

Article

Corrosion Behavior of Al₁₀Cr₃₀Fe₂₅Mn₃₀Ti₅ High-Entropy Alloy: Microstructural, Electrochemical, and Surface Analysis

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Abstract: In this work, the corrosion performance of a new developed high-entropy alloy (HEA) of the composition Al₁₀Cr₃₀Fe₂₅Mn₃₀Ti₅ (at. %) was studied. The corrosion testing of the Al₁₀Cr₃₀Fe₂₅Mn₃₀Ti₅ HEA was carried out in 2.5 M NaOH, 0.6 M NaCl, and in 0.5 M H₂SO₄. The correlation between the microstructure, elemental composition, density, hardness, and corrosion resistance of the new developed Al₁₀Cr₃₀Fe₂₅Mn₃₀Ti₅ HEA was investigated. The impedance response showed protective corrosion behavior for the neutral and acidic pH, while the alkaline environment led to a passivity breakdown due to dissolution of Al forming Al(OH)₃. The outcome of the presented study suggests that new developed HEA is suitable to be used in industrial environments with a neutral and acidic pH.

Keywords: high-entropy alloys (HEA); electrochemical impedance spectroscopy (EIS); X-ray photoelectron spectroscopy (XPS); high-energy X-ray diffraction (HEXRD); passive film



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1. Introduction

High-entropy alloys (HEA) are new materials composed of four to five elements in similar ratios with high mixing entropy, and they generally have a stable solid solution phases such as face-centered cubic (FCC), body-centered cubic (BCC), and/or hexagonal close-packed (HCP) [1,2]. HEAs have outstanding properties, both mechanical (hardness, strength, density, or wear), and corrosion protection (high-temperature oxidation, pitting corrosion, atmospheric corrosion resistance), making the HEA really appealing for industrial applications [3]. The main factor for the outstanding properties is the design selection matrix and ratios of their elemental composition, granting them specific boost depending on the desired application [4].

In the case of HEA corrosion in harsh environments, several studies are found using HEA compositions, such as the CoCrFeNi, which promoted an enriched Cr₂O₃ passive oxide film in 0.6 M chloride solution, leading to a more noble corrosion potential value (E_{corr}) with a low corrosion current density (i_{corr}) [3]. Similar HEAs with Al additions lead to a formation of Al- and Ni-rich film; however, the BCC phase was Cr-depleted, becoming more susceptible to localized corrosion, thus promoting pitting corrosion [5]. Similarly, the Al_xCrFe_{1.5}MnNi_{0.5} HEA showed increasing corrosion resistance with decreasing Al content in both acid (H₂SO₄) and neutral (NaCl) solutions [6]. When the HEA has some Ti additions, FeCoCrAlNiTi was able to form a stable oxide film at a much higher rate than those without it, inducing low i_{corr} in a neutral 3.5 wt.% NaCl solution [7]. Additions of Mn have been reported to decrease the Cr content in the passive film of the FeCrNiCoMn HEA, reducing the corrosion protection properties of the HEA [4]. Even more, for a high Mo content HEA, there was an increased σ -phase precipitation, which was rich in Cr and Mo, thus promoting a preferential site for dissolution, inducing higher current densities in the FeCrNiCoMo HEA [8]. The deleterious effect of the σ -phase precipitation was also

seen by additions of V, which triggered the formation of the σ -phase in the AlFeNiCrCoTiV HEA, promoting pitting corrosion at these sites [9].

The aim of this study is to reveal the corrosion performance of the Al₁₀Cr₃₀Fe₂₅Mn₃₀Ti₅ HEA. A combination of electrochemical techniques, such as cyclic potentiodynamic polarization (CPP) and electrochemical impedance spectroscopy (EIS), in three different pH electrolyte solutions—alkaline (NaOH, pH 14), neutral (NaCl, pH 7), and acidic (H₂SO₄, pH 0.3)—will allow setting the suitability of the HEA for industrial applications. In depth characterization of the passive film is performed by XPS, SEM, and EDX, with correlation to the environment, electrochemical response, microstructure, and elemental composition.

2. Materials and Methods

2.1. Material and Microstructure Characterization

The nominal composition of the HEA, expressed in the atomic percentage, is Al₁₀Cr₃₀Fe₂₅Mn₃₀Ti₅ (see Table 1). Stoichiometric amounts of the pure elements, purity > 99.5%, were melted in an induction furnace and poured in a steel mold. As-cast ingot was homogenized at 1200 °C for 1 h in an inert Ar atmosphere and subsequently quenched in water. Finally, the ingot was heated at 1200 °C for 30 min and subsequently forged with a final reduction of 65%. The forged sheet was cooled down in air. Hardness of the new designed HEA was tested in a microhardness Tukon 1202 (Instron Co., Canton, MA, USA) with a HV/10 cone indenter applying 10 N for 15 s.

Table 1. Elemental composition of Al₁₀Cr₃₀Fe₂₅Mn₃₀Ti₅ HEA.

Element	Cr	Mn	Fe	Al	Ti
Content (at.%)	30	30	25	10	5
Content (wt.%)	30.5	32.2	27.3	5.3	4.7

After the ingots were processed, the samples were cut and polished with SiC paper up to 1200 grid, and further finished with 1 μ m diamond powder. Then, the samples were rinsed with DI water, cleaned with ethanol, and air dried. The microstructural study was performed by optical microscopy (OM) using a Nikon SMZ 745T stereomicroscope (Nikon Metrology Inc., Brighton, MI, USA), and scanning electron microscopy (SEM) using a JEOL 6500 microscope (JEOL USA Inc., Peabody, MA, USA) equipped with an energy dispersive X-ray spectrometer (EDS) microanalysis. Samples were etched with an etchant solution containing 10 mL HNO₃, 30 mL HCl, 10 mL DI water, 2 mL H₂O₂, and 2 mL picric acid. The identification of the phases present in the alloy was done using high-energy X-ray diffraction (HEXRD) measurements in the P07 beamline of PETRA III at the Deutsches-Elektronen-Synchrotron (DESY, Hamburg, Germany). The wavelength of the X-ray source was 0.1424 Å, corresponding to an energy of 87.1 keV. The diffraction patterns were recorded using a Perkin-Elmer XRD1621 (PerkinElmer Inc., Fremont, CA, USA) flat panel detector located at 1390 mm from the sample. The flat panel was an array of 2048 $\times$ 2048 pixels with an effective pixel size of 200 $\times$ 200 μ m². LaB₆ standard powder was used as reference material for calibrating the acquired diffraction spectra.

2.2. Electrochemical Techniques

The electrochemical corrosion properties of the new designed Al₁₀Cr₃₀Fe₂₅Mn₃₀Ti₅ HEA were tested under three different environments: alkaline 2.5 M NaOH (pH 14), neutral with chloride influence 0.6 M NaCl (pH 7) [10], and acidic 0.5 M H₂SO₄ (pH 0.3). A pH probe was used to measure the pH of each electrolyte solution, and before the measurements were taken, the pH probe was calibrated with fresh standard solutions. These three electrolyte solutions represent a wide spectrum of industrial environments where the HEA could be under service, thus providing a comprehensive study to better understand the electrochemical corrosion kinetics and mechanisms. A three-electrode configuration electrochemical cell setup was used, consisting of a saturated calomel electrode

(SCE) as the reference electrode (RE), a platinum mesh counter electrode (CE), and the $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA as the working electrode (WE). The samples were mounted in resin and polished with SiC paper up to 1200 grid, finishing with 1 μm diamond powder; then, the samples were rinsed with DI water, cleaned with ethanol, and air dried. The sample exposed area for all electrochemical tests was set to 1 cm^2 by means of nonconductive red lacquer. For each of the electrolyte solutions at a different pH, a set of electrochemical testing was conducted. An open circuit potential (OCP) was conducted over 1 h prior to each electrochemical measurement until a steady-state OCP value was reached [11]. Then, electrochemical impedance spectroscopy (EIS) gathered information of the corrosion mechanisms of the electrolyte/passive film and the passive film/metal interface. The EIS measurements were recorded at the OCP, with a frequency range between 10^5 and 10^{-2} Hz, using an AC excitation signal of 10 mV and at a step rate of 10 points per decade, following ASTM G106-89 [12]. Finally, a cyclic potentiodynamic polarization (CPP) test was carried out to study the electrochemical reaction kinetics and activation/transport limiting processes. The CPP tests were performed from $-0.6 V_{\text{OCP}}$ to $+0.6 V_{\text{OCP}}$ at a potential scan rate of 1.667 mV s^{-1} in accordance with ASTM G61-86 [13]. Both EIS and CPP were accelerated electrochemical corrosion tests performed after the 1 h of exposure from the OCP in accordance with ASTM G61-86 and ASTM G106-89 [14,15]. These accelerated tests, with a short exposure time, were selected due to their validity and acceptance based on previous literature for determining the corrosion behavior of HEAs, even more in the case of HEAs containing Al [5,6,16–18]. All the electrochemical tests were done in triplicate to check reproducibility.

