NEW BINDERS, LESS CORROSION - DURIT RESULTS

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The limited corrosion resistance of conventional WC-Co hardmetals remains a major challenge in applications exposed to aggressive environments. Responding to this limitation, DURIT has investigated alternative binder systems designed to enhance the durability and performance of cemented carbides operating under corrosive conditions.

In this study, DURIT developed and characterised industrially relevant WC-based composites containing alternative binders such as Ni, CoNi, NiCr, CoNiCr, and NiCrMo, applied at different binder contents. Their corrosion behaviour in 0.5 M NaCl solution was systematically compared with standard WC-Co grades using electrochemical techniques, including corrosion potential monitoring and Potentiodynamic polarization testing.

The results clearly demonstrate that these alternative binders significantly improve corrosion resistance, particularly the Co-free alloys, which showed superior stability in neutral saline media. These developments represent a major step toward extending the lifetime of tools and components, minimising maintenance needs, and reducing operational costs while promoting more sustainable material solutions for corrosion-prone environments.

KEYWORDS:
HARDMETALS; ALTERNATIVE BINDERS; MECHANICAL CHARACTERISATION; CORROSION RESISTANCE.

INTRODUCTION

Hardmetals, more precisely termed cemented carbides, represent a class of composite materials engineered for superior wear resistance. Composed primarily of tungsten carbide (WC) particles embedded in a metallic binder, typically cobalt (Co) at 3.5% to 27% by weight, these alloys exhibit a unique microstructure that confers high hardness coupled with adequate toughness. The Vickers hardness (HV30) of such materials ranges from 770 to 1980, while transverse rupture strength reaches 2200-3800 N/mm^2, and fracture toughness varies from 7 to 27 $MPa{\cdot}M^{1}/^{2}$ depending on grain size and binder phase distribution. This combination arises from the immiscible nature of WC and Co, where WC provides the abrasive resistance akin to diamond, and Co acts as a ductile matrix to absorb energy during deformation [1-3].

DURIT, formally known as Metalurgia Portuguesa do Tungsténio, Lda. is a Portuguese industrial manufacturer focused on hardmetal (cemented carbide) components and wear-protection solutions for demanding service conditions, high abrasion, erosion, impact, and (in many cases) corrosion. From its start as a family business in 1982 in Albergaria-a-Velha, Portugal, the company grew into an international player with modern production and operational facilities. Today, DURIT positions itself as a one-stop supplier: from the design of the component and selection of carbide grade, through powder-metallurgy manufacturing, finishing, inspection, and, where needed, advanced coatings to extend service life [1].

This one-source manufacturing approach is particularly relevant in the context of modern hardmetal applications, where performance is determined not only by bulk material properties but also by microstructural control, dimensional precision, and surface condition. DURIT currently develops and manufactures more than 60 proprietary hardmetal grades, tailored to specific wear mechanisms and service environments. A comprehensive overview of DURIT's grades, including technical data sheets is available on their website at www.durit.com, which serves as an invaluable resource for engineers seeking application-specific guidance. DURIT's products are deployed across a wide range of industrial applications, including crushing and milling equipment, extrusion and conveying systems, renewable energy machinery, pharmaceutical tooling, and components for energy and chemical processing installations [1].

However, in many of these applications, particularly those involving exposure to aggressive media such as saline brines, acidic process streams, or humid offshore conditions, the corrosion susceptibility of conventional WC-Co hardmetals emerges as a critical limita-tion [4 - 9]. Galvanic coupling between the noble WC phase and active Co binder drives selective dissolution, pitting, embrittlement, and accele-rated wear, potentially halving component lifespan in neutral saline environments such as 0.5 M NaCl. This increases maintenance costs, downtime, and sustainability challenges for industries demanding exten-ded service intervals. To mitigate this, DURIT has developed alternative binder systems, including Ni-based and alloyed CoNi variants with Cr and Mo additions, for improved passivation and stability without sacrificing mechanical properties. This study evaluates these scalable compositions using electrochemical testing and microstructural analysis, yielding quantitative corrosion insights relative to WC-Co standards and supporting DURIT's goal of optimized solutions for wear-intensive sectors.

MATERIALS AND METHODS

Table 1 presents the studied compositions, with Co-based and Ni-based binders. Besides CoNi and NiCrMo, the remaining binder compositions are based on commercial grades from DURIT. The hardmetals are divided into fine-grained low binder content and coarse-grained high binder content compositions. When necessary, metallic W or C powders were added to adjust the carbon balance, to obtain a biphasic microstructure, based on the respective phase diagrams.

