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Passivation of Ni-Cr and Ni-Cr-Mo Alloys in Low and High pH Sulfate Solutions

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Abstract

The kinetics of passive oxide film formation, its thickening, and composition on Ni-22Cr and Ni-22Cr-6Mo wt.% alloys were investigated selected anodic potentials. Experiments were performed in acidic and alkaline sulfate environments using a number of characterization techniques including a combination of potentiodynamic polarization, on-line atomic emission spectro-electrochemistry (AESEC), *in situ* potentiostatic passive film growth, along with *in situ* neutron reflectometry (NR) and *ex situ* X-ray photoelectron spectroscopy (XPS). The roles of solution pH and Mo on the passivation behavior were discussed in terms of thermodynamic and kinetic factors governing passivation. The pH was found to have an impact on the relative chemical compositions of passive film of the Ni-22Cr alloy but not noticeably for the Ni-22Cr-6Mo alloy. Ni-rich films formed early during the passivation process while Cr(III) enrichment was observed at longer times albeit less extensively than observed previously in Cl⁻ solutions. The fraction of Cr(III) cations also increased with alloying of Mo at low and high pH demonstrating a strong effect of Mo on Cr(III) content during aqueous passivation in Ni based superalloys however a larger

effect is seen in Cl⁻. This is a noteworthy finding as Mo is usually assumed to mainly influence pit and crevice stabilization.

Introduction

The passivation of pure Ni metal¹⁻¹² and Ni-based alloys^{3,9,12-20} in sulfate environments has been studied to understand the formation, dissolution mechanisms, and the stability of the passive film. For Ni, its passive film is often described by a bilayer structure with an inner crystalline NiO and an outer porous, and hydrated Ni(OH)₂ layers. This structure is observed on alloys exposed to sulfuric and perchloric acidic, as well as to alkaline solutions with limiting thicknesses measured on the order of a few nanometers¹.

Electrochemical passivation can be greatly improved with the addition of alloying elements. At lower Cr concentrations, the passive film formed is predominantly NiO-based as there is not sufficient Cr present for formation of a continuous film^{16,21,22}. Previous work reported that the addition of a few at.% of Cr to Ni altered the preferred oxidation mechanism from one dominated by outward cation diffusion to one where oxygen ingress was substantial²³. Above approximately 13 at.% Cr, Ni-Cr alloys preferentially form a continuous Cr-rich oxide/hydroxide film because these particular compounds are more thermodynamically stable and also kinetically favored than Ni-rich ones^{15,22}. In the case of high temperature oxidation at 700 °C, it was observed that NiO formed first, followed by subsurface Cr₂O₃ enrichment at the inner interface and eventually the emergence of large NiCr₂O₄ islands¹⁷. While in general, the addition of Cr to Ni introduces excellent resistance to localized corrosion²⁴⁻²⁹ and increases passive film stability in halide-free acidic solutions^{18,30}, transpassive dissolution is possible for Cr-rich passive films in highly oxidizing environments^{27,29}. This can be remediated through alloying with other elements³¹⁻³³.

One of the most common alloying elements used in the Ni-Cr system for corrosion resistance improvement is Mo. Addition of Mo to pure Ni metal provides a less significant effect on the passive film structure compared to the effect of Cr. Ni alloyed with 13 wt.% Mo and passivated in 1 N Na₂SO₄ solution acidified to pH 2.8 has been studied using scanning transmission electron microscopy. The electron diffraction results indicated only the presence of crystalline NiO particles with approximately 3 nm diameters. Mo, however, was found to be either finely dispersed in the NiO film or present as an amorphous species that did not appear in the electron diffraction

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2
3 60 patterns⁹. While the addition of Cr alone improves the passivity of Ni-based alloys, Mo addition
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5 61 has been argued to impair passivity as evidenced by increases in the passive current density and
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7 62 the film growth rate²⁴. A defective, amorphous $(\text{Mo}^{+4}, \text{Mo}^{+6})_x\text{O}_y$ layer was produced which
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9 63 increases the defect concentrations in NiO, accounting for the observed increase in passive current
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11 64 density²⁵.

12 65 Alloying with both Cr and Mo, however, usually results in a highly synergistic relationship
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14 66 with regards to the passivity as seen in both the Fe and Ni-based systems³⁴. This effect is especially
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16 67 notable in chloride containing environments but corrosion resistance is similarly improved in
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18 68 acidic sulfate environments. For instance, Alloy 59 (Ni-22.5Cr-15.5Mo-0.9Fe, wt.%) has been
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20 69 studied in sulfuric acid solutions using potentiodynamic polarization, electrochemical impedance
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22 70 spectroscopy (EIS), X-ray photoelectron spectroscopy (XPS), and sputter depth profiling via
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24 71 Auger spectroscopy²⁶. The results indicated a substantial increase in the passivity of the material
25
26 72 when alloyed with high concentrations of Cr and Mo compared to pure Ni and its binary alloys.
27
28 73 Passive films formed in air exhibited (Cr, Ni)-oxide films whereas those formed in solutions were
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30 74 hydrated (Cr, Ni)-hydroxides²⁶. Additionally, the air-oxidized films were thicker by approximately
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32 75 a nanometer in sulfuric acid likely due to the competition between film growth and dissolution
33
34 76 absent in the case of the air films oxide. The passive film was not found to exhibit a bi-layered or
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36 77 multi-layered structure. Instead, XPS and Auger depth profiling suggested that the aforementioned
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38 78 oxide species were distributed throughout the film with no preferential segregation to the inner or
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40 79 outer interfaces²⁶. Additional work has been reported in aggressive sulfuric acid solutions (0.5 M)
41
42 80 deaerated by Ar and characterization by Time-of-Flight Secondary Ion Mass Spectrometry (ToF-
43
44 81 SIMS) as well as XPS^{30,35}. Passivation was achieved in this study at potentials of 0.25 V/SCE and
45
46 82 0.3 V/SCE, for Ni-20Cr and Ni-20Cr-10Mo (wt.%) respectively (by stepping the potential from
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48 83 OCP to the selected potential, and maintaining the polarization for 4 h. The film was found to be
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50 84 enriched in Cr(III) for both alloys, and Mo oxide was suggested to form between the outer/inner
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52 85 layers interface for the Mo-containing alloy^{30,35}. At higher potentials, soluble Mo species were
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54 86 formed. Cycles of spontaneous passivation after cathodic reduction supported the continuous
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56 87 accumulation of Mo cations in passive films. In other recent study, the potentiodynamic
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58 88 passivation of Ni-22%Cr and Ni-22%Cr-6%Mo, wt.%, alloys were investigated using elemental
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60 89 resolved polarization curves in aerated and deaerated sulfuric acid solutions¹⁸. Alloying with Mo