2.3. Surface Characterization Techniques

Surface analysis by X-ray photoelectron spectroscopy (XPS) was performed on the $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA samples after the CPP testing for each pH electrolyte solution. XPS spectra were recorded on a PHI 5000 VersaProbe II X-ray photoelectron spectrometer (Physical Electronics, Chanhassen, MN, USA) with an Al K_{α} source ($h\nu = 1486.6 \text{ eV}$), a working residual pressure below 10^{-6} Pa, a high-voltage excitation of 30 kV, and a current of 30 mA. The high resolution XPS used a CLAM2 hemispherical electron analyzer (VG Microtech Ltd., London, UK) with a nonmonochromatic Mg K_{α} X-ray source operated at 300 W, with a pass energy of 23.5 eV, and at energy step size of 0.2 eV/step. The depth profile sputtering was performed using an EX05 Ar⁺ ion gun (ThermoFisher Scientific, Waltham, MA, USA) operating at 1 kV and 1 μA [19].

By the means of scanning electron microscopy (SEM) in a Hitachi-TM3030, the microstructure and surface morphology of the tested samples were analyzed. The SEM analysis was performed using secondary electron (SE) mode at an accelerating voltage of 15 kV and at a working distance of 8 mm. In addition, local compositional analysis was obtained by the energy dispersive X-ray spectroscopy (EDX) technique.

3. Results

3.1. Microstructure and Hardness

The choice of the $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA composition was based on three empirical approaches: the enthalpy of mixing ($\Delta H_{\text{mix}} = -6.5 \text{ kJ/mol}$), and the atomic size mismatch parameter ($\delta = 5.5\%$) to evaluate the stability of a single-phase alloy; and the valence electron concentration ($\text{VEC} = 6.4$) was used to choose the crystalline structure. Therefore, with these design parameter values, a HEA with a single-phase BCC structure is predicted.

The microstructure of the as-cast ingot consists of equiaxed grains with a bright secondary phase mainly located at the grain boundaries as long laths, although it can also appear more sparsely dispersed within the grains (see Figure 1). According to semiquantitative EDX microanalysis, the composition of the alloy is slightly deviated from the nominal composition, as can be checked in Table 2, likely due to the low vapor pressure of manganese, which led to some manganese losses by volatilization. Microanalysis data also evidenced that the matrix was enriched in chromium while the secondary phases were

enriched in titanium, iron, and manganese. The hot-forged alloy, however, was left to cool down in air, which explains the nucleation of the secondary phases in the alloy (see Figure 2), but in lower amounts than that found in the as-cast processing [20].

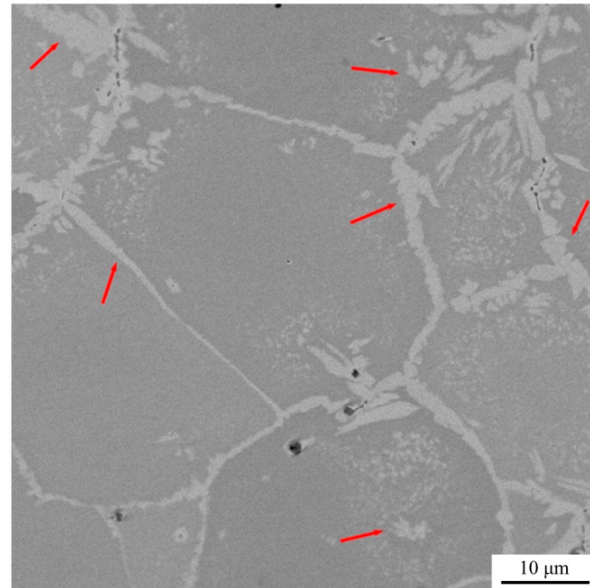


Figure 1. Microstructure of the as-cast $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA. Red arrows label some examples of the secondary phases present in the alloy.

Table 2. Average composition (at.%) of the as-cast $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA and compositions of the matrix and secondary phase particles.

Region	Cr	Mn	Fe	Al	Ti
Average	31.5	28.9	25.6	8.0	6.0
Matrix	38.1	25.8	23.6	8.3	4.2
Secondary phase	24.3	29.6	28.8	6.1	11.1

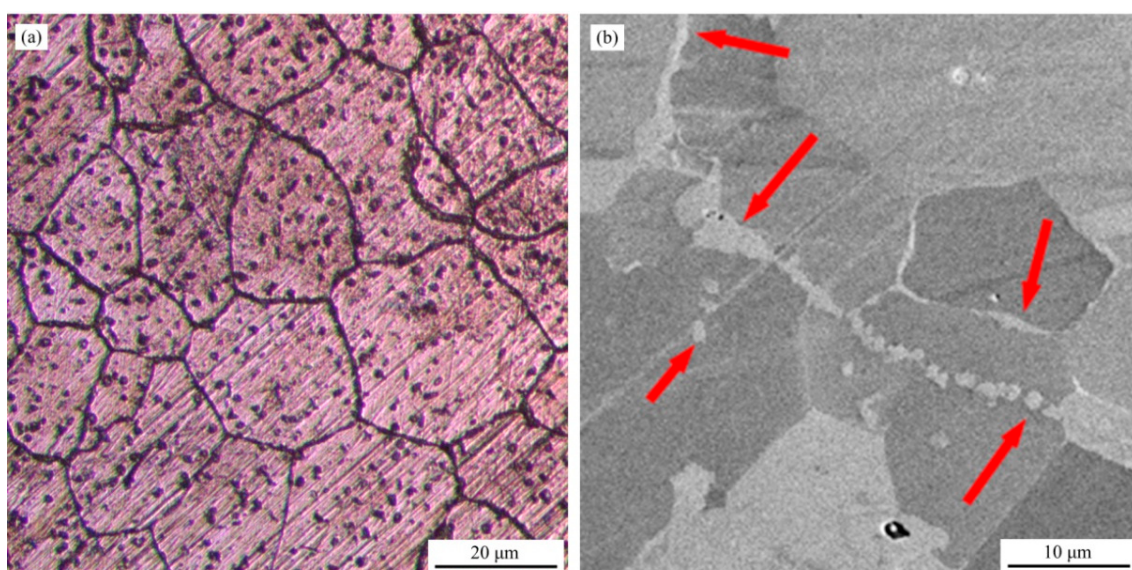


Figure 2. Microstructure of the forged $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA at 1200 °C. (a) Optical micrograph showing a general view of the microstructure, and (b) SEM image, in which can be distinguished small secondary phases, particles (labeled by red arrows) along the grain boundaries of BCC grains.

The equiaxed grain microstructure presents an average grain size of 26 μm with a standard deviation of 3 μm , as obtained by ImageJ software (NIH–LOCI, WI, USA) (see Figure 1).

The hardness and the density values were measured as part of the HEA study, obtaining 660 HV and 6.84 g/cm^3 , respectively [21].

3.2. High-Energy X-ray Diffraction (HEXRD)

According to the HEXRD pattern obtained for the $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA, the more intense peaks correspond to the BCC matrix while the minor peaks are due to β -Mn particles (see Figure 3). The microstructure of the as-cast ingot evolved after homogenization heat treatment at 1200 $^\circ\text{C}$ for 1 h and subsequent quenching in such a way that only the BCC peaks of the matrix are found on the HEXRD pattern shown in Figure 3. This means that at 1200 $^\circ\text{C}$, the HEA moves in the BCC single phase region. The applied quenching permitted to stabilize this single BCC structure at room temperature, preventing the formation of secondary phases.

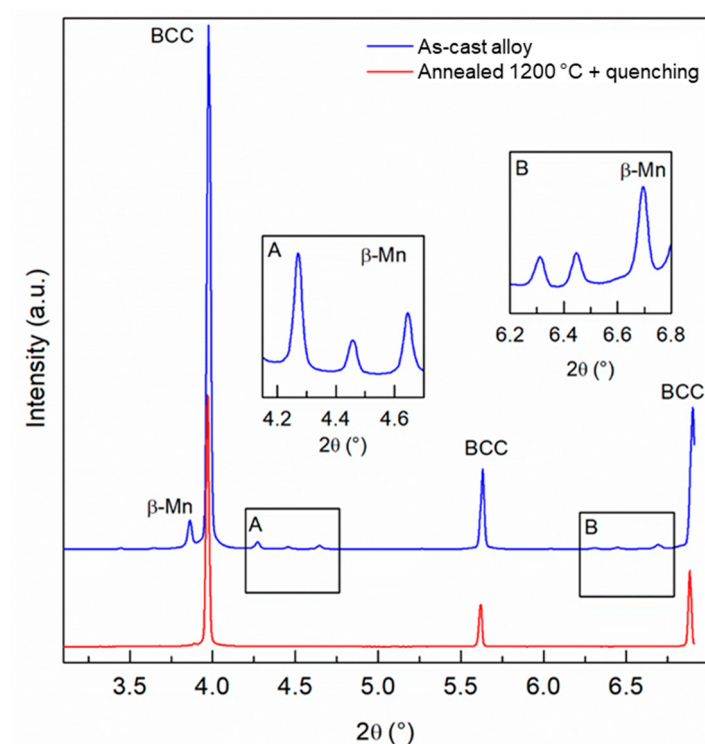


Figure 3. HEXRD patterns for the as-cast and annealed $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA at 1200 $^\circ\text{C}$, and subsequently quenched in water.

