of the Co–Cr matrix and the dense incorporation of WC particles, which is consistent with the typical structure of well-consolidated WC–Co-Cr coatings with good mechanical properties. In the WC–Ni coating, nickel dominates (33.44 wt.%), forming a continuous metallic matrix. The W content is comparatively lower (5.65 wt.%), which is attributed to the structural characteristics of the mechanical powder mixture. The WC particles are discrete and finely dispersed throughout the nickel matrix. As shown in Figure 2b, the elemental maps confirm the uniform distribution of Ni and the

homogeneous embedding of WC particles, which contributes to the low porosity of this coating.

The WC–NiCr coating is characterized by a combination of Ni (22.13 wt.%) and Cr (5.63 wt.%) in the binder, along with a moderate W content (13.35 wt.%). As evident from Figure 2c, the elemental distribution maps indicate a non-uniform distribution of chromium and WC particles. The presence of Cr increases the viscosity of the binder and promotes the formation of local pores, which is reflected in the higher porosity of this coating compared to WC–Ni and WC–Co-Cr.

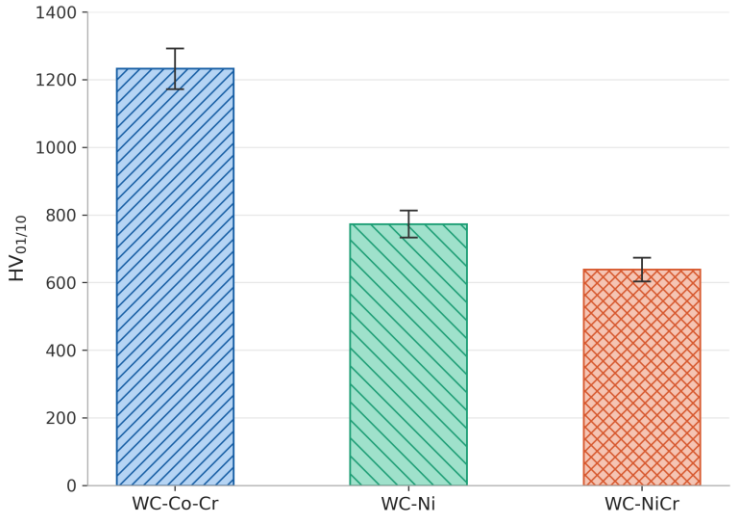


Figure 3 - Microhardness values ($HV_{01/10}$) of WC-based coatings deposited by detonation spraying

Microhardness measurements revealed significant differences among the three coatings, governed by the type of metallic binder and the proportion of the WC phase (Figure 3).

The WC–Co-Cr coating exhibits the highest microhardness of 1232.55 HV, which is attributed to the high WC content and the effective distribution of the Co–Cr binder, ensuring good compaction and minimal decarburization. According to the literature, this structure provides enhanced wear resistance and stable performance under operational loads [22, 23]. The WC–Ni coating demonstrates intermediate microhardness values of 773.0 HV. Despite the more ductile nickel matrix and low porosity, the lower proportion of the WC phase and the softer binder result in reduced hardness compared to WC–Co-Cr [20, 21]. The WC–NiCr coating shows the lowest microhardness of 638.37 HV. This is attributed to the increased viscosity of the Ni–Cr binder, higher porosity, and less uniform distribution of WC particles. Chromium segregation within the matrix further reduces the local hardness of the coating. Measurements of the average coefficient of friction revealed that the coatings exhibit distinct tribological behavior depending on the type of metallic binder. The WC–Co-Cr coating demonstrates the lowest coefficient of friction of 0.515, indicating high contact interaction stability and minimal intensity of adhesive and abrasive processes. The low friction is attributed to the high hardness of the coating, reduced porosity, and the effective performance of the Co–Cr binder. The WC–Ni coating is characterized by a higher average coefficient of friction of 0.661, which is associated with the greater plasticity of the nickel matrix and its increased tendency toward adhesion in the contact zone. Although the friction value is higher than that of WC–Co-Cr, it remains stable throughout the test, reflecting the moderate wear resistance of this coating [22].

The WC–NiCr coating exhibits the highest coefficient of friction of 0.673, which is linked to its higher porosity, reduced plasticity of the Ni–Cr binder, and the possible formation of brittle surface fragments during sliding contact.

