



EFFECT OF CHROMIUM ON THE TRIBOCORROSION BEHAVIOR IN ACIDIC CHLORIDE MEDIA OF WC-NiCrMo COMPOSITES

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Resumo

Os carbonetos cimentados à base de WC são amplamente utilizados em aplicações industriais severas devido à sua elevada dureza e resistência ao desgaste. No entanto, os sistemas convencionais WC-Co apresentam limitações importantes em ambientes agressivos, particularmente em meios ácidos contendo cloretos, devido à dissolução preferencial do ligante metálico e à elevada suscetibilidade à tribocorrosão. Neste contexto, os sistemas alternativos WC-NiCrMo surgem como candidatos promissores para substituir o cobalto, combinando elevada resistência à corrosão com propriedades mecânicas competitivas.

O presente trabalho teve como objetivo avaliar o efeito do teor de crômio no comportamento eletroquímico e tribocorrosivo de compósitos WC-NiCrMo em meio ácido cloretado, comparando três composições experimentais (Cr-11, Cr-13 e Cr-18) com um material de referência WC-Co. Para tal, foi realizada caracterização microestrutural e química por microscopia eletrônica de varrimento (SEM/EDS), avaliação mecânica através de dureza Vickers e tenacidade à fratura, ensaios eletroquímicos (potencial de circuito aberto, polarização potenciodinâmica e espectroscopia de impedância eletroquímica) e ensaios de tribocorrosão com monitorização simultânea do potencial e do coeficiente de atrito.

Os resultados demonstraram que a substituição do ligante Co por NiCrMo promove uma melhoria muito significativa da resistência à corrosão, reduzindo a densidade de corrente de corrosão em duas a três ordens de grandeza e aumentando substancialmente a estabilidade eletroquímica através da formação de uma camada superficial semi-protetora rica em crômio. Verificou-se ainda que o aumento do teor de crômio promove refinamento microestrutural e aumento da dureza, embora acompanhado por uma redução da tenacidade à fratura. Foi identificado um teor crítico de aproximadamente 13 wt.% de Cr para garantir um regime de baixa dissolução estável; abaixo deste valor observaram-se ciclos de destabilização local e restauro desta condição semi-protetora, enquanto teores superiores conduziram à formação de heterogeneidades microestruturais e segregação local de crômio.

Nos ensaios de tribocorrosão, os materiais WC-NiCrMo apresentaram desempenho global superior ao WC-Co, com menor tribo-oxidação, menor degradação do ligante e maior preservação da integridade superficial sob ação simultânea de desgaste mecânico e corrosão. Os resultados indicam que a resistência à tribocorrosão não depende exclusivamente do teor absoluto de crômio, mas também da homogeneidade da sua distribuição na matriz metálica. Globalmente, os resultados confirmam o elevado potencial dos compósitos WC-NiCrMo como alternativa ao WC-Co para aplicações em ambientes tribocorrosivos severos.

Palavras-chave: Carbonetos cimentados; WC-NiCrMo; Tribocorrosão; Caracterização eletroquímica; Desgaste por deslizamento.

Abstract

WC-based cemented carbides are widely used in severe industrial applications due to their high hardness and wear resistance. However, conventional WC-Co systems present significant limitations in aggressive environments, particularly in acidic media containing chlorides, due to the preferential dissolution of the metallic binder and their high susceptibility to tribocorrosion. In this context, alternative WC-NiCrMo systems emerge as promising candidates to replace cobalt, combining high corrosion resistance with competitive mechanical properties.

The present work aimed to evaluate the effect of chromium content on the electrochemical and tribocorrosion behavior of WC-NiCrMo composites in an acidic chloride medium, comparing three experimental compositions (Cr-11, Cr-13, and Cr-18) with a WC-Co reference material. To this end, microstructural and chemical characterization was performed using scanning electron microscopy (SEM/EDS), alongside mechanical evaluation through Vickers hardness and fracture toughness, electrochemical tests (open-circuit potential, potentiodynamic polarization, and electrochemical impedance spectroscopy), and tribocorrosion tests with simultaneous monitoring of the potential and friction coefficient.

The results demonstrated that replacing the Co binder with NiCrMo promotes a highly significant improvement in corrosion resistance, reducing the corrosion current density by two to three orders of magnitude and substantially increasing electrochemical stability through the formation of a chromium-rich semi-protective surface layer. It was also found that increasing the chromium content promotes microstructural refinement and an increase in hardness, although this is accompanied by a reduction in fracture toughness. A critical chromium content of approximately 13 wt.% was identified to ensure a stable low-dissolution regime; below this value, cycles of local destabilization and restoration of this semi-protective condition were observed, while higher contents led to the formation of microstructural heterogeneities and local chromium segregation.

In the tribocorrosion tests, the WC-NiCrMo materials exhibited a superior overall performance compared to WC-Co, showing lower tribo-oxidation, reduced binder degradation, and greater preservation of surface integrity under the simultaneous action of mechanical wear and corrosion. The results indicate that tribocorrosion resistance does not depend exclusively on the absolute chromium content, but also on the homogeneity of its distribution within the metallic matrix.

Overall, the results confirm the high potential of WC-NiCrMo composites as an alternative to WC-Co for applications operating in severe tribocorrosive environments.

Keywords: Cemented carbides; WC-NiCrMo; Tribocorrosion; Electrochemical characterization; Sliding wear.

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List of abbreviations

BSE	Backscattered Electron
CE	Counter Electrode
CPE	Constant Phase Element
EDS	Energy-Dispersive X-ray Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
HV	Vickers Hardness
K_{Ic}	Fracture Toughness
OCP	Open Circuit Potential
RE	Reference Electrode
SCE	Saturated Calomel Electrode
SEM	Scanning Electron Microscopy
WE	Working Electrode

1. Introduction

Cemented carbides are high-hardness materials widely recognized for their excellent combination of mechanical properties, namely high hardness, wear resistance, and impact toughness [1-3]. These composites are typically composed of carbide grains (with tungsten carbide, WC, being the most common and hardest) held together in a matrix of a more ductile metallic binder [1,4]. Historically, cobalt (Co) has been the standard binder for WC, due to its excellent wettability on WC grains and its low affinity for carbon, resulting in dense composites with superior mechanical properties [2,3].

The unique properties of WC-Co have made it the standard in various industrial applications, such as cutting and rock drilling tools, extrusion dies, and components subjected to high wear, including valves for pumping systems, mechanical seals, and nozzles [1-3]. These applications are found in critical industries, such as mining, petrochemical, and other high-demand industrial sectors [2,5]. In these environments, the performance of cemented carbides does not only depend on their intrinsic mechanical properties but is strongly influenced by their resistance to corrosion caused by the aggressive media to which they are exposed [1].

Despite its exceptional mechanical properties, the WC-Co composite exhibits poor corrosion resistance when exposed to specific environments, which can significantly decrease their service life [1]. In service environments, particularly those involving acidic media (common in oil, gas and petrochemical industries), the Co binder is particularly vulnerable, which leads to premature deterioration of tools and components [3]. This limitation is compounded by environmental and economic concerns: cobalt is a toxic element associated with health problems, and faces uncertainties in global supply, raising its price (Table 1) [2-5].

Table 1 - Current market prices of cobalt compared to alternative industrial metals. Values are expressed in US Dollars per metric tonne (USD/t) based on data sourced from Trading Economics on 2 July 2026 [6].

Metal	Price (USD/t) - 2/07/2026
Cobalt (Co)	56290
Nickel (Ni)	16224
Copper (Cu)	13445
Titanium (Ti)	6414
Aluminum (Al)	3059.5
HRC steel	1171.1
Chromium (Cr)	9149.26

These factors have driven a significant effort in the partial or total substitution of Co in the development of new composites. Alloys based on nickel (Ni) have emerged as promising alternatives, demonstrating superior corrosion resistance to conventional WC-Co grades, especially in neutral and acidic media [1,3,4]. Nickel, besides being more economical than cobalt, exhibits lower affinity for carbon and better performance against strong oxidizing media [3]. The development of the WC-NiCrMo system aims to capitalize on the characteristics of corrosion-resistant superalloys and stainless steels, where Cr promotes the formation of a passive protective film, and Mo increases the resistance to pitting corrosion in chloride media [3,5]. Recent studies demonstrate that WC-NiCrMo composites may outperform WC-Co in terms of corrosion resistance while retaining competitive mechanical behavior, making them strong candidates for severe-service applications [1-3,5].

In many of these industrial environments, such as pumping and flow control systems, the material is subject not only to chemically aggressive media but also to constant mechanical stresses (friction or impact) [1]. In this context, wear and corrosion act simultaneously, leading to a more complex and severe degradation phenomenon: tribocorrosion. Tribocorrosion is defined as the deterioration or transformation of the material resulting from the simultaneous action of wear and corrosion [7,8]. Knowledge of the tribological behavior in the absence of corrosion and the electrochemical behavior in the absence of wear is not sufficient to predict their combined performance, as there is a synergy between the two phenomena: wear modifies the material's sensitivity to corrosion, and vice versa [7]. Due to the inherent complexity and the high number of variables involved, the intricate interaction between these chemical and mechanical factors remains a continuous challenge in research, and there is a need to deepen the investigation into the underlying mechanisms [7,8].

The study of tribocorrosion in acidic environments is of extreme relevance to chemical processing, pumping systems, and other critical industrial applications, as this combination of factors leads to the premature failure of components [1,3,7]. Although the WC-NiCrMo system is promising as a substitute for WC-Co, its tribocorrosion behavior is still largely unknown, and the impact of elemental contents, namely Cr, on its performance is sparsely reported in the literature [3].

The present Master's thesis is situated within this context, focusing on the effect of Cr content on the tribocorrosion susceptibility in acidic chloride media of WC-NiCrMo composites. Furthermore, this research directly aligns with the United Nations Sustainable Development Goals (SDGs), specifically contributing to SDG 3 (Good Health and Well-being), SDG 9 (Industry, Innovation, and Infrastructure), and SDG 12 (Responsible Consumption and Production). By developing safer, cobalt-free WC-NiCrMo alternatives, this study addresses occupational health hazards in metallurgical processing while reducing reliance on a critical raw material. Concurrently, enhancing tribocorrosion resistance significantly extends the operational lifespan of industrial components in severe environments, mitigating premature equipment failures, reducing raw material and energy consumption, and supporting more resilient industrial infrastructure.

2. Literature Review

2.1. Cemented Carbides

Cemented carbides are a mature class of powder metallurgical, liquid-phase sintered composite materials consisting of at least one hard and wear-resistant phase – in the majority of cases being tungsten carbide (WC) and a ductile metallic phase from the iron group of metals, mainly cobalt (Co) and its alloys [9]. Currently representing a cornerstone of the global tool manufacturing industry [9], the production of cemented carbides has grown rapidly in the past 30 years, increasing from 30,000 tons in 2000 to almost 60,000 tons in 2008, particularly due to the entry of China onto the market [10]. Compared to other hard materials, cemented carbides make up 50% of the total world market, while high-speed steels account for 45% and ceramics about 4% [10].

The outstanding performance of these materials derives from the synergy between their constituents. The WC phase (hexagonal close-packed) possesses an extremely narrow homogeneity range but ensures high hardness, thermal conductivity, and excellent wettability by metallic liquids [10]. Cobalt, which also exhibits a hexagonal close-packed structure at room temperature, acts as the ideal binder. It possesses a temperature-dependent solubility for WC (tungsten and carbon) that aids liquid-phase sintering and results in a fully dense product with exceptional strength and ductility [9].

The resulting microstructure consists of faceted WC grains embedded in a Co-rich matrix [11]. In compositions with low to medium binder contents, this structure forms two interconnected skeletons of the carbide and metallic phases [9]. The mechanical properties of these cemented carbides can be tailored over a wide range by adjusting the two key variables of this interplay: the WC grain size and the Co binder content (Figure 1) [9,10]. According to ISO standards (ISO 4499-2:2010), these materials are classified based on the WC mean grain size, ranging from nano ($<0.2\ \mu\text{m}$) to extra coarse ($>6.0\ \mu\text{m}$) [12].

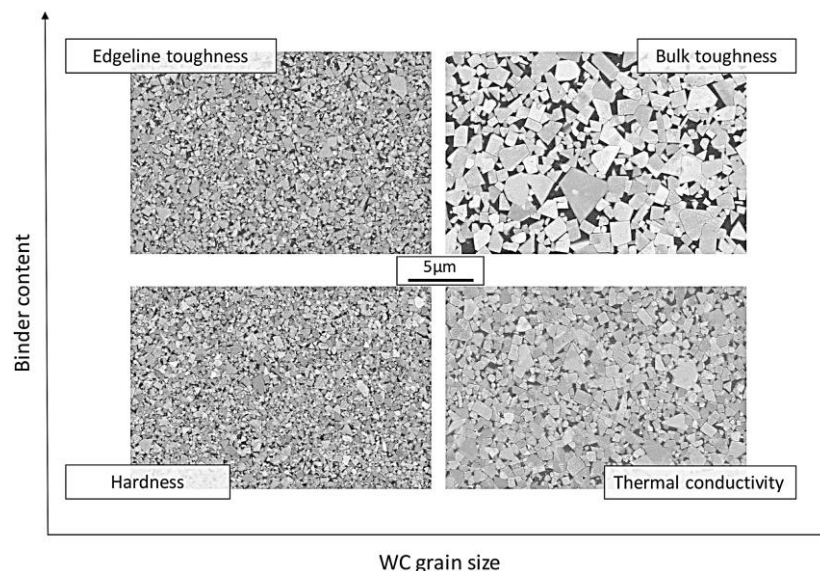


Figure 1- Influence of WC grain size and binder content on the microstructure and key properties of cemented carbides [10].

As illustrated in Figure 1, the performance of these materials is governed by a fundamental inverse relationship between hardness and toughness. Maximum hardness—which is critical for mechanical wear resistance—is achieved in microstructures characterized by a fine WC grain size and a low binder volume fraction. Conversely, increasing the Co binder content enhances the overall toughness of the material, providing the necessary resilience to prevent brittle fracture and micro-chipping under load. Ultimately, the precise microstructural design must carefully balance the WC grain size and binder content to achieve an optimal compromise between wear resistance and structural integrity for the intended application [10].

2.1.1. Applications

Owing to this highly tunable microstructural flexibility, hardmetals remain the material of choice for demanding applications that require a strict balance of wear resistance, toughness, and strength [9]. Rather than applying a universal formulation, manufacturers tailor these phases to specific industrial working conditions (Figure 2).

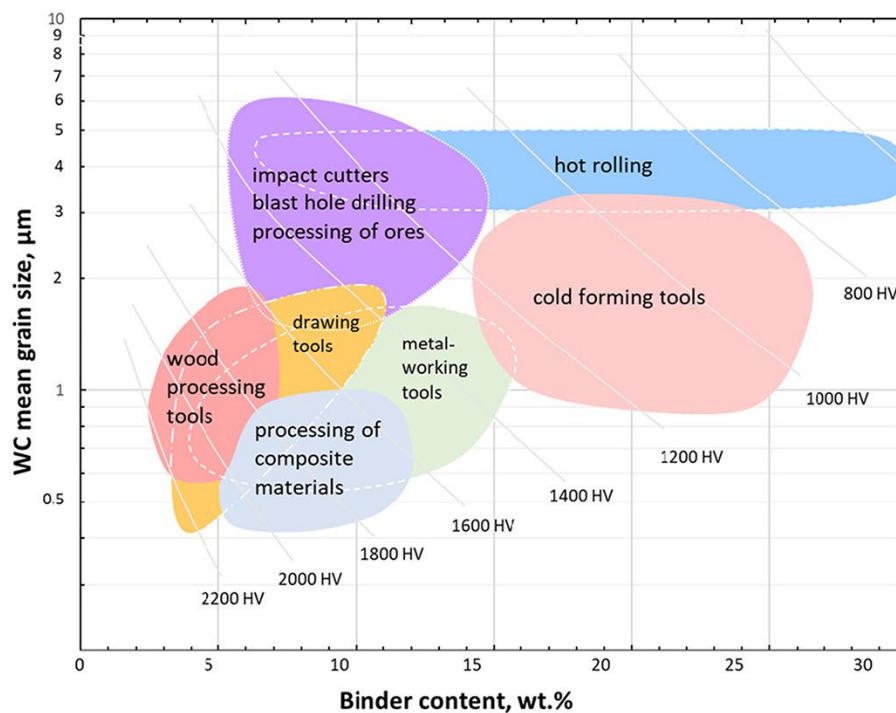


Figure 2 - Combinations of WC grain size and cobalt in cemented carbides, showing a wide range of applications. The lines indicate values of isohardness [12].

As observed in Figure 2, distinct regions are defined for specific uses. Grades for metal cutting typically utilize medium to fine grain sizes with moderate cobalt contents. Applications such as woodworking often require finer grains, while mining tools (such as drill bits) and wear parts might employ coarser grains or higher cobalt contents to withstand high impact loads [10,12]. Furthermore, to improve performance in metal cutting, cubic transition metal carbides (TiC, TaC, NbC) are often added to improve hot hardness and crater wear resistance [9,10].

2.2. Corrosion Resistance of WC-Co

While mechanically robust, the chemical stability of WC-Co in corrosive media is a major industrial limitation. Degradation is primarily driven by a strong galvanic couple: the noble WC grains act as the cathode, while the active cobalt binder acts as the anode, suffering continuous dissolution through oxidation [2,13]. In chloride solutions, WC-Co displays low open-circuit potentials (around -330 mV vs. SCE), high corrosion current densities, and extremely low polarization resistance [2,14]. During polarization, the composite typically exhibits a pseudo-passive plateau. However, when the potential elevates above 800 mV vs. SCE, current density surges again due to the oxidation of the WC grains [14]. As the active cobalt leaches away, it recedes deeply below the surface, leaving the WC skeleton structurally unsupported. Morphological analyses demonstrate that the resulting corrosion layer is highly porous, covered in corrosion products, and riddled with microcracks that allow the electrolyte to maintain contact with the fresh metal underneath [2,14]. The severe visual and microscopic consequences of this specific active degradation mechanism are clearly illustrated by Rocha et al. [2] (Figure 3). After two weeks of prolonged immersion in 0.5 M NaCl, the WC-Co surface becomes heavily coated with loose corrosion products. Once removed, it reveals a completely depleted binder matrix and a structurally unsupported, highly vulnerable WC skeleton.

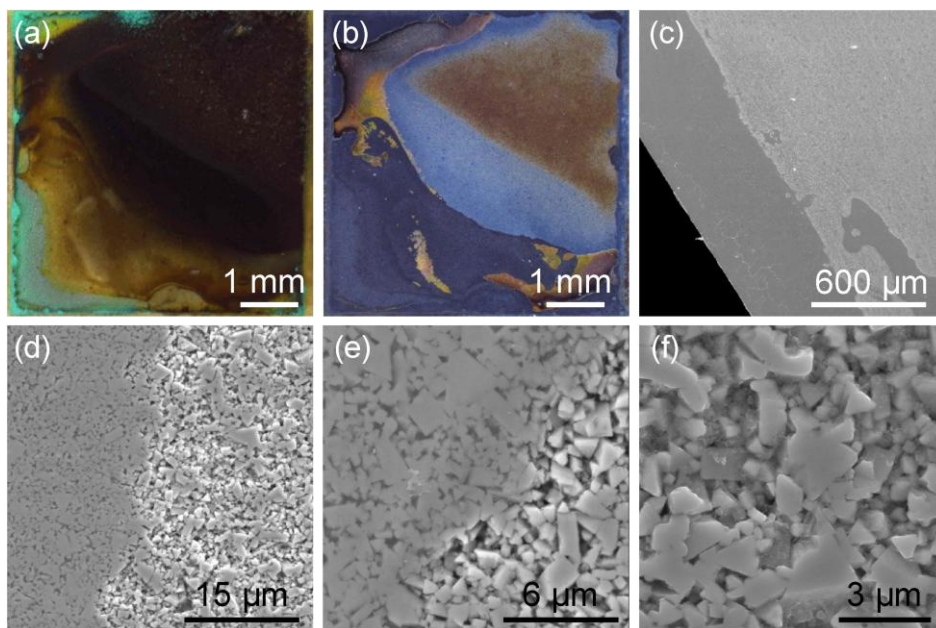


Figure 3 - Optical and SEM images of WC-Co composite after 2 weeks of immersion in 0.5 M NaCl [2].

The severity, kinetics, and specific mechanisms of WC-Co corrosion are radically dependent on environmental chemistry, particularly pH and electrolyte concentration. Acidic environments are notably aggressive. In purely acidic solutions, the global corrosion potential of the alloy is naturally more noble than that of pure cobalt due to the highly cathodic nature of the WC phase. However, rather than offering protection, this elevated mixed potential increases the anodic driving force on the cobalt matrix, severely accelerating its preferential galvanic dissolution [15]. This inherent galvanic problem was clearly illustrated by Sutthiruangwong et al. [16], who evaluated the constituent phases

individually; as demonstrated by their potentiodynamic polarization curves, pure Co exhibits massive active dissolution at low potentials, whereas pure WC remains completely passive up to high anodic potentials (Figure 4).

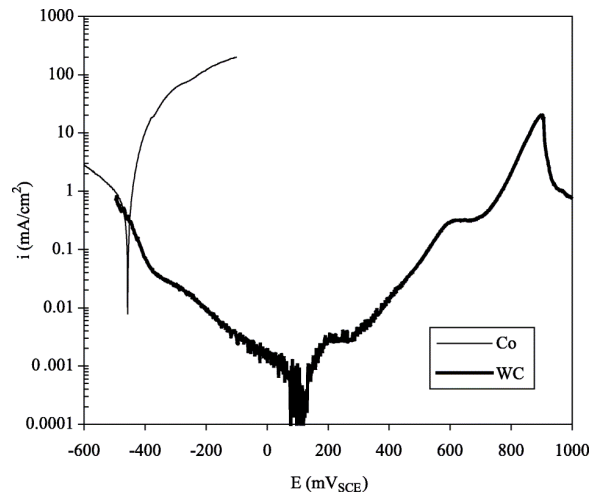


Figure 4 - Potentiodynamic polarization curves of pure Co and WC in an aerated 1M H_2SO_4 solution [16].

Crucially, Sutthiruangwong et al. [16] refuted the theory that the pseudo-passive plateau in WC-Co is caused by a solid protective film. Instead, they proved it is a diffusion-controlled mass transport phenomenon. As the acid rapidly leaches the cobalt, it leaves behind a thick, highly porous skeleton of unbonded WC grains (Figure 5). Newly dissolved cobalt ions (Co^{2+}) must then travel through this tortuous network to reach the bulk solution, physically limiting the mass transport and slowing the corrosion rate. Eventually, at extreme electrical potentials (above 900 mV), the WC skeleton itself oxidizes into an insulating tungsten trioxide (WO_3) barrier that halts the process. To mitigate this extreme susceptibility, partial substitution of Co with small amounts of Ni (e.g., 2 wt%) has been shown to optimize fracture toughness and reduce active dissolution in acidic media without sacrificing overall hardness [17].

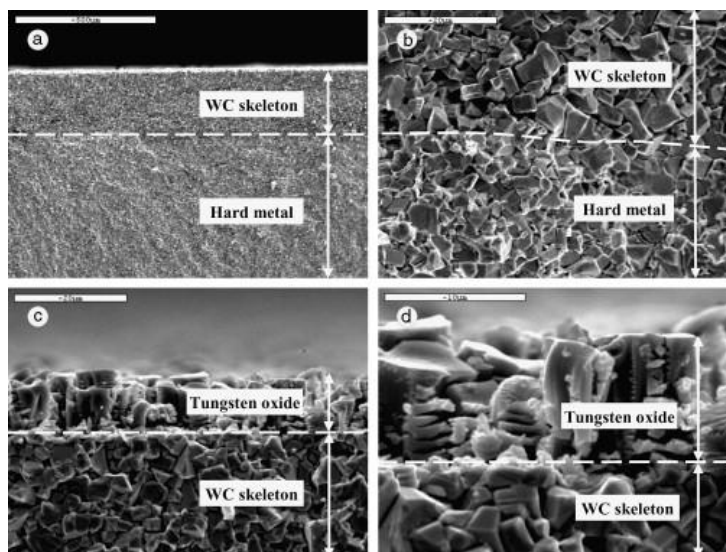


Figure 5 - SEM cross-sectional views of a WC-Co composite after polarization in 1 M H_2SO_4 [16].

Transitioning to neutral and chloride-rich environments, baseline corrosion rates are generally lower than in strong acids. However, raising the salinity from 3.5% to 5% NaCl dramatically accelerates surface degradation and promotes aggressive pitting, as evidenced by the higher anodic currents in potentiodynamic testing (Figure 9) [13]. In these highly saline media, intense galvanic dissolution eventually causes massive grain detachment, forming isolated "islets" of the remaining WC skeleton.

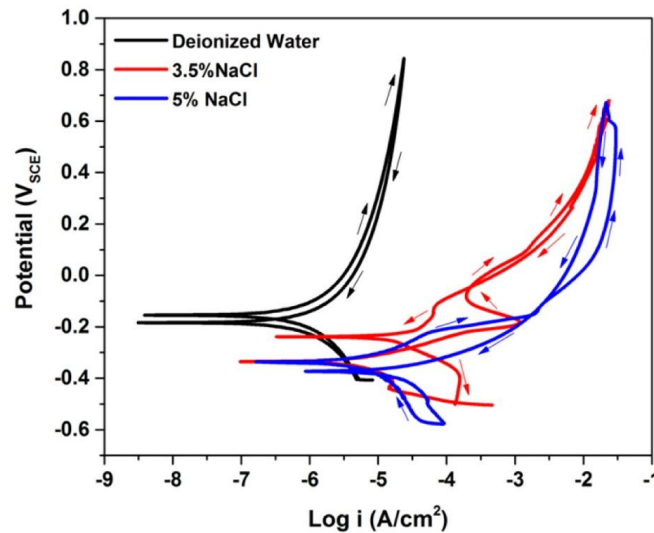


Figure 6 - Potentiodynamic polarization curves of WC-Co in deionized water, 3.5% NaCl solutions [13].