3.3. Cyclic Potentiodynamic Polarization (CPP)

Electrochemical analysis of the $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA samples was conducted to reveal the electrochemical corrosion reaction mechanisms at room temperature (RT, 25 $^\circ\text{C}$) and under different pH aqueous electrolyte solutions: acidic 0.5 M H_2SO_4 (pH 0.3), neutral 0.6 M NaCl (pH 7), and alkaline 2.5 M NaOH (pH 14).

In order to study the electrochemical reaction kinetics of the $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA in each of the environments, CPP tests were performed after a steady-state OCP value was reached (see Figure 4). Tafel fitting was performed using the Gamry software, selecting ± 50 mV from the E_{corr} . In the alkaline environment, 2.5 M NaOH (pH 14), the recorded E_{corr} was -331 mV_{SCE}, which shows to be more active than for the other electrolyte solutions tested (see Table 3). However, an active i_{corr} of 16.12 $\mu\text{A}/\text{cm}^2$ was found, which indicates dissolution as the current density is above the 1 $\mu\text{A}/\text{cm}^2$. While during the anodic polarization the current kept increasing, after reaching the upper potential limit, the HEA

sample experienced a negative hysteresis and a more positive mixed potential than the E_{corr} , indicating that no pit was formed. In the neutral 0.6 M NaCl (pH 7) [22], the HEA had a nobler E_{corr} value of $-198 \text{ mV}_{\text{SCE}}$, with a lower i_{corr} of $4.10 \times 10^{-7} \text{ A/cm}^2$, which is three orders of magnitude less than the i_{corr} value registered for the high alkaline pH 14. The stable BCC phase matrix, providing a stable and protective passive film, made for the enhanced passivity compared to the alkaline environment. Similarly, to the 2.5 M NaOH, the 0.6 M NaCl did not promote any pitting to the HEA sample, developing a negative hysteresis and obtaining an even nobler mixed potential in the backward scan than the E_{corr} . Finally, the sample exposed to 0.5 M H_2SO_4 showed the best corrosion performance of all three electrolyte solutions, presenting the lowest i_{corr} of $1.36 \times 10^{-8} \text{ A/cm}^2$. The acidic environment helped the HEA to form a stable passive film, similar to the passivation treatment applied in industry for stainless steels [23,24]. The 0.5 M H_2SO_4 presented a negative hysteresis (same as all three solutions); however, the ennoblement was not as pronounced as the 0.6 M NaCl. From all three environments, the pH 14 was the most damaging due to the reactivity of Al forming hydroxides. Even though the elemental percentage of the aluminum was kept below 4.62 wt.%, high dissolution reaction kinetics in alkaline environment was found. That is the reason for the deterioration of the corrosion protection properties of $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA as the pH increases.

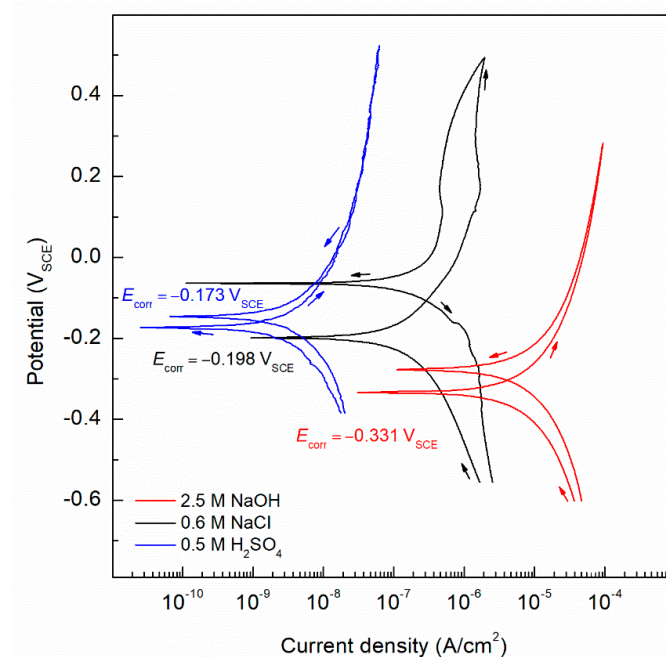


Figure 4. CPP curves for $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA in acidic 0.5 M H_2SO_4 (pH 0.3), neutral 0.6 M NaCl (pH 7), and alkaline 2.5 M NaOH (pH 14) electrolyte solutions.

Table 3. Electrochemical parameters from the CPP curves for $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA in acidic 0.5 M H_2SO_4 (pH 0.3), neutral 0.6 M NaCl (pH 7), and alkaline 2.5 M NaOH (pH 14) electrolyte solutions.

Electrolyte Solution	E_{corr} mV_{SCE}	i_{corr} A/cm^2	β_a mV/dec	β_c mV/dec	B mV	α_a	α_c
2.5 M NaOH	−331	1.61×10^{-5}	592	−601	129	0.165	0.121
0.6 M NaCl	−198	4.10×10^{-7}	549	−573	121	0.047	0.045
0.5 M H_2SO_4	−173	1.36×10^{-8}	719	−820	161	0.036	0.031

A standard deviation below 10% for all values was obtained.

3.4. Electrochemical Impedance Spectroscopy (EIS)

To further analyze the electrochemical corrosion mechanisms of the $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA in the different environments, an EIS study was conducted for all three different pH electrolyte solutions at RT and at the OCP (see Figure 5). The Nyquist plots present a depressed semicircle at intermediate frequencies, which can be attributed to the rough and porous passive oxide film surface, where a nonuniform distribution of the alternating current (AC) takes place on the electrode (Figure 5a). The passive film is a porous film with imperfections and inhomogeneities, thus introducing the concept of a nonideal capacitor. This can be modeled using a constant phase element (CPE), the CPE accounts for the nonideal capacitance response of an active electrode, and its impedance is described by $Z_{\text{CPE}} = (Y)^{-1} (j\omega)^{-n}$, where Y is the admittance ($\text{S cm}^{-2} \text{s}^n$), ω is the angular frequency (rad s^{-1}), j is the imaginary number, and n is a dimensionless variable that represents the nonideality of the CPE. The values of n range from 1, which would make the CPE an ideal capacitor, to 0, which will represent an ideal resistor.

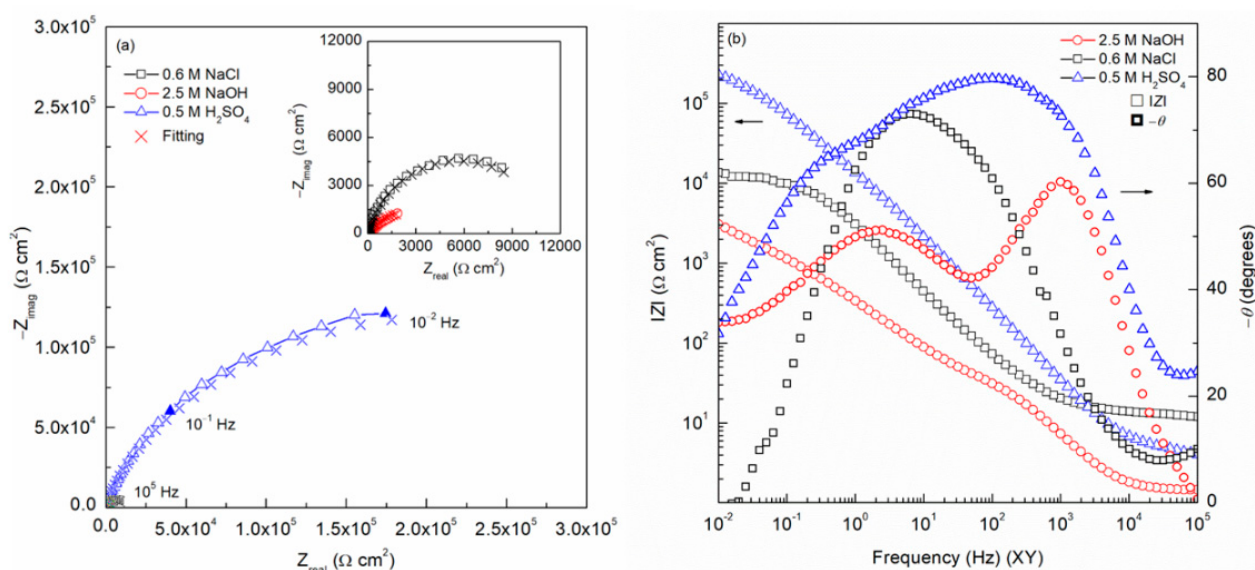


Figure 5. EIS plots for $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA in acidic 0.5 M H_2SO_4 (pH 0.3), neutral 0.6 M NaCl (pH 7), and alkaline 2.5 M NaOH (pH 14) electrolyte solutions: (a) Nyquist plots, and (b) Bode plots.

