

Article

Microstructure, Sliding Wear, and Electrochemical Corrosion of a High-Entropy Alloy–Cermet Composite Thermal Spray Coating

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Highlights

What are the main findings?

- A dense, well-bonded ~400 μm composite coating was successfully fabricated using HVOF.
- Rapid cooling stabilized a complex structural mix of FCC, BCC, and σ -NiCr phases.
- Adding 50 wt.% Cr_3C_2 -Ni₈₀Cr₂₀ drastically enhanced sliding wear resistance versus pure HEA.
- Wear behavior shifted from adhesive wear to mild third-body abrasion and protective tribo-oxidation.
- Heterogeneous phases triggered micro-galvanic cells, raising corrosion current density in NaCl.

What are the implications of the main findings?

- The hybrid design yields a synergistic balance between matrix ductility and load-bearing capacity.
- The system offers a green alternative by removing industrial reliance on toxic cobalt and tungsten.
- Post-deposition treatments are vital next steps to seal porosities and mitigate galvanic corrosion.

Abstract

This study investigates the design, microstructure, and performance profile of a novel composite coating combining a high-entropy alloy (HEA) matrix with cermet reinforcement. A 50wt.%CoCrFeMnNi_{0.8}V–50wt.% Cr_3C_2 -Ni₈₀Cr₂₀ powder mixture was successfully deposited onto steel substrates via high-velocity oxy-fuel (HVOF) thermal spraying. Microstructural analysis revealed a highly dense, well-bonded coating architecture (450–500 μm thick) where partially melted, spherical HEA splats were uniformly surrounded by the Cr_3C_2 -Ni₈₀Cr₂₀ phase. X-ray diffraction confirmed a complex multiphase evolution consisting of FCC, BCC, and σ -NiCr phases driven by the rapid solidification inherent to the HVOF process. Tribological evaluations via ball-on-disc testing demonstrated that in-

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incorporating the $\text{Cr}_3\text{C}_2\text{-Ni}_{80}\text{Cr}_{20}$ reinforcement significantly improves wear resistance compared to the monolithic HEA coating. The composite's wear behavior is governed by a synergistic mechanism: the ductile HEA matrix accommodates plastic deformation, while the harder carbide particles enhance load-bearing capacity, transitioning from adhesive wear to mild third-body abrasion and protective tribo-oxidation. Conversely, electrochemical testing in a 3.5 wt.% NaCl solution showed that the composite coating exhibits higher corrosion current densities ($10.53 \times 10^{-6} \text{ A/cm}^2$) and more active corrosion potentials than the pure HEA matrix. This behavior is attributed to localized micro-galvanic cells forming at the heterogeneous interfaces between the different phases, alongside chloride-induced destabilization of the surface oxide film. Overall, the novel composite coating offers a compelling, sustainable alternative for surface engineering applications requiring a balanced trade-off between mechanical toughness and acceptable environmental durability. This behavior is also verified by the comparison with previous results dealing with monolithic $\text{CoCrFeMnNi}_{0.8}\text{V}$ and 75wt.% $\text{CoCrFeMnNi}_{0.8}\text{V}$ –25wt.% $\text{Cr}_3\text{C}_2\text{-Ni}_{80}\text{Cr}_{20}$ thermal sprayed coatings, where it is evident that the increase of the reinforcing phase leads to an optimum combination of properties.

Keywords: high-entropy alloys; thermal spray coatings; microstructure; wear; corrosion

1. Introduction

1.1. High-Entropy Alloys

High-entropy alloys (HEAs) represent a paradigm shift in alloy design by incorporating five or more principal elements in near-equimolar proportions. This design significantly increases configurational entropy, stabilizing simple solid-solution phases (face-centered cubic (FCC), body-centered cubic (BCC), or hexagonal close-packed (HCP)) over complex intermetallics. This high entropy promotes the stabilization of simple solid-solution phases, such as FCC, BCC, or HCP structures, despite their complex chemical composition [1,2].

The introduction of HEAs in 2004 through independent pioneering studies marked a milestone in material science, demonstrating that multi-principal-element systems could form more single-phase structures than complex intermetallic compounds [3,4]. The formation of solid-solution phases in HEAs is primarily driven by high entropy, further influenced by factors such as lattice distortion, slow atomic diffusion, and the “cocktail effect”, a result of differences in atomic sizes, melting points, and crystal structures among the elements. Together, these effects contribute to enhanced wear and corrosion resistance, improved thermal stability, and notable mechanical performance [5]. These characteristics make HEAs suitable candidates for demanding structural and functional applications in aerospace, energy, automotive, and surface engineering sectors [6,7].

In recent years, research has increasingly focused on tailoring microstructures through multiphase HEA design to overcome the traditional strength–ductility trade-off. By carefully controlling composition and processing, it is possible to engineer dual-phase or multiphase systems that combine the high strength of BCC phases with the ductility of FCC phases. The design of such advanced HEAs relies on empirical thermodynamic parameters, CALPHAD modeling, and advanced machine learning techniques capable of predicting phase stability and properties by efficiently analyzing complex datasets. However, significant challenges remain, such as the need for precise feature descriptions and the inclusion of manufacturing parameters, including cooling rate, which strongly influence microstructure evolution and hence mechanical properties [8].

From the engineering perspective, HEAs offer compelling advantages over conventional coating materials. HEAs provide a flexible compositional platform that enables property optimization while potentially reducing dependency on materials that may be limited in availability, environmentally harmful, or subject to regulatory restrictions.

1.2. The Rising Demand for Innovative Alloys/Composite Coatings in Surface Engineering and the Main Idea for This Study.

High-entropy alloys have recently emerged as promising feedstock materials for thermal spray coatings due to their compositional flexibility, phase stability under rapid solidification, and ability to combine high hardness, wear, and corrosion resistance within a single matrix [9]. Several studies have demonstrated that thermally sprayed HEA coatings produced by HVOF, HVAF, APS, or cold spray exhibit a refined microstructure, enhanced hardness, and improved tribological and corrosion performance compared to the conventional Ni-, Co-, or Fe-based coatings, confirming their suitability for severe service environments [10,11]. While monolithic HEA coatings show considerable potential, further performance enhancement can be achieved through ceramic or cermet reinforcement, a strategy widely applied in thermal spray systems using carbides, such as WC, W₂C, TiC, and Al₂O₃ [12,13].

The strategic development of hybrid protective coatings is driven by the urgent demands of industries, such as aerospace, power generation, mechanical engineering, and marine sectors, where components are simultaneously exposed to severe mechanical wear and aggressive chemical or high-temperature environments [14–16].

Traditional monolithic coatings often fail to meet these multifaceted requirements; for instance, pure cermets can suffer from high brittleness and decarburization, while monolithic high-entropy alloys (HEAs) may lack sufficient structural hardness to withstand intense abrasive forces [17]. The integration of a ductile CoCrFeMnNi-based matrix with a robust Cr₃C₂-Ni₈₀Cr₂₀ cermet phase addresses these critical performance gaps by creating a synergistic balance between structural compliance and high load-bearing capacity [18]. Consequently, this composite architecture holds potential for application in engineering components requiring high wear resistance and environmental durability, such as hydraulic actuators, compressor blades, pump impellers, and marine infrastructure operating under combined tribological and localized corrosive attacks [19–21]. Furthermore, because this design utilizes Cr₃C₂-Ni₈₀Cr₂₀ to bypass standard industrial reliance on cobalt and tungsten binders, it offers a sustainable, eco-friendly surface engineering solution tailored to modern regulatory constraints without sacrificing operational longevity in harsh environments [22].

Based on these crucial points, the selection of CoCrFeMnNi_{0.8}V as a base for new HEA compositions stems from machine learning insights, theoretical analysis, and experimental data, pinpointing vanadium's crucial role in enhancing alloy properties. Vanadium promotes a dual-phase FCC and σ microstructure with increased hardness and wear resistance while maintaining corrosion performance [23,24]. Compared to refractory HEAs (such as WMoTaNb), which exhibit high melting points, high density, and processing challenges in thermal spray processes, CoCrFeMnNi_{0.8}V offers a more suitable melting range, low density, and easier processability. The incorporation of CrC-NiCr into this HEA matrix is, therefore, strategically justified by its balanced hardness, oxidation and corrosion resistance, and metallurgical compatibility, leading to a hybrid strengthening approach that integrates entropy-driven solid-solution strengthening, σ -phase precipitation, and carbide dispersion hardening [25].

It is important to mention at this point, nevertheless, the crucial role the different coating deposition methods may play to their performance. As such, to successfully deploy high-entropy alloy (HEA)–cermet composites in harsh engineering environments,

the selection of an appropriate coating preparation methodology is critical [26]. Conventional surface modification techniques present distinct operational trade-offs regarding coating thickness, deposition rates, and microstructural preservation [27]. Thin-film technologies, such as physical vapor deposition (PVD) and chemical vapor deposition (CVD), excel at producing highly uniform, atomically dense coatings with exceptional interfacial adhesion; however, they are intrinsically restricted by slow deposition rates and ultra-thin processing limits (typically $<10\text{ }\mu\text{m}$), rendering them unsuitable for thick hard-facing applications requiring structural load-bearing capabilities [28]. Conversely, metallurgical cladding methods, such as laser cladding and plasma translucent arc welding, offer thick, heavily bonded overlays but generate massive heat inputs [29]. This thermal surge leads to prolonged cooling cycles that can trigger significant substrate dilution, macroscopic distortion, and macro-segregation, which completely disrupts the formation of metastable, simple solid-solution phases crucial to HEA design.

In this context, thermal spray technologies—and specifically high-velocity oxy-fuel (HVOF) deposition—emerge as a uniquely balanced approach that bridges the gap between thin-film precision and heavy cladding thickness [30]. The novelty and advantage of the HVOF method lie in its high kinetic energy and rapid cooling rates ($104\text{--}106\text{ K/s}$), which accelerate combustion gases up to Mach 2.7 to generate exceptionally dense, well-bonded coatings ($450\text{--}500\text{ }\mu\text{m}$ thick) with minimized porosity and strong mechanical interlocking [31]. Crucially, the extremely brief dwell time of the particles in the HVOF flame prevents total core melting of the high-melting-point HEA matrix [32]. This preserves the gas-atomized primary phase structure while simultaneously enforcing rapid peripheral solidification that restricts chromium carbide decarburization and traps desirable high-temperature phases, such as the FCC, BCC, and σ -NiCr structural mix. Despite these clear advantages, a recognized limitation of thermal spray processing is the heterogeneous ‘splat-by-splat’ architecture it yields. This multiphase morphology inevitably generates micro-porosities and phase boundaries that can act as stress concentration zones during tribological loading or initiate micro-galvanic corrosion pathways. Nonetheless, optimizing HVOF parameters presents a highly effective and innovative pathway to engineer high-volume-fraction cermet–HEA hybrid structures that cannot be replicated through conventional liquid metallurgy or vapor deposition routes.

This study aims to evaluate the performance of the composite coating and to compare its performance with previously studied systems, assessing its potential as a competitive and more sustainable alternative for advanced surface engineering applications. It has to be mentioned that the present effort is the continuance of our previous work [18]. In our previous effort we compared the monolithic CoCrFeMnNi_{0.8}V coating with the 75% CoCrFeMnNi_{0.8}V–25% Cr₃C₂–Ni₈₀Cr₂₀ coating composite system (composition in wt.%). In this effort we expanded the work to compare the previous results with a new system comprised of 1–1 ratio between the matrix and the reinforcement and ascertain whether the increase of the reinforcing phase would lead to an optimum combination of the examined properties.

2. Materials and Methods

2.1. Feedstock Materials

Gas-atomized CoCrFeMnNi_{0.8}V particles consist of a single BCC solid solution with an average size of $20\text{--}50\text{ }\mu\text{m}$ (Figure 1a), developed by Castolin Eutectics [24]. The particles appear to have been properly melted and solidified with no porosity and minimal defects (Figure 1b). The chemical composition of the powder is close to the nominal composition of the system, with slightly lower V content and higher Cr content (Table 1). Elemental mapping of the powder indicates the good distribution of the elements, with Ni appearing to be segregated (Figure 2).