Conversely, in highly alkaline environments (such as 1 M NaOH), the WC-Co composite suffers a staged synergistic corrosion process. Initially, the galvanic couple leads to the active dissolution of the cobalt binder. As the cobalt is depleted, the WC abruptly loses its cathodic protection. The exposed sharp edges of the WC crystals promote a localized concentration of hydroxide ions that directly attacks the tungsten carbide itself. This simultaneous dual-phase degradation causes the rapid flaking of ceramic particles and a staggering 71% drop in transverse rupture strength [17]. This stark contrast in structural degradation is visually confirmed in Figure 7, which highlights the deep, porous WC skeleton layer formed in the cobalt-bonded composite compared to the minimal surface impact on the binderless material.

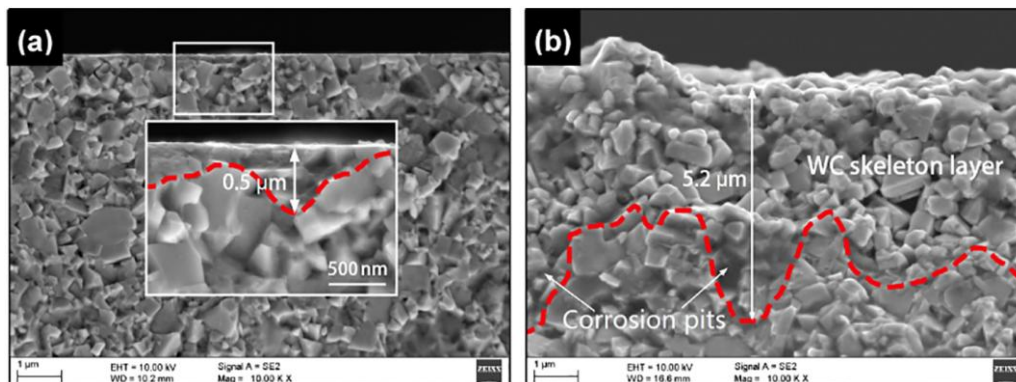


Figure 7 - FESEM images of fractured surfaces of specimens continuously immersed in 1 M NaOH for 28 days: (a) binderless WC and (b) WC-10Co [18].

2.3. Alternative Binders for WC Hardmetals

Despite its dominance, WC-Co faces two critical limitations. First, cobalt is highly toxic, subject to strict occupational exposure limits, and classified as a critical raw material with supply chain uncertainties [19]. Second, the Co binder is highly susceptible to preferential corrosion in aggressive media, leading to pitting that acts as stress concentration points and severely compromises the tool's fatigue resistance and lifespan [1,2]. These health, economic, and performance challenges drive the transition towards safer and more chemically stable alternative binders, primarily Ni-based alloys [1,10]. While simple WC-Ni composites suffer a drop in mechanical strength, strategically alloying the nickel matrix with chromium and molybdenum (e.g., WC-NiCrMo) successfully recovers the required industrial mechanical profile (Figure 8) while providing vastly superior corrosion resistance [1,4,5].

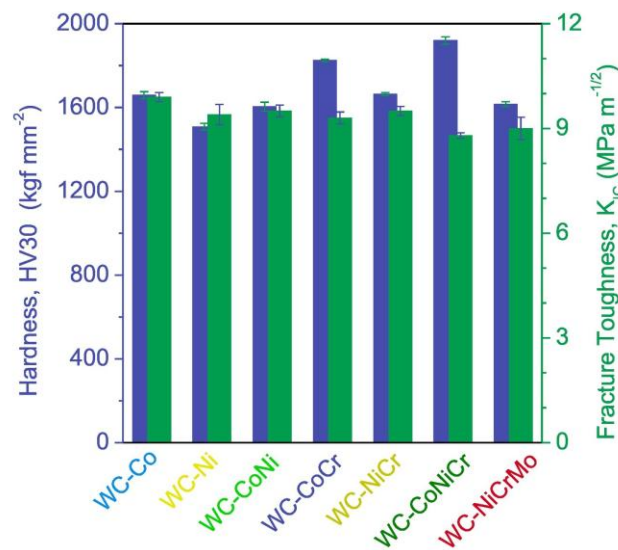


Figure 8 - Comparison of hardness (HV30) and fracture toughness K_{IC} , for WC composites with different binder systems [1].

Table 2 summarizes the specific structural, mechanical, and anti-corrosive impacts of the most thoroughly studied alternative binder systems in the current literature.

Table 2 - Effect on corrosion resistance and mechanical properties of different binder systems.

Binder System	Effect on corrosion resistance	Effect on mechanical properties
WC-Ni	Significantly higher resistance than WC-Co (up to 100x). Prevents severe matrix degradation in chloride/sulfate media, but minor localized pitting may occur after long-term exposure [1,20].	Lowest hardness and mechanical strength compared to Co. Promotes coarser WC microstructures due to higher W solubility and moderate strain hardening [4,10].

WC-NiCr	Cr improves passivation, eliminates pitting, and lowers corrosion rate by an order of magnitude vs. WC-Ni[1]. <i>Caveat:</i> Requires low-carbon formulations to prevent Cr depletion and passive layer breakdown [4].	Higher hardness than pure WC-Ni; Cr acts as an excellent WC grain growth inhibitor [4].
WC-FeCoNi	Highly susceptible to corrosion, similar to pure Co. Exhibits active dissolution, low polarization resistance, and localized pitting [2].	Eliminates porosity. Hardness similar to WC-Co; offers high abrasive wear resistance (if Fe-rich) or high toughness/fatigue resistance (if Co-rich) [2,21].
WC-CoNi	Marginal improvement over WC-Co. Displays high corrosion rates and active degradation (greenish Ni-ion release) [1].	Acceptable hardness and toughness profile, though slightly softer than pure Co [1].
WC-CoNiCr	Superior to simpler Co-alloys in neutral media (no visible attack after one month). However, completely corrodes under prolonged harsh seawater tests [4].	Exceptionally high elastic modulus (up to 560 GPa); allows formulations with lower binder volume fractions [1].
WC-CoCr	Virtually no corrosion improvement over pure Co. Weak passivation; suffers rapid active dissolution in acids and catastrophic localized breakdown in seawater [1,4].	Retains very high mechanical strength, achieving the highest composite and metallic binder microhardness among standard alloys [4].
WC-NiCrCoMo	True passive behavior with excellent stability. Highly positive corrosion potentials (+400 mV vs. WC-Co) and massive polarization resistance ($\sim 10^6 \Omega \cdot \text{cm}^2$) [2].	Hardness equal to or slightly higher than traditional WC-Co, while maintaining acceptable fracture toughness [2].
WC-NiCrMo	The most corrosion-resistant binder. Exhibits true passivation, extremely low corrosion rates, and extreme polarization resistance. Forms dense double passivation layers that withstand severe acidic/marine environments [1,2,4].	Hardest Ni-based alloy. Mo and Cr synergistically inhibit grain growth, yielding a highly refined microstructure with solid solution strengthening [3,4].

2.4. Corrosion Resistance of Alternative Binders

To overcome cobalt's chemical limitations, industry has shifted towards complex face-centered cubic (fcc) solid solutions, culminating in the highly successful WC-NiCrMo

system. Electrochemical evaluations in aggressive 0.5 M NaCl environments confirm its superiority [1]. As observed in Figure 9, Co-based alloys stabilize at highly negative potentials, whereas the WC-NiCrMo and WC-NiCr composites experience a rapid anodic shift, indicating the swift formation of a protective passive film on the binder's surface.

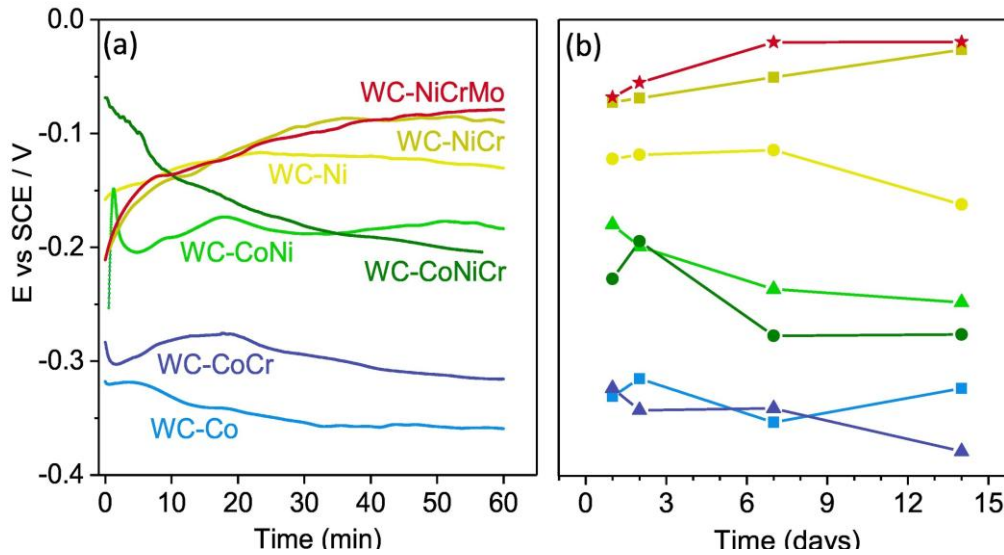


Figure 9 - Open-circuit potential (E vs SCE) evolution over time for various WC composites immersed in 0.5 M NaCl solution: (a) initial 60 minutes; (b) 14-day exposure [1].

Potentiodynamic polarization curves (Figure 10) corroborate this behavior. While cobalt-rich composites exhibit unabated active dissolution, the NiCr and NiCrMo systems display a highly stable, low-current pseudo-passive plateau over a wide potential range.

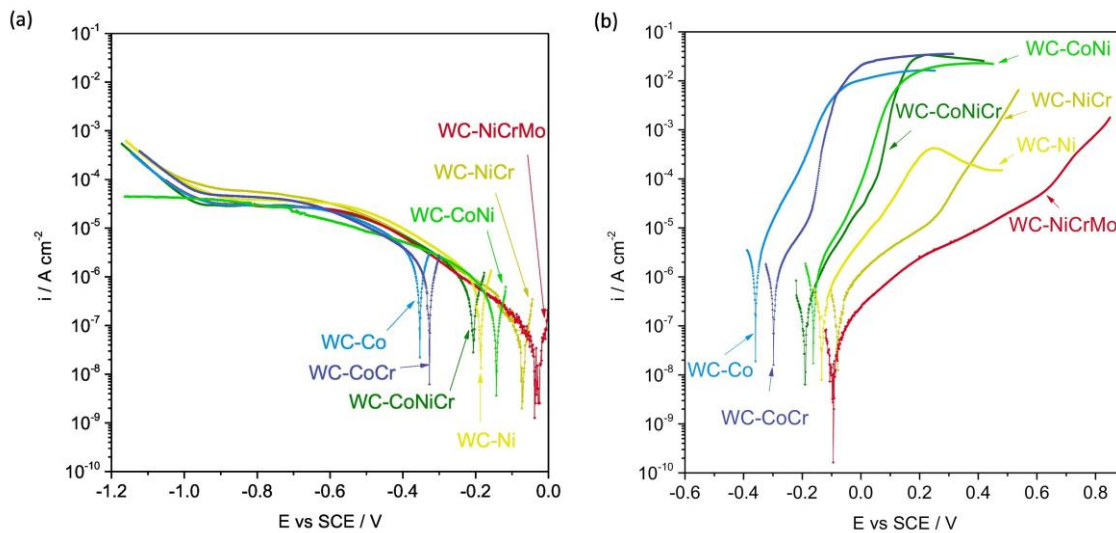


Figure 10 - Potentiodynamic polarization curves for WC binder systems (a) Cathodic branch, (b) Anodic branch in 0.5 M NaCl [1].

These distinct behaviors directly impact the calculated corrosion current densities (i_{corr}) (Figure 11). The traditional WC-Co benchmark yields the highest dissolution rates, whereas the WC-NiCrMo system exhibits a reduction in current density of about two orders of magnitude. Extended Electrochemical Impedance Spectroscopy (EIS) measurements (Figure 12) further attest to this stability, with the highly alloyed Ni-based matrices

maintaining massive impedance values (in the order of 10^5 to $10^6 \Omega \cdot \text{cm}^2$) over several weeks of continuous immersion.

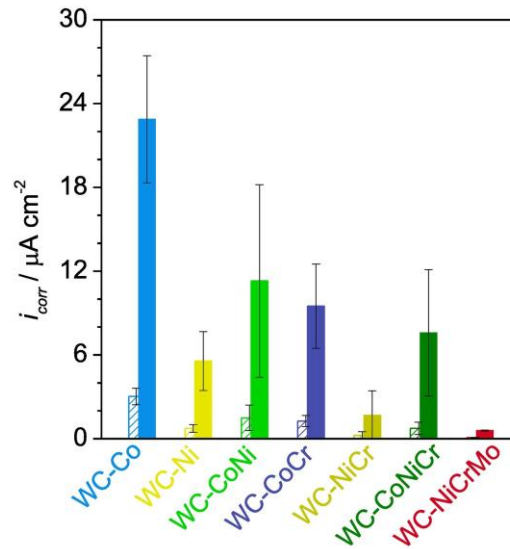


Figure 11 - Calculated corrosion current densities (i_{corr}) for the evaluated WC composites [1].

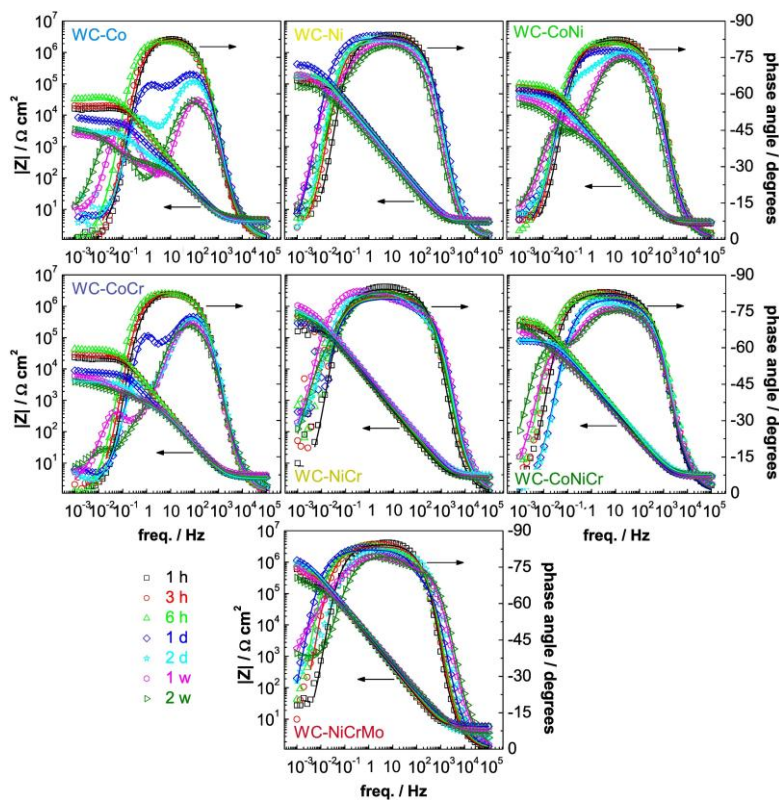


Figure 12 - Electrochemical Impedance Spectroscopy (EIS) Bode plots for the studied WC composites over a 14-day immersion period in 0.5 M NaCl [1].

Visual and microscopic examinations by Rocha et al. [2] confirm this exceptional chemical stability. As depicted in Figure 13, after two weeks of continuous immersion in 0.5 M NaCl,

the WC-NiCrMo and WC-NiCrCoMo specimens retained their pristine surface integrity without any signs of localized corrosion or binder leaching.

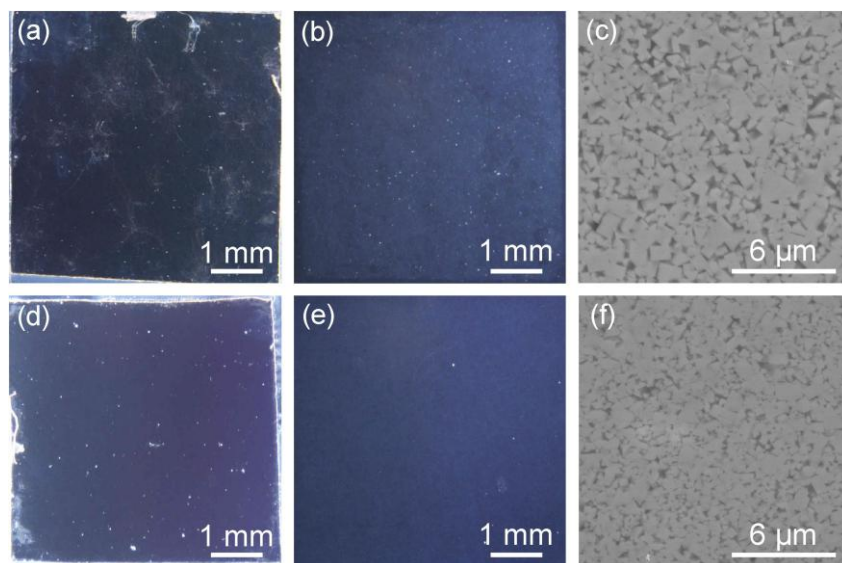


Figure 13 - Optical and SEM images of the WC-NiCrCoMo (a-c) and WC-NiCrMo (d-f) composites after 2 weeks of immersion in 0.5 M NaCl [2].

The underlying mechanism defining this superior protection relies heavily on the intricate elemental roles within the binder, especially in combatting chloride attacks. Chlorides are notoriously destructive because they do not directly alter the dissolution reaction but strongly interfere with the formation of protective oxide films. In localized defect areas, dissolving metal attracts chloride ions and increases local acidity via cation hydrolysis; this completely inhibits the oxide's ability to repassivate itself, initiating severe pitting corrosion [22]. To combat this, nickel serves as the foundational matrix because it possesses a higher standard electrode potential than cobalt, offering better intrinsic thermodynamic stability and a natural tendency to form a superficial nickel oxide film. However, in severe environments containing chlorides or strong acids, pure nickel is insufficient to sustain long-term passivation and remains highly susceptible to pitting [10,20].

Therefore, chromium is introduced as it is essential for forming a robust primary passive film rich in chromium oxide. This physical and dielectric barrier increases the charge transfer resistance at the metal-electrolyte interface by up to two orders of magnitude compared to pure nickel or cobalt matrices, effectively preventing ionic diffusion and protecting the matrix against localized pitting in chloride- and sulfate-rich environments [20]. However, incorporating chromium must be carefully balanced with the material's mechanical properties. As detailed by Santos et al. [3], in severe acidic media (0.5 M NaCl + HCl at pH=2), the protective efficacy of the material depends strictly on this threshold, which is clearly demonstrated through electrochemical evaluations. Open-circuit potential (OCP) measurements reveal that composites with higher chromium contents (specifically 13 wt% and 18 wt% in the binder) exhibit a rapid anodic shift over time, indicating superior surface nobility and a strong tendency toward passivation (Figure 14).

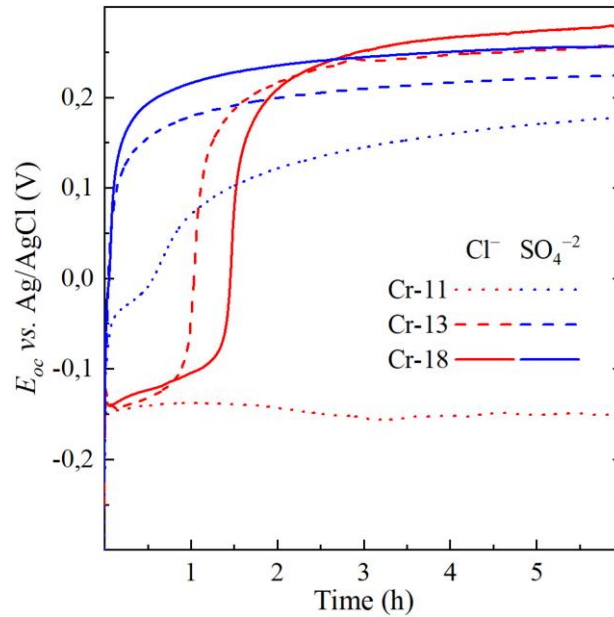


Figure 14 - Open-circuit potential evolution over time for WC-Ni-Cr-Mo composites with varying Cr contents in acidic chloride and sulfate media [3].

Furthermore, potentiodynamic polarization (PD) curves show that reaching these elevated chromium levels reduces the active corrosion current by almost an entire order of magnitude. In stark contrast, a specimen with only 11 wt% chromium fails to passivate effectively under these aggressive conditions (Figure 15).

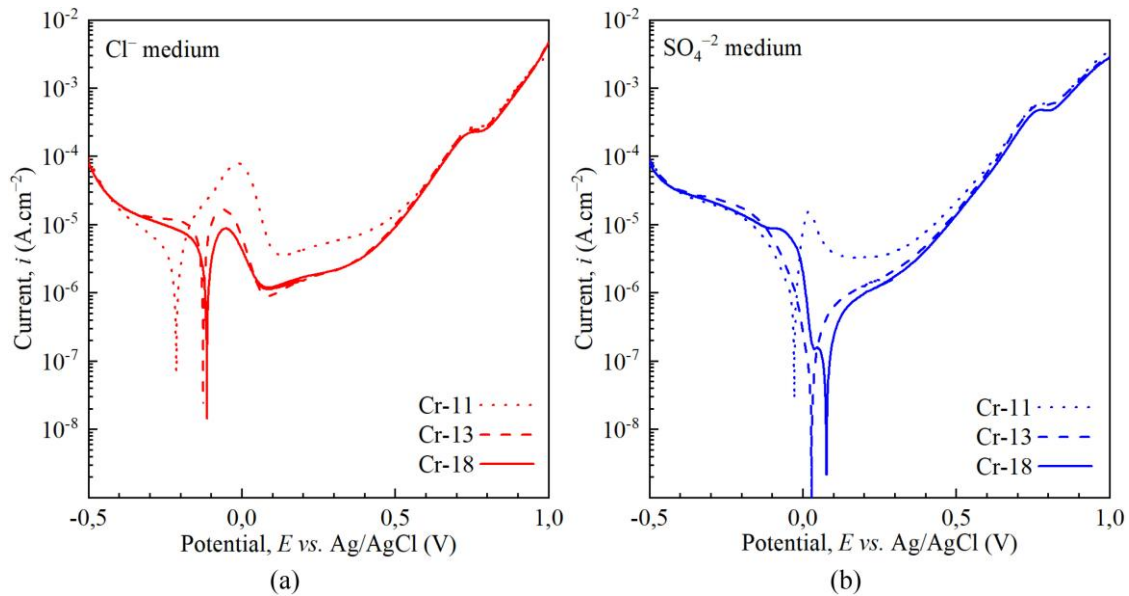


Figure 15 - Potentiodynamic polarization curves demonstrating the critical Cr threshold required to suppress active dissolution in acidic chloride (a) and sulfate media [3].

Finally, Electrochemical Impedance Spectroscopy (EIS) confirms that below this approximate 11 wt% threshold, the resulting passive film is porous and discontinuous, offering virtually no protection. Exceeding this limit exponentially increases the

polarization resistance, highlighting the strict necessity of a sufficient chromium content to ensure robust surface protection (Figure 16) [3,5].

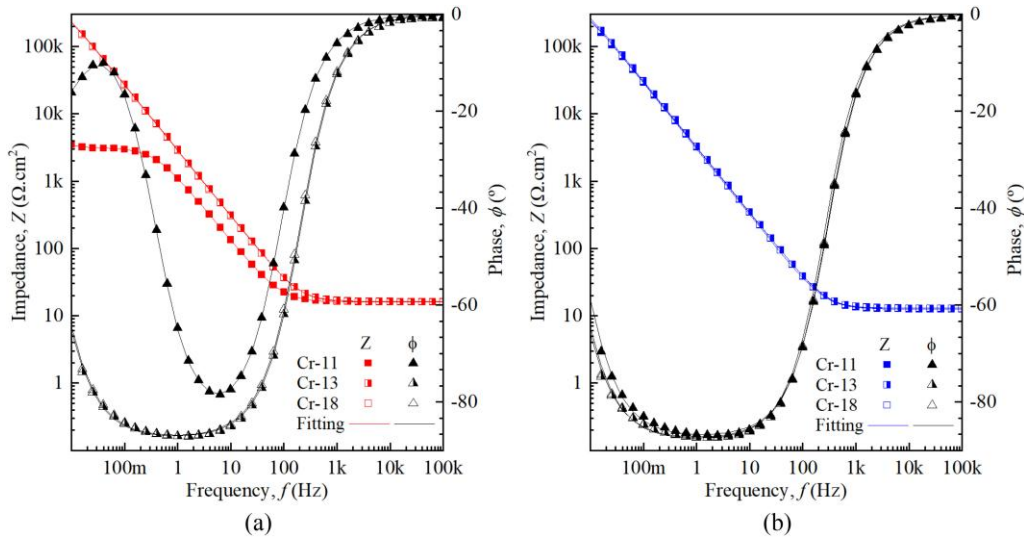


Figure 16 - EIS Bode plots in (a) chloride medium and (b) sulfate medium, showing higher resistance with increased Cr content [3]-

Molybdenum works alongside chromium to significantly enhance the stability of the protective passive film. It strengthens the film's structure to prevent breakdown and helps rapidly repair any localized damage that might occur [23]. However, the molybdenum content must be carefully optimized. A precise addition, such as 0.6 wt%, provides the best balance for rapid protection, whereas incorrect amounts can actually delay the passivation process and increase corrosion rates [5].

