



Corrosion behaviour of HVOF-sprayed TiC + high-entropy alloy (HEA) hardmetal coatings

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ABSTRACT

Hardmetal coatings with a High-Entropy Alloy (HEA) matrix have been shown to provide intermediate wear performance between conventional WC-CoCr and Cr₃C₂-NiCr compositions. Thus, they may overcome the traditional dichotomy between a more performing material that is however based on strategic (W, Co) and carcinogenic (Co) elements, and one based on less critical materials but with poorer performance. However, little is known about their corrosion response in aqueous environments. Therefore, in this work, we selected four High-Velocity Oxygen Fuel (HVOF)-sprayed HEA + 60 vol% TiC coatings, namely Cr₂₀Mn₂₅Fe₄₀Ni₁₅ + 60TiC, Al₁₄(Cr₂₀Mn₂₅Fe₄₀Ni₁₅) + 60TiC, Al_{0.5}CuCrFeNi₂ + 60TiC and CrMnFeCoNi+60TiC (matrix compositions in atomic ratios), and we investigated their corrosion behaviour in a common model environment, a 3.5% NaCl (wt./vol.) aqueous solution, through electrochemical polarization and chronoamperometry tests.

We found that the electrochemical polarization responses of all HEA-based hardmetals were much more similar to each other than their widely different matrix compositions would have suggested. Coupling with the TiC hard phase, indeed, had a levelling effect, promoting pseudo-passivation of compositions where the matrix alone would hardly exhibit any passivity, such as Al₁₄(Cr₂₀Mn₂₅Fe₄₀Ni₁₅), while worsening the response of better-passivating matrices.

There were, however, differences in the long-term stability of the pseudo-passive state, studied by potentiostatic chronoamperometry. Al_{0.5}CuCrFeNi₂ + 60TiC and CrMnFeCoNi+60TiC experienced progressive destabilization during 3 h of testing at +0.15 V vs. OCP, while Cr₂₀Mn₂₅Fe₄₀Ni₁₅ + 60TiC and Al₁₄(Cr₂₀Mn₂₅Fe₄₀Ni₁₅) + 60TiC developed a more stable pseudo-passive film based on Fe, Cr, and Ti oxides (from XPS analyses), which was destabilized only at higher anodic overpotentials of +0.20 and +0.25 V vs. OCP.

1. Introduction

Hardmetal coatings deposited by thermal spraying find numerous applications to protect industrial components subjected to severe wear conditions e.g. in the aeronautical, pulp and paper, and petrochemical industries, in hydroelectric plants, automatic industrial machinery, etc. [1–7]. The most widely used material category in many of these applications consists of WC-based hardmetals with Co-based matrix, because the unique wettability between these two constituents results in an optimal combination of hardness and fracture toughness [8]. The thermal spray technique of choice in the industry is the High Velocity Oxygen-Fuel (HVOF) process, which produces dense coatings with low porosity, strong adhesion to the substrate, and limited thermal

alterations like carbide dissolution, oxidation, and carbon loss [9]. Newer processes like High Velocity Air-Fuel (HVOF) are also being considered, with extremely promising results, as recently reviewed by Torkashvand et al. [10], but their industrial usage is still limited.

In many of the applications listed above, together with severe contact conditions, corrosive environments are also encountered; therefore, hardmetal coatings also need to possess good corrosion resistance. For this purpose, the material of choice is usually WC-10wt%Co-4wt%Cr, or similar compositions with Cr [11], because Cr confers passivation ability to the Co matrix, which would otherwise have limited corrosion resistance [12]. Studies on the corrosion resistance of HVOF-sprayed WC-CoCr compositions have been conducted in many application fields. In particular, the HCAT team carried out extensive corrosion testing in the

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1990s and 2000s as part of a wider effort to validate the use of these coatings in aircraft landing gears as a replacement for hard chromium [13].

When particularly good corrosion resistance is needed, Cr_3C_2 -25 wt % (Ni-20wt.%Cr) coatings can be employed [14], despite a lower hardness than WC-based ones. These two formulations, namely WC-CoCr and Cr_3C_2 -NiCr, currently dominate the market of thermal spray hardmetal coatings. Other compositions, such as Cr_3C_2 -WC-NiCr [15] or WC-(W, Cr) $_2$ C-Ni [14,16,17] hardmetals, combine the carbides of chromium and tungsten to obtain a compromise between corrosion and wear resistance, as well as high-temperature resistance.

However, the development of novel compositions could be of considerable practical significance. All formulations based on WC rely on an element, namely tungsten, which is often considered among the most critical raw materials for many industrialized economies, including, e.g., the European Union [18] and the USA [19]. It is indeed subjected to significant market price fluctuations and export control measures [20]. Cobalt, too, is regarded as a critical raw material, and it is also classified as a human carcinogen [21,22]. Furthermore, the performance gap between WC-CoCr and Cr_3C_2 -NiCr coatings in terms of hardness and wear resistance is considerable. Therefore, finding compositions that provide a proper balance between wear and corrosion resistance other than those based on WC + Cr_3C_2 mixes, which still contain considerable amounts of tungsten, would be of particular significance.

In our previous work, we reported on TiC-based hardmetals with Fe-and/or Ni-based matrices [23–25]: the compositions with Ni-based matrices like Ni-20wt.%Cr or Ni-Fe-Cr alloys, did provide interesting results in terms of achieving intermediate wear resistance between WC-CoCr and Cr_3C_2 -NiCr, and corrosion resistance approaching that of Cr_3C_2 -NiCr itself.

More recently, we have undertaken a research effort to further improve the properties of these hardmetals by switching from the “simple” matrices listed above to High-Entropy Alloy (HEA) matrices. The idea is to take advantage of the unique combination of properties offered by HEAs, that is, equiatomic or near-equiatomic mixtures of five or more elements [26–29]. Their particularly interesting properties are usually believed to stem from four so-called “core effects”, [30] namely:

- Entropy stabilization: despite being a combination of multiple elements, HEAs usually consist of one or, at the most, two random solid solutions with highly symmetric lattices, because this maximizes the entropy term of the Gibbs' free energy, which thus prevails over the enthalpy term, at least at high temperature.
- Lattice distortion effect: combining several elements with slightly different atomic radii distorts the crystalline lattice. This provides an effective solid solution strengthening effect. Thus, it is usually maintained that high-entropy alloys provide a superior combination of strength and toughness, compared to conventional alloys [31].
- Sluggish diffusion effect: the distorted lattice hinders the atomic movement, which means that undesirable phenomena such as grain growth or precipitation of second phases, even when thermodynamically possible, are kinetically hindered.
- “Cocktail” effect, i.e. the possible occurrence of unexpected synergies that result in unique, unpredictable properties.

Actually, some of these “core effects” have sometimes been criticized or found not to be true in all cases. For example, the sluggish diffusion effect has been called into question by more than one author and is apparently not true for all HEAs but should be verified on a case-by-case basis [27,32–34]. The superiority of the strength-toughness combination in comparison with conventional alloys may also not be true in all cases, as a recent study showed that, under cryogenic conditions, ordinary austenitic stainless steels offer a better performance than CoCr-FeMnNi and CoCrNi alloys [35]. Even the entropy stabilization effect, which is the basis of the “high entropy” name, has been criticized [36].

Miracle and Senkov showed that it is not always true that multi-element systems are fully entropy-stabilized against the formation of intermetallics, because entropy and enthalpy of both solid solutions and intermetallics depend on multiple contributions, the magnitude of which can vary considerably from one system to another, making a generalizable conclusion more elusive than it originally seemed [36]. However, the review confirmed that there indeed are multi-element systems that can fall within extended solid-solution ranges and develop a single crystalline phase.

While all these considerations call for a more balanced approach to the family of HEAs, the considerable potential of these systems is undeniable. In particular, in the current context of corrosion resistance, the ability to form single-phase solid solutions in nearly equiatomic elemental mixtures is the most interesting one. A single-phase material does not suffer from the galvanic coupling phenomena that would lead to accelerated degradation of the less noble phase(s) in multi-phase systems. At the same time, the multi-element combination means that a HEA can be formulated to be rich in both primary passivating elements such as Cr [31,37], and in elements such as Co and Ni that enhance the passivating effect itself. Thus, several HEAs reportedly exhibit excellent corrosion resistance in bulk form, even better than that of austenitic stainless steels [38], making them attractive materials also as matrices for hardmetals operating under corrosive conditions.

In our previous report [39], we presented the microstructure, mechanical properties, and wear resistance of HVOF-sprayed TiC+HEA hardmetals, showing promising results, although not always superior to those of TiC hardmetals with “simple” matrices. Not much, however, is known about the corrosion resistance of these TiC+HEA hardmetal coatings. In fact, no research paper has yet studied in depth the electrochemical response of a wide range of thermally sprayed hardmetal coatings with HEA matrices. Most of the literature on thermally sprayed HEAs only concerns metallic coatings, as reviewed e.g. by Meghwal et al. [40]. Among the very few examples of studies on the corrosion resistance of thermal spray hardmetal coatings with HEA matrices, Bosi et al. [41] investigated HVOF-sprayed WC-20 wt% CoCrFeNi, highlighting promising corrosion resistance in seawater in comparison with conventional hardmetals. However, this study still employed WC as the hard phase and only considered one HEA composition. Thus, there is a clear need to expand the research toward other hard phases and a comparison between multiple HEA matrices. Therefore, the present work focuses specifically on the corrosion resistance of TiC+HEA hardmetals in an aqueous environment, characterized by means of two types of electrochemical tests, electrochemical polarization and potentiostatic chronoamperometry, respectively aimed to assess the short-term response and the long-term stability. The tests are carried out in a simple model environment, i.e. a 3.5 wt./vol% NaCl aqueous solution, which is pertinent to a number of application fields that involve the contact with chlorine-containing environments, such as seawater, contaminated industrial waters or wastewaters, etc.

The chosen hardmetal compositions all feature 60 vol% TiC with four matrices, selected among HEAs studied in the literature, so that reference information is available on the bulk form of the alloys:

- A Cr-Mn-Fe-Co-Ni equiatomic alloy (“Cantor” alloy), a widely studied material with known corrosion resistance though still containing substantial amounts of cobalt [28,29];
- Two $\text{Al}_x(\text{Cr}_{20}\text{Mn}_{25}\text{Fe}_{40}\text{Ni}_{15})_{1-x}$ compositions with $x = 0$ and $x = 14$, which should correspond to a mainly face-centred cubic (FCC) or body-centred cubic (BCC) lattice, respectively [42]. They are Co-free alternatives to the “Cantor” alloy and are suitable to assess both a change from FCC to BCC lattice, and the effect of adding Al to a solid solution of transition metal elements. This, indeed, sometimes seem to degrade the corrosion resistance of multi-element systems [43,44];
- An $\text{Al}_{0.5}\text{CuCrFeNi}_2$ composition, which complements the mentioned study on the effects of Al because it is an Al-rich composition, like

Table 1

HVOF deposition parameters for all coatings (parameters for the TiC+HEA coatings from [39]).

Parameter setting	Run 1	Run 2	Run 3	WC-CoCr	Cr ₃ C ₂ -NiCr
O ₂ pressure (psi/MPa)	170/1.20				
O ₂ flow rate (SLPM)	201	214	228	234	214
H ₂ pressure (psi/MPa)	140/0.98				
H ₂ flow rate (SLPM)	574	635	656	666	635
Air pressure (psi/MPa)	100/0.7				
Air flow rate (SLPM)	274			235	235
Stoichiometric ratio	0.9	0.86	0.87	0.85	0.83
Powder feed rate (g/min)	20			60	50
Stand-off distance (mm)	250			240	250
Torch-substrate speed (mm/s)	750				
Pitch distance (mm)	5			6	6
N° of passes per cycle	3				
N° of deposition cycles	13			8	9
N° of preheating cycles	1				
Pause between cycles (s)	20				

Al₁₄(Cr₂₀Mn₂₅Fe₄₀Ni₁₅)₈₆, but possesses a mainly FCC lattice because of its content of Ni and Cu [45].

2. Experimental

2.1. Powders and coatings

Full details of the choice of coating materials, the production of feedstock powders, the deposition of coatings, and the microstructure and phase composition of powders and coatings were provided in our previous paper [39]. The most salient features are reported here for the sake of clarity.

Feedstock materials were prepared by high-energy ball milling (HEBM) under proprietary process conditions. The chosen chemical compositions; the particle size distribution, measured by laser scattering with wet dispersion; and the phase composition, obtained by semi-quantitative Rietveld refinement on XRD patterns, were as follows:

1. Cr-Mn-Fe-Co-Ni (“Cantor” alloy) + 60 vol% TiC – hereafter “Cantor+60TiC”

Particle size distribution [$d_{10}/d_{50}/d_{90}$, μm]: 18/35/62.

Phase composition (wt%): TiC 39.4 ± 0.6 ; FCC matrix 52.4 ± 0.3 ; BCC matrix 8.2 ± 0.4

2. Cr₂₀Mn₂₅Fe₄₀Ni₁₅ + 60 vol% TiC – hereafter “Al₀(CrFeMnNi) + 60TiC”

Particle size distribution [$d_{10}/d_{50}/d_{90}$, μm]: 16/31/55.

Phase composition (wt%): TiC 57.7 ± 0.2 ; FCC matrix 33.5 ± 0.4 ;

BCC matrix 8.8 ± 0.2

3. Al₁₄(Cr₂₀Mn₂₅Fe₄₀Ni₁₅)₈₆ + 60 vol% TiC – hereafter “Al₁₄(CrFeMnNi) + 60TiC”

Particle size distribution [$d_{10}/d_{50}/d_{90}$, μm]: 18/35/61.

