Corrosion Behavior and Galvanic Corrosion Resistance of WC and Cr₃C₂ Cermet Coatings in Madeira River Water

Leonardo Augusto Luiz¹ · Juliano de Andrade² · Camila Melo Pesqueira² · Irene Bida de Araújo Fernandes Siqueira¹ · Gustavo Bavaresco Sucharski¹ · Milton Jakson de Sousa³

Submitted: 18 August 2020 / in revised form: 21 December 2020 / Accepted: 2 January 2021 / Published online: 21 January 2021
© ASM International 2021

Abstract Thermally sprayed cermet coatings are adequate solutions to improve cavitation and wear resistance of hydraulic turbines made of stainless steel (SS), especially in rivers with a high sediment load, such as the Madeira River in Brazil. However, some cermets are easily dissolved in river water, leading to premature failure of the coating and costly maintenance. Moreover, galvanic corrosion induced by coupling the cermet to a SS can accelerate the coating dissolution. Therefore, the corrosion resistance of six cermets (WC-12Co, WC-10Ni, WC-10Co-4Cr, Cr₃C₂-25NiCr, Cr₃C₂-10NiCr and Cr₃C₂-10Ni) and the galvanic corrosion resistance of these materials coupled to CA6NM SS were evaluated in a solution that simulated Madeira River water. WC-12Co and WC-10Ni cermets exhibited the highest corrosion rates, 0.077 and 0.068 mm/year, respectively, whereas the Cr content in the WC-10Co-4Cr (0.017 mm/year) and Cr₃C₂-based coatings (0.005 to 0.007 mm/year) led them to corrode at slower rates. Moreover, the WC-10Co-4Cr and Cr₃C₂-based cermets exhibited negligible galvanic corrosion current when coupled to the CA6NM SS, making them good options to

coat hydraulic turbines. In contrast, WC-12Co and WC-10Ni coatings underwent a more severe galvanic corrosion process, which would drastically reduce the lifespan of these materials as hydraulic turbine coatings.

Keywords corrosion resistance · Cr₃C₂-based coatings · galvanic corrosion · power plant · turbines · WC-based coatings

Introduction

Cavitation is one of the main wear mechanisms that affects hydro-turbine components, causing material loss through the implosion of vapor bubbles (Ref 1, 2). As a result, martensitic stainless steels such as CA6NM alloy are the most used materials in turbine components due to their microstructure composed of low-carbon martensite and retained austenite, providing high hardness and toughness (Ref 1, 3). However, rivers such as the Madeira River have high abrasive particle density (sediment load of 2.76×10^9 tonnes/year) (Ref 4), which can also cause severe abrasive wear to components made of stainless steel (Ref 5, 6). A solution to this problem is to thermally spray the components with cermet coatings, providing synergy of cavitation and abrasive wear resistance.

The most widely studied and applied cermet systems are coatings based on WC (WC-Co, WC-Co-Cr, WC-Ni) and Cr₃C₂ (Cr₃C₂-NiCr, Cr₃C₂-Ni), due to their synergy of high hardness and toughness (Ref 7–10). The carbides provide wear resistance, while the distribution of these ceramic materials in a ductile metallic matrix guarantees resistance to impact (Ref 7–10). Ludwig et al. showed that WC-CoCr coatings sprayed by the HVOF process enhanced the slurry erosion resistance of stainless steels (Ref 11). Goyal et al.

This article is an invited paper selected from abstracts submitted for the 2020 International Thermal Spray Conference, ITSC2020, that was to be held from June 10–12, 2020, in Vienna, Austria. The conference was canceled due to the coronavirus (COVID-19) pandemic. The paper has been expanded from the planned presentation.

✉ Leonardo Augusto Luiz
leonardoal2012@gmail.com; leonardo.l Luiz@lactec.org.br

¹ Mechanical Systems Department - Lactec Institute, Curitiba, Brazil

² Materials Department - Lactec Institute, Curitiba, Brazil

³ Santo Antônio Energia S/A, Porto Velho, Brazil

also analyzed the slurry erosion resistance of Cr_3C_2 -NiCr coating in comparison with an uncoated CA6NM stainless steel. In all test conditions, the HVOF coating improved the wear resistance (Ref 12). In general, many authors have reported that WC- and Cr_3C_2 -based coatings can reduce material loss caused by cavitation and slurry erosion by improving superficial properties (Ref 2, 9–14).

However, cavitation and abrasive wear are not the only degradation mechanisms affecting hydropower plants. Hydraulic turbines are also susceptible to corrosion due to the corrosiveness of the aqueous environment. Although stainless steel components are corrosion resistant in river water due to the formation of a passive film consisting of Cr_2O_3 , thermally sprayed coatings can be susceptible to dissolution. That can lead to corrosion of the coating and deterioration of its wear and cavitation resistance, leading to further damage to the substrate (Ref 7). Therefore, thermally sprayed coatings should also be corrosion resistant in river water and properly selected to avoid premature and costly maintenance of hydro-turbines.

It is widely reported that WC-Co and WC-Ni coatings tend to have low corrosion resistance as a result of micro-galvanic cells formed between the ceramic phase and the metal binder (Ref 15–18). Many authors have found that the formation of porous non-protective cobalt oxide (CoO) leads to low corrosion resistance of WC-Co coatings (Ref 8, 15, 19). Nevertheless, Cr_3C_2 coatings with a matrix of NiCr and Ni tend to have high corrosion resistance in a variety of corrosive media (Ref 8, 15, 20–23). Li et al. confirmed that the corrosion resistance of Cr_3C_2 -based coatings is the result of oxide formation, such as Cr_2O_3 and Ni_2O_3 , protecting the substrate (Ref 8). The corrosion resistance of WC-10Co-4Cr, as widely reported, is improved by the Cr content in solid solution (Ref 8, 15, 24, 25). Hong et al. studied the electrochemical behavior of WC-10Co-4Cr in 3.5% NaCl, reporting that aside from the Cr content, the amorphous structure of the coating enhanced the ability to form dense and protective oxide films. The authors also reported that the main mechanism of corrosion is the formation of micro-galvanic cells between the carbide and metal binder (Ref 24).

Most of these reports focus in the corrosion behavior of cermets in seawater or acid media (Ref 8, 15, 19–27). To the best of our knowledge, to date no study of the corrosion resistance of these materials in river water has been published. This is an important gap in the literature, since these cermet materials are being widely applied as coatings for hydro-turbines, and knowledge of their corrosion and mass rates in river water is necessary for proper coating selection as well as lifespan prediction.

Another problem related to corrosion is the formation of galvanic coupling between substrate and coating. This theme is extremely important, since WC and Cr_3C_2

coatings are normally the anodes of a galvanic couple when combined with stainless steel, which leads to more severe dissolution of the coating (Ref 21, 26, 27). The damage caused by galvanic corrosion can be increased by the area of the cathode in relation to the anode (A_c/A_a), as pointed out by Mansfeld (Ref 28). The higher the A_c/A_a is, the greater will be the corrosion rate of the anode. This situation is critical, especially for turbine components, since it is common to coat only damaged parts of the turbines for maintenance purposes (Ref 29). Unfortunately, the galvanic corrosion in coupling formed by thermally sprayed coatings and stainless steel is not widely discussed in the literature, especially for immersion in river water.

Therefore, this work evaluated the corrosion resistance, estimated the corrosion and mass loss rates and analyzed the severity of the galvanic couple formed between a stainless steel widely used as hydro-turbine material (grade CA6NM) and WC/ Cr_3C_2 -based coatings in Madeira River water. Such analysis has not yet been reported and knowledge of corrosion rates and galvanic corrosion resistance is of major practical importance for the hydropower generation sector. Moreover, all the electrochemical studies have been carried out in a solution simulating water typical of the Madeira River, which supplies two important Brazilian hydroelectric plants.

Materials and Methods

Materials and Coating Deposition

The CA6NM stainless steel alloy and six thermally sprayed coatings were studied in the present work. The coatings were deposited in a carbon steel substrate as it is a more readily available material and also because the substrate did not influence in the electrochemical results. The carbon steel substrate was grit blasted with alumina (36 mesh) before coating deposition, resulting in medium surface roughness (R_a) of $4.64 \pm 0.13 \mu\text{m}$. Their chemical compositions are shown in Tables 1 and 2, respectively. The CA6NM stainless steel's electrochemical performance in river water was also analyzed, since it is one of the most used materials in hydro-turbine components (Ref 1, 3, 5, 6). Therefore, the corrosion resistance of CA6NM steel as well as the severity of the galvanic couple formed between the stainless steel and cermet coatings must be evaluated.