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2
3 90 improved the long-term passivity by favoring the formation of Cr_2O_3 in the film, and also resulted
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5 91 in significant Mo accumulation within the oxide. The most recent studies of the passive film
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7 92 growth on the Ni-Cr alloy systems with alloying elements in chloride deaerated solutions were
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9 93 conducted for long periods of exposure up to 10^5 s ^{31,36} and 10^6 s ³⁷. These studies showed that Ni(II)
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11 94 formed early, Cr(III) enrichment occurred with time changing the overall oxide film composition.
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13 95 Cr oxides and hydroxides were formed at short passivation times while spinels were detected at
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15 96 longer times^{31,36,37}. Mo was incorporated into these oxides. Therefore, while the studies in Cl^-
16
17 97 solutions provide information on the influence of Mo on Cr(III) enrichment in the passive film
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19 98 with time, the up-to-date ones in sulfate solutions do not contain such information. However, it is
20
21 99 essential to know how the minor alloying elements influence on the growth and the composition
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23 100 of the passive film in sulfate solutions, at both acidic and alkaline pH.

24
25 101 The objective of this study is to revisit the effects of Mo at fixed solution pH on the kinetics
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27 102 of passive film growth on Ni-based alloys over second to 10 ks times frames without the effect of
28
29 103 Cl^- on film dissolution. *In operando* film growth is analyzed by atomic emission
30
31 104 spectroelectrochemistry (AESEC), and single frequency-electrochemical impedance spectroscopy
32
33 105 (SF-EIS) measurements in both acidic and alkaline sulfate environments. The film composition,
34
35 106 thickness, and their variations with passivation time during a potentiostatic film growth are
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37 107 characterized using *ex situ* XPS and *in situ* neutron reflectometry (NR). The role of pH on passive
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39 108 film growth is investigated through direct comparison of a mildly acidic (pH 4) solution with a
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41 109 mildly alkaline one (pH 10). The results provide more insights into the role of Mo during acidic
42
43 110 and alkaline passive film growth and its synergistic relationship when alloyed with Cr.

44 111 **Materials and Experiments**

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46 112 The samples used in this study were polycrystalline, solid solution Ni-based alloys with
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48 113 the compositions of Ni-22Cr and Ni-22Cr-6Mo^A that model common Cr and Mo concentrations
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50 114 in commercial Ni-based superalloys. The materials were arc-melted, cast, rolled, recrystallized at
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52 115 $1100 \text{ }^\circ\text{C}$ for 40 min, quenched, and sectioned²⁷. Prior to each experiment, the samples were wet-
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54 116 polished up to 1200 grit using SiC paper, ultrasonically cleaned in ethanol and rinsed with

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60
^A In this study, Ni-22Cr (wt.%) and Ni-22Cr-6Mo (wt.%) alloys are denoted as Ni-22Cr and Ni-22Cr-6Mo, respectively. For XPS and AESEC calculations the alloys compositions in at. % - Ni-24Cr and Ni-24.7Cr-3.7Mo - were used.

117 deionized water (Milli-Q, resistivity of 18.2 M Ω -cm) before being placed into the electrochemical
118 cell.

119 The solutions used in film passivation experiments were 0.1 M Na₂SO₄ adjusted to pH 4
120 by 1.0 M H₂SO₄, and 0.1 M Na₂SO₄ pH 10 adjusted by 1.0 M NaOH. All solutions were prepared
121 using reagent grade chemicals and deionized water. During electrochemical experiments the
122 solutions were deaerated using N₂ gas.

123 An initial cathodic reduction step at -1.3 V vs. saturated calomel electrode (SCE) for 10
124 min was conducted before all electrochemical experiments in order to minimize the effect of air-
125 formed oxides on the alloy surface²⁸. Following the cathodic reduction step, potentiodynamic
126 polarization was performed from -1.3 V_{SCE} to +0.8 V_{SCE} with 1 mV/s scan rate, while *in situ*
127 monitoring the imaginary impedance (Z'') at 1 Hz using a 20 mV_{rms} AC signal. Similarly, after a
128 cathodic reduction step, potentiostatic passive film growth experiments were performed using the
129 single frequency EIS method at +0.2 V_{SCE} where the current density and Z'' was monitored at 1
130 Hz for 10 ks. The oxide thickness (l_{ox}) was estimated at the end of measurement. A full frequency
131 EIS spectrum was acquired from 100 kHz to 1 mHz to obtain the constant phase element exponent
132 (α), via a circuit model fit²⁸ and correlate $-Z''(t)$ to an oxide thickness, $l_{ox}(t)$ ²⁹. From these
133 results, the oxidation current density, $i_{ox}(t)$, may be calculated as:

$$l_{ox}(t) = \frac{-Z''(t)(2\pi f \epsilon \epsilon_0)^\alpha A}{\rho_\delta^{1-\alpha} \sin\left(\frac{\alpha\pi}{2}\right) [1 + 2.88(1 - \alpha)^{2.375}]} \quad \text{Equation 1}$$

$$i_{EC}(t) = i_{ox}(t) + i_{diss}(t) \quad \text{Equation 2}$$

$$i_{ox}(t) = \frac{n\rho_{ox}F}{M_{ox}} \frac{dl_{ox}}{dt} \quad \text{Equation 3}$$

$$\eta = \frac{i_{ox}}{i_{EC}} \quad \text{Equation 4}$$

134 Here f is the applied frequency, ϵ is the dielectric constant (30 assumed³⁸), ϵ_0 is the
135 vacuum permittivity of free space, A is the exposed sample area, ρ_δ is the boundary interfacial
136 resistivity (450 Ω - cm assumed³⁹), i_{EC} is the total anodic current density, i_{diss} is the total
137 measured dissolution current density, n is the cation valency, ρ_{ox} is the oxide or hydroxide density,
138 F is Faraday's constant, M_{ox} is the oxide molar mass, and η is the oxidation efficiency²⁹.