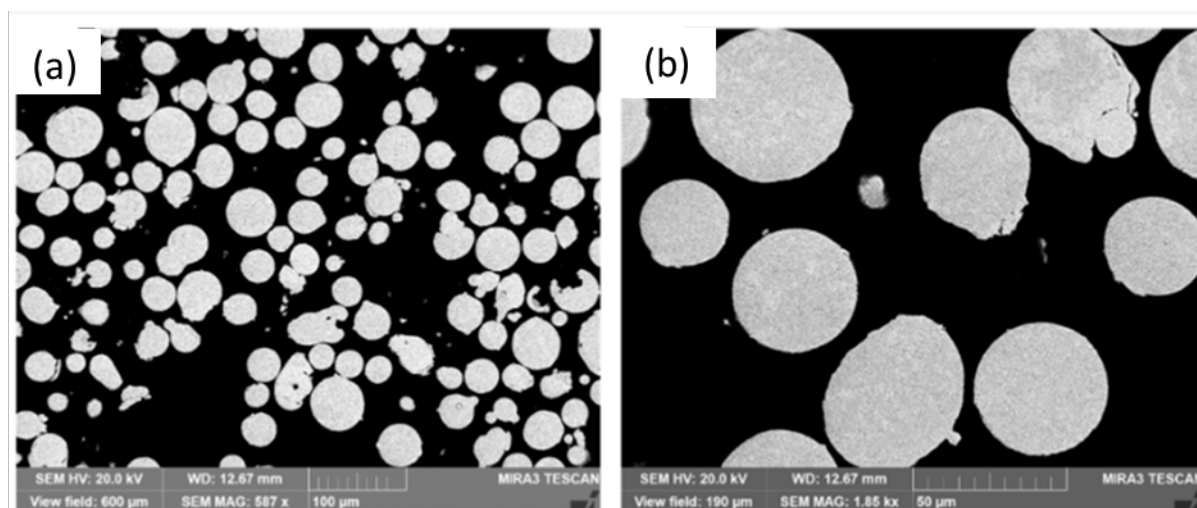


Figure 1. Microstructure of CoCrFeMnNi_{0.8}V powder: (a) low magnification and (b) high magnification [24].

Table 1. Chemical composition (at%) of CoCrFeMnNi_{0.8}V gas-atomized powder [14].

	V	Cr	Mn	Fe	Co	Ni
Nominal	17.2	17.2	17.2	17.2	17.2	13.8
Powder	15.9 ± 0.2	18.1 ± 0.2	17.9 ± 0.4	17.1 ± 0.4	17.3 ± 0.2	13.8 ± 0.3

Figure 3 shows the SEM micrographs of the Cr₃C₂-Ni₈₀Cr₂₀ powder [18]. The powder comprises spherical, agglomerated, and sintered powders specifically designed for thermal spraying, consisting of 80% chromium carbide (density 6.68 g/cm³, melting point ≈ 1620 °C) for enhanced hardness and resistance to wear, complemented by a nickel–20% chromium matrix (hereafter Ni₈₀Cr₂₀) that serves multiple functions. This Ni–Cr matrix (density 7.49 g/cm³, melting point ≈ 1440 °C) not only prevents the chromium carbide from decomposing (decarburization) during thermal spraying but also acts as an adhesive for the carbides during use. Upon application via the HVOF (high-velocity oxy-fuel) spray process, the resultant coatings are notably dense, exhibit robust bond strength, and present greater uniformity when compared to coatings applied through plasma spraying or combustion powder techniques. In the top micrograph, a cluster of spherical particles is visible, uniform in shape and with a rough surface texture. These particles are densely packed together, and their size is relatively consistent throughout the field of view. The nominal size is −45 µm (D₉₅) + 15 µm (D₅). The bottom image is a cross-sectional view of the Cr₃C₂-Ni₈₀Cr₂₀ powders used for thermal spraying. The interior of the particles in the bottom image displays a heterogeneous texture, which indicates variations in the material composition due to the presence of Ni–Cr.

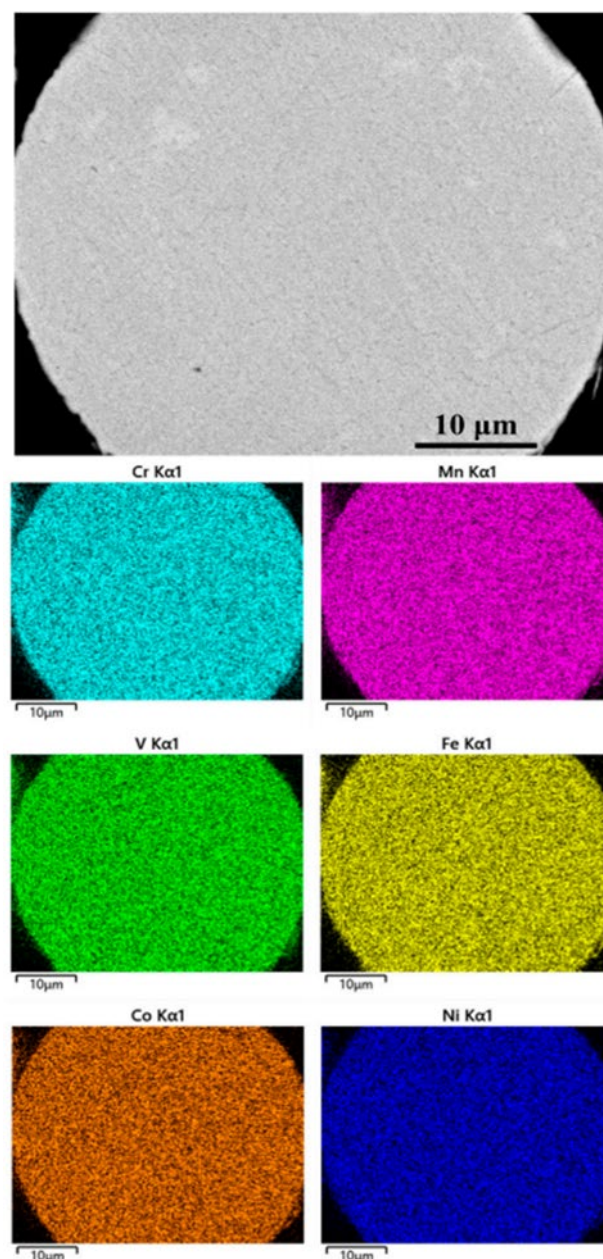


Figure 2. EDS elemental mapping of CoCrFeMnNi_{0.8}V powder [18,24].

2.2. Coating Application

Composite coatings were produced from a powder blend containing 50 wt.% HEA and 50 wt.% CrC-NiCr and deposited onto steel substrates using the high-velocity oxy-fuel (HVOF) method. Prior to deposition, the substrates were prepared properly by abrasive blasting with 46 µm alumina particles from a 100 mm distance, followed by compressed air cleaning. The HVOF system employed a nozzle capable of accelerating combustion gasses to Mach 2.7, resulting in high particle velocities and dense coating formation. The spraying parameters were optimized in house to obtain coating characterized by low porosity and a high-volume fraction of chromium carbide phase while maintaining high microhardness. The optimization also aimed to minimize decarbonization by controlling the flame temperature and particle impact velocity during deposition [24].

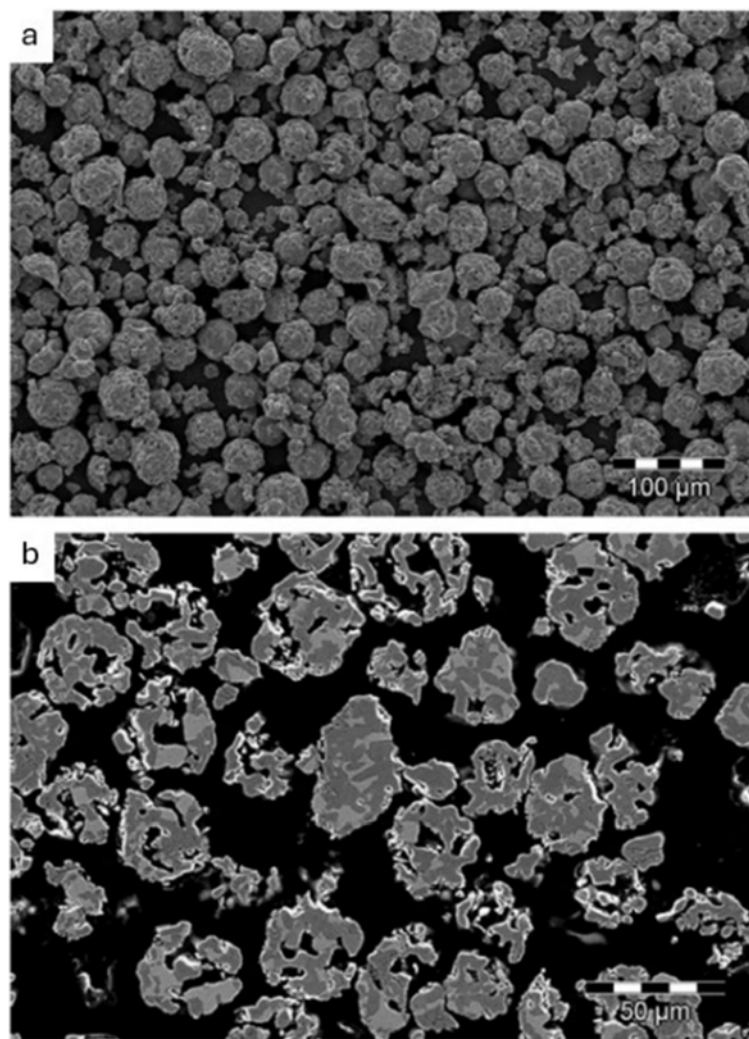


Figure 3. SEM micrographs showing the morphology (a) and the microstructure (b) of the Cr₃C₂-Ni₈₀Cr₂₀ powder [18].

2.3. Structural Analysis and Phase Identification

The coating microstructure and phase were analyzed by scanning electron microscopy (JEOL 6510 LV SEM, Akishima, Tokyo, Japan) equipped with energy-dispersive X-ray spectroscopy (Oxford Instruments Ltd., Abingdon, Oxfordshire, UK; 20 kV acceleration voltage, 15 mm working distance, 60 spot size). Diffraction patterns were recorded over a 2θ range from 10 to 120° with a scan rate of 0.01°/s utilizing a Bruker D8 Advance diffractometer (Billerica, MA, USA).

In order to gain information on the relative fraction of the involved phases, image analysis was performed using Image J software (Image J 1.54 g, Wayne Rasband and Contributors, National Institutes of Health, USA; <http://imagej.org> (accessed on 17 July 2026), java 1.8.0_345).

2.4. Hardness Evaluation

Hardness measurements were performed using an HMV hardness tester (Innovatest IN-700M, Universal Hardness Tester, Maastricht, The Netherlands) with a Vickers diamond indenter, under an applied load of 306 N. Average values and standard deviations were calculated from a minimum of ten measurements per sample.

2.5. Sliding Wear Assessment

Tribological performance was evaluated using a ball-on-disc tribometer (CSM Instruments, Needham, MA, USA). Tests were conducted under a normal load of 5N with sliding velocity of 10 cm/s against an Al₂O₃ counter-body with a diameter of 6 mm. Each test was performed over a total sliding distance of 2000 m. To track mass evolution and evaluate wear progression, the sliding wear tests were periodically interrupted at cumulative sliding distance intervals of 200 m. At each 200 m interval, a standardized cleaning and weighing protocol was systematically repeated for every specimen. The specimens were completely immersed in high-purity acetone, which served as the cleaning medium, and subjected to ultrasonic cleaning for a duration of 5 min to thoroughly detach any loosely adhered wear debris and ambient contaminants from both the wear tracks and surrounding surfaces. Following the ultrasonic cleaning cycle, the specimens were dried in air until all residual solvent completely evaporated. The specimens were then allowed to thermally equilibrate to room temperature before being weighed on a high-precision analytical balance to calculate mass loss. This exact cleaning and drying procedure was uniformly executed after every 200 m interval throughout the entire sliding distance to ensure high accuracy and reproducibility of the gravimetric measurements. A minimum of three tests were conducted to ensure reproducibility, and the wear rate was calculated from mass loss and sliding distance. It should be clarified that while gravimetric measurements were recorded at 200 m intervals, SEM morphological observations of the wear tracks were performed solely at the end of the sliding test. This post-test analysis captures the final cumulative state of the worn surface, reflecting the long-term interaction between the composite coating and the counterface after steady-state wear conditions were established.

To provide some further insight of the sliding wear testing, it should be noticed that the ball-on-disc sliding wear tests were performed over a total sliding distance of 2000 m at a constant sliding velocity of 10 cm/s. Based on these kinematic parameters, the total net sliding duration for each test repetition was exactly 20,000 s (approximately 5.56 h or 333.3 min), excluding the brief periodic interruptions at intervals of 200 m for specimen cleaning and mass-loss measurements. All tribological runs were carried out under controlled ambient laboratory environmental conditions at a room temperature of 23 ± 2 °C and a relative humidity of $45 \pm 5\%$. These atmospheric conditions are critical, as they directly govern the rate of local tribo-oxidation and the stability of the protective oxide-rich transfer film identified across the wear track during subsequent scanning electron microscopy and energy-dispersive X-ray spectroscopy examinations.

2.6. Electrochemical Behavior Evaluation

Electrochemical corrosion behavior was investigated by cyclic polarization in a 3.5 wt.% NaCl aqueous solution using a Gamry Reference 600 potentiostat/galvanostat (Warminster, PA, USA). A conventional three-electrode electrochemical cell was employed, consisting of the coated sample as the working electrode, a graphite plate as the counter-electrode, and a saturated calomel electrode (SCE) as the reference electrode. Prior to polarization testing, the specimens were immersed in the electrolyte for one hour to stabilize the open circuit potential. Polarization scans were then performed at a scan rate of 10 mV/min. The exposed surface was 0.785 cm². The electrolyte temperature was ~25 °C and the pH was kept at ~7.