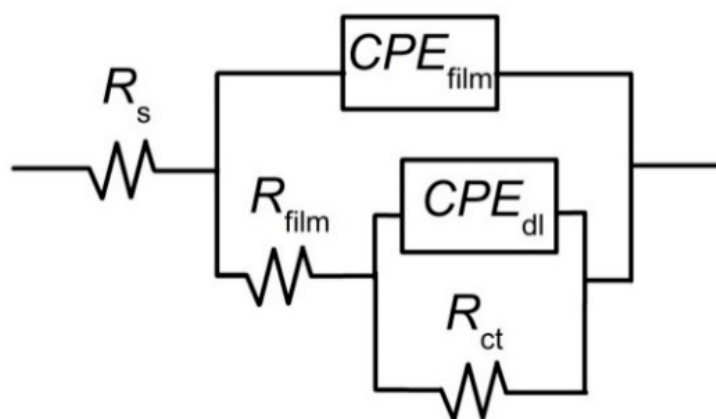
The shape of the Bode plots (Figure 5b) show a capacitor behavior at intermediate frequencies, indicated by the phase angle values between 60 and 80 degrees, while resistor behavior is seen at high frequencies with theta angles (θ) close to 0 degrees [18]. The plateau at high frequencies corresponds to the electrolyte resistance. The difference in the modulus of impedance ($|Z|$), found at low frequencies values (10^{-2} Hz), is used to compare the overall corrosion performance between solutions. Comparing the $|Z|$, the highest impedance value of $10^5 \Omega \text{ cm}^2$ was obtained for the 0.5 M H_2SO_4 solution, followed by the 0.6 M NaCl, and ending with the high alkaline 2.5 M NaOH (pH 14), showing a decreased impedance value of two orders of magnitude down to $10^3 \Omega \text{ cm}^2$. This trend clearly aligns with the CPP trend previously seen.

Table 4 presents the electrochemical results found in the literature for several HEAs to evaluate the corrosion behavior as a function of the testing electrolyte solution [16,25–28].

Table 4. Corrosion properties comparison between different HEAs.

HEA	Electrolyte Solution	E_{corr} (mV _{SCE})	i_{corr} (A/cm ²)	$ Z $ (Ω cm ²)	Ref.
Al ₁₀ Cr ₃₀ Fe ₂₅ Mn ₃₀ Ti ₅	2.5 M NaOH	−331	1.61×10^{-5}	3.21×10^3	This work
	0.6 M NaCl	−198	4.10×10^{-7}	1.26×10^4	
	0.5 M H ₂ SO ₄	−173	1.36×10^{-8}	2.25×10^5	
Cr ₁₈ Mn ₁₈ Fe ₂₁ Co ₂₁ Ni ₂₂	0.05 M H ₂ SO ₄	−320	8.0×10^{-6}	1.25×10^5	[25]
Cr _{19.6} Ni _{20.2} Co _{21.3} Mn _{20.5} Fe _{18.4}	0.4 M Na ₂ CO ₃ 1 M NaHCO ₃	−250	3.0×10^{-6}	1.0×10^5	[26]
CoCrFeNi Cu 5 wt.% + AlCoCrFeNi	0.6 M NaCl	−130	2.11×10^{-6}	1.2×10^4	[16]
		−197	12.97×10^{-6}	1.7×10^3	
FeCrSiNb thin film	0.6 M NaCl	+60	8.66×10^{-10}	–	[27]
	0.6 M H ₂ SO ₄	+360	1.22×10^{-8}	–	
Co ₂₁ Cr ₁₉ Fe ₂₀ Mn ₁₉ Ni ₂₀	0.5 M H ₂ SO ₄	−366	57.9×10^{-6}	1.0×10^3	[28]

To fit the EIS experimental data, a hierarchical ladder distributed electrical equivalent circuit (EEC) with two time-constants was used. The two time-constant EECs proposed are also shown by the two changes in slope in the θ phase angle, indicating two relaxation processes (see Figure 6). The high- and low-frequency processes represent the response of the passive film and the electrochemical double-layer, respectively. The passive film (at intermediate frequencies) is indicated by the distributed constant phase element (CPE_{film}) in parallel with the resistance of the film (R_{film}) ($CPE_{\text{film}} // R_{\text{film}}$), while the electrochemical double-layer (at low frequencies) is represented by a capacitance (CPE_{dl}) in parallel with the charge transfer resistance (R_{ct}) ($CPE_{\text{dl}} // R_{\text{ct}}$) [29–31]. The value and order of magnitude of the R_{ct} will indicate the corrosion resistance against the aggressive environment, providing information on susceptibility to localized depassivation and pit incubation [32]. The solution resistance (R_s) is connected in series, indicating the ohmic drop related to the ionic conductivity of the electrolyte.

**Figure 6.** EEC with two time constants proposed to model the EIS response of the Al₁₀Cr₃₀Fe₂₅Mn₃₀Ti₅ HEA.

After the fitting of the EIS experimental data with the proposed EEC, the following fitting parameters were gathered in Table 5.

Table 5. Fitting EIS parameters for Al₁₀Cr₃₀Fe₂₅Mn₃₀Ti₅ HEA exposed to different pH electrolyte solutions at RT.

Electrolyte Solution	R_s $\Omega \text{ cm}^2$	R_{film} $\text{k}\Omega \text{ cm}^2$	Y_{film} $\mu\text{S}/\text{cm}^2 \text{ s}^{n_{\text{film}}}$	n_{film}	R_{ct} $\text{k}\Omega \text{ cm}^2$	Y_{dl} $\mu\text{S}/\text{cm}^2 \text{ s}^{n_{\text{dl}}}$	n_{dl}	$C_{\text{eff, film}}$ F/cm^2	χ^2 (*)
2.5 M NaOH	3.91	0.52	3.65	0.82	5.35	987.62	0.79	8.36×10^{-5}	2.69×10^{-3}
0.6 M NaCl	13.44	1.53	3.29	0.85	11.39	35.01	0.81	6.56×10^{-5}	1.91×10^{-3}
0.5 M H ₂ SO ₄	2.48	2.45	1.12	0.93	494.28	9.28	0.74	1.54×10^{-5}	1.45×10^{-3}

* Error < 10% for all values.

4. Discussion

4.1. Microstructure and Hardness Analysis

The hardness of the Al₁₀Cr₃₀Fe₂₅Mn₃₀Ti₅ HEA was obtained as 660 HV, which, compared to the other BCC HEAs listed in Table 6, is around the average, leaving aside some exceptions such as the 3000 HV of the Co₂₁Cr₁₉Fe₂₀Mn₁₉Ni₂₀ [17] (for further comparisons between HEA see data base [33]). Although the BCC materials have a higher number of slip systems than the FCC, the slip planes in the BCC systems are not as closely packed as in the FCC, and therefore the BCC materials present a lower deformation ability and higher hardness than the FCC materials. Furthermore, the elemental composition, the manufacturing process, and the thermal treatment also influenced the final hardness. Thus, the hardness of this Al₁₀Cr₃₀Fe₂₅Mn₃₀Ti₅ HEA in the as-cast condition is 730 HV, decreasing up to 490 HV after the homogenization heat treatment at 1200 °C due to dissolution of the β -Mn phase. Then, after the forging process and the air quenching treatment, the hardness of the Al₁₀Cr₃₀Fe₂₅Mn₃₀Ti₅ HEA increases again due to the generation of a high dislocation density, as well as the precipitation of a low-volume fraction of β -Mn phase, as can be seen in Figure 3b.

Table 6. Hardness and density properties comparison between HEAs.

HEA	Hardness (HV)	Density (g/cm ³)	Ref.
Al ₁₀ Cr ₃₀ Fe ₂₅ Mn ₃₀ Ti ₅	660	6.84	This work
CoCrFeNi	676	—	[34]
FeNiCoCrMo	1000	8.86	[35]
CoCrFeNi	225	8.34	[16]
Cu 5 wt. %	400	7.21	
AlCoCrFeNi			
FeCrSiNb thin film	1530	—	[27]
CoCrFeMnNiC _{0.6}	566.4	—	[36]
Co ₂₁ Cr ₁₉ Fe ₂₀ Mn ₁₉ Ni ₂₀	3000	—	[28]
Al ₂₀ Fe ₂₀ Mg ₂₀ Ni ₂₀ Ti ₂₀	94.5	4.64	[37]

Finally, it is worth mentioning that the density of the new designed Al₁₀Cr₃₀Fe₂₅Mn₃₀Ti₅ HEA was 6.84 g/cm³, which was below most of the other HEAs except the Al₂₀Fe₂₀Mg₂₀Ni₂₀Ti₂₀ due to the higher amount of Al and Ti compared to the one studied in this work, making for an HEA of only 4.64 g/cm³. This new designed Al₁₀Cr₃₀Fe₂₅Mn₃₀Ti₅ HEA had the highest hardness-to-density ratio as compared to the other HEAs, which confers suitable application for lightweight materials exposed to strong mechanical stimulus and extreme environments.