The AESEC was used to monitor the elemental dissolution rates during passivation. The detailed principles of this technique are available elsewhere^{40,41}. The specimen was vertically placed in a specially designed electrochemical flow cell. The electrolyte containing the cations released from the specimen were transferred to an inductively coupled plasma atomic emission spectrometer (ICP-AES, Ultima ExpertTM Horiba Jobin Yvon) for chemical analysis. The elemental concentration of the electrolyte as a function of time, $C_M(t)$, was calculated from the atomic emission intensity with a characteristic wavelength of the element M, $I_\lambda(t)$, as:

$$C_M(t) = \kappa[I_\lambda(t) - I_\lambda^0(t)] \quad \text{Equation 5}$$

where $I_\lambda^0(t)$ is the background signal, and κ is the sensitivity factor of M obtained separately from a standard ICP calibration method. The elemental current density ($i_{diss}^M(t)$), equivalent to the elemental dissolution rates, may be calculated as:

$$i_{diss}^M(t) = \frac{zFfC_M(t)}{A M_M} \quad \text{Equation 6}$$

where z is the oxidation state, f is the flow rate of the electrolyte (2.8 mL min⁻¹), F is Faraday constant, A is the exposed surface area (0.7 cm²), and M_M is the atomic mass of M.

Electrochemical control was achieved using a Gamry Reference 600 potentiostat. After the cathodic reduction at - 1.3 V_{SCE} for 10 min^{28,42}, a potentiostatic step to +0.2 V_{SCE}, was implemented to grow the passive film for up to 10,000 s. This potential is relevant to the long-term open circuit potential of Ni-Cr-Mo alloys in seawater and other natural environments where passivation occurs sometimes punctuated by crevice corrosion⁴³. Under this applied potential and at pH 4 and 10, the thermodynamically predominant oxidation states of the metals are Ni⁺², Cr⁺³, and Mo⁺⁶⁴⁴. The element-specific current density contributions for the cation species, M^{z+}, released into solution and not retained in the oxide as determined by the AESEC measurements, $i_{diss}^M(t)$, were summed to obtain the total current density for dissolution and cation ejection reactions:

$$i_{diss}(t) = \sum i_{diss}^M(t) \quad \text{Equation 7}$$

The $i_{diss}(t)$ value was then subtracted from the total electrochemically measured DC current density, i_{EC} , to estimate the total oxide formation current density, $i_{ox}(t)$ in equation 8:

$$i_{ox}(t) = i_{EC}(t) - i_{diss}(t) \quad \text{Equation 8}$$

In order to evaluate the contribution of a specific element M towards passivation rather than direct cation ejection or film dissolution, the expected element-specific dissolution current density based on congruent alloy dissolution^B where E_{app} is well above the oxidation potential for each element, $i_{cong\ diss}^M(t)$, was estimated:

$$i_{cong\ diss}^M(t) = z(at.\% M)i_{EC}(t) \quad \text{Equation 9}$$

and the oxidation current density contribution of element M may be obtained as follows:

$$i_{ox}^M(t) = i_{cong\ diss}^M(t) - i_{diss}^M(t) \quad \text{Equation 10}$$

The atomic composition of M cations at the surface, N_M , may be calculated as:

$$N_M = \frac{N_A}{zF} q_{ox}^M = \frac{N_A}{zF} \int_0^t i_{ox}^M(t) dt \quad \text{Equation 11}$$

$$A_M(t) = \frac{N_M(t)}{\sum N_M(t)} \quad \text{Equation 12}$$

where N_A is Avogadro's number and q_{ox}^M is the integrated oxidation charge for element M. It is recognized that this estimated cation composition does not account for potential layering nor say anything about the type of oxide or hydroxide formed just the moles oxidized but not dissolved and solubilized per unit area. Equation 12 gives the cation fraction again with no consideration of phase separation or solute capture (in other words the structure and layering cannot be determined). This was used to estimate the oxidized cation fraction that joined the surface layer over 10 ks as a comparison to XPS and NR.

The changes in film composition and thickness was characterized by *ex situ* XPS using PHI VersaProbe III instrument. The spectra were obtained for native air oxides, and periodically after 10 min of cathodic reduction at -1.3 V_{SCE} and potentiostatic passive film growth of 100s, 1000s and 10 ks at +0.2 V_{SCE}. This technique has been well-established for the analysis of the identity, concentration, and thicknesses of individual compounds present in surface thin films⁴⁵, especially for the case of Ni-based alloys^{28,46,47}. All XPS spectra were obtained using a monochromatic Al-K α photon source ($E = 1,486.7$ eV). The take-off angles between the sample

^B Congruent dissolution is a starting point and a reasonable assumption when there are large thermodynamic driving forces for dissolution of each alloying element, i.e. $i_{diss} \gg i_{ox}$.

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3 182 and detector were adjusted to 45 and 90°, whereas that between the detector and the X-ray source
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5 183 was fixed at 54.7° (Figure 1). The instrument was calibrated to the 4f_{7/2} binding energy (E = 84
6
7 184 eV) of a metallic Au reference measured at the same time. Survey spectra were recorded on all
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9 185 samples using a pass energy of 200 eV, followed by high resolution analysis of the Ni 2p, Cr 3p,
10
11 186 Mo 3d, and O 1s regions using a pass energy of 20 eV. No charge neutralization system was
12
13 187 employed. The samples were in the electrical contact with the stage.

