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The grain size effect on corrosion property of Al₂Cr₅Cu₅Fe₅₃Ni₃₅ high-entropy alloy in marine environment

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Abstract

The influence of grain size on the localized corrosion properties of a new high-entropy alloy ($Al_2Cr_5Cu_5Fe_{53}Ni_{35}$) in seawater is investigated in the present study. After $Al_2Cr_5Cu_5Fe_{53}Ni_{35}$ alloy undergoes cold rolling and annealing, its grain size will vary accordingly, resulting in different corrosion behaviors. The microstructural evolutions after different treated conditions are characterized by XRD, SEM, EDS and EBSD, whereas the corrosion properties are measured by potentiodynamic, potentiostatic and EIS experiments. The properties of the passive layer was studied with XPS and SIMS. The Point Defect Model approach is employed to analysis the data obtained from electrochemical experiments. The results show that by decreasing the grain size, the localized corrosion resistance of the material is enhanced.

Keywords: High-entropy alloys, grain size effect, localized corrosion, Point Defect Model

1. Introduction

The concept of the well known advanced high-entropy alloys (HEAs) was proposed by Yeh et al. [1-5] and Cantor et al. [6] independently in 2004. The high-entropy alloys are more often referred to as complex-concentrated alloys (CCAs), which contain five or more elements with near-equimolar elemental fractions (between 5 and 35 atomic percent) [1]. The high configurational entropy of mixing (ΔS_{mix}^{conf}) in HEAs tends to promote the formation of single solid solution or a single matrix structure rather than complex intermetallics [7-9]. HEAs might also contain minor amount of elements to obtain specific properties [10]. Compared with conventional alloys, HEAs possess high strength, fracture toughness and improved fatigue resistance [10–15], giving the opportunity to be highly-promising candidate for several engineering applications, including corrosion resistant structures in marine environments [16]. As reported in the previous study by Xue et al. [17], a single-phased Al₂Cr₅Cu₅Fe₅₃Ni₃₅ high-entropy alloy ex-10 hibits better localized corrosion resistance compared with conventional martensitic stainless steel UNS \$40300 whose 11 average grain size is in the order of hundreds of microns ($\approx 500 \,\mu$ m). However, large grain sizes usually give rise 12 concerns regarding suitable mechanical responses as they tend to perform poorly when compared with similar alloys 13 with smaller grain dimensions (Hall-Petch effect). Hence, grain refinement may be an option to counteract this effect 14 by increasing grain boundary obstacles for dislocation movement, and thus enhancing mechanical properties to meet 15 certain specific requirements [18, 19]. One alternative method to manipulate the properties of alloys is by adjusting 16 the microstructure through cold-rolling and subsequent annealing [20, 21]. The grains would significantly elongated 17 in the rolling direction and fragmented into smaller grains after the cold-rolling process, while annealing would be 18 responsible of removing residual stresses and recrystallization under specific temperature and time exposure. For 19 instance, in magnesium alloys when the annealing time is in the range of $t \le 30$ mins, the average grain size increases 20 with increasing of the annealing time, while it began to decrease when $t \ge 40$ mins. This is because recrystallization, 21 which takes place during the first 30 mins of exposure, leads to the enhancement of the texture, while it is impaired 22

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for times greater than 40 mins [22]. The effect of grain size could play a significant role in corrosion behavior of 23 alloys and varies depending upon the type of microstructure and constituents [23]. It has been reported that the grain 24 boundary acts as a physical corrosion barrier for magnesium alloys, thus the corrosion resistance increases while there 25 are finer grains [24]. Moreover, for the aluminum alloys, majority of literature pertaining to Al suggest that as grain 26 size decreases, susceptibility to corrosion decreases as a result of the ability of fine grained materials to more readily 27 passivate [25-27]. The opposing view, that corrosion resistance decreases as grain size decreases for aluminum alloys, 28 has also been presented [28, 29]. For the ferrous alloys, improved corrosion resistance from grain refinement of Fe 29 alloys is generally attributed to improved passive film stability, which could be the result of increased rates of diffu-30 sion in fine-grained structures [30-32]. Nonetheless, other authors who previously reported increased rates of general 31 corrosion as grain size decreased attributed the behavior to a passive film destabilization [33, 34]. The grain size 32 effect on the corrosion resistance of the newly designed HEA Al₂Cr₅Cu₅Fe₅₃Ni₃₅ hasn't been determined. Therefore, 33 investigating how the grain size changes after cold-rolling and annealing, and its effect on corrosion characterstics of 34 Al₂Cr₅Cu₅Fe₅₃Ni₃₅ HEA is essentially important to understand as its comprehension would ultimately leads to the 35 development of new type of impervious alloys capable of withstand harsh conditions. 36 In the present study, the influence of cold-rolling and annealing processes on $Al_2Cr_5Cu_5Fe_{53}Ni_{35}$ HEA's microstruc-37 ture is investigated. The various microstructures after grain refinement were systematically probed by means of 38 state-of-the-art techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive 39 spectrometer (EDS), and electron-backscattered diffraction (EBSD). Moreover, the effect of the grain size on the 40 corrosion properties is also study when the material immersed in seawater through electrochemical analyses using 41 potentiodynamic-polarization, potentiostatic staircases and electrochemical impedance spectroscopy (EIS). To sim-42 ulate the marine environment, the solutions were prepared containing inorganic salts in proportions and concentra-43 tions representative of seawater [35], diluted or condensed to $0.1 \times$, $10 \times$ chloride concentration solutions respectively. 44 45 Additionally, X-ray photoelectron spectroscopy (XPS) and Secondary Ion Mass Spectrometer (SIMS) were used to

account for the properties of the passive film as well as the Point Defect Model (PDM) was employed to interpret the
 obtained electrochemical experimental data [36–38]. By revealing the grain size effect on the corrosion resistance of
 Al₂Cr₅Cu₅Fe₅₃Ni₃₅ alloy after several treated conditions, the present work is envisaged to offer additional compre hension of the corrosion properties of this high-entropy alloy system, therefore contributing to the already extensive

⁵⁰ body of results on the subject matter.

52 2. Experiments

53 2.1. Test material

The current high-entropy alloy system, Al₂Cr₅Cu₅Fe₅₃Ni₃₅, was prepared using Al, Cr, Cu, Fe and Ni elements 54 of high purity (99.99 wt.%) and was synthesized by means of induction-melting furnace. The as-cast rectangular 55 ingots were then hot rolled at 900°C for 40% thickness reduction and were solution treated at 1200°C for 2 hours in 56 Ar atmosphere followed by water quenching, whose stage was called as-received in this study. The grain refinement 57 of the as-received Al₂Cr₅Cu₅Fe₅₃Ni₃₅ alloys were cold-rolled with a thickness reduction of 50% and 85% to avoid 58 significant grain growth with subsequent annealing at short time periods. The first set of 50% thickness reduction 59 sheets were annealed at 900°C for 5min, 10min and 15min; while the second one of 85% was annealed only for 3min 60 at the same temperature. All followed by water quenching afterward. Here, the notation for the treated condition 61 of 85% thickness reduction followed by 3minutes annealing time is "3min", and for the 50% thickness reduction 62 followed by 5, 10 and 15min the notations are "5min", "10min" and "15min", respectively. The specimens for the 63 microstructural characterization with SEM were cut into rectangular cuboids of $10 \times 10 \times 3$ mm³, then wet polished 64 with SiC papers up to 1200 grit number. After that, the specimens were mechanically polished using 3 μ m, 1 μ m and 65 $0.04 \,\mu m$ diamond suspensions in sequence. The EBSD specimens were vibrationally polished by employing $0.04 \,\mu m$ 66 suspension to remove the polishing scratches after being mechanically polished up to 0.04 μ m as the SEM samples, 67 then cleaned with alcohol before dried with nitrogen. The specimens for the electrochemical tests were machined out 68 as cylinders with 3 mm radius and 43 mm height. Prior to each electrochemical experiment, the exposed sample areas 69 (0.6 cm²) were wet grounded with SiC papers up to 1200 grit number, ultrasonic vibrated to clean the surface and then 70 dried. Moreover, to study the passive film formation on the surface, the polished cubic XPS sample was immersed in 71 artificial seawater solution at room temperature $(20 \pm 2^{\circ}C)$ for 24 hours. 72