The corrosion behavior of the WC-Ni-Cr-Mo composite is dynamic and highly dependent on environmental pH and electrical potential (Figure 17). In highly acidic media (pH 1), the tungsten carbide (WC) matrix is protected by a stable WO_3 film, whereas the metallic binder undergoes preferential dissolution, leaving cavities within the ceramic skeleton. In neutral to weakly basic environments (pH 4 to 10), the binder successfully passivates, and both phases are protected at low potentials; however, above 0.3 V, the carbide's passive layer breaks down, leading to its severe dissolution while the binder remains intact. This behavior completely inverts in highly alkaline media (pH 13), where the nickel-based binder perfectly passivates while the WC matrix undergoes aggressive dissolution, resulting in a spongy pure-nickel skeleton. Furthermore, molybdenum dissolves across all tested pH conditions—alongside the binder in acidic media and the ceramic matrix in basic media—due to its partial diffusion into the carbide phase during sintering [24].

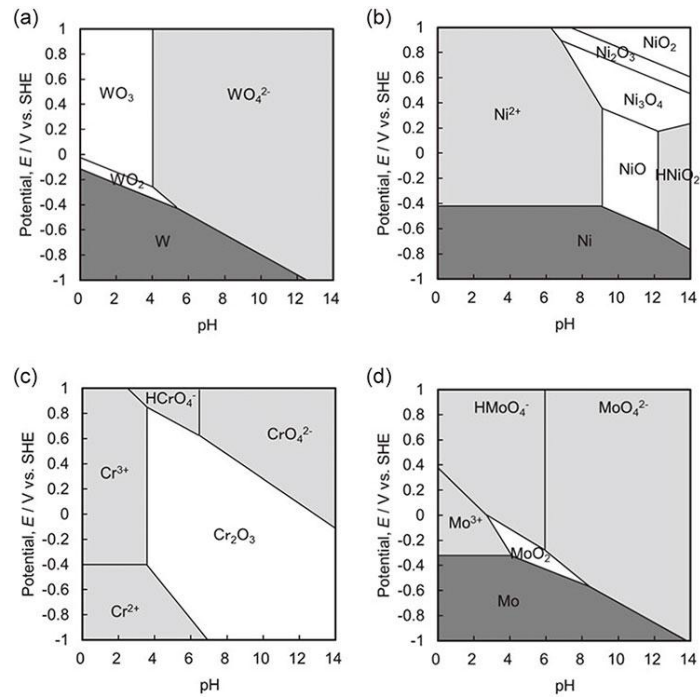


Figure 17 - Pourbaix diagrams in sodium chloride solution demonstrating the thermodynamic stability of W, Ni, Cr and Mo phases as a function of pH and potential [24].

2.5. Tribocorrosion

Tribocorrosion is the degradation of material surfaces resulting from the combined and simultaneous action of corrosion (chemical and electrochemical processes) and mechanical wear (friction) between parts in contact with relative motion [25]. (Figure 18). The central concept is the synergistic effect: knowing a material's isolated wear and corrosion behavior is insufficient to predict its performance when both act simultaneously. Corrosion accelerates mechanical wear, and mechanical wear accelerates corrosion [25,26].

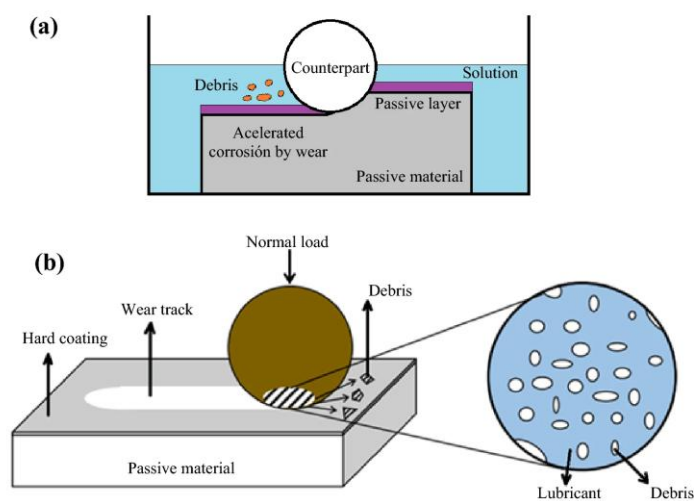


Figure 18 - Tribocorrosion phenomena. (a) Schematic representation for the tribopair, and (b) Different parameters and the products that affect the behavior [27].

This phenomenon critically impacts various engineering fields, particularly in heavy industrial applications such as oil and gas pumps [25,27]. Economically, the cost of material degradation is severe: wear alone is responsible for approximately 30% of all mechanical system malfunctions, consuming between 6% and 10% of the Gross Domestic Product (GDP) in industrialized countries. Because the synergistic effect of tribocorrosion exponentially aggravates this damage, it is estimated to be responsible for up to 70% of these massive GDP losses, highlighting the critical need for highly resistant components [25].

2.5.1. Degradation Mechanisms

The degradation mechanisms in a tribocorrosion system are highly dependent on the intrinsic physicochemical properties of the materials in contact, their surface reactivity, and the nature of the surrounding electrolyte. Consequently, different classes of materials respond distinctly to the simultaneous action of mechanical wear and electrochemical corrosion. In passivating metals, the base mechanism involves depassivation and repassivation [7,25]. Continuous friction mechanically removes the protective passive film (depassivation), exposing bare metal to the electrolyte and triggering localized corrosion. The worn area becomes the anode, while the surrounding untouched passive area acts as the cathode, creating a galvanic cell that lowers the corrosion potential [8,25,26] (Figure 19).

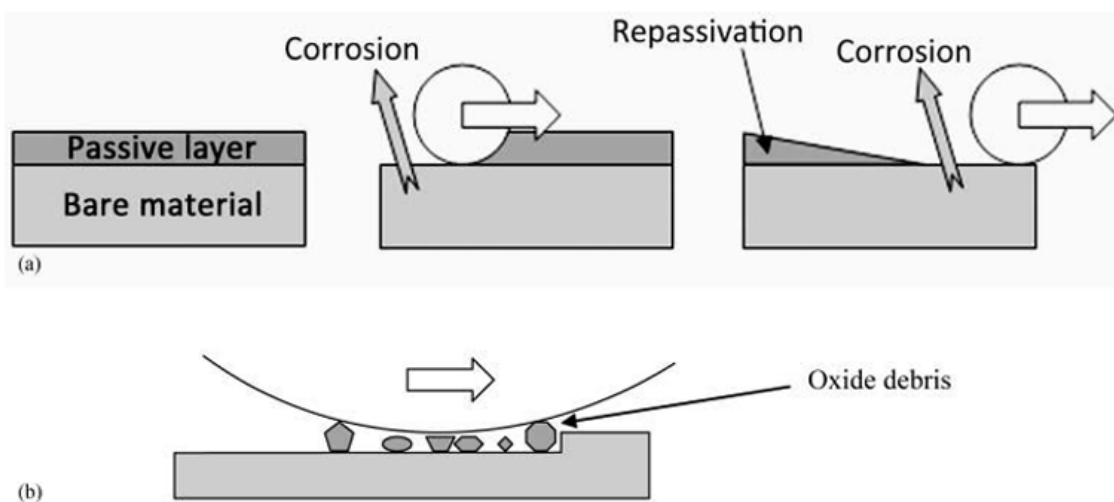


Figure 19 - Synergistic effect of corrosion on wear and vice versa: (a) corrosion accelerated by friction through depassivation; (b) abrasion accelerated by corrosion products (oxide debris) acting as a third body [25].

The "third body" effect is critical: solid products like oxide debris often remain trapped in the contact zone [7,25]. These elements act as an additional abrasive, intensifying both mechanical damage and chemical reaction rates [25] (Figure 20).

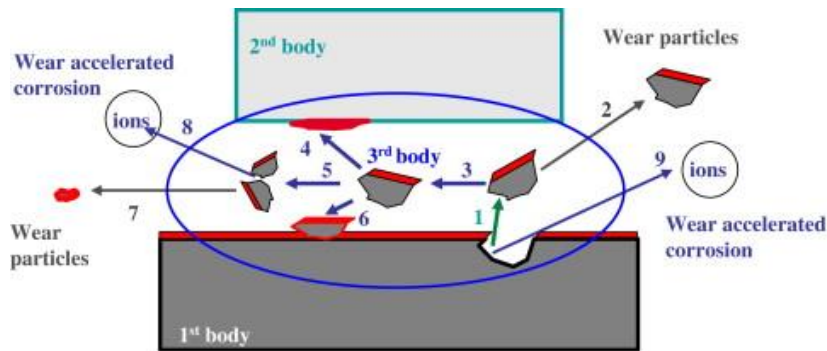


Figure 20 - Schematic illustration of material flows and reactions in a tribocorrosion system involving a passive metal (first body) an inert counter body (second body) and wear particles (third body) [7].

2.5.2. In Situ Evaluation Techniques

Macroscopic measurements like mass loss are insufficient to understand tribocorrosion. *In situ* electrochemical techniques are essential to reveal dynamic reactions in real-time [7,8,25]:

- Open Circuit Potential (OCP): Registers the spontaneous potential difference. Friction onset causes a potential drop, indicating film destruction and active metal exposure [7,8] (Figure 21).

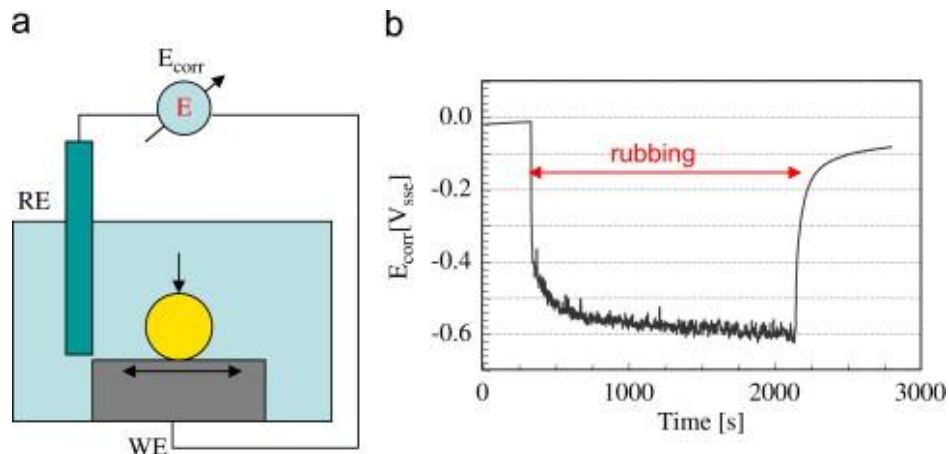


Figure 21 - Schematic view of a tribocorrosion setup for measuring the corrosion potential (OCP) and its evolution during rubbing [7].

- Potentiostatic and Potentiodynamic Tests: Potentiostatic tests impose a fixed potential to quantify material removed by oxidation via Faraday's Law. Potentiodynamic tests reveal synergies through large anodic currents in the wear track [7,8].
- Electrochemical Impedance Spectroscopy (EIS): The most effective technique for detailed kinetic analysis without disturbing the system. It differentiates a fully passive surface from one recently subjected to friction [8].
- Galvanic Cells: Measures current between a sample under friction and an identical plate not subjected to wear [7].

2.6. Tribocorrosion of WC-Based Composites

According to Pereira et al. [28], the intricate relationship between wear and corrosion in WC-based composites is critical, particularly when comparing conventional WC-Co with alternative binders (Ni, NiCr, NiMo, and NiCrMo) in severe environments like 0.5 M NaCl + 0.05 M HCl. While WC-Co suffers from severe active dissolution, highly alloyed binders—especially WC-NiCrMo—form robust protective oxide films that heavily resist chemical attack. During tribocorrosion, these passivating systems undergo dynamic depassivation and repassivation. As mechanical sliding begins, the action violently removes the protective layer, causing an abrupt cathodic shift; once friction ceases, the binder rapidly repassivates and the potential recovers (Figure 22).

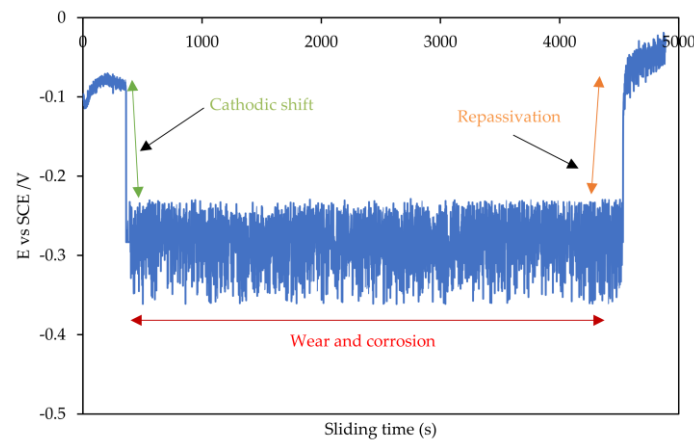


Figure 22 - Evolution of the open circuit potential (OCP) for WC-NiCr specimen before, during, and after the tribological test [28].

Interestingly, the corrosive aqueous electrolyte fundamentally alters the physical wear dynamics by acting as a lubricating agent. This fluid hydrodynamic effect effectively halves the steady-state coefficient of friction compared to unlubricated dry conditions (Figure 23).

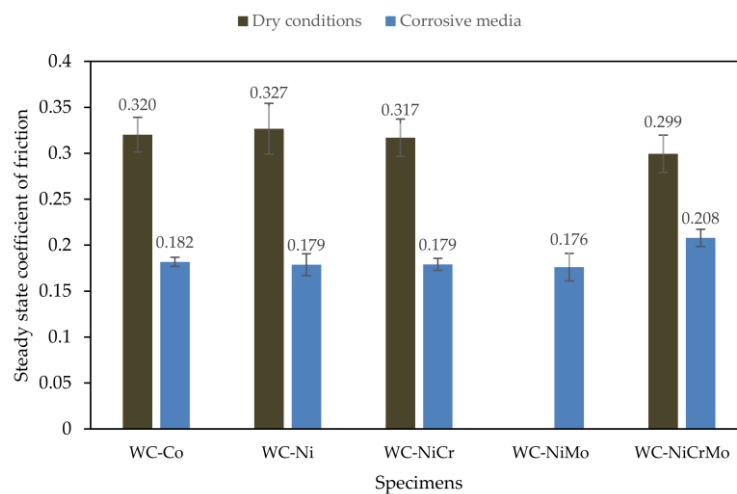


Figure 23 - Steady state coefficient of friction values for the four specimens (WC-Co, WC-Ni, WC-NiCr, WC-NiMo, and WC-NiCrMo) for normal load of 23N in dry/unlubricated and on the presence of the corrosive media/lubricated conditions [28].

Despite this mechanical mitigation, the overall material degradation is ultimately dictated by the chemical resilience of the binder. Wear occurs primarily through the preferential dissolution of the metallic matrix, which undermines the carbide grains and leads to their pull-out. While WC-Co and simpler Ni-based specimens suffer massive crater formations and widespread damage, the extraordinary chemical stability of the WC-NiCrMo matrix prevents this rapid dissolution.

At the atomic level, first-principles calculations based on Density Functional Theory (DFT) indicate that the co-addition of chromium and molybdenum (Cr+Mo) beneficially alters the adhesion energies at the interface. Although the isolated presence of Cr or Mo can theoretically weaken the adhesion at the Ni/WC interface, their simultaneous presence (Ni-Cr-Mo) generates a synergistic effect that strengthens the bonding energy and the intergranular mechanical stability of the interface [29]. This excellent intergranular cohesion, combined with the rapid repassivation kinetics promoted by free chromium in the matrix, is crucial under wear-corrosion conditions. Under continuous friction (tribocorrosion), the chromium exposed on the wear track repassivates almost instantaneously after the passage of the counter-body, minimizing active galvanic dissolution and stabilizing both the mechanical and chemical material removal rates [30]. Consequently, the Ni-Cr-Mo system restricts damage to highly localized areas, proving its superiority in surviving severe tribocorrosive environments (Figure 24) [28].

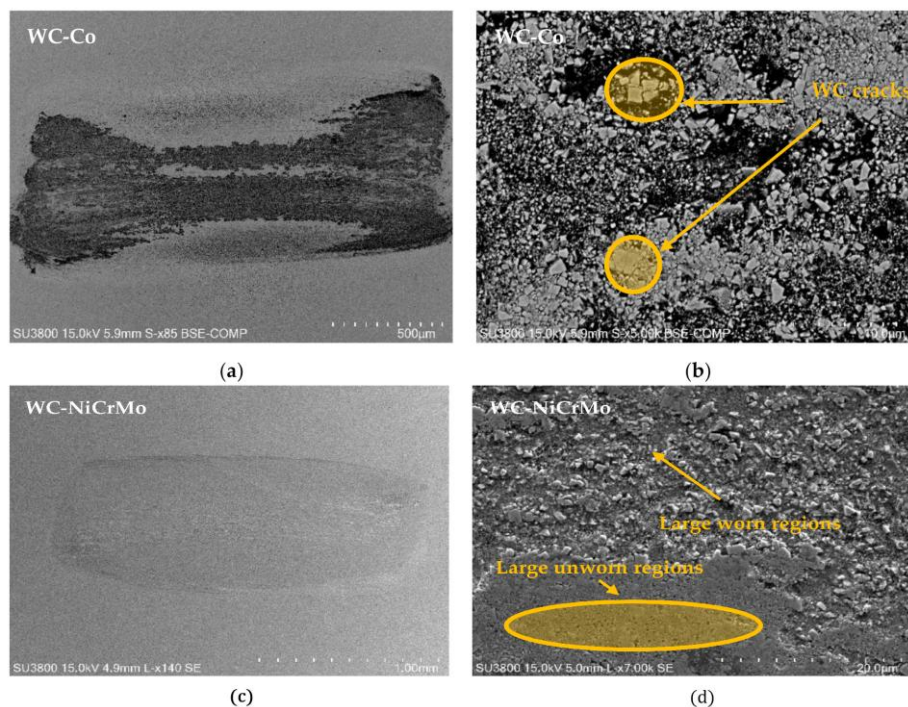


Figure 24 - SEM micrographs of the wear tracks for the five different specimens for 17 N applied load, showing the wear mechanisms: (a,b) WC-Co and (c,d) WC-NiCrMo [28].

3. Material and methods

3.1. Material

The materials investigated in this work comprised a reference WC-Co cemented carbide with a 13 wt.% nominal binder content, and three experimental WC-NiCrMo composites containing 10 wt.% nominal binder with varying chromium (Cr) concentrations ranging from 1.1 to 1.8 wt.%.

All experimental specimens were synthesized following procedures described in previous work by Santos et al. [3,5]. The starting powders included WC and Cr_3C_2 from H.C. Starck GmbH (Germany), Mo_2C from Treibacher Industrie AG (Austria), and Ni from Umicore (Belgium). Appropriate amounts of each powder were weighed to prepare three distinct chemical compositions. Each mixture was ball-milled in ethanol using laboratorial equipment for roughly 70 hours, then dried and uniaxially compressed at 15 MPa into shallow cylinders (20 mm in diameter). Subsequently, the green compacts were synthesized via a sinter-HIP cycle, holding a temperature between 1440-1460 °C for 90 minutes under 2-3 MPa in an Argon atmosphere.

For each of the experimental WC-NiCrMo grades (designated as Cr-11, Cr-13, and Cr-18), multiple specimens sharing the same chemical composition were tested to ensure data reliability. Conversely, for the reference WC-Co material, only a single specimen with that specific chemical composition was evaluated. The nominal chemical composition of the investigated WC-NiCrMo specimens is summarized in Table 3.

Table 3 – Nominal chemical composition (wt.%) of the investigated specimens.

Sample	Ni	Cr	Mo	WC
Cr-11	8.5	1.1	0.4	Bal.
Cr-13	8.3	1.3	0.4	Bal.
Cr-18	9.0	1.8	0.4	Bal.

3.2. Methods

3.2.1. Chemical and microstructural characterization

Scanning Electron Microscopy (SEM) coupled with Energy-Dispersive X-ray Spectroscopy (EDS) was utilized at different stages of the experimental work to characterize the material's microstructure, determine chemical compositions, and evaluate degradation mechanisms. The chemical and microstructural analyses were conducted as follows:

Pre-test Characterization: Microstructural observations and elemental chemical analyses via EDS were performed immediately after the metallographic preparation described in Section 3.2.3. to establish the baseline condition of the studied composites. Additionally, a quantitative phase analysis was carried out using ImageJ software. For this purpose, six

distinct image fields were captured via SEM at a magnification of x15000 per specimen, covering a total analyzed area of approximately 4410 μm^2 for each evaluated condition, to ensure statistical relevance.

Post-Electrochemical Characterization: Following the completion of the sequential electrochemical tests, the surfaces were examined by SEM and EDS to analyze the morphology, chemical composition of corrosion products, and the specific type of the resulting corrosive attack.

Post-Tribocorrosion Characterization: Prior to the SEM/EDS analyses, the specimens were ultrasonically cleaned for 15 min in ethanol, followed by 10 min in distilled water to remove any loose debris. Detailed SEM and EDS analyses were then performed on the resulting wear tracks, as well as on the corresponding alumina balls used as the counter-face material, to investigate the chemical evolution, mechanical wear tracks, and active degradation mechanisms.

3.2.2. Mechanical Characterization

The mechanical behavior of the specimens was evaluated through hardness and fracture toughness measurements. Hardness was measured using a DuraVision G5 EMCotest hardness tester, following the Vickers test procedure in accordance with the ISO 6507-1 standard [31], executing a total of 5 indentations per specimen with an applied load of 294 N (HV30).

Furthermore, the Palmqvist method was employed to determine the Palmqvist fracture toughness (K_{Ic}) from the radial cracks propagating from the hardness indentations in accordance with the ISO 28079 (2026) standard [32]. The radial crack lengths required for this analysis were measured using a Leica DM4000M Optical Microscope, and the final toughness values were calculated according to Equation 1 [33]:

$$K_{Ic} = A\sqrt{H} \sqrt{\frac{P}{\sum_{i=1}^4 l_i}} \quad (1)$$

where A is an empirical constant equal to 0.0028, H is the Vickers hardness value expressed in N/mm^2 , P is the applied indentation load in N , l_i represents the crack length measured from each corner of the indentation in mm .

3.2.3. Electrochemical Measurements

To evaluate the electrochemical behavior of the samples, a rigorous metallographic preparation was first performed to ensure a standardized surface finish. The grinding process involved the use of 54 μm and 18 μm diamond embedded discs, followed by a polishing stage using cloths impregnated with 6 μm and 1 μm diamond suspensions.

The electrochemical tests were carried out using a conventional three-electrode cell configuration (Figure 25), consisting of the prepared specimen as the working electrode (WE), a silver/silver chloride (Ag/AgCl , 3 M KCl) reference electrode (RE), and a platinum-

coated titanium (Pt-coated Ti) coil as the counter electrode (CE). The electrical contact with the working electrode was established using an aluminum (Al) foil. The corrosive medium used was a 0.5 M sodium chloride (NaCl) solution, with the pH adjusted to 2 using hydrochloric acid (HCl) to simulate an acidic environment. A set of electrochemical tests was executed sequentially for each specimen using a Gamry Interface 1000E potentiostat/galvanostat (Gamry Instruments, USA) (Table 4). Each experimental set was performed at room temperature under stagnant conditions, starting approximately 10 min after the metallographic surface preparation and 1 min after immersion. To ensure reproducibility, each set of measurements was repeated at least four times for each condition. To control the testing region, a protective mask in the shape of a circle was applied to the specimen surface, delimiting an exposed surface area of 0.50 cm².

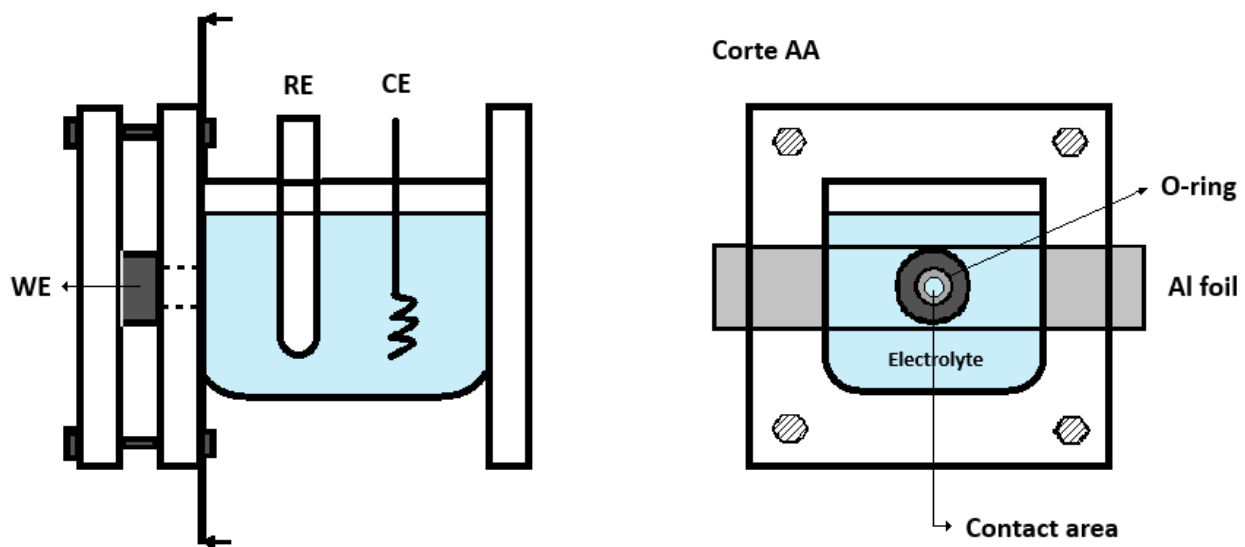


Figure 25 - Experimental setup used for the electrochemical measurements: (left) side view of the three-electrode cell configuration); (right) Section A-A view detailing the sealing O-ring, the aluminum (Al) foil, and the delimited contact area of the working.