14 188 Commercial CasaXPS software was used to perform Shirley background corrections and
15
16 189 spectra fitting based on the peaks and parameters for the expected oxide species⁴⁸⁻⁵⁰. The charge
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18 190 correction was done by shifting the C 1s peak binding energy to 284.8 eV, and then shifting all
19
20 191 other peaks to the same number of eV. The concentrations of Ni(II), Cr(III), and Mo(IV,VI) species
21
22 192 in the passive films were computed by fitting the spectra to their observed metallic and
23
24 193 oxide/hydroxide peaks, as established in previous literature^{46,47,50-53} and correcting these integrated
25
26 194 peak areas to atomic sensitivity factors for Ni, Cr, and Mo (4.044, 2.427, and 3.321 for this detector
27
28 195 and source configuration, respectively)⁵⁰ (Appendix A).

29 196 The calculation of XPS enrichment/depletion factor $f_{(Cr(III))}$ in passive film was
30
31 197 accomplished using equation⁵⁴:

$$f_A = \frac{A^{n+}/(A^{n+} + B^{m+} + C^{l+})}{A/(A+B+C)} \quad \text{Equation 13}$$

32
33 199 where A^{n+} , B^{m+} , C^{l+} – the cationic fraction of the element in the oxide; A, B, C – the atomic fraction
34
35 200 of the element in the alloy.

36
37 201 The molecular identity and the layering of passive films were also analyzed using *in situ*
38
39 202 neutron reflectometry. The experiments were conducted at the D3 beamline at the National
40
41 203 Research Universal (NRU) reactor (Chalk River, Ontario, Canada), shown schematically in Figure
42
43 204 B1 (Appendix B). This setup allowed NR measurements to be performed concurrently with
44
45 205 electrochemical experiments^C. Thin film samples for NR experiments were prepared by a sputter
46
47 206 deposition system (Plasmionique Inc., Quebec, Canada) to produce approximate 25 nm thick Ni-
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49 207 Cr and Ni-Cr-Mo alloys on 100 mm diameter x 6 mm thick polished Si (111) wafers. XPS analysis
50
51 208 following thin film preparation yielded bulk compositions of Ni-20Cr and Ni-20Cr-10Mo. The

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53
54 ^C Because of the unfortunate shutdown of the D3 neutron beam line, *in situ* passivation measurements were only
55 performed for 0.1 M Na₂SO₄ acidified to pH 4.

thin film samples for NR experiments were stored in a vacuum desiccator and, prior to experiments, were cleaned with methanol and dried in air.

A conventional three-electrode electrochemical cell with a Pt thin foil counter electrode and a KCl saturated Ag/AgCl reference electrode ($V_{\text{Ag/AgCl}} = +47 \text{ mV}_{\text{SCE}}$) was used. The electrochemical experiments were conducted under a Solartron 1287A potentiostat control. Similarly, to all mentioned above electrochemical experiments, the cathodic potential of $-1.3 \text{ V}_{\text{SCE}}$ was applied for 5 min^D. Then potentiostatic polarization from was performed from $-0.8 \text{ V}_{\text{SCE}}$ to $+0.2 \text{ V}_{\text{SCE}}$ (potentials were adjusted to SCE values for better data comparability) with 0.2 V steps every 6 hours (Figure B2, Appendix B). The NR measurements started 1 hour after the applied potential was switched to the set value and each measurement took approximately 90 min to complete. At least two measurements were performed in each potential step to ensure a steady-state was achieved before moving to the next applied potential. The D3 neutron beam characteristics could be found in²⁹ and Appendix B.

For analysis of the passive film composition and thickness, the SLD profiles of the unoxidized alloys deposited on Si, and of H₂O exposed to vacuum were simulated using GenX software with the interfacial roughness and SLD values of each layers obtained from experiments (Figure 2)⁵⁵. The SLD for the simulated base metals and electrolyte were then subtracted from the experimental SLD profiles, as indicated in Figure 2, in order to extract the SLD versus depth data for only the passive films.

Results

Electrochemistry of Ni-Alloys in Aqueous Sulfate Environments

The E-log(*i*) and $-Z''$ vs E curves of Ni-22Cr and Ni-22Cr-6Mo in the acidic and alkaline solutions of interest were established in Figure 3(a) & 3(b), respectively. The oxide thickness was estimated from $-Z''$ using Equation 1 and the results were plotted in the same graph as the impedance data (Figure 3(b)). In both solutions, the alloys exhibited a large passive range extending from the corrosion potential to above $+0.5 \text{ V}_{\text{SCE}}$ (Figure 3(a)). In addition, Ni-22Cr-6Mo exhibited lower passive current density than Ni-22Cr indicating the beneficial effect of Mo addition to the Ni-Cr system (Figure 3(a)).

^D A shorter time was used for the cathodic reduction for the NR experiments in order to minimize possible damage to the thin film sample caused by H₂ evolution.

237 The difference in passivity of Ni-22Cr and Ni-22Cr-6Mo near +0.2 V_{SCE} is evident in the
238 alkaline environment. At small anodic overpotentials (e.g., from -0.5 to 0 V_{SCE}), a lower passive
239 current density and a thicker oxide (or passive layer with different dielectric constant) according
240 to the impedance results were observed for the Mo-containing alloy which could be attributed to
241 the effect of the minor solute on inhibiting dissolution. In addition, the films formed on the same
242 alloy during cyclic polarization were, in general, thicker in the acidic environment compared to
243 those formed in the alkaline. The characteristic thickening and thinning rates of each alloy (i.e.,
244 the slopes of the oxide thickness vs. E curves in Figure 3(b)) were similar and were consistent with
245 passivity theory positing a few nm/V, with notably Ni-Cr film dissolution initiating at a lower
246 potential and occurring more rapidly than Ni-Cr-Mo alloy in the acidic environment. This is due
247 to a known electrochemical stabilization benefit of Mo⁴⁴.