73 2.2. Microstructure characterization

The X-ray diffraction (XRD) was used to probe the crystal structure of the proposed alloy (Bruker D8 Discover 74 at Materials Development and Characterization Center (MDC2) of Texas A&M University) in which a sample is 75 secured by a holder along with a goniometer enclosed in a radiation safety chamber. The sample is aligned by using 76 a laser source equipped with a video camera. The X-ray source is a 3 kW Cu X-ray tube that works at an operating 77 current of 40 kV and 40 mA whose wavelength is 1.54060 Å. The diffraction angle, 20, is defined between the 78 incident beam and the detector. The incident angle ω is equivalent to 1/2 of the diffraction angle 2 θ . The 250 mm 79 diameter $\theta - 2\theta$ goniometer is a computer controlled electronic device with independent stepper motors and optical encoders for the θ circle with the angular step size of 0.005°. Scanning electron microscopy (SEM) experiments 81 were conducted with JCM - 6000PLUS at National Corrosion and Materials Reliability Laboratory of Texas A&M 82 University, the concentration of elements in various phases were measured by energy-dispersive spectrometer (EDS) 83 linked to the SEM equipment. The electron-backscattered diffraction (EBSD) was carried out using a Tescan FERA-84 3 Model GMH Focused Ion Beam Microscope of Texas A&M University Materials Characterization Core Facility 85 (RRID:SCR 022202). 86

87 2.3. Electrochemical analyses

A high-performance potentiostat workstation GAMRY Reference 600+ in a three-electrode electrochemical cell 88 was used to conduct the potentiodynamic polarization, potentiostatic and EIS experiments. The three-electrode cell 89 was composed by a platinum sheet as contour electrode, a tungsten/tungsten oxide reference electrode, and a working electrode, the values of electrochemical potential vs. the W/W_{oxide} reference electrode obtained from the tests were 91 converted to potential vs. saturated calomel electrode (SCE) [39]. The potentiodynamic-polarization measurements 92 were conducted at 25°C in three different chloride concentration solutions containing inorganic salts in proportions and 93 concentrations representative of seawater [35]. Different chloride concentration solutions were prepared by diluting 94 or condensing the artificial seawater solution to $0.1 \times$ chloride concentration seawater, or $10 \times$ chloride concentration 95 seawater. The samples were immersed into the solutions overnight to stabilized and reach a quasi-stationary value of 96 the open circuit potential (OCP) before each measurement was taken. Three different scan-rate (0.1 mV/s, 1 mV/s, 97 and 10 mV/s) were used for each potentiodynamic-polarization test condition, the scanned potential started from -400 98 99 mV vs. OCP until either the potential exceeds the pitting potential or the current density reaches 1 mA/cm^2 . The summary of the experimental matrix is detailed Tab. 1. The potentiostatic staircases were used to assess the presence 100 of metastable pits and the transition to stable pit growth, this staircase method is described in detail in the literature 101 [40, 41]. In the context of the present study, the bias steps were applied at 50 mV intervals from the OCP and kept 102 103 constant for 2 hours, until the current density exceeds 0.2 mA/cm². The EIS tests were carried out at the OCP, running from 10 kHz to 10 mHz with a sinusoidal potential amplitude of 10 mV. 104

Solution						0.1 ×	Seav	vater							-
Material notation	As-	received	d	3min			5min		1	0min	ı]	15min	1	-
Scan rates (mV/s)	0.1	1 1	10 0.1	1	10	0.1	1	10	0.1	1	10	0.1	1	10	
Solution				T		Se	awat	er					-		-
Material notation	As-	received	d	3min			5min		1	0min	L	1	15min	i i	yan
Scan rates (mV/s)	0.1	1 1	10 0.1	1	10	0.1	1	10	0.1	1	10	0.1	1	10	
Solution						$10 \times$	Seav	vater							-
Material notation	As-	received	d	3min			5min		1	0min	I	I	15min	i .	_
Scan rates (mV/s)	0.1	1 1	10 0.1	1	10	0.1	1	10	0.1	1	10	0.1	1	10	
															-

Table 1: Sequence of experimental conditions used in the present work.

105 2.4. Corrosion by-products identification

The Omicron XPS system with Argus detector at Materials Characterization Facility (MCF) of Texas A&M University (RRID:SCR_022202) was employed to conduct the X-ray photoelectron spectrometer. XPS measurements were performed using a Mg/Al X-ray source. The spot size is 0.311mm × 3.22mm, and the base pressure in the analysis chamber was < 5×10^{-8} mbar. XPS peak fitting was done employing software CasaXPS. FERA FIB-SEM ToF

Secondary Ion Mass Spectrometer (ToF SIMS) attached to FERA FIB-SEM (Materials Characterization Facility of TAMU) was used for the depth profiling. The analyzed surface was sputtered by the 30 keV Xe⁺ beam with a current

of 6 nA. The diameter of the beam was $< 1\mu m$; the raster was $100 \times 100 \ \mu m^2$. The angle of incidence of the beam was

 113 90° (angle between surface and beam direction). The depth profiles were measured for two randomly chosen surface 114 areas.

115 3. Results

116 3.1. Microstructure analysis

The Tetrataenite phase (PDF card number 01-71-8321) was used to analyze the X-ray diffraction (XRD) pattern. 117 The XRD patterns for the HEAs after different treatments are shown in Fig. 1, the super-lattice peak (111) is the most 118 intense peak in each pattern, followed by the (2 0 0), (2 2 0), (3 1 1) and (2 2 2) peaks, which can be exclusive to the 119 disordered FCC phase (comparable with the common FeNi intermetallic compound). The XRD patterns reveal that 120 although the intensity of each peak varies within the alloy, the coordinates of the peaks are the same, indicating that 121 after cold rolling and annealing processes, there was no significant change in the full width at half maxima (FWHM) 122 [42]. This means that there are no extra peaks in addition to the FCC phase after different grain refinement treated 123 conditions. 124



Figure 1: X-ray diffraction patterns of different treated Al2Cr5Cu5Fe53Ni35 system alloys.

The micrographs of the $Al_2Cr_5Cu_5Fe_{53}Ni_{35}$ alloys after different treated conditions are presented in Fig. 2. The coarse grains of the as-received $Al_2Cr_5Cu_5Fe_{53}Ni_{35}$ alloy could easily be observed due to the boundaries with lengthy edges, while a more finer and uniform spreading of fine grains is observed in the material subjected to 3min. Somewhat diffuse images are appreciable for the other material states in terms of grain boundary and size (see Figs. 2c, d and e), which will be elucidated next. As indicated in the same figure, the red spots mark the locations of EDS point analysis.