The coatings were deposited onto the carbon steel substrate by high-velocity oxy-fuel (HVOF) spraying, using a Sulzermetco DJ2700 pistol, propane (C_3H_8) as the fuel and 20 torch passes. HVOF is the most recommended thermal spraying process for corrosion resistant coatings since it reduces porosity and produces coatings with good

Table 1 Chemical composition (wt.%) of Cr₃C₂- and WC-based coatings

Coating	Cr ₃ C ₂ -25NiCr	Cr ₃ C ₂ -10NiCr	Cr ₃ C ₂ -10Ni	WC-12Co	WC-10Co-4Cr	WC-10Ni
Chemical composition	75% Cr ₃ C ₂ , 20% Ni, 5% Cr	90% Cr ₃ C ₂ , 8% Ni, 2% Cr	90% Cr ₃ C ₂ , 10% Ni	88% WC, 12% Co	86% WC, 10% Co, 4% Cr	90% WC, 10% Ni

adhesion, making it more difficult for the electrolyte to reach the substrate (Ref 9, 26, 30). Table 3 reports the optimized parameters used in the deposition.

X-ray Diffraction

X-ray diffraction was used to characterize the phases formed in the coating, assisting in identifying oxidation of the coating and decarbonization of carbides. The equipment used was a Shimadzu XRD-6000 diffractometer with CuK_α ($\lambda = 1.544 \text{ \AA}$) radiation. The 2θ range analyzed was of 30° to 95° , with a scan rate of 1°min^{-1} .

Microstructure

Microstructural analysis was carried out to study features, such as porosities, grain morphology and oxide inclusions. The samples were prepared as follows: The CA6NM stainless steel and cross sections of the coatings sprayed on substrates of carbon steel were cut and cold mounted in epoxy resin; after which the samples were ground with silica paper with 180-240-400-600-1500-2000 mesh. The samples were also polished with alumina particles of $1 \mu\text{m}$ and then finely polished with $0.3 \mu\text{m}$ alumina. The CA6NM stainless steel was electrochemically etched in a solution of 10% oxalic acid at 6 V during 10 s, followed by over-etching during 30 s. Over-etching was done to highlight regions with retained austenite and estimate its amount. The microstructure under both low ($200\times$) and high magnifications ($3000\times$) was evaluated using a VEGA3 Tescan scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS). Porosities of the coatings and retained austenite content in the CA6NM steel were estimated through image analysis using five micrographs with magnification of $200\times$ in the Image-J software.

Tafel Extrapolation

Extrapolation of potentiodynamic curves was used to obtain the current density and corrosion potential of the coatings, thus indicating the severity of the corrosion process in Madeira River water. The samples were

prepared as follows: Rectangular samples were sectioned, and copper wires were soldered in the opposite surface of the coating (carbon steel substrate) to create an electrical contact. Afterward, the samples were cold mounted in epoxy resin. The surface of the coatings was then ground with silica paper of 180-240-400-600-1500-2000 mesh, and the surface area was limited to 0.5 cm^2 for the electrochemical tests. The final thickness of each coating after grounding is exhibited in Table 4.

The open circuit potential (E_{OCP}) of the ground samples was monitored for 15 minutes followed by the potentiodynamic polarization conducted in a potential range of -300 versus E_{OCP} to $+1200 \text{ mV}$ versus SCE, at a scan rate of 1 mV s^{-1} . After the potentiodynamic polarization, each coating cross-section and corroded surface was investigated through EDS. The reference electrode used was a saturated calomel electrode (SCE—Hg, Hg₂Cl₂, KCl_{sat}), with a platinum wire as counter electrode and the coatings as working electrodes. A Gamry Reference 3000 potentiostat/galvanostat was used to perform the electrochemical experiments. Every measurement was carried out in triplicate to assure the reproducibility of the experiment.

The electrolyte composition obtained by analysis of the water used to simulate Madeira River water is shown in Table 5. The formulation was produced in the laboratory mainly using sodium salts such as sodium chloride (NaCl), sodium nitrite (NaNO₂), sodium nitrate (NaNO₃), sodium bromide (NaBr), sodium phosphate (Na₃PO₄), sodium sulfate (Na₂SO₄) and calcium carbonate (CaCO₃).

Galvanic Coupling Analysis with Zero-Resistance Ammeter (ZRA)

Measurements using a zero-resistance ammeter (ZRA) were obtained to evaluate the severity of the galvanic couple formed by the stainless steel/thermally sprayed coating. The galvanic corrosion current (i_g) and potential (E_c) of the couple were monitored for 11 days, since that was the time necessary to stabilize the system and obtain a precise measurement of i_g and E_c . The electrochemical cell was set using SCE as the reference electrode, the coatings as working electrodes and the CA6NM stainless steel as the counter electrode. In this experiment, the Gamry Reference

Table 2 Chemical composition (wt.%) of stainless steel CA6NM according to standard ASTM A743/A743M

Material	Cr, wt.%	Ni, wt.%	Mo, wt.%	Mn, wt.%	Si, wt.%	C, wt.%	Fe, wt.%
CA6NM	12.75	4.00	0.70	0.50	0.50	0.06	Bal.

Table 3 Parameters used in the HVOF spraying process

O ₂ flow rate, L min ⁻¹	Air flow rate, L min ⁻¹	Fuel flow rate, L min ⁻¹	Spraying distance, mm	Feed rate, g min ⁻¹
256.67	3516.67	56.67	250	40

3000 potentiostat functions as a ZRA, short circuiting the counter and working electrodes to simulate the galvanic corrosion process.

Results and Discussion

Characterization of the CA6NM Stainless Steel and HVOF-Sprayed Coatings

The microstructure of the CA6NM stainless steel is depicted in Fig. 1(a) and (b). The stainless steel microstructure is composed of low-carbon martensite with acicular morphology as well as bright unetched grains of retained austenite (indicated by arrows), highlighted by over-etching in Fig. 1(b). Both phases, austenite and low-carbon martensite, are desired in steels employed in hydro-turbines due to their inherent high toughness, which provides high cavitation resistance (Ref 1, 3). Also, the retained austenite, estimated at 2.7 vol.%, can turn into martensite if deformed, offering an extra protective mechanism against cavitation (Ref 31).

Figure 2(a), (b), and (c) exhibits the microstructures of the Cr₃C₂-based coatings. Through analysis of the SEM cross sections under low magnification (200×), all Cr₃C₂-based coatings showed a dense structure, with mechanical interlocking with the substrate and without the presence of interconnected pores. The absence of such paths for the electrolyte to reach the substrate improves the electrochemical resistance of these coatings, hindering the formation of galvanic cells with the substrate (Ref 26, 30). Also, no cracks or voids were seen in the interface between the coating and substrate, indicating good adhesion.

The microstructure of the Cr₃C₂-based coatings, as shown in the SEM high-magnification images, consisted of lamellar morphology, a result of the high-speed impact promoted by the HVOF process (Ref 17, 21, 31, 32). In the Cr₃C₂-25NiCr coating, rounded carbide particles uniformly

distributed in the lamellar structure of the coating were also visible. Besides high coating density, these morphologies provide substantial cohesive strength between each deposited layer. The Cr₃C₂-10Ni and Cr₃C₂-10NiCr coatings (Fig. 2(a) and (b)) exhibited a contrast of clearer gray tone layers, while other layers exhibited a darker gray tone which might suggest a different chemical composition. Through EDS analyses of these regions, it was concluded that the clearer regions are composed by the metallic matrix, only having Cr and Ni in its composition, while the darker regions are composed by Cr and C, being the areas with a high content of chromium carbides. However, for the Cr₃C₂-25NiCr cermet, this contrast of gray tones is not so evident. Through EDS it was confirmed that the rounded shaped particles are chromium carbides, while the lamellar structures are composed mainly by Cr and Ni, but also have some C content in it. It confirms that for the Cr₃C₂-25NiCr a higher degree of carbide dissolution in the metallic matrix occurred, which is beneficial for corrosion resistance as it reduces the composition gradient between carbides and metallic matrix (Ref 32).