4.2. Crystallographic HEXRD Analysis

By means of the peak integration method, the quantification of the BCC phase and the β -Mn phase present in the $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA was 94.76 and 5.24%, respectively, showing that most of the phase volume belongs to the BCC phase (see Equation (1)).

$$\text{Vol.\% Phase} = \frac{\sum_i^{\text{peak}} \int_{2\theta_i}^{2\theta_f} \text{Phase}}{\sum_i^{\text{phase}} \left(\sum_i^{\text{peak}} \int_{2\theta_i}^{2\theta_f} \text{Phase} \right)} \quad (1)$$

4.3. Cyclic Potentiodynamic Polarization (CPP)

The CPP plots were performed to understand the electrochemical kinetics of the $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA, and analyzed to obtain the anodic (β_a) and cathodic (β_c) Tafel slopes and the Stern–Geary constant (B), as well as the electrochemical transfer coefficients of the anodic (α_a) and cathodic (α_c) electrode reaction kinetics (see Equations (2)–(4)) [38]:

$$B = \frac{\beta_a \beta_c}{2.303 (\beta_a + \beta_c)} \quad (2)$$

$$\alpha_a = \frac{RT}{nF} \frac{1}{\beta_a} \quad (3)$$

$$\alpha_c = \frac{RT}{nF} \frac{1}{\beta_c} \quad (4)$$

where R is the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the temperature in K (at RT), n is the number of electrons, and F is the Faraday constant ($96,485 \text{ C mol}^{-1}$).

The β_a and β_c for both 2.5 M NaOH and 0.6 M NaCl electrolyte solutions are around 600 mV/dec, while the 0.5 M H_2SO_4 increases its value up to the 700–800 mV/dec, indicating lower dissolution kinetics and therefore better corrosion performance. Both equations, the Tafel slope, and the electrochemical transfer coefficients are inversely related, meaning that higher Tafel slopes exhibit low electrochemical activity and vice versa [39]. Similarly, as was seen on the E_{corr} and i_{corr} , as the pH decreased, both α_a and α_c decreased as well, confirming the better performance of the $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA in the acid medium.

Comparing the electrochemical corrosion properties of the new designed $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA to other HEA with similar compositions found in the literature, the corrosion protection of the new designed $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA is superior in all environments, regardless of the pH. The only HEA which behaves better in alkaline environment is the $\text{Cr}_{19.6}\text{Ni}_{20.2}\text{Co}_{21.3}\text{Mn}_{20.5}\text{Fe}_{18.4}$, which is Al-free, thus explaining the nobler E_{corr} and lower dissolution kinetics as found on the lower value of i_{corr} and higher modulus of the impedance $|Z|$, thus conferring superior corrosion protection properties. Nevertheless, in acidic and neutral environments contaminated with chlorides, the i_{corr} is lower than most HEAs, and also large modulus of impedance $|Z|$ values are found at 10^{-5} – 10^{-8} A/cm^2 and $10^5 \text{ } \Omega \text{ cm}^2$, respectively.

4.4. Electrochemical Impedance Spectroscopy (EIS)

The EIS fitting data of the $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA revealed a similar corrosion behavior trend as the one seen in the CPP, where the most damaging environment was the alkaline (2.5 M NaOH). The time constant for the film ($R_{\text{film}}/CPE_{\text{film}}$) had the lowest R_{film} value of $0.52 \text{ k}\Omega \text{ cm}^2$ and the highest Y_{film} $3.65 \text{ } \mu\text{S cm}^{-2} \text{ s}^{n_{\text{film}}}$, with a n_{film} value of 0.82. Similarly, a low R_{ct} value of $5.35 \text{ k}\Omega \text{ cm}^2$ was found. Such a low R_{ct} value indicates the low resistance for the electron transfer, thus indicative of the higher susceptibility to the environment. Then, 0.6 M NaCl showed a considerable increase on the corrosion properties, increasing its R_{film} , decreasing its Y_{film} , and increasing the n_{film} , with $1.53 \text{ k}\Omega \text{ cm}^2$, $3.29 \text{ } \mu\text{S cm}^{-2} \text{ s}^{n_{\text{film}}}$, and 0.85, respectively. Finally, the most acidic environment (0.5 M H_2SO_4) displayed the highest R_{film} value as well as the lowest Y_{film} [40]. Comparing the R_{ct} values between the different samples, which are inversely related with the corrosion

rate, a decreased R_{ct} value as the pH increased can be seen, showing the lower R_{ct} value of $5.35 \text{ k}\Omega \text{ cm}^2$ at the alkaline pH (see Table 5). The charge transfer resistance value of the sample exposed to $0.5 \text{ M H}_2\text{SO}_4$ ($R_{ct} = 494.28 \text{ k}\Omega \text{ cm}^2$) indicates that sulfuric acid promotes the formation of a protective passive oxide film on the $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA, as it is also found on the higher R_{film} value of $2.45 \text{ k}\Omega \text{ cm}^2$, in addition to a low CPE_{film} value of $1.54 \times 10^{-5} \text{ F/cm}^2$. The time constant attributed to the electrochemical double layer (CPE_{dl}/R_{ct}) shows the ease for the electron transfer, and thus the rate for the electrochemical corrosion reaction, which indicates the kinetics of the anodic dissolution of the passive film. The aluminum reaction at higher $[\text{OH}^-]$ leads to the formation of $\text{Al}(\text{OH})_3$, which is the responsible for the faster anodic dissolution kinetics of $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA at the alkaline pH.

While an ideal capacitor (non-defective interface) allows to measure directly the capacitance, the CPE elements which represent a defective interface need to be modeled with a branched ladder hierarchically distributed RC network [41,42]. To calculate the effective capacitance of the CPE , the resistance is also considered. In the case of the effective capacitance of the passive film ($C_{eff, film}$), the equation from Mansfeld et al. considers the Y_{film} , n_{film} , and the frequency (ω_m'') value where the imaginary impedance has a maximum to correct the CPE (see Equation (5)) [43]:

$$C_{eff, film} = Y_{film} (\omega_m'')^{n_{film}-1} \quad (5)$$

As can be seen from Table 5, the values of the $C_{eff, film}$ were calculated, giving the highest value for the 2.5 M NaOH with $8.36 \times 10^{-5} \text{ F cm}^{-2}$, followed by the 0.6 M NaCl with $6.56 \times 10^{-5} \text{ F cm}^{-2}$, and $0.5 \text{ M H}_2\text{SO}_4$ with $1.54 \times 10^{-6} \text{ F cm}^{-2}$. The higher the capacitance, the lower the corrosion protection, as indicated by the lower impedance values as well as the higher current densities seen in the CPP. The effective capacitance value of the passive oxide film, $C_{eff, film}$, which is inversely proportional to the passive film thickness (see Equation (6)), indicates a more protective passive film in $0.5 \text{ M H}_2\text{SO}_4$. The lowest $C_{eff, film}$ value is attributed to the more protective passive film and the highest value to the most defective and doped passive oxide film. The doping process of the passive film is related to higher interstitial vacancies, which may be attributed to the detrimental effect of the OH^- in the 2.5 M NaOH electrolyte solution. The passive film time constant also includes the higher R_{film} value of $2.45 \text{ k}\Omega \text{ cm}^2$. In addition, the tested electrode in $0.5 \text{ M H}_2\text{SO}_4$ electrolyte revealed the higher R_{ct} value of $494.28 \text{ k}\Omega \text{ cm}^2$, which is in good agreement with the i_{corr} values trend seen in the CPP.

With the $C_{eff, film}$ values, the estimated thickness (d_{film}) is also added using the inverse relationship seen in Equation (6):

$$C_{eff, film} = \frac{\epsilon_0 \epsilon_{film} A}{d_{film}} \quad (6)$$

where ϵ_0 is the dielectric constant of the permittivity of the vacuum (8.84×10^{-14}), ϵ_{film} is the dielectric constant of the passive oxide film (considered as 12 for HEA [44,45]), and A is the exposed surface area [46,47]. The obtained d_{film} of the passive film is 1.27, 1.62, and 6.89 nm for HEA samples exposed to 2.5 M NaOH , 0.6 M NaCl , and $0.5 \text{ M H}_2\text{SO}_4$, respectively. These d_{film} values are in the same order of magnitude of the other HEA passive films found in the literature [45]. In addition, it coincides with the other electrochemical results, where the worst corrosion behavior was for 2.5 M NaOH and the best performance was for $0.5 \text{ M H}_2\text{SO}_4$. The reason for the bad corrosion behavior of the presented HEA in the high alkaline environment is the Al content, as previously stated by several authors [3]. The addition of Al content enhances the growth of the BCC phase increasing the elemental segregation degree, besides promoting a less stable passive film compared to Cr oxides [6].