Treated condi	tions	Al (wt%)	Cu(wt%)	Cr(wt%)	Ni(wt%)	Fe(wt%)
	Pt. 1	1.78	5.08	5.41	33.04	54.68
A	Pt. 2	1.86	4.44	5.20	34.20	54.30
As-received	Pt. 3	1.88	4.99	5.21	33.88	54.05
	Ave.	1.84	4.84	5.27	33.71) Fe(wt%) 54.68 54.30 54.30 54.34 53.16 54.34 53.16 54.16 53.49 53.22 53.19 55.03 53.81 54.77 54.84 53.77 54.84 53.77 54.46 54.24 54.01 53.76 54.00
2min	Pt. 1	2.29	4.69	5.30	34.55	53.16
	Pt. 2	2.12	4.77	5.32	34.64	53.16
Simin	Pt. 3	2.20	4.86	5.33	33.46	54.16
	Ave.	2.20	4.77	5.32	34.22	53.49
5min	Pt. 1	1.88	5.45	5.54	33.92	53.22
	Pt. 2	1.90	4.91	5.22	34.78	53.19
	Pt. 3	1.71	4.72	5.30	33.24	55.03
	Ave.	1.83	5.03	5.35	33.98	53.81
	Pt. 1	1.34	4.81	5.26	33.82	54.77
10	Pt. 2	1.43	4.61	5.55	33.57	54.84
TOIMIN	Pt. 3	1.50	5.35	5.57	33.81	53.77
	Ave.	1.42	4.92	5.46	33.73	54.46
	Pt. 1	1.61	4.54	5.33	34.29	54.24
15	Pt. 2	1.61	4.99	5.25	34.14	54.01
131010	Pt. 3	1.84	4.98	5.26	34.16	53.76
	Ave	1.60	4.84	5.28	34.20	54.00

Table 2: EDS point quantitative analysis results for each treated conditions Al2Cr5Cu5Fe53Ni35 alloys.



Figure 2: Scanning electron microscopy (SEM) result shows the morphology of the (a) as-received, (b) 3min, (c) 5min, (d) 10min, (e) 15min $Al_2Cr_5Cu_5Fe_{53}Ni_{35}$ alloys. EDS point analysis locations are indicated in red spots.

¹³⁰ The chemical composition of $Al_2Cr_5Cu_5Fe_{53}Ni_{35}$ alloys after different treatments is given in Tab. 2. As indicated by ¹³¹ the EDS point analysis results, for every conditions, each element distributes homogeneously in the matrix space and ¹³² the chemical composition closely matches with as-received $Al_2Cr_5Cu_5Fe_{53}Ni_{35}$ alloys. This result is consistent with

¹³³ the XRD analysis previously discussed.

¹³⁴ The electron-backscattered diffraction (EBSD) maps are presented in the column 1, 2, 3 of Fig. 3, the EBSD



Figure 3: Electron-backscattered diffraction (EBSD) mapping of the microstructure of Al₂Cr₅Cu₅Fe₅₃Ni₃₅ alloys for (a) as-received, (b) 3min, (c) 5min, (d) 10min, (e) 15min along different axis.

pattern was indexed with iron FCC phase which is shown in the column 4. Column 5 shows the grain size distributions 135 for each treated conditions of Al₂Cr₅Cu₅Fe₅₃Ni₃₅ alloys. It can be concluded that after each treated condition, the 136 Al2Cr5Cu5Fe53Ni35 alloys keep a single-phase FCC similar to the as-received state, which is consistent with previous 137 XRD and EDS results. The grain size changes significantly after cold-rolling process, especially for large thickness 138 reduction (85%) and short exposure annealing time (3min). Conversely, for lesser thickness reduction (50%) and 139 larger annealing times (t > 3 min), recrystallization is easily surpasses by the grain growth stage where the elongation 140 and possibly the strength would be seriously affected by an exponentially growth of grains at low temperature rate 141 [43, 44]. Moreover, the microstructures exhibit a stripe-shape grains preferentially elongated in the rolling direction. 142

¹⁴³ The statistical information of the grain dimensions for each treated condition is presented in Tab. 3. According to ¹⁴⁴ them, it can be inferred that the larger the thickness reduction, the smaller the grain size with the shorter exposure

¹⁴⁵ annealing time. Conversely, the longer the exposure time, the greater the grain dimension is. This time-dependent

phenomenon, which is called recrystallization and grain growth is normally found in physical metallurgy literature as

¹⁴⁷ well as several studies [43, 45, 46].

Treated conditions	Grain Count	Mean (µm)	Min. (µm)	Max. (µm)	St. Dev. (µm)
As-received	65	227.2	71.4	828.6	141.1
3min	284	12.3	7.1	48.1	6
5min	309	61.3	35.7	406.4	49.5
10min	29	140.4	40.5	983.1	176.5
15min	21	178.3	37.4	536.4	175.1

Table 3: Grain size of Al2Cr5Cu5Fe53Ni35 alloys after different treated conditions.

148 3.2. Electrochemical analyses

149 3.2.1. Potentiodynamic-polarization measurements

150 Potentiodynamic-polarization is a standard test method to evaluate formation and breakdown of passive oxide films on the sample surface [47]. According to the conceptual interpretation of typical potentiodynamic-polarization 151 curve, several important parameters can be obtained to characterize the corrosion properties of materials. As shown 152 in Fig. 4, E_{corr} stands for the corrosion potential in open circuit (OCP), I_{corr} is the corrosion current density, β_a and 153 β_c are anodic and cathodic Tafel slopes, whereas E_p and I_{pass} specify the critical pitting potential and the current 154 density in the passivation area, respectively. The so-called Tafel extrapolation of polarization curves was used to 155 determine above parameters, which takes advantage of potentiodynamic polarization test outcomes to associate with 156 the corrosion process and its rate. In fact, this method supersedes greatly traditional techniques such as weight 157 loss as it estimates the numerous reactions involved in the corrosion process, especially in multicomponent alloys 158 accurately. For corrosion parameters calculation, the classic Tafel analysis is performed by extrapolating the linear 159 portions of a logarithmic current versus potential plot back to their intersection, see Fig. 4. Unfortunately, many 160 real world corrosion systems do not provide a sufficient linear region to permit accurate extrapolation, therefore the 161 measured data is numerically fit to the Butler-Volmer equation by adjusting the values of E_{corr} , I_{corr} , β_a , and β_c . Some 162 illustrative examples to support the usage of this methodology can be found in [16, 48-51] 163

Figure 5 shows the typical potentiodynamic result of Al₂Cr₅Cu₅Fe₅₃Ni₃₅ alloy after different treated conditions 164 in distinct chloride concentration solutions with a 0.1 mV/s scan rate. The chloride concentration of the simulated 165 seawater is 0.55 mol/L, the concentration of $0.1 \times$ diluted seawater and the condensed 10× seawater are 0.055 mol/L 166 167 and 5.5 mol/L, respectively. As illustrated by the curves in Fig. 5, the Al₂Cr₅Cu₅Fe₅₃Ni₃₅ alloy after 3 min treated condition exhibits the best corrosion resistance compared to others in the $0.1 \times$ and $1 \times$ seawater solutions, while it is 168 slightly surpasses by its as-received alternative in $10 \times$ seawater concentration solvent. Overall, the 3 min treated con-169 figuration possesses the best corrosion resistance followed by the as-received, while the remaining treated conditions 170 display a somewhat similar behavior. To quantitatively study the corrosion properties of these Al₂Cr₅Cu₅Fe₅₃Ni₃₅ 171 alloys after different grain refinement treated conditions, the electrochemical parameters are measured and displayed 172 in Tab. 4. According to the data, it can be concluded that in the seawater solution the 3 min treated condition alloy 173 (the smallest grain size), not only the E_p is larger compared with other treated conditions, but also the I_{pass} is the 174 smallest, indicating its superior resistance to localized corrosion. For instance, the corrosion resistance order in 1× 175 seawater is $3\min > as$ -received $\cong 5\min \cong 10\min \cong 15\min$; while in $0.1 \times seawater$ solution, the order swapped to $3\min$ 176 > as-received > 5min \approx 10min \approx 15min. Moreover, when the chloride concentration increases to 10× seawater, this 177 order becomes as-received >3min > 15min \approx 10min \approx 5min. Related to the EBSD analysis, the potentiodynamic po-178 larization results suggest that the smaller the grain size and the more recrystallized the alloy is, the better the corrosion 179

180 behavior will be.