Figure 3(a), (b), and (c) shows the microstructures of the WC-based coatings. In the low SEM magnification images (200×), all the WC cermets exhibited good adhesion to the substrate and low porosity, along with no interconnected pores. Therefore, we expected porosity would not have a major influence in the electrochemical analysis of the WC- and Cr₃C₂-based coatings, since both cermet systems had low porosity, below 2%, as well as no micro-cracks or interconnected pores. In the SEM high-magnification images, a refined structure of carbides was observed homogeneously distributed in the metallic matrix of all the WC-based coatings (Ref 2, 17, 21). Differently from the Cr₃C₂-based coating, the WC cermets exhibited a clearer gray tone in all the SEM images. As widely discussed, in SEM backscattering images, heavier elements, such as the main element of these coatings (tungsten), appear with clearer gray tones (Ref 14). It suggests that a high degree of carbide dissolution occurred in the metallic matrix of the

Table 4 Porosity content and thickness in the as-sprayed state and after grinding of the Cr₃C₂- and WC-based coatings thermally sprayed by the HVOF process

Material	Porosity	Thickness—as sprayed, μm	Thickness after grinding, μm
Cr ₃ C ₂ -25NiCr	1.91 ± 0.34	230 ± 8	200 ± 21
Cr ₃ C ₂ -10NiCr	1.93 ± 0.10	153 ± 34	104 ± 19
Cr ₃ C ₂ -10Ni	1.79 ± 0.09	187 ± 22	90 ± 14
WC-10Co-4Cr	1.13 ± 0.17	210 ± 13	90 ± 11
WC-12Co	1.56 ± 0.39	321 ± 16	118 ± 7
WC-10Ni	1.69 ± 0.15	435 ± 21	277 ± 13
CA6NM	...	...	...

Table 5 Madeira River water composition reproduced in the laboratory

Electrolyte composition, mg L^{-1}							
Cl ⁻	NO ₂ ⁻	Br ⁻	NO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻	CaCO ₃	pH
0.75	0.50	0.50	0.46	1.00	6.70	29.47	7.1

WC-based coatings, which was further confirmed through EDS analyses.

Moreover, Table 4 summarizes the porosity content and thickness, in the as-sprayed state and after grinding for polarization tests, of the Cr₃C₂ and WC coatings. All the coatings showed porosity levels below 2%, which is consistent with the HVOF process (Ref 33–35). Low porosity is of great importance to corrosion resistance, due to the absence of free paths for the electrolyte to reach the substrate.

Even though optical microscopy and SEM analysis provides valuable information about the coating structure, XRD can lead to a better understanding of phase formation, as shown in Fig. 4(a) and (b). The Cr₃C₂-based coatings (Fig. 4(a)) are consisted of Cr₃C₂ carbides, having also peaks with low intensity assigned to Cr₇C₃ and Cr₂O₃ (Ref 9, 20, 21). Similarly, the WC-based coatings (Fig. 4(b)), did not show any oxide peaks while presenting little decomposition of carbide WC into W₂C (Ref 2, 9, 14). This is due to the high velocities applied in the HVOF process, leaving little or no time for the carbides to react with the oxygen in the atmosphere, limiting the amount of oxide formation and decarbonization of the carbides. Hence, the XRD analysis corroborates the results obtained by metallography: the HVOF process produced coatings with a structure almost free of oxides/decarbonization allied with high density and good adhesion to the substrate (Ref 2, 9, 14, 21).

Potentiodynamic Polarization of the Coatings Thermally Sprayed by HVOF

Figure 5(a) and (b) displays the graphs of the potentiodynamic curves of the CA6NM stainless steel, carbon steel

Fig. 1 Optical microscopy of the CA6NM stainless steel electrochemically etched with a solution of 10% oxalic acid for 10 s (a) and over-etched for 30 s (b)

substrate, Cr₃C₂ and WC coatings. Also, Table 6 summarizes the values of corrosion current density (i_{corr}), corrosion potential (E_{corr}), transpassive potential (E_{tr}), anodic (β_a) and cathodic (β_c) Tafel slopes, corrosion (CR) and mass loss rates (MR) of all the coatings.

The corrosion potential is a parameter directly related to the thermodynamics of the corrosion process, whereas the corrosion current density is related to the kinetics of corrosion. According to Fig. 5(a) and (b) and Table 6, the

Fig. 2 SEM cross-section microstructures with low (indication 01) and high (indication 02) magnification of the Cr_3C_2 -10Ni (a), Cr_3C_2 -10NiCr (b) and Cr_3C_2 -25NiCr (c) coatings

coatings containing Cr in the metallic matrix (WC-10Co-4Cr and Cr_3C_2 -based coatings) not only exhibited higher corrosion potential but also had lower corrosion current densities compared to the WC-12Co and WC-10Ni coatings. This implies that in Madeira River water, corrosion processes are more prone to start in WC-Co and WC-Ni-based coatings, as indicated by their lower E_{corr} values, and dissolution of these coatings is more severe, as exhibited by the higher i_{corr} values.

Each cermet system possesses a complex corrosion mechanism due to its interaction with the corrosive media, that results in substantial differences in dissolution resistance, as exhibited by the E_{corr} and i_{corr} values of these materials. These results reveal the importance of evaluating the corrosion resistance of cermets in river water, even though it is a media without high concentration of corrosive ions. As shown in the river water composition (Table 5), the main corrosive agents are chloride (Cl^-) and sulfate (SO_4^{2-}), anions that exist in small concentrations, 0.75 and 6.70 mg/L^{-1} , respectively. Moreover, many studies have reported that sulfate acts as an inhibitor of localized corrosion in solutions containing Cl^- , and this inhibitive effect increases with rising $[\text{SO}_4^{2-}]/[\text{Cl}^-]$ ratio, which is about 8.93 for Madeira River water (Ref 36–38). Additionally, as reported by Zuo et al. (Ref 38), PO_4^{3-} and NO_3^- also acts as pitting inhibitors. Therefore, based on these data, the river water is not highly corrosive consisting mainly of corrosion inhibitors. However, the combined effects of these different parameters can affect the

corrosion mechanisms and the materials corrosion resistance. This confirms the relevance of evaluating each cermet's corrosion resistance in river water, especially with the rising application of these materials as coatings for hydro-turbines.

The higher dissolution of the WC-12Co and WC-10Ni cermets can be explained by their corrosion mechanisms. As widely reported, WC-based coatings undergo micro-galvanic corrosion between the metallic matrix (Ni, Co) and the ceramic phase (WC), in which the metallic matrix acts as the anode and is preferentially corroded, maintaining the surface of these cermets under active dissolution conditions (Ref 15–18, 24, 25). This can be related to the more negative corrosion potentials, ranging from -372 mV versus SCE (WC-10Ni) to -414 mV versus SCE (WC-12Co). Moreover, according to Li et al., the corrosion resistance of WC-12Co can be affected by the oxidation of the Co matrix, leading to formation of non-protective oxides such as Co_3O_4 and CoO at neutral pH, which are easily dissolved and can promote the continuous dissolution of the coating (Ref 8, 19).

The same observations apply to the corrosion current densities, which were up to 15 times higher than in the other coatings, in which the micro-galvanic corrosion and constant dissolution of porous oxides increased the flow rate of electrons from the anodic dissolution, leading to high i_{corr} values (Ref 15–19, 24, 25). Based on the use of these materials as coatings for hydro-turbines, these electrochemical properties in river water are concerning,

Fig. 3 SEM cross-section microstructures with low (indication 01) and high (indication 02) magnification of the WC-10Ni (a), WC-12Co (b) and WC-10Co-4Cr (c)

especially because of the synergistic effect of erosion and cavitation, which can increase the interfacial area between the ceramic particles and the electrolyte, promoting corrosion of the carbides as well as mechanic detachment of these particles due to preferential dissolution of the metallic matrix (Ref 15).

The better electrochemical performance in Madeira River water of Cr_3C_2 -based coatings (Fig. 5(a)) may be the result of the NiCr/Ni matrix and the Cr content in solid solution (Ref 15, 20–23), leading to formation of protective oxides such as Cr_2O_3 and Ni_2O_3 . Unlike oxides formed in WC-Co coatings, these act as barriers against corrosion (Ref 20–23). Additionally, as exhibited in the diffractogram of Fig. 4(a), Cr_2O_3 is also formed during the deposition of the coating. According to Espallargas et al. (Ref 21), the Cr_2O_3 formed during deposition has high adherence to the substrate and improves the corrosion resistance of these cermets. The formation of these protective oxides hinders the general surface activity as well as reducing the effect of micro-galvanic corrosion between the carbides and metallic matrix, as reported by many authors (Ref 8, 15, 16, 21, 22). These widely reported protective mechanisms may be the main reason for the higher corrosion potentials, around -250 mV versus SCE, of the Cr_3C_2 -based coatings. Moreover, these oxides can hinder the electron transfer through metal dissolution, resulting in lower corrosion current densities. Another important feature is that the corrosion resistance in river water of these cermets is directly affected by the Cr content rather than

the Ni content, as indicated by the increase in i_{corr} of the Cr_3C_2 cermets with the reduction of Cr content in the matrix (Ref 8, 15, 21).