Moreover, it is well known that the Al does not provide corrosion protection in alkaline environments due to the metal dissolution by the hydroxides, which follows the electrochemical reaction $\text{Al} \rightarrow \text{Al}(\text{OH})_3 \rightarrow \text{Al}(\text{OH})_4^-$ [48]. Where the corrosion rate

depends on the OH^- concentration based on $\text{Al} + 3 \text{H}_2\text{O} + \text{OH}^- \rightarrow 3/2 \text{H}_2 + \text{Al}(\text{OH})_4^-$, a higher alkaline pH would thus lead to higher corrosion rates [49]. Even with the short exposure times, the differences in the electrochemical response of the passive oxide film can be seen from both the EIS data as well as by the analysis of the CPP. The one-hour exposure is enough to develop a passive oxide film in the HEA, as previously seen in the literature [18].

4.5. X-ray Photoelectron Spectroscopy (XPS)

The $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA samples were analyzed by XPS to study the different oxide products and correlate with the electrochemical dissolution mechanism. The XPS surface analysis of the HEA samples exposed to the three different electrolyte solutions included a depth profile analysis, which can be seen in Figures 7–9. The initial XPS surface analysis of the $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA in the alkaline environment (2.5 M NaOH) showed a high carbon content due to atmospheric contamination, followed by oxygen (see Figure 7a). After sputtering down to 2 nm, the carbon content decreased in values between 15 and 10 at.% for the following depth profile analyses performed; in addition, the oxygen showed its highest content value of 35 at.%, and thereafter decreased as the depth increased. During the first 10 nm, the passive film is mainly composed out of chromium and iron oxides formation, including Cr_2O_3 , Fe_2O_3 , and the spinel FeCr_2O_4 . The Al and Mn content increased after the first 10 nm, the point where Cr and Fe contents are plateauing (see Figure 7b).

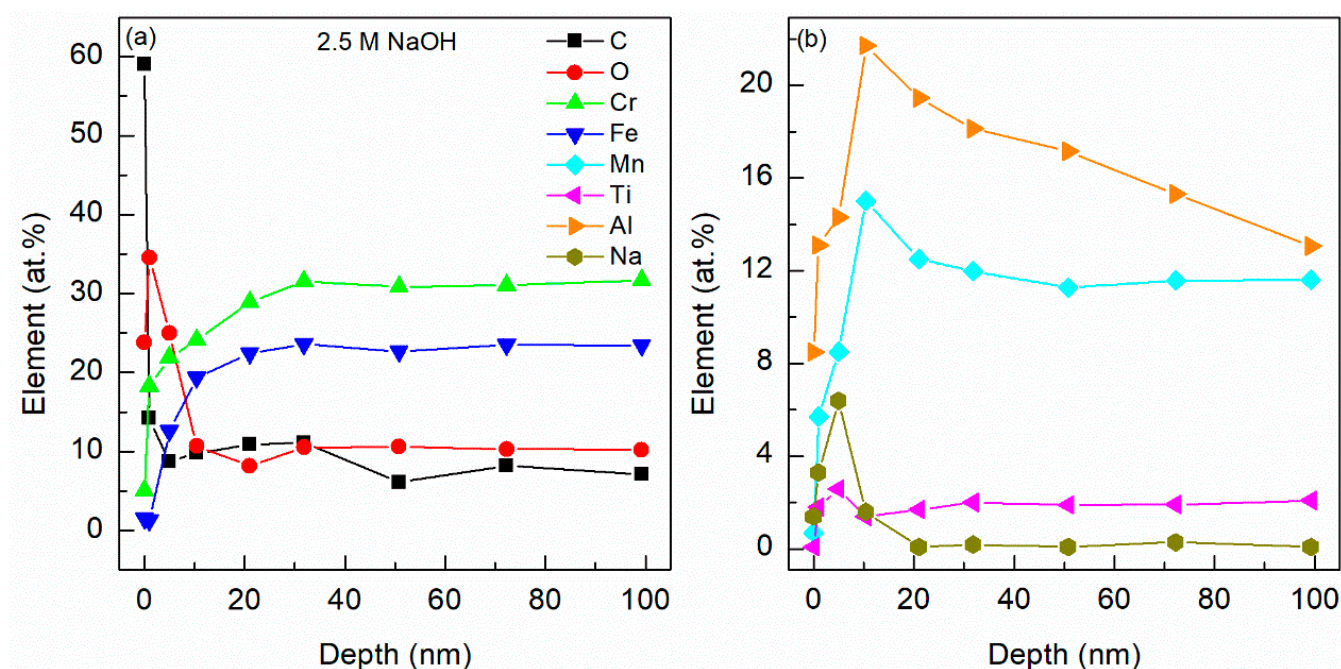


Figure 7. XPS showing depth profiles and elemental analysis (at.%) for $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA in 2.5 M NaOH: (a) C, O, Cr, Fe, and (b) Mn, Ti, Al, and Cl.

Thus, after the formation of the chromium and iron oxides in the outermost layer, the Al and Mn oxides are formed in the inner layer close to the metal surface. This inner layer is less dense, as the oxygen concentration decreases after the first 10 nm; hence, the main components of the passive film are the Cr_2O_3 , Fe_2O_3 , and FeCr_2O_4 . The passive film thickness of $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ in the alkaline environment had a thickness of 10 nm, and it was rich in Cr, Fe, and some Al; however, the protectiveness came from the Cr and Fe oxides, as the Al present was as hydroxides ($\text{Al}(\text{OH})_3$), which then reacted with the high alkaline environment to dissolve into $\text{Al}(\text{OH})_4^-$. As discussed, the Al content enhanced the corrosion susceptibility in this environment due to the high OH^- concentration [49].

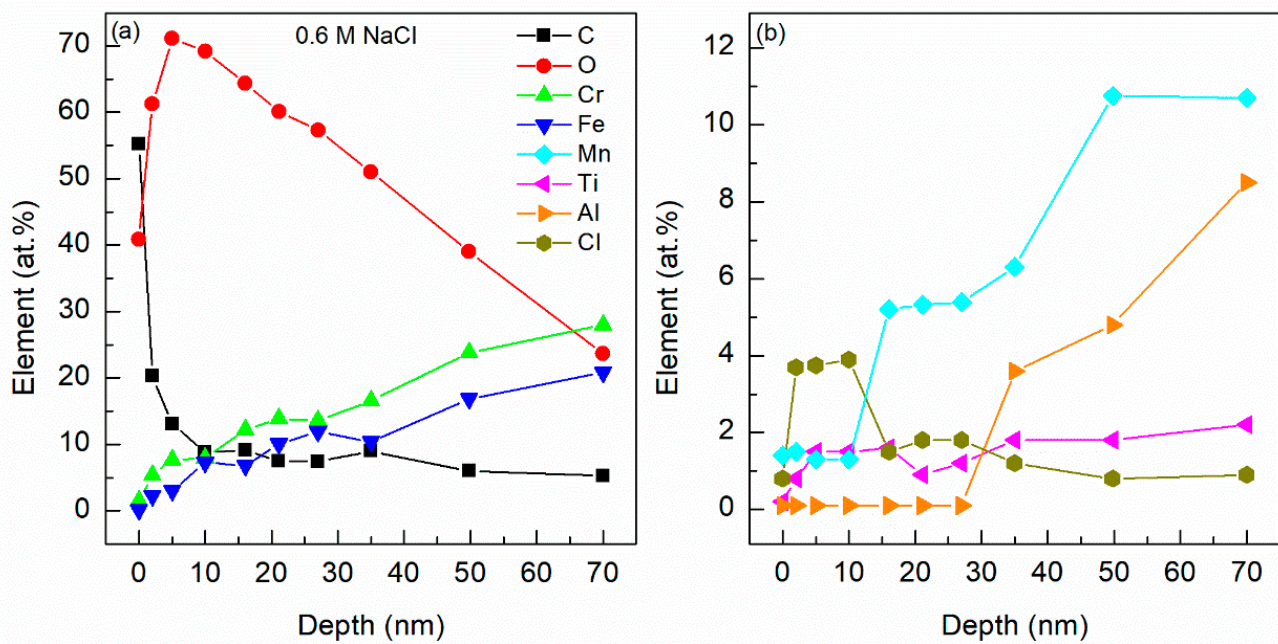


Figure 8. XPS showing depth profiles and elemental analysis (at.%) for Al₁₀Cr₃₀Fe₂₅Mn₃₀Ti₅ HEA in 0.6 M NaCl: (a) C, O, Cr, Fe, and (b) Mn, Ti, Al, and Cl.