The following techniques were performed sequentially:

Table 4 -Summary of the electrochemical experimental routines and parameters

Routine	Objective	Parameters
Open Circuit Potential (OCP)	Monitored to evaluate the potential stability over time.	≈22 h vs. Ag/AgCl
Electrochemical Impedance Spectroscopy (EIS)	Performed to characterize the interfacial resistance and corrosion mechanisms.	100 000 to 0.005 Hz (± 7 mV rms vs. E _{oc})
Potentiodynamic Polarization	Conducted to determine the corrosion kinetic parameters.	-0.25 to 1.5 V (at 1 mV.s)

3.2.4. Tribocorrosion Measurements

Tribocorrosion assessments were performed to investigate the synergetic effects of mechanical wear and electrochemical degradation on the samples. The experimental sequence began with a two-step OCP monitoring protocol, utilizing a conventional reference electrode (saturated Ag/AgCl) and a 0.5 M NaCl solution adjusted to pH 2 as the electrolyte.

Initially, a first OCP step was scheduled for 2 h to ensure the electrochemical stability of the sample. To optimize testing time, a stability criterion was adopted: if the potential variation was lower than 60 mV during the first hour of immersion, the first step was manually bypassed, and the system was advanced to the second OCP step (1 h duration) using the same reference electrode and electrolyte, as sufficient stability had already been achieved. Exactly 3 minutes after the initiation of the second OCP step, the tribological test was launched. During this stage, an alumina ball (10 mm in diameter, supplied by CERATEC, Belgium) was rubbed against the sample surface, WE, in a sliding motion for 30 minutes, according to the operational parameters summarized in Table 5. A total normal force (F_N) of 40 N was applied, resulting from the combination of the tribometer arm's baseline weight (5 N) and an additional dead weight of 35 N. To ensure proper electrical conductivity and reliable OCP measurements throughout the test, a copper billet was positioned beneath the sample to serve as the electrical back-contact. The electrochemical potential was continuously monitored throughout the entire sliding period, as well as during the subsequent relaxation phase, to evaluate the electrochemical recovery and post-sliding behavior of the sample. The setup used for the tribocorrosion tests is shown in Figure 26.

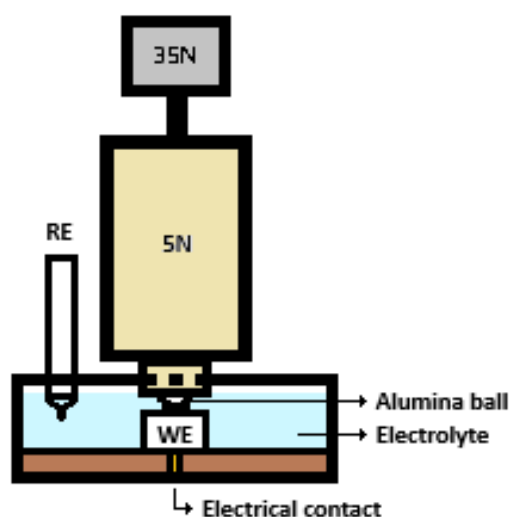


Figure 26 - Schematic diagram of the tribocorrosion test setup.

Table 5 - Operational parameters used in the tribological mechanical tests.

Normal force (N)	Stroke (mm)	amplitude	Test duration (s)	Max. sliding speed (mm/s)
40	6		1800	18.85

4. Results and discussion

4.1. Microstructural and Chemical Characterization

The microstructure and elemental distribution of the sintered WC-Co hardmetal cement were evaluated using SEM combined with EDS mapping (Figure 27) and spot analysis (Figure 28).

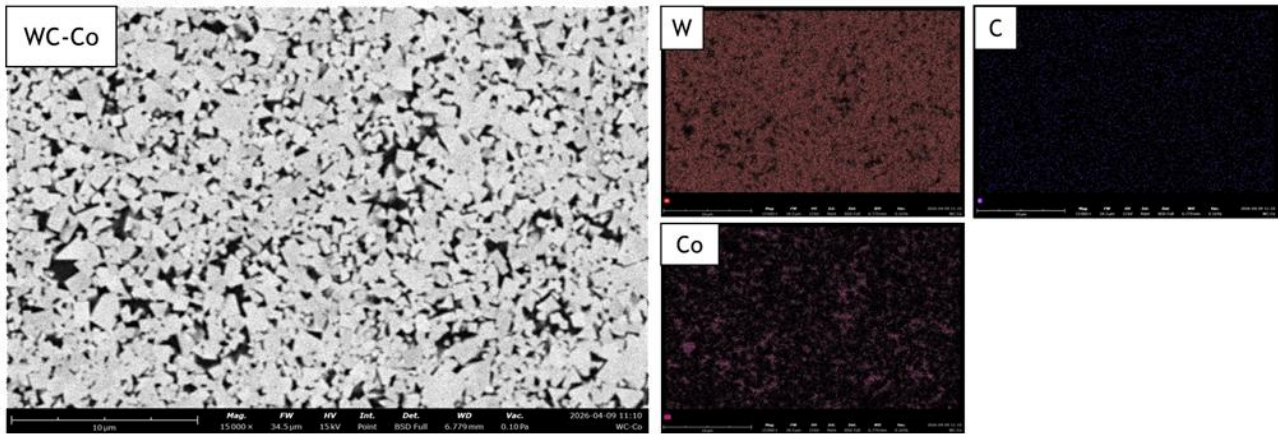


Figure 27 - SEM-BSE micrograph of the reference WC-Co hardmetal and corresponding EDS elemental mapping for Tungsten (W), Carbon (C), and Cobalt (Co).

Figure 27 illustrates the typical microstructure of the WC-Co composite along with its respective EDS elemental mapping interfaces. The backscattered electron (BSE) micrograph (Figure 27, left) reveals a homogeneous and dense structure characterized by two distinct phases: faceted, sharp-edged prismatic grains with light grey contrast, and a continuous, interconnected network of a darker matrix filling the interstitial spaces. This morphology is characteristic of liquid-phase sintered WC-Co hardmetals [34]. The EDS elemental mapping confirms the spatial distribution of the constituent elements across the analyzed area. The tungsten (W) and carbon (C) maps exhibit a strong spatial correlation, predominantly localizing within the sharp angular geometric grains, which confirms their identity as the hard tungsten carbide (WC) phase. Conversely, the cobalt (Co) map demonstrates that the binder phase is uniformly distributed throughout the microstructure, effectively wetting the WC grains and forming a continuous skeleton that acts as a tough matrix. This uniform distribution of the metallic binder is crucial for preventing localized stress concentration and ensuring high fracture toughness [35].

To further investigate the chemical composition, a localized EDS spot analysis was performed directly within an interstitial region containing a high concentration of the binder phase, as highlighted by the target marker in Figure 28 (left).

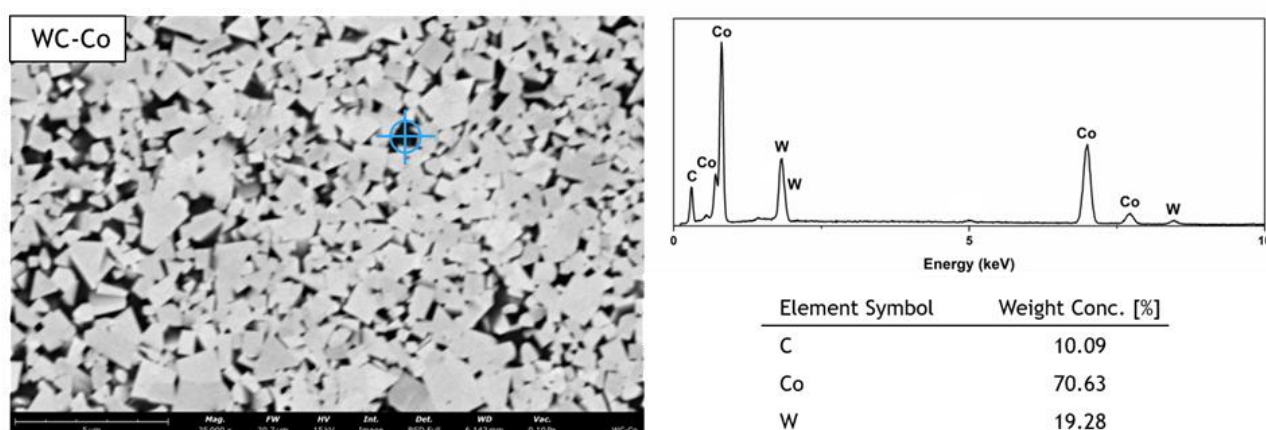


Figure 28 - EDS point analysis performed on the metallic binder of the reference WC-Co hardmetal, including the obtained spectrum and elemental composition.

The corresponding EDS spectrum and the semi-quantitative elemental analysis are presented in Figure 28 (right). The spot analysis yielded a chemical composition comprising 70.63 wt.% cobalt, 19.28 wt.% tungsten, and 10.09 wt.% carbon. While the high concentration of Co confirms the successful identification of the binder pool, the W and C contents significantly exceed their thermodynamic solid solubility limits in solid cobalt at room temperature[10]. This discrepancy does not reflect the true matrix composition but rather stems from the EDS interaction volume. Because the electron beam penetration depth exceeds the sub-micron dimensions of the binder pools, the generated X-rays inevitably capture signals from adjacent and subsurface WC grains [36]. Furthermore, the disproportionately high carbon content is a well-known artifact in EDS analysis, typically associated with surface contamination and the technique's low accuracy for light elements [37].

Despite these measurement artifacts, a genuine – albeit strictly limited by thermodynamic boundaries – dissolution of W and C into the Co matrix does occur during the high-temperature liquid-phase sintering stage. Upon cooling, while the majority of the dissolved WC reprecipitates onto existing carbide grains (contributing to grain growth and facet formation), a specific fraction of tungsten along with trace amounts of carbon, remains trapped in solid solution within the cobalt matrix [10].

To improve the corrosion and oxidation resistance of the hardmetal, the conventional Co matrix was substituted with a multi-component NiCrMo binder system. The microstructural evolution and elemental distribution of three distinct formulations, designated as Cr-11, Cr-13, and Cr-18 (containing nominal concentrations of 11 wt.%, 13 wt.%, and 18 wt.% of Cr within the binder phase, respectively), were investigated. Figure 29 presents the phase distribution map of the Cr-11 sample, as representative of the composites with a NiCrMo binder.

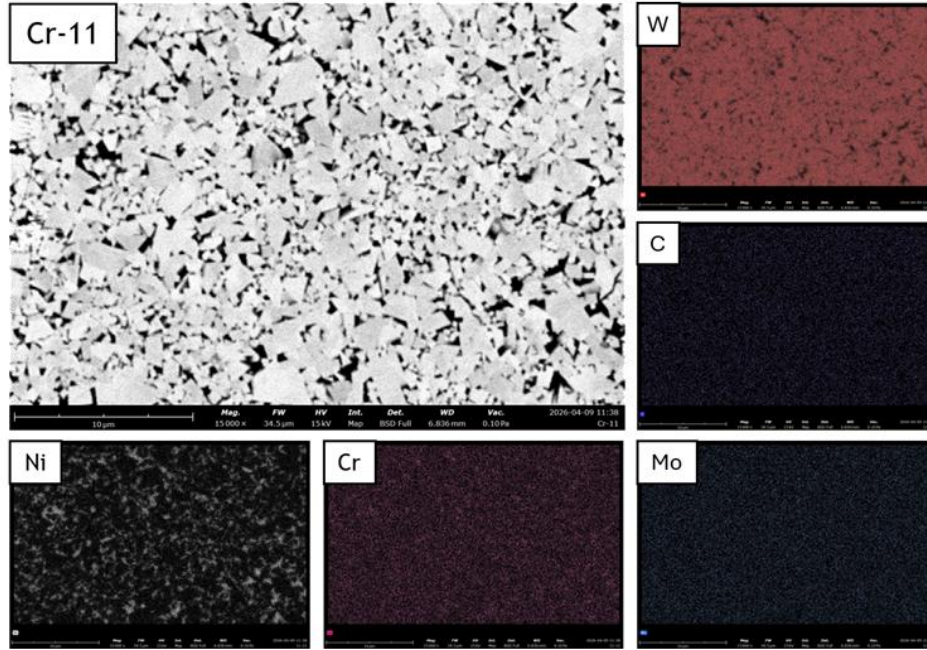


Figure 29 - SEM-BSE micrograph of the alternative Cr-11 composite and corresponding EDS elemental mapping for W, C, Ni, Cr, and Mo.

Figure 29 displays the SEM surface micrographs alongside the respective EDS elemental mappings for the W, C, Ni, Cr and Mo phases across the three compositions. In all samples, a homogeneous distribution of WC grains embedded in the Ni-based alloy matrix is initially observed. The mapping confirms that Ni and Mo are uniformly distributed within the binder pools, effectively wetting the angular WC grains.

However, despite the intended enrichment of the matrix, the corporate distribution of Cr undergoes a notable transition at the highest doping level. As illustrated in Figure 30, the Cr-18 sample exhibits microstructural anomalies characterized by localized Cr-rich clusters or "pockets" (Figure 30). The EDS map clearly delineates these irregular concentration regions where Cr has accumulated preferentially instead of remaining completely dissolved in the Ni solid solution.

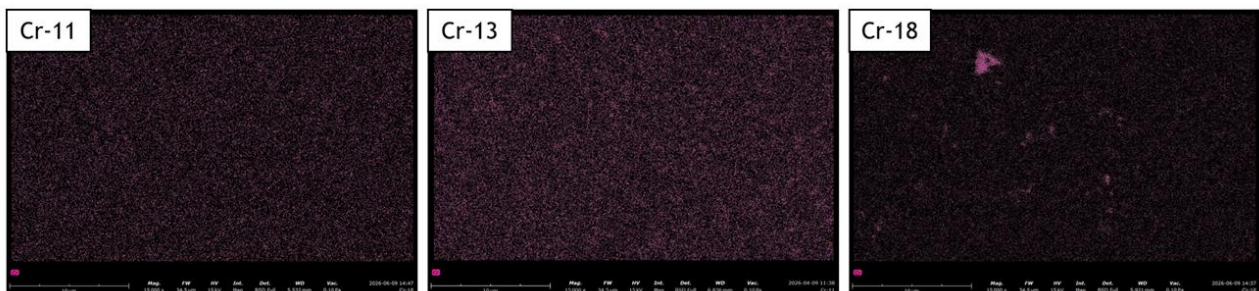


Figure 30 - Comparative EDS elemental mapping illustrating the distribution of Cr across the microstructures of the Cr-11, Cr-13, and Cr-18 composites.

This localized heterogeneity indicates that at an explicit 18 wt.% nominal Cr addition, the thermodynamic solubility limit of Cr within the Ni-base matrix during liquid-phase

sintering has been exceeded [4]. The excess Cr, driven by its high chemical affinity, precipitates out or segregates into distinct secondary phases (Cr_3C_2 , Cr_7C_3) or elemental pockets during the cooling cycle [4]. The formation of these macro-heterogeneities in the Cr-18 alloy can be detrimental, as these Cr-rich pockets often act as stress concentrators, potentially compromising the mechanical integrity of the composite and leading to a localized reduction in fracture toughness [38].

To evaluate the impact of this segregation on the remaining metallic matrix, a localized quantitative analysis was conducted on the binder pools outside of these segregated pockets. As summarized in the compositional data presented in Figure 31, the effective Cr concentration within the analyzed binder solution increases progressively from 7.60 wt.% in the Cr-11 sample, to 9.40 wt.% in Cr-13, and reaches 9.80 wt.% in the Cr-18 sample.

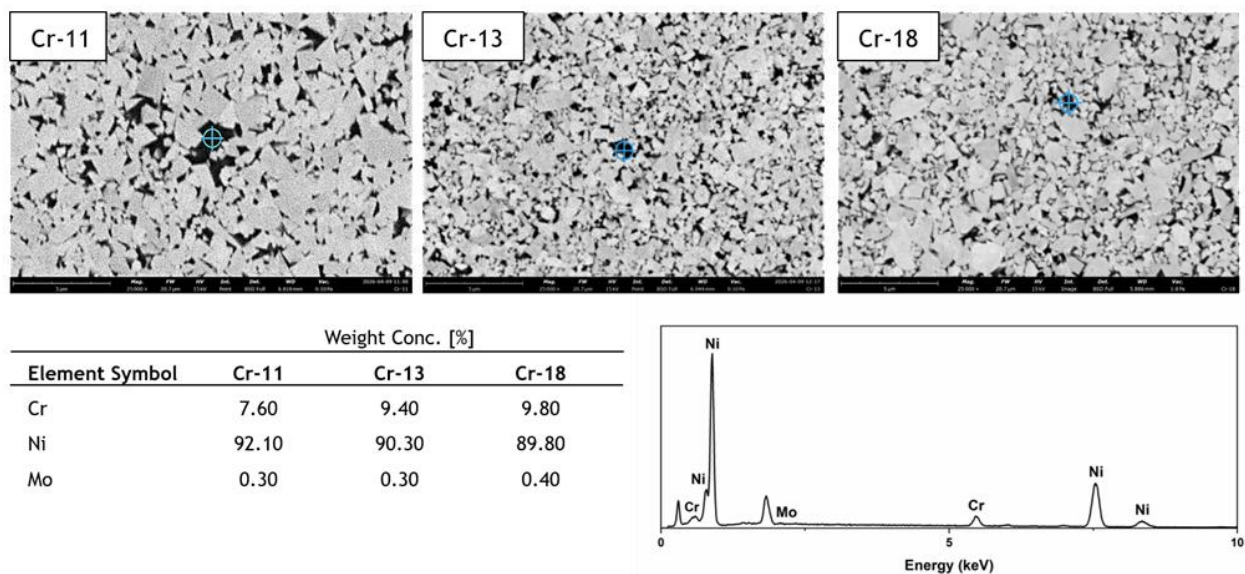


Figure 31 - EDS point analyses performed on the metallic binder pools of the Cr-11, Cr-13, and Cr-18 hardmetals, including a representative spectrum and the corresponding elemental compositions.

This systematic increase in Cr content within the continuous matrix phase matches the initial experimental design. Experimental investigations focused on WC-NiCr systems demonstrate that, to avoid the formation of chromium precipitates, the Cr concentration should not exceed a maximum of 9 to 11 wt.% [4]. This behavior is consistent with the thermodynamic stabilization limit reported for WC-NiCoCr systems, where the upper limit for effective Cr addition is typically found between 9.0 and 13.5 wt.%. [39]. Accordingly, the small difference in dissolved Cr between Cr-13 (9.40 wt.%) and Cr-18 (9.80 wt.%) reflects exactly this thermodynamic restriction, demonstrating that the matrix has reached a saturation plateau and cannot accommodate more Cr in solid solution. Consequently, once this thermodynamic solubility limit is exceeded, the remaining excess chromium from the 18 wt.% nominal addition is not diluted; instead, it is forced to precipitate as segregated secondary phases, being confined into the aforementioned segregated pockets [4]. Thermodynamically, this excess predominantly precipitates in the form of chromium carbides, such as Cr_3C_2 in carbon-rich formulations or Cr_7C_3 in lower-carbon domains [4]. The corresponding EDS spectrum (Figure 31, bottom) confirms the

simultaneous presence of Ni, Cr, and Mo peaks, verifying the formation of the intended multi-component solution within the non-segregated matrix regions.

A comparative analysis of the microstructures, performed at equivalent magnification levels (Figure 28 and 31), reveals a significant evolution in the average WC grain size across the studied compositions. The WC-Co sample and the Cr-11 alloy exhibit a coarser microstructure, characterized by larger, faceted WC grains. In contrast, the Cr-13 and Cr-18 samples demonstrate a marked refinement in grain size, with a more uniform and significantly finer carbide distribution. This grain growth inhibition is directly linked to the increase in Cr content within the Ni-base binder. During the liquid-phase sintering process, chromium segregates to the WC/binder interface, where it acts as a kinetic barrier. This accumulation of Cr at the interface reduces the solubility of WC in the liquid binder and hinders the diffusion of W and C atoms, thereby slowing down the dissolution-reprecipitation mechanism that drives grain coarsening [35,40].

The transition from the coarser structures observed in the Cr-11 alloy to the refined, sub-micron scale of the Cr-13 and Cr-18 samples highlights the efficiency of Cr as a grain growth inhibitor in Ni-bonded composites [40]. By maintaining a finer carbide skeleton, these higher-chromium compositions are expected to provide superior hardness and mechanical resistance.

In addition to the qualitative and compositional analysis, a quantitative stereological evaluation was performed to determine the precise area fraction of the metallic binder phase across the different sintered samples (Figure 32). Table 6 summarizes the quantified binder phase fractions obtained via image analysis of the representative SEM micrographs.

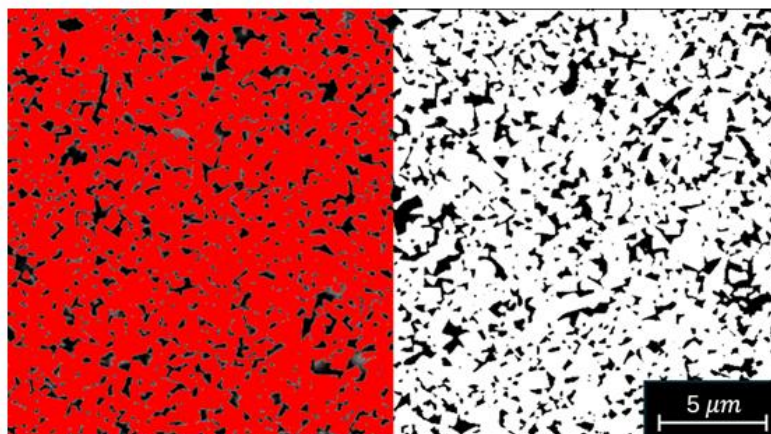


Figure 32 - Representative binarized SEM micrograph illustrating the image analysis thresholding method used to quantify the binder phase.

Table 6 - Volumetric binder content (%) of the investigated composites determined via quantitative image analysis.

	Binder content (%)
WC-Co	21 ± 0.3
Cr-11	18 ± 0.4
Cr-13	20 ± 0.3
Cr-18	19 ± 0.4

The quantitative data reveals that despite the variations in the chemical composition of the binder pools (i.e., the different Cr additions in the Ni-base matrix and the standard Co-binder), the overall geometric distribution and area fraction occupied by the metallic phase remain consistent across all specimens. This determination is essential to ensure that subsequent comparative property evaluations are not biased by macro-differences in the total content of the soft matrix phase.

Crucially, the precise quantification of the binder's phase fraction serves a dual purpose in this study. Beyond completing the fundamental microstructural characterization of the processed composites, this area fraction assessment is vital for the upcoming electrochemical corrosion and passivation behavior analyses. In WC-based composites, the ceramic WC phase is chemically inert across a wide range of potentials, meaning that the degradation, dissolution, and electrochemical active surface area are overwhelmingly governed by the exposed metallic binder network [41-43]. Therefore, the area fractions established in Table 6 establish the baseline parameters required to accurately normalize the electrochemical current densities, ensuring a scientifically rigorous comparison of the intrinsic corrosion rates and passivation dynamics of the multi-component NiCrMo and conventional Co matrices.

4.2. Mechanical Characterization

The mechanical performance of the sintered composites was evaluated through Vickers hardness (HV) and indentation fracture toughness (K_{Ic}) measurements. Unlike conventional structural alloys, whose performance is typically defined by parameters such as yield strength or elongation at break, the mechanical viability of cemented carbides is fundamentally governed by the delicate balance between hardness and fracture toughness [35]. In these materials, these two properties act as the ultimate design criteria, dictating their wear resistance and ability to withstand catastrophic failure under impact [35]. The comparative results for all tested compositions are summarized in Figure 33a. The fracture toughness was determined based on the crack lengths propagating from the corners of the Vickers indents, as illustrated by the representative optical micrograph in Figure 33b.

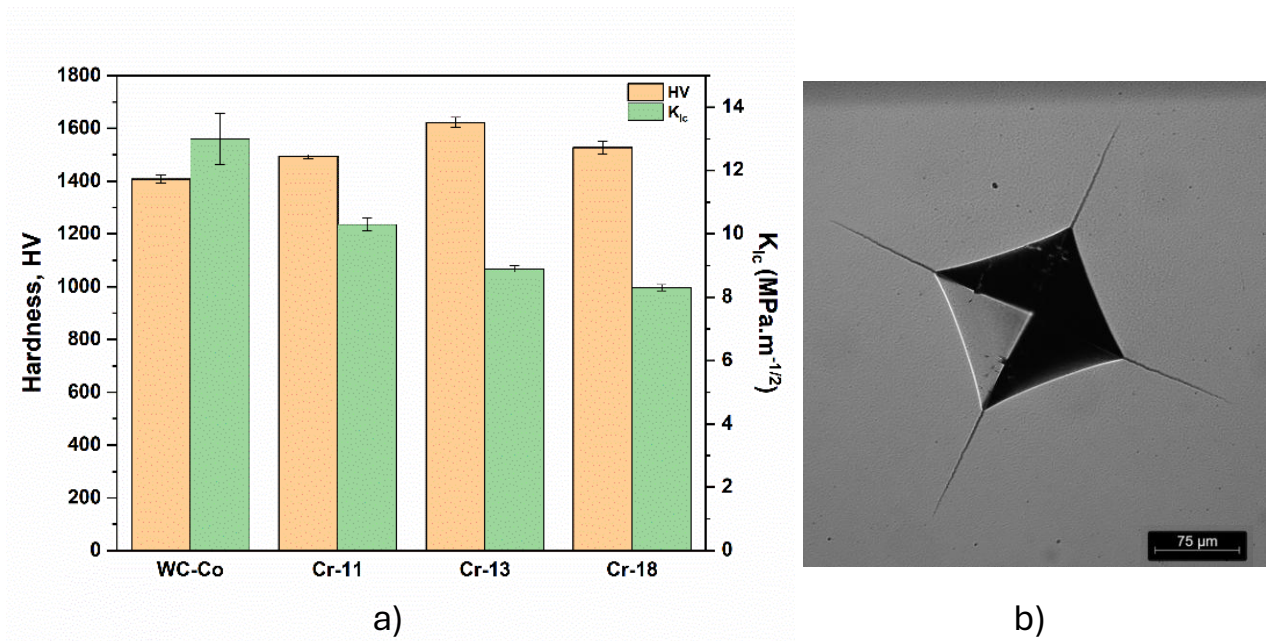


Figure 33 - Mechanical properties of the investigated composites (a) and representative optical micrograph of a Vickers indentation (b).