The compositions were prepared by conventional powder metallurgy methods. The powders were mixed in a roller ball stainless-steel mill, using ethanol and hardmetal balls. The milling time applied was based on industrial know-how. The powder slurries were vacuum dried (~65°C) and the powders de-agglomerated with a 350 µm sieve.

Cylindrical samples were uniaxially pressed (150 MPa) and sintered using sinterHIP (3 MPa bar of Ar) and sinterVAC industrial furnaces, at a maximum temperature of 1450°C. All sintered samples were characterised according to industrial quality control procedures, detailed in Table 2, including: coercive force (HC), and magnetic saturation (σm); density (ρ), according to Archimedes method; Vickers hardness (HV30); and Palmqvist indentation toughness (KIC), when applicable.

Sintered samples were ground and polished down to a 3 µm diamond paste finishing and chemically etched using Murakami reagent (10 g potassium ferricyanide and 10 g sodium hydroxide in 100 ml distilled water). For Scanning Electron Microscopy (SEM) analysis, the samples were further polished with 1 µm colloidal silica suspension and etched with Caro's acid (7 ml hydrogen peroxide, at 30%, and 0.5 ml hydrochloric acid, at 37%). Optical microscopy was used to characterise porosity, free-carbon and eta phase content and analyse the microstructures. The samples were analysed in SEM to assess the WC grain size (dWC), following the mean linear intercept method.

The binder mean free path (λ) was calculated by Equation 1, where dWC is the average grain size and VBinder the binder volume fraction.

$$\lambda = d_{WC} \times (0.1 + 2V_{Binder}) \qquad (1)$$

Samples (~H10 mm x Ø20 mm) of each composition were tested in 0.5 M NaCl (pH = 7.0),

~~TABELA~~ 1
Nominal compositions of the prepared hardmetal compositions

Hardmetal Composition	Sintering Method	WC FSSS (µm)	Composition (wt.%)					Binder Composition (wt.%)				Binder volume (vol.%)
			WC	Co	Ni	Cr_3C_2	Mo_2C	Co	Ni	Cr	Mo	
8Co	SinterHIP	0.8 (fine)	92.0	8.0				100.0				13.3
8CoNi			92.0	5.5	2.5			68.8	31.2			13.3
6CoNiCr			94.2	3.5	1.5	0.8		61.5	26.3	12.2		10.2
8Ni			92.0		8.0				100.0			13.2
8NiCrMo			90.6		8.0	0.8	0.6		86.4	7.5	6.1	15.8
8NiCr			91.2		8.0	0.8			92.0	8.0		14.9
27Co	SinterVAC	4.0* (coarse) *25% WC x 2.5 µm + 75% WC x 6 µm	73.0	27.0				100.0				39.6
27CoNi			73.0	18.9	8.1			70.0	30.0			39.5
27CoNiCr			71.1	17.5	7.4	4.0		61.7	26.1	12.2		41.3
25Ni			75.5		24.5				100.0			36.0
27NiCrMo			71.6		24.6	1.9	1.9		87.8	5.9	6.4	41.0

TABELA 2
Samples' characterisation methods, standards and equipment

	Property	Method	Standard	Equipment
	Density(ρ)	Archimedes method	ISO 3369	Mettler ToledoMS204S scale
Magnetic properties	Coercive Force (HC)	-		Foerster Koerzimat cs 1.097 HCJ
	Magnetic Saturation (σm)	-		Fischer Feritscope MP30E-S
	Hardness (Hv30)	Vickers Hardness (294.2 N)	ISO 6507	Buehler Wilson VH3300 durometer
	Fracture toughness (K_{IC})	Palmqvist toughness test	ISO 28079	
	Microstructure	Characterisation of porosity, free-carbon and eta phase	ISO 4499-4	LEICA DMLM microscope
	WC Grain Size (d_{WC})	Mean linear intercept method	ISO 4499-2	Hitachi SU70 SEM and Image J software

prepared with distilled water and pro-analysis grade reagents. Before testing, the specimens were electrically connected to insulated copper wires with a conductive silver paint (PELCO), before cold mounting in epoxy resin (BUEHLER EpoKwick™ FC). After polymerisation, the mounted specimens were mirror-polished and cleaned in distilled water and ethanol. An insulating electroplating tape (Scotch 3M) was used to delimit the surface exposed to the electrolyte solution to a constant circular area of 0.24 cm^2.