3. Results and Discussions

3.1. Microstructure of the Composite Coating

Figure 4 presents SEM panoramic views of the surface and the cross-section areas of the produced composite coating. A rough surface topography can be observed in Figure

4a,b with some evidence of localized surface porosity. The cross-section areas (Figure 4c,d) provide a brief distribution of the involved phase. It has to be mentioned that, based on images similar to Figure 4c,d, the thickness of the coating was measured (at least five measurements by Image J image analysis software) at different areas and was calculated to be $406 \pm 10 \mu\text{m}$. This small error indicates a very homogeneous distribution of the coating thickness as a result of the coating application optimization process, already mentioned in the Materials and Method Section.

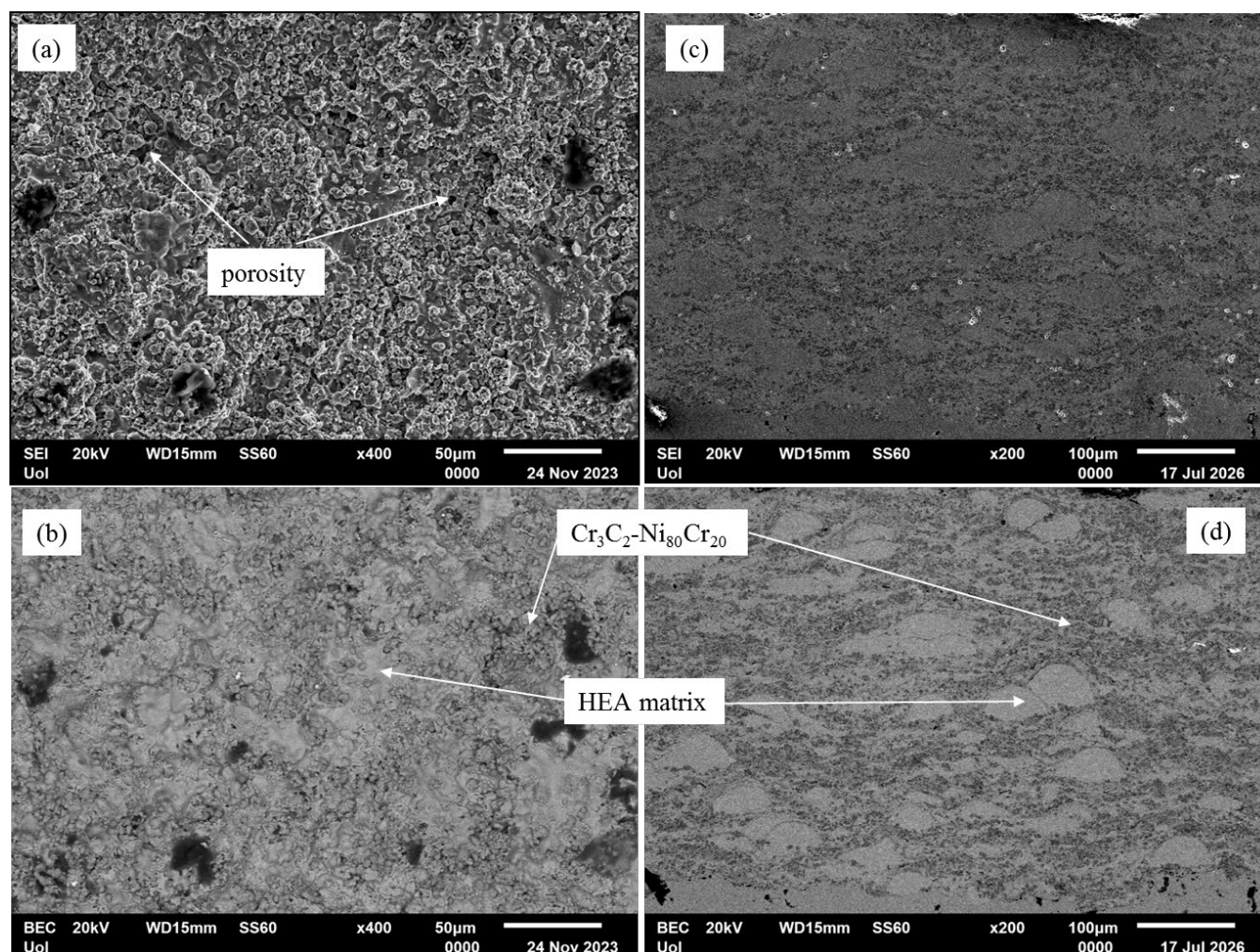


Figure 4. SEM panoramic views of the produced coating. (a,b) Surface morphology after SEI and BSC mode. Some surface porosity is present. (c,d) Cross-section after SEI and BSC mode. Brief notification of the involved phases is indicated.

Figure 5 presents a characteristic EDS elemental mapping analysis of the deposited coating showing the elemental distribution. Three different EDS elemental mapping analyses, similar to that of Figure 5, were conducted and their quantitative results are presented in Table 2. This quantitative analysis confirms the uniform compositional elements' distribution throughout the coating area.

Table 2. Elemental composition at different coating areas after various EDS mapping measurements (trials).

Elemental Composition in at%						
Trial	V	Cr	Mn	Fe	Co	Ni
EDS mapping 1	7.50	47.05	8.15	8.69	8.54	20.07
EDS mapping 2	7.41	48.24	7.86	8.13	8.41	19.95

EDS mapping 3	6.86	49.87	7.44	8.05	7.98	19.80
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Figure 6a,b present a higher magnification of the interfacial area between the coating and the substrate. The coating–substrate interface exhibits a slightly roughened profile, which indicates mechanical interlocking that contributes to strong adhesion. The lack of cracking or delamination at that interface further demonstrates the structural integrity of the coating deposition. Both the HEA matrix and the $\text{Cr}_3\text{C}_2\text{-Ni}_{80}\text{Cr}_{20}$ are present at the interfacial area, both showing a significantly enhanced bonding with the substrate.

Further information concerning the presence of porosity can be subtracted by the use of SEM images at higher magnification. Indicatively, Figure 7a,b presents in more detail the presence of porosity within the coating. It can be observed that isolated micropores are located throughout the cross-section area of the coating and some micropore clusters are especially located at the sequential boundaries of the deposited layers. By using images similar to the top of Figure 6 and by utilizing Image J image analysis software, the porosity was measured to be $1.89\% \pm 0.1$ (percentage of area coverage), which can be considered to be limited.

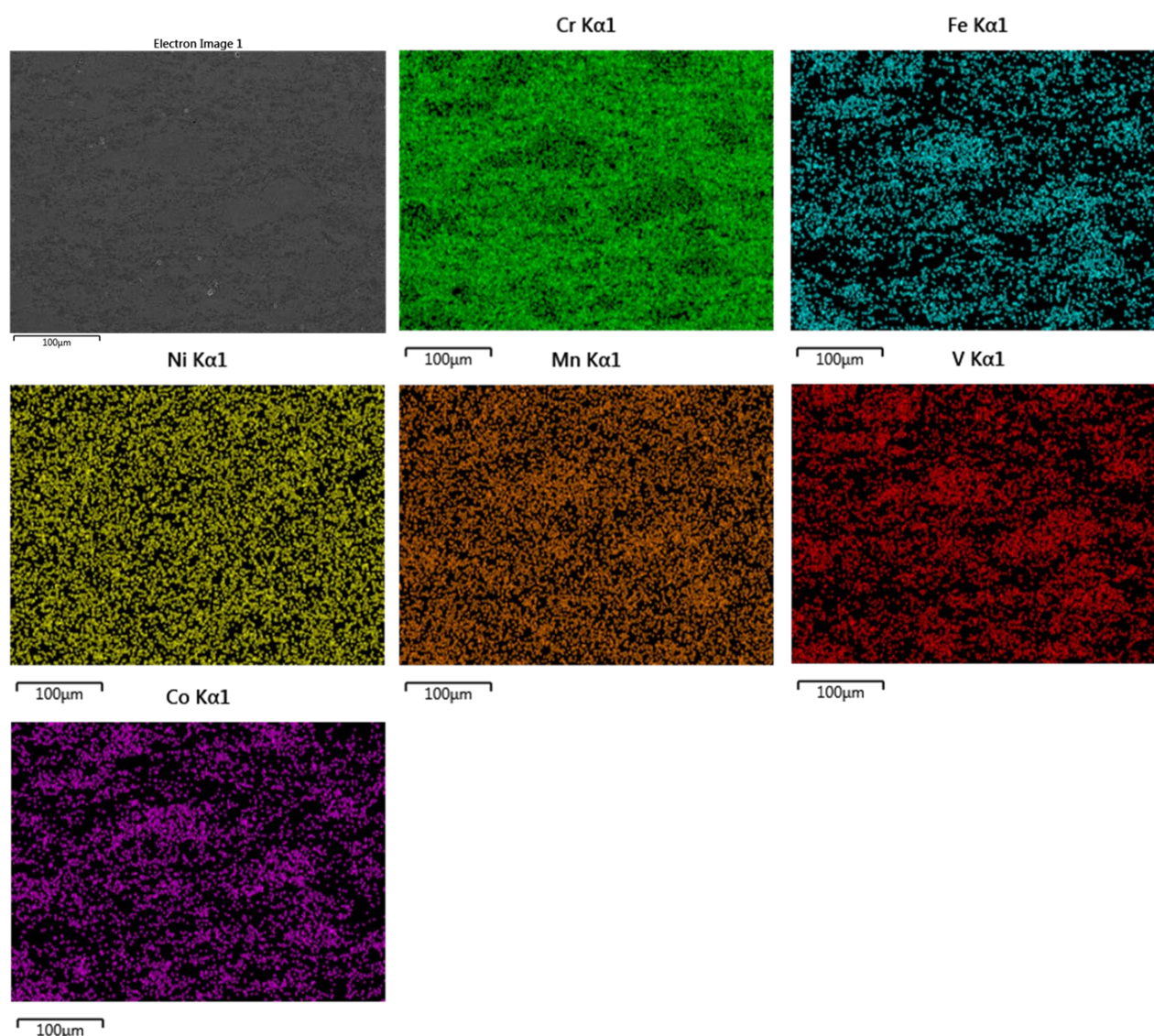


Figure 5. EDS elemental mapping analysis presenting the distribution of elements within the produced coating.

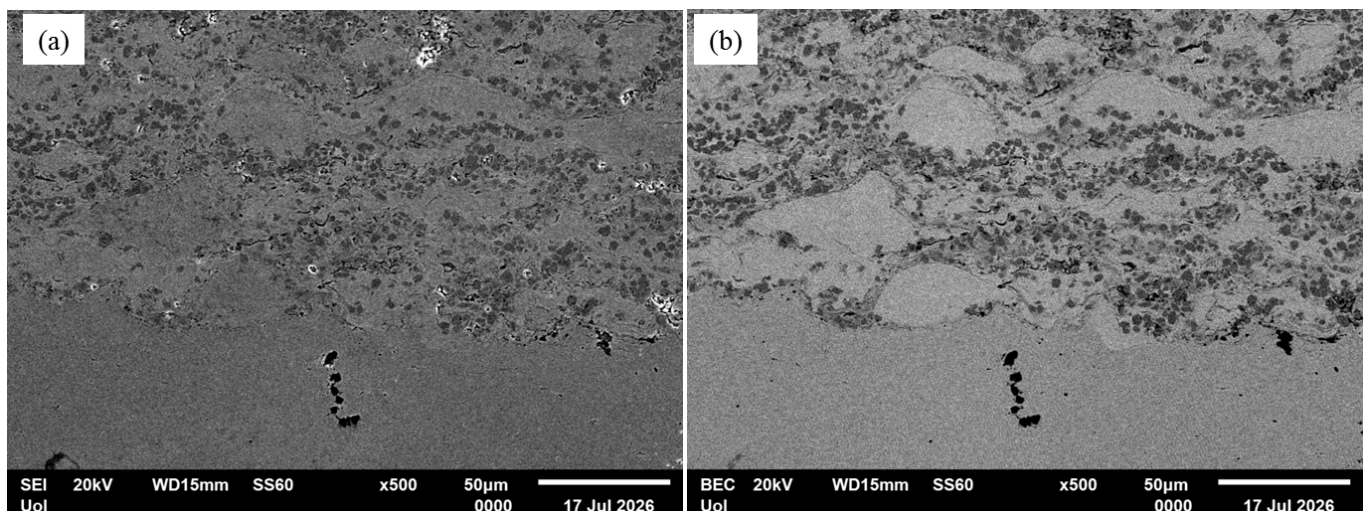


Figure 6. Closer examination of the coating-substrate interfacial area. (a) SEI and (b) BSC modes. The region shows a good adhesion with significant mechanical interlocking and limited defects. Both matrix partially melted particles and $\text{Cr}_3\text{C}_2\text{-Ni}_{80}\text{Cr}_{20}$ reinforcing phase are located at the interfacial area, showing significant bonding.