The results demonstrate a clear inverse relationship between hardness and fracture toughness, which is a classic behavior in cemented carbide systems. The reference WC-Co sample exhibits the highest fracture toughness ($K_{Ic} \approx 13.0 \text{ MPa}\cdot\text{m}^{1/2}$) but the lowest hardness ($\text{HV} \approx 1400$). Upon transitioning to the NiCrMo binder system, a general increase in hardness is observed for all alloyed samples.

This hardening effect is primarily attributed to two factors: first, the solid-solution strengthening of the Ni-based matrix by Cr and Mo [29]; and second, the microstructural refinement – specifically the reduction in WC grain size [40]– previously discussed in Section 4.1. The Cr-13 sample achieves the peak hardness value ($\text{HV} \approx 1620$), indicating an optimal balance of microstructural grain refinement and binder strengthening at this chromium level. However, this increase in hardness is accompanied by a concurrent reduction in fracture toughness. The K_{Ic} values decrease systematically as the chromium content increases, dropping from $\approx 10.5 \text{ MPa}\cdot\text{m}^{1/2}$ in Cr-11 to approximately $8.5 \text{ MPa}\cdot\text{m}^{1/2}$ in the Cr-18 sample. The decline in fracture toughness observed as chromium content increases can be attributed to a combination of metallurgical and structural factors. Primarily, the substitution of the conventional cobalt matrix with a NiCrMo binder system, while highly beneficial for corrosion resistance, generally results in lower intrinsic ductility compared to the cobalt matrix [10]. Furthermore, the microstructural anomalies identified in the Cr-18 alloy play a critical role; the presence of chromium-rich pockets and potential secondary brittle phases acts as significant sites for crack initiation [38]. These local heterogeneities disrupt the plasticity of the binder skeleton, effectively hindering its ability to accommodate the plastic deformation required to blunt crack tips during propagation. Finally, the reduction in WC grain size, while successfully increasing hardness via the Hall-Petch effect [44], inevitably reduces the mean free path of the binder [10,35,44]. Consequently, these narrower binder channels limit the plastic zone

formation at the crack tip, which reduces the energy required for crack propagation and ultimately lowers the overall fracture toughness of the composite [35].

In summary, while the Cr-13 composition represents a superior compromise for applications requiring high hardness, the Cr-18 alloy demonstrates that exceeding the thermodynamic solubility limit of Cr in the binder significantly degrades the mechanical reliability of the material.

4.3. Electrochemical results

4.3.1. Open Circuit Potential

The evolution of the OCP over ≈ 22 hours of immersion is shown in Figure 34, and the steady-state OCP values (E_{oc}) for the samples that reached stability are summarized in Table 7. To ensure a representative equilibrium value, the E_{oc} for each sample was calculated by averaging the potential recorded during the final 600 seconds of the immersion period.

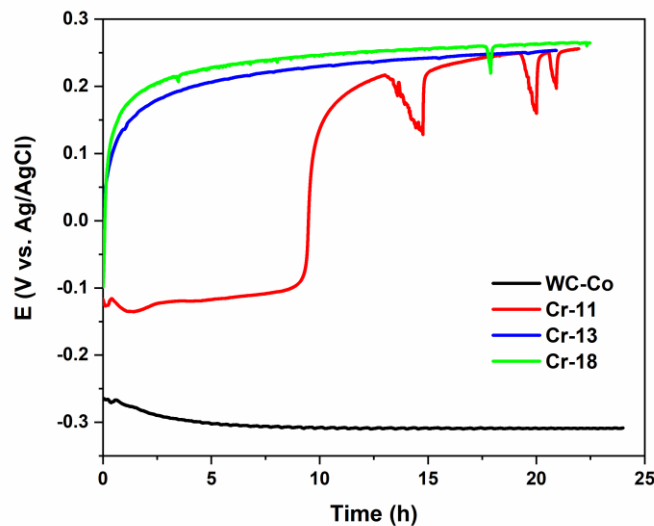


Figure 34 - OCP evolution over ≈ 22 hours for the reference WC-Co and the alternative composites.

Table 7 - Steady-state open-circuit potential (E_{oc}) values of the investigated composites after 22 hours of immersion.

Sample	E_{oc} (mV)
WC-Co	-310 ± 6
Cr-11	Unstable – not determined
Cr-13	247 ± 16
Cr-18	259 ± 20

The WC-Co reference exhibited a strongly negative and continuously decreasing OCP ($E_{oc} = -310 \pm 6$ mV vs. Ag/AgCl), indicative of a thermodynamically unstable surface with

a high driving force for anodic dissolution. This behavior is consistent with the well-documented susceptibility of cobalt binders to corrosion in acidic and chloride-containing media through a process known as preferential binder leaching, in which the Co matrix is selectively dissolved, leaving the WC skeleton structurally unsupported [45].

In contrast, the Cr-13 and Cr-18 samples exhibited a rapid evolution toward more noble (positive) potentials, followed by stabilization after a short immersion period. Such a positive shift in OCP generally indicates a progressive decrease in the thermodynamic tendency for active dissolution and the establishment of a more corrosion-resistant surface condition [41]. At this stage, based solely on OCP measurements, several mechanisms may account for this behavior, including the formation of a Cr-rich passive or semi-protective surface layer, the accumulation or restructuring of corrosion products, selective dissolution leading to surface enrichment in more noble elements, or the establishment of a dynamic balance between surface dissolution and oxide formation [1,17,41,43]. The rapid increase and subsequent stabilization of the potential suggest that Cr contributes to shifting the binder surface toward a less reactive electrochemical state. The similar stabilized potentials observed for Cr-13 and Cr-18 further indicate that beyond approximately 13 wt.% Cr in the binder, additional chromium provides limited further improvement in the thermodynamic stabilization of the surface under the present condition [39]. However, it is critical to emphasize that a noble OCP alone does not guarantee low corrosion rates or true passivity [46]. The precise nature and protectiveness of the surface state cannot be established from OCP measurements alone and are therefore further examined through the potentiodynamic polarization and EIS results discussed in subsequent sections.

The Cr-11 sample displayed a markedly different and inherently unstable behavior. Rather than converging to a steady-state potential, its OCP fluctuated significantly throughout the monitoring period, characterized by repeated drops and sharp rises. This unstable response suggests the existence of competing surface processes occurring simultaneously during immersion. Such fluctuations are commonly associated with transitions between electrochemical states of different stability and may reflect localized changes occurring at the binder/electrolyte interface [43,46].

Several mechanisms may contribute to these potential transients. Periods of decreasing OCP may indicate episodes of enhanced local dissolution, activation of previously protected regions, or local destabilization of the surface condition. Conversely, upward shifts toward more noble potentials may correspond to temporary reductions in dissolution kinetics resulting from processes such as the formation or local restoration of a passive or semi-protective surface layer, accumulation or restructuring of corrosion products, selective surface enrichment in Cr-containing species, or the establishment of a temporary balance between dissolution and surface stabilization processes [39,43,46]. These transient events may originate from localized corrosion phenomena initiated at microstructural heterogeneities, particularly at interfaces between WC grains and the metallic binder, where local chemistry can evolve due to hydrolysis of dissolved metal ions and local variations in chloride concentration [43]. The observed OCP oscillations

therefore suggest that the surface of Cr-11 does not evolve toward a single stable electrochemical condition but instead alternates between competing surface states.

This behavior may indicate that a Cr content of 11 wt.% lies close to a compositional threshold for achieving sustained stabilization of the binder surface under this highly aggressive environment [39,43]. Unlike Cr-13 and Cr-18, which evolve rapidly toward stable noble potentials, Cr-11 appears to repeatedly transition between more and less protective surface conditions during exposure. As a reliable steady-state E_{oc} could not be extracted, Cr-11 is excluded from Table 7, and its potentiodynamic and EIS behavior is instead analysed separately according to OCP state.

To capture this behavior in more detail, Figure 35 presents the OCP curves of Cr-11 with the three characteristic potential regions explicitly identified, while the accompanying Table 8 quantifies the specific E_{oc} ranges established for each state. These include: a low OCP region, corresponding to a more active surface condition; a medium OCP region, representing an intermediate and transitional state; and a high OCP region, associated with more noble potentials approaching those observed for Cr-13 and Cr-18 and potentially reflecting a more developed or stabilized surface condition. This classification provides the basis for the OCP-based subdivision of the potentiodynamic polarization and EIS results discussed in Sections 4.3.2 and 4.3.3. Furthermore, it illustrates that the instability of Cr-11 corresponds to cyclic transitions between distinct electrochemical surface states rather than a single, well-defined corrosion regime.

Table 8 - Steady-state open-circuit potential (E_{oc}) ranges for the three defined Cr-11 subgroups.

Cr-11	E_{oc} Range (mV)
Cr-11_High OCP	213 - 256
Cr-11_Medium OCP	121 - 153
Cr-11_Low OCP	27 - 54

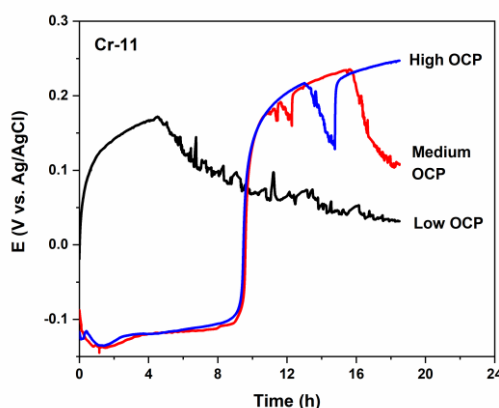


Figure 35 - Open-circuit potential (OCP) evolution of the Cr-11 alloy over time, illustrating the three distinct stabilization

behaviors: high, medium, and low OCP.

4.3.2. Potentiodynamic Polarization

The potentiodynamic polarization curves are presented in Figure 36, and the extracted corrosion potential ($E_{(i=0)}$) and corrosion current density (i_{corr}) values are summarized in Table 9. These electrochemical parameters were determined via Tafel extrapolation using the Gamry Echem Analyst software. To ensure methodological consistency and maintain a uniform margin of error across the entire dataset, the linear Tafel regions were systematically selected at an exact interval of ± 100 mV relative to the $E_{(i=0)}$ of each respective curve. For Cr-11, the high OCP subgroup was selected for this comparison, as it represents the best-case passivation scenario and allows the most meaningful contrast with the stable Cr-13 and Cr-18 samples. The full analysis of Cr-11 across all OCP states is presented in Section 4.3.2.1.

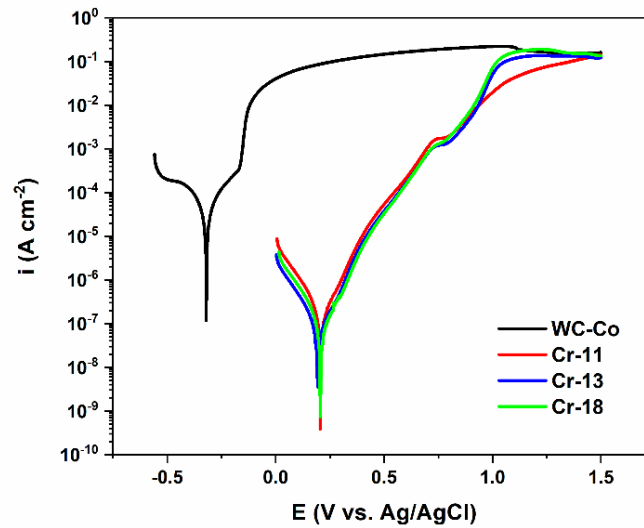


Figure 36 - Potentiodynamic polarization curves for the reference WC-Co and the alternative composites.

Table 9 - Electrochemical parameters (corrosion potential, $E_{(i=0)}$, and corrosion current density, i_{corr} extracted from the potentiodynamic polarization curves.

	$E_{(i=0)}(\text{mV})$	$i_{\text{corr}} (\mu\text{A}.\text{cm}^{-2})$
WC-Co	-316 ± 4	108 ± 65
Cr-11	188 ± 15	0.28 ± 0.05
Cr-13	178 ± 21	0.11 ± 0.00
Cr-18	201 ± 20	0.19 ± 0.00

The results reveal two clearly distinct electrochemical regimes: the highly active behavior of WC-Co and the markedly reduced dissolution behavior exhibited by all Cr-containing composites. The WC-Co reference exhibited a corrosion potential of $E_{(i=0)} = -316 \pm 4$ mV and a corrosion current density of $i_{\text{corr}} = 108 \pm 65 \mu\text{A}\cdot\text{cm}^{-2}$, values that are dramatically inferior to those of all Cr-containing materials. The corrosion current density is approximately two to three orders of magnitude higher than that measured for the Cr-bearing samples, demonstrating that the conventional Co binder provides limited corrosion resistance under these highly aggressive conditions (0.5 M NaCl, pH 2).

The potentiodynamic response of the WC-Co reference is characterized by high anodic current densities across the polarization range, confirming its poor corrosion resistance. Following the corrosion potential, the anodic current increases rapidly, indicating sustained dissolution of the metallic binder. At higher anodic potentials, the curve exhibits a region in which the rate of current increase becomes less pronounced. The high measured corrosion current density ($i_{\text{corr}} = 108 \pm 65 \mu\text{A}\cdot\text{cm}^{-2}$), together with the absence of a low-current region characteristic of stable passivation, indicates that corrosion remains dominated by continued binder dissolution and progressive cobalt leaching [1,45]. The reduced sensitivity of current to increasing potential at elevated polarization may instead result from non-passivating effects, including transport limitations within the electrolyte, temporary accumulation of corrosion products at the interface, progressive reduction of the exposed metallic binder area as dissolution proceeds, or a combination of these processes [43].

In contrast, all Cr-containing samples displayed substantially more noble corrosion potentials, ranging from 178 to 201 mV vs. Ag/AgCl, together with extremely low corrosion current densities (0.11-0.28 $\mu\text{A}\cdot\text{cm}^{-2}$). Although their potentiodynamic curves do not exhibit a classical passive plateau, the marked reduction in corrosion current relative to WC-Co indicates a substantial suppression of active dissolution[41,46]. Following the current minimum near $E_{(i=0)}$, the anodic current increases progressively with applied potential, suggesting that the surface enters an incipient passive state rather than developing a fully stable passive regime [38]. Under the highly aggressive conditions of 0.5 M NaCl at pH 2, any protective surface layer formed through Cr oxidation appears unable to maintain a constant passive current density and instead only slows the dissolution kinetics of the binder [42].

The potentiodynamic curves of Cr-11 (high OCP), Cr-13, and Cr-18 are visually very similar and largely superimposed, indicating that the dominant corrosion mitigation mechanism remains comparable across all three compositions. Among the NiCrMo binder samples, Cr-13 exhibited the lowest corrosion current density ($0.11 \pm 0.00 \mu\text{A}\cdot\text{cm}^{-2}$), suggesting that this composition provides the most effective suppression of anodic dissolution under the tested conditions. Despite containing the highest Cr concentration, Cr-18 showed a slightly higher i_{corr} ($0.19 \pm 0.00 \mu\text{A}\cdot\text{cm}^{-2}$), while also exhibiting the most noble $E_{(i=0)}$ (201 ± 20 mV). This apparent discrepancy may be associated with the microstructural heterogeneity of the Cr-18 sample, which contains Cr-rich pockets resulting from incomplete homogenization during processing [4,38,39]. This interpretation is consistent with the

corrosion behavior of WC-based composites, which is known to be strongly influenced by micro-galvanic interactions between regions of different composition and, consequently, different local corrosion potentials [47]. An uneven distribution of Cr within the binder is expected to generate local electrochemical gradients between Cr-rich and Cr-depleted regions, promoting preferential local dissolution. This effect has been previously demonstrated in WC-based coatings, where Cr segregation reduced corrosion resistance, whereas homogenization of Cr distribution across the binder and hard phase reduced local potential differences and improved corrosion performance by approximately one order of magnitude [48]. By analogy, the localized Cr-rich regions observed in Cr-18 may promote microscale galvanic coupling and contribute to the slightly increased measured corrosion current despite the higher bulk Cr content.

Overall, these results indicate that the corrosion performance of WC-NiCrMo composites is governed not only by the total Cr content but also by the homogeneity of Cr distribution within the binder. Under the present conditions, approximately 13 wt.% Cr appears sufficient to maximize corrosion resistance, while further Cr addition does not translate into proportional electrochemical benefit.

4.3.2.1. Effect of OCP State on the Polarization Behavior of Cr-11

Given the OCP instability of Cr-11, potentiodynamic polarization tests were conducted on specimens grouped according to their OCP at the time of measurement: high OCP, medium OCP, and low OCP (Figure 37). This subdivision was adopted to reduce the experimental error associated with the highly variable surface state of Cr-11 and to allow a physically meaningful interpretation of its electrochemical response. The $E_{(i=0)}$ and i_{corr} values for each subgroup are presented in Table 10.

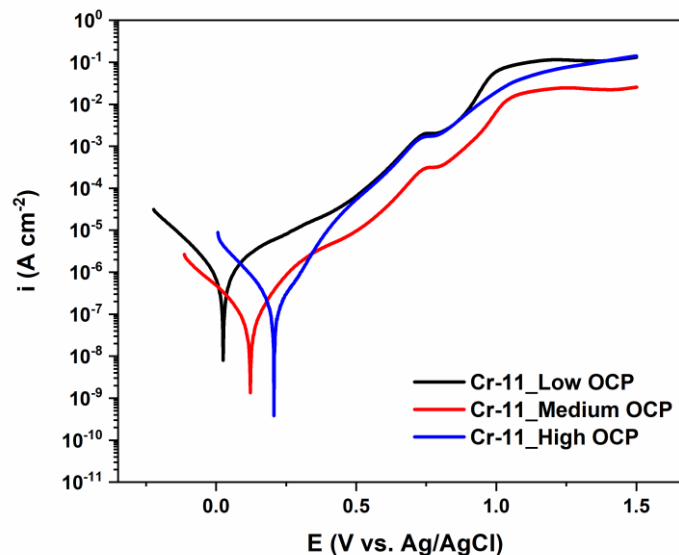


Figure 37 - Potentiodynamic polarization curves corresponding to the distinct high, medium, and low OCP states of the Cr-11 composite.

Table 10 - Electrochemical parameters ($E_{(i=0)}$ and i_{corr}) extracted from the polarization curves for the different OCP states of the Cr-11 composite.

	$E_{(i=0)}$ (mV)	i_{corr} ($\mu\text{A}\cdot\text{cm}^{-2}$)
Cr-11	136 ± 60	0.48 ± 0.29
Cr-11_High OCP	188 ± 15	0.28 ± 0.04
Cr-11_Medium OCP	148 ± 33	0.45 ± 0.03
Cr-11_Low OCP	36 ± 10	0.99 ± 0.06

The data in Table 10 reveal a clear and systematic trend: as the OCP state decreases from high to low, both $E_{(i=0)}$ and i_{corr} progressively deteriorate. Specimens measured at high OCP ($E_{(i=0)} = 188 \pm 15$ mV; $i_{\text{corr}} = 0.28 \pm 0.05 \mu\text{A}\cdot\text{cm}^{-2}$) behave comparably to Cr-13 and Cr-18, demonstrating that when the surface remains in its less active electrochemical state, the response of Cr-11 approaches that of the more Cr-rich compositions. At medium OCP (148 ± 33 mV; $0.45 \pm 0.03 \mu\text{A}\cdot\text{cm}^{-2}$), both parameters worsen, and the larger standard deviation in $E_{(i=0)}$ reflects the transitional and unstable nature of the surface in this intermediate condition. At low OCP (36 ± 10 mV; $0.99 \pm 0.06 \mu\text{A}\cdot\text{cm}^{-2}$), the corrosion potential drops dramatically and i_{corr} nearly doubles compared to the Medium OCP condition, indicating that the surface has shifted towards a more active dissolution regime with reduced corrosion resistance.

This behavior suggests that the OCP fluctuations observed in Figure 35 for Cr-11 correspond to cyclic transitions between an incipient passive state (or strongly reduced active dissolution state) and a more active dissolution state. Such cyclic behavior, alternating between local loss of surface protection and recovery of corrosion resistance, is characteristic of materials operating close to the active-passive transition threshold rather than systems exhibiting stable and fully developed passivation [46,49]. The corrosion current density extracted from each subgroup therefore remains a reliable and standard metric for comparing their relative corrosion severity. The large overall standard deviations observed for the undivided Cr-11 dataset ($i_{\text{corr}} = 0.48 \pm 0.29 \mu\text{A}\cdot\text{cm}^{-2}$) are thus interpreted as a consequence of averaging measurements acquired across different electrochemical surface states, and the subdivision approach effectively separates this variability into physically meaningful contributions.

In summary, these results indicate that a nominal addition of 11 wt.% Cr represents a transitional threshold in this system. Although this composition substantially suppresses corrosion and reduces the dissolution rate relative to the conventional Co binder, the surface state developed in Cr-11 appears metastable under the tested conditions. Cr concentrations of 13 wt.% or higher appear necessary to promote a more stable low-

dissolution regime and a more reproducible electrochemical response under local perturbations.

4.3.3. Electrochemical Impedance Spectroscopy

The EIS results are presented as Bode plots (Figure 38a) and Nyquist plots (Figure 38b). The corresponding equivalent circuits used to fit these experimental data are depicted in Figure 39.

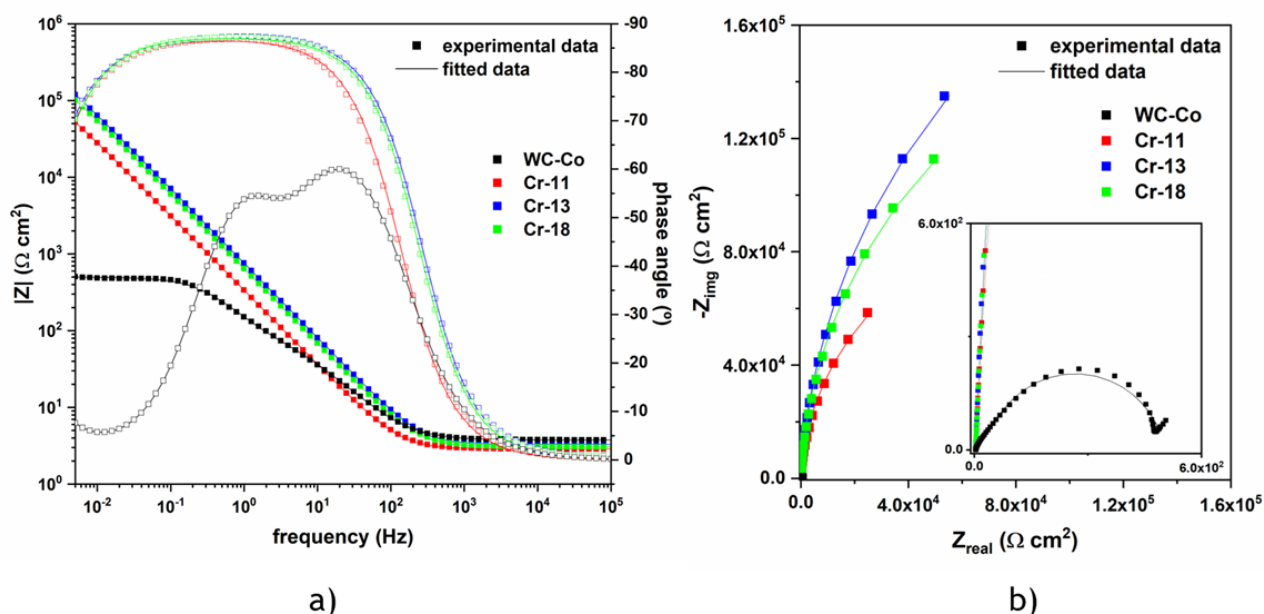


Figure 38 - Electrochemical impedance spectroscopy (EIS) spectra of the investigated composites: (a) Bode plots and (b) Nyquist plots.

The impedance modulus at low frequency ($|Z|_{f \rightarrow 0}$) constitutes a direct measure of the overall corrosion resistance of each sample [50]. As is immediately evident from Figure 38a, the WC-Co reference exhibits $|Z|_{f \rightarrow 0}$ in the order of $\approx 500 \Omega \cdot \text{cm}^2$, while the Cr-containing samples reach values of $10^5 \Omega \cdot \text{cm}^2$, a difference of more than two orders of magnitude. This contrast confirms, in full consistency with the potentiodynamic polarization results, the dramatic improvement in corrosion resistance afforded by the NiCrMo binder system. In the Bode phase angle plot, all Cr-containing samples display a single broad plateau, reaching values close to -90° and extending over approximately three decades of frequency ($\approx 10^{-2} - 10^1$ Hz), before decreasing smoothly to 0° at higher frequencies. The WC-Co sample, in contrast, exhibits a narrower, lower-amplitude peak (maximum phase angle of approximately -60°) centered around 20-30 Hz, together with a low-frequency tail at the lowest frequencies measured.