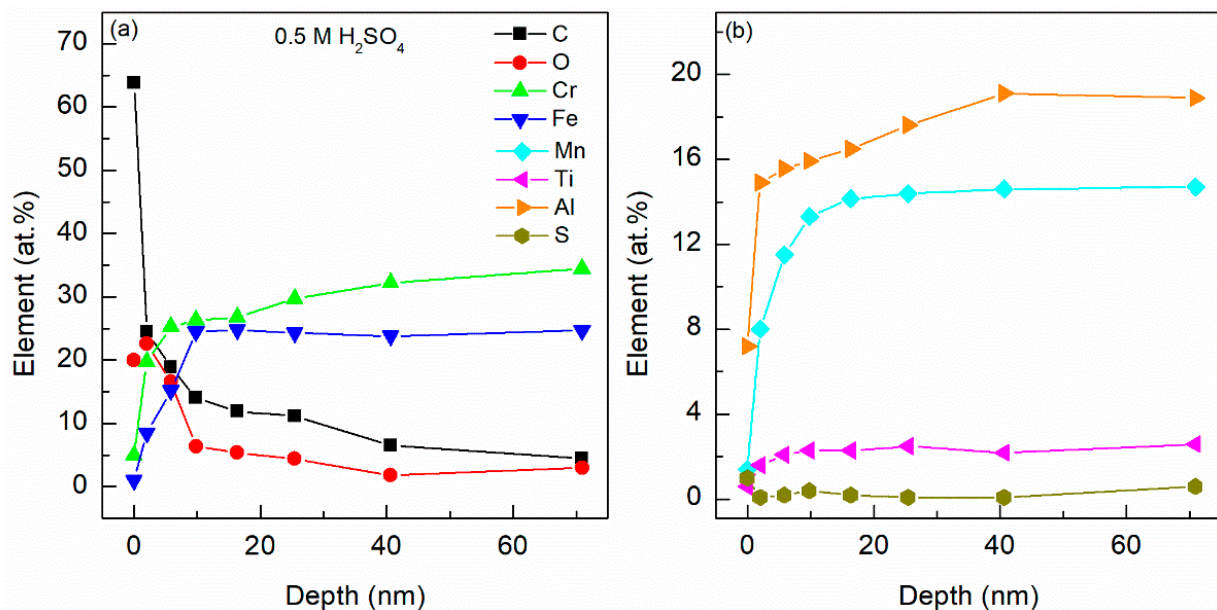


Figure 9. XPS showing depth profiles and elemental analysis (at.%) for Al₁₀Cr₃₀Fe₂₅Mn₃₀Ti₅ HEA in 0.5 M H₂SO₄: (a) C, O, Cr, Fe, and (b) Mn, Ti, Al, and Cl.

The XPS analysis of the Al₁₀Cr₃₀Fe₂₅Mn₃₀Ti₅ HEA in the neutral pH (0.6 M NaCl) showed a high carbon content on the surface; however, it dropped drastically within the first 5 nm (see Figure 8). After the 5 nm depth, a maximum oxygen concentration was found to be 71.1 at.%, which decreased linearly down to 23.7 at.% after 70 nm depth. The two main alloying elements, Cr and Fe, gradually increased with depth, being below 15 at.% for depths below 25 nm. Nevertheless, as the depth increases, both metal concentrations increase, being that of Cr above that of Fe. While the tendency for the passive films is to form the Fe oxides on the outer layer and the Cr oxides underneath, the elemental composition of the Al₁₀Cr₃₀Fe₂₅Mn₃₀Ti HEA has a higher Cr content than Fe, 34.48 and 28.94 at.%, respectively, making the Cr to react even faster and produce Cr oxides on the

outer layers (see Figure 8a) [50]. The Mn oxides do not play a significant role until reaching the 10 nm depth, where the Mn concentration is raised from 1.3 to 5.2 at.%, stabilizing around 30 nm, with another step found up to 11.7 at.% at 50 nm (see Figure 8b). The Al oxides were detected after 30 nm depth, increasing linearly thereafter as the depth increases. The Ti content keeps constant throughout the entire 70 nm range around 1.5 at.%. Finally, the Cl influenced the first 10 nm, as its concentration remained similar to that in the testing solution, around 3.8 at.%, after that the concentration dropped around 1 at.%. Even more, in this 70 nm passive film, it can be seen that the oxides composition also changes, reacting on the outermost surface the Cr and Fe oxides, and further inside, the Mn and Al oxides start getting some relevance after 30 nm.

The XPS analysis of the $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA in the acidic solution (0.5 M H_2SO_4 , pH 0.3) exhibited the highest Cr and Fe concentrations at the surface (Figure 9a,b), with values in the 25 at.%. The acid environment enhances the formation of the passive film rich in Cr oxides, as well as in Cr-Fe mixed oxides, thus conferring enhanced corrosion protection properties. In this acidic environment, the passive film is not as dense as that generated in the 0.6 M NaCl solution, where the XPS analyses revealed an oxygen peak content around 25 at.%. (5 nm depth) compared to the almost 70 nm of the neutral pH environment. The Al and Mn contents play a critical role in the formation of a stable and protective passive oxide film, where an enrichment in Mn was found after the 30 nm depth. A high Al content is seen in the film composition due to the stability of Al in an acidic pH 0.3. The great amount of Cr and Fe oxides confirms the outstanding corrosion performance of the $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA in the acidic medium, showing the lowest i_{corr} and high $|Z|$ values, with 1.36×10^{-8} A/cm² and 2.30×10^5 Ω cm², respectively.

4.6. Energy Dispersive X-ray Spectroscopy (EDX)

A visual inspection of the $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA samples was first conducted, looking for pits or signs of dissolution. Both acidic and neutral pH showed no pitting, but the alkaline environment 2.5 M NaOH did show clear signs of dissolution. After inspection, the 2.5 M NaOH sample was analyzed by SEM and EDX to further study the preferential dissolution of the HEA in the alkaline environment (see Figure 10).

From the EDX mapping, the outermost surface of the $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA sample was rich in Mn, Fe, and Cr, while the inside of the pit revealed a region mainly formed out of Ti and Al.

This shows how the alkaline environment preferentially dissolves the Al forming $\text{Al}(\text{OH})_3$ to then dissolve into $\text{Al}(\text{OH})_4^-$, indicated by the lower impedance response seen in the Nyquist plots. A selective elemental analysis of the surface of the pit and surroundings showed that, inside the pit, the Al concentration increases (see Figure 11). This agrees with the higher Al content measured by XPS, where it sharply increased once the passive film was gone (approximately 10 nm).

As a summary, the studied $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA showed outstanding corrosion performance in the acidic solution (0.5 M H_2SO_4), with low i_{corr} values and high impedance values. In the neutral solution (0.6 M NaCl), while still being above the average compared to the literature, decreased its corrosion efficiency. Nevertheless, the high alkaline electrolyte solution (2.5 M NaOH) favors dissolution kinetics due to the spontaneous reaction of Al and OH^- , yielding $\text{Al}(\text{OH})_3$ and promoting passivity breakdown, which, under a high alkaline pH environment, evolves to $\text{Al}(\text{OH})_4^-$, thus dissolving the electrode surface film $\text{Al} \rightarrow \text{Al}(\text{OH})_3 \rightarrow \text{Al}(\text{OH})_4^-$ [48]. Where the corrosion rate depends on the OH^- concentration based on the electrochemical reaction of $\text{Al} + 3 \text{H}_2\text{O} + \text{OH}^- \rightarrow 3/2 \text{H}_2 + \text{Al}(\text{OH})_4^-$, therefore high-concentration alkaline solutions would lead to higher corrosion rates [49].