Phase composition (wt%): TiC 42.9 ± 0.2 ; Ti 16.2 ± 0.7 ; FCC matrix 7.8 ± 0.3 ; BCC matrix 33.1 ± 0.3 .

4. Al_{0.5}CuCrFeNi₂ + 60 vol% TiC – hereafter “AlCuCrFeNi+60TiC”

Particle size distribution [$d_{10}/d_{50}/d_{90}$, μm]: 21/33/53.

Phase composition (wt%): TiC 48.5 ± 0.2 ; FCC matrix 49.7 ± 0.4 ; BCC matrix 1.8 ± 0.4 .

All coatings were deposited by hydrogen-fuelled HVOF spraying (Diamond Jet 2600 system with DJ8W torch) on grit-blasted AISI 304 stainless steel plates with three distinct sets of deposition parameters (Table 1).

Commercially available WC-10wt%Co-4wt%Cr (Woka 3652, Oerlikon Metco WOKA GmbH, Barchfeld, Germany) and Cr₃C₂-25 wt%(Ni-20wt.%Cr) (Woka 7202, Oerlikon Metco WOKA GmbH) feedstock powders, hereafter designated simply as “WC-CoCr” and “Cr₃C₂-NiCr”, were also sprayed by the same HVOF process using parameters optimized in previous experiments (Table 1).

The HVOF deposition of the TiC+HEA powders resulted in ~ 300 μm -thick coatings with porosity <1 vol% (by image analysis on SEM micrographs) and hardness values roughly in the range 750–900 HV (measured at 3 N load with a Vickers indenter) - Table 2. Although TiC was retained as the main phase in all coatings, some decarburization occurred, with the formation of a hexagonal TiC_{1-x} phase, and the matrix composition tended to change with an increase in the amount of FCC phase and a corresponding decrease or disappearance of the BCC phase, as summarized by the results of the Rietveld refinements on the XRD patterns provided in [39] (Table 3). Additionally, in-flight oxidation resulted in oxygen contents of 5–9 wt% in all samples. Oxides appeared mainly in the form of Ti-rich stringers along the lamellar boundaries.

2.2. Electrochemical corrosion testing

Electrochemical corrosion tests were performed on the polished sample surfaces in a neutral 3.5% (wt./vol.) NaCl aqueous solution at room temperature under aerated conditions, using a three-electrode cell with the sample as the working electrode, an Ag/AgCl/KCl_(sat.) reference electrode, and a Pt mesh as the counterelectrode. The exposed sample surface, delimited by a Teflon gasket, was 1 cm². The cell was filled with approximately 300 mL of the test solution and the electrodes were connected to a VersaStat 3 potentiostat (Ametek – Princeton Applied Research, USA).

Specifically, electrochemical polarization tests were performed after a stabilization period of 1 h by first polarizing the samples cathodically from the open circuit potential (OCP) to -0.4 V vs. OCP and then

Table 2

Porosity, thickness (by image analysis), oxygen content (by EDX analysis on polished cross-sections), and Vickers microhardness of all coatings, from [39].

Sample ID	Porosity (%)	Thickness [μm]	Oxygen content (wt.%)	HV _{3N}	BCC/FCC
Cantor+60TiC Run1	0.35 ± 0.15	294 ± 13	5.45 ± 0.21	884 ± 91	0
Cantor+60TiC Run2	0.27 ± 0.09	332 ± 11	5.90 ± 0.26	933 ± 102	0
Cantor+60TiC Run3	0.07 ± 0.04	307 ± 11	6.20 ± 0.19	904 ± 97	0
Al ₁₄ (CrFeMnNi) + 60TiC Run1	0.33 ± 0.05	363 ± 10	7.69 ± 0.18	745 ± 81	1.33
Al ₁₄ (CrFeMnNi) + 60TiC Run2	0.25 ± 0.07	339 ± 8	7.77 ± 0.07	786 ± 82	1.24
Al ₁₄ (CrFeMnNi) + 60TiC Run3	0.23 ± 0.07	326 ± 11	8.29 ± 0.15	816 ± 70	1.24
Al ₀ (CrFeMnNi) + 60TiC Run1	0.06 ± 0.03	323 ± 21	8.20 ± 0.07	747 ± 80	0.06
Al ₀ (CrFeMnNi) + 60TiC Run2	0.06 ± 0.01	310 ± 20	8.46 ± 0.28	813 ± 60	0.08
Al ₀ (CrFeMnNi) + 60TiC Run3	0.08 ± 0.07	281 ± 18	9.65 ± 0.15	740 ± 73	0.08
AlCuCrFeNi+60TiC Run1	0.007 ± 0.004	321 ± 15	5.38 ± 0.32	772 ± 78	0.01
AlCuCrFeNi+60TiC Run2	0.003 ± 0.002	311 ± 15	5.47 ± 0.16	793 ± 64	0.01
AlCuCrFeNi+60TiC Run3	0.021 ± 0.013	308 ± 13	5.07 ± 0.05	819 ± 77	0.02

Table 3

Summary of the phase composition of the powders and the coatings by Rietveld refinement on XRD patterns, reproduced from [39].

Sample	FCC	BCC	TiC	Ti	TiC _{1-x}	MO	MTiO ₃
Cantor + 60TiC powder	52.4 ± 0.3	8.2 ± 0.4	39.4 ± 0.6	–	–	–	–
Cantor + 60TiC Run1	39.6 ± 0.3	–	29.1 ± 0.2	–	23.6 ± 0.4	–	7.7 ± 0.5
Cantor + 60TiC Run2	41.1 ± 0.3	–	28.9 ± 0.2	–	21.8 ± 0.4	–	8.2 ± 0.6
Cantor + 60TiC Run3	37.4 ± 0.3	–	27.8 ± 0.2	–	26.2 ± 0.5	–	8.6 ± 0.6
Al ₀ (CrMnFeNi) + 60TiC Powder	33.5 ± 0.4	8.8 ± 0.4	57.7 ± 0.2	–	–	–	–
Al ₀ (CrMnFeNi) + 60TiC Run1	34.5 ± 0.3	2.0 ± 0.1	36.8 ± 0.2	–	15.5 ± 0.4	3.5 ± 0.9	7.7 ± 0.3
Al ₀ (CrMnFeNi) + 60TiC Run2	31.3 ± 0.2	2.5 ± 0.4	34.4 ± 0.2	–	18.6 ± 0.4	4.0 ± 0.4	9.2 ± 0.3
Al ₀ (CrMnFeNi) + 60TiC Run3	29.7 ± 0.4	2.5 ± 0.4	33.5 ± 0.2	–	19.8 ± 0.4	4.4 ± 0.9	10.1 ± 0.3
Al ₁₄ (CrMnFeNi) + 60TiC Powder	7.8 ± 0.3	33.1 ± 0.3	42.9 ± 0.2	16.2 ± 0.7	–	–	–
Al ₁₄ (CrMnFeNi) + 60TiC Run1	20.5 ± 0.5	27.3 ± 0.3	38.2 ± 0.2	–	3.8 ± 0.5	8.1 ± 0.8	2.1 ± 0.4
Al ₁₄ (CrMnFeNi) + 60TiC Run2	20.8 ± 0.5	25.7 ± 0.3	36.1 ± 0.2	–	3.9 ± 0.5	10.9 ± 0.9	2.6 ± 0.5
Al ₁₄ (CrMnFeNi) + 60TiC Run3	20.3 ± 0.4	25.2 ± 0.2	34.1 ± 0.2	–	4.6 ± 0.5	12.4 ± 0.9	3.4 ± 0.5
AlCuCrFeNi + 60TiC Powder	49.7 ± 0.4	1.8 ± 0.2	48.5 ± 0.2	–	–	–	–
AlCuCrFeNi + 60TiC Run1	43.4 ± 0.2	0.5 ± 0.1	46.6 ± 0.1	–	1.1 ± 0.1	7.9 ± 0.5	0.5 ± 0.2
AlCuCrFeNi + 60TiC Run2	44.7 ± 0.2	0.6 ± 0.1	45.4 ± 0.1	–	0.5 ± 0.2	8.5 ± 0.3	0.3 ± 0.1
AlCuCrFeNi + 60TiC Run3	44.3 ± 0.2	0.7 ± 0.6	45.0 ± 0.2	–	0.6 ± 0.1	9.1 ± 0.3	0.4 ± 0.1

performing a potential sweep from -0.4 V vs. OCP to $+1.6$ V vs. OCP to record the full (cathodic and anodic) electrochemical polarization curve. The scan rate was 0.0005 V/s. Two repeats were performed for each type of sample. The corrosion potential (E_{Corr}) and the corrosion current density (I_{Corr}) were obtained by the Tafel extrapolation method. To this end, a linear fit was applied to the first linear sections of the anodic and cathodic branches of the polarization curves that occurred at overpotentials of at least $|0.05|$ V away from the equilibrium potential.

On selected samples (see Section 3.2), chronoamperometric tests were also performed in the same 3.5% (wt./vol.) NaCl aqueous solution with the experimental setup described above. Once again, the samples were allowed to stabilize in contact with the test solution for 1 h, then they were first polarized cathodically from the open circuit potential (OCP) to -0.4 V vs. OCP, so that the initial surface condition of the sample was the same as at the beginning of the electrochemical polarization sweep. Subsequently, the sample was polarized to a fixed potential value, which was kept constant for 3 h while continuously monitoring the current flowing through the system (1 acquisition per second). Potential values were set so that the samples were polarized to overpotentials of $+0.15$ V, $+0.20$ V, and $+0.25$ V above their OCP value established after the cathodic pre-polarization. The solution was not changed during the 3 h-long chronoamperometric tests.

2.3. Characterization of tested samples

The cross-sections of the samples after both electrochemical polarization and chronoamperometric testing, and some selected surfaces after chronoamperometric testing were observed by scanning electron microscopy (SEM: Quanta-200 and Nova NanoSEM 450, FEI Thermo Fisher Scientific, Eindhoven, NL) equipped with an energy-dispersive X-ray (EDX) detector (INCA, Oxford Instruments Analytical, Abingdon, UK and Quantax-200 with XFlash10 detector, Bruker Nano GmbH, Berlin, Germany). The samples were hot-mounted in a transparent acrylic resin using a mounting press, sectioned with a metallographic cutting disc, ground with SiC-based abrasive papers (from P400 to P4000), and polished using a polycrystalline diamond slurry ($3\ \mu\text{m}$ average particle size) and colloidal silica. Resin-mounted samples were coated with a ~ 10 nm-thick layer of Au by sputtering to provide the necessary electrical conductivity.

Identification of compounds on the surfaces of samples subjected to chronoamperometric tests was further carried out by micro-Raman spectroscopy (LabRAM HR Evolution, Horiba Jobin-Yvon) and X-ray Photoelectron Spectroscopy (XPS). Raman spectra were acquired using a Nd:YAG laser with a wavelength of 532 nm and a maximum emission power of 100 mW. The laser beam was filtered to 10% of its maximum power and focused on the surface of the sample through a $100\times$ objective. The signal coming from the sample was detected using a 600

g/mm diffraction grating and a CCD camera with a Peltier cell. Spectra were obtained as the sum of 6 accumulations (wear tracks) or 10 accumulations (corroded surfaces) with a counting time of 20 s each. XPS spectra were acquired using a custom system consisting of a Mg-K α X-ray gun (photon energy 1253.6 eV) and a SPECS Phoibos HSA 3500 analyser. The analysed area was approximately $1\ \text{mm}^2$ and was located around the centre of the tested sample. High-resolution spectra of detectable elements were acquired with a resolution of 0.1 eV. The binding energies for the interpretation of the XPS spectra were taken from the NIST (National Institute of Standards and Technology) XPS database [46].

3. Results and discussion

3.1. Electrochemical polarization testing

All TiC+HEA coatings exhibited similar polarization curves, with little influence from matrix composition and process parameters, at least within the range explored in this study (Fig. 1). The anodic branches showed an initial activation stage that was employed for Tafel fitting. Specifically, linear portions of the anodic and cathodic curves located approximately between 0.05 V and 0.1 V above and below (respectively) the rest potential were employed for linear fitting, and the coordinates of the intersection point between the extrapolated linear fits were taken as the corrosion potential and corrosion current density (Table 4).

The resulting corrosion potentials were roughly between -0.5 and -0.45 V vs. Ag/AgCl/KCl_(sat.) for most samples except for the AlCuCrFeNi+60TiC composition, which exhibited slightly nobler values around -0.3 V vs. Ag/AgCl/KCl_(sat.). The corrosion current densities were also mostly between 3 and $10\ \mu\text{A}/\text{cm}^2$, although there were some composition-based systematic differences. The Al₀(CrMnFeNi) + 60TiC and Al₁₄(CrMnFeNi) + 60TiC compositions showed higher values (~ 7 – $11\ \mu\text{A}/\text{cm}^2$) than the Cantor+60TiC (~ 4 – $5\ \mu\text{A}/\text{cm}^2$) and AlCuCrFeNi+60TiC samples (~ 3 – $4\ \mu\text{A}/\text{cm}^2$). The narrow error ranges in Table 4 mean that these differences can be considered significant, albeit small. A comparison between all polarization curves is provided in the Supplementary Material (Fig. S1) to further corroborate the repeatability of the polarization curves.

The corrosion current densities and corrosion potentials of the AlCuCrFeNi+60TiC samples were comparable to or even slightly better than those obtained with the benchmark WC-CoCr coating, though the Cr₃C₂-NiCr benchmark was significantly nobler and its corrosion current density was more than one order of magnitude lower (Table 4).