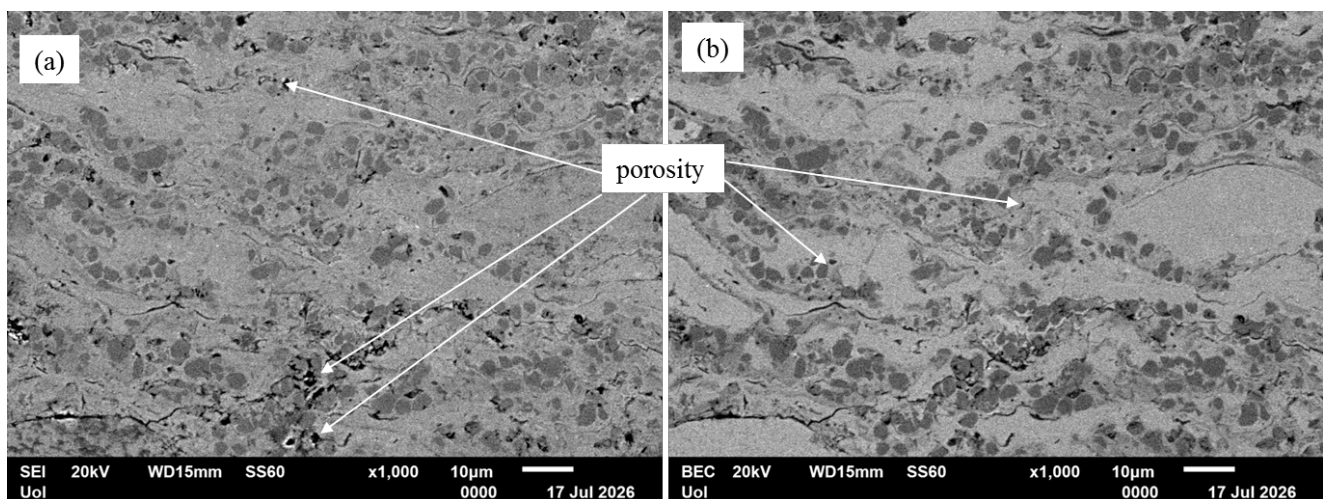


Figure 7. Higher magnification SEM images revealing the presence of porosity. (a) SEI mode and (b) BSE mode. Partially isolated micropores can be observed within the cross-section area and concentrated pore clusters are located at the sequential deposition layers. The extent of porosity, nevertheless, can be characterized as limited.

To further analyze the possible phases being present, XRD analysis was performed and the results are presented in Figure 8. The diffractogram confirms the complex multi-phase structure of the sprayed coating. The diffractogram shows a face-centered cubic (FCC) phase, attributed to the solid solution and/or CrC, a body-centered cubic (BCC) solid solution, and a Sigma NiCr phase. The detection and coexistence of these distinct phases point to a complex solidification process, with the final phase stability being dependent on the rapid cooling rates, which is characteristic of thermal spray coatings. As emphasized by Kamnis et al. [23], extreme cooling rates fundamentally alter the empirical phase boundaries of $\text{CoCrFeMnNi}_{0.8}\text{V}$ systems, trapping high-temperature phases and triggering rapid σ -phase precipitation that deviates from conventional equilibrium CALPHAD predictions. Furthermore, no profound evidence of carbide decomposition and/or secondary carbide formation can be drawn from the diffractogram. We have to recall from the Introduction Section that one of the important HVOF characteristics is that it restricts chromium carbide decarburization and traps desirable high-temperature phases, such as

the FCC, BCC, and σ -NiCr structural mix [32,33]. This observation could explain the possible stability of the carbide phase. On the other hand, however, the rapid cooling rates experienced upon the coating deposition can be responsible for the development of residual stresses and microstructural grain refinement that could explain some peak broadening observed in the received diffractogram. The authors do recognize, however, that further experimentation (possible TEM examination) is required toward this direction.

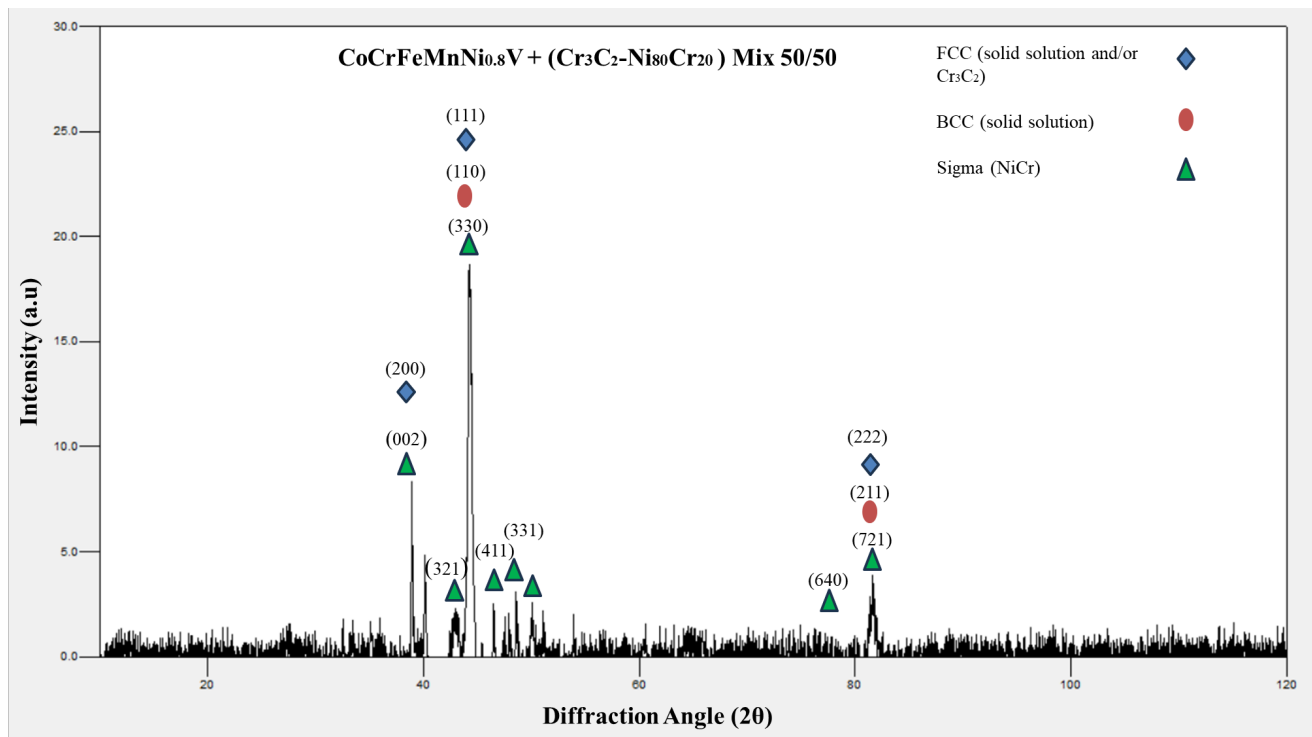


Figure 8. X-ray diffractogram (XRD) of the sprayed coating. Potentially present phases are listed along with the corresponding indexing.

A feature of high importance is the splat morphology created upon thermal spraying and presented in more detail in Figure 9a,b. Within the microstructure of the coating, the presence of splats from the HEA alloy (brighter regions) and $\text{Cr}_3\text{C}_2\text{-Ni}_{80}\text{Cr}_{20}$ particles (darker regions) was noticeable. Notably, a significant portion of the HEA alloy splats maintained their spherical shape, suggesting that these specific particles were partially melted during the spraying process. The high melting point of the HEA relative to the dwell time in the HVOF flame prevents complete core melting, which actually helps preserve the original gas-atomized phase structure. This phenomenon aligns with observations by Sfikas et al. [24], where the rapid flight times and high thermal mass of specialized multi-component powders often restrict melting to the particle periphery, safeguarding the core composition. Based on the measurements of ten of those ellipsoidal HEA alloy splats, their average diameter was found to be roughly 40 to 50 μm . Furthermore, the uniform distribution of the $\text{Cr}_3\text{C}_2\text{-Ni}_{80}\text{Cr}_{20}$ around the HEA splats creates a microstructure that is desirable to block crack propagation and improves the overall toughness of the coating. Furthermore, by conducting image analysis at different areas (at least five different regions) within the produced coatings, the extent of the partially melted HEA particles was measured and found to be $28.5 \pm 3\%$ area coverage.

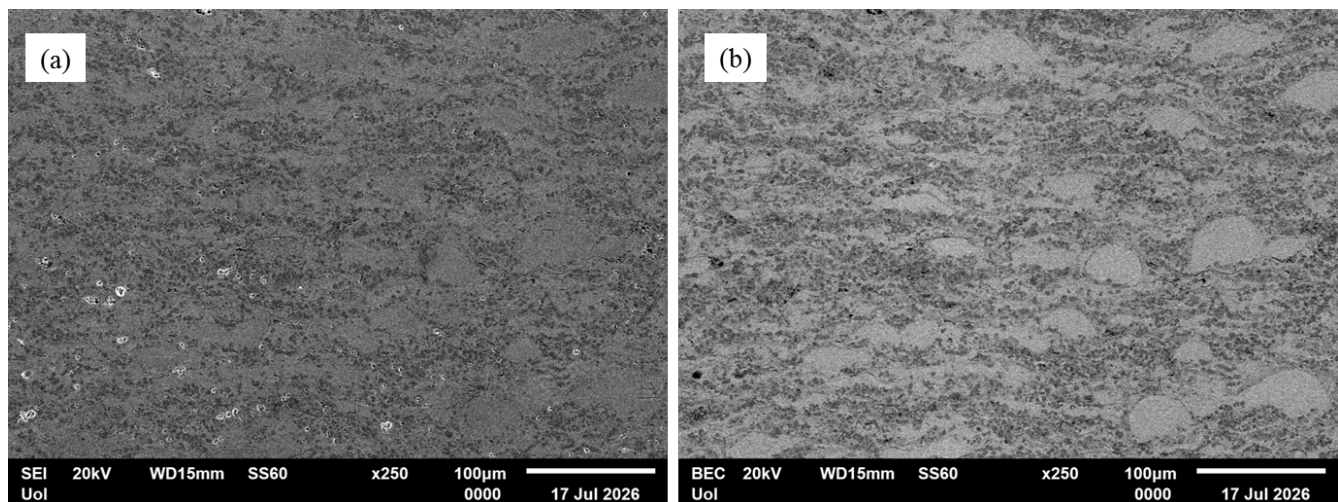


Figure 9. Higher magnification SEM images showing the splats' morphologies and the distribution of partially melted HEA matrix particles. (a) SEI mode and (b) BSC mode.

One of the crucial factors in thermal spray coatings is the presence of oxide phases in the form of stringers, developed especially at the boundary regions between the sequentially deposited layers. The presence of such oxide phases may deteriorate the integrity and quality of the interfacial regions and may lead to premature failure phenomena upon servicing. Figure 10a,b present, in higher magnification SEM images, the presence of such oxide stringers. To confirm their existence, EDS point analysis was performed and shown in Figure 11. The presence of oxide phases is evident. Having taken into consideration, however, the high magnification of Figure 11, it can be said that the presence of the oxide stringer is remarkably limited, a fact that indicates the quality of the produced coating and eliminates potential risks for accumulated failure phenomena. This limited presence of the oxide phases is due to the optimization process upon developing the thermal spray parameters, as already stated in previous paragraphs.