The scratch test results for all three coatings are presented in Figure 5. The profiles of normal force (Fn), frictional force (Ft), and acoustic emission (Ae) were recorded as a function of scratch length to evaluate the adhesion strength and cohesive integrity of the coatings. For the WC–Co-Cr coating (Figure 5a), the frictional force increases gradually and steadily with increasing normal load, while the acoustic emission signal remains relatively low and stable throughout the test. This behavior indicates good adhesion to the substrate and high cohesive strength of the coating, with no pronounced delamination or cracking events observed during scratching.

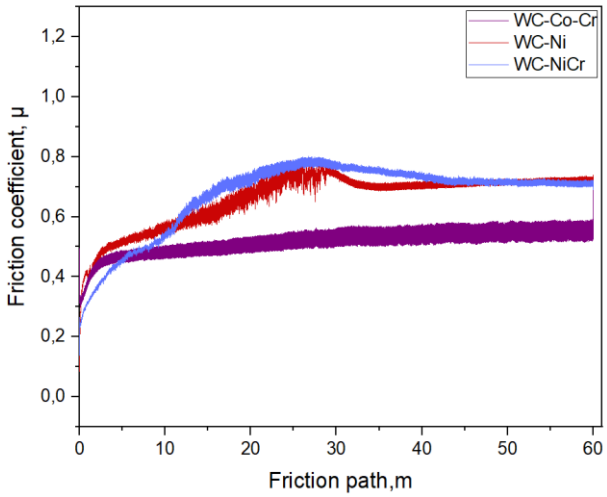


Figure 4 – Friction coefficient as a function of sliding distance for WC-based coatings deposited by detonation spraying