248 ***SF-EIS Application to Ni-alloys over a range of pH levels***

249 Potentiostatic passivation of Ni-22Cr and Ni-22Cr-6Mo at +0.2 V_{SCE} in acidic (pH 4) and
250 alkaline (pH 10) 0.1 M Na₂SO₄ was monitored using SF-EIS to investigate the formation of passive
251 film. The $-Z''(t)$ as a function of time in the acidic environment for Ni-22Cr and Ni-22Cr-6Mo
252 obtained from the SF-EIS measurements at 1 Hz and +0.2 V_{SCE} are shown in Figure 4. The $-Z''(t)$
253 and the corresponding $l_{ox}(t)$, calculated from Equation 1, (assuming a Cr rich passive film) were
254 slightly smaller in alloys containing Mo. This can be seen in both the early stage of passive film
255 formation (i.e., a few seconds after potentiostatic experiment) and at longer periods during film
256 formation (i.e., above 1000 s). In addition, the passive film thickness did not change much after
257 approximately 1000 s for both Mo-free and Mo-containing alloys.

258 The passivation-time behavior of Ni-22Cr and Ni-22Cr-6Mo in 0.1 M Na₂SO₄ solution
259 adjusted to various pH values are shown in Figures 6a and 6b, respectively. It can be seen that at
260 all pH levels i_{ox} is below i_{EC} and η is less than 1 even in the most alkaline solution. At early
261 passivation times such as 10–100 s efficiency increases with increasing pH. At later times such as
262 1ks–10ks, efficiency approaches very low levels as the passive current density maintains a nearly
263 constant passive film thickness. The film thickness estimated by SF-EIS on both Ni-22Cr and Ni-
264 22Cr-6Mo increases with pH (Figure 5), likely due to the chemical stability of certain hydroxides
265 or oxides. This was confirmed through the analysis of the oxidation rate, i_{ox} , and the efficiency, η

(Equation 4), for the alloys, shown in Figure 6. As predicted by the faster passivation with increasing pH values, η generally increases for each alloy.

AESEC passivation of Nickel Alloys in 0.1 M Na₂SO₄

The equivalent elemental dissolution current densities, i_{diss}^M , determined using Equation 6 for the Ni-22Cr (Figure 7(a)) and Ni-22Cr-6Mo (Figure 7(b)) alloys in 0.1 M Na₂SO₄ pH 4 solution are shown by solid lines with a comparison to the partial electrochemical current densities for each element ($i_{cong\ diss}^M$) calculated using Equation 9. The differences between the i_{diss} versus time for each element (i_{diss}^{Ni} , i_{diss}^{Cr} , i_{diss}^{Mo}) and the corresponding $i_{cong\ diss}^M$ indicates the elemental contributions to the non-dissolved oxidized species accumulating on the surface in some manner. It should be noted that the i_{EC} for the AESEC figures were convoluted, taking into account the residence time distribution of the elemental dissolution signal in the flow cell⁴¹.

The low values of i_{diss} compared to i_{EC} indicates that there is a higher efficiency but less than 1 for oxide growth versus dissolution at early stage of passivation. However, a significant role of cation ejection during passivation in acidic sulfate solutions is evident. In the case of the Ni-22Cr, the AESEC data shown in Figure 7(a) indicates that there were non-dissolved oxidized Ni-species present for the initial stage of passivation, followed by later enrichment of a passive, Cr-rich oxide film.

The Ni-22Cr-6Mo shown in Figure 7(b) has similar initial Ni(II) formation accumulating on the surface over the first 10 s followed by Ni(II) mostly dissolving when oxidized during subsequent Cr-enrichment of the passive film. A gradual decrease in i_{diss}^{Ni} , nearly matches i_{EC} whereas i_{diss}^{Cr} and i_{diss}^{Mo} remain below i_{EC} at all times indicating that these cations accumulate on the surface or join the passive film. At longer times, a quasi-limiting thickness is attained (Figure 5(b)) and dissolution observed using AESEC corresponds to ejection of the alloying elements from the passive film and oxidation of elements to maintain the thickness in Figure 5. The gradual enrichment of Cr(III) accumulated continually occurs after 100 s, as shown in Figure 8(a), presumably as a result of favorable oxide film formation with Mo-alloying⁵⁶. The i_{diss}^{Mo} indicates that, after early Mo release during Cr-film enrichment, it likely becomes incorporated in the oxide at small concentrations.

294 Elemental dissolution rates of Ni-22Cr and Ni-22Cr-6Mo in the alkaline media, 0.1 M
295 Na₂SO₄ pH 10, were under the detection limits, therefore, are not presented herein. The cation
296 concentrations at the surface given in Figure 8(b) were approximated using the base metal alloying
297 content.

298 *Neutron Reflectometry of Nickel Alloys*

299 The reflectivity curves for the two alloys in 0.1 M Na₂SO₄ pH 4 are given in Figure 9.
300 These data sets were fitted using an algorithm developed by Parratt^{55,57-59} to produce neutron SLD
301 profiles versus depth (Figure 10). The reflectivity curves were best fitted using a passive film
302 model comprised of a single-phase inner oxide layer and an outer hydroxide layer rather than a
303 model comprised of separated inner oxide layers of NiO and Cr₂O₃ and an outer hydroxide layer.
304 At low depths, the SLDs were close to $-0.5 \times 10^{-6} \text{ \AA}^2$ corresponding to the electrolyte layer. At
305 greater depths (i.e., between approximately 50 and 110 Å in Figure 10(a) and between
306 approximately 150 and 270 Å in Figure 10(b)), the SLDs gradually increased to ca. $1.5 \times 10^{-6} \text{ \AA}^2$,
307 corresponding to the outer hydrated oxide layer. A steep increase in the SLD at higher depths (i.e.,
308 between approximately 110 and 130 Å in Figure 10(a) and between approximately 270 and 290 Å
309 in Figure 10(b)) corresponded to the interface between the outer hydrated oxide layer and the inner
310 oxide layer of the passive film. The humps in the SLD profiles at the depth between ca. 130 and
311 160 Å in Figure 10(a) and between ca. 290 and 320 Å in Figure 10(b) corresponded to the inner
312 oxide layers. Finally, the SLD of the base metal alloys was reached at greater depths. Annotated
313 on Figure 10 as horizontal lines are the theoretical SLD of several stoichiometric oxides and
314 hydroxides. SLD values of the inner oxide layers formed on the two alloys suggest the layers were
315 rich in Ni-oxide species.