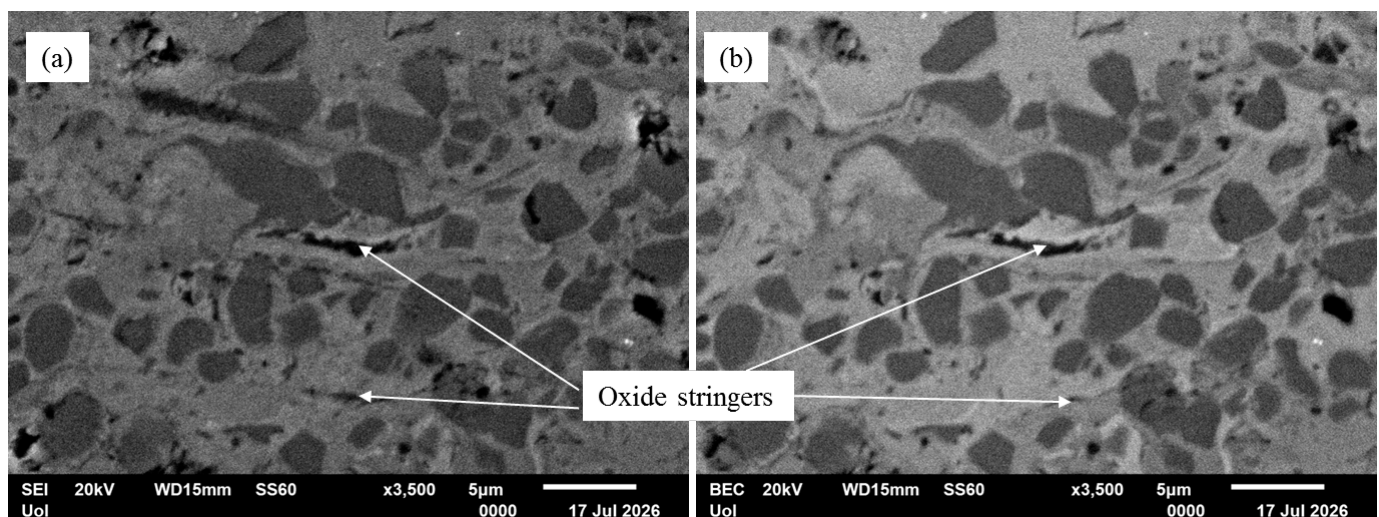


Figure 10. High-magnification SEM images showing the limited presence of oxide stringers. (a) SEI mode and (b) BSC mode.

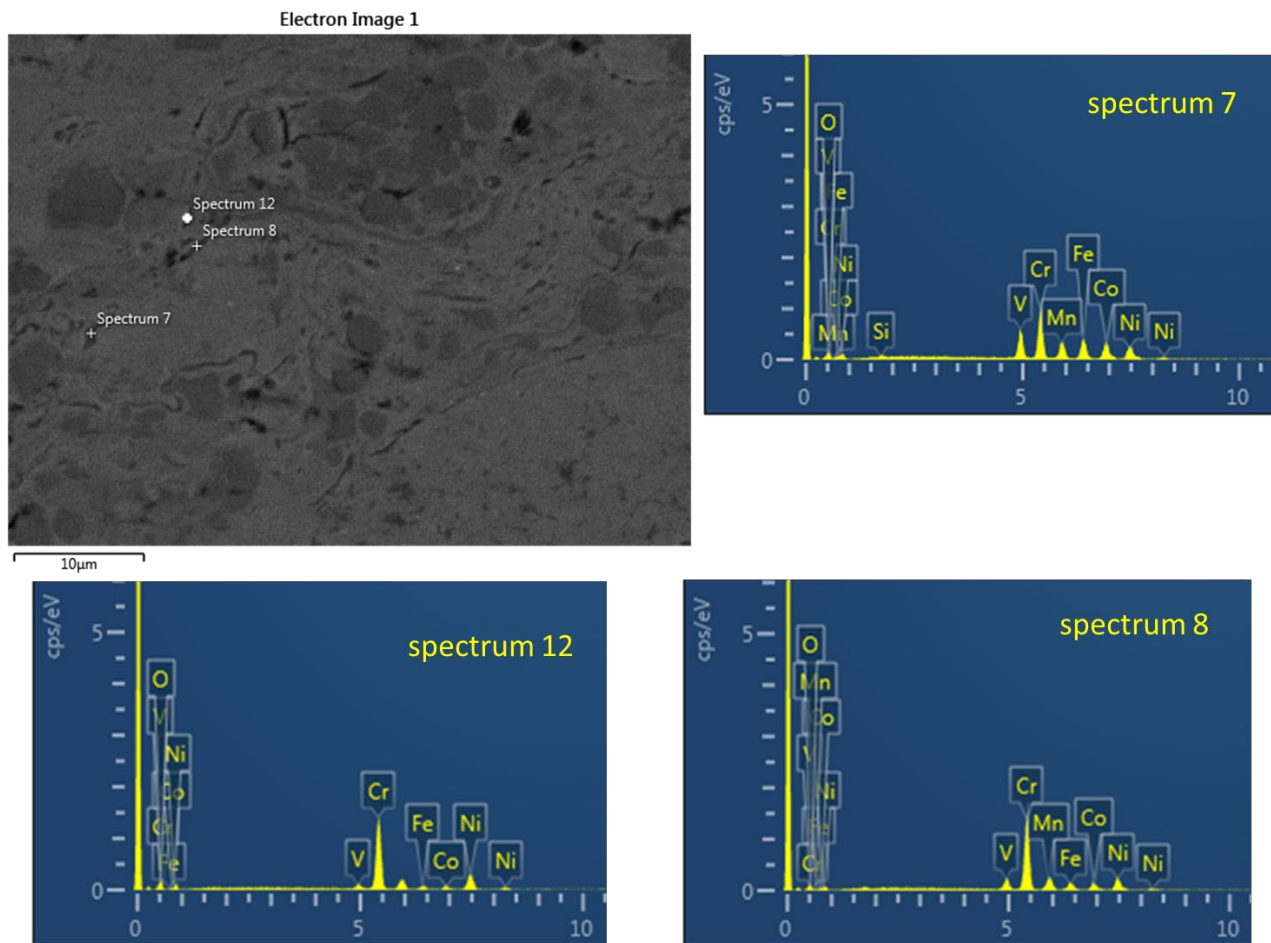


Figure 11. EDS point analysis verifying the presence of oxide stringers within the produced coating.

Last but not least, Figure 12a,b present the distribution of the Cr_3C_2 carbide phases within the produced coating. A uniform pattern of the Cr_3C_2 - $\text{Ni}_{80}\text{Cr}_{20}$ cermet as the reinforcing phase can be observed throughout the coating area, which (the cermet) seems to homogeneously engulf and surround the HEA matrix particles. Uniform distributions such as these can indeed ensure homogeneity in the microstructure with a corresponding positive impact on the overall coating's performance. Based on a series of images similar to Figure 12, the content of the carbide phase was measured through image analysis and calculated to be $34.5 \pm 2.5\%$ (area of coverage).

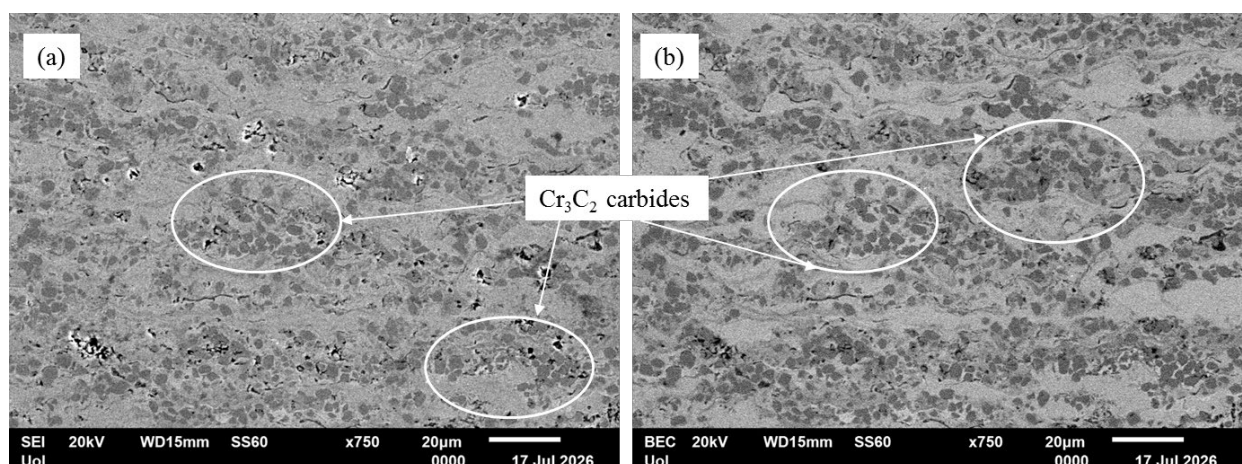


Figure 12. SEM images showing the distribution of the carbide phases within the coating area. (a) SEI mode and (b) BSC mode.

3.2. Sliding Wear Response of the Composite Coating

Prior to the analysis of the testing results, it is necessary to comment on the selection of the externally applied load. In our study, a normal load of 5 N was selected for the ball-on-disc sliding wear tests using a 6 mm-diameter Al_2O_3 counter-body. This specific testing configuration is not merely an arbitrary laboratory setup but directly simulates the localized contact mechanics and extreme stress regimes encountered by surface overlays in real-world industrial machinery. Given the high elastic modulus of both the alumina ball (~380 GPa) and the cermet-HEA composite (~220–250 GPa), this 5 N load generates an initial localized peak contact pressure exceeding 1.2–1.5 GPa.

This range in the contact pressure accurately mirrors the severe localized stress concentrations experienced by high-wear mechanical components in field applications. Specifically, such stress profiles are highly representative of the extreme operating conditions found in heavy-duty components protected by thermal spray overlays, including high-pressure hydraulic ram sleeves, severe-service industrial valve seats, slurry pump impellers, and rotating shaft seals operating under abrasive conditions [34].

In these applications, misalignments, particle entrapment, and concentrated mechanical loading routinely subject the coating surface to localized pressures that easily reach or exceed the yield strength of the metallic matrix. Furthermore, keeping the nominal load at 5 N avoids macro-fracture or excessive thermal cracking of the brittle carbide reinforcements at the onset of testing. This allows for a controlled evaluation of the steady-state synergistic wear mechanisms—such as adhesive deformation, interface fatigue, and protective tribo-oxidation—that dictate the actual service life of these engineering coatings in industrial environments.

Another important issue, prior to data analysis, is that the intermittent cleaning of the specimens in acetone at every 200 m interval inevitably removed loose, un-adhered wear debris from both the worn track and the counterface. This periodic interruption could have temporarily altered the wear dynamics by mitigating continuous third-body abrasion that would otherwise persist or intensify during uninterrupted, long-term sliding. Consequently, the observed third-body abrasive wear mechanism, characterized by micro-ploughing and micro-cutting, was likely driven primarily by debris that was generated, trapped, and highly compacted into stable tribo-layers within each discrete 200 m sliding cycle, rather than from a cumulative accumulation of loose particles over the entire 2000 m distance. This limitation implies that under continuous, uninterrupted field conditions, the contribution of loose debris to third-body abrasion might be more pronounced or lead to different wear rates. Nevertheless, the rapid formation of highly adherent and compacted oxide-rich patches during each interval demonstrates that a significant portion of the debris was mechanically alloyed back onto the wear track surface almost immediately upon formation, thereby maintaining the protective and load-bearing role of the tribo-layers despite the periodic cleaning protocol.

The mass loss as a function of sliding distance is presented in Figure 13, where the three different curves represent the repetitions of the test, to ensure reproducibility. The curves show an approximately linear increase in mass loss when increasing the sliding distance, indicating that the wear process proceeds at a relatively stable rate under the applied load. Based on the slope of the curves and the applied normal load, the average specific wear rate of the investigated coating was calculated following the simple expression:

$$\text{Wear rate (g/N.m)} = \text{mass loss} - \text{sliding distance slope/external load.}$$

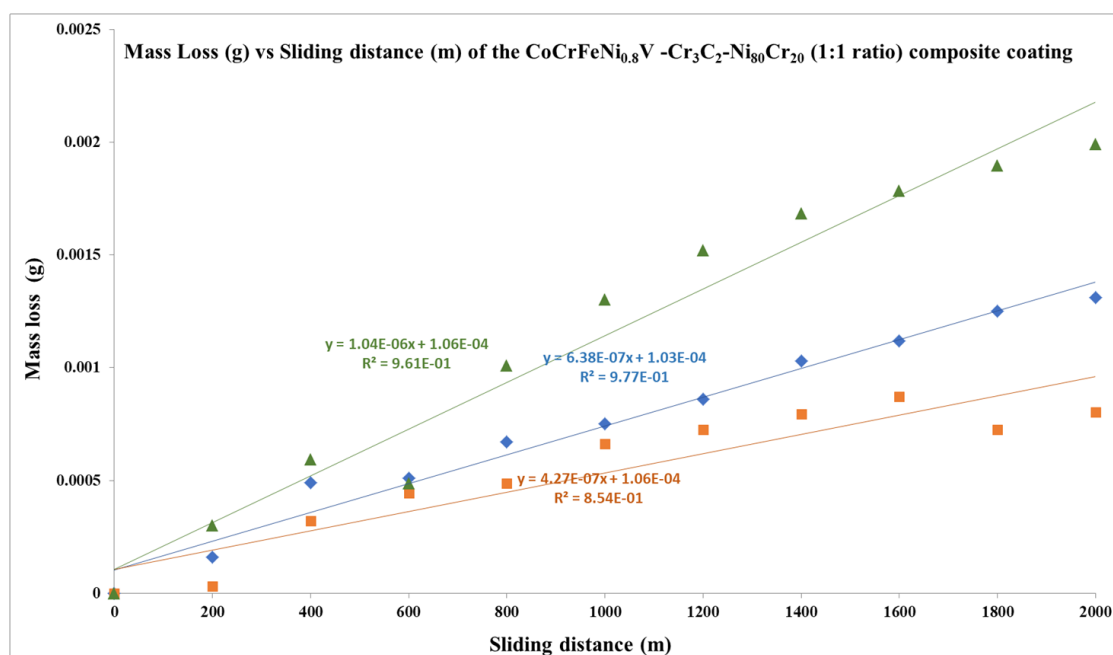


Figure 13. Mass loss versus sliding distance for the CoCrFeMnNi_{0.8}V + Cr₃C₂-Ni₈₀Cr₂₀ (1:1 ratio in wt.%) composite coating. The three different curves correspond to three different repetitions. The linear regression lines along with the related equations and standard deviations have been included.