The electrochemical experiments were conducted in a standard three-electrode electrochemical cell (shown in Figure 1), inside a Faraday cage, in aerated and quiescent conditions, at room temperature (23 ± 2°C), using Autolab potentiostats. The Reference Electrode (RE) was a Saturated Calomel Electrode (SCE), the Counter Electrode (CE) a platinum rod, and the immersed sample the working electrode (WE). The Open Circuit Potential (OCP) was monitored during the first hour of immersion, and then after 1 day, 2 days, 7 days and 14 days. Potentiodynamic cathodic and anodic polarization curves were obtained, after 1 hour of immersion, from near OCP to -1.2 V and +0.8 V (vs. SCE), respectively, with a scan rate of 1 mV/s for both branches.

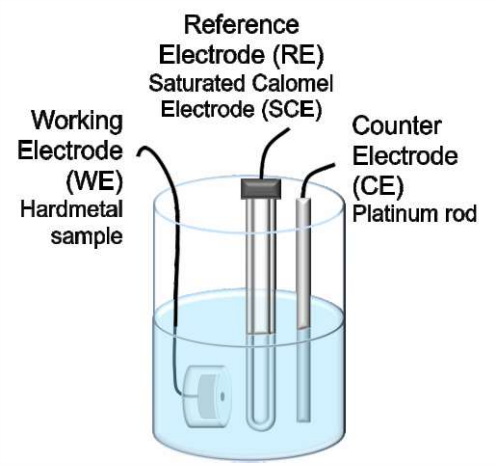


FIGURE 1
Electrochemical tests' setup

RESULTS

Structural and microstructural characteristics of the studied hardmetal grades are presented in Table 3. The overall performance of hardmetals is affected by microstructural features, such as the WC particle size. Figure 2 shows the microstructures of the hardmetal compositions. All sintered samples are fully dense and showed a uniform microstructure, free of defects or porosity (A00B00C00).

TABELA 3
Characteristics of the sintered hardmetals samples

Hardmetal Composition	ρ (g/cm^3)	HC (Oe)	σ_m (emu/g)	HV30 (kgf/mm^2)	KIC ($MPa.m^{1/2}$)	d_{wc} (μm)	λ (nm)
8Co	14.72	263	132	1659 ± 16	9.9 ± 0.1	0.56 ± 0.03	203
8CoNi	14.62	297	149	1604 ± 22	9.5 ± 0.2	0.55 ± 0.04	200
6CoNiCr	14.82	409	123	1920 ± 18	8.8 ± 0.1	0.54 ± 0.03	160
8Ni	14.69			1508 ± 16	9.4 ± 0.3	0.57 ± 0.01	207
8NiCrMo	14.55			1616 ± 11	9.0 ± 0.3	0.53 ± 0.02	216
8NiCr	14.58			1664 ± 8	9.5 ± 01	0.54 ± 0.01	211
27Co	13.06	71	136	787 ± 5		1.15 ± 0.66	1029
27CoNi	12.99	64	148	730 ± 7		1.46 ± 0.97	1299
27CoNiCr	12.85	84	97	909 ± 10		0.82 ± 0.48	731
25Ni	13.22			701 ± 7		1.56 ± 1.14	1278
27NiCrMo	12.89			793 ± 7		0.84 ± 0.50	753