316 Simulated SLD profiles for a non-equilibrium film with varying Cr(III) content were
317 produced using GenX software (Figure 11). One notable change in the SLD profiles of a non-
318 equilibrium film with varying Cr(III) is that when the content of Cr(III) increased, the SLD of the
319 oxide layer gradually decreased until it reached the theoretical SLD value of Cr₂O₃.

320 The SLD profiles of the stand-alone passive film after subtraction of the metal and
321 electrolyte SLDs (Figure 2) are shown in Figure 12. These results additionally allow for the
322 estimation of l_{ox} and the Cr(III) cation fraction using the width and height of the profile,
323 respectively. Films with an SLD closer to the theoretical SLD value of NiO ($8.7 \times 10^{-6} \text{ \AA}^2$) will

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3 324 have a lower % Cr(III) compared to those near the theoretical SLD value of Cr_2O_3 ($5.1 \times 10^{-6} \text{ \AA}^{-2}$),
4 325 2), and the non-stoichiometric film possessing an SLD in-between the two. The SLDs of the inner
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6 326 layer on both alloys were close to the theoretical SLD value of NiO suggesting the oxide films on
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8 327 both alloys were rich in Ni, similar to previous work^{46,60,61}. For Ni-Cr-Mo, the SLD of the outer
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10 328 layer decreased with increased potential suggesting a selective dissolution of Ni(II) in favor of Cr-
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12 329 enrichment as the potential increased (Figure 12(b)). The small SLD of the outer layer is attributed
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14 330 to a highly hydrated nature of the layer. The thickness of the outer layer was estimated to be several
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16 331 nm from the SLD profiles.

17 332 Analysis of the Cr(III) metal cation fraction and the passive film thickness was conducted
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19 333 using the profile width and peak SLD values in Figure 12. The Ni-Cr-Mo alloy exhibited greater
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21 334 Cr-enrichment in the oxide film than the Ni-Cr alloy across all potentials (Figure 13(a)). The film
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23 335 thickness was also consistently greater on the Ni-Cr-Mo alloy at every potential investigated in
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25 336 this work, suggesting the effect of Mo on promoting Cr-oxidation and passive film formation
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27 337 (Figure 13(b)). There is small variation in both Cr(III) cation fraction and film thickness with
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29 338 applied potentials due to relatively slow dissolution kinetics in sulfate environments. The slight
30
31 339 thinning of the film at higher potentials can be attributed to the transpassive oxide dissolution. At
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33 340 higher potentials (e.g. $+550 \text{ mV}_{\text{SCE}}$)⁴⁴, fast transpassive dissolution of Cr(III) would result in more
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35 341 noticeable thinning⁶².

342 *XPS Analysis of Nickel Alloys*

36 343 An example of the deconvolution of the XPS spectra for the Ni-Cr-Mo alloy passivated at
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38 344 $+0.2 \text{ V}_{\text{SCE}}$ for 10 ks after 600 s of cathodic potential step at $-1.3 \text{ V}_{\text{SCE}}$ in $0.1 \text{ M Na}_2\text{SO}_4$ pH 4 is
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40 345 shown in Figure 14. The fitted peaks are consistent with the presence of $\text{Ni}(\text{OH})_2$, NiO, $\text{Cr}(\text{OH})_3$,
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42 346 Cr_2O_3 , MoO_2 , and MoO_3 in the passive film but contain no structural verification. It should be
43
44 347 noted that previous literature has additionally identified spinel compounds (e.g. NiCr_2O_4)^{16,17,63-65},
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46 348 but it was found that during peak fitting these phases only constituted an insignificant fraction (\leq
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48 349 1%) of the total integrated area and as such were excluded from the current analysis.

49 350 The comparison of the XPS fitted data of native-formed oxide film (Figure 8(a) & (b)) and
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51 351 that of the film after cathodic reduction (Table 1) showed a slight higher cation fraction of Cr(III)
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53 352 for Ni-22Cr alloy after cathodic reduction step at $-1.3 \text{ V}_{\text{SCE}}$ in both acidic and alkali solutions but
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55 353 only for Ni-22Cr-6Mo in acidic solution. At the same time, the composition of the film on Ni-

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3 354 22Cr-6Mo after cathodic reduction in 0.1 Na₂SO₄ pH10 solution remained close to the native-
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5 355 formed oxide. It must be mentioned that the thickness of the film after the cathodic reduction step
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7 356 was much lower (according to a comparison of the intensity of metal and metal oxides/hydroxides
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9 357 peaks), and the composition of the film underlying alloy layer remained almost unchanged.

10 358 The XPS enrichment/depletion factor $f_{Cr(III)}$ in passive film calculated by equation 13⁵⁴
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12 359 (Figure 15) shows that at pH 4, the Ni-22Cr alloy (Figure C1, Appendix C) exhibited lower
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14 360 enrichment of Cr-species in its passive film than Ni-22Cr-6Mo (Figure C2, Appendix C), resulting
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16 361 in a higher cation fraction of Cr(III) in the passive film when Mo was alloyed. Upon comparing
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18 362 passivation in an acidic environment (Figure 8(a)) to that in an alkaline one (Figure 8(b)), there is
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20 363 an apparent difference in the composition between the films. The fraction of Ni(II) measured using
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22 364 XPS peak fitting and AESEC analysis remained steady for the Ni-22Cr alloy, whereas there was
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24 365 slight but statistically significant enrichment of Cr(III) within the film on the Ni-22Cr-6Mo alloy
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26 366 throughout the passivation time (Figure 15). For all times, there was additionally a slightly greater
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28 367 fraction of Cr(III) within the film on the Ni-22Cr-6Mo alloy than on the Ni-22Cr alloy after 10 ks
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30 368 (Figure 8(a)). Finally, the calculated cation fractions of Mo(IV,VI) in the passive film were lower
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32 369 for pH 10 (Figure 8(b)) than that observed at pH 4 (Figure 8(a)) probably due to MoO₃²⁻ stability
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34 370 at high pH.