Average specific wear rates for other coating materials from previous work are also listed in Table 3.

Table 3. Average specific wear rates for the different coating materials.

Coating System	Average Specific Wear Rate ($\times 10^{-7}$ gr/Nm)	Coefficient of Friction	Hardness, HV	Wear Mechanism
Cr ₃ C ₂ -Ni ₈₀ Cr ₂₀	1.12 ± 0.60	0.493 ± 0.04	893 ± 45	Abrasive + Fatigue [18]
CoCrFeMnNi _{0.8} V	7.13 ± 1.1	0.595 ± 0.05	500 ± 30	General [18]
Composite (75%HEA-25%Cr ₃ C ₂ -Ni ₈₀ Cr ₂₀)	1.70 ± 0.55	0.654 ± 0.05	540 ± 35	Combined [18]
Composite (50%HEA-50%Cr ₃ C ₂ -Ni ₈₀ Cr ₂₀) (present effort)	1.40 ± 0.68	0.536 ± 0.045	610 ± 40	Combined

Representative SEM images of the wear track obtained at different magnifications are shown in Figure 14a–c. At low and intermediate magnifications (Figure 14a,b), the wear track displays a continuous profile consisting of distinct dark and bright regions. The darker zones represent the highly deformed, softer, ductile face-centered cubic (FCC) high-entropy alloy (HEA) matrix phase, which shows smooth sliding tracks.

This behavior is characteristic of ductile metal matrices under sliding contact, as widely documented by Kiapé et al. [18] and Anupam et al. [13] regarding thermally sprayed multi-component systems.

High-magnification micrographs (Figure 14c) reveal irregular cavities, interface discontinuities, and localized pockets of fragmented debris. This directly captures the particle pull-out mechanism. Because a significant mismatch in mechanical properties (elastic modulus and hardness) exists between the soft HEA binder and the hard chromium carbide phase, severe cyclic stress concentrations accumulate at their mutual boundaries during repeated sliding passes. This induces interfacial micro-cracking and eventual detachment of the cermet reinforcement fragments. This liability at heterogeneous interfaces under

cyclic loading is a classic failure mode for cermets, aligning perfectly with observations made by Bolelli et al. [35] on the sliding wear behavior of $\text{Cr}_3\text{C}_2\text{-Ni}_{80}\text{Cr}_{20}$ hard metal overlays.

Debris amassment is visible in localized depressions within the sliding track (Figure 14b), yet the wear track conspicuously lacks severe, long, continuous parallel ploughing grooves or deep micro-cutting lines. The loose particles detached via pull-out become entrapped between the counter-body Al_2O_3 and the coating surface, prompting a transition into mild third-body abrasion. However, because the exposed harder carbide phases successfully shield the remaining matrix by increasing the coating's global load-bearing capabilities, severe abrasive wear is mitigated. This phenomenon represents the beneficial hybrid shielding approach highlighted by Katranidis et al. [36], where carbide phases act as primary load-bearing structures that limit macro-abrasion.

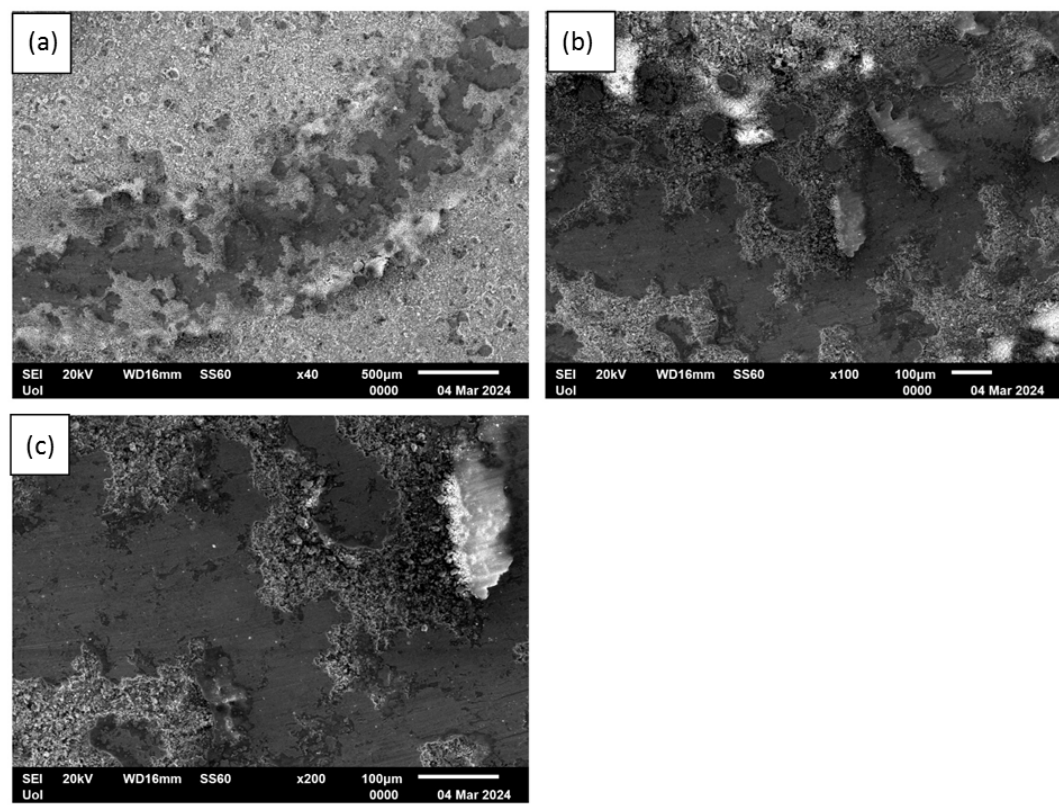


Figure 14. Composite coating wear track at different magnifications (a–c).

In addition to mechanical damage, the EDS elemental map (Figure 15) was also performed to gain further insight on the potential wear mechanisms. The accompanying EDS elemental map (Figure 15) confirms a prominent presence and uniform dispersion of oxygen across the worn track area. This provides clear evidence of protective tribo-oxidation. Frictional heating during sliding contact promotes rapid localized oxidation, creating a thin tribo-film. This layer acts as a solid lubricant or protective barrier that prevents direct metal-to-metal adhesion, effectively stabilizing the wear rate and maintaining a linear mass-loss progression. This dynamic matches the findings of Akhtari Zavareh et al. [37], where native oxides generated during tribological contact reduce friction coefficients and lower wear rates in Cr_3C_2 -based cermet composites.

During the SEM (Figure 14) and energy-dispersive X-ray spectroscopy (EDS; Figure 15) examinations of the worn surface, clear evidence of a mechanically mixed transfer layer—specifically a tribo-oxidative film—was observed. As detailed in the intermediate and high-magnification SEM micrographs, the sliding track exhibits flattened, smooth

plateaus alongside localized patches of compacted wear debris. The elemental map explicitly confirms that these smeared zones are highly enriched with oxygen, alongside chromium and the metallic elements of the high-entropy alloy (HEA) matrix. This localized chemistry indicates that under the severe frictional heating and flash temperatures generated during the 2000 m sliding distance, the dislodged debris from the sacrificial multi-element HEA matrix and the fragmented $\text{Cr}_3\text{C}_2\text{-Ni}_{80}\text{Cr}_{20}$ particles undergoes continuous comminution, oxidation, and mechanical compaction. Rather than being swept away completely, this material is dynamically smeared back onto the wear track by the sliding action of the Al_2O_3 counter-body, stabilizing into a protective, self-lubricating transfer layer. This mechanically mixed layer effectively shields the underlying composite from severe, direct metal-to-metal contact with the counter-body, which directly explains the transition from severe adhesive wear to mild abrasion and the highly reproducible, linear mass-loss rates recorded in our experiments.

The wear behavior of the novel 50wt.% $(\text{CoCrFeMnNi})_{0.8}\text{V}$ –50wt.% $\text{Cr}_3\text{C}_2\text{-Ni}_{80}\text{Cr}_{20}$ composite coating is governed by a synergistic, evolving process, where each mechanism plays a distinct role. Initially, the primary wear mode is dominated by adhesive wear, which exerts a high relative contribution localized within the softer, inherently ductile face-centered cubic (FCC) high-entropy alloy (HEA) matrix. At the onset of sliding contact against the rigid Al_2O_3 counter-body, this metallic binder phase accommodates the applied normal load through localized plastic deformation. Under repeated sliding passes, microscopic friction junctions continuously form and fracture at the mating asperities. This adhesive mechanism manifests in the intermediate-magnification SEM micrographs as smooth sliding tracks and zones of plastically deformed matrix material. Adhesive material removal from the matrix continues until the harder chromium carbide reinforcement particles become progressively exposed at the surface to support a significant portion of the applied load.

As the sliding process transitions into a steady-state regime, fatigue wear provides a moderate yet highly critical relative contribution by acting as the primary trigger for structural micro-damage at the phase boundaries. Because a severe mismatch in elastic modulus and hardness exists between the highly compliant HEA matrix and the rigid cermet particles, intense cyclic stress concentrations accumulate at their mutual interfaces under the repeating passes of the counter-body. Over time, this cyclic contact fatigue drives interfacial debonding and micro-cracking along the matrix–particle boundaries, leading to the eventual detachment or pull-out of the reinforcement phases. High-magnification SEM observations directly capture this fatigue-induced damage, revealing numerous irregular cavities and structural discontinuities where carbide particles have been plucked from the surrounding matrix.

Once these hard carbide fragments and associated matrix debris are liberated from the coating architecture, they become entrapped within the sliding interface, introducing an abrasive wear component. The relative contribution of this third-body abrasion remains low to moderate and is effectively localized. Although these trapped hard fragments scratch the sliding tracks, the worn surface conspicuously lacks severe, long, continuous parallel ploughing grooves or deep micro-cutting lines, proving that macro-abrasion is not the dominant failure mode. This mitigation occurs because the remaining, well-embedded carbide particles form an exposed, highly resilient network that enhances the coating's global load-bearing capacity, successfully shielding the softer matrix from severe abrasive cutting.

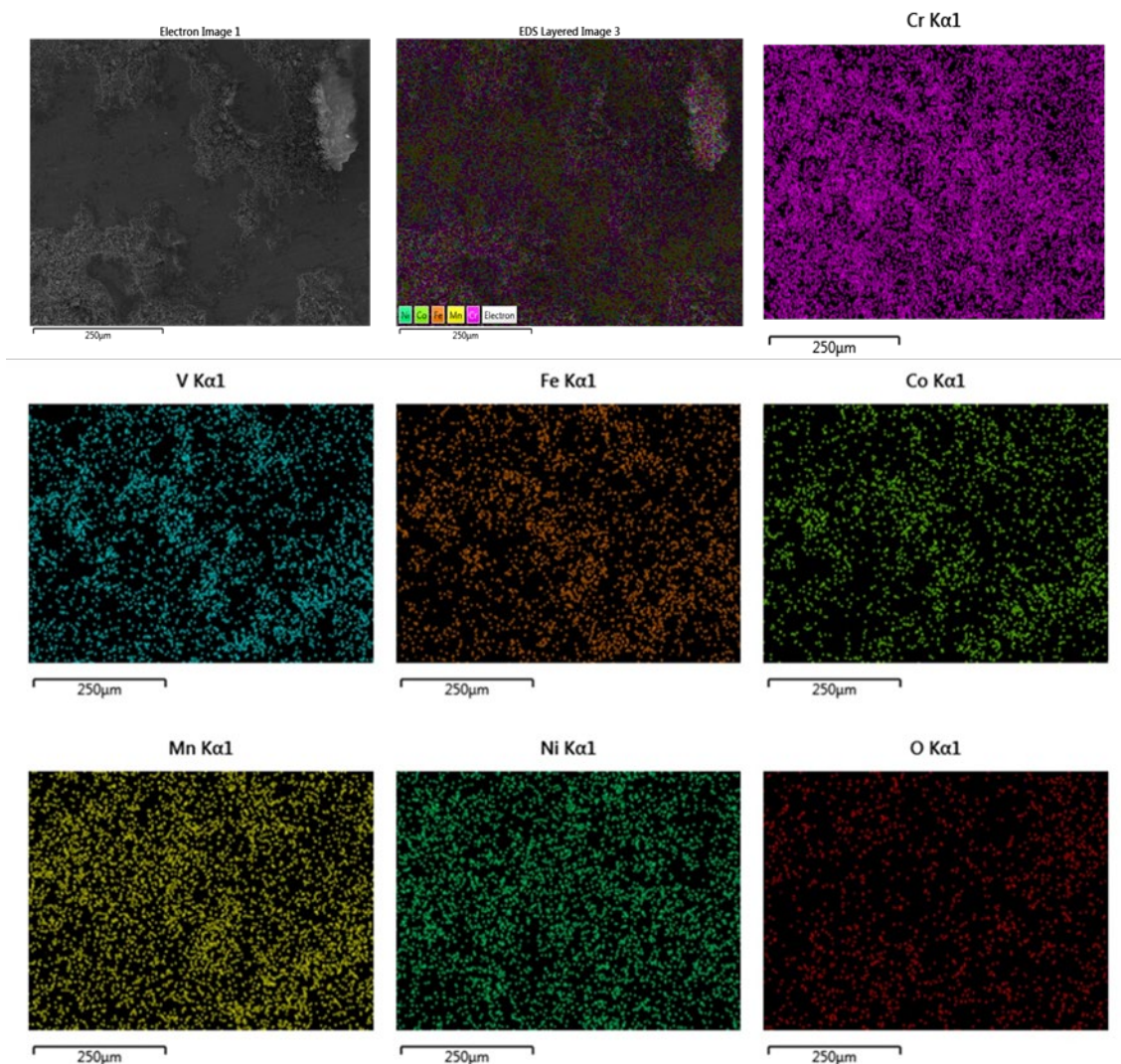


Figure 15. EDS elemental mapping on a selective area of the wear track.