Among the WC-based cermets, the one containing a matrix of Co-Cr exhibited the highest positive corrosion potential (-267 mV versus SCE) and up to four times lower corrosion current density ($1.743 \mu\text{A cm}^{-2}$) compared to the WC-12Co ($7.758 \mu\text{A cm}^{-2}$) and WC-10Ni ($7.340 \mu\text{A cm}^{-2}$) coatings in Madeira River water, supporting the beneficial effect of adding chromium in WC cermets. Many authors have report that the addition of Cr in WC-Co cermets improves the corrosion resistance due to the formation of Cr_2O_3 and CoCr_2O_4 , oxides, which act as barriers, hampering the dissolution kinetics, which is not possible for WC-Co coatings since cobalt forms porous oxides that are easily dissolved in water (Ref 8, 16, 39). Therefore, these results indicate that addition of Cr in WC-based coatings can greatly improve the corrosion resistance of these materials, making them suitable options to coat hydro-turbine components from an electrochemical point of view, whereas WC-12Co and WC-10Ni are more prone to undergo dissolution as well as corrode at rates up to fifteen times higher than the coatings containing Cr, limiting their application in river water.

All the coatings exhibited active dissolution followed by a stabilization of the current density, suggesting a passivation process. However, the high current density values in these regions (on the order of 10^{-5} A/cm^2) implies a pseudopassive state rather than true passivity, which was

only attained by the stainless steel (Ref 10, 27, 40). Pseudopassivity is a common protective mechanism in WC and Cr_3C_2 cermet systems, having been widely reported in acid, alkaline and neutral media (Ref 10, 27, 40, 41).

Fig. 4 Diffraction patterns of the Cr_3C_2 -based (a) and WC-based (b) coatings

WC-12Co and WC-10Ni were the only coatings that retained the pseudopassive state until 1200 mV versus SCE, while all the coatings containing Cr (WC-10Co-4Cr and Cr_3C_2 -based coatings) exhibited a sharp increase in current at some point of the anodic polarization process, leading to transpassive dissolution of these materials. The pseudopassivity of WC-Co cermets is generally ascribed to a complex structure of Co and W oxides that hinders the electron transfer of the anodic reaction (Ref 10, 27, 39, 40).

Figure 5(b) shows two pseudopassive regions in the polarization curve of the WC-12Co coating. According to Li et al. (Ref 8), the first stage can be assigned to the preferential dissolution and oxidation of cobalt as well as oxidation of W dissolved in the metallic binder, while a second region with higher anodic potential is related to further oxidation of W from the carbide particles. Lekatou et al. (Ref 10, 27) also reported a similar two-stage pseudopassive protective mechanism of WC-Co cermets. Therefore, it is possible to assume that the behavior observed in the polarization curves of the WC-12Co (Fig. 5(b)) was due to pseudopassive stage (I) related to oxidation of cobalt and tungsten in the metallic binder, while pseudopassive stage (II) was related to further oxidation of cobalt oxides and of the tungsten in WC particles.

The possible reaction route for pseudopassive stage (I) is exhibited in reactions (1) and (2), while a possible reaction route for pseudopassive stage (II) is depicted in reactions (3) and (4) (Ref 8, 39). For the WC-10Ni coating, the pseudopassive range might be related, besides the oxidation of tungsten, to dissolution of the Ni matrix, leading to Ni_2O_3 and $\text{Ni}(\text{OH})_2$ formation, protecting the substrate, as described by Zhang et al. (Ref 7):

Fig. 5 Potentiodynamic curves of the Cr_3C_2 -based (a) and WC-based (b) coatings in comparison with the CA6NM stainless steel in Madeira River water

Table 6 Corrosion potential (E_{corr}), corrosion current density (i_{corr}), transpassive potential (E_{tr}), corrosion (CR) and mass loss (MR) rates, anodic (β_a) and cathodic (β_c) Tafel slopes obtained from thepotentiodynamic curves for the CA6NM stainless steel, carbon steel substrate and Cr₃C₂- and WC-based coatings

Material	E_{corr} versus SCE, mV	i_{corr} , $\mu\text{A cm}^{-2}$	E_{tr} versus SCE, mV	β_a , mV	β_c , mV	CR, mm/year	MR, g/m ² d
Cr ₃ C ₂ -25NiCr	− 224 ± 3	0.494 ± 0.016	704 ± 3	548 ± 47	209 ± 30	0.0045	0.0874
Cr ₃ C ₂ -10NiCr	− 248 ± 2	0.711 ± 0.036	700 ± 9	588 ± 66	218 ± 51	0.0068	0.1267
Cr ₃ C ₂ -10Ni	− 261 ± 4	0.750 ± 0.051	567 ± 7	401 ± 44	199 ± 36	0.0071	0.1341
WC-10Co-4Cr	− 267 ± 5	1.743 ± 0.035	502 ± 4	528 ± 25	298 ± 15	0.0168	0.6708
WC-10Ni	− 372 ± 6	7.340 ± 0.254	...	517 ± 33	358 ± 12	0.0683	2.7975
WC-12Co	− 414 ± 3	7.758 ± 0.311	...	500 ± 62	367 ± 58	0.0777	3.1509
CA6NM	− 263 ± 6	0.173 ± 0.026	...	511 ± 21	122 ± 15	0.0019	0.0405
Carbon steel	− 568 ± 4	18.871 ± 0.472	...	546 ± 47	315 ± 19	0.2257	4.8567

For the coatings containing Cr (WC-10Co-4Cr and Cr₃C₂-based coatings), formation of chromium oxide was the main protective mechanism leading to pseudopassive behavior. However, a sharp increase in the current density at potentials around 500–700 mV versus SCE suggested transpassivation (Ref 40). According to Langberg et al. (Ref 41), under higher anodic potentials, chromium oxide can undergo oxidation from Cr (III) to Cr (VI). This might have been the cause of the transpassive dissolution of these coatings. Nevertheless, even though the CA6NM stainless steel also formed a layer of Cr₂O₃, it exhibited passive behavior at high anodic potentials without undergoing transpassive dissolution. This is a result of the Cr content above 10.5% in the CA6NM stainless steel, which provides the formation of a continuous protective film of Cr₂O₃ (Ref 1, 6). Even though the WC-10Co-4Cr and Cr₃C₂-based coatings had Cr content ranging between 2.5 and 6%, these were not enough to form a continuous film of chromium oxide. As described by Picas et al., this chromium content leads to the formation of non-uniform isolated regions with Cr₂O₃, enhancing the dissolution resistance, but not as effectively as a stainless steel that contains approximately 12.75% Cr (Ref 16).

Considering the corrosion resistance of these cermets, the ability to retain the pseudopassive state in such a wide range of overpotentials is the only advantage of the WC-12Co and WC-10Ni cermets over the other tested materials. Nevertheless, considering the practical application as coatings for hydro-turbines, neither passivity nor pseudopassivity is a real advantage, since the constant friction with the river water, implosion of vapor bubbles and the wear caused by the sediment load of the Madeira River can constantly remove the oxide layer of these materials, maintaining them in an active dissolution state. Therefore, due to their high corrosion resistance, the WC-10Co-4Cr

and Cr₃C₂-based coatings are more suitable materials to coat hydro-turbines, while the application of WC-10Ni and WC-12Co is limited by their low corrosion resistance in river water.

The anodic (β_a) and cathodic (β_c) Tafel slopes also supported the previous results. The slopes of the anodic and cathodic polarization are directly related to the rate of the anodic (coating/stainless steel dissolution) and cathodic (oxygen reduction) reactions (Ref 42). The CA6NM stainless steel exhibited β_a values up to three times higher than the β_c values, indicating that the protective mechanisms act on the anodic dissolution. Similar results were obtained by Gerald et al. (Ref 42) and are related to passive Cr₂O₃ film formation, since it hampers the electron transfer from the anodic reaction rather than acting to reduce oxygen. Similarly, the cermet coatings exhibited anodic Tafel slopes two to three times higher than the cathodic slopes. Analogously to the stainless steel, all these cermets can form a structure of oxides on their surfaces, directly hindering the anodic dissolution, as indicated by their pseudopassive behavior and high β_a values.

According to Fig. 5(a) and (b) and Table 6, the carbon steel substrate has a much more active behavior and underwent a more severe corrosion process when compared to all the cermet coatings. This major difference in the corrosion potential and current density also sustains that the substrate did not influence in the electrochemical results, thus confirming that the dense cermet coatings inhibited any contact between the electrolyte and substrate during the polarization tests. Moreover, the coatings with a higher thickness (WC-12Co and WC-10Ni) exhibited the higher corrosion current densities, indicating that the corrosion results are influenced only by the coating structure and composition, regardless of its thickness.

The stainless steel, the WC-10Co-4Cr coating and the Cr₃C₂-based coatings have a similar tendency to corrode, since their corrosion potentials are all close to − 250 mV in Madeira River water. According to Schneider et al., if

two materials have a difference in corrosion potential smaller than 50 mV, galvanic corrosion between these materials may not occur because of electrochemical similarity (Ref 43). The maximum difference of E_{corr} between the coatings containing Cr in solid solution and the CA6NM stainless steel was 29 mV, while these differences were 109 mV for the WC-10Ni and of 151 mV for the WC-12Co coatings. Therefore, based on the previous results, the WC-10Co-4Cr and Cr_3C_2 cermets may not undergo galvanic corrosion in Madeira River water when applied in a CA6NM substrate, while the WC-12Co and WC-10Ni can be substantially corroded by the galvanic effect.