At an overpotential greater than $+0.1$ V vs. OCP, the anodic polarization curves of the TiC+HEA coatings (Fig. 1) entered a pseudo-passive regime characterized by current densities that increased slowly in the range 10^{-5} A/cm²– 10^{-4} A/cm². This behaviour persisted up to a

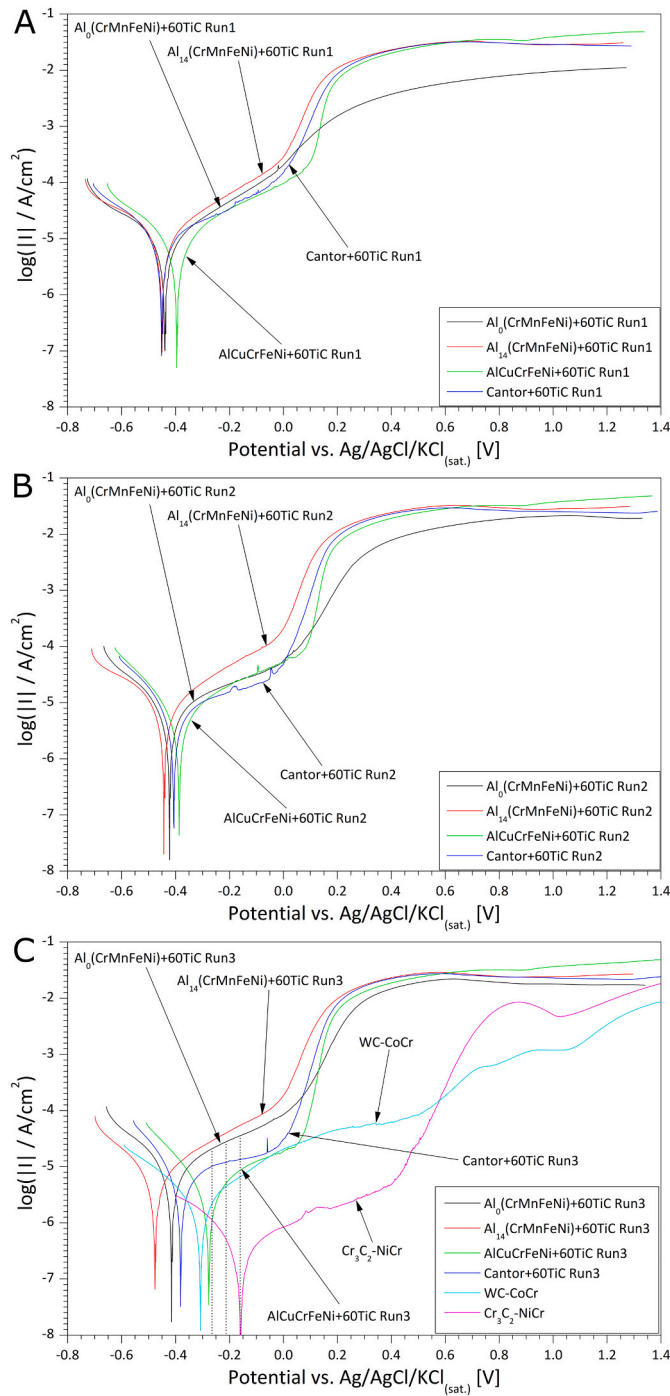


Fig. 1. Electrochemical polarization curves for all deposition runs (see Table 1) of each of the TiC+HEA coating materials: Run 1 (A), Run 2 (B), and Run 3 (C). Panel (C) also shows the electrochemical polarization curves of the benchmark WC-CoCr and Cr₃C₂-NiCr coatings.

potential of about -0.05 V vs. Ag/AgCl/KCl_(sat.), when a rapid increase in current density signalled the breakdown of passivity and the transition to a transpassivation regime. In the pseudo-passive regime, the current densities were comparable to those of the WC-CoCr benchmark (Fig. 1C), though the breakdown of pseudo-passivity of WC-CoCr occurred at much higher overpotentials of around $+0.5$ V vs. Ag/AgCl/KCl_(sat.) and did not feature an equally abrupt jump in current density magnitude. In fact, Human et al. [47,48] showed that the Co-based alloy matrices do not enter a transpassivation regime: the increase in the current density exhibited by WC-Co-based materials at high

Table 4

Corrosion potential (E_{Corr}) and corrosion current density (I_{Corr}) values (average $\pm$ half-difference) obtained by Tafel extrapolation from the electrochemical polarization curves.

Sample ID	E_{Corr} [V]	I_{Corr} [$\mu\text{A}/\text{cm}^2$]
Cantor+60TiC Run1	-0.447 ± 0.004	5.19 ± 0.58
Cantor+60TiC Run2	-0.410 ± 0.006	4.01 ± 0.22
Cantor+60TiC Run3	-0.385 ± 0.005	3.55 ± 0.14
Al ₀ (CrMnFeNi)+60TiC Run1	-0.433 ± 0.003	9.71 ± 0.09
Al ₀ (CrMnFeNi)+60TiC Run2	-0.418 ± 0.002	8.15 ± 0.26
Al ₀ (CrMnFeNi)+60TiC Run3	-0.414 ± 0.011	10.01 ± 0.51
Al ₁₄ (CrMnFeNi) + 60TiC Run1	-0.463 ± 0.025	11.13 ± 1.50
Al ₁₄ (CrMnFeNi) + 60TiC Run2	-0.443 ± 0.003	6.94 ± 0.49
Al ₁₄ (CrMnFeNi) + 60TiC Run3	-0.467 ± 0.019	6.97 ± 0.16
AlCuCrFeNi+60TiC Run1	-0.261 ± 0.043	4.28 ± 1.29
AlCuCrFeNi+60TiC Run2	-0.321 ± 0.003	2.71 ± 0.02
AlCuCrFeNi+60TiC Run3	-0.293 ± 0.019	2.99 ± 0.40
WC-CoCr	-0.329 ± 0.023	3.95 ± 1.78
Cr ₃ C ₂ -NiCr	-0.157 ± 0.001	0.165 ± 0.050

overpotentials is due to the onset of the corrosion of WC itself, while the matrix remains in a pseudo-passive regime even at the highest applied anodic overpotential. By contrast, the Cr₃C₂-NiCr benchmark does exhibit a proper transpassivation with a rapid increase in current density above $+0.45$ V vs. Ag/AgCl/KCl_(sat.), but at lower potentials, its current density around 10^{-6} A/cm² (Fig. 1C) indicates that the material is capable of a true passivation: the film formed on its surface is denser and more protective than that formed on the TiC+HEA samples. Thus, it can be concluded that the TiC+HEA samples, though overall competitive with WC-CoCr in terms of electrochemical corrosion resistance, do not match the superior corrosion protection afforded by Cr₃C₂-NiCr.

Notably, we reported analogous electrochemical polarization responses in our previous work on TiC-based hardmetal coatings with simpler non-HEA matrices [23–25]. SEM inspection of the cross-section of the present samples after the polarization tests also revealed features analogous to those reported in our previous work (Fig. 2). The corrosion damage seen at the end of the test, which reflected the degradation mechanism occurring in the transpassive regime, consisted of selective dissolution of the matrix. A uniform corrosion front advanced into the coating (Fig. 2A, C, E, G: label 1), with fine TiC particles left “floating” amidst a dissolved matrix, as seen in magnified views of Fig. 2B, D, F, H. Only a few splats remained partially unaffected, which might be due to differences in local chemical composition.

EDX spectra acquired on the entire corroded areas (Fig. 3 – spectrum 1, quantitative results in Table 5), as well as spectra acquired specifically on the dissolved regions (spectrum 3), exhibited a stronger oxygen signal and a substantial decrease in the relative amounts of the matrix elements, especially Mn, Fe and Ni, compared to spectra acquired on the underlying, unaffected coating (spectrum 2), and on the few undissolved splats (spectrum 4). Therefore, it is inferred that Fe, Mn, and Ni were selectively leached out of the matrix in the transpassive regime, leaving behind the undissolved TiC particles together with Cr-based corrosion products. The relative intensity of the Cr K- α peak with respect to the Fe, Mn and Ni K- α lines was indeed higher in spectra 1 and 3 compared to spectra 2 and 4. The presence of Si in spectra 1 and 3 was probably an artefact, because some colloidal silica from the final polishing step (see Section 2.3) was retained within the recesses of the corroded region. Likewise, S and Ca (also seen in spectra 1 and 3) came from the running water used for grinding and polishing, while Cl reflected the presence of corrosion products originated by interaction with the NaCl-containing test solution.

Notably, after the polarization test, the Al₀(CrMnFeNi) + 60TiC and AlCuCrFeNi+60TiC samples showed significant corrosion also below the dissolution front (Fig. 2C: label 4) and at the substrate interface (Fig. 2G: label 5). The Cantor+60TiC and Al₁₄(CrMnFeNi) + 60TiC samples (Fig. 2A and E) did not show a comparable damage. Fig. 2C showed blistering of the coating due to the pressure exerted by the corrosion

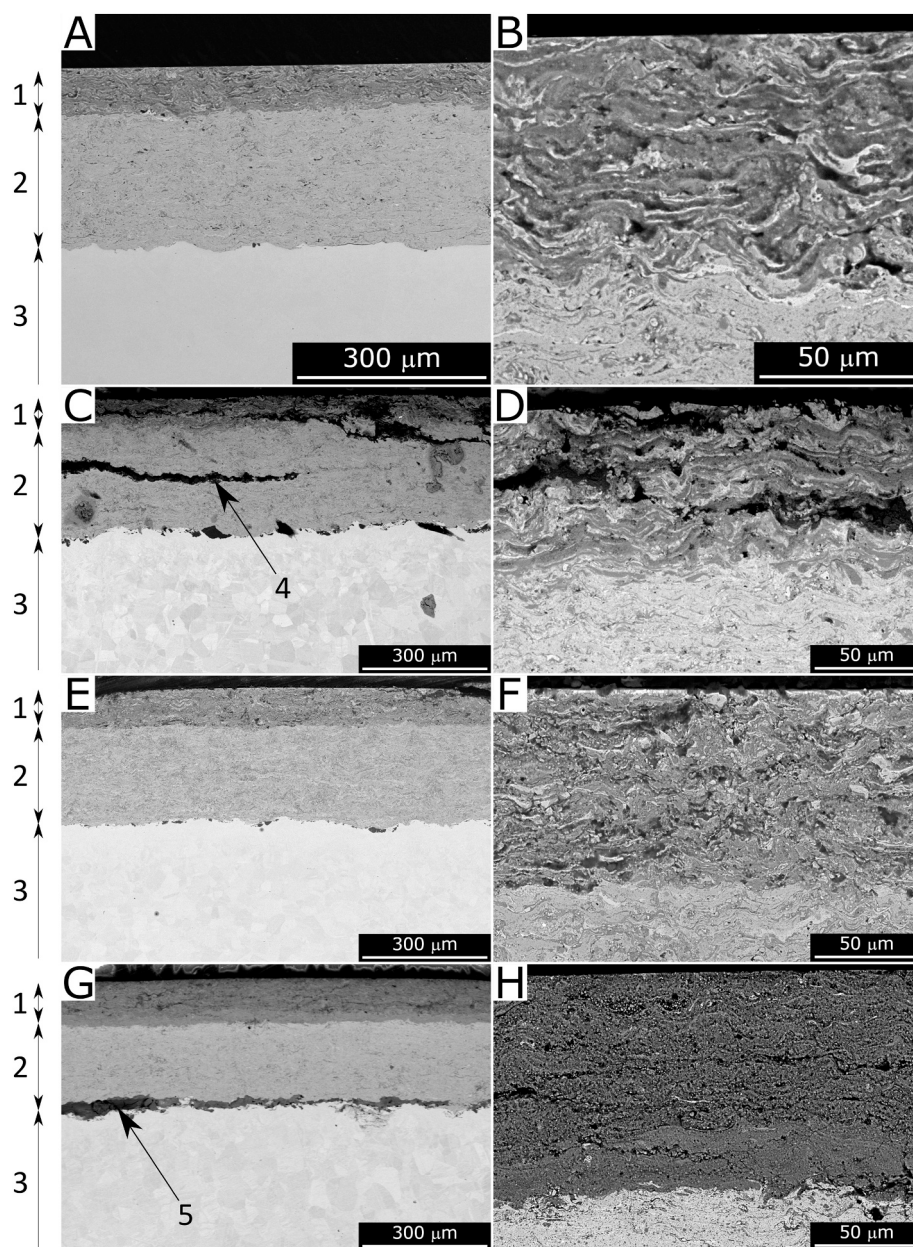


Fig. 2. Backscattered-electron SEM micrographs of polished cross-sections of the Cantor+60TiC Run 1 (A, B), $\text{Al}_0(\text{CrMnFeNi}) + 60\text{TiC}$ (C, D) Run3, $\text{Al}_{14}(\text{CrMnFeNi}) + 60\text{TiC}$ Run3 (E, F) and $\text{AlCuCrFeNi}+60\text{TiC}$ (G, H) samples after electrochemical polarization testing. Labels: 1 = dissolution area; 2 = undissolved coating; 3 = substrate; 4 = blistering crack; 5 = interface corrosion.

products accumulating at the interface. As the corrosion front advanced into the coating during the transpassive stage, the undamaged portion of the coating became increasingly thin. In some cases, this remaining layer contained interconnected pores that allowed corrosive agents to reach the substrate. The latter was then selectively corroded due to galvanic coupling and crevice corrosion phenomena. However, this did not translate into a visible difference among the polarization curves, even in the transpassive regime. Namely, the transpassive portions of the curves of the samples with visible substrate corrosion did not exhibit higher current densities than those of the samples without substrate corrosion. This means that most of the current flowing through the system was, anyway, that due to the transpassive dissolution of the matrix. The substrate corrosion, albeit visibly severe, gave a minor contribution in terms of overall current. Indeed, if the substrate was exposed through interconnected pores, its reacting area was small and gave a correspondingly small contribution to the measured current, although the

current density in those localized spots was high and resulted in the accumulation of corrosion products. Thus, the polarization curves can be taken to be representative of the coating response in all cases.