Cr_3min Cr_5min 10 10 10-10 Cr 10min 10⁻¹⁰ Cr_15min 10 -0.4 -0.2 0.0 0.2 Potential (V) vs. SCE -0.4 -0.2 0.0 Potential (V) vs. SCE -0.6 0.2 -0.8 0.4 0.6 -0.8 -0.6 0.4 -0.6 -0.4 -0.2 Potential (V) vs. SCE -0.8 0.0 (c) (b) (a)

Figure 5: Potentiodynamic-polarization curves for $Al_2Cr_5Cu_5Fe_{53}Ni_{35}$ alloys after different treated conditions in (a) $0.1 \times$ seawater, (b) seawater and (c) $10 \times$ seawater with 0.1 mV/s scan rate.

181 3.2.2. Potentiostatic measurements

The mass transport of electroactive species (available ions in the solution) under diffusion controlled conditions can be realized by a potential step method known as potentiostatic [52]. It basically consists of increasing the potential of the working electrode by certain amount above or below OCP and hold it constant while the current density is measured as a function of time as shown in Fig. 6. This method is also known as chronoamperometry and for this particular study the target potential was OCP + 50 mV applied to all samples immersed at three different seawater solution concentrations to represent the anodic polarization reaction (dissolution/oxidation) of the working electrode.

Solution	Treated conditions	Ecorr (mV vs. SCE)	I_{corr} (μ A/cm ²)	β_a (mV/dec)	β_c (mV/dec)	E _p (mV vs. SCE)	$\frac{\Delta E}{(\text{mV vs. SCE})}$	I_{pass} (μ A/cm ²)
	As-received	-249.98	0.058	136.8	-78.3	479.44	727.42	0.373
	3min	-238.13	0.049	155.2	-76.1	504.72	742.85	0.334
$0.1 \times \text{seawater}$	5min	-222.84	0.046	124.9	-75.2	276.12	498.96	0.661
	10min	-401.98	0.041	112.2	-72.2	262.12	664.11	0.709
	15min	-451.80	0.030	113.0	-77.7	264.52	716.32	0.681
	As-received	-250.03	0.022	26.4	-33.9	238.22	488.25	0.605
	3min	-199.97	0.008	77.3	-45.1	351.42	551.39	0.212
seawater	5min	-249.56	0.108	25.2	-33.8	230.72	480.28	1.036
	10min	-180.04	0.217	79.2	-46.6	226.27	406.31	0.591
	15min	-210.63	0.168	36.4	-38.5	243.05	453.68	0.915
	As-received	-364.51	0.089	95.2	-91.8	-8.13	356.34	0.762
	3min	-320.19	0.083	88.5	-58.7	-42.48	277.71	0.529
$10 \times \text{seawater}$	5min	-519.59	0.143	55.6	-78.0	-191.77	327.82	1.897
	10min	-497.65	0.384	72.1	-51.5	-161.48	336.17	2.698
	15min	-339.36	0.257	82.2	-61.6	-136.75	202.62	1.675

Table 4: Electrochemical parameters for Al₂Cr₅Cu₅Fe₅₃Ni₃₅ alloys after different treated conditions in different solutions.

As it can be seen in Fig. 6(a) the current density decays exponentially with increasing time until approximately 2000 188 s, from which the current reaches a plateau. This stage is known as diffusion controlled and denotes the mass transfer 189 of electroactive species present in the solution under a steady-state regime. This behavior is less remarkable for the 190 alloys as received and 3min which yield almost zero faradaic current, indicating that passivation is taking place over 191 the sample surface without film instability. However, evidences of metastable pitting formation along repassivation 192 193 are observable in the remaining configurations. On the other hand, in more dense ionized solutions like seawater and 10x seawater, a lesser kinetic controlled stage (exponential decay) is exhibited for most of the different microstructures 194 herein considered. Being dominantly mass-transfer limited process with uniform oxide film formation and very few 195 metastable pitting peaks presence especially in 5min and 15min alloys. 196

197 3.2.3. EIS results

The electrochemical impedance spectroscopy (EIS) is usually used as a steady state method to characterize the 198 199 electrical properties of oxide films formed on surface's alloys and their interfaces of electronically conducting electrodes [53]. Figs. 7(a1), (b1) and (c1) display the Nyquist (complex) plots, (a2), (b2) and (c2) present the Bode 200 201 plots of the studied alloys, in the (a) $0.1 \times$ seawater, (b) seawater and (c) $10 \times$ seawater solutions. The impedance components in the Nyquist representation tend to resemble circular arcs whose radius magnitudes are associated with 202 the impedance of the passive film on the surface. The greater the radius, the better the impedance. As it can be seen, 203 all selected cases display capacitive loops being the largest the 3min Al₂Cr₅Cu₅Fe₅₃Ni₃₅ alloy for the three solution 204 concentrations herein analyzed, whereas the other treated configurations present significant smaller capacitive loops 205 indicating poor protective characteristics of the film. However, even though the tendency in the above treated ma-206 terial conditions is quite similar (impedance reduces as annealing time increases, especially in lighter and normal 207 solution concentrations) including as-received alloy, the 5min alloy depicts the wider response variation. In particular, 208 209 this alloy has the second larger diameter in seawater solution, while the lowest in 0.1x and 10x seawater solutions, respectively. In the Bode representation, on the other hand, the total impedance, Z_{mod} varies strongly with respect 210 to applied frequency, especially in the range of 10^{-2} to 10^{2} Hz, while for high frequencies (> 10^{2} Hz) the plateau 211 region indicates the electrolyte resistance, which appears to be considerable low for highly dense solutions as the cor-212 responding impedance that is less than $\approx 3.3 \,\Omega \, \text{cm}^2$ compared with 1x and 0.1x seawater compounds. Moreover, the 213 phase angle curves for each treated alloys in the three chloride concentration solutions show a slightly constant mid 214 to low frequency phase angle magnitudes in the range of $-60 \sim -80$ degrees. The shapes of the Bode curves indicate 215 the characteristics of a capacitor-like behavior resulted in a two-time constants in the range of low to mid frequencies, 216



Figure 6: The chronoamperometry transients obtained at the recorded OCP + 50 mV for $Al_2Cr_5Cu_5Fe_{53}Ni_{35}$ alloys after different treated conditions in (a) $0.1 \times$ seawater, (b) seawater and (c) $10 \times$ seawater.

²¹⁷ whereas in high frequencies a resistor-like behavior with almost zero phase angle is visible [54, 55].