Using the corrosion current densities obtained through Tafel extrapolation of the polarization curves and Eq 5 and 6 as described in ASTM standard G102, we were able to estimate both the corrosion and mass loss rates in river water, parameters of major relevance for proper selection of materials to coat hydro-turbines, a topic that is scarce in the literature. In Eq 5 and 6, i_{corr} is the corrosion current density, in $\mu\text{A}/\text{cm}^2$; MR is the mass loss rate, in $\text{g}/\text{m}^2 \text{ d}$; K_2 is a constant equivalent to 8.954×10^{-3} ($\text{g cm}^2/\mu\text{A m}^2 \text{ d}$); EW is the equivalent weight of the material; CR is the corrosion rate, in mm/year ; ρ is the density of the coating, in g/cm^3 , and K_1 is a constant equivalent to 3.27×10^{-3} ($\text{mm g}/\mu\text{A cm year}$). The equivalent weight was calculated based on the valences exhibited in Table 7 for each metallic element and calculated through Eq 7, where n_i is the valence, f_i is the mass fraction and W_i is the atomic weight of the i th element of the cermet coating:

$$\text{MR} = K_2 \cdot i_{\text{corr}} \cdot \text{EW} \quad (\text{Eq 5})$$

$$\text{CR} = \frac{K_1 \cdot i_{\text{corr}} \cdot \text{EW}}{\rho} \quad (\text{Eq 6})$$

$$\text{EW} = \frac{1}{\sum \frac{n_i f_i}{W_i}} \quad (\text{Eq 7})$$

The corrosion and mass loss rates (Fig. 6(a) and (b)) are proportional to the i_{corr} values, corroborating the previous analysis, i.e., the chromium carbide coatings had less severe rates, followed by WC-10Co-4Cr and last by WC-12Co and WC-10Ni coatings, both lacking Cr in their chemical compositions. Also, Fig. 6(a) and (b) highlights the large difference in the dissolution rate between the Cr_3C_2 - and WC-based coatings. The WC coatings showed CR and MR values up to 10 times higher than the values obtained for the Cr_3C_2 -based coatings.

The maximum and minimum CR and MR values of the WC-based coatings are shown in Fig. 6(a) and (b). Tungsten dissolution forms different corrosion products, such as WO_3 and WO_4^{2-} if the dissolved species is W^{6+} , or WO_2 if the dissolved species is W^{4+} (Ref 7, 8, 16, 39). Therefore, to calculate the CR and MR, we assumed a condition

in which tungsten dissolves in the W^{4+} state (maximum) and another in which it dissolves in the W^{6+} state (minimum). However, the real CR and MR values of the WC-based coatings may be closer to the minimum value, since the predominant corrosion products found for WC dissolution are WO_3 and WO_4^{2-} (Ref 7, 16, 39–41), possibly through reactions 8 and 9 (Ref 39). The Pourbaix diagram of tungsten also supports this hypothesis, implying that the corrosion product formed in neutral solutions is WO_4^{2-} (Ref 44):

SEM and EDS Analyses of Corroded Surfaces/Cross Sections

The SEM cross-section images of the cermet coatings after potentiodynamic polarization in Madeira River water are exhibited in Fig. 7. All the cermet coating exhibited cross sections without corrosion paths as well as no corrosion was detected in the coating/carbon steel substrate. This is in accordance with the previous results obtained through the potentiodynamic polarization tests, where all the coatings exhibited higher E_{corr} and lower i_{corr} values when compared to the carbon steel, in other words, it is confirmed that the coatings successfully prevented any contact between the electrolyte and the carbon steel substrate. Therefore, the HVOF process proved to be an excellent technique to obtain cermet coatings with a dense structure, with low porosity and no interconnected pores, which reflects in higher corrosion resistance in Madeira River water.

Analysis of the corroded surface of these coatings (Fig. 8) corroborates the previous results. In Table 8 are exhibited the EDS results of the corrosion products formed in the surface of the cermet coatings, as depicted in Fig. 8. The Cr_3C_2 -based coatings surfaces were mainly composed of Cr, Ni, C and expressive O content, indicating formation of oxides. Moreover, the darker gray tone regions (areas 2 and 5) exhibited higher oxygen content when compared to the clearer gray tone regions (areas 1 and 6), suggesting that the surface was not fully covered by oxides. This is in accordance with the findings of Picas et al. (Ref 16), where the authors states that Cr_3C_2 -based coatings can form isolated islands of oxides rather than a continuous passive film.

Similarly, the WC-based coatings surface composition was constituted of its main matrix elements (Co, Ni, CoCr), W, C and oxygen, also suggesting formation of oxides which is in accordance with the pseudopassive mechanism previously discussed. The morphology of the corroded surfaces also sustains that no severe corrosion process took

Table 7 Oxidation state and valence (n) of the elements considered for the calculation of the equivalent weight (EW) of the Cr_3C_2 - and WC-based coatings.

Element	Oxidation state	n
W	$\text{W}^{6+}/\text{W}^{4+}$	6/4
Co	Co^{2+}	2
Ni	Ni^{3+}	3
Cr	Cr^{3+}	3

place in these cermets as well as no localized corrosion was detected.

The coatings that exhibited a higher degree of porosity in its surface, i.e. Cr_3C_2 -25NiCr, WC-10Ni, WC-12Co and WC-10Co-4Cr, showed a higher content of oxygen inside pores (areas 3, 8, 10 and 11), while most of the free surface did not present any oxygen (areas 4, 7, 9 and 12). This shows that the porosities were active anodic sites for occurrence of corrosion, but that due to the low corrosiveness of the river water, these regions were readily protected by formation of oxides, as was similarly stated by Liu et al. (Ref 2).

Galvanic Corrosion of the CA6NM/Cermet Coatings

Figure 9(a), (b), (c), (d), (e), and (f) displays the graphs of the variation in galvanic current density and potential of the couple as a function of time. All the galvanic couples formed by CA6NM stainless steel and Cr_3C_2 -based coatings showed positive values of galvanic current density. This means, for the cell setup (CA6NM—counter electrode; Cr_3C_2 -based coatings—working electrode), that stainless steel is the cathode and the coating is the anode. Therefore, under galvanic corrosion conditions, the coating will have accelerated dissolution, while the stainless steel is under cathodic protection (Ref 21, 26, 27). Nevertheless, these coatings exhibited negligible galvanic current densities, on the order of $10^{-3} \mu\text{A cm}^{-2}$, as indicated in Table 9. This shows that the kinetics of the process is slow, not leading to severe corrosion of the Cr_3C_2 cermets. Also, all the Cr_3C_2 coatings had high and stable couple potentials (E_c) during the immersion time of 11 days, resulting in a lesser tendency for galvanic corrosion to occur, as was predicted in the Tafel analysis.

The WC-based coatings also acted as the anode of the couple, while the stainless steel was the cathode, leading to cathodic protection of the stainless steel and more severe dissolution of the coating (Ref 21, 26, 27). Among all the cermets, WC-10Co-4Cr showed the lowest value of i_g , even compared to the Cr_3C_2 -based coatings. Furthermore, the E_c value of WC-10Co-4Cr was the highest among all the cermets analyzed, making galvanic corrosion between the CA6NM/WC-10Co-4Cr couple less likely to occur. Analysis of the corrosion potential obtained by Tafel

Fig. 6 Corrosion (a) and mass loss rate (b) of the cermet coatings. WC-based coatings had maximum and minimum values due to two possible species in dissolution (W^{4+} and W^{6+})

extrapolation indicated a minimum difference of 7 mV between the corrosion potentials of the stainless steel and the WC-10Co-4Cr, corroborating the results obtained through ZRA.

The WC-10Ni and WC-12Co coatings underwent more severe galvanic corrosion, exhibiting i_g values on the order of 10^{-2} to $10^{-1} \mu\text{A cm}^{-2}$, up to 100 times higher than the other coatings. These values can be explained by the dissimilarity between the cermets and the CA6NM steel, in addition to the corrosion susceptibility of these coatings in river water, as predicted in the Tafel extrapolation analysis (Ref 8, 19). For these reasons, both WC-10Ni and WC-12Co are prone to undergo severe galvanic corrosion when coupled to CA6NM stainless steel, which will cause faster deterioration of these coatings.