According to [49], the equilibrium potentials of stoichiometric TiC and slightly sub-stoichiometric $\text{TiC}_{0.9}$ in 3.5 wt% NaCl are +0.050 V and +0.105 V, respectively. Thus, at the beginning of the anodic sections of the curves shown in Fig. 1, the TiC particles acted as cathodes. On the other hand, various HEA compositions in Al-Cr-Mn-Fe-Co-Ni-Cu systems exhibit corrosion potentials in the range -0.2 to -0.3 V [50–54] or even <-0.5 V [53,55]. The equilibrium potentials seen in Fig. 1 were indeed consistent with these values. Therefore, the HEA matrices acted as the anode, and the anodic sections of the curves in Fig. 1 reflected their corrosion behaviour.

Many of the HEAs described in the literature [50–55], in bulk form, exhibit passive or pseudo-passive behaviour in 3.5 wt% NaCl aqueous solutions, with breakdown reportedly occurring at potentials ranging

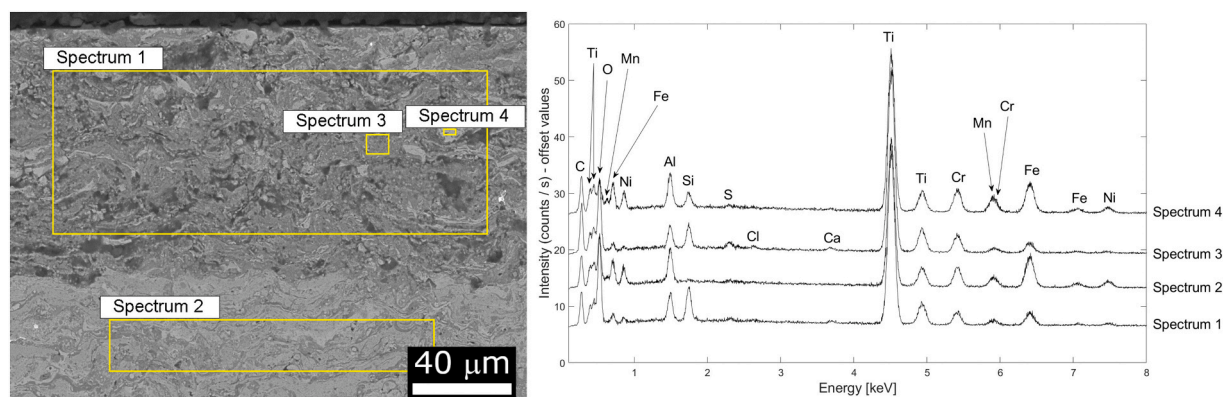


Fig. 3. Backscattered-electron SEM micrograph of the polished cross-section of $\text{Al}_{14}(\text{CrMnFeNi}) + 60\text{TiC}$ Run3 after electrochemical polarization testing, and the corresponding EDX spectra.

Table 5

Quantitative results from the EDX spectra in Fig. 3B, in wt%.

Element (wt%)	O	Al	Si	S	Cl	Ca	Ti	Cr	Mn	Fe	Ni
Spectrum 1	30.25	2.35	2.87	0.25	0.12	0.31	45.41	5.76	1.82	8.59	2.28
Spectrum 2	15.26	3.24	0.14	–	–	–	38.78	8.87	4.43	22.06	7.21
Spectrum 3	27.31	2.00	1.96	0.58	0.23	0.46	49.62	7.99	1.32	7.02	1.50
Spectrum 4	9.29	3.20	1.34	0.22	–	0.20	41.53	9.99	7.25	20.76	6.21

from <0 V up to even 1 V in some cases. Therefore, the breakdown of pseudo-passivity in the present coatings occurred earlier than for many bulk HEAs. The pseudo-passive current density values seen in Fig. 1 were also higher than those reported for several types of bulk, unreinforced HEAs. The passive current densities of bulk HEAs are usually not greater than 10^{-5} A/cm², and sometimes even $<10^{-6}$ A/cm². However, it should also be noted that high-Cu HEAs similar to the AlCuCrFeNi composition were reported to exhibit no passivation or pseudo-passivation at all [52], because the segregation of Cu-rich phases induced galvanic couples that resulted in active anodic dissolution of the less noble phase [52,53]. Likewise, adding Al up to levels where a two-phase structure (BCC + FCC) is produced, as in the case of the $\text{Al}_{14}(\text{CrMnFeNi})$ composition (see Table 3), is generally reported to be detrimental to passivation [53,54], as also laid out in the Introduction.

Therefore, it seems that in our coatings there was a considerable “levelling” of responses, compared to what would have been expected considering the diverse behaviours of our matrix alloys taken in bulk form. Those expected to have better passivation ability showed a degradation, while those expected not to passivate, such as the AlCuCrFeNi and $\text{Al}_{14}(\text{CrMnFeNi})$ compositions, showed improved corrosion resistance. This levelling is consistent with the previous considerations on the similarities in the electrochemical polarization responses of TiC-based hardmetals with HEA matrices and with simpler matrices. It suggests that being part of a cermet has a major influence on the anodic response of metal matrices.

Impact quenching of the particles during HVOF spraying probably helped suppress solute segregation (e.g. Cu segregation), which, as noted above, is responsible for the lack of pseudo-passivation in some bulk HEAs. The microstructural investigation of the $\text{AlCuCrFeNi}+60\text{TiC}$ coatings reported in [39], for example, did not suggest any Cu segregation, and the matrix consisted almost exclusively of an FCC phase (Table 3). The dissolution of Ti and C in the matrix during the HVOF process, as reported in [39] for the present samples and in [24] for TiC-based hardmetals with Ni–Cr and Ni–Fe–Cr matrices, and as evidenced by the formation of a partly decarburized TiC_{1-x} phase (Table 3), also played a role. According to [56], for example, small amounts of dissolved carbon can improve the corrosion resistance of HEAs. On the contrary, the few extant pores and the oxide inclusions limited the

passivation ability, compared to that of a bulk material. These combined effects might account for the mentioned “levelling”. Above all, however, the present results were dictated by the numerous micro-galvanic couples between the anodic metal and the cathodic TiC phase. Galvanic couples accelerated the oxidation of the matrices; thus, they promoted the passivation of those that would have had more a limited passivation ability. As a result, the matrices showed far more similar passivation behaviour than they would in bulk form. However, the same galvanic couples also facilitated the breakdown of passivity when the anodic overpotential increased.

It is important to note that, although WC–CoCr hardmetals are also known to exhibit an apparent breakdown in pseudo-passivity at high anodic overpotentials, this is in fact due to the oxidation rate of WC becoming faster than that of the CoCr(W,C) alloy matrix [47,48,57]. In fact, the CoCr matrix remains passive, without any breakdown, up to remarkably high overpotentials. In the current TiC-based hardmetals, in contrast, there was a true breakdown of the matrix passivity, as clearly seen in Fig. 2. While the polarization curves of WC–Co-based hardmetals start to coincide with those of pure WC at high overpotentials, the anodic current densities of pure TiC and $\text{TiC}_{0.9}$ are still $<10^{-4}$ A/cm² even at potentials of +1 V, where the present samples exhibited current densities above 10^{-2} A/cm². Thus, any contribution of TiC to the current measured in the present systems was negligibly small, even though TiC made up a substantial fraction of the sample surface.

Despite the mentioned “levelling”, there were slight differences between the polarization curves of the samples as a function of the matrix composition. In particular, the $\text{AlCuCrFeNi}+60\text{TiC}$ and $\text{Cantor}+60\text{TiC}$ coatings exhibited slightly lower current density in the pseudo-passive range than the other samples, and the corrosion current density values obtained by Tafel extrapolation (Table 4) were also slightly lower, as mentioned above. In contrast, no meaningful differences emerged between the corrosion current density values of samples with the same composition deposited under different spray conditions.

3.2. Chronoamperometry tests

To check the longer-term stability of the (pseudo-)passivity, chronoamperometric tests were carried out on the “Run3” samples of both

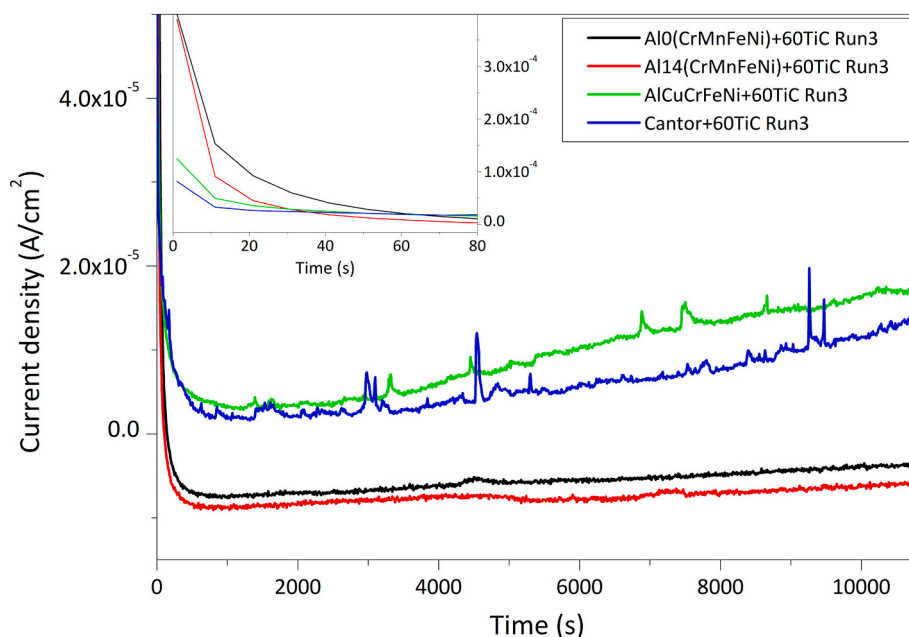


Fig. 4. Chronoamperometric curves (current density vs. time) recorded at a fixed overpotential of +0.15 V vs. OCP on the AlCuCrFeNi+60TiC Run3, Cantor+60TiC Run3, Al₀(CrMnFeNi) + 60TiC Run3 and Al₁₄(CrMnFeNi) + 60TiC Run3 samples.

series. The analysis was limited to these samples because of the mentioned absence of any significant influence of the process parameters on the polarization results discussed so far. The first overpotential value of +0.15 V vs. OCP for the chronoamperometric test (Section 2.2) was selected because it fell within the pseudo-passivity range seen in the polarization curves of Fig. 1. This is shown in Fig. 1C in the case of the Al₀(CrMnFeNi) + 60TiC coating with a dashed line illustrating where an overpotential of +0.15 V vs. OCP falls in the polarization curve of this sample.

At this potential, the current density dropped rapidly in less than 2 min at the beginning of the test (Fig. 4). This is consistent with what would be expected for a passivating system. In agreement with the polarization results of Fig. 1, the inset of Fig. 4 indicates that the current density of the AlCuCrFeNi+60TiC and Cantor+60TiC coatings was initially lower than that produced by the Al₀(CrMnFeNi) + 60TiC and Al₁₄(CrMnFeNi) + 60TiC coatings.

However, after the initial drop, the current density produced by the AlCuCrFeNi+60TiC and Cantor+60TiC coatings settled to a higher level. The minimum of 10^{-6} A/cm² can be ascribed to the growth of the pseudo-passive film, but the subsequent slow increase in current density throughout the test suggests a gradual destabilization of the passive film

in the chlorine-rich environment. On the contrary, the current density produced by the Al₀(CrMnFeNi) + 60TiC and Al₁₄(CrMnFeNi) + 60TiC coatings became negative (slightly higher than -1×10^{-5} A/cm²), i.e. cathodic, and despite also increasing slowly through the test, it remained negative until the end. This means that the passive film developed in the initial stages was so stable and protective that it increased the practical nobility of the samples, which became cathodic with respect to the reference electrode when kept at a fixed potential of +0.15 V above the initial OCP value. Indeed, the formation of the film made the sample so much nobler that such a fixed potential ended up becoming cathodic. Therefore, the Al₀(CrMnFeNi) + 60TiC and Al₁₄(CrMnFeNi) + 60TiC samples, despite their initially higher current densities, exhibited much better long-term stability. This result was verified by performing a repetition of the chronoamperometric tests on the Al₀(CrMnFeNi) + 60TiC and Al₁₄(CrMnFeNi) + 60TiC samples – see the Supplementary Material (Fig. S2).