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36 371 In the alkaline environment, the measured Ni 2p^{3/2} spectra were predominantly
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38 372 representative of Ni metal and Ni(OH)₂ (Figures C3 and C4, Appendix C) and Cr metal and
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40 373 Cr(OH)₃ for the Cr 2p_{3/2} spectra. Spectral fitting suggests there were some oxide species present at
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42 374 all times in the acidic environment because of its favorable thermodynamics over the hydroxides,
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44 375 whereas both were stable at pH 10 and the oxides became hydrated Ni(OH)₂ and Cr(OH)₃. Less
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46 376 Mo(IV,VI) was found within the alkaline passive film. This can be attributed to its poor
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48 377 thermodynamic stability in high pH environments⁴⁴.

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50 378 Following the 10 ks passivation, the films formed on Ni-22Cr and Ni-22Cr-6Mo in both
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52 379 the acidic and alkaline environments were analyzed using an XPS take-off angles of 45° and 90°
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54 380 (Figure C5 to Figure C7, Appendix C). The spectra are normalized to the intensity of the metal
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56 381 peaks to demonstrate the increased sensitivity for the surface chemistry and suggest any
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58 382 preferential outer environment of certain oxide species. The spectra were representative of the
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60 383 same oxide/hydroxide species. Spectral fitting, however, demonstrated that there was slight

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3 384 enrichment of Ni(II) species and depletion of Cr(III) at the film/solution interface following
4 385 passivation in the alkaline environment for both Ni-Cr and Ni-Cr-Mo (Figure 16). Notably,
5 386 Mo(IV,VI) was not affected by the preferential Ni(II) surface enrichment and appears to be present
6 387 at a similar concentration throughout the film. No clear surface enrichment was observed for the
7 388 films formed in the acidic environment.

389 Discussion

390 Passive film formation is rapid during single step passivation and efficiency lower than
391 100% for Ni(II), Cr(III) and Mo(IV, VI). For every nanometer of oxide formed, 0.5 nm of metal
392 is dissolved at 100% efficiency. The results strongly suggest an early pre-dominance by
393 hydroxylated NiO or Ni(OH)₂, possibly containing solute captured Cr(III), followed by very slow
394 enrichment of Cr(III) within the passive film during single step passivation. Evidence of solute
395 capture are suggested by initial oxide cation fractions very close to the alloy element fractions and
396 the slow dissolution rate of Ni in sulfate at pH 10 relative to Cl⁻ where Cr(III) enrichment is faster.
397 During single step passivation a pseudo steady state is reached after 1000 s⁶⁶ and in pH 10 sulfate
398 remain rich in Ni(II). Alloying with Mo supports some later and gradual preferential oxidation of
399 Cr to Cr(III) within the film, resulting in Ni(II) cation ejection. Mo, when included as a minor
400 alloying element, becomes incorporated into the passive film in low concentrations.

401 The results performed in the mildly acidic (pH 4) and mildly alkaline (pH 10) sulfate
402 environments demonstrate different characteristics of the passive films formed in each
403 environment. Less preferential Ni-dissolution and subsequent Cr-enrichment was observed in the
404 alkaline environment, probably due to the increased thermodynamic stability of these oxides and
405 the lower solubility of NiSO₄ compared to NiCl₂⁶⁷ (Figure 8(b)). This is supported by Pourbaix's
406 predictions⁴⁴, where NiO and Ni(OH)₂ are thermodynamically stable at pH > 5. The lack of
407 significant Cr enrichment in the passive films compared to previous studies performed in chloride
408 environments²⁹ demonstrates the influence of preferential dissolution of Ni(II) on the evolution of
409 passive film compositions. Passivation in a sulfate environment still supports the previous theory⁶⁶
410 that Mo alloying promotes the oxidation of Cr. The calculated enrichment of Mo(IV,VI) cations
411 was lower for pH 10 (Figure 8(b)) than that observed at pH 4 (Figure 8(a)), due to its
412 thermodynamic instability and likely selective dissolution in the alkaline environment as MoO₄²⁻.

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3 413 The passive films formed in the acidic sulfate environment exhibited a distribution of
4 414 cations that suggests nonequilibrium solute capture (Figure 11(a)), where a mixed oxide is
5 415 speculated (e.g. $\text{Ni}_{1-x}\text{Cr}_x\text{O}_y$) was observed instead of the traditionally expected, phase-distinct,
6 416 bilayer structure (e.g. $\text{NiO}/\text{Cr}_2\text{O}_3/\text{Ni-Cr(-Mo)}$) (Figure 11(b)). For the film formed in the alkaline
7 417 sulfate environment, however, angle-resolved XPS exhibited some outer enrichment of
8 418 predominantly NiO (Figure 16). The difference was, albeit, slight but the stability of Ni(II) in the
9 419 film resulted in some segregation to the film/solution interface. Interestingly, Mo was not observed
10 420 to vary in composition throughout the film formed in either environment as a result of solute
11 421 capture. Due to the low concentration within the alloy, no segregation was observed.

12 422 The passive dissolution rate and breakdown of the oxide are often attributed to and rates
13 423 regulated by the features and properties of the passive film. It is clear that the passive films of Ni-
14 424 Cr-X alloys take on many forms depending of exposure conditions and aging (exposure time).
15 425 Caution is therefore warranted in assigning corrosion properties under any one condition given a
16 426 that a large variety of passive film characteristics can be realized depending on anion (i.e., Cl^- vs
17 427 sulfate), pH, growth rate and potential, exposure aging time. These variable need to be precisely
18 428 controlled in order to produce a particular passive film which then governs the electrochemical
19 429 corrosion properties likely in many cases to rely heavily on the exact make-up of the oxide.