Concurrently, oxidative wear provides a high and highly beneficial relative contribution by acting as a rate-stabilizing chemical mechanism throughout the 2000 m sliding distance. Frictional heating generated across the contacting asperities drives rapid localized oxidation of the metallic elements. This process is explicitly validated by the EDS elemental mapping, which demonstrates a strong, widespread oxygen signal across the active wear track. The continuous development of these thin oxide layers leads to a protective tribo-film that acts as a solid lubricant barrier, physically minimizing direct metal-to-metal contact and preventing severe adhesion. This oxidative shielding is directly responsible for stabilizing the wear rate and maintaining the highly reproducible, linear mass-loss progression observed experimentally. By integrating this comprehensive breakdown of adhesive deformation, interface contact fatigue, mild third-body abrasion, and protective tribo-oxidation into the revised manuscript, we have shifted the focus from a simplistic hardness-based interpretation to a holistic, mechanism-driven analysis.

The calculated average specific wear rates presented in Table 3 demonstrate that the incorporation of $\text{Cr}_3\text{C}_2\text{-Ni}_{80}\text{Cr}_{20}$ reinforcement significantly improves the wear resistance of the HEA coating. The pure HEA coating exhibits the highest wear rate, whereas the carbide coating exhibits the lowest wear rate. The composite of this study exhibits intermediate behavior (and lower than the 75/25 composite, which was studied in our previous

work [18]). This reflects a highly beneficial synergistic interaction between matrix plasticity and carbide reinforcement. The HEA matrix efficiently accommodates the deformation during sliding via its inherently ductile FCC phase, while the carbide reinforcement enhances load-bearing capacity and resists material removal. Consequently, the wear behavior of the composite coating is governed by a combination of the wear mechanisms analyzed above.

3.3. Corrosion Resistance of the Composite Coating

The potentiodynamic polarization curves obtained for the investigated coating system in 3.5 wt.% NaCl solution are presented in Figure 16. Three polarization measurements were performed to evaluate the reproducibility of the electrochemical response. The solid lines represent the forward scan, while the dashed lines represent the reverse scan of the polarization's curves. The corrosion potential (E_{corr}) and corrosion current density (I_{corr}) were determined using Tafel fitting, and the corresponding values are presented in Table 4, including values for coatings from our previous work [18]. The Tafel extrapolation method was based on the use of the Gamry equipment (Echem Analyst software). The Tafel slopes were calculated within a range of -100 to $+100$ mV relative to E_{corr} , which is a common practice to calculate I_{corr} densities.

Table 4. Polarization testing comparative summary.

Coating System	E_{corr} (mV)	I_{corr} ($\times 10^{-6}$) A/cm ²	Remarks
CoCrFeMnNi0.8V	-302.00 ± 45	4.06 ± 0.4	Local corrosion. Very low I_{corr} . [18]
Cr ₃ C ₂ -Ni ₈₀ Cr ₂₀	-359.00 ± 40	4.77 ± 0.5	General corrosion. Passivation. [18]
CoCrFeMnNi0.8V + Cr ₃ C ₂ -Ni ₈₀ Cr ₂₀ (75–25) % Mix	-462.00 ± 50	10.80 ± 2.0	Local corrosion. Very low I_{corr} . [18]
CoCrFeMnNi0.8V + Cr ₃ C ₂ -Ni ₈₀ Cr ₂₀ (50–50) % Mix (present effort)	-552.00 ± 50	10.53 ± 2.0	Local corrosion. Very low I_{corr}

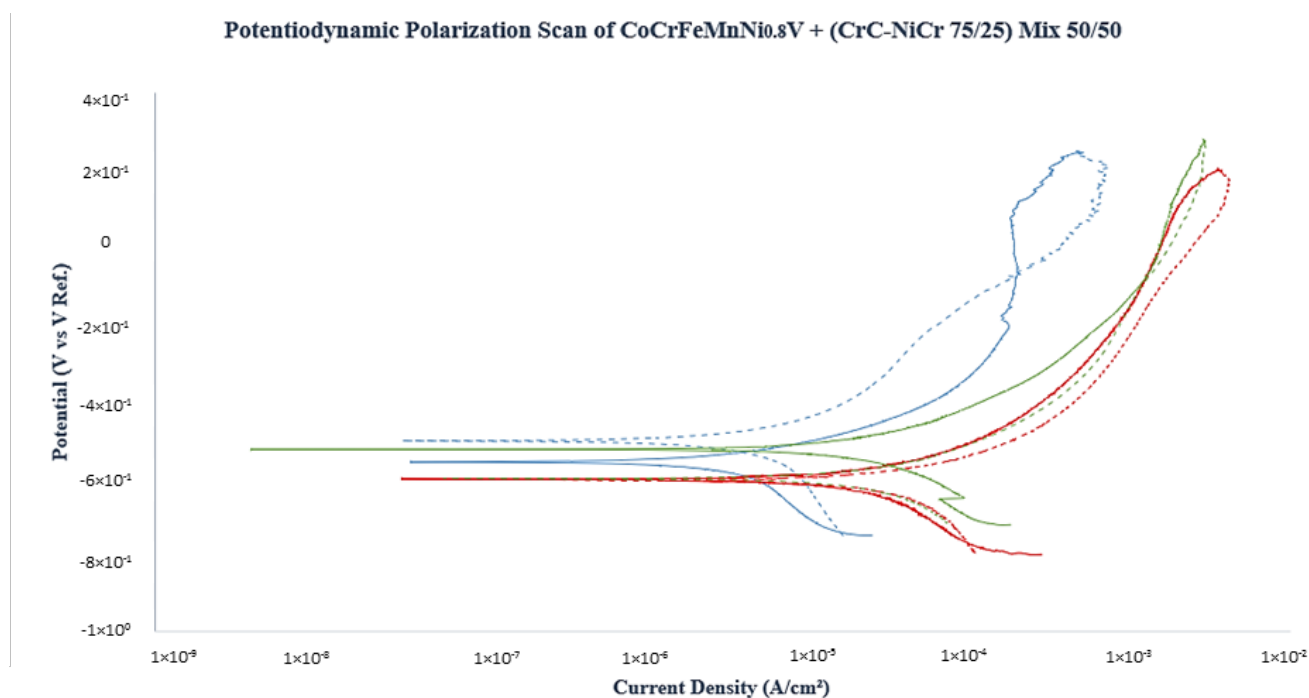


Figure 16. Potentiodynamic polarization curves of the composite coating. The different curves represent three different repetitions. Solid lines correspond to the forward polarization stage, whereas dashed lines correspond to the reverse polarization scans. The scanning rate was 10 mV/min, the electrolyte temperature was 25 °C, the pH was kept at 7, and a resting time of 1 h prior to the scanning initiation was retained to stabilize and reach the OPC (open circuit potential).

The measured corrosion potentials vary between -302 mV and -552 mV, indicating differences in the thermodynamic tendency for electrochemical dissolution among the systems compared [24]. The CoCrFeMnNi_{0.8}V HEA coating shows the most noble corrosion potential (-302 mV). On the contrary, the composite coating of this study displays more negative potential, reaching -552 mV, indicating that the composite coating has higher susceptibility to be corroded [38]. The HEA coating exhibits a corrosion current density of 4.06×10^{-6} A/cm², which is slightly lower than that of the Cr₃C₂-Ni₈₀Cr₂₀ coating (4.77×10^{-6} A/cm²). In contrast, the composite coating exhibited significantly higher corrosion current densities, reaching 10.80×10^{-6} A/cm² for the 75/25 composite, which was studied in our previous work [18], and 10.53×10^{-6} A/cm² for the 50/50 composite. These values indicate that the corrosion rate increases when the carbide phase is incorporated into the HEA matrix [38].

The forward scan of the polarization curves for the investigated coating shows a continuous increase in current density with increasing potential without the presence of a well-defined passive plateau. This behavior suggests that the oxide films formed on the coating surfaces are not sufficiently stable to provide strong passivation in the chloride-containing electrolyte. Chloride ions are known to destabilize passive films by penetrating oxide layers and promoting localized breakdown, which can lead to sustained anodic dissolution [39]. A small hysteresis between the forward and reverse scans is observed in the polarization curves. The reverse scans generally exhibit slightly higher current densities than the forward scans, indicating that the surface condition changes during the polarization, likely due to the formation of corrosion products or localized dissolution sites. Such behavior is commonly observed in heterogeneous coating systems where different phases may exhibit different electrochemical responses [38].

SEM images of the corroded surface (Figure 17) at different magnifications offer further insight into the corrosion mechanisms. Higher magnification images (Figure 17b,d) reveal the presence of small pits and irregular surface features that correspond to localized corrosion sites. These features suggest that corrosion preferentially initiates at specific microstructure locations within the coating rather than occurring uniformly across the entire surface [38,39].

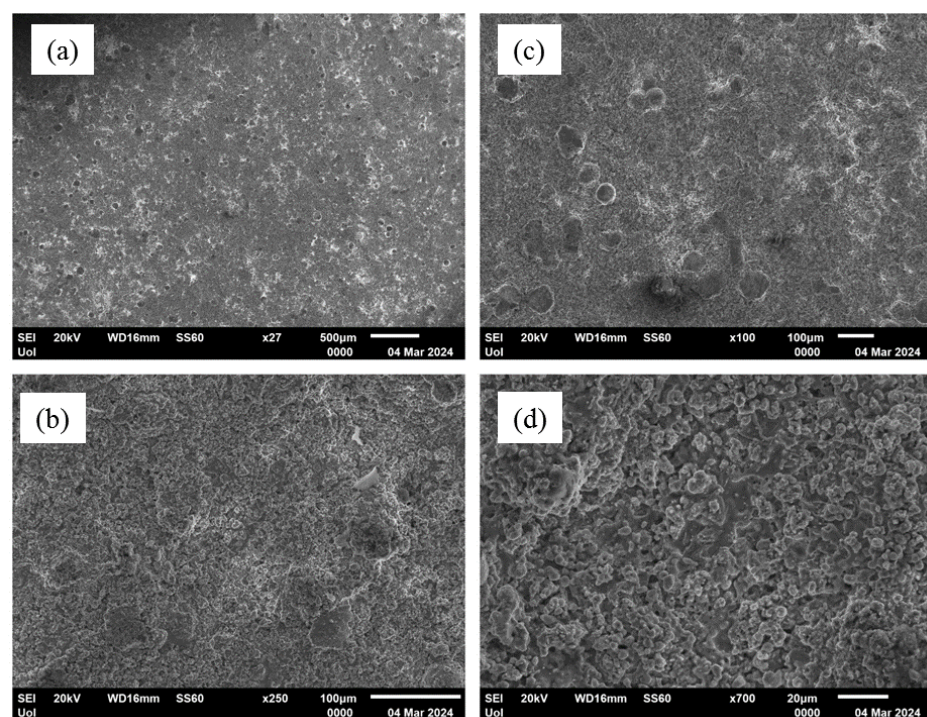


Figure 17. SEM images from the corroded surface of the composite coating at different magnifications. (a) $\times 27$. (b) $\times 250$. (c) $\times 100$ and (d) $\times 700$.