Two main factors contribute to reducing the severity of the galvanic couple formed between CA6NM and the coatings containing chromium (WC-10Co-4Cr and Cr_3C_2 -based coatings): electrochemical similarity and passivation of the cathode (Ref 26, 27, 43, 45). As reported by Schneider et al., galvanic corrosion will not occur if the difference in corrosion potentials is under 50 mV (Ref 43). As

shown in Table 6, the greatest difference between corrosion potentials of the coatings alloyed with Cr (WC-10Co-4Cr and Cr_3C_2 -based cermets) and the stainless steel was 35 mV. This is an indication of the similarity between these coatings and the turbine material, which results in small

values of galvanic current density between these couples. Furthermore, both the coatings and the stainless steel form Cr_2O_3 on their surfaces, reducing the corrosion severity due to the barrier effect of the oxide (Ref 26, 27, 43, 45).

Fig. 7 SEM cross-section images of the Cr_3C_2 - and WC-based coatings after potentiodynamic polarization in Madeira River water

Fig. 8 SEM images of the Cr_3C_2 - and WC-based coatings surface after potentiodynamic polarization tests

Table 8. Chemical compositions of the areas exhibited in Fig. 10 obtained through SEM–EDS analysis of the Cr₃C₂- and WC-based coatings after potentiodynamic polarization in Madeira River water.

Area	Coating	Cr, wt. %	Ni, wt. %	Co, wt. %	W, wt. %	C, wt. %	O, wt. %
1	Cr ₃ C ₂ -10Ni	23.6	76.4	...	...	...	...
2	Cr ₃ C ₂ -10Ni	76.9	5.2	...	...	11.7	6.2
Total area	Cr ₃ C ₂ -10Ni	60.6	19.5	...	...	9	10.9
3	Cr ₃ C ₂ -25NiCr	55.9	14.9	...	...	28.1	1.1
4	Cr ₃ C ₂ -25NiCr	61	26.2	...	...	12.9	...
Total area	Cr ₃ C ₂ -25NiCr	60.6	22.3	...	...	13.2	3.9
5	Cr ₃ C ₂ -10NiCr	62	15.6	...	...	12.6	9.9
6	Cr ₃ C ₂ -10NiCr	39.9	47	...	...	6	7.1
Total area	Cr ₃ C ₂ -10NiCr	59.9	19.9	...	...	9.1	11.1
7	WC-10Ni	...	7.0	...	93.0	...	...
8	WC-10Ni	...	5.7	...	66.5	23.7	4.1
Total area	WC-10Ni	...	6.7	...	75.4	13.7	4.2
9	WC-12Co	...	...	7.9	92.1	...	...
10	WC-12Co	...	...	5.3	5.8	75.1	13.9
Total area	WC-12Co	...	...	10.3	52.1	26.1	11.5
11	WC-10Co-4Cr	2.7	...	12.2	45.7	29.5	9.9
12	WC-10Co-4Cr	2.5	...	8.9	88.6	...	...
Total area	WC-10Co-4Cr	3.7	...	9.0	69.3	14.3	3.7

The passivation of the stainless steel, that is, the formation of a uniform and continuous film of Cr₂O₃ on the cathode, is an important parameter to analyze, since it influences the reactions in both cathode and anode. The main reaction in the cathode (stainless steel), for neutral and aerated aqueous solutions, is the reduction of the oxygen dissolved in the water, while in the anode (cermet coatings), the main reaction is the dissolution of metal. Equations 10 and 11 display both reactions (Ref 43, 45):

The cathodic reaction is dependent on the diffusion of oxygen dissolved in the electrolyte (mass transfer) and on the transport of electrons produced by the anodic reaction on the surface of the anode (charge transfer) (Ref 43, 45). When the cathode is a metal susceptible to passivation, the oxide layer hinders the diffusion of oxygen, slowing the kinetics of the cathodic reaction (Ref 26, 43, 45). Hence, with less oxygen available to complete the reaction, fewer electrons provided by the anodic reaction will be attracted, reducing the dissolution of the anode. Figure 10 illustrates the reactions in cathode and anode of a stainless steel/cermet coating couple. Besides all those factors, Madeira River water does not have a large content of corrosive ions that can destabilize the protective Cr₂O₃ oxide, which can

also contribute to lower values of galvanic current density for the WC-10Co-4Cr and Cr₃C₂ coatings.

The Madeira River's seasonality and its correlation with the operation of a hydro-turbine can affect the corrosion behavior of the galvanic couples. In periods of drought, the Madeira River's average flow rate is of 2000 m³/s, but reaches up to 52,000 m³/s in flood periods due to the hydrological regime (Ref 4). For a hydropower plant, this huge variation in flow rate can lead to the shutdown of some turbines, especially in flood periods.

While a turbine is rotating, the removal of the passive stainless steel film can occur as a result of friction with the fluid, cavitation or erosion by sediment particles. This makes it easier for the oxygen to diffuse to the substrate, increasing the galvanic current density to the values indicated by arrows in Fig. 9(a), (b), (c), (d), (e), and (f). These peaks at the initial moments of immersion in the i_g versus t profiles correspond to an active surface of the stainless steel, since the passive film is not yet completely formed. However, when a turbine is not in operation, the Cr₂O₃ film tends to form and remain stable, leading the galvanic current density to drop to the values estimated for 11 days of immersion, as exhibited in Table 9. The variation of the galvanic current density as a function of the previously reported mechanisms is illustrated in Fig. 11.

For the WC-based coatings (Fig. 9(d), (e), and (f)) and the Cr₃C₂-10Ni (Fig. 9(c)), the peak of galvanic current

Fig. 9 Couple potential (E_c) and galvanic current density (i_g) of the Cr_3C_2 -25NiCr (a), Cr_3C_2 -10NiCr (b), Cr_3C_2 -10Ni (c), WC-10Co-4Cr (d), WC-12Co (e) and WC-10Ni (f) coatings coupled to CA6NM stainless steel in Madeira River water.

was in the positive direction of the current, that is, it increased the dissolution of the coating. However, for the cermets Cr_3C_2 -25NiCr and Cr_3C_2 -10NiCr (Fig. 9(a) and (b)), the peak current was in the anodic direction, that is, the stainless steel acted as the anode and underwent galvanic dissolution. This suggests that without the passive

film, the CA6NM stainless steel had a more active surface than the Cr_3C_2 -25NiCr and Cr_3C_2 -10NiCr coatings and would corrode under these galvanic corrosion conditions.

The area ratio between the cathode and anode should also be considered. According to Mansfield (Ref 28), the higher the ratio of the cathode area in relation to the anode

area (A_C/A_A), the greater will be the galvanic current density. It is common practice to coat only small damaged areas of a hydraulic turbine, meaning the cathode area (stainless steel) will be much larger than the area of the coating, leading to severe galvanic corrosion of the latter. For the WC-10Co-4Cr and Cr_3C_2 -based coatings, this area effect may not induce severe corrosion, since these coatings exhibited negligible values of i_g . Nevertheless, this can be critical for the WC-12Co and WC-10Ni coatings, since they exhibited high galvanic current densities at an area ratio equal to 1.

Through these results, the WC-10Co-4Cr and the Cr_3C_2 cermets proved to be strong options to avoid premature electrochemical dissolution and enhance the lifespan of coatings in Madeira River water, under both active and galvanic corrosion. However, WC-10Ni and WC-12Co coatings exhibited high corrosion rates and were prone to undergo severe galvanic corrosion when coupled to CA6NM stainless steel, limiting their durability due to corrosive degradation.

Table 9. Couple potential (E_g) and galvanic current density (i_g) values of the cermet coatings coupled to CA6NM stainless steel.

Coating	i_g , $\mu\text{A cm}^{-2}$	E_c versus SCE, V
Cr_3C_2 -25NiCr	0.00275	– 0.1814
Cr_3C_2 -10NiCr	0.00129	– 0.1630
Cr_3C_2 -10Ni	0.00134	– 0.1417
WC-10Co-4Cr	0.000946	– 0.1360
WC-10Ni	0.0889	– 0.2990
WC-12Co	0.531	– 0.4510

Fig. 11 Schematic representation of the influence of the wear mechanisms on the galvanic current density. The breakage of the passive film in the cathode due to these degradation mechanisms facilitates the oxygen diffusion, increasing the i_g and consequently the corrosion of the anode.