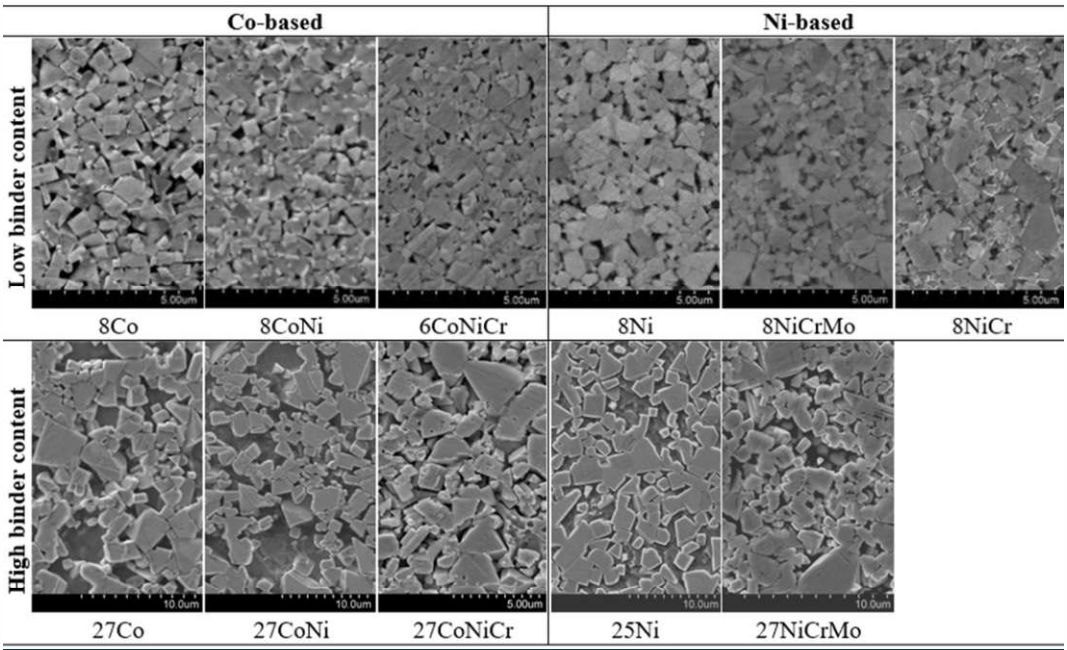


FIGURE 2
SEM micrographs of the different sintered composites. Note the different scale lines

Despite the different binder compositions, the hardmetals with equivalent binder contents present similar density values. The hardness and, when applicable, coercive force, evolve inversely to the WC grain size and the binder contents, as expected. In turn, the binder mean free path is proportional to dWC. The compositions with Ni-based binders present lower hardness values in comparison to Co-based hardmetals. However, the introduction of Cr and Mo carbides increased the materials' hardness, presumably due to their known grain growth-inhibiting effect [3]. These additions did not significantly affect the fracture toughness of low binder content compositions (8CoNiCr, 8NiCrMo, and 8NiCr) in comparison to hardmetals with plain Co and Ni binders (8Co and 8Ni).
Figure 3 shows the evolution of the OCP of all the hardmetal compositions studied during the first hour of immersion and after 1, 2, 7, and 14 days in the neutral solution (0.5 M NaCl). In general, all the compositions containing Co present a more negative potential than Ni-based hardmetals, except for the CoNiCr binder at high binder contents (27CoNiCr).

Additionally, the partial substitution of Co with Ni significantly improves the corrosion resistance in both low and high binder content hardmetals (8CoNi and 27CoNi). Moreover, the Co-free compositions (8Ni, 8NiCr, 8NiCrMo, 25Ni, and 27NiCrMo) show an initial increase in corrosion potential, which indicates the passivation of the surface in the first minutes of immersion. This was also observed for composition 27CoNiCr. After the first days of immersion, the OCP of the studied compositions seems to stabilise and is kept constant for up to 2 weeks. Conversely, the composition 6CoNiCr exhibits a significant improvement in corrosion potential after 2 weeks of immersion. After 2 weeks, the corrosion potential of low binder content hardmetals ranks in the order: 8NiCrMo = 8NiCr > 6 CoNiCr > 8Ni > 8CoNi > 8Co. In high binder

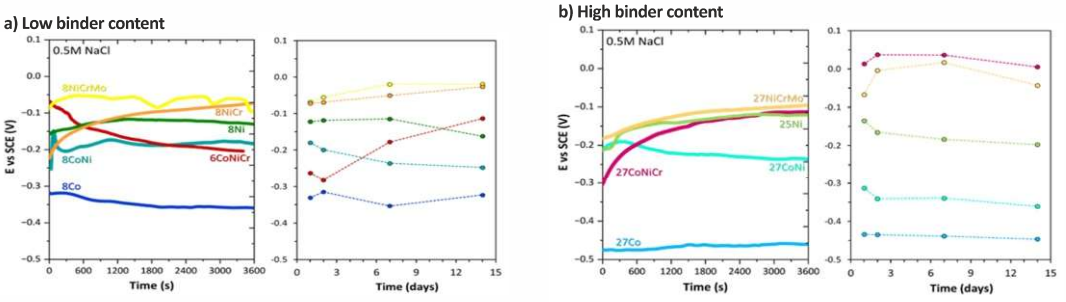


FIGURE 3
Evolution of the Open Circuit Potential (OCP) of low binder content (a) and high binder content (b) hardmetals during the first hour of immersion and after 1, 2, 7, and 14 days in 0.5 M NaCl

content compositions, the corrosion potential evolves as: 27Co < 27CoNi < 25Ni < 27NiCrMo > 27CoNiCr.
The presence of Mo in the NiCrMo binder (8NiCrMo) did not significantly improve the corrosion potential in comparison to the 8NiCr composition. On the other hand, Cr-containing compositions always present a more positive potential, and presumably less susceptibility to corrosion, than hardmetals with plain Co and Ni or CoNi binders. The gap between simple (8Co, 8CoNi, 8Ni, 27Co, 27CoNi, and 25Ni) and complex binder compositions (6CoNiCr, 8NiCr, 8NiCrMo, 27CoNiCr, and 27NiCrMo) becomes more evident for longer immersion times.