The equivalent electrical circuit designed to fit the experimental results is presented in Fig. 8, which corresponds to the ladder circuit type [56]. The equivalent electrical circuit is constituted by two parts: (1) one constant phase element (CPE_{pass}) is employed to characterize the pseudo-capacitance properties of the passive layer [57] and (2) a series-connected circuit to the charge-transfer resistance (R_{pass}) which is used to describe the corrosion process might occur in the vulnerable area where local attack (pits) are likely to form due to the surface defects [58], this active mechanism of metal dissolution can be idealized as an equivalent circuit having a charge-transfer resistance (R_{ct}) and



Figure 7: Nyquist (first row) and Bode (second row) plots of $Al_2Cr_5Cu_5Fe_{53}Ni_{35}$ alloys measured at open circuit potential with a sinusoidal potential amplitude of 10mV, running from 10 kHz to 10 mHz in (a) 0.1 × seawater, (b) seawater and (c) 10 × seawater.



 $Figure \ 8: \ The \ equivalent \ electrical \ circuit \ representative \ of \ the \ electrode \ interface \ for \ the \ Al_2 Cr_5 Cu_5 Fe_{53} Ni_{35} \ alloys.$

 $_{224}$ a pseudo-double-layer capacitance (CPE_{dl}). The impedance [59] of the CPE can be calculated by the expression

$$Z_{\rm CPE} = Y_0^{-1} (i\omega)^{-\alpha} \tag{1}$$

where Z_{CPE} is the impedance of the CPE, Y_0 is the proportionality factor, *i* is the imaginary unit, ω is the angular frequency, and α is the phase shift [60]. The effective capacitance [61] associated with the CPE can be expressed by the formula proposed by Hsu and Mansfeld for studies on passive film [59, 62]

$$C_{\rm eff} = Y_0^{1/\alpha} R_{\rm f}^{(1-\alpha)/\alpha}$$

According to the equivalent electrical circuit, the corresponding fitting curves for the Nyquist and Bode responses 228 are included in Fig. 7 as solid lines, while measured data are depicted in solid circles accompany with open symbols 229 depicting the frequency band. Good agreement between experimental data and model can be observed which provides 230 solid evidence of the suitability of the above proposed model to describe the polarization resistance of passive films of 231 232 Al₂Cr₅Cu₅Fe₅₃Ni₃₅ alloys in different chloride concentration solutions and annealing time periods. The corresponding polarization resistance parameters are summarized in Tab. 5. Note that among all considered alloys, the 3min has 233 234 the largest CPE_{pass} , indicating that the passive film formed on the surface is highly stable under steady-state condition and thus has the best protective characteristics. Moreover, by comparing the alloys' response in different chloride 235 concentration solutions, the lower chloride concentration appears to have lesser impact on oxide films stability, which 236 means the chloride ions degrade less the passive film. That is, compared with R_{pass}, R_{et} is practically negligible 237 (smaller in $\approx 10^5$ order of magnitude), indicating that the surface is mostly occupied by dispersive, thinner passive 238 film. Based on the data obtained from EIS, the effective thickness of the passive film $(d_{\rm eff})$ can be estimated as follow 239 240 [61]

$$d_{\rm eff} = \frac{\varepsilon \varepsilon_0}{C_{\rm eff}} \tag{3}$$

(2)

where ε is the relative dielectric constant taken equal 12, which is suitable for HEAs [63], ε_0 stands for the permittivity 241 of vacuum, which equals to 8.8542×10^{-14} F/cm. The estimate film thickness of each treated Al₂Cr₅Cu₅Fe₅₃Ni₃₅ 242 alloys are presented in Tab. 5. As it can be seen, the 3min film thickness in the seawater condition has the smallest 243 value, 5.9 nm, while its apparent corrosion resistance surpasses the others indicating that thickening is not synonym 244 of good anticorrosive properties. Therefore, the composition and density of the passive film should also be taken into 245 consideration besides the thickness [50]. This phenomenon reveals that the density and the composition of passives 246 film formed on the surface of each treated alloys is different, the 3min would have a thinner but denser protective layer 247 while the others may have a thicker but porous-like surface films [50, 64]. 248

249 3.3. Chemical composition analysis of the surface film

250 3.3.1. XPS analysis

According to EIS analysis, the composition and density of the protective oxide film formed on surface of each 251 252 treated condition of Al₂Cr₅Cu₅Fe₅₃Ni₃₅ are different. The X-ray Photoelectron Spectroscopy (XPS) can be utilized to obtain more information about the oxide layer composition resulting from the dissolution process of the working 253 electrode [65]. For critical comparison of chemical composition of passive films, the 3min configuration is analyzed 254 in conjunction with as-receive condition. Fig. 9 shows the Fe 2p_{3/2}, Ni 2p_{3/2}, Cr 2p_{3/2}, Al 2p, Cu 2p_{3/2}, and O 1s 255 peak spectra used to fit the measured data for (a) as-received and (b) 3min treated Al₂Cr₅Cu₅Fe₅₃Ni₃₅ alloys. The 256 Al 2p spectra, Figs. 9a4 b4 contain metallic-state aluminum, aluminum oxide, and hydroxide [66]. Similarly, the 257 Fe 2p_{3/2}, Ni 2p_{3/2}, Cr 2p_{3/2} spectra contain the metallic-state metal with their corresponding oxides and hydroxides 258 species [67]. Likewise, the Cu $2p_{3/2}$ spectra contain metallic-state Cu with its oxide product only without hydroxides 259 [68]. Moreover, the O 1s spectra are comprised by O^{2-} and OH^{-} peaks. The peak-area ratios of $Fe^{2+,3+}/Fe$, Ni^{2+}/Ni , 260 Cr^{3+}/Cr , Al^{3+}/Al , Cu^{2+}/Cu , and OH^{-}/O^{2-} species present in the passive films of the $Al_2Cr_5Cu_5Fe_{53}Ni_{35}$ alloys are 261 summarized in Tab. 6. From Fig. 9 and Tab. 6, it can be seen that the ratios of $Fe^{2+,3+}/Fe$ and Ni^{2+}/Ni in the passive 262 film of as-received $Al_2Cr_5Cu_5Fe_{53}Ni_{35}$ are much more significant than the 3min one. It can be assumed that the 263 spectra peaks of the oxide states correspond to signals from the passive film while the metallic states correspond to 264 the alloy matrix [69] if the detecting area and depth in XPS experiments are the same for each sample. Similar ratio 265 of other metal elements but deceased peak-area ratio of Fe^{2+,3+}/Fe, Ni²⁺/Ni in the 3min Al₂Cr₅Cu₅Fe₅₃Ni₃₅ alloy 266 indicates that the thickness of its passive films reduced, which is consistent with the EIS estimation. 267

To give a quantitative results of the passive film compositions, the percentage atomic concentration of metal elements can be calculated by the equation [50]