Consequently, the Al₀(CrMnFeNi) + 60TiC and Al₁₄(CrMnFeNi) + 60TiC coatings exhibited no signs of corrosion detectable by unaided visual inspection at the end of the test, while reddish corrosion products emerged on the surface of the AlCuCrFeNi+60TiC and Cantor+60TiC coatings. The chronoamperometric curves of the latter were

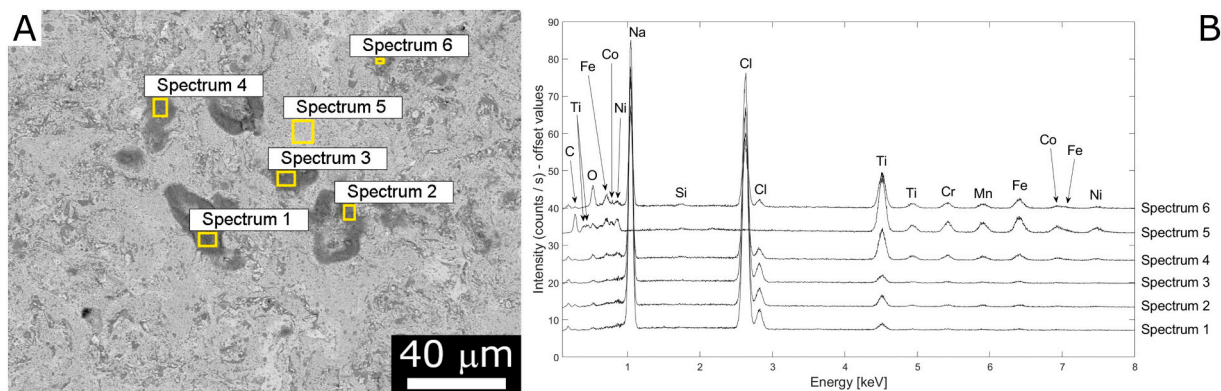


Fig. 5. SEM micrograph acquired on the surface of the Cantor+60TiC Run3 sample after the chronoamperometric test at +0.15 V vs. OCP (A), and the corresponding EDX spectra (B).

Table 6

Quantitative results from the EDX spectra in Fig. 5B, in wt%.

Element (wt%)	O	Na	Si	Cl	Ti	Cr	Mn	Fe	Co	Ni	Others
Spectrum 1	1.07	40.33	0.04	50.82	3.28	0.91	0.68	1.57	0.77	0.51	–
Spectrum 2	1.71	38.33	0.06	45.54	5.90	1.48	1.59	2.45	1.39	1.55	–
Spectrum 3	1.32	39.49	0.06	49.43	4.10	1.01	0.79	2.16	0.85	0.79	–
Spectrum 4	2.70	31.83	0.16	27.07	16.26	3.96	3.33	7.38	3.69	3.62	–
Spectrum 5	3.41	–	0.25	–	30.10	9.44	10.47	22.35	11.36	11.75	Nb: 0.87
Spectrum 6	11.62	23.41	0.35	17.31	18.86	4.58	4.00	12.35	3.88	3.63	–

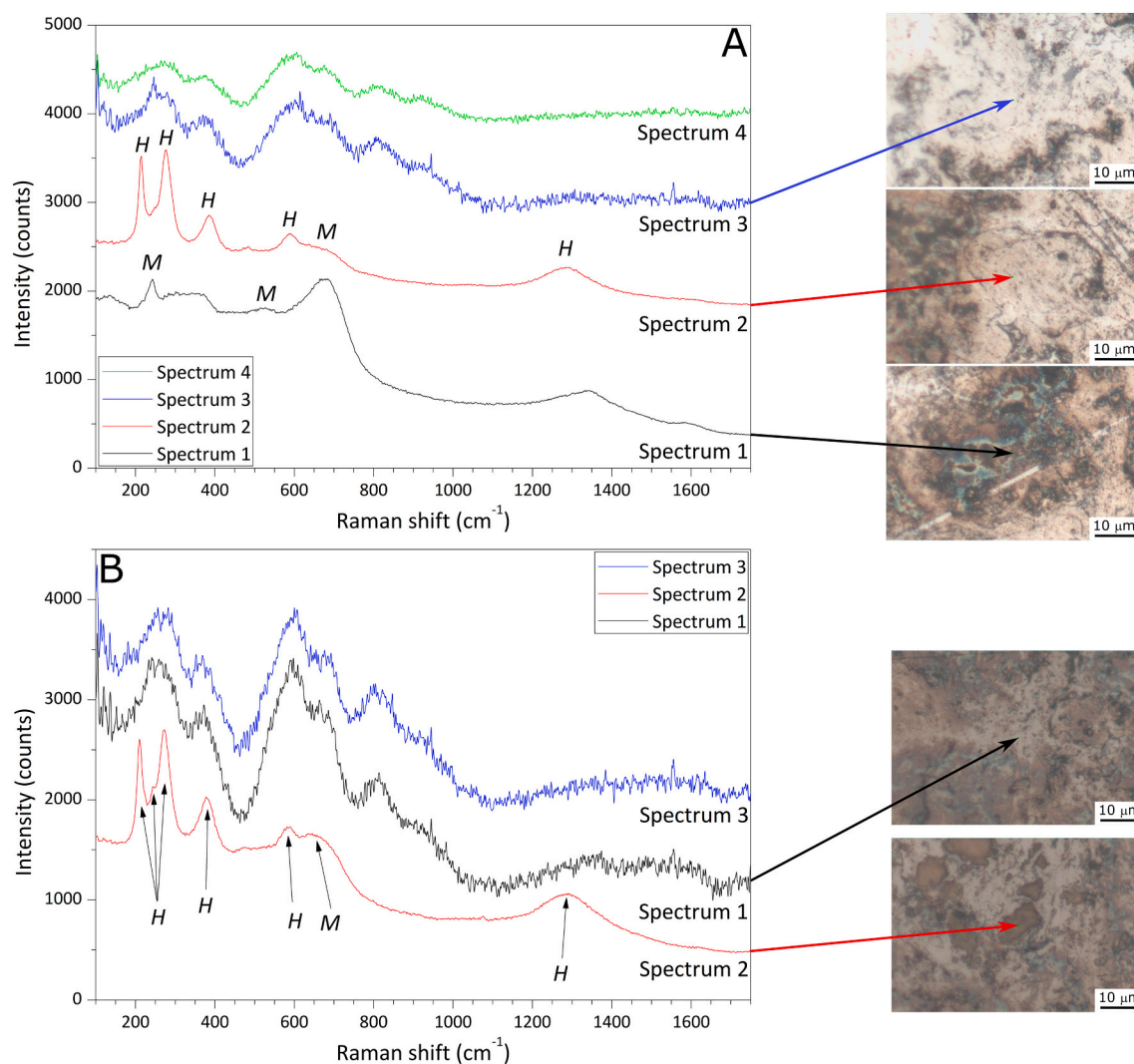


Fig. 6. Micro-Raman spectra acquired on the surfaces of the Cantor+60TiC Run3 (A) and AlCuCrFeNi+60TiC Run3 (B) samples after the chronoamperometric tests at +0.15 V vs. OCP, with optical micrographs of the acquisition locations of the spectra. Spectrum 4 in panel A and spectrum 3 in panel B were acquired outside the tested area. Labels: H = hematite; M = magnetite.

characterized not only by positive and increasing current density values, but also by local spikes, which indicated the opening of pits. Consistently, there were more reddish corrosion products on the Cantor+60TiC coating, whose chronoamperometric curve showed more current spikes.

SEM + EDX analyses of the surfaces of Cantor+60TiC and AlCuCrFeNi+60TiC samples after the chronoamperometry test at +0.15 V vs. OCP consistently revealed localized accumulations of corrosion products based on Fe, O, and Cl (Fig. 5: spectra 1–4, 6; quantitative results in Table 6). The micro-Raman spectra (Fig. 6A – spectra 1 and 2) indicated that these products were based on hematite and magnetite: the Raman peaks were assigned according to [58]. It is inferred that such products

originated from substrate corrosion: the opening of the pits in the coating allowed the corrosive medium to penetrate through the coating to the substrate and attack it, following a crevice corrosion mechanism. In particular, the polarization curve of the Cantor+60TiC sample (Fig. 1) also showed a few current spikes indicative of transient pit formation.

Fe-based corrosion products were less frequent on the AlCuCrFeNi+60TiC coating. In fact, fewer current spikes in its chronoamperometric response at +0.15 V vs. OCP (Fig. 4) indicated fewer pits opening during the test. One of them is seen in Fig. 6B – spectrum 2.

In any case, the cross-sectional observation of the AlCuCrFeNi+60TiC coating confirmed that, although the overall damage was quite limited, some interconnected paths, identifiable by their darker

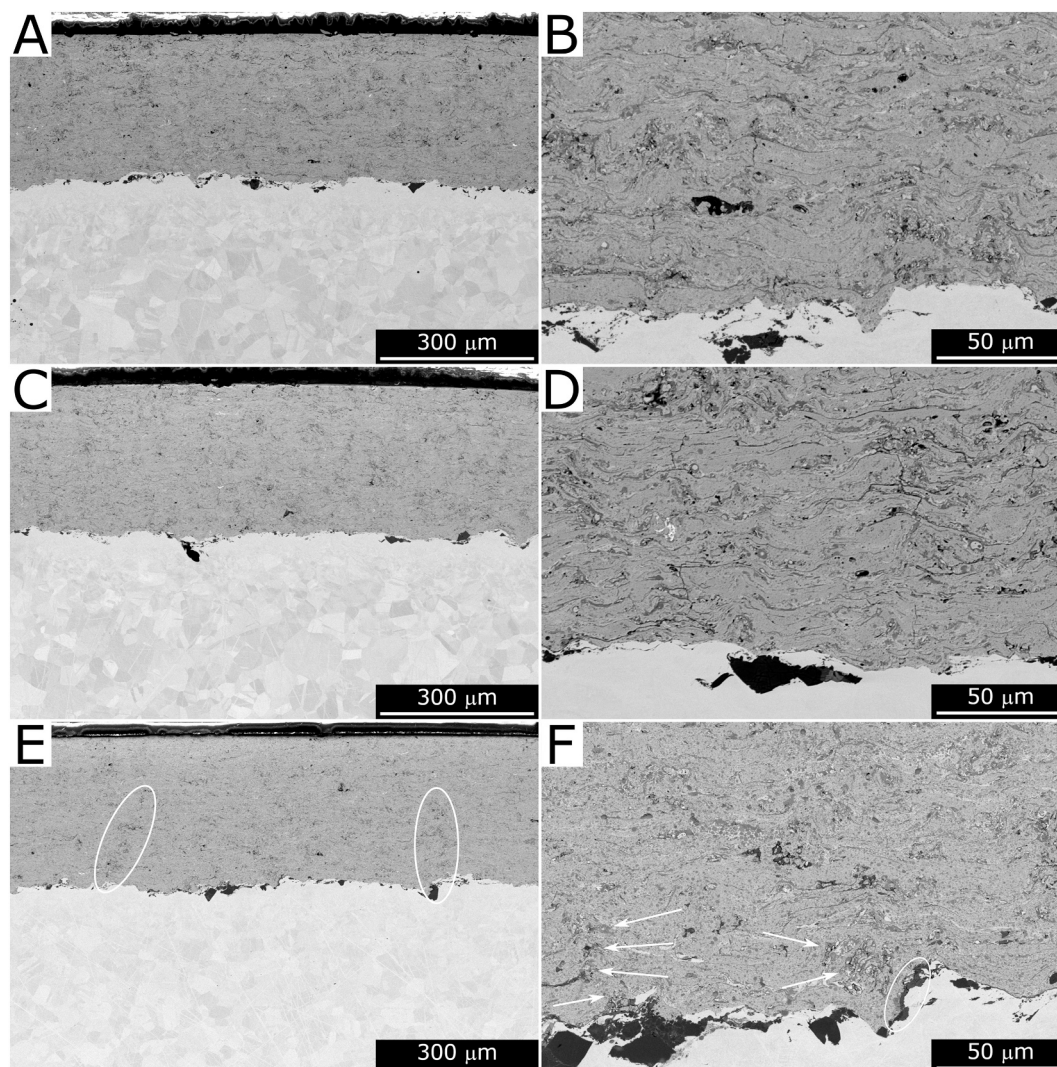


Fig. 7. Cross-sectional SEM micrographs of coated samples after chronoamperometric tests at +0.15 V vs. OCP: $\text{Al}_0(\text{CrMnFeNi}) + 60\text{TiC}$ Run3 sample in the tested region (A, B) and in a region away from the test area (C, D), and $\text{AlCuCrFeNi} + 60\text{TiC}$ Run3 sample in the tested region (E, F) – overviews (A, C, E) and details of the interface with the substrate (B, D, F). In panel E, the circles indicate interconnected paths; in panel F, the circle indicates Fe-based corrosion products on the substrate and the arrows indicate interconnected paths.

contrast (due to the local increase in porosity and the presence of corrosion products), were opened across the coating (Fig. 7E, F: see the circles in panel E and the arrows in panel F). The substrate was accordingly attacked by the liquid medium and developed corrosion products along the interface (Fig. 7F: circle). In backscattered electron imaging mode, the corrosion products on the substrate can be distinguished from embedded residuals of the alumina grits because of their slightly brighter contrast. The EDX maps in Fig. 8 also show that on the substrate there were some oxygen-rich areas that contained some Fe but no Al, indicating that they were Fe-based corrosion products (see the circles in panels A–D). Some Fe-rich spots within the interconnected pores opened in the coating (Fig. 8D: arrows) indicate that corrosion products from the substrate were moving upwards across the coating, explaining how Fe-based corrosion products made it to the outer surface.