Figure 4a presents the corrosion rates determined by the Tafel extrapolation of the polarization curves. As in neutral environments, the corrosion of hardmetals is dominated by the binder dissolution mechanism, the icorr results were corrected (Figure 4) to account only for the binder area (same as vol.%, see Table 1), using Equation 2. This correction did not alter the relative ranking of the binder compositions.

$$i_{corr\,corrected} = i_{corr} / \text{Binder area fraction} \quad (2)$$

The corrosion rates follow the trend observed in OCP monitoring, with the corrosion resistance of the binders ranking as NiCr = NiCrMo > CoNiCr = Ni > CoNi > Co in low binder compositions and CoNiCr > Ni > CoNi > NiCrMo > Co in high binder content hardmetals. Compositions 8Co and 27Co present the lowest corrosion resistance, while 8NiCr has the lowest corrosion rate. The addition of Cr to Ni and to CoNi significantly decreases the corrosion rates, but the addition of Mo (8NiCrMo) has a negligible effect on the icorr. Moreover, at high binder contents, the NiCrMo binder (27NiCrMo) showed a higher corrosion rate than all compositions except 27Co, as the corrosion resistance is also dependent on the WC grain size and binder distribution. This is also supported by the lower corrected icorr of coarse-grained 27Co in comparison to fine-grained 8Co.

In general, Ni-based binders are more corrosion resistant. However, the studied CoNiCr and plain Ni binders result in similar corrosion rates in both low and high binder content compositions, despite the different corrosion potentials.

CONCLUSIONS

Industrially promising Co-based and Ni-based hardmetals were produced and characterised, with fine (0.8 μm) and coarse (4 μm) WC grains. The alternative binders include CoNi, CoNiCr, Ni, NiCr, and NiCrMo compositions, applied in low (8 wt.%) and high (27 wt.%) binder content grades. The evaluation of their mechanical properties and corrosion resistance in 0.5 M NaCl produced the following conclusions:

1. The addition of Cr_3C_2 and Mo_2C increased the hardness of hardmetals, without compromising the fracture toughness in low binder content compositions.
2. In general, Ni-based hardmetals are more corrosion resistant than Co-based compositions, which often present more negative corrosion potentials and higher corrosion rates.
3. Compositions with plain Co binders present the lowest corrosion resistance. The partial or complete substitution of Co by Ni improves the corrosion potential and decreases the corrosion rate of hardmetals.
4. The corrosion resistance is further enhanced with the introduction of Cr in Co-based and Ni-based binders.
5. NiCr and NiCrMo binders have the lowest corrosion rates and more positive corrosion potentials in low binder content compositions, while the CoNiCr binder excels in high binder content hardmetals. Compositions with CoNiCr and Ni binders presented similar corrosion rates.

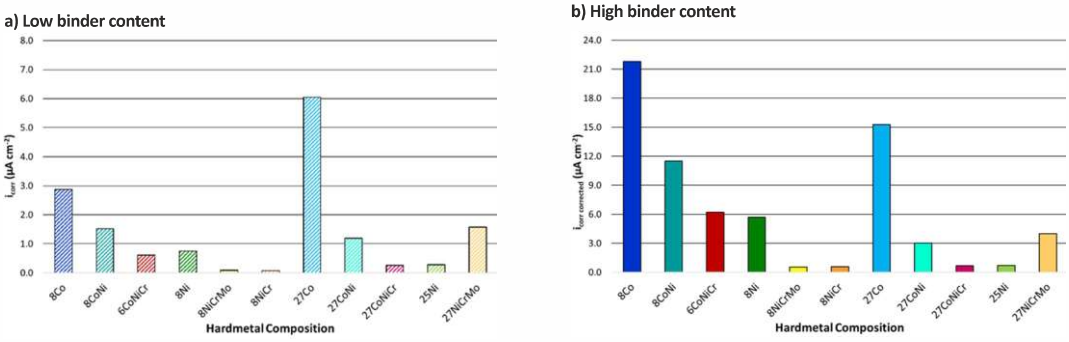


FIGURE 4
Absolute (a) corrosion rates (i_{corr}) of all the samples after 1 h of immersion in 0.5 M NaCl and i_{corr} corrected (b) for the binders' area fraction

6. The presence of Mo in the binder did not improve the corrosion potential or the corrosion rate of NiCrMo compositions.

7. All the studied alternative binders, especially Co-free compositions, outperform plain Co in terms of corrosion resistance in saline neutral environments, preventing corrosion-induced mechanical damage.

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