The Nyquist plots (Figure 38b) corroborate these observations. Rather than well-developed semicircular arcs, the Cr-containing samples display a steeply rising, near-linear trajectory with no curvature towards closure anywhere within the measured frequency window, indicating that the corresponding relaxation time constant lies beyond the lowest frequency probed and that the true charge-transfer resistance is substantially higher than the maximum $|Z|$ value directly read from the plot [51-53]. The inset in Figure

38b resolves the response of WC-Co on an appropriately small scale, revealing a depressed semicircle of small radius ($\approx 400 \Omega \cdot \text{cm}^2$) followed by a low-frequency deviation attributable to a finite-length diffusion element.

Based on these qualitative observations, two equivalent circuit models were employed for data fitting. For Cr-11, Cr-13, and Cr-18, the circuit represented in Figure 39a was selected, in which R_s represents the solution resistance, and the remaining elements are arranged as two nested time constants – one capturing the high-frequency semi-protective layer response (CPE_{HF} , R_{HF}) and the other the low-frequency double-layer/charge-transfer processes occurring at electrochemically active regions exposed to electrolyte penetration through the porous surface layer (CPE_{dl} , R_{ct}). Although the Cr-containing samples show only a single broad phase angle plateau rather than two clearly separated maxima, this is consistent with two relaxation processes whose characteristic frequencies are too close to be resolved as distinct peaks, an outcome that is common when the high and low frequency loops of a two-time-constant system are not well separated [50]. This does not preclude the use of the two-loop circuit, as confirmed by the excellent agreement subsequently obtained between the experimental and fitted data (Figures 38). Conversely, for the WC-Co reference sample, the equivalent circuit depicted in Figure 39b was employed. This model specifically incorporates a diffusion element to account for the mass transport limitations that characterize its active corrosion regime at low frequencies.

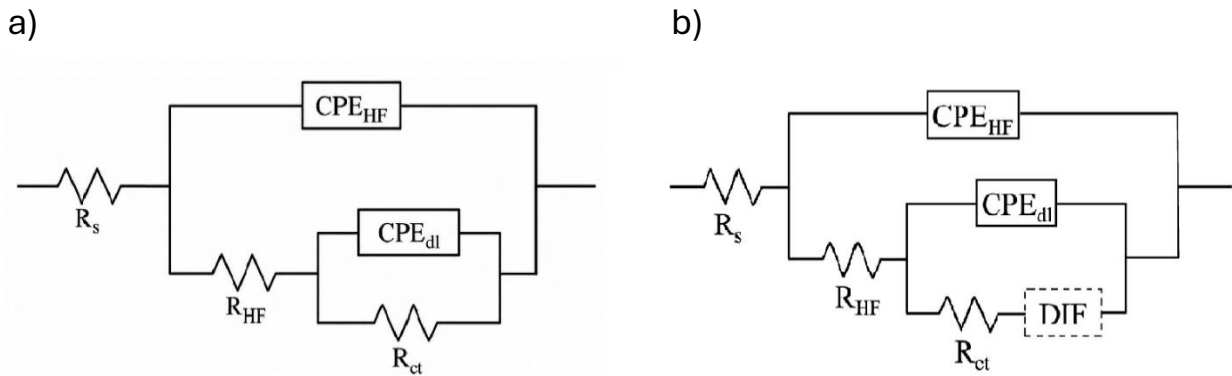


Figure 39 - Equivalent electrical circuits used to fit the experimental EIS data: (a) model with two-time constants and (b) model including a diffusion element.

In both loops of the two circuits, a constant phase element (CPE) was used instead of an ideal capacitor, since the surfaces studied are not perfectly smooth or homogeneous and therefore do not behave as ideal dielectrics. The CPE impedance is defined as:

$$Z_{\text{CPE}} = \frac{1}{Y_0(j\omega)^a} \quad (2)$$

where Y_0 (in $\Omega^{-1} \cdot \text{s}^a \cdot \text{cm}^{-2}$) is the admittance prefactor and a is the CPE exponent a , bounded between 0 and 1. A value of $a = 1$ corresponds to an ideal capacitor, while lower values represent increasing deviation from ideal capacitive behavior, generally attributed to surface roughness, porosity, or a distribution of local time constants across the electrode surface [52,54]. This deviation from ideality is routinely observed for both passive oxide

films and double-layer responses on real, non-uniform electrode surfaces [55], which justifies the use of CPE_{HF} and CPE_{dl} , rather than ideal capacitances, in the equivalent circuit adopted.

A practical limitation of Y_o is that, since its units depend on the value of a , it cannot be directly compared between samples or states with different CPE exponents – a situation that arises repeatedly in this study (seen in Tables 11 and 12). To allow physically meaningful comparison, the CPE parameters were converted into equivalent capacitances (C) using the Hsu-Mansfeld relation for the high-frequency loop (Equation 3) and the Brug relation for the low-frequency loop (Equation 4) [52,55]:

$$C_{HF} = Y_o^{\frac{1}{a}} \times R_{HF}^{\frac{(1-a)}{a}} \quad (3)$$

$$C_{dl} = Y_o^{\frac{1}{a}} \times \left(\frac{1}{R_s + R_{HF}} + \frac{1}{R_{ct}} \right)^{\frac{a-1}{a}} \quad (4)$$

where R_{HF} is the resistance of the high-frequency loop and R_{ct} is the charge transfer resistance, both normalised by the binder area ($\Omega.cm^2$), consistent with the area-normalised Y_o . For C_{HF} (Eq. 3), the expression accounts for the parallel resistance R_{HF} associated with the surface film/pore behavior. For C_{dl} (Eq. 4), the formulation incorporates both the charge transfer resistance (R_{ct}) and the uncompensated ohmic series resistance preceding the double layer ($R_s + R_{HF}$). Carrying out dimensional analysis confirms that both expressions yield C directly in $F.cm^{-2}$ (in this study expressed in $\mu F.cm^2$), independent of the value of a , thereby providing a rigorous basis for cross-sample comparison that Y_o alone cannot offer. The resulting C_{HF} and C_{dl} values are reported in Tables 11 and 12 alongside the raw CPE parameters and are used throughout the discussion below wherever a direct physical comparison between samples is required.

The physical interpretation of the equivalent electrical circuits rests on modeling a duplex interfacial structure, composed of a porous outer surface layer and an underlying reactive metal interface located at the base of the pores. Within this framework, R_s represents the uncompensated ohmic resistance of the bulk electrolyte between the reference electrode and the working electrode surface. Within the porous outer surface film, R_{HF} accounts for the pore solution resistance confined inside the open channels formed during corrosion. The non-ideal capacitive response of this outer layer is modeled by CPE_{HF} , which encompasses both the dielectric behavior of the semi-passive corrosion product film and the double-layer capacitance associated with the exposed WC skeleton surfaces along the pore walls. Deep within the porous structure at the base of the pore channels, where binder dissolution primarily takes place, the response of the active metallic matrix interface is captured by CPE_{dl} and R_{ct} . Specifically, CPE_{dl} describes the non-ideal double-layer capacitance at this underlying metallic interface, while R_{ct} measures the charge-transfer resistance associated with the faradaic reactions. Circuit of Figure 39a is applied under conditions where the electrochemical process at the base of the pores is purely governed by charge-transfer kinetics, indicating that the transport of electroactive species through the pore network occurs without significant mass-transport hindrance.

For WC-Co specifically, the low-frequency tail observed in the Nyquist plot (Figure 38b) could not be captured by the two-loop circuit alone. This response indicates that the faradaic processes taking place at the metallic interface are governed by mixed kinetic control, being restricted simultaneously by charge-transfer kinetics and mass-transport limitations. To describe this combined response, a diffusion element (DIF) was incorporated in series with the charge-transfer resistance (R_{ct}) (Figure 39b), represented by a bounded (finite-length) Warburg element. This element is characterized by the Warburg admittance Y_{o_dif} and the time-constant parameter B_{dif} , as reported directly by the fitting software [56].

On a mechanistic level, this element accounts for the low-frequency diffusional contribution associated with the transport of dissolved Co^{2+} ions away from the actively corroding binder and the ingress of aggressive ionic species (Cl^- , H^+) through the porous surface layer [45]—a transport restriction that the simpler two-loop circuit, sufficient for the passivated Cr-containing samples, does not need to describe. Crucially, as a macroscopic phenomenological model, the Bounded Warburg element captures this combined mass-transport hindrance without requiring individual parameterization for each specific ionic species, thereby offering a robust physical description of both the resistive and capacitive features of the diffusion-limited faradaic response. The bounded Warburg impedance is given by:

$$Z = \frac{1}{Y_{o_dif}\sqrt{i\omega}} \cdot coth(B_{dif}\sqrt{j\omega}) \quad (5)$$

where $Y_{o_dif}(\Omega^{-1}.s^{1/2}.cm^{-2})$ is the Warburg admittance, related to the diffusion coefficient D and concentration of the electroactive species, and $B_{dif} = L/\sqrt{D}$ is a diffusion parameter (units of $s^{1/2}$) associated with the finite diffusion length L [50,51,56].

The EIS fitted parameters for all samples are compiled in Table 11. Additionally, the goodness of fit, evaluated via the chi-squared (χ^2) parameter, was lower than 5.31×10^{-4} for all fitted curves, confirming the high statistical reliability of the proposed equivalent circuit models. The high OCP subgroup of Cr-11 is used for comparison, consistent with the approach adopted in the potentiodynamic analysis.

Table 11 - Equivalent circuit parameters extracted from the EIS fitting for the investigated composites.

	WC-Co	Cr-11	Cr-13	Cr-18
$R_{sol} (\Omega.cm^2)$	3.75 ± 0.03	2.97 ± 0.07	3.37 ± 0.10	2.95 ± 0.10
$Y_{o_HF} (\mu\Omega^{-1}.s^a.cm^{-2})$	670 ± 142	421 ± 44	219 ± 4	252 ± 4
a_{HF}	0.87 ± 0.01	0.96 ± 0.02	0.98 ± 0.00	0.97 ± 0.00
$R_{HF} (\Omega.cm^2)$	159 ± 27	52 ± 38	143 ± 30	2197 ± 1292
$C_{HF} (\mu F.cm^{-2})$	478 ± 101	359 ± 78	201 ± 5	246 ± 7

$Y_{o_dl} (\mu\Omega^{-1}.s^a.cm^{-2})$	1047 ± 142	36 ± 14	10 ± 5	6 ± 3
a_{dl}	0.96 ± 0.00	0.89 ± 0.02	0.67 ± 0.07	0.67 ± 0.07
$R_{ct} (\times 10^3 \Omega.cm^2)$	0.35 ± 0.09	138 ± 42	487 ± 45	375 ± 52
$C_{dl} (\mu F.cm^{-2})$	985 ± 137	17 ± 8	0.76 ± 0.77	0.34 ± 0.33
$Y_{o_dif} (\times 10^5 \mu\Omega^{-1}.s^a.cm^{-2})$	3.21 ± 0.82			
$B_{dif} (s^{1/2})$	1.78 ± 0.31			

The solution resistance R_s is consistently low ($\approx 3 \Omega.cm^2$) across all samples, as expected for a highly conductive electrolyte (0.5 M NaCl + HCl, pH 2). The negligible variation between samples confirms that observed differences in impedance response arise from interfacial phenomena and not from experimental artefacts [51,53,56].

Protective layer response (CPE_{HF} , R_{HF} , C_{HF})

Because a_{HF} varies between samples (0.87-0.98), Y_{o_HF} values are not strictly comparable across the dataset, and the converted equivalent capacitance C_{HF} (Equation 3) is used here instead. C_{HF} decreases in the order WC-Co ($478 \pm 101 \mu F.cm^{-2}$) > Cr-11 ($359 \pm 78 \mu F.cm^{-2}$) > Cr-18 ($246 \pm 7 \mu F.cm^{-2}$) > Cr-13 ($201 \pm 5 \mu F.cm^{-2}$). The physical significance of this trend is defined by the fundamental relationship for the capacitance of a dielectric layer:

$$C = \frac{\epsilon_o \epsilon_r A}{d} \quad (6)$$

where ϵ_o is the vacuum permittivity, ϵ_r is the relative permittivity of the dielectric film, A is the electroactive area, and d is the film thickness [52]. The lower CPE-derived capacitance for Cr-13 suggests the formation of a more compact and/or thicker corrosion product layer, which is consistent with improved corrosion resistance observed in potentiodynamic tests. In contrast, the higher apparent capacitance for WC-Co may be associated with a more porous and hydrated surface film, which increases the effective dielectric constant and electrochemically active area. However, given the non-ideal nature of the CPE response, these interpretations should be considered qualitative rather than direct measurements of film thickness or true capacitance [50,57,58]. The CPE exponent a_{HF} approaches unity for all Cr-containing samples (0.96-0.98), indicating a high degree of uniformity and homogeneity in the semi-protective layers formed. The slightly lower value for WC-Co (0.87) confirms the greater surface heterogeneity of the unpassivated reference.

The high-frequency resistance (R_{HF}), which characterizes the ionic resistance through the outer surface layer (the first boundary in direct contact with the electrolyte), reveals critical differences in interfacial porosity. For Cr-11, the low R_{HF} ($52 \pm 38 \Omega.cm^2$) reflects a highly porous interface caused by cyclic surface destabilization [57]. Conversely, Cr-13 shows a higher R_{HF} ($143 \pm 30 \Omega.cm^2$) which, coupled with a lower C_{HF} , confirms a more compact and restrictive Cr-rich semi-protective layer [58]. The WC-Co reference displays a numerically similar R_{HF} ($159 \pm 27 \Omega.cm^2$), but its high capacitance indicates this

resistance originates from a thick, porous sludge of actively leaching corrosion products rather than a true barrier [59]. Finally, the Cr-18 R_{HF} values must be interpreted with caution: this anomalously high R_{HF} ($2197 \pm 1292 \Omega \cdot \text{cm}^2$) is accompanied by an extremely large standard deviation, directly reflecting the microstructural inhomogeneity of this sample. Depending on the local surface composition probed in each measurement — whether Cr-rich pockets or binder-matrix regions — the high-frequency impedance response varies considerably, resulting in poor reproducibility of R_{HF} for this composition [48,49].

Double-layer response (CPE_{dl} , R_{ct} , C_{dl})

The same comparability issue applies to $Y_{0,dl}$, given the large spread in a_{dl} between WC-Co (0.96) and the Cr-containing samples (0.67-0.89); the equivalent double-layer capacitance C_{dl} is therefore used for comparison. C_{dl} is dramatically higher for WC-Co ($985 \pm 137 \mu\text{F} \cdot \text{cm}^{-2}$) than for the Cr-containing samples ($0.34\text{-}17 \mu\text{F} \cdot \text{cm}^{-2}$), representing values typical of an actively corroding bare metal surface versus a kinetically hindered interface, respectively [52]. A large C_{dl} reflects an extensive, accessible electrochemically active interface: in WC-Co, continuous binder leaching progressively exposes fresh metallic Co surface, maintaining a large and reactive double-layer area [59]. Conversely, in the Cr-containing samples, the semi-protective surface layer physically shields the metal from the electrolyte, drastically reducing the effective electrochemically active area [53]. Among the Cr-containing samples, C_{dl} decreases monotonically from Cr-11 ($17 \mu\text{F} \cdot \text{cm}^{-2}$) to Cr-13 ($0.76 \mu\text{F} \cdot \text{cm}^{-2}$) to Cr-18 ($0.34 \mu\text{F} \cdot \text{cm}^{-2}$), indicating that Cr-18 presents the smallest effective electroactive double-layer area — a trend that was not evident from $Y_{0,dl}$ alone. The lower a_{dl} values observed for Cr-13 and Cr-18 (0.67) compared to WC-Co (0.96) reflect an electrochemically heterogeneous and geometrically restricted interface, although the underlying microstructural causes for this deviation from ideality differ between the two alloys [50]. For the microstructurally homogeneous Cr-13, this restricted charge transfer is likely confined to microscopic defects or phase boundaries within its highly protective Cr-rich film, creating a non-uniform metal-electrolyte contact zone [52]. Conversely, for Cr-18, this localized charge transfer is further exacerbated by its inherent microstructural segregation. While its extremely low capacitance confirms that the overall binder surface is extensively shielded, the few unprotected gaps in the protective layer may coincide with underlying compositional gradients (Cr-rich pockets versus a depleted matrix). These specific sites act as focal points for intense micro-galvanic coupling [48,60]. This distinction perfectly explains why Cr-18, despite having the smallest exposed area (lowest C_{dl}), exhibits faster local dissolution kinetics and a slightly lower charge-transfer resistance than the more homogeneous Cr-13.

Charge-transfer resistance (R_{ct})

The charge-transfer resistance R_{ct} is widely regarded as the single most informative EIS parameter for corrosion resistance assessment, being inversely related to the corrosion current density i_{corr} through the Stern-Geary relationship [61]:

$$i_{corr} = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)R_p} \quad (7)$$

where β_a and β_c are the anodic and cathodic Tafel slopes, respectively, and R_p is the polarization resistance, which is effectively equivalent to R_{ct} in these systems. The difference in R_{ct} between WC-Co ($(0.35 \pm 0.09) \times 10^3 \Omega \cdot \text{cm}^2$) and the Cr-containing samples ($\approx 10^5 \Omega \cdot \text{cm}^2$) spans approximately three orders of magnitude, unambiguously confirming the superiority of the NiCrMo binder in resisting charge-transfer driven corrosion processes. Among the Cr-containing samples, Cr-13 exhibits the highest R_{ct} ($(487 \pm 45) \times 10^3 \Omega \cdot \text{cm}^2$), consistent with its lowest i_{corr} in the potentiodynamic polarization tests, reinforcing the identification of Cr-13 as the optimal composition under these conditions. Cr-18 yields an intermediate R_{ct} ($(375 \pm 52) \times 10^3 \Omega \cdot \text{cm}^2$), slightly below that of Cr-13, which is again attributable to the detrimental effect of microstructural heterogeneity. Cr-11 presents the lowest R_{ct} among the Cr-containing samples ($138 \pm 42 \times 10^3 \Omega \cdot \text{cm}^2$), in full agreement with its higher i_{corr} and reflecting the lower integrity and metastable nature of its semi-protective surface condition.

For WC-Co specifically, the relative significance of the diffusional contribution captured by the bounded Warburg element can be assessed directly through the magnitude of its admittance parameter (Y_{o_dif}). In electrochemical impedance, admittance represents the ease with which a charge or mass transport process occurs, acting inversely to impedance[50]. As shown in Table 11, the fitted Warburg admittance for the WC-Co sample is exceptionally high ($(3,21 \pm 0.82) \times 10^5 \mu\Omega^{-1} \cdot \text{s}^a \cdot \text{cm}^{-2}$) which corresponds to $0.321 \Omega^{-1} \cdot \text{s}^a \cdot \text{cm}^{-2}$ in base units. This massive admittance value indicates that the mass transport process offers virtually negligible impedance to the overall electrochemical system. Consequently, the bottleneck of the reaction is heavily dominated by the charge-transfer resistance at the metal interface ($R_{ct} = (0.35 \pm 0.09) \times 10^3 \Omega \cdot \text{cm}^2$) [59]. This substantial contrast in magnitudes confirms that the active corrosion process in the conventional WC-Co hardmetal is predominantly charge-transfer controlled [58]. The diffusional contribution acts merely as a minor secondary phenomenon at very low frequencies, characterized by a finite diffusion time constant parameter ($B_{dif} = 1.78 \pm 0.31 \text{ s}^{1/2}$) [50,58].

4.3.3.1. EIS Analysis of Cr-11 Subgroups

The EIS Bode and Nyquist plots for the three Cr-11 subgroups are shown in Figure 40, respectively, and the corresponding fitted parameters are compiled in Table 12. The goodness of fit, evaluated via the chi-squared (χ^2) parameter, was consistently lower than 6.12×10^{-4} for all fitted curves, confirming the high statistical reliability of the applied equivalent circuit models.

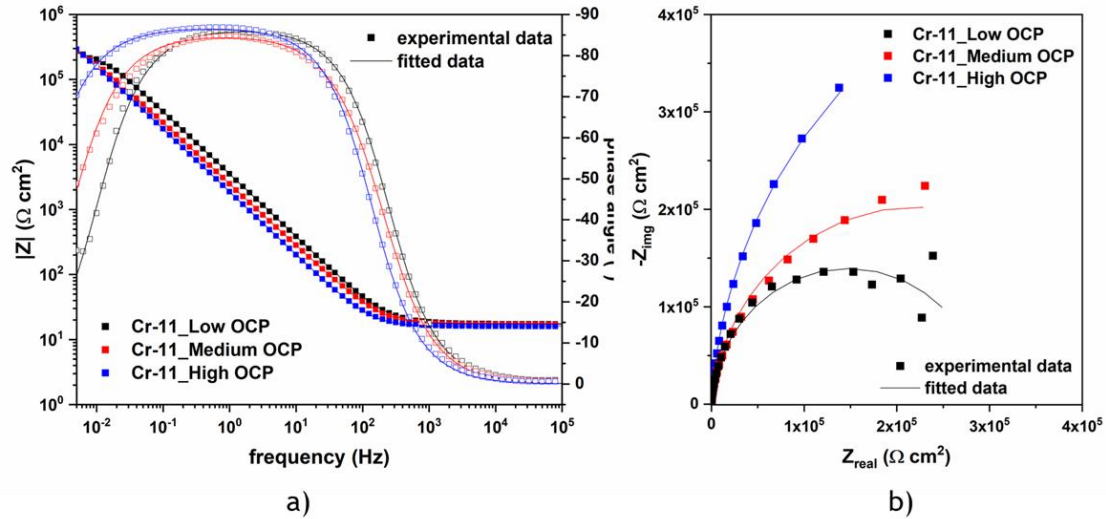


Figure 40 - Electrochemical impedance spectroscopy (EIS) spectra for the different OCP states of the Cr-11 alloy: (a) Bode plots and (b) Nyquist plots.

Table 12 - Equivalent electrical circuit parameters extracted from the EIS fitting for the distinct OCP states of the Cr-11 composite.

Cr-11	Cr-11_Low OCP	Cr-11_Medium OCP	Cr-11_High OCP
$R_{sol} (\Omega.cm^2)$	3.19 ± 0.03	2.94 ± 0.13	2.97 ± 0.07
$Y_{o_HF} (\mu\Omega^{-1}.s^a.cm^{-2})$	267 ± 3	369 ± 47	421 ± 44
a_{HF}	0.97 ± 0.00	0.96 ± 0.01	0.96 ± 0.02
$R_{HF} (\Omega.cm^2)$	382 ± 143	146 ± 29	52 ± 38
$C_{HF} (\mu F.cm^{-2})$	245 ± 3	330 ± 47	359 ± 78
$Y_{o_dl} (\mu\Omega^{-1}.s^a.cm^{-2})$	3.15 ± 3.01	23 ± 2	36 ± 14
a_{dl}	0.89 ± 0.03	0.86 ± 0.07	0.89 ± 0.02
$R_{ct} (\times 10^3 \Omega.cm^2)$	65.4 ± 12.4	94.2 ± 15.5	138 ± 42
$C_{dl} (\mu F.cm^{-2})$	1.31 ± 1.25	10 ± 4	17 ± 8

The Bode plots (Figure 40a) reveal that all three Cr-11 subgroups share the same qualitative shape at mid-to-high frequencies – characterized by two closely spaced relaxation processes and a similar phase angle maximum of approximately -80° to -85° – confirming that the fundamental corrosion mechanism is identical across the three OCP states. However, significant differences emerge in the low-frequency region. Alongside the systematic increase in the magnitude of $|Z|$ from low to high OCP, the phase angle profiles also diverge: the phase angle of the low OCP subgroup begins to decay towards 0° at noticeably higher frequencies than the high OCP state. This earlier transition from

capacitive to resistive behavior reflects the compromised integrity of the semi protective surface layer [57]. The Nyquist plots (Figure 40b) reinforce this, showing capacitive arcs with clearly distinguishable diameters that grow progressively larger from low to high OCP. This confirms that the initial OCP state directly dictates the varying extent and effectiveness of the protective barrier.

Analysis of the fitted parameters in Table 12 reveals several physically significant trends. As previously established, the equivalent capacitance C (Equation 6) is used for direct physical interpretation. C_{HF} increases monotonically from low to high OCP ($245 \rightarrow 330 \rightarrow 359 \mu\text{F.cm}^{-2}$). Since capacitance is inversely proportional to film thickness, this trend mathematically indicates that the high-frequency layer present at Low OCP is effectively thicker than the barrier at high OCP. From an electrochemical standpoint, this suggests that the low OCP surface is covered by a thicker, less compact accumulation of hydrated corrosion products (precipitated following the localized film breakdown), rather than the compact Cr-rich semi-protective layer characteristic of the kinetically hindered high OCP state. Furthermore, this thick, porous sludge exhibits a higher ionic resistivity, which physically explains the counter-intuitive increase in R_{HF} observed at low OCP ($382 \Omega.\text{cm}^2$) compared to High OCP ($52 \Omega.\text{cm}^2$). In established duplex film models, the high-frequency response (R_{HF}) characterizes the ionic resistance through the pores of the outer surface layer [51,57]. Upon local destabilization of this surface layer and subsequent enhanced active anodic dissolution, precipitated corrosion products accumulate and thicken the outer interface, restricting the physical transport of ions from the electrolyte and thereby increasing the apparent high-frequency resistance [51,57]. Importantly, the true protection of the alloy is governed by the charge-transfer resistance at the metal interface (R_{ct}), which drops drastically under these localized breakdown conditions. Importantly, the CPE exponent a_{HF} remains constant across all three states (0.96-0.97), demonstrating that the local homogeneity of this outer interface is preserved.