SEM observation of the cross-section of the $\text{Al}_0(\text{CrMnFeNi}) + 60\text{TiC}$ sample after the chronoamperometric test at +0.15 V vs. OCP, by contrast, revealed the absence of any significant corrosion across the coating and at the substrate interface. Indeed, the overall appearance of the coating in the region subjected to the chronoamperometry test (Fig. 7A) was the same as that seen away from the tested area, which was representative of an unaffected coating (Fig. 7C). There were no signs of interconnected pores and no corrosion products at the interface with the

substrate (Fig. 7B), which was also unaltered compared to the unaffected region (Fig. 7D). This can be contrasted with the appearance of the same sample after the polarization test (Fig. 2C, D). This difference between the chronoamperometry and polarization tests means that:

- The selective leaching of the matrix seen after the polarization tests in Fig. 2 was indeed a consequence of the breakdown of the passive film, as stated in Section 3.1. It did not happen as long as the pseudo-passive film was stable.
- Because substrate corrosion products emerged after chronoamperometric testing of a sample (Cantor+60TiC) that did not exhibit substrate damage after the polarization test, and vice versa (for the $\text{Al}_0(\text{CrMnFeNi}) + 60\text{TiC}$ sample), it is inferred that the substrate corrosion phenomena seen in the two types of tests were unrelated. Substrate corrosion during the polarization test started in the transpassive regime, because, in the pseudo-passive regime, the opening of pits capable of exposing the substrate took a longer time than was available during the polarization tests (the pseudo-passive section of the anodic curves in Fig. 1 corresponded to a measurement duration of no more than 10 min, at a rate of 0.0005 V/s). Thus, we can confirm that substrate corrosion had no effect on the polarization response around the rest potential and in the pseudo-passive stage, as

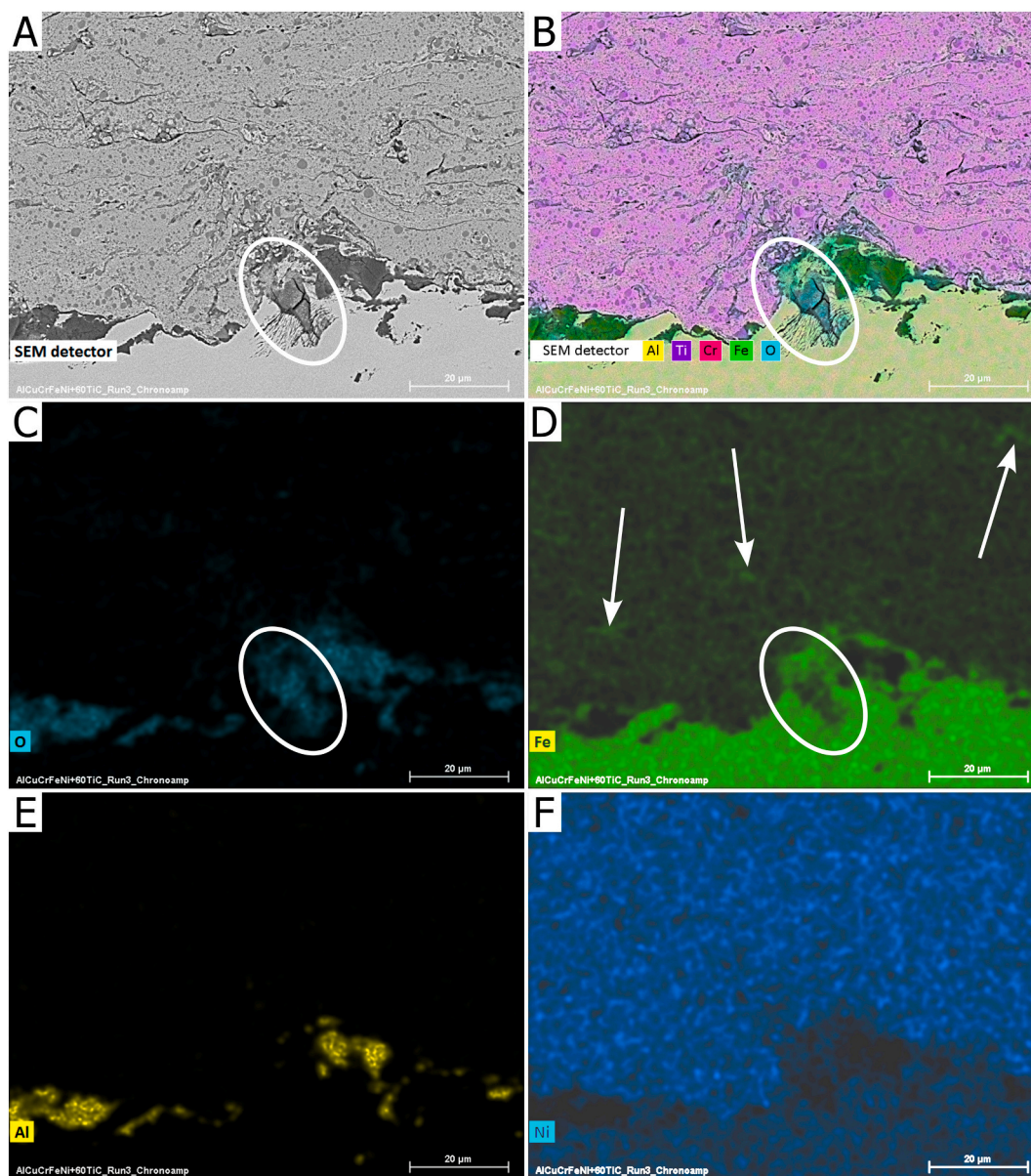


Fig. 8. Cross-sectional SEM micrograph of the AlCuCrFeNi+60TiC Run3 sample after the chronoamperometry test at +0.15 V vs. OCP (A), and the corresponding EDX maps: overall map (B) and maps of oxygen (C), iron (D), aluminium (E), and nickel (F).

previously stated in Section 3.1, and it did not influence the corrosion current density and corrosion potential values of Table 4. Moreover, substrate corrosion was not the consequence of interconnected pores existing in the pristine coating, otherwise, the same sample should have exhibited substrate corrosion in both tests.

Because, after the chronoamperometry test at +0.15 V vs. OCP, there were fewer pits and fewer corrosion products on the AlCuCrFeNi+60TiC Run3 sample than on the Cantor+60TiC Run3 sample, most of the Raman spectra acquired on the tested surface of AlCuCrFeNi+60TiC, like spectrum 1 in Fig. 6B, corresponded to the typical spectrum of titanium carbide [59,60], which was also found outside the corroded area (Fig. 6B – spectrum 3). Accordingly, this type of spectrum was found also on the corroded surface of the Cantor+60TiC sample when the signal was collected far from the visible pits, as in spectrum 4 of Fig. 6A.

TiC has a rock-salt FCC structure; therefore, its centre of symmetry should forbid any Raman-active vibration mode. However, defects such as carbon vacancies, which are inevitable in a product obtained by HEBM and subsequently subjected to a thermal spraying process, may

break down this symmetry. Therefore, a Raman-active response is provided by the defect sites themselves [59,60]. The spectrum of TiC was observed in all areas not covered by thick corrosion products, because the distance between the TiC particles was smaller than the lateral resolution of micro-Raman spectroscopy ($\sim 1 \mu\text{m}$), i.e. some TiC particles were always present in the laser-irradiated area. Note that the metal matrix, instead, does not return a Raman signal. Furthermore, the presence of the TiC spectrum within the tested area means that the portions that were free of pits developed a passive layer whose thickness was much lower than the penetration depth of the laser beam. Therefore, the passive film could not be detected by Raman spectroscopy. A thin passive layer is desirable for (pseudo-)passivity: thicker passive films have been reported to be generally more porous and less protective than thinner ones [54].

Because micro-Raman spectroscopy was not useful to analyse the composition of the pseudo-passivating layer, XPS analyses were carried out on the $\text{Al}_0(\text{CrMnFeNi}) + 60\text{TiC}$ and $\text{Al}_{14}(\text{CrMnFeNi}) + 60\text{TiC}$ samples after the chronoamperometric test at +0.15 V vs. OCP to clarify the composition of their passive films. This technique indeed probes a depth

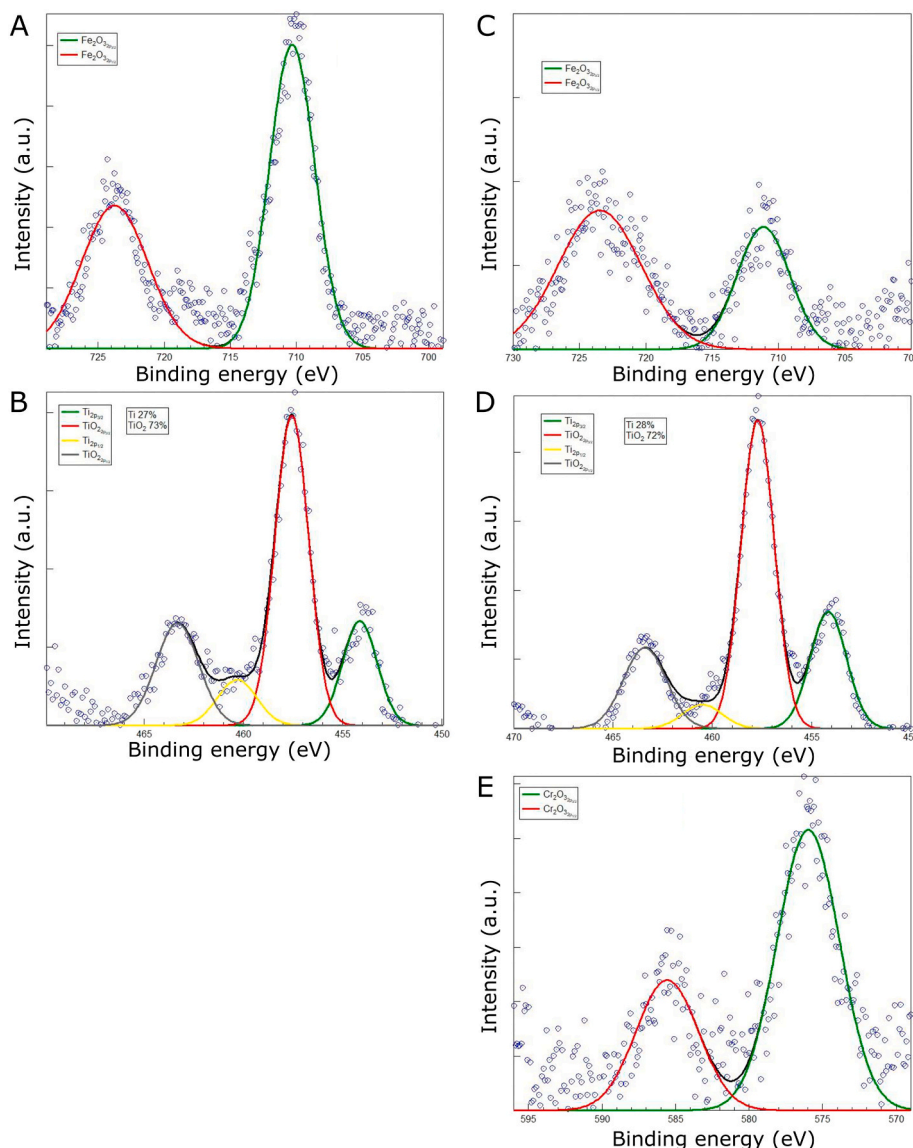


Fig. 9. XPS spectra acquired on coating surfaces after the chronoamperometry tests at +0.15 V vs. OCP: Fe2p (A) and Ti2p (B) spectra of the $\text{Al}_0(\text{CrMnFeNi}) + 60\text{TiC}$ sample; Fe2p (C), Ti2p (D), and Cr2p (E) spectra of the $\text{Al}_{14}(\text{CrMnFeNi}) + 60\text{TiC}$ sample.

Table 7

Fitted positions of the XPS peaks seen in Fig. 9.

Sample	Peak position (eV)	Assignment
$\text{Al}_0(\text{CrMnFeNi}) + 60\text{TiC}$	454.1	Ti 2p _{3/2}
	457.5	TiO ₂ 2p _{3/2}
	460.3	Ti 2p _{1/2}
	463.3	TiO ₂ 2p _{1/2}
	710.3	Fe ₂ O ₃ 2p _{3/2}
	723.7	Fe ₂ O ₃ 2p _{1/2}
	454.2	Ti 2p _{3/2}
	457.7	TiO ₂ 2p _{3/2}
	460.5	Ti 2p _{1/2}
$\text{Al}_{14}(\text{CrMnFeNi}) + 60\text{TiC}$	463.4	TiO ₂ 2p _{1/2}
	711.1	Fe ₂ O ₃ 2p _{3/2}
	723.4	Fe ₂ O ₃ 2p _{1/2}
	576	Cr ₂ O ₃ 2p _{3/2}
	585.6	Cr ₂ O ₃ 2p _{1/2}

of less than 10 nm below a surface. XPS analyses were not performed on the $\text{AlCuCrFeNi} + 60\text{TiC}$ and $\text{Cantor} + 60\text{TiC}$ samples because the experimental apparatus we used in this work did not allow precise positioning

of the 1 mm² large acquisition region. Therefore, this region could have ended up encompassing some of the corrosion products emerging from the substrate, making it impossible to discern the contribution of the passive film from that of the corrosion products themselves.