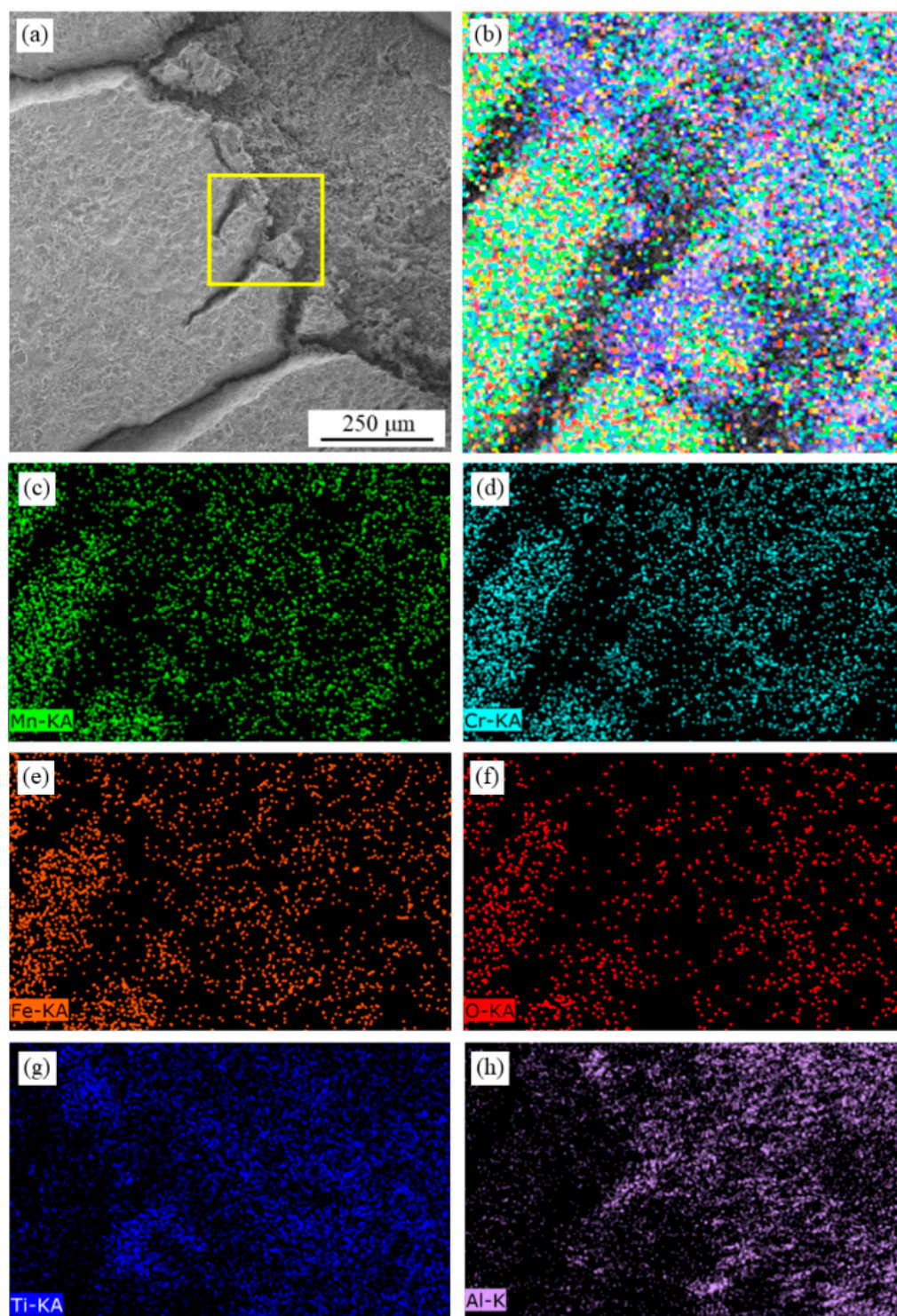


Figure 10. EDX analysis of $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA in 2.5 M NaOH after the CPP: (a) SEM micrograph $\times 120$, (b) EDX mapping, and EDX mapping of (c) Mn, (d) Cr, (e) Fe, (f) O, (g) Ti, and (h) Al.

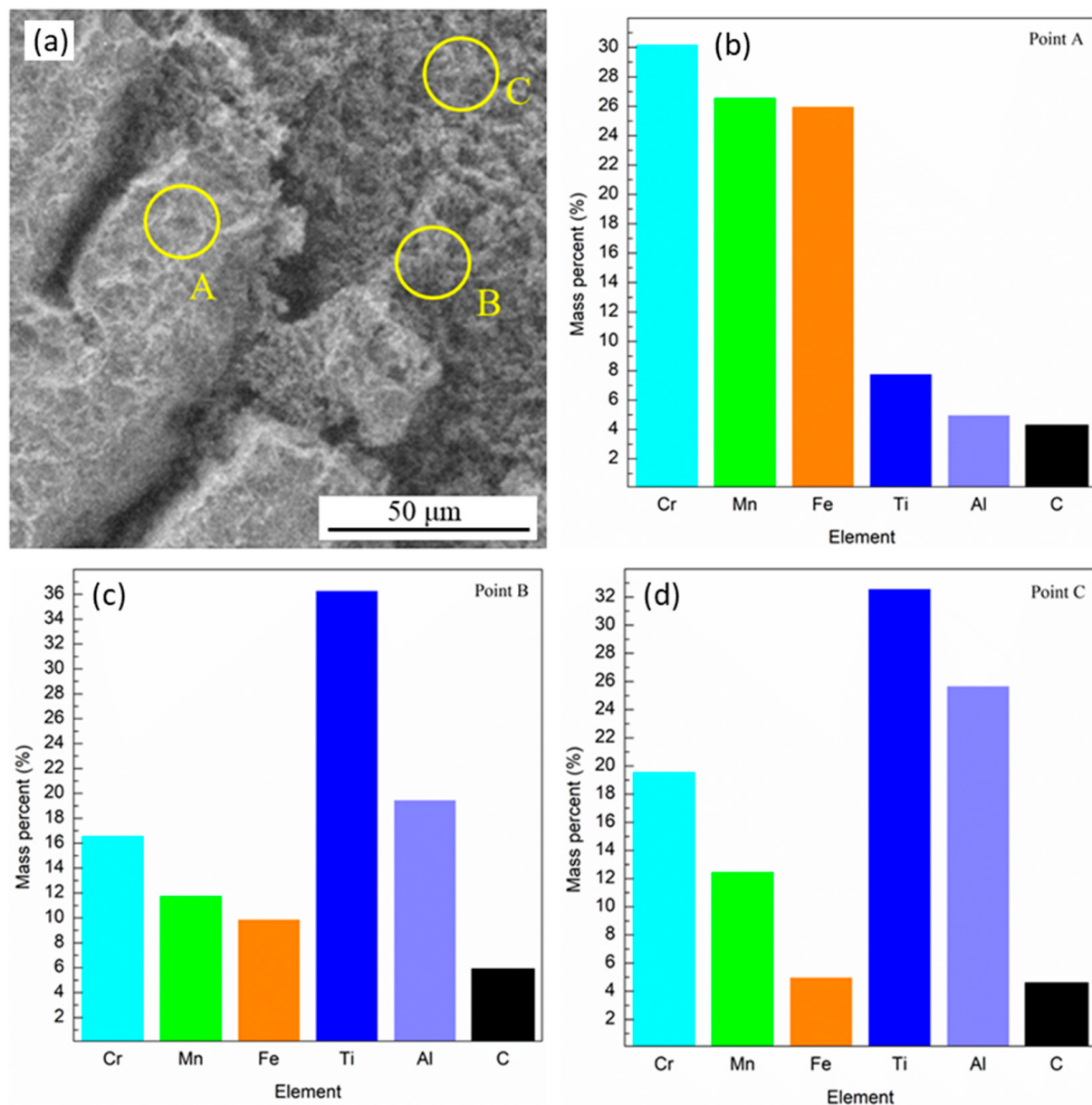


Figure 11. EDX analysis of Al₁₀Cr₃₀Fe₂₅Mn₃₀Ti₅ HEA in 2.5 M NaOH after the CPP: (a) SEM micrograph $\times 120$, and EDX elemental composition of: (b) region A, (c) region B, and (d) region C.

5. Conclusions

After studying the crystallography, microstructure, and electrochemical corrosion properties in different environments and pHs for the Al₁₀Cr₃₀Fe₂₅Mn₃₀Ti₅ HEA, the following conclusions are drawn:

The Al₁₀Cr₃₀Fe₂₅Mn₃₀Ti₅ HEA is mainly composed of a BCC crystal structure with some β -Mn, having a ratio of 94.76% and 5.24%, respectively.

The Al₁₀Cr₃₀Fe₂₅Mn₃₀Ti₅ HEA shows hardness values similar to other BCC HEAs at 660 HV, being also a light alloy compared to other HEAs, having a density of 6.84 g/cm³, thereby showing that the mechanical properties of the Al₁₀Cr₃₀Fe₂₅Mn₃₀Ti₅ HEA exceed the conventional HEAs.

The anodic kinetics are activated as the pH increases, being that the high alkaline (2.5 M NaOH) environment is the most aggressive for the Al₁₀Cr₃₀Fe₂₅Mn₃₀Ti₅ HEA. The preferential dissolution of the Al due to the high OH[−] concentration promotes the

formation of $\text{Al}(\text{OH})_3$, thus showing the highest i_{corr} and lowest E_{corr} values from all three environments.

The modulus of impedance response of the $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA is maximized in the acid and neutral pH, with a $|Z|$ in the $10^5 \Omega \text{ cm}^2$, thus indicating corrosion protection, while in alkaline environment, the impedance decreases to $10^3 \Omega \text{ cm}^2$.

By the XPS surface analysis, the formation of a stable passive film on the $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA for the neutral and acidic environments was revealed, showing high Cr and Fe contents, with d_{film} values within the range from 30 to 70 nm thickness.

The elemental composition of the $\text{Al}_{10}\text{Cr}_{30}\text{Fe}_{25}\text{Mn}_{30}\text{Ti}_5$ HEA makes it suitable for acid to neutral conditions, being able to form a stable passive film which protects it from the aggressive agents. However, the new HEA fails to withstand alkaline environments due to the Al alloying, because of the fast dissolution kinetics experienced by $\text{Al}(\text{OH})_3$.

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