In a nested equivalent circuit modeling passivity, the low-frequency capacitance (C_{dl}) characterizes the inner semi-protective barrier layer at the metal interface. C_{dl} is drastically lower for the low OCP subgroup ($1.31 \pm 1.25 \mu\text{F.cm}^{-2}$), compared to the high OCP subgroup ($17 \pm 8 \mu\text{F.cm}^{-2}$). This sharp contrast highlights a fundamental structural difference between the tested states. The high capacitance of the high OCP sample reflects an extremely thin, highly compact inner barrier layer, which is characteristic of stable passivity [55,58]. Conversely, the severely diminished capacitance of the low OCP sample indicates the absence of this pristine barrier; its metal interface is instead characterized by a thicker, ill-defined, and non-protective active structure associated with destabilization of the semi-protective layer [55,58].

Consequently, the charge-transfer resistance (R_{ct}) exhibits a systematic correlation with the respective OCP subgroup, recording values of $(65.4 \rightarrow 94.2 \rightarrow 138) \times 10^3 \Omega.\text{cm}^2$ for the low, medium, and high OCP samples, respectively. This confirms a direct structural correspondence between the open-circuit stabilization level and the semi-protective layer integrity: samples that stabilized at lower OCP values possess a inherently weaker barrier to charge transfer, corresponding to inherently faster corrosion kinetics [58,59]. This

correlation is quantitatively consistent with the i_{corr} values extracted from the potentiodynamic polarization tests for these distinct subgroups, robustly validating the internal coherence of the dataset. Crucially, even the low OCP sample retains an R_{ct} of $65.4 \times 10^3 \Omega \cdot \text{cm}^2$, which is approximately 185 times higher than that of the WC-Co reference ($0.35 \times 10^3 \Omega \cdot \text{cm}^2$). This establishes that even the subgroup exhibiting the least protective surface condition provides substantially superior corrosion protection, underlining the fundamental benefit of Cr incorporation in the binder.

4.3.4. Corroded Surfaces Analysis

To physically validate the degradation mechanisms proposed by the electrochemical techniques, the surfaces of the composites were examined using SEM and EDS after the severe electrochemical testing in the 0.5 M NaCl + HCl (pH 2) solution. The analysis compares the uncorroded reference surfaces (top images, a) with the post-corrosion morphologies (bottom images, b) for each composition, accompanied by their respective localized chemical analyses (Figure 41, 43, 45, 46).

At a microscopic level, the post-corrosion SEM analysis of the WC-Co sample may not immediately exhibit a completely collapsed sponge-like structure, as the hard tungsten carbide skeleton remains physically intact (Figure 41b). However, a macroscopic visual inspection of the tested sample (Figure 42a) provides undeniable evidence of severe active dissolution. The circular area exposed to the acidic electrolyte developed a thick, distinctly colored yellowish/bluish film, which is characteristic of accumulated solid corrosion products and metal-oxide sludge on the surface [16,58]. The EDS analysis perfectly correlates with this macroscopic observation. The chemical quantification reveals a drastic depletion of the metallic binder, with the Co content dropping from an initial 14.61 wt.% down to 6.90 wt.%. Concurrently, a massive surge in oxygen is detected, reaching 9.60 wt.%. These combined results indicate that while the WC grain network remains visible, the underlying cobalt binder has undergone deep, active anodic dissolution (leaching) (Figure 42b). The visible macroscopic film and the high oxygen content in the EDS confirm the formation of a thick, non-protective layer of mixed oxides/hydroxides (e.g., hydrated tungsten oxides and dissolved cobalt species) [13,16]. This degraded, highly oxidized surface physically validates the massive active dissolution and the enormous double-layer capacitance (C_{dl}) previously modeled in the EIS data.

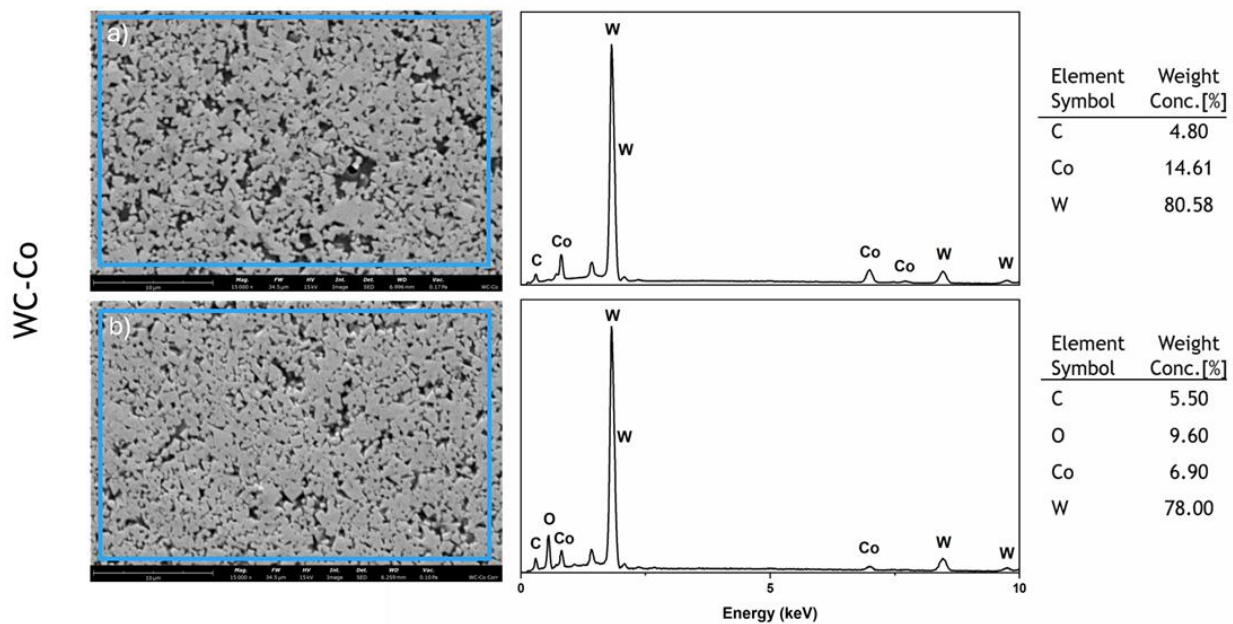


Figure 41 - Surface morphology and EDS compositional analysis of the reference WC-Co hardmetal: (a) uncorroded surface and (b) corroded surface.

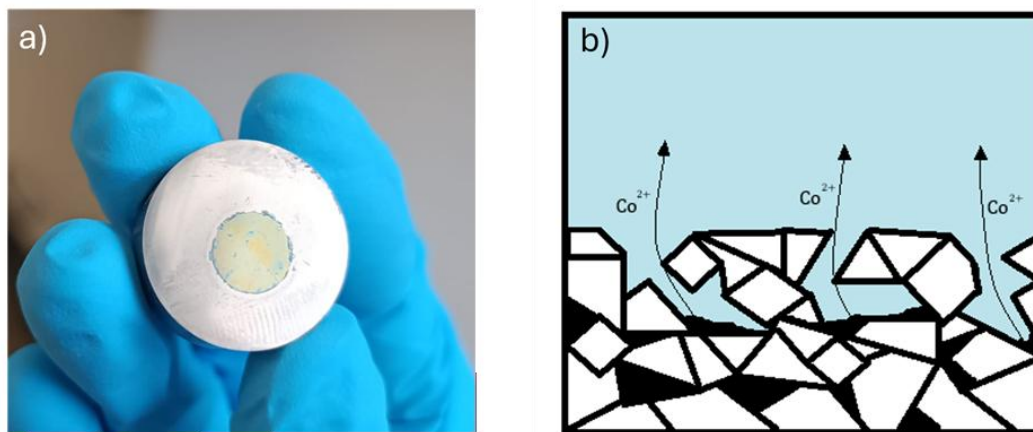


Figure 42 - Post-corrosion analysis of the WC-Co sample: (a) macroscopic view of the corroded surface, and (b) schematic illustration of the deep binder leaching process.

The uncorroded Cr-11 sample displays a uniform distribution of the Ni-based binder (Figure 43a). Following the corrosion test, the surface reveals clear intergranular voids where the metallic matrix has been leached away by the aggressive acidic chloride electrolyte, exposing the sharp, faceted edges of the WC grains. The localized chemical analysis highlights a severe drop in Ni concentration, plummeting from an initial 7.79 wt.% to a mere 0.60 wt.%. Unlike the WC-Co reference, the oxygen content remains remarkably low at 1.70 wt.%. This confirms that the Cr-11 composite does not undergo massive, generalized oxidation. Instead, it suffers from localized active dissolution (leaching) precisely at the sites where its metastable semi-protective film ultimately failed (Figure 44)[4,28]. The low oxygen content proves the absence of a thick corrosion product scale [58].

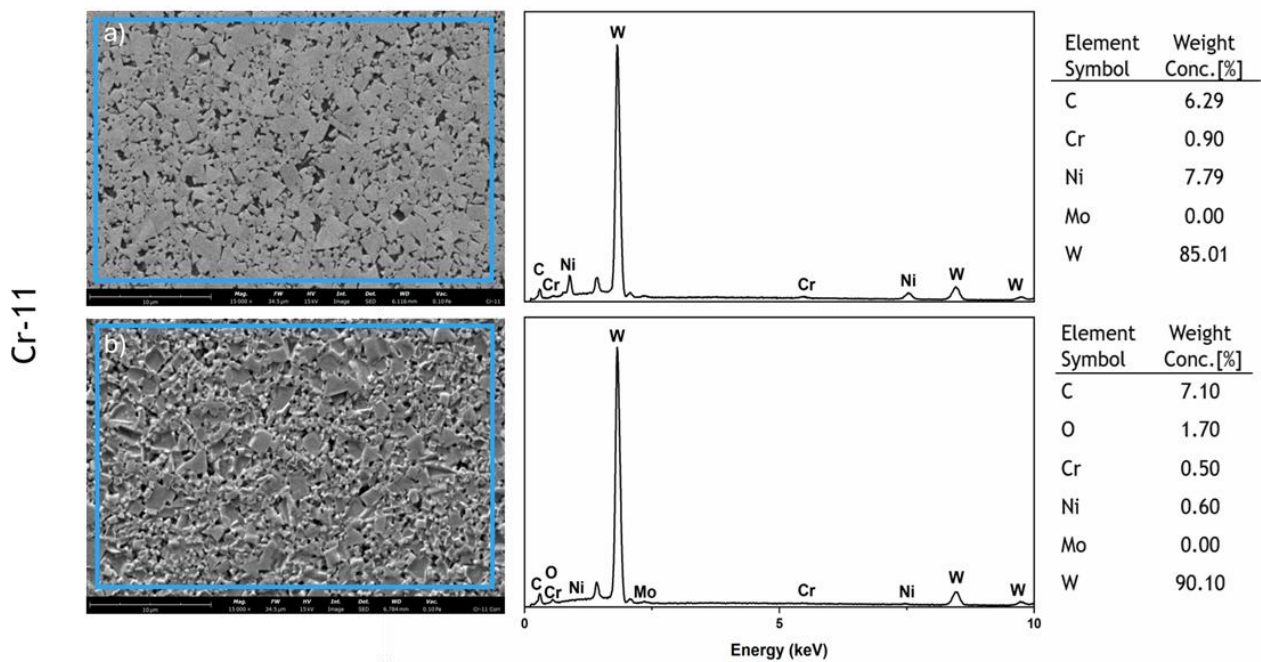


Figure 43 - Surface morphology and EDS compositional analysis of the reference Cr-11 hardmetal: (a) uncorroded surface and (b) corroded surface.

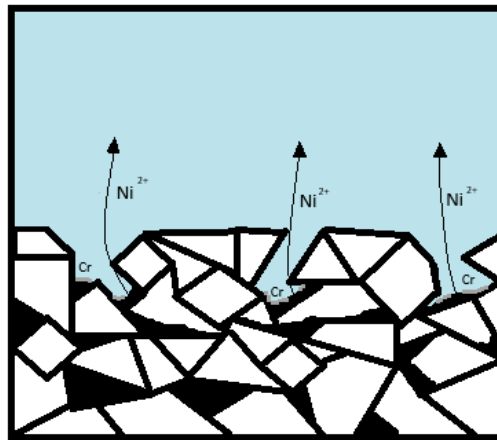


Figure 44 - Schematic representation of the corrosion mechanism in the NiCrMo binder, illustrating the selective anodic dissolution (leaching) of Ni^{2+} and the formation of a semi-protective Cr-rich passive layer at the metal-electrolyte interface.

The corroded morphology of the Cr-13 sample is visually similar to that of the Cr-11, exhibiting localized binder depletion (Figure 45b) [4,28]. However, the structural integrity of the composite appears slightly better preserved, with fewer deep voids. The EDS data reveals that the Ni content drops from 8.99 wt.% to 2.00 wt.%. The oxygen concentration remains low, matching the Cr-11 sample at 1.70 wt.%. While selective leaching still occurs upon the localized breakdown of the semi protective layer at high anodic potentials, the Cr-13 sample retains a significantly higher fraction of its initial binder (2.00 wt.% compared to the 0.60 wt.% of Cr-11) [4,58]. This compositional retention physically

supports the electrochemical data, confirming its superior stability and higher restoration capability in the highly aggressive medium [23].

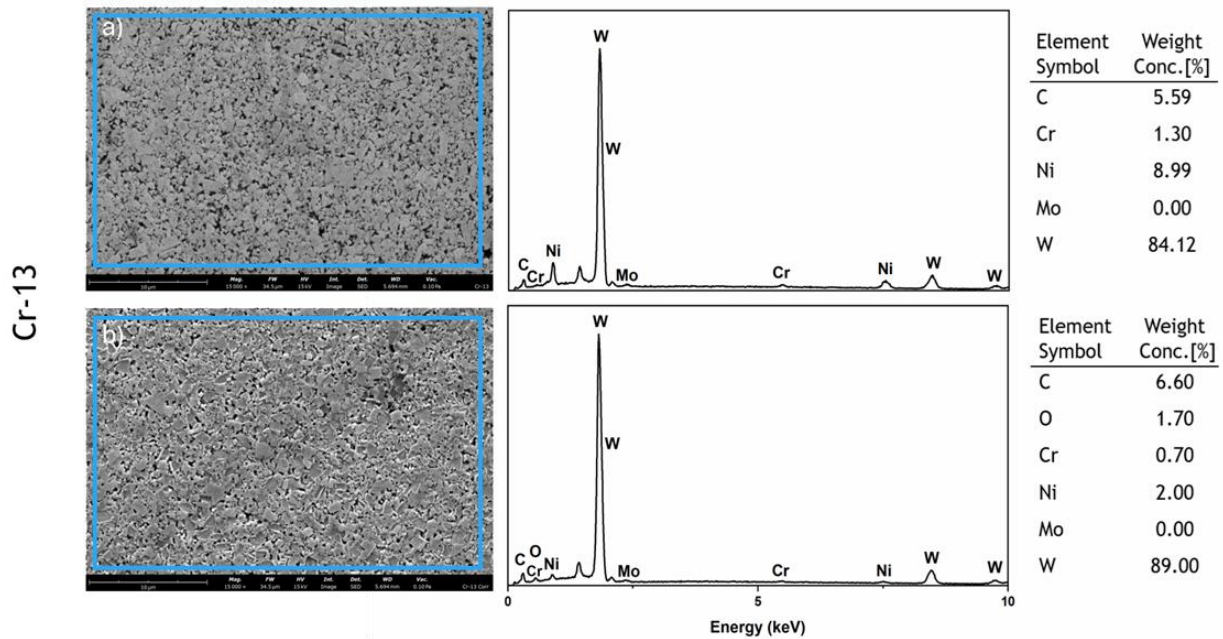


Figure 45 - Surface morphology and EDS compositional analysis of the reference Cr-13 composite: (a) uncorroded surface and (b) corroded surface.

The Cr-18 sample presents a highly distinct post-corrosion signature (Figure 46b). The uncorroded surface already hints at microstructural heterogeneities. After corrosion, the morphology reveals the emergence of distinct, brightly contrasting particles protruding across the surface in relief, while the surrounding matrix appears excavated. The overall Ni content drops from 8.89 wt.% to 1.40 wt.%. Paradoxically, despite its excellent overall corrosion resistance, it records an unexpectedly high oxygen concentration (9.01 wt.%), which is comparable to the severely degraded WC-Co sample. The protruding morphological features are, in fact, the primary WC grains. During the electrochemical test, the surrounding Ni solid solution undergoes severe localized leaching. As the binder dissolves, the hard WC grains are left standing in relief, creating a skeletonized surface. However, EDS analysis reveals that while Ni is heavily depleted, Cr is preferentially retained in the remaining binder pools. The high oxygen content is the direct chemical signature of a thick, robust, and highly oxidized semi-passive layer that grew preferentially within these Cr-enriched intergranular regions and on the exposed surfaces [4,23]. This visual and compositional evidence aligns seamlessly with the EIS modeling: the extreme chromium content promotes a highly resistive, heavily oxidized surface barrier, which perfectly justifies the anomalous surge in the high-frequency film resistance ($R_{HF} \approx 2197 \Omega \cdot \text{cm}^2$) and successfully chokes further charge transfer despite the textural alteration of the surface.

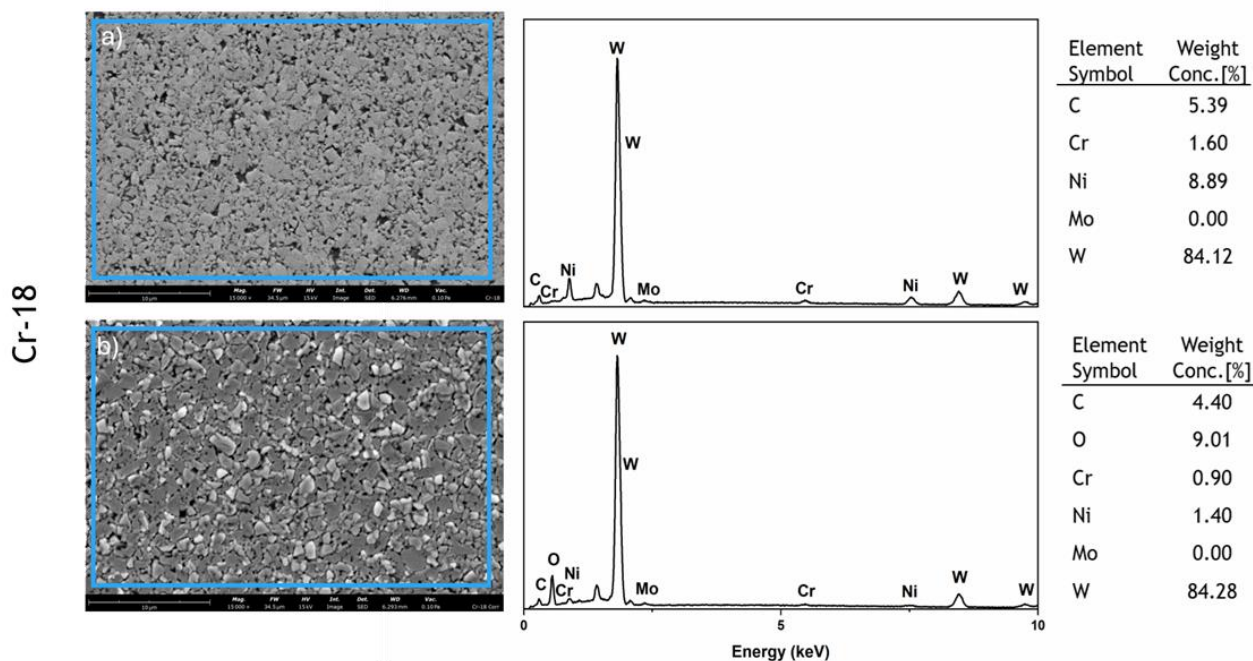


Figure 46 - Surface morphology and EDS compositional analysis of the reference Cr-18 composite: (a) uncorroded surface and (b) corroded surface.

4.3.5. Overall Electrochemical Remarks

The combined OCP, potentiodynamic polarization, EIS, and SEM/EDS results converge on a consistent and physically coherent picture of the corrosion behavior of WC-NiCrMo composites as a function of Cr content. Five principal conclusions can be drawn.

First, the substitution of Co by a NiCrMo binder dramatically improves corrosion resistance in aggressive chloride-acid environments. The corrosion current density is reduced by two to three orders of magnitude, the corrosion potential shifts approximately 500 mV in the noble direction, and the charge-transfer resistance increases by approximately three orders of magnitude relative to WC-Co. This improvement is driven by the formation of a Cr-rich semi-protective surface layer — likely comprising oxide/hydroxide islands and surface enrichment driven by selective Ni dissolution — which partially separates the metal from the electrolyte and kinetically suppresses electrochemical dissolution.

Second, a critical minimum Cr content exists within the binder, estimated at approximately 13 wt.%, below which a stable kinetically hindered state cannot be maintained. At 11 wt.% Cr, the semi-protective condition is repeatedly disrupted by chloride attack and undergoes cyclic destabilization and local restoration, resulting in metastable OCP behavior, elevated corrosion current variability, and a reduced charge-transfer resistance compared to higher Cr compositions. At and above 13 wt.%, the establishment of this low-dissolution surface regime is prompt, stable, and highly reproducible.

Third, increasing Cr content beyond 13 wt.% does not yield proportional corrosion benefits and may be detrimental if it results in microstructural inhomogeneity. The Cr-18 sample,

which contains Cr-rich pockets due to incomplete homogenization, exhibits a slightly higher i_{corr} and lower R_{ct} than Cr-13, and displays anomalously large variability in R_{HF} . This demonstrates that compositional homogeneity within the binder matrix is as important as the absolute Cr content in determining electrochemical performance.

Fourth, the OCP-state subdivision applied to Cr-11 reveals that the corrosion mechanism of this sample does not change qualitatively between surface states – only the extent and coverage of the semi-protective layer vary. The consistent a_{HF} values across high, medium, and low OCP states confirm that the local quality of this kinetically hindered interface is independent of the overall stabilization state, and that the observed variability arises from differences in the fraction of the surface that is effectively protected at any given moment.

Fifth, SEM and EDS analysis of the corroded surfaces provides direct morphological and compositional confirmation of the mechanisms inferred electrochemically. The sharp decrease in surface Co content and the appearance of oxygen-rich corrosion products in WC-Co confirm massive binder leaching, while the preferential loss of Ni relative to Cr in all three Cr-containing samples confirms the selective protective role of Cr-driven surface enrichment. The elevated post-corrosion oxygen content and pronounced morphological alteration observed for Cr-18 directly support the hypothesis that microstructural inhomogeneity compromises local protection efficiency, while the well-preserved surface morphology and low oxygen content of Cr-13 confirm it as the most corrosion-resistant composition.

Taken together, these findings suggest that a Cr content of approximately 13 wt.% in the NiCrMo binder represents the optimal composition for corrosion resistance under the tested conditions, balancing effective and stable passivation with microstructural homogeneity.

4.4. Tribocorrosion results

The synergistic effect of mechanical wear and electrochemical corrosion was evaluated through tribocorrosion tests. Figure 47 illustrates the simultaneous evolution of the coefficient of friction (μ) and the OCP before, during, and after the mechanical sliding action.

It is important to emphasize that the baseline OCP values recorded at the beginning of these tribocorrosion tests differ from those obtained in the pure electrochemical assays detailed in Section 4.3. This variation is primarily attributed to distinct experimental parameters inherent to the tribo-electrochemical setup itself. Specifically, factors such as differences in the sample mounting system, the galvanic coupling effect between the exposed wear track area and the unworn surface area, ambient humidity, and localized temperature all contribute to the shift in the initial thermodynamic stabilization of the samples [7,8].

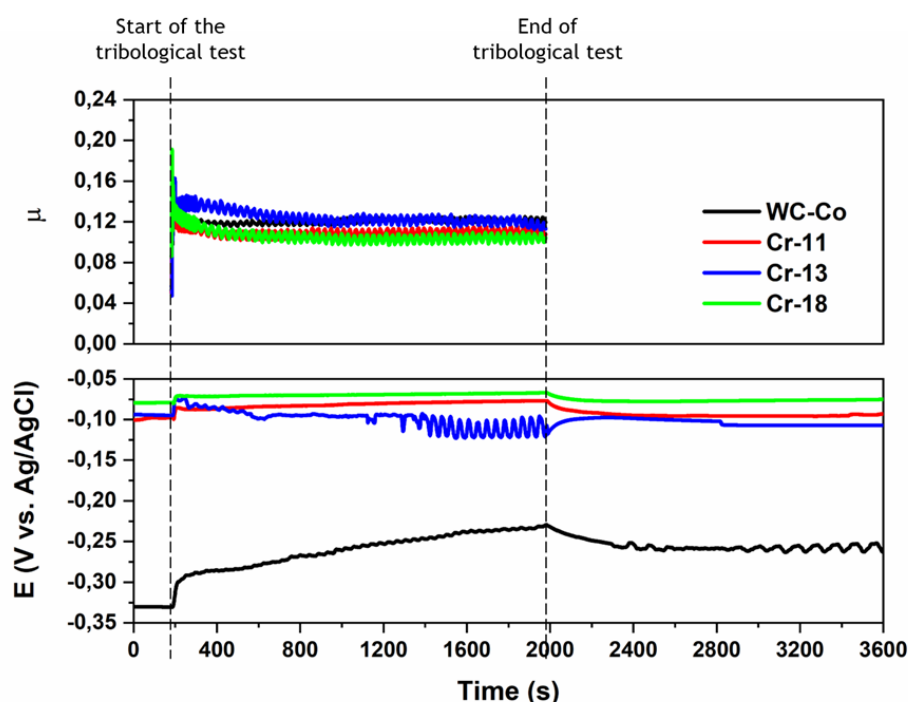


Figure 47 - Evolution of the coefficient of friction (μ) and open-circuit potential (OCP) over time during the tribocorrosion tests.