The results (Fig. 9, Table 7) showed that for the $\text{Al}_0(\text{CrMnFeNi}) + 60\text{TiC}$ sample, the strongest XPS signals came from the Fe 2p and Ti 2p regions of the spectrum (Fig. 9A, B). Fe 2p, Cr 2p, and Ti 2p signals were correspondingly the strongest ones to emerge from the $\text{Al}_{14}(\text{CrMnFeNi}) + 60\text{TiC}$ sample (Fig. 9C, D, E). The Fe and Cr signals were entirely due to Fe³⁺ and Cr³⁺ in the forms of Fe₂O₃ and Cr₂O₃, respectively (Table 7), suggesting that these were the compounds responsible for the passivation of the matrix. The Ti signal was more intense, since more than half of the volume fraction of the material is made of TiC. It comprised a dominant component due to TiO₂, which passivated the surface of the TiC particles, as well as a secondary component due to Ti⁰ (Fig. 9B, D and Table 7). The latter might have originated from metallic Ti that resulted from the partial decarburization of TiC, as shown by our previous work [39]. The lack of comparable signals from the Fe⁰ or Cr⁰ species was likely due to the lower overall intensity of the respective spectra. However, it is also possible to speculate that the passivating film on the TiC particles was very thin, in the nanometre range. This might

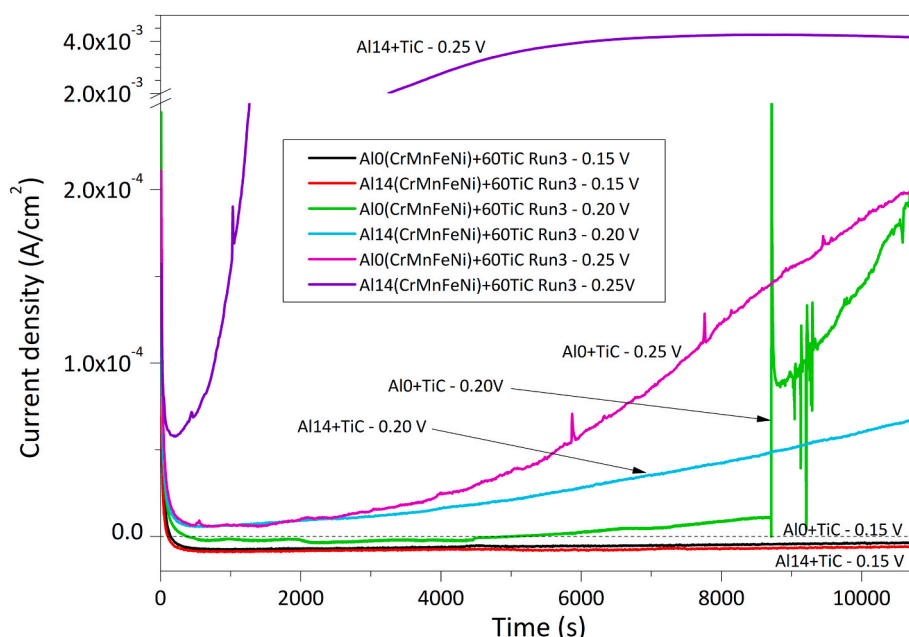


Fig. 10. Chronoamperometric curves recorded on the $\text{Al}_0(\text{CrMnFeNi}) + 60\text{TiC}$ Run3 and $\text{Al}_{14}(\text{CrMnFeNi}) + 60\text{TiC}$ Run3 samples at fixed overpotentials of +0.15 V vs. OCP, +0.20 V vs. OCP, +0.25 V vs. OCP.

have allowed the detection of the Ti^0 signal below the passive film itself. From this, it also follows that, if the passive layer on the TiC particles was of only a few nanometres, the high intensity of the TiO_2 signal might have been due to some of it originating from the matrix. That is, the passive film protecting the matrix consisted of mixed oxides of Fe^{3+} , Cr^{3+} and Ti^{4+} . This would corroborate the previous assumptions that the dissolution of TiC during the spraying process had a considerable influence on the corrosion behaviour of the matrix. According to this interpretation, indeed, the fraction of titanium entering the matrix would have contributed to its passivation. In contrast, the XPS signals from other elements, such as Ni, Mn, as well as Al in the $\text{Al}_{14}(\text{CrMnFeNi}) + 60\text{TiC}$ sample, were barely detectable and are not shown in Fig. 9. Thus, they were not major constituents of the passive film.

The observation that the TiC particles were covered by a thinner oxide film than the matrix is consistent with the corrosion potential values of stoichiometric and sub-stoichiometric TiC quoted in Section 3.1. In fact, TiC was still cathodic at the overpotential of +0.15 V above the initial OCP of the coated system, which corresponded to an absolute potential value < 0 V vs. $\text{Ag}/\text{AgCl}/\text{KCl}_{(\text{sat.})}$. Thus, the tendency of the carbide particles to grow an oxide layer during the chronoamperometric test was very low because they rather acted as cathodes.

To determine the stability limits of the passive film on the $\text{Al}_0(\text{CrMnFeNi}) + 60\text{TiC}$ and $\text{Al}_{14}(\text{CrMnFeNi}) + 60\text{TiC}$ samples, additional chronoamperometric tests were performed at overpotentials of +0.20 V and +0.25 V vs. OCP (Fig. 10). Both values were still within the pseudo-passive range of the polarization curves in Fig. 1, as shown by the corresponding dashed lines in Fig. 1C in the case of the $\text{Al}_0(\text{CrMnFeNi}) + 60\text{TiC}$ sample. Nevertheless, these potential levels imposed more severe working conditions than the tests at +0.15 V vs. OCP.

All chronoamperometric curves acquired at these higher overpotential levels (Fig. 10) still exhibited a rapid drop in current density during the initial 100–200 s. However, overall trends differed from those seen at +0.15 V vs. OCP (also shown in Fig. 10 for comparison). Specifically, the $\text{Al}_0(\text{CrMnFeNi}) + 60\text{TiC}$ sample developed slightly cathodic current density values during the first half of the test at +0.20 V vs. OCP but subsequently turned anodic again. At a certain point, it exhibited an abrupt increase in current density by two orders of magnitude. At +0.25 V vs. OCP, its current density never turned

cathodic and continued to increase continuously throughout the test, ending at about 2×10^{-4} A/cm².

The $\text{Al}_{14}(\text{CrMnFeNi}) + 60\text{TiC}$ sample never turned cathodic at both overpotentials. At +0.20 V vs. OCP, its current density increased steadily, with values that were above those that the $\text{Al}_0(\text{CrMnFeNi}) + 60\text{TiC}$ sample exhibited before the above-mentioned jump. At +0.25 V vs. OCP, the current density was, from the very beginning of the test, orders of magnitude higher than in all other cases. The current density increased quickly during the test and reached values of around 4×10^{-3} A/cm².

Therefore, it is inferred that increasing the overpotential above +0.15 V vs. OCP destabilized the passive films of these two coating formulations. The $\text{Al}_{14}(\text{CrMnFeNi}) + 60\text{TiC}$ composition, perhaps due to its two-phase (BCC + FCC) matrix (Table 3), was more readily destabilized and degraded.

Specifically, SEM micrographs (Fig. 11) showed that cracking of the passive film caused interlamellar corrosion of the coating, the severity being correlated with the measured current densities. Damage was quite limited, for both coatings, after the test at +0.20 V vs. OCP ($\text{Al}_{14}(\text{CrMnFeNi}) + 60\text{TiC}$: Fig. 11A–B; $\text{Al}_0(\text{CrMnFeNi}) + 60\text{TiC}$: Fig. 11E–F). At low magnification, there is no macroscopic damage (Fig. 11A, E). The test solution, however, penetrated through the interlamellar boundaries and corroded the matrix phase in some specific lamellae, such as the ones circled in panels A and F. The details (Fig. 11B, F) revealed TiC particles that were left unsupported by the dissolution of the matrix. EDX spectra (Fig. 12A, C and quantitative results in Table 8) accordingly show that, in the corroded lamellae (spectrum 1), the Ti peaks remained as intense as in unaffected areas (spectrum 2), while the peaks of the elements constituting the matrix (Cr, Mn, Fe, and Ni) became weaker, resulting in an increase in the overall concentration of Ti when normalizing the quantitative analysis to 100 (Table 8). Moreover, in the corroded area, the relative concentration of Cr increased compared to those of Mn, Fe, and Ni (compare again spectrum 1 to spectrum 2 in Table 8), indicating that the selective dissolution primarily affected the latter three elements. This is the same selective dissolution phenomenon observed after the electrochemical polarization test in Section 3.1. The EDX spectra of corroded areas (spectrum 1) were also clearly distinguishable from that of the pre-existing oxide inclusions (spectrum 3). The oxide inclusions contained

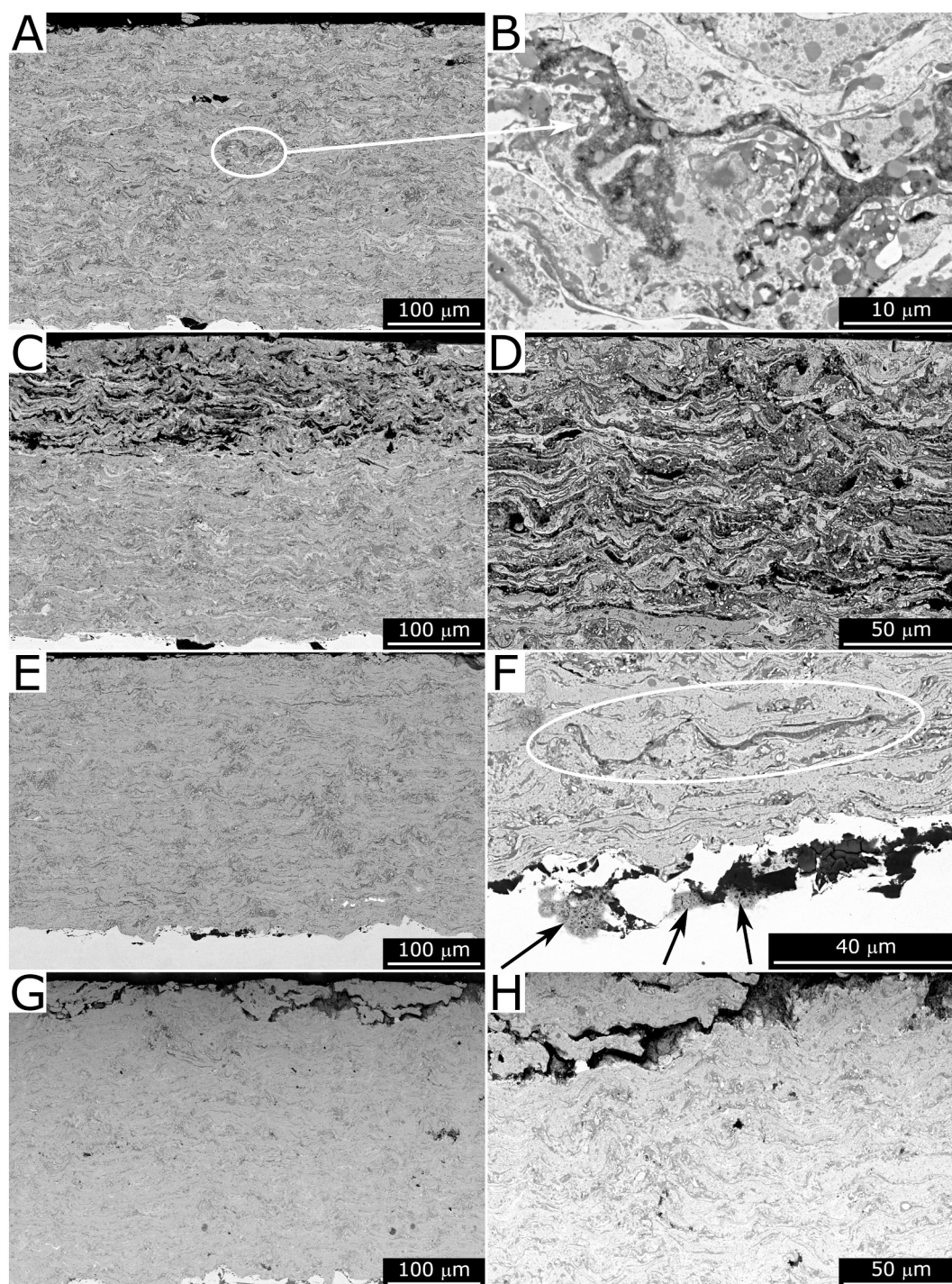


Fig. 11. Cross-sectional SEM micrographs of the $\text{Al}_{14}(\text{CrMnFeNi}) + 60\text{TiC}$ Run3 (A–D) and $\text{Al}_0(\text{CrMnFeNi}) + 60\text{TiC}$ (E–H) samples after chronoamperometric tests at +0.20 V (A–B, E–F) and + 0.25 V vs. OCP (C–D, G–H): overviews (A, C, E, G) and details of the corroded area (B, D, F, H). The circles in panels A and F indicate corroded lamellae; the arrows in panel F indicate substrate corrosion.

more Al but even less Cr, Mn, Fe, and Ni than the corroded areas (quantitative results in Table 8). In fact, Ti and, secondarily, Al were preferentially oxidized during the deposition process because of their higher oxygen affinity.