Solution	Treated	R _{pass}	Relectrolyte	CPE _{pass} parameter	rs	R _{ct}	CPE _{dl} parameters		C _{eff}	d_{eff}
Bolution	conditions	$(\Omega \ cm^2)$	$(\Omega \ cm^2)$	Y_0 (F cm ⁻² s ⁿ⁻¹)	α	$(\Omega \text{ cm}^2)$	Y_0 (F cm ⁻² s ⁿ⁻¹)	α	(Fcm ⁻²)	(nm)
	As-received	2.13×10^7	114.4	3.13×10^{-5}	0.830	163.4	2.29×10^{-5}	0.814	7.92×10^{-5}	13.4
	3min	9.20×10^7	539.4	4.12×10^{-5}	0.864	102.6	4.50×10^{-6}	0.891	1.18×10^{-4}	9.0
$0.1 \times \text{seawater}$	5min	1.46×10^7	123.7	2.55×10^{-5}	0.775	185.0	2.77×10^{-5}	0.743	$6.25 imes 10^{-5}$	17.0
	10min	1.43×10^7	190.4	$2.38 imes 10^{-5}$	0.697	228.7	7.77×10^{-5}	0.732	$4.93 imes 10^{-5}$	21.6
	15min	1.59×10^7	130.7	2.10×10^{-5}	0.674	188.4	$5.64 imes 10^{-5}$	0.727	3.79×10^{-5}	28.0
	As-received	8.46×10^{6}	19.1	3.38×10^{-5}	0.741	76.2	1.70×10^{-5}	0.843	7.78×10^{-5}	13.7
	3min	1.90×10^7	104.1	5.36×10^{-5}	0.727	318.0	1.14×10^{-6}	0.890	1.78×10^{-4}	5.9
seawater	5min	1.22×10^7	28.2	3.92×10^{-5}	0.756	311.7	1.41×10^{-5}	0.833	1.05×10^{-4}	10.1
	10min	4.82×10^{6}	36.2	5.04×10^{-5}	0.755	116.4	1.40×10^{-5}	0.869	1.17×10^{-4}	9.1
	15min	6.44×10^{6}	56.7	5.27×10^{-5}	0.760	347.5	1.54×10^{-5}	0.816	1.33×10^{-4}	8.0
	As-received	1.99×10^{6}	2.6	8.23×10^{-5}	0.721	67.0	1.57×10^{-5}	0.790	$1.71 imes 10^{-4}$	6.2
	3min	1.97×10^6	19.6	$1.34 imes 10^{-4}$	0.896	139.1	$1.84 imes 10^{-6}$	0.862	2.39×10^{-4}	4.4
$10 \times \text{seawater}$	5min	2.33×10^5	4.0	2.18×10^{-4}	0.726	114.0	9.64×10^{-5}	0.790	3.68×10^{-4}	2.9
	10min	1.94×10^5	7.1	$2.40 imes 10^{-4}$	0.694	79.2	8.46×10^{-5}	0.805	$3.64 imes 10^{-4}$	2.9
	15min	1.37×10^5	5.4	2.52×10^{-4}	0.747	94.2	4.18×10^{-5}	0.841	4.06×10^{-4}	2.6

 $Table 5: Equivalent circuit element values for EIS data of Al_2 Cr_5 Cu_5 Fe_{53} Ni_{35} alloys after different treated conditions in different chloride concentration of the state of t$ tration solutions.

Table 6: The peak-area ratios of $Fe^{2+,3+}/Fe$, Ni^{2+}/Ni , Cr^{3+}/Cr , Al^{3+}/Al , Cu^{2+}/Cu , and OH^{-}/O^{2-} in the passive films on the as-received and 3min alloys.

Treated conditions	Fe ^{2+,3+} /Fe	Ni ²⁺ /Ni	Cr ³⁺ /Cr	Al ³⁺ /Al	Cu ²⁺ /Cu	OH^{-}/O^{2-}
As-received	12.6	6.83	27.16	5.48	0.77	1.17
3min	4.82	1.75	28.58	5.55	1.55	2.67

$$X_i = 100 \frac{A_i}{\sum_{i=1}^n A_i} \tag{4}$$

- where X_i is the atomic percentage for the *i*th element, *n* is the total number of elements in the material, which is 5 in 270 271
 - the present study, and A_i is the adjusted intensity that corresponds to the area under the peak of each element

$$A_i = \frac{J_i}{R_i K} \tag{5}$$

- where J_i is the measured area under peaks, R_i is the relative sensitivity factor which could be obtained from the 272
- SPECSLab2 software, K is the kinetic energy. The chemical composition of the passive film formed on the as-received 273
- and 3min Al₂Cr₅Cu₅Fe₅₃Ni₃₅ alloys are illustrated in Tab. 7. 274

Table 7: XPS calculated chemical compositions in at.% (or wt.%) of passive film for as-received and 3min alloys after immersed in seawater for 24 hours at room temperature.

Treated conditions	Al	Cr	Cu	Fe	Ni
As-received	69.2 (51.7)	4.4 (6.3)	1.9 (3.3)	15.8 (24.5)	8.7 (14.2)
3min	70.7 (53.7)	5.5 (8.1)	0.8 (1.4)	15.8 (24.9)	7.2 (11.9)



Figure 9: The XPS spectra for (a) as-received, (b) 3min Al₂Cr₅Cu₅Fe₅₃Ni₃₅ alloys after immersed in seawater for 24 hours at room temperature.

According to the information presented in Tab. 7, the XPS analysis indicates that the dissolution rate of each 275 element has significant differences. Aluminum takes up the most large ratio among the metallic elements in the 276 oxide layer in both treated alloys. The beneficial role of Al when incorporated into surface films for passive alloys 277 (in passive conditions) has already been documented [70-72]. Thus the large amount of Al serves as a significant 278 279 protective role at the outer surface of the alloys, which contributes to the stable passive behavior of the alloys consistent with potentiodynamic-polarization and EIS outcomes. As mentioned previously that the estimate thickness of the 280 passive film formed on the surface of 3min Al₂Cr₅Cu₅Fe₅₃Ni₃₅ alloy is more compared with the as-received 281 configuration, its superior stability casts better corrosion properties due to compositional configuration. As shown in 282 Tab. 7, in the passive film of 3min, there exist more elemental fraction of Al, and significantly less fractional amount 283 of Cu, and Ni. It was investigated that increasing Cu content will resulted in a higher i_{corr} and lower E_p for the system 284 [73]. Moreover the inferior corrosion resistance of the Ni-containing HEAs is also reported, which is related to the 285 small atomic radius of Ni. The small atomic radius would result in a large distortion in alloys and thereby could 286 decrease the corrosion resistance [74]. Therefore, it is plausible to argue that the thinning of the 3min oxide film is 287 more related to the abundant presence of Al regarding others elements such as Cu and Ni, which yields major stability 288 and steady-state species diffusion in the barrier layer. 289

290 3.3.2. SIMS analysis

The Secondary Ion Mass Spectrometer (SIMS) is a well-known high-sensitivity chemical analysis technique widely used for the investigation of chemical composition [75, 76]. In order to study the elemental profile distribution in the passive film formed on the $Al_2Cr_5Cu_5Fe_{53}Ni_{35}$ alloy, the 3min material condition was selected.

The ToF SIMS positive ion depth profiles for the passive film formed in seawater over the $3\min Al_2Cr_5Cu_5Fe_{53}Ni_{35}$ alloy's surface is presented in Fig. 10. Note that due to strong matrix effect on ion emission, the intensity of the plotted ions in the depth profiles cannot be compared directly and do not reflect the concentrations of the associated species in the substrate. The depth profiles are plotted versus the sputtering time, the sputtering time can be directly translated into oxide thickness. The sputtering rate was computed using the TRIM code(The sputtering rate was computed using the TRIM code (http://www.srim.org/SRIM/SRIMLEGL.htm). It is crucial to determine the position of the metal/oxide interface in the depth profiles for understanding the composition of the passive film. The Al³⁺ ion profile



 $Figure \ 10: \ ToF \ SIMS \ depth \ profiles \ of \ the \ passive \ film \ formed \ on \ the \ 3min \ Al_2 Cr_5 Cu_5 Fe_{53} Ni_{35} \ alloy \ immersed \ in \ seawater \ for \ 24 \ h.$

is used to define the oxide film region I, which ends at 80% of the maximum intensity of the depth profile. The region III is defined with the intensity plain which corresponds to the metallic substrate of the alloy. The remaining region II is assigned to a modified alloy layer under the oxide film in the vicinity of the oxide-metal interface [77]. It can be concluded from Fig. 10 that the passive film formed on the $3min Al_2Cr_5Cu_5Fe_{53}Ni_{35}$ alloy is mainly composed of Al, and the thickness is approximate 7 nm, which is close to the EIS estimated result, 5.9 nm.