The localized corrosion behavior can be directly explained by the heterogeneous microstructure of the composite coating. The coatings consist of multiple phases, including the HEA matrix and the carbide particles, which display substantial differences in electrochemical potentials. This mismatch results in the formation of numerous micro-galvanic cells, where certain regions behave as anodic sites and preferentially dissolve, while nobler regions act as cathodic sites [38,39]. Usually, the metallic matrix (especially containing elements like Mn and V) acts as the sacrificial anode relative to the nobler chromium carbide reinforcement. This pattern follows the broader literature on cemented cermet corrosion mechanisms, where the potential gradients between binder matrices and hard carbide phases accelerate binder leaching. The prevalence of these widespread micro-galvanic interactions explains the higher corrosion current densities for the composite coating compared to the individual, monolithic coating systems [38,39].

Additional evidence of these corrosion processes is provided by the EDS elemental analysis shown in Figure 18. The presence of chromium within both the HEA matrix and the carbide contributes to the formation of chromium-rich oxides on the coating surface. Although such oxides may provide a localized baseline level of protection against further corrosion, the chloride ions present in the electrolyte continuously destabilize these films, allowing sustained electrochemical activity and driving the development of the localized corrosion features observed [38,39].

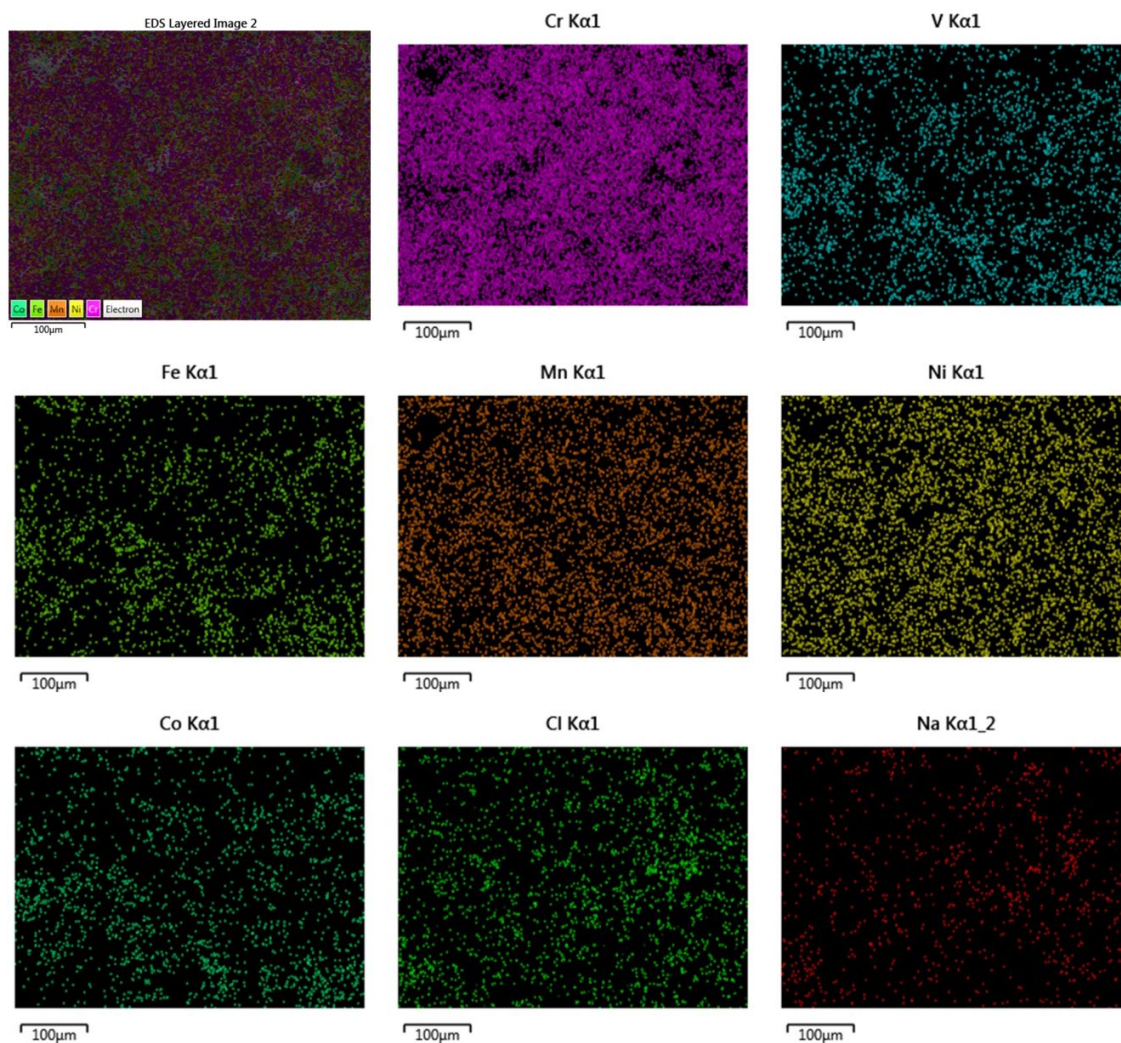


Figure 18. EDS analysis from the corroded surface of the composite coating.

Last but not least, the role of porosity is of crucial importance. Although the high-velocity oxy-fuel (HVOF) spraying parameters were optimized to achieve a highly dense composite architecture with low baseline porosity, the presence of residual micro-porosity, splat boundaries, and interphase micro-voids plays a definitive role in facilitating electrolyte infiltration. These structural defects function as direct interconnected channels that allow the aggressive 3.5 wt.% NaCl solution to penetrate deep into the coating interior. Once the chloride-rich electrolyte penetrates these pathways, it causes localized destabilization and breakdown of the native oxide passive films. This penetration stagnates within the micropores, establishing localized concentration cells that severely restrict oxygen replenishment and generate aggressive micro-environments. Consequently, this electrolyte infiltration directly accelerates the activation of widespread micro-galvanic cells at the highly heterogeneous phase boundaries between the sacrificing metallic CoCrFeMnNi_{0.8}V matrix and the nobler Cr₃C₂-Ni₈₀Cr₂₀ cermet particles. The presence of these porous pathways directly explains the absence of a stable passive plateau and the elevated corrosion current densities (10.53×10^{-6} A/cm²) observed during testing.

In summary, taking into consideration both the sliding wear and corrosion response, it can be said that while the incorporation of the 50 wt.% Cr₃C₂-Ni₈₀Cr₂₀ cermet phase effectively enhances the mechanical durability and structural load-bearing capacity of the hybrid coating, it introduces an intrinsic operational trade-off by increasing vulnerability to localized electrochemical corrosion in chloride environments due to severe micro-galvanic coupling between the heterogeneous phases. Remedying this compromise to achieve simultaneously optimal tribological and corrosion protection remains an essential objective for subsequent research. Future efforts will systematically investigate targeted post-deposition sealing interventions—such as the infiltration of liquid polymeric or organic inhibitors—alongside advanced surface modification strategies, including high-density laser surface melting or localized post-weld heat treatments. These sealing and microstructural homogenization methods aim to minimize interconnected micro-porosities, refine phase boundaries, and eliminate localized active galvanic paths, thereby transforming this cobalt- and tungsten-free composite architecture into a fully resilient, multi-functional coating solution for aggressive marine and industrial settings.

As a summarizing comment concerning the overall coating's characteristics and behavior, it can be said that microstructurally, the developed composite displays a highly dense, dual-phase core-shell architecture. This distinct structure consists of partially melted, gas-atomized spherical CoCrFeMnNi_{0.8}V splats uniformly wrapped by a continuous network of the Cr₃C₂-Ni₈₀Cr₂₀ cermet phase. This structural arrangement shares strong similarities with the pioneering multi-component architectures fabricated by Bosi et al. [40] and Kiape et al. [18]. Those studies confirmed that rapid thermal spray solidification traps high-temperature FCC, BCC, and secondary intermetallic σ phases. However, a key microstructural difference in our system is that optimizing the flame temperature and particle impact velocities specifically preserved the un-melted core composition of the gas-atomized HEA splats. This preservation successfully maintained baseline mechanical toughness and avoided the full chemical macro-homogenization often seen in high-power atmospheric plasma-sprayed (APS) variations, which can experience excessive matrix oxidation.

From a tribological standpoint, our composite matches the broad trends observed in current literature, where adding a cermet or ceramic second phase transitions the wear mechanism from severe adhesive deformation to a stable combination of mild third-body abrasion and rate-controlling tribo-oxidation. The average specific wear rate of our hybrid coating remains intermediate, showing significantly better performance than the monolithic HEA but yielding a slightly higher mass loss than pure, highly brittle chromium carbide overlays. This intermediate behavior highlights a beneficial synergistic trade-off. The ductile FCC matrix of the HEA safely accommodates plastic deformation and arrests

propagating cracks under cyclic loading, while the surrounding exposed hard carbides act as primary load-bearing boundaries to restrict large-scale abrasive cutting. This performance compares favorably with the findings of Liu et al. [25], confirming that such cermet-HEA hybrid designs effectively balance structural ductility with surface erosion shielding.

Conversely, the electrochemical profile of our composite coating reveals a distinct performance trade-off that matches the broader literature regarding heterogeneous overlays. In a 3.5 wt.% NaCl solution, the 50/50 composite exhibits an active corrosion potential (-552 mV) and higher corrosion current densities (10.53×10^{-6} A/cm²) compared to the pristine, monolithic HEA matrix. This acceleration in degradation is fundamentally driven by the widespread activation of localized micro-galvanic cells forming at the vast interfaces between the distinct phases. Here, the multi-element metallic matrix acts as a sacrificial anode relative to the nobler chromium carbide reinforcements. This behavior aligns with the corrosion trends described by Mehmood et al. [41], who demonstrated that while multi-principal-element binders can provide protective native chromium-rich passivating layers, the high density of heterogeneous phase boundaries and micro-voids inherent to thermal spraying offers a path for aggressive chloride ions to penetrate and continuously destabilize these films.

4. Conclusions

In this study, a novel 50 wt.% CoCrFeMnNi_{0.8}V–50 wt.% Cr₃C₂-Ni₈₀Cr₂₀ composite coating was successfully deposited via the high-velocity oxy-fuel (HVOF) thermal spray process. Its microstructural evolution, tribological behavior, and electrochemical properties were systematically investigated. Based on the experimental findings and discussions, the following primary conclusions can be drawn:

1. **Successful architectural deposition:** The HVOF technique successfully generated a highly dense, well-bonded coating architecture with a thickness of 406 ± 10 μ m and no visible cracking or delamination at the substrate interface. The microstructure is uniquely characterized by a uniform distribution of Cr₃C₂-Ni₈₀Cr₂₀ surrounding partially melted, gas-atomized spherical HEA splats (40–50 μ m in diameter). Rapid cooling rates inherent to the process successfully stabilized a complex multiphase structural coexistence of FCC, BCC, and σ -NiCr phases.
2. **Synergistic sliding wear resistance:** Tribological evaluations demonstrated that the incorporation of 50 wt.% Cr₃C₂-Ni₈₀Cr₂₀ cermet reinforcement significantly enhances the sliding wear resistance compared to the pure, monolithic HEA coating. The wear process is governed by a highly effective synergistic interaction: the ductile FCC matrix of the HEA accommodates localized plastic deformation under cyclic loading, while the harder, exposed chromium carbide particles successfully shield the matrix by enhancing the overall load-bearing capacity. This mechanism effectively limits severe abrasive wear, transitioning the damage profile toward mild third-body abrasion and protective tribo-oxidation.
3. **Micro-galvanic corrosion activation:** In contrast to its superior wear performance, electrochemical testing in a 3.5 wt.% NaCl solution revealed that the composite coating displays a more active corrosion potential (-552 mV) and higher corrosion current densities (10.53×10^{-6} A/cm²) than the pristine HEA matrix. This accelerated degradation is fundamentally driven by the heterogeneous nature of the composite. Widespread micro-galvanic cells form at the interfaces of the distinct phases, wherein the multi-element metallic matrix acts as a sacrificial anode to the nobler chromium carbide reinforcements. Furthermore, the lack of a well-defined passive plateau confirms that aggressive chloride ions continuously destabilize the surface oxide film, promoting localized pitting and sustained anodic dissolution.

4. Engineering trade-offs and sustainability: Despite the trade-off in corrosion rate, the environmental durability of the composite coating remains entirely acceptable for a broad range of demanding surface engineering applications. By significantly mitigating dependencies on critical raw materials, such as cobalt and tungsten (common to conventional industrial WC-Co hard metals), this hybrid design offers a highly competitive and sustainable alternative for structural sectors requiring exceptional mechanical toughness coupled with balanced environmental resilience.
5. Pathways for future optimization: Because the electrochemical performance of thermal spray overlays is tightly dictated by structural heterogeneity, porosity, and phase configuration, future research should target precise microstructural refinement. Implementing post-deposition surface treatments—such as optimized vacuum heat treatments or ultrasonic nanocrystal surface modification (UNSM)—holds substantial promise to homogenize the phase boundaries, seal residual micro-porosities, and enhance baseline corrosion resistance while preserving or augmenting the coating's excellent tribological performance.

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