Although the interface with the substrate was apparently unaffected (Fig. 11A, E), detailed views, especially in the case of the $\text{Al}_0(\text{CrMnFeNi}) + 60\text{TiC}$ sample, revealed isolated corrosion spots. Fig. 12B, C show corrosion products with a needle-like morphology, based on Fe, O and Cl (Table 8: spectra 4 and 5), which can be easily differentiated from the Al_2O_3 residuals left by grit-blasting both through their different contrast

level in backscattered electron imaging mode, and their EDX spectrum (compare with spectrum 6). It is possible that the increase in current density observed during this test was associated with the onset of substrate corrosion, meaning that the corrosive agents, by selective dissolution of specific lamellae, managed to open an interconnected path across the entire coating. This would again be consistent with the analogous finding in the electrochemical polarization tests (Section 3.1 and Fig. 2C–D). It corroborates the above discussion on the fact that substrate corrosion was not the consequence of interconnected pores existing in the pristine coating and that it takes some time for the

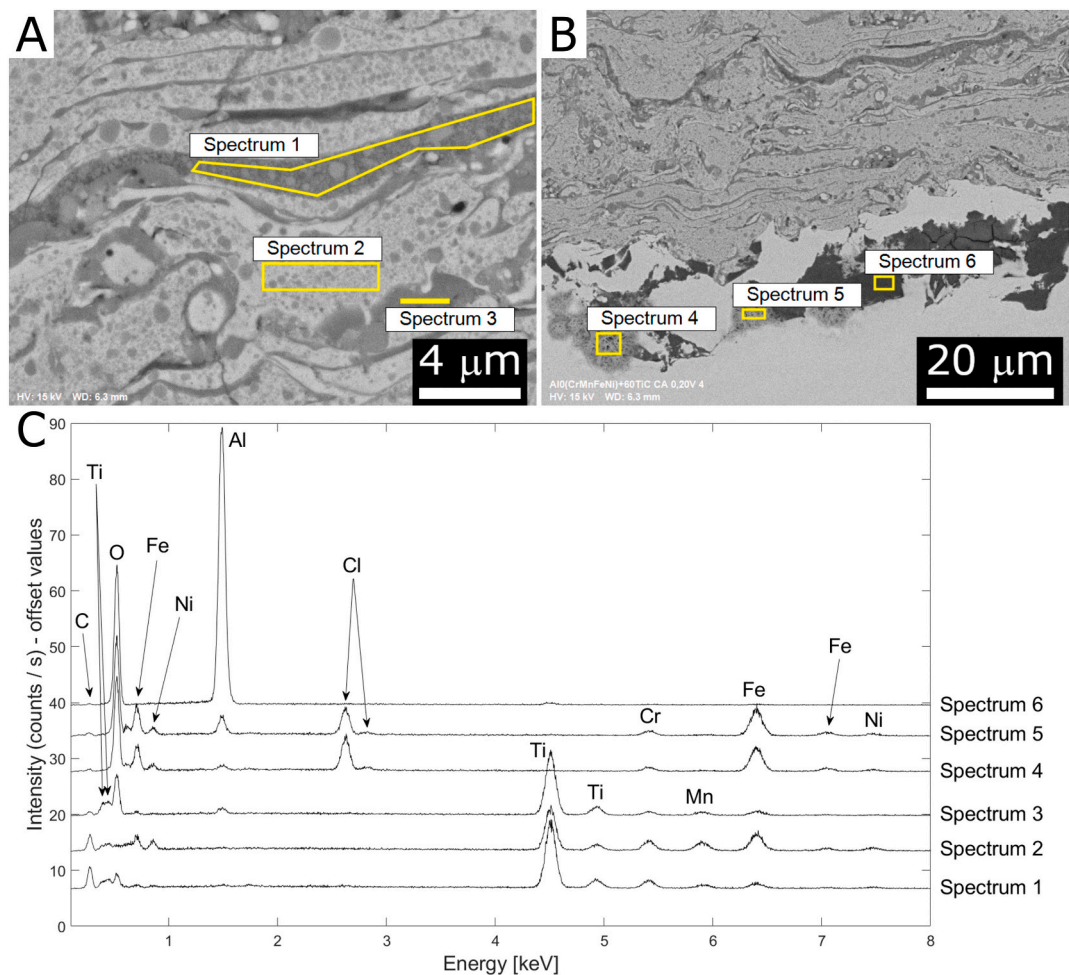


Fig. 12. Cross-sectional SEM micrographs of the $\text{Al}_0(\text{CrMnFeNi}) + 60\text{TiC}$ Run3 sample after the chronoamperometric test at +0.20 V (A-B) and corresponding EDX spectra (C).

Table 8
Quantitative results from the EDX spectra in Fig. 12C, in wt%.

Element (wt%)	O	Al	Si	Cl	Ti	Cr	Mn	Fe	Ni
Spectrum 1	15.95	0.35	0.36	0.27	53.77	11.15	4.20	10.25	3.69
Spectrum 2	1.60	0.24	0.09		31.46	11.81	12.11	33.15	9.54
Spectrum 3	36.97	1.30			44.76	4.20	4.42	7.37	0.98
Spectrum 4	33.59	1.08	0.24	10.35		3.83	0.24	45.03	5.63
Spectrum 5	31.46	4.33		7.68	0.31	4.34		46.10	5.78
Spectrum 6	47.77	49.80			1.16	0.45		0.82	

corrosive agents to open up a path across a coating. As the higher applied anodic overpotential accelerated the dissolution process, this time became shorter.

Corrosion along lamellar boundaries was more severe in the samples tested at +0.25 V (Fig. 11C-D, G-H), consistent with the higher current densities recorded during the chronoamperometric test in Fig. 10. The $\text{Al}_0(\text{CrMnFeNi}) + 60\text{TiC}$ sample (Fig. 11G, H) exhibited some highly corroded interlamellar pathways leading to the interior of the coating. The $\text{Al}_{14}(\text{CrMnFeNi}) + 60\text{TiC}$ sample (Fig. 11C, D) was even more affected, with widespread interlamellar corrosion. Therefore, as the current density recorded during the chronoamperometric tests increased, the corrosion morphology became more and more similar to that seen after transpassive corrosion in the electrochemical polarization tests (Fig. 2 and Fig. 3). This means that in all cases the main corrosion mechanism triggered by the destabilization of the passive film was the penetration of corrosive agents along the lamellar boundaries, followed

by a selective attack to the metallic matrix, moving from the boundary toward the interior of each splat. Looking at the bottom of the degraded portion of the $\text{Al}_{14}(\text{CrMnFeNi}) + 60\text{TiC}$ sample in great detail, this mechanism is particularly apparent through the incipient corrosion of isolated splats (Fig. 13: some of these splats are outlined). The matrix indeed started to dissolve from lamellar boundaries, even where these did not show apparent pores, indicating that the corrosive species could penetrate through even the tiniest interlamellar channels. As dissolution progressed toward the interior, the surrounding oxide inclusions were left unaffected, as were the TiC particles. The oxide inclusions present in all coatings could in fact have had a role in worsening the resistance against this type of corrosive attack: (1) they interrupt the continuity of the pseudo-passive film, thus facilitating corrosion along the splat boundaries, (2) they may facilitate the presence of nanometric defects along the splat boundaries, where the corrosive species could infiltrate, and (3) if they are electrically conductive, which can indeed be the case

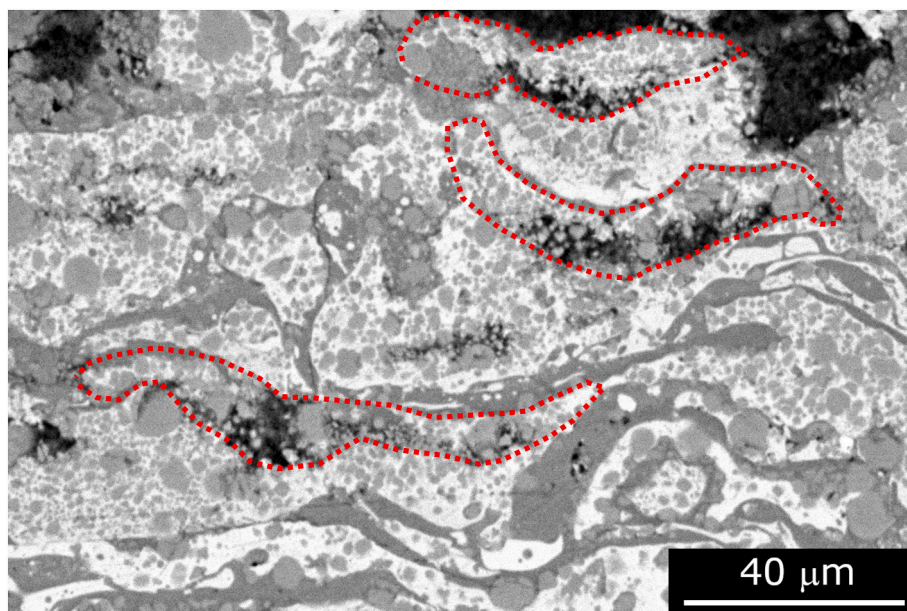


Fig. 13. Magnified SEM micrograph showing the bottom edge of the degraded area of the $\text{Al}_{14}(\text{CrMnFeNi}) + 60\text{TiC}$ Run3 sample after the chronoamperometric test at +0.25 V. Partially corroded lamellae are outlined by dashed lines.

if they are slightly sub-stoichiometric, they can act as cathodic sites and further accelerate the dissolution of the adjacent metal matrix.

Local corrosion spots again appeared on the substrate, and reddish products could be observed by the unaided eye on the surface of the samples tested at +0.25 V vs. OCP.

4. Conclusions

We found for the first time a “levelling effect” in the electrochemical response of TiC+HEA hardmetal coatings, in comparison to the response of pure alloys. Specifically, the polarization response of all coatings in a 3.5% (wt./vol.) NaCl solution was similar and featured a pseudo-passive regime with current densities of 10^{-5} – 10^{-4} A/cm² up to a potential of ~ -0.05 V vs. Ag/AgCl/KCl_(sat.). Beyond the pseudo-passive stage, transpassive dissolution of the matrix took place. Thus, the corrosion of the coatings was primarily due to the corrosion of their matrix, but the differences among the performances of the different coatings were smaller than what would have been expected based on the known corrosion behaviour of the high-entropy alloy matrices alone. It is inferred that the galvanic coupling between the various matrices and the TiC phase, and the alloying of the matrices with Ti and C released by partial dissolution of TiC, levelled the electrochemical polarization performance of all samples.

Nonetheless, minor differences could still be identified among the samples. The Cantor+60TiC and AlCuCrFeNi+60TiC coatings exhibited slightly lower corrosion current densities and slightly lower current density values in the pseudo-passive stage of electrochemical polarization tests, suggesting better short-term corrosion behaviour. However, it is particularly interesting to note that the short-term polarization behaviour is not representative of longer-term performances. In fact, chronoamperometric tests indicated that the pseudo-passive state of the $\text{Al}_0(\text{CrMnFeNi}) + 60\text{TiC}$ and $\text{Al}_{14}(\text{CrMnFeNi}) + 60\text{TiC}$ coatings was more stable. Their practical electrochemical nobility was increased by the growth of a protective film, up to the point that they turned cathodic with respect to the reference electrode, when the test was carried out at a fixed potential corresponding to +0.15 V with respect to the initial open circuit potential (OCP) value. The AlCuCrFeNi+60TiC and Cantor+60TiC coatings, on the other hand, experienced some pitting corrosion during the chronoamperometric test at the same overpotential level, indicating a progressive destabilization of the pseudo-passive film

in the chlorine-containing medium. The passive film developed on the $\text{Al}_0(\text{CrMnFeNi}) + 60\text{TiC}$ and $\text{Al}_{14}(\text{CrMnFeNi}) + 60\text{TiC}$ coatings was based on oxides of Fe^{3+} , Cr^{3+} and Ti^{4+} , which confirmed the role of dissolved Ti in the corrosion behaviour of the matrix. If the potential applied in the chronoamperometric tests was further increased (to overpotential levels of +0.20 V vs. OCP and +0.25 V vs. OCP), the passive film on the $\text{Al}_0(\text{CrMnFeNi}) + 60\text{TiC}$ and $\text{Al}_{14}(\text{CrMnFeNi}) + 60\text{TiC}$ coatings was also destabilized, triggering interlamellar penetration of the corrosive agents followed by matrix dissolution. The $\text{Al}_{14}(\text{CrMnFeNi}) + 60\text{TiC}$ coating, in particular, seemed more prone to destabilization with increasing applied potential.

The present results indicate that the TiC+HEA hardmetal coatings have potential for applications where protection against corrosion by aqueous environments is required in addition to wear resistance. Examples are ball and gate valves and seats especially in marine environments; water pump parts such as impellers, bearing faces, etc.; rotary joints in liquid distributor units; and hydroelectric parts. However, further research is needed to find improved matrix compositions that, despite the “levelling effect” exerted by the mixing with TiC particles (and the dissolution of Ti in the matrix itself), can exhibit improved resistance against transpassive dissolution and even better long-term stability, since the present coatings are not yet at the same level of corrosion resistance as HVOF-sprayed $\text{Cr}_3\text{C}_2\text{-NiCr}$.

CRediT authorship contribution statement

Giovanni Bolelli: Writing – original draft, Visualization, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Maria Francesca Bonilauri:** Writing – review & editing, Investigation, Formal analysis. **Luca Bortolotti:** Writing – review & editing, Investigation, Formal analysis. **Alessia Bruera:** Writing – review & editing, Investigation, Formal analysis. **Lorenzo Ferrari:** Investigation, Formal analysis. **Luca Lusvarghi:** Supervision, Funding acquisition, Conceptualization. **Stefania Morelli:** Writing – review & editing, Investigation, Formal analysis. **Alvise Bianchin:** Writing – review & editing, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. **Enrico Forlin:** Writing – review & editing, Methodology, Investigation, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

All authors report financial support was provided by European Union under GA no 101092211. Alvise Bianchin, Enrico Forlin report a relationship with MBN Nanomaterialia S.r.l. that includes: employment. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.surfcoat.2026.133632>.

Data availability

Data will be made available on request.

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