306 4. Point defect model (PDM) analysis

The Point Defect Model (PDM) was developed by Macdonald to study the passivity breakdown of metals [78–81]. Over the past 40 years, large amount of empirical evidence attests to the ability of PDM to successfully account for the properties of the passive films [82]. It was proposed that the passivity breakdown was expected to happen at the points on the metals surface which can be characterized by high cation vacancy $(V_M^{\lambda'})$ diffusivity along with anion vacancy $(V_{\bar{O}})$ migration as indicated in Fig. 11. The reactions shown are not assumed, they are the only possible elementary reactions for vacancy generation and annihilation [83].Therefore, pitting can be viewed as a local damage process originated from vacancy condensation at the metal-film interface.

As PDM describes, the aggressive chloride anion (Cl⁻) absorbed by oxygen vacancies (V_{O}°) into the barrier layer (bl), giving rise to the generation of cation vacancies ($V_{M}^{\lambda'}$) at the barrier layer/solution interface (bl/s). The cation vacancies then enhance their flux (J_{ca}) to penetrate the barrier layer toward the metal/barrier layer interface (m/bl). The vacancies are usually annihilated by injection of cations from the metal [78]

 $m + V_{\rm M}^{\chi'} \to M_{\rm M} + v_{\rm m} + \chi e' \tag{6}$

where the *m* and v_m are the metal atom and a vacancy in the metal substrate respectively, M_M is a normal cation site on the cation sub-lattice of the barrier layer, χ is the oxidation number of the host cation within the bl. The J_m

parameter is used to describe the annihilation rate of the $V_M^{k'}$ at the m/bl interface. If the $J_{ca} > J_m$, the cation vacancies

will condense locally at the m/bl interface leading to the separation of the barrier layer from the metal substrate.



Figure 11: Process leading to the breakdown of the passive film according to PDM.

- ³²² Furthermore, when the critical areal cation vacancy concentration exceeds a critical value (ξ , cm⁻²), the remnants of
- the barrier layer form a blister at the condensation areal and the barrier layer is prevented from growing into the metal
- by generating V_{Ω}° , which will generates new film at the m/bl interface [78]

$$m \to M_{\rm M} + \frac{\chi}{2} V_{\rm O}^{\circ} + \chi e' \tag{7}$$

The reaction shown in Eq. 6 results in oxide/hydroxide outer layer growth by the reaction between the cation and the solvent, and the reaction shown in Eq. 7 leads to the growth of the oxide film by shifting the oxide/metal interface into the metal. However, at where is identified as high local discontinuous area, the condensation continues at the periphery of the blister making the blister expand and dissolve at the bl/s interface, these 'weak points' on the defective barrier layer are where passivity breakdown occurs [78–81, 83–85].

According to the PDM theory, an expression for the dependence of the critical pitting potential on temperature, pH and anion activity can be demonstrated [78]

$$E_{\rm p} = \frac{4.606RT}{\chi \alpha F} \log\left(\frac{b}{D}\right) - \frac{2.303RT}{\alpha F} \log[\rm Cl^{-}]$$
(8)

$$b = \frac{RT J_{\rm m}\Omega}{F\chi\varepsilon N_{\rm v}} \times \exp\left(\frac{\Delta G_{\rm s}^0 + \frac{\chi}{2}\Delta G_{\rm A}^0 - \frac{\chi}{2}\beta F \rm pH}{RT}\right)$$
(9)

$$\phi_{f/s} = \phi_{f/s}^0 + \alpha E + \beta p H \tag{10}$$

is

where the term χ is the oxide stoichiometry, α and β are functionals of the potential drop across the film/solution interface $\phi_{f/r}$ and pH, respectively. The *D* represents for the cation vacancy diffusion coefficient, while Ω indicates

³³³ interface $\phi_{f/s}$, and pH, respectively. The *D* represents for the cation vacancy diffusion coefficient, while Ω indicates ³⁴⁴ the volume per mole of the cation in the barrier film. The ε is the electric field strength. The energy term $\Delta G_s^0 + \frac{\chi}{2} \Delta G_a^0 - \frac{\chi}{2} \Delta G_a^0$

 $\frac{\chi}{2}F\phi_{f/c}^{0}$ is used to describe the free-energy related to the absorption of aggressive anions into V_{0}^{0} [86], whereas $\phi_{f/c}^{0}$

the value of $\phi_{f/s}$ in the standard state of E = 0 and pH = 0. The T is the temperature, F is Faraday's constant, R is the

gas constant, and N_v is Avogadro's number which is equal to 6.023×10^{23} No./mol.

In the view of the PDM, the relative stability of the passive layer is largely defined by the behavior of the polarizability of the film/solution interface, α , and the rate of annihilation of the cation vacancies at the metal/film interface, J_{m} [87]. The PDM provides a linear relationship between the critical pitting potential (E_p) and the chloride concentration (log[Cl⁻]) as indicated in Eq. 8. The slope related to the polarizability of the film/solution interface (α). Furthermore, from the relationship between E_p and log[Cl⁻] described in Eq. 8, the slope-intercept form at low chloride concentration can be used to measure the cation vacancy diffusion coefficient D, which can be used to describe

- how fast the metal cations are used at the metal/film interface, it can be used as an indication of the passive film property [88].
- The relationship between E_p and $\log[Cl^-]$ is presented in Fig. 12a. It can be seen that E_p decreases linearly with increasing of $\log[Cl^-]$, which is consistent with prediction of the PDM theory. With the help of the data obtained from Fig. 12a, the value of α can be calculated. Moreover, the relationship between E_p and the scan rate (v) is needed to evaluate the rate of cation annihilation at the metal/film interface, J_m . An analytical relationship between E_p and v is
- 350 given by the PDM as [52]

$$E_{\rm p}(v) = \left(\frac{2\xi RT}{J_{\rm m}\chi\alpha}\right)^{1/2} v^{1/2} + E_{\rm p}(v=0)$$
(11)

where $\xi = 3.5 \times 10^{14} \text{cm}^{-2}$, is the critical areal cation vacancy concentration which is related to the crystal structure of the metal oxide and the corresponding metal substrate [36]. As shown in Fig. 12b, the relationship between the E_p and $v^{1/2}$ obtained from potentiodynamic-polarization experiments is a linear dependency relationship, which agrees with Eq. 11. Based on the slope obtained from the fitted curves in Fig. 12b, the value of J_m can be calculated.



Figure 12: The relationship between the pitting potentials and chloride concentration at room temperature of the $Al_2Cr_5Cu_5Fe_{53}Ni_{35}$ alloys after different treated conditions.

Table 8: The slope and intercept of the fitted results about the linear relationship (y = Ax + B) between E_p vs. log[Cl⁻] shown in Fig. 12a and E_p vs. $v^{1/2}$ shown in Fig. 12b.