Conclusions

Cermet coatings are used in hydro-turbines to mitigate the degradation by abrasion and cavitation. However, if they are not corrosion resistant, those properties can be lost after short operation periods. Thus, the subject of this work was to study the active and galvanic corrosion resistance of six different HVOF thermally sprayed coatings in Madeira River water. The results led to the following major conclusions:

The HVOF process proved to be an important tool for the development of corrosion resistant coatings, since all the cermets showed porosity level below 2% and good adhesion to the substrate, inhibiting any contact between the electrolyte and the substrate. Also, all the cermet coatings exhibited a pseudopassive behavior in Madeira River water. However, considering their applicability as coatings for hydro-turbines, pseudopassivity is not a real advantage, since the operational conditions involving friction with water, cavitation and wear caused by

Fig. 10 Schematic representation of the galvanic corrosion mechanism in neutral aerated solutions. In the anode (cermet), dissolution of the coating takes place, while in the cathode, oxygen reduction occurs. The presence of a passive film on the cathode can hinder the cathodic reaction kinetics, reducing the severity of galvanic corrosion.

sediments in the water can constantly remove the protective oxide layer of these materials. Lastly, WC-10Co-4Cr and Cr₃C₂-based coatings were more suitable options to coat hydro-turbines since they exhibited negligible galvanic corrosion when coupled to the CA6NM stainless steel in Madeira River water as well as corrosion rates up to ten times lower than the WC-12Co and WC-10Ni cermets. Moreover, addition of Cr in the metallic matrix greatly increased the corrosion resistance of WC- and Cr₃C₂-based coatings in river water.

Acknowledgments The authors would like to thank the laboratories and companies that provided substantial assistance with this work: Revesteel Metalização Ltda., Brazil, the Laboratory of Corrosion and Electrochemistry and Laboratory of Coatings and Welding of the LACTEC Institute.

References

1. R. Singh, S.K. Tiwari, and S.K. Mishra, Cavitation Erosion in Hydraulic Turbine Components and Mitigation by Coatings: Current Status and Future Needs, *J. Mater. Eng. Perform.*, 2012, **21**, p 1539–1551. <https://doi.org/10.1007/s11665-011-0051-9>
2. J. Liu, T. Chen, C. Yuan, and X. Bai, Performance Analysis of Cavitation Erosion Resistance and Corrosion Behavior of HVOF-Sprayed WC-10Co-4Cr, WC-12Co, and Cr₃C₂-NiCr Coatings, *J. Therm. Spray Technol.*, 2020, **29**, p 798–810. <https://doi.org/10.1007/s11666-020-00994-y>
3. B.A. Tabatabae, F. Ashrafzadeh, and A.M. Hassanli, Influence of Retained Austenite on the Mechanical Properties of, *ISIJ Int.*, 2011, **51**, p 471–475.
4. D.R. do Nascimento, A.O. Sawakuchi, C.C.F. Guedes, P.C.F. Giannini, C.H. Grohmann, and M.P. Ferreira, Provenance of Sands from the Confluence of the Amazon and Madeira Rivers Based on Detrital Heavy Minerals and Luminescence of Quartz and Feldspar, *Sediment. Geol.*, 2015, **316**, p 1–12. <https://doi.org/10.1016/j.sedgeo.2014.11.002>
5. M. Sharma, D.K. Goyal, and G. Kaushal, Tribological Investigation of HVOF Sprayed Coated Turbine Steel under Varied Operating Conditions, *Mater. Today Proc.*, 2020, **24**, p 869–879.
6. D.K. Goyal, H. Singh, H. Kumar, and V. Sahni, Slurry Erosive Wear Evaluation of HVOF-Spray Cr₂O₃ Coating on Some Turbine Steels, *J. Therm. Spray Technol.*, 2012, **21**, p 838–851. <https://doi.org/10.1007/s11666-012-9795-5>
7. X. Zhang, J. Zhou, C. Liu, K. Li, W. Shen, Z. Lin, Z. Li, Y. He, and N. Lin, Effects of Ni Addition on Mechanical Properties and Corrosion Behaviors of Coarse-Grained WC-10(Co, Ni) Cemented Carbides, *Int. J. Refract. Met. Hard Mater.*, 2019, **80**, p 123–129. <https://doi.org/10.1016/j.jrmhm.2019.01.004>
8. S. Li, Z. Guo, J. Xiong, Y. Lei, Y. Li, J. Tang, J. Liu, and J. Ye, Corrosion Behavior of HVOF Sprayed Hard Face Coatings in Alkaline-Sulfide Solution, *Appl. Surf. Sci.*, 2017, **416**, p 69–77. <https://doi.org/10.1016/j.apsusc.2017.04.149>
9. N. Vashishtha, R.K. Khatirkar, and S.G. Sapate, Tribological Behaviour of HVOF sprayed WC-12Co, WC-10Co-4Cr and Cr₃C₂-25NiCr coatings, *Tribol. Int.*, 2017, **105**, p 55–68. <https://doi.org/10.1016/j.triboint.2016.09.025>
10. A. Lekatou, D. Sioulas, A.E. Karantzalis, and D. Grimanis, A Comparative Study on the Microstructure and Surface Property Evaluation of Coatings Produced from Nanostructured and Conventional WC-Co Powders HVOF-Sprayed on Al7075, *Surf. Coatings Technol.*, 2015, **276**, p 539–556. <https://doi.org/10.1016/j.surfcoat.2015.06.017>
11. G.A. Ludwig, C.F. Malfatti, R.M. Schroeder, V.Z. Ferrari, and I.L. Mueller, WC10Co4Cr Coatings Deposited by HVOF on Martensitic Stainless Steel for Use in Hydraulic Turbines: Resistance to Corrosion and Slurry Erosion, *Surf. Coatings Technol.*, 2019, **377**, p 124918.
12. D. Goyal, H. Singh, H. Kumar, and V. Sahni, Erosive Wear Study of HVOF Spray Cr₃C₂-NiCr Coated CA6NM Turbine Steel, *J. Tribol.*, 2014, **136**, p 1–11. <https://doi.org/10.1115/1.4027621>
13. H. Zhang, Y. Gong, X. Chen, A. McDonald, and H. Li, A Comparative Study of Cavitation Erosion Resistance of Several HVOF-Sprayed Coatings in Deionized Water and Artificial Seawater, *J. Therm. Spray Technol.*, 2019, **28**, p 1060–1071. <https://doi.org/10.1007/s11666-019-00869-x>
14. T. Varis, T. Suhonen, J. Laakso, M. Jokipii, and P. Vuoristo, Evaluation of Residual Stresses and Their Influence on Cavitation Erosion Resistance of High Kinetic HVOF and HVAF-Sprayed WC-CoCr Coatings, *J. Therm. Spray Technol.*, 2020, **29**, p 1365–1381. <https://doi.org/10.1007/s11666-020-01037-2>
15. S.A. Galedari, A. Mahdavi, F. Azarmi, Y. Huang, and A. McDonald, A Comprehensive Review of Corrosion Resistance of Thermally-Sprayed and Thermally-Diffused Protective Coatings on Steel Structures, *J. Therm. Spray Technol.*, 2019, **28**, p 645–677. <https://doi.org/10.1007/s11666-019-00855-3>
16. J.A. Picas, M. Punset, E. Rupérez, S. Menargues, E. Martin and M.T. Baile, Corrosion Mechanism of HVOF Thermal Sprayed WC-CoCr Coatings in Acidic Chloride Media, *Surf. Coatings Technol.*, 2019, **371**, p 378–388. <https://doi.org/10.1016/j.surfcoat.2018.10.025>
17. L.J. Wang, P.X. Qiu, Y. Liu, W.X. Zhou, G.Q. Gou, and H. Chen, Corrosion Behavior of Thermal Sprayed WC Cermet Coatings Containing Metallic Binders in Saline environment, *Trans. Nonferrous Met. Soc. China*, 2013, **23**, p 2611–2617. [https://doi.org/10.1016/S1003-6326\(13\)62775-2](https://doi.org/10.1016/S1003-6326(13)62775-2)
18. J.E. Cho, S.Y. Hwang, and K.Y. Kim, Corrosion Behavior of Thermal Sprayed WC Cermet Coatings Having Various Metallic Binders in Strong Acidic Environment, *Surf. Coatings Technol.*, 2006, **200**, p 2653–2662. <https://doi.org/10.1016/j.surfcoat.2004.10.142>
19. M. Takeda, N. Morihiro, R. Ebara, Y. Harada, R. Wang, and M. Kido, Corrosion Behavior of Thermally Sprayed WC Coating in Na₂SO₄ Aqueous Solution, *Mater. Trans.*, 2003, **43**, p 2860–2865. <https://doi.org/10.2320/matertrans.43.2860>
20. Q. Wang, S. Luo, S. Wang, H. Wang, and C.S. Ramachandran, Wear, Erosion and Corrosion Resistance of HVOF-Sprayed WC and Cr₃C₂ Based Coatings for Electrolytic Hard Chrome Replacement, *Int. J. Refract. Met. Hard Mater.*, 2019, **81**, p 242–252. <https://doi.org/10.1016/j.jrmhm.2019.03.010>
21. N. Espallargas, J. Berget, J.M. Guilemany, A.V. Benedetti, and P.H. Suegama, Cr₃C₂-NiCr and WC-Ni Thermal Spray Coatings as Alternatives to Hard Chromium for Erosion–Corrosion Resistance, *Surf. Coatings Technol.*, 2008, **202**, p 1405–1417. <https://doi.org/10.1016/j.surfcoat.2007.06.048>
22. C.D. Arrieta-González, J. Porcayo-Calderon, V.M. Salinas-Bravo, J.G. Chacon-Nava, A. Martinez-Villafañe, and J.G. Gonzalez-Rodriguez, Corrosion Behavior of Ni-Cr Based Coatings in Simulated Human Body Fluid Environment, *Int. J. Electrochem. Sci.*, 2011, **6**, p 3644–3655.
23. P.H. Suegama, C.S. Fugivara, A.V. Benedetti, J. Fernández, and J. Delgado, Electrochemical Behaviour of Thermally Sprayed Cr₃C₂-NiCr Coatings in 0.5 M, *J. Appl. Electrochem.*, 2002, **32**, p 1287–1295.
24. S. Hong, Y. Wu, Y. Zheng, B. Wang, W. Gao, and J. Lin, Microstructure and electrochemical properties of nanostructured WC-10Co-4Cr coating prepared by HVOF spraying, *Surf.*