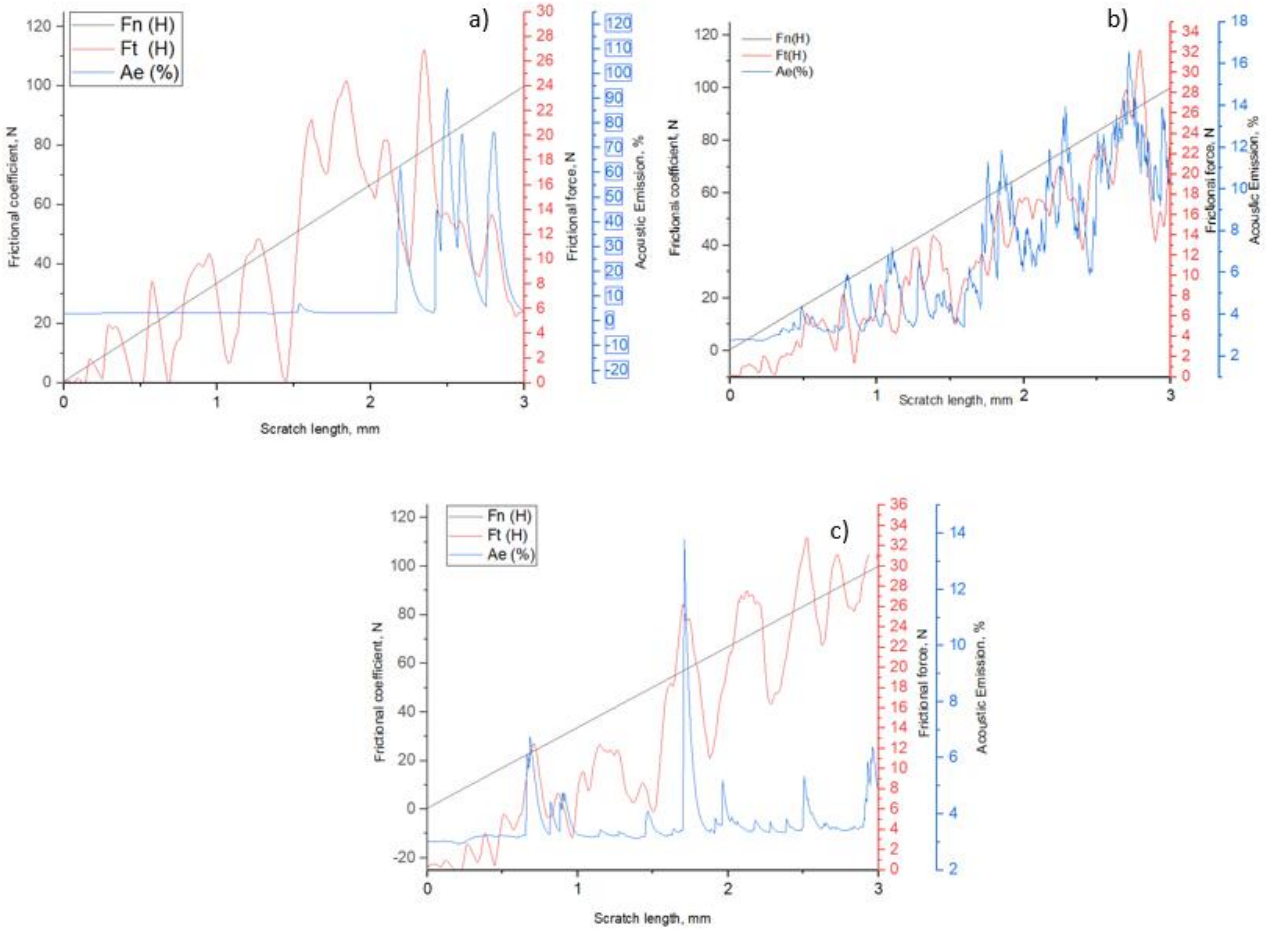


Figure 5 – Scratch test profiles showing normal force (Fn), frictional force (Ft), and acoustic emission (Ae) as a function of scratch length for detonation-sprayed WC-based coatings:
a) WC–Co-Cr, b) WC–Ni, c) WC–NiCr.

The WC–Ni coating (Figure 5b) exhibits a more irregular frictional force profile with notable fluctuations, accompanied by a progressive increase in acoustic emission. This suggests that localized cracking and partial delamination occur at higher loads, which is consistent with the more ductile nature of the nickel binder and the lower hardness of this coating compared to WC–Co-Cr. The WC–NiCr coating (Figure 5c) demonstrates the most unstable behavior, characterized by significant oscillations in both frictional force and acoustic emission signals, including sharp emission peaks at scratch lengths of approximately 0.8 mm, 1.8 mm, and 2.0 mm. These peaks are indicative of brittle fracture events and progressive coating failure, which correlates with the higher porosity and reduced mechanical integrity of this coating. Overall, the scratch test results confirm that the WC–Co-Cr coating possesses the highest adhesion and cohesive strength among the three systems studied, while WC–NiCr exhibits the greatest susceptibility to cracking and delamination under progressive loading [23-25].

Conclusion

In this study, WC–Co-Cr, WC–Ni, and WC–NiCr coatings were successfully deposited by detonation spraying and comprehensively characterized. The following conclusions can be drawn based on the experimental results:

All three coatings exhibit a dense lamellar microstructure with strong adhesion to the Steel 45 substrate. The WC–Co-Cr coating forms the most uniform and compact structure, while WC–NiCr shows a higher degree of structural heterogeneity due to chromium segregation and non-uniform WC particle distribution. Coating porosity varies significantly with binder type: WC–Ni achieves the lowest porosity (0.40%) owing to the high fluidity of the nickel binder, WC–Co-Cr shows intermediate porosity (1.23%), and WC–NiCr exhibits the highest porosity (2.78%), attributed to the increased viscosity of the Ni–Cr phase and reduced wettability of WC particles. Microhardness follows the order WC–Co-Cr (1232.55 HV) > WC–Ni (773.0 HV) > WC–NiCr (638.37 HV), reflecting the combined effect of WC content, binder hardness, and coating density. Tribological testing under dry sliding conditions revealed that WC–Co-Cr exhibits the lowest average coefficient of friction (0.515) and the most stable contact behavior, while WC–Ni (0.661) and WC–NiCr (0.673) show progressively higher friction values associated with greater binder plasticity and structural porosity. Scratch test analysis confirmed that WC–Co-Cr possesses the highest adhesion and cohesive integrity, with no significant delamination events observed. In contrast, WC–NiCr demonstrated the greatest susceptibility to brittle fracture under progressive normal loading. Electrochemical corrosion testing in 3.5 wt.% NaCl solution showed that WC–Co-Cr provides the best corrosion protection, characterized by the most positive corrosion potential and the lowest corrosion current density. WC–NiCr showed moderate corrosion resistance due to the passivating role of chromium, while WC–Ni exhibited the highest corrosion activity among the coated samples.

Overall, the WC–Co-Cr coating deposited by detonation spraying demonstrates the most balanced and superior combination of structural, mechanical, tribological, and corrosion properties, making it the most suitable candidate for protective applications in the oil and gas sector, particularly for gate valves and other components subjected to simultaneous wear and corrosive attack.

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Author Contributions

N.M. Magazov: Conceptualization, Methodology; **N. Muktanova**: Formal Analysis, Data Curation, Writing – Review & Editing; **G.K. Uazyrkhanova**: Investigation, Data Curation, Visualization; **Z.E. Aringozhina**: Formal Analysis, Resources, Validation. Supervision, Funding Acquisition; Project Administration.

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