Looking at the mechanical response (Figure 47, top), all samples exhibit a typical running-in period immediately following the start of the tribological test (at $t = 180$ s), characterized by a sharp initial spike in the friction coefficient. This is associated with the initial contact and fracture of superficial asperities [62]. After this brief period, the friction coefficient stabilizes into a steady-state regime for the remainder of the sliding period. The steady-state μ values are relatively low and comparable across all samples (ranging approximately between 0.10 and 0.14), as expected for ceramic-ceramic contact in the presence of an electrolyte, which can promote partial lubrication and reduce friction [63]. The Cr-11 and Cr-18 samples display a very stable and smooth friction profile. In contrast, the Cr-13 sample exhibits slightly higher friction values accompanied by continuous oscillations, suggesting a more dynamic interface, possibly due to the entrapment of wear debris or the cyclic formation and detachment of a tribolayer [64].

The electrochemical response to mechanical sliding (Figure 47, bottom) reveals remarkably distinct behaviors depending on the binder composition. Prior to sliding, the NiCrMo samples (Cr-11, Cr-13, and Cr-18) stabilize at more noble potentials compared to the WC-Co reference, confirming their superior intrinsic thermodynamic stability even in this severe acidic chloride environment [65].

Typically, the onset of sliding by a hard ceramic counterbody removes the protective semi-protective layer, exposing the bare, highly reactive metal to the electrolyte, which translates into an abrupt drop in the OCP (cathodic shift) [7,66]. However, the NiCrMo modified binders exhibit exceptional resistance to this mechanical depassivation. The Cr-11 and Cr-18 samples show practically no significant potential drop upon sliding against the alumina sphere, maintaining a highly stable OCP throughout the entire 1800 second

friction period. This remarkable stability indicates that either the mechanical action is insufficient to completely breach the surface layer, or the surface restoration kinetics of these specific Cr-alloyed matrices are virtually instantaneous, preventing any measurable macroscopic active dissolution despite the highly acidic conditions [66].

The Cr-13 sample, on the other hand, exhibits noticeable potential fluctuations during the sliding phase, mirroring its friction coefficient behavior. These oscillations correspond to a cyclic process of localized destabilization (layer removal by the alumina counterbody) and subsequent surface restoration, highlighting a continuous struggle to maintain a protective condition under mechanical stress in the pH 2 solution [66,67].

Interestingly, the conventional WC-Co sample presents an atypical response. Instead of a potential drop, the application of mechanical wear induces a gradual ennoblement (positive shift) of the OCP, rising from approximately -0.33 V to -0.23 V. Since cobalt dissolves actively in acidic media and does not form a robust passive film, this continuous positive shift is likely driven by tribochemical reactions [68]. The localized frictional heating and mechanical mixing at the sliding interface against the chemically inert alumina can promote the accelerated oxidation of the exposed tungsten carbide grains and the cobalt binder, leading to the gradual formation of a pseudo-protective, mixed-oxide tribolayer (e.g., containing WO_3 or CoWO_4) [69,70]. Once the sliding ceases (at ≈ 2000 s), the OCP of the WC-Co sample begins to slowly drop again, indicating that this mechanically-induced oxide layer is chemically unstable and slowly dissolves back into the aggressive acidic electrolyte when the mechanical stimulus is removed [70].

4.4.1. Surface analysis of the wear tracks

To validate the degradation mechanisms hypothesized from the electrochemical and tribological data, the wear tracks of the samples were analyzed after the tribocorrosion tests using SEM and EDS (Figure 48 and 49).

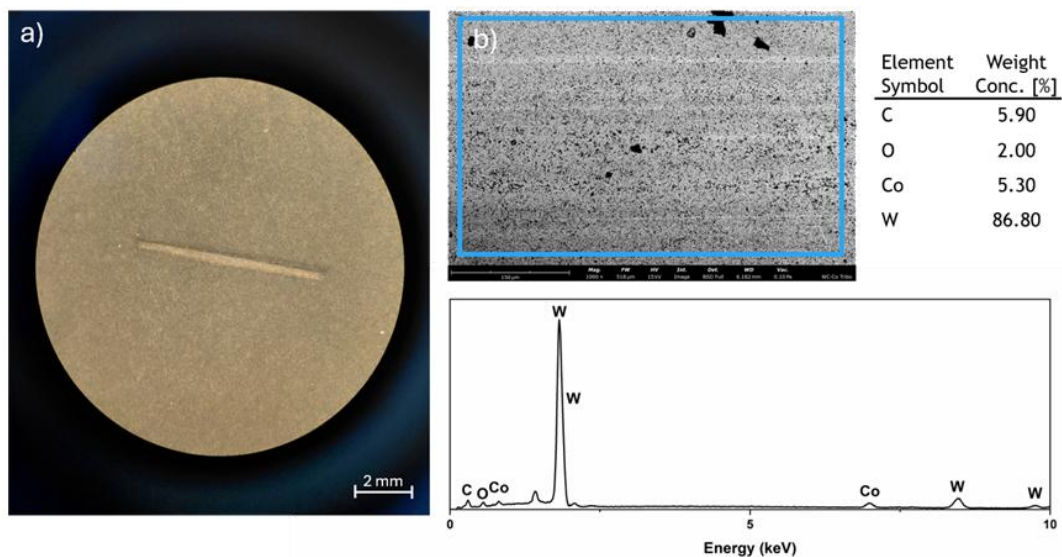


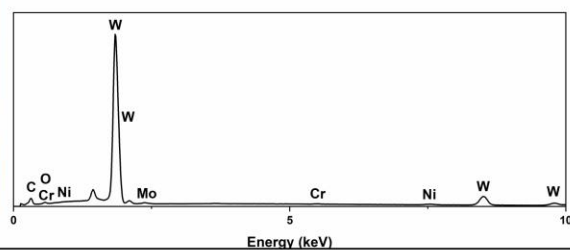
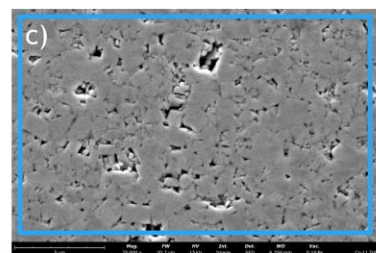
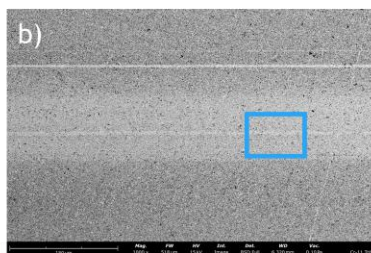
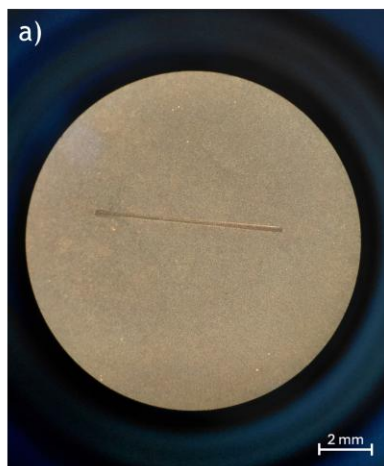
Figure 48 - Surface analysis of the WC-Co sample after tribocorrosion: (a) macroscopic view of the wear track and (b) SEM micrograph with the corresponding EDS area analysis.

Figure 48 presents the post-test analysis of the reference WC-Co hardmetal. The macroscopic view (Figure 48a) reveals a distinct, well-defined wear scar. It should be noted that obtaining SEM micrographs at higher magnifications within the wear track was not possible. Because the cobalt binder is highly magnetic (ferromagnetic), it strongly interferes with the microscope's electron beam and magnetic lenses. This interference causes severe image distortion and blurring, preventing any clear observation at higher magnifications [71].

Nevertheless, the corresponding EDS analysis conducted inside the wear track provides a critical piece of information: the presence of approximately 2.00 wt.% of oxygen. This elevated oxygen concentration provides direct physical evidence supporting the hypothesis formulated previously. The continuous ennoblement (positive shift) of the OCP observed during sliding is indeed driven by the tribochemical oxidation of the surface, leading to the formation of a mixed-oxide tribofilm (e.g., tungsten and cobalt oxides) under the localized frictional heating [68,69]. While this tribolayer may temporarily influence the potential, the degradation of the Co binder is still evident.

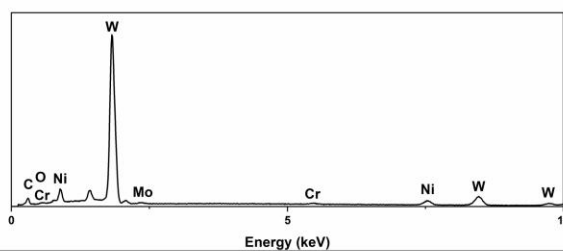
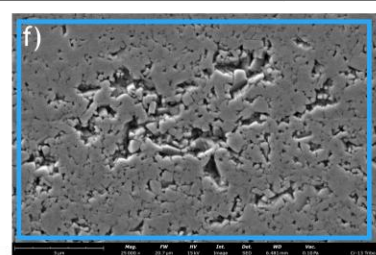
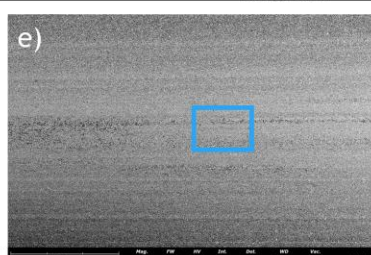
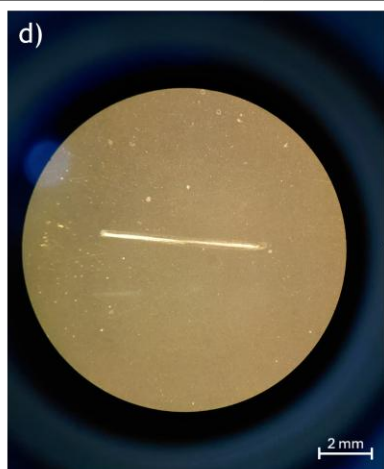
Figure 49 illustrates the wear tracks for the alternative Cr-11, Cr-13, and Cr-18 compositions. The optical micrographs (a, d, g) confirm that sliding occurred, but the compositional and microscopic analyses reveal a fundamentally different wear mechanism compared to the Co reference.

Cr-11



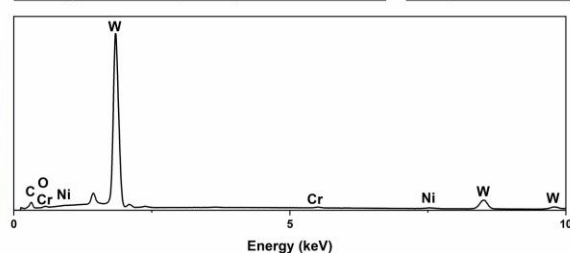
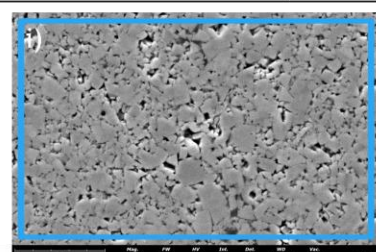
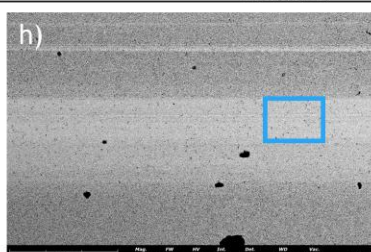
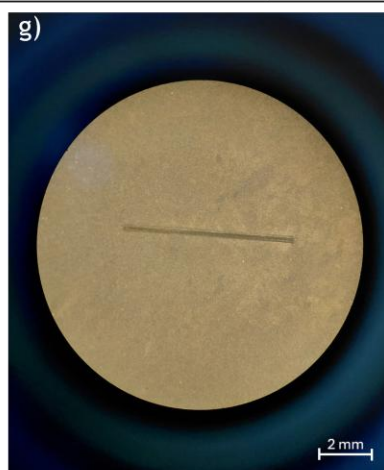
Element Symbol	Weight Conc. [%]
C	6.89
O	0.90
Cr	0.40
Ni	0.60
Mo	0.00
W	91.21

Cr-13



Element Symbol	Weight Conc. [%]
C	6.81
O	0.80
Cr	0.70
Ni	3.00
Mo	0.00
W	88.69

Cr-18



Element Symbol	Weight Conc. [%]
C	6.50
O	0.70
Cr	0.70
Ni	0.60
Mo	0.00
W	91.50

Figure 49 - Surface analysis of the alternative composites (Cr-11, Cr-13, and Cr-18) after tribocorrosion: (a, d, g) macroscopic views of the wear tracks, (b, e, h) SEM micrographs, and (c, f, i) higher magnification views of these regions with their corresponding EDS area analyses.

Chemically, the most prominent feature across all three NiCrMo samples is the drastically lower oxygen content detected inside the wear tracks (0.90 wt.% for Cr-11, 0.80 wt.% for Cr-13, and 0.70 wt.% for Cr-18). This demonstrates that the Cr-alloyed matrices are highly resistant to the severe tribo-oxidation that afflicted the WC-Co sample, successfully inhibiting the formation of massive oxide scales even under the severe mechanical action in the pH 2 solution.

However, the EDS tables also reveal a severe depletion of the binder elements within the sliding contact area. For instance, the Ni content drops to negligible levels in the Cr-11 (0.60 wt.%) and Cr-18 (0.60 wt.%) wear tracks, leaving behind a heavily tungsten-rich surface (W > 91 wt.%). This indicates a mechanism of preferential binder removal. During tribocorrosion, the softer metallic binder is selectively leached by the acidic electrolyte and mechanically extruded or worn away by the alumina counterbody, leaving the harder WC grains exposed [65,72].

The progression of magnification, from left to right in Figure 49, provides crucial morphological context that perfectly correlates with the real-time tribocorrosion data. For the Cr-11 and Cr-18 samples, the high-magnification SEM micrographs (Figures 49c and 49i, respectively) show multiple micro-voids where the metallic binder has been selectively depleted by the acidic electrolyte. However, despite this localized binder extraction, the remaining WC skeleton appears relatively planar, polished, and structurally intact. This uniform surface morphology explains the highly stable, smooth friction coefficient profiles and the unwavering OCP stability observed for these two specific alloys during sliding.

Conversely, the high-magnification image for the Cr-13 sample (Figure 49f) presents a strikingly different and severely degraded topography. Rather than a planar skeleton with empty binder pools, the surface is disrupted by deep jagged craters. This morphology is a classic signature of severe micro-fracturing and the catastrophic physical pull-out of entire clusters of WC grains (*spalling*) [67]. The lack of adequate binder support leads to the collapse of the WC skeleton under the applied shear stress. Once ripped from the matrix, these exceedingly hard WC fragments become entrapped within the contact zone, acting as aggressive third-body abrasives [7,66]. Furthermore, this jagged, excavated morphology directly correlates with the continuous oscillations previously observed in both its friction coefficient and OCP profiles, confirming the presence of a highly dynamic, destructive, and mechanically unstable sliding interface [66].

4.4.2. Counterbody Surface Analysis

To substantiate the proposed degradation mechanisms, the contact surfaces of the alumina (Al₂O₃) spheres were examined using SEM and EDS after the tribocorrosion tests. Figure 50 displays the resulting micrographs and localized compositional analysis of the debris adhered to the sliding wear scar of the counterbody.

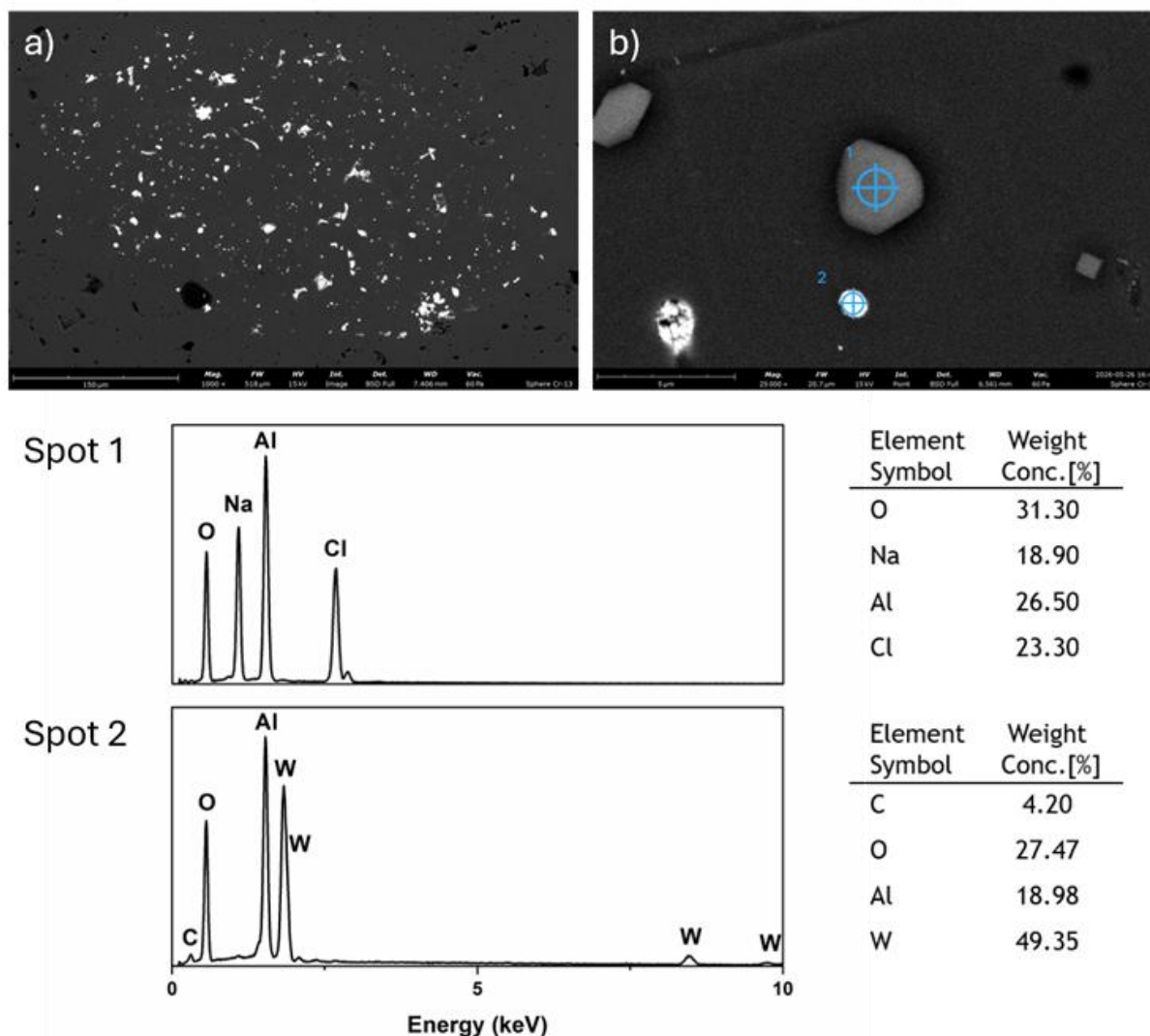


Figure 50 - Surface analysis of the alumina sphere after tribocorrosion testing: (a) SEM micrograph of the sphere surface (b) detailed view with corresponding EDS point analyses.

The low-magnification micrograph (Figure 50a) reveals a significant accumulation of scattered, highly reflective debris firmly adhered across the sliding contact zone of the ceramic sphere. A detailed inspection at higher magnification (Figure 50b), coupled with targeted EDS point analysis, allows for the precise identification of these transferred materials.

The EDS spectrum for Spot 1, which targets a larger, geometric particle, exhibits prominent peaks for sodium (Na) and chlorine (Cl), alongside aluminum (Al) and oxygen (O) from the underlying sphere. This clearly corresponds to crystallized NaCl salt. It represents a residual artifact originating from the evaporation of the highly concentrated and aggressive electrolyte (0.5 M NaCl + HCl, pH 2) that remained trapped within the contact interface after the sliding test concluded.

Crucially, the compositional analysis of the bright, irregular particles (represented by Spot 2) reveals a substantial concentration of W and C. This provides direct, irrefutable physical

evidence of macroscopic WC grain pull-out. As hypothesized in the wear track analysis, the severe acidic attack selectively depletes the metallic binder phase, leaving the hard carbide grains structurally unsupported [65]. Under the applied shear stress of the sliding alumina sphere, these exposed WC grains detach from the composite matrix and become entrapped within the tribological interface [64,65].

The adhesion of these exceedingly hard, fragmented carbide particles to the counterbody firmly corroborates the occurrence of third-body abrasive wear [7,66]. These transferred WC grains act as active abrasive indenters against their own parent matrix, mechanically justifying the jagged wear track morphologies (particularly observed in the Cr-13 sample) and the dynamic oscillations recorded in both the real-time friction coefficient and OCP profiles [64].

Taken together, these results establish that the incorporation of a NiCrMo binder, particularly at Cr contents of 11 and 18 wt.%, confers a substantial and multi-faceted improvement in tribocorrosion resistance relative to the conventional WC-Co benchmark. The superior performance of these compositions arises not from a single mechanism, but from a synergistic combination of enhanced electrochemical stability, resistance to tribo-oxidation, and the ability to maintain a structurally coherent surface under concurrent mechanical and chemical attack. The anomalous behavior of the Cr-13 composition, which underperformed relative to both its lower and higher chromium counterparts, suggests that the relationship between Cr content and tribocorrosion resistance is non-monotonic, and that microstructural factors – such as binder phase homogeneity or carbide grain distribution [72] – may critically mediate the macroscopic response at intermediate alloying levels.

5. Conclusions

This thesis investigated the influence of chromium content on the electrochemical and tribocorrosion behavior of WC-NiCrMo cemented carbides in acidic chloride environments, aiming to evaluate their potential as alternatives to conventional WC-Co hardmetals for demanding industrial applications.

The results demonstrated that replacing the conventional Co binder with a NiCrMo metallic matrix significantly enhances corrosion resistance while maintaining competitive mechanical performance. All WC-NiCrMo compositions exhibited superior electrochemical behavior compared with the WC-Co reference material, showing lower corrosion current densities and greater stability in aggressive environments. This improvement was primarily associated with the formation of a Cr-rich semi-protective surface layer that effectively reduced binder dissolution and delayed surface degradation.

Chromium content was shown to play a decisive role in determining the overall performance of the materials. Increasing chromium promoted microstructural refinement and contributed to higher hardness values, confirming its beneficial strengthening effect. However, this improvement occurred at the expense of fracture toughness, highlighting the need to balance mechanical and chemical performance when designing binder compositions.

Electrochemical characterization revealed the existence of a critical chromium concentration close to 13 wt.% required to ensure an effective and stable low-dissolution regime. Chromium contents below this threshold led to cyclic local breakdown and restoration of this semi-protective condition, resulting in lower electrochemical stability. Conversely, increasing chromium beyond this level did not produce proportional improvements, as higher concentrations promoted local heterogeneity and chromium segregation within the binder phase.

Under tribocorrosion conditions, all WC-NiCrMo materials outperformed the conventional WC-Co grade. The combined action of mechanical wear and electrochemical attack showed that the enhanced corrosion resistance of the alternative binders translated into lower tribo-oxidation, reduced binder degradation and improved preservation of surface integrity. Nevertheless, the results also demonstrated that tribocorrosion resistance is not governed exclusively by chromium content but depends strongly on the homogeneity of chromium distribution and the stability of the semi-protective layer during sliding.

Overall, this work confirms that WC-NiCrMo cemented carbides constitute a promising alternative to conventional WC-Co systems for applications operating under severe tribocorrosive conditions. The findings contribute to a deeper understanding of the relationship between composition, microstructure and degradation mechanisms in alternative composite binders and provide useful guidelines for the development of next-generation cemented carbides with improved durability.

6. Future Works

The findings and hypotheses formulated in this dissertation establish a strong foundation regarding the tribological and electrochemical behavior of alternative NiCrMo binders, yet they also open critical avenues for advanced research. To thoroughly validate the proposed degradation mechanisms and fully understand the dynamic nature of these interfaces, future investigations should focus on three primary approaches.

Advanced *In-Situ* Tribocorrosion Dynamics: Given the complex mechanical-electrochemical synergy observed, particularly the cyclic macro-oscillations in the friction coefficient, future research must prioritize real-time transient analysis. This can be achieved by performing tribocorrosion tests with the simultaneous high-frequency acquisition of both the friction coefficient and the Open Circuit Potential (OCP). This setup will allow for a precise correlation between mechanical wear events and electrochemical voltage drops, effectively mapping the continuous formation, fracture, and ejection of the protective tribofilm. Furthermore, employing dynamic Electrochemical Impedance Spectroscopy (d-EIS) during sliding, or immediately after it ceases, would be vital to capture the true electrical resistance and protective quality of the transient mixed-oxide tribolayer before it undergoes chemical dissolution in the aggressive electrolyte.

Post-Sliding Dissolution Kinetics and High-Resolution Characterization: To unequivocally prove the hypothesis that the relatively low oxygen content detected *ex situ* inside the wear track is a consequence of the transient tribofilm dissolving during the post-test stabilization period, a combination of chemical and advanced microscopic analyses is required. Future works should utilize Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to analyze the testing solution immediately after the sliding ceases, quantifying the release of dissolved metal ions to confirm the active dissolution of the mechanically induced oxides. To overcome the penetration depth limitations of standard EDS, this must be paired with X-ray Photoelectron Spectroscopy (XPS) and cross-sectional Transmission Electron Microscopy (FIB-TEM) inside the wear track. These high-resolution techniques will allow for the direct physical measurement of the nanometric tribolayer thickness, its exact stoichiometry, and the precise depth of the localized binder leaching.

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