- Coatings Technol.*, 2013, **235**, p 582–588. <https://doi.org/10.1016/j.surfcoat.2013.08.029>
25. Q. Wang, S. Zhang, Y. Cheng, J. Xiang, X. Zhao, and G. Yang, Wear and Corrosion Performance of WC-10Co4Cr Coatings Deposited by Different HVOF and HVAF Spraying Processes, *Surf. Coatings Technol.*, 2013, **218**, p 127–136. <https://doi.org/10.1016/j.surfcoat.2012.12.041>
 26. V.A.D. Souza and A. Neville, Linking Electrochemical Corrosion Behaviour and Corrosion Mechanisms of Thermal Spray Cermet Coatings (WC-CrNi and WC/CrC-CoCr), *Mater. Sci. Eng. A.*, 2003, **352**, p 202–211. [https://doi.org/10.1016/S0921-5093\(02\)00888-2](https://doi.org/10.1016/S0921-5093(02)00888-2)
 27. A. Lekatou, D. Zois, A.E. Karantzalis, and D. Grimalis, Electrochemical Behaviour of Cermet Coatings with a Bond Coat on Al7075: Pseudopassivity, Localized Corrosion and Galvanic Effect Considerations in a Saline Environment, *Corros. Sci.*, 2010, **52**, p 2616–2635. <https://doi.org/10.1016/j.corsci.2010.04.010>
 28. F. Mansfeld, Area Relationships in Galvanic Corrosion, *Corrosion*, 1971, **27**, p 436–442. <https://doi.org/10.5006/0010-9312-27.10.436>
 29. A. Kumar, J. Boy, R. Zatorski, and L.D. Stephenson, Thermal Spray and Weld Repair Alloys for the Repair of Cavitation Damage in Turbines and Pumps: A Technical Note, *J. Therm. Spray Technol.*, 2005, **14**, p 177–182. <https://doi.org/10.1361/10599630523737>
 30. J.M. Guilemany, J. Fernández, J. Delgado, A.V. Benedetti, and F. Climent, Effects of Thickness Coating on the Electrochemical Behaviour of Thermal Spray Cr3C2-NiCr Coatings, *Surf. Coatings Technol.*, 2002, **153**, p 107–113. [https://doi.org/10.1016/S0257-8972\(01\)01679-6](https://doi.org/10.1016/S0257-8972(01)01679-6)
 31. Z. Wang and J. Zhu, Effect of Phase Transformation on Cavitation Erosion Resistance of Some Ferrous Alloys, *Mater. Sci. Eng. A.*, 2003, **358**, p 273–278. [https://doi.org/10.1016/S0921-5093\(03\)00306-X](https://doi.org/10.1016/S0921-5093(03)00306-X)
 32. X. Zhang, F. Li, Y. Li, Q. Lu, Z. Li, H. Lu, X. Ran, and X. Qi, Comparison on Multi-Angle Erosion Behavior and Mechanism of Cr3C2-NiCr Coatings Sprayed by SPS and HVOF, *Surf. Coatings Technol.*, 2020, **403**, p 126366. <https://doi.org/10.1016/j.surfcoat.2020.126366>
 33. Y. Liu, Z. Hang, G. Yang, H. Fu, N. Xi, and H. Chen, Influence of Rare Earth on the High-Temperature Sliding Wear Behavior of WC-12Co Coating Prepared by HVOF Spraying, *J. Therm. Spray Technol.*, 2018, **27**, p 1143–1152. <https://doi.org/10.1007/s11666-018-0764-5>
 34. W. Tillmann, I. Baumann, P. Hollingsworth, and I.A. Laemmerhirt, Influence of the Spray Angle on the Properties of HVOF Sprayed WC-Co Coatings Using (−10 + 2 μm) fine powders, *J. Therm. Spray Technol.*, 2013, **22**, p 272–279. <https://doi.org/10.1007/s11666-013-9882-2>
 35. W. Tillmann, I. Baumann, P.S. Hollingsworth, and L. Hagen, Sliding and Rolling Wear Behavior of HVOF-Sprayed Coatings Derived from Conventional, Fine and Nanostructured WC-12Co Powders, *J. Therm. Spray Technol.*, 2014, **23**, p 262–280. <https://doi.org/10.1007/s11666-013-0038-1>
 36. T. Aoyama, Y. Sugawara, I. Muto, and N. Hara, In Situ Monitoring of Crevice Corrosion Morphology of Type 316L Stainless Steel and Repassivation Behaviour Induced by Sulfate Ions, *Corr. Sci.*, 2017, **127**, p 131–140.
 37. Y.L. Chou, Y.C. Wang, J.W. Yeh, and H.C. Shih, Pitting Corrosion of the High-Entropy Alloy Co_{1.5}CrFeNi_{1.5}Ti_{0.5}Mo_{0.1} in Chloride-Containing Sulphate Solutions, *Corr. Sci.*, 2010, **52**, p 3481–3491. <https://doi.org/10.1016/j.corsci.2010.06.025>
 38. Y. Zuo, H. Wang, J. Zhao, and J. Xiong, The Effects of Some Anions on Metastable Pitting of 316L Stainless Steel, *Corr. Sci.*, 2002, **44**, p 13–24.
 39. V.A.D. Souza and A. Neville, Mechanisms and Kinetics of WC-Co-Cr High Velocity Oxy-Fuel Thermal Spray Coating Degradation in Corrosive Environments, *J. Therm. Spray Technol.*, 2006, **15**, p 106–117. <https://doi.org/10.1361/105996306X92677>
 40. G. Bolelli, A. Colella, L. Lusvarghi, S. Morelli, P. Puddu, E. Righetti, P. Sassatelli, and V. Testa, TiC-NiCr Thermal Spray Coatings as an Alternative to WC-CoCr and Cr₃C₂-NiCr, *Wear*, 2020, **450–451**, p 203273. <https://doi.org/10.1016/j.wear.2020.203273>
 41. M. Långberg, C. Örnek, J. Evertsson, G.S. Harlow, W. Linpé, L. Rullik, F. Carlà, R. Felici, E. Bettini, U. Kivisäkk, E. Lundgren, and J. Pan, Redefining Passivity Breakdown of Super Duplex Stainless Steel by Electrochemical Operando Synchrotron Near Surface X-ray Analyses, *Npj Mater. Degrad.*, 2019, **3**, p 1–11. <https://doi.org/10.1038/s41529-019-0084-3>
 42. O.J. Gerald, L. Wenge, L. Zhang, Z. YuanTao, and L.C. Long, Corrosion Behaviour of 2205 Duplex Stainless Steel in Marine Conditions Containing *Erythrobacter pelagi* Bacteria, *Mat. Chem. Phys.*, 2020, **239**, p 1222010. <https://doi.org/10.1016/j.matchemphys.2019.122010>
 43. M. Schneider, K. Kremmer, C. Lämmel, K. Sempf, and M. Herrmann, Galvanic Corrosion of Metal/Ceramic Coupling, *Corros. Sci.*, 2014, **80**, p 191–196. <https://doi.org/10.1016/j.corsci.2013.11.024>
 44. S.B. Lyon, Corrosion of Tungsten and Its Alloys, *Sheir Corrosion*, Vol III, 1st ed., T.J.A. Richardson Ed., Elsevier, Amsterdam, 2009, p 2151–2156
 45. J.W. Oldfield, Electrochemical Theory of Galvanic Corrosion, *STP978 Galvanic Corrosion*. H.P. Hack Ed., ASTM International, West Conshohocken, 1988, p 5–22

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.