Treated conditions	Ep	vs. log[C]	[-]	$E_{\rm p}$ vs. $v^{1/2}$			
freuted conditions	A	В	R^2	Α	В	R^2	
As-received	-0.2438	0.1728	0.9999	0.7200	0.2108	0.9850	
3min	-0.2785	0.1968	0.9392	0.9960	0.2977	0.8439	
5min	-0.2409	0.0442	0.8782	0.6320	0.1809	0.9175	
10min	-0.2109	0.0561	0.8163	0.4802	0.2101	0.9965	
15min	-0.2055	0.0696	0.7971	0.4678	0.2205	0.9012	

The calculated values of the polarizability of the passive layer/solution interface (α) and the rate of annihilation of the cation vacancies at the metal/film interface ($J_{\rm m}$), combined with the grain size data obtained from EBSD



Figure 13: Effect of temperature on the polarizability of the passive layer/solution interface (α) and the rate of annihilation of the cation vacancies at the metal/ film interface (J_m) for Al₂Cr₅Cu₅Fe₅₃Ni₃₅ alloys in seawater.

experiments are presented in Fig. 13. It can be observed that both α and J_m values are in the increasing tendency 357 when grain size is getting larger. Following the PDM description of passivity, this suggests that the increasing in the 358 grain size is responsible for the wakening of the passive layer formed on the surface of Al₂Cr₅Cu₅Fe₅₃Ni₃₅ alloys. 359 Herein, a hypotheses is raised, which is the smaller values of α and J_m for the grain-refined Al₂Cr₅Cu₅Fe₅₃Ni₃₅ alloy 360 is attributed to its increased grain boundary density, where the cation vacancy generates slower and its diffusion is 361 obstructed by the boundaries due to the lower cation diffusivity. Moreover, The upper limit of the J_m value within the 362 barrier layer of Cr_2O_3 , which is 2×10^{17} [89], is also shown in Fig. 13. It can be observed that the $Al_2Cr_5Cu_5Fe_{53}Ni_{35}$ 363 alloys have higher J_m values than Cr_2O_3 , which indicate that there are more other elements rather than Cr in the 364 passive film. This results can be proved by the XPS results, limited amount of Cr was detected in the passive film 365 formed on the surface HEAs. 366

On the basis of the values of α and $J_{\rm m}$, the metal cation diffusivity at the metal barrier, D, can be calculated using 367 the relationship shown in Eq. 8 to 11 [90, 91]. The estimated results of D for the passive film formed on the surface of 368 Al₂Cr₅Cu₅Fe₅₃Ni₃₅ alloys are presented in Fig. 14. It can be seen that the cation vacancies diffusivity has an increase 369 tendency with grain size of the HEAs, and the smallest grain size Al₂Cr₅Cu₅Fe₅₃Ni₃₅ alloys, corresponding to the 370 371 3min treated condition owns the smallest D value. According to the description of the PDM theory, lower value of Dindicates better passive film properties. Thus it can be easily concluded that the 3min Al₂Cr₅Cu₅Fe₅₃Ni₃₅ possesses 372 the best localized corrosion resistance among these HEAs, and larger grain size of the Al₂Cr₅Cu₅Fe₅₃Ni₃₅ HEA will 373 have a detrimental effect on its corrosion behavior. The primary reason for improvements in corrosion resistance for 374 grain-refined alloys is due to the increasing in the grain boundary density. The grain boundaries possess lower ability 375 to generate the cation vacancies which attribute to the smaller polarization α and the annihilation rate J_m , the diffusion 376 for the cation vacancy across the boundary is more difficult due to its smaller cation diffusivity value, making the grain 377 boundaries more passivate stable area. 378

The pitting potential (E_p) and the potential difference between OCP and pitting potential (ΔE) in seawater solution of Al₂Cr₅Cu₅Fe₅₃Ni₃₅ alloys after different treated conditions are also included in Fig. 14. As indicated in Fig. 14, the values of E_p and ΔE decline as the grain size grows, which implies that larger grain size of Al₂Cr₅Cu₅Fe₅₃Ni₃₅ alloys has a deleterious effect not only on the limit but also on the stability of the passive film. This can be associated



Figure 14: Pitting potential (E_p) and the potential difference between OCP and pitting potential (ΔE), combined with the metal cation diffusivity (D) of Al₂Cr₅Cu₅Fe₅₃Ni₃₅ alloys in seawater.

with the increasing of D within the passive films as described by the PDM framework in Eq. 8. That is, the greater

the value of *D*, the lower the pitting potential due to mobility's increment of the cation vacancies at the metal/film

interface. This explanation was also pointed out in several previous studies [87, 92].

386 5. Conclusions

The microstructure and localized corrosion behavior of Al₂Cr₅Cu₅Fe₅₃Ni₃₅ HEAs after different treated conditions were thoroughly characterized by a series of comprehensive microstructural and electrochemical experiments. After cold rolling and annealing processes, the grain size of treated Al₂Cr₅Cu₅Fe₅₃Ni₃₅ alloys and corrosion properties were drastically modified whose primary conclusions can be drawn as follows:

The newly created Al₂Cr₅Cu₅Fe₅₃Ni₃₅ high entropy alloy is a single-phase FCC solid solution bulk metallic material. Cold rolling will decrease its grain size and make the material inhomogeneous. Annealing will recrystallize and grow the grains of Al₂Cr₅Cu₅Fe₅₃Ni₃₅ alloys. But after different treated conditions, the phase and the solid solution of the alloys doesn't change regarding as-received condition. The alloy system that underwent 85% thickness reduction by cold rolling and 3minutes annealing produced the best grain refinement with almost equibiaxially shaped grains whose average size was 12.3 μm.

- In simulated seawater solutions, the Al₂Cr₅Cu₅Fe₅₃Ni₃₅ alloys after all treated condition exhibits improved passivation properties, especially the 3min configuration compared with the as-received condition. Moreover, as expected, the localized corrosion resistance decreases with the increasing of chloride concentration as result of the amount of electroactive species present in the solution. On the other hand, the larger the grain size is, the worsen the anticorrosive characteristics of the material is.
- The EIS and XPS analyses results show that the thickness and the composition of the passive film formed on surface of different grain refinement of $Al_2Cr_5Cu_5Fe_{53}Ni_{35}$ alloys are different. The thickness of the passive film formed on the surface of 3min treated alloy is compact regarding the as-received configuration, which is attributed to the lower volume fraction of Cu and Ni considered detrimental elements in the passive layer
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ingredients. Therefore, decreasing the Cu or Ni amount in the passive film of $Al_2Cr_5Cu_5Fe_{53}Ni_{35}$ alloys can increase protective ability of the passive film.

• The Point Defect Model (PDM) approach provides a convincing argument with the passive film properties of the $Al_2Cr_5Cu_5Fe_{53}Ni_{35}$ alloys formed in seawater solutions. The values of polarizability (α), the cation vacancies at the metal/film interface (J_m) and the metal cation diffusivity at the metal barrier (D) increase along with larger grain sizes in the microstructure, indicating that the average grain dimension has a relevant impact on the stability of the passive film. According to the PDM analysis, the localized corrosion resistance of $Al_2Cr_5Cu_5Fe_{53}Ni_{35}$ alloys after 85% thickness reduction and annealing time period of 3min is remarkable superior than the other treated alloys in this study.

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420 Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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HIGHLIGHTS

- A new high entropy alloy system is developed whose compositional configuration is Al₂Cr₅Cu₅Fe₅₃Ni₃₅ especially developed for marine applications with the corresponding anticorrosive properties expected for this adverse operating environment.
- Anticorrosive surface properties of the alloy are greatly improved by grain refinement through cold rolling and annealing processes.
- Combine 85% thickness reduction with 3 min annealing time period yields the best material corrosion resistance properties after comprehensive electrochemical analyses campaign performed over all the considered heat treatment configurations.
- This salient noble behavior of this material condition also prevails when subjected to different seawater concentration solutions herein studied.

CRediT author statement

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Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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