30 430 **Conclusions**

31 431 The passivation and dissolution of Ni-22Cr and Ni-22Cr-6Mo (wt.%) alloys, were
32 432 investigated in both acidic and alkaline Na_2SO_4 environments under potentiostatic conditions using
33 433 *in operando* AESEC and SF-EIS, *in situ* NR, and *ex situ* XPS. The combination of the AESEC
34 434 technique may enable determination of i_{ox} distinctly from i_{EC} with high temporal resolution. It
35 435 was determined that Ni-rich films form early during the passivation process, indicating the
36 436 substantial influence of kinetic factors. At longer times, Cr(III) enrichment was observed when
37 437 thermodynamics predominated the film composition. Surface films formed during potentiostatic
38 438 polarization at $+0.2 \text{ V}_{\text{SCE}}$ were consistent with non-stoichiometric solid solution rock salt and
39 439 corundum oxide structures, likely containing solute captured Ni(II), Cr(III), and Mo(IV,VI)
40 440 cations. No substantial layering was observed during oxide formation, with the films instead being
41 441 Ni-rich at the film/electrolyte and Cr-rich at the metal/film interfaces. Oxides were first formed,
42 442 with compositions governed by non-equilibrium solute capture. The electrochemical stability of

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3 443 Cr(III) cations also increased with alloying of Mo in the base metal, noted by the respective
4 444 dissolution currents being measured below the detection limit for the Ni-22Cr-6Mo alloy in each
5 445 environment. Surface films formed during anodic polarization in the alkaline environment were
6 446 found to be enriched in Ni(II) cations because of the increased stability of NiO and Ni(OH)₂.

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Appendix A – The Cation Concentrations Calculation from the XPS Data

$$x_{Ni^{2+}} = \frac{\frac{A_{NiO}^{tot} + A_{Ni(OH)_2}^{tot}}{S_{Ni}}}{\left[\frac{A_{NiO}^{tot} + A_{Ni(OH)_2}^{tot}}{S_{Ni}} + \frac{A_{Cr_2O_3}^{tot} + A_{Cr(OH)_3}^{tot}}{S_{Cr}} + \frac{A_{MoO_2}^{tot} + A_{MoO_3}^{tot}}{S_{Mo}} \right]} \quad \text{Equation A1}$$

$$x_{Cr^{3+}} = \frac{\frac{A_{Cr_2O_3}^{tot} + A_{Cr(OH)_3}^{tot}}{S_{Cr}}}{\left[\frac{A_{NiO}^{tot} + A_{Ni(OH)_2}^{tot}}{S_{Ni}} + \frac{A_{Cr_2O_3}^{tot} + A_{Cr(OH)_3}^{tot}}{S_{Cr}} + \frac{A_{MoO_2}^{tot} + A_{MoO_3}^{tot}}{S_{Mo}} \right]} \quad \text{Equation A2}$$

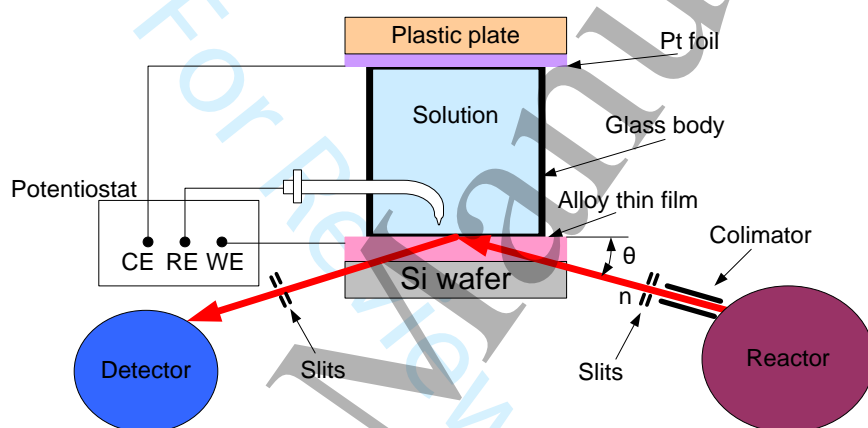
$$x_{Mo^{4,6+}} = \frac{\frac{A_{MoO_2}^{tot} + A_{MoO_3}^{tot}}{S_{Mo}}}{\left[\frac{A_{NiO}^{tot} + A_{Ni(OH)_2}^{tot}}{S_{Ni}} + \frac{A_{Cr_2O_3}^{tot} + A_{Cr(OH)_3}^{tot}}{S_{Cr}} + \frac{A_{MoO_2}^{tot} + A_{MoO_3}^{tot}}{S_{Mo}} \right]} \quad \text{Equation A3}$$

621 where χ_{M^+} is the cation fraction of a generic cation, M^+ , $A_{M^+}^{tot}$ is the integrated XPS peak area for
 622 a generic metal oxide/hydroxide, and S_M is the atomic sensitivity factor for different metals given
 623 above.

624

625 Appendix B – Neutron Reflectometry Experiment

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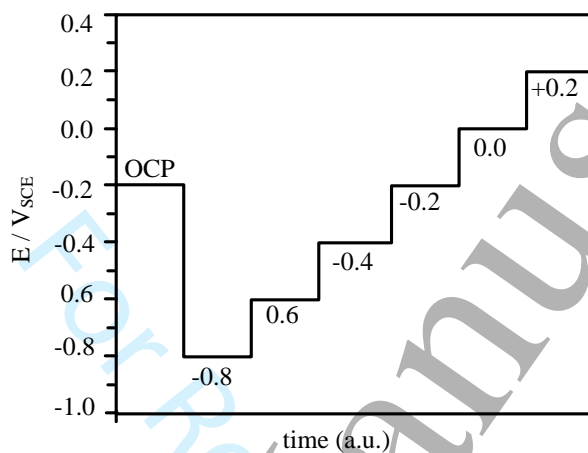


627
 628 Figure B1. Schematic of the *in situ* neutron reflectometry (NR) experiment at the D3 beamline in
 629 the NRU reactor. Collimated neutron beam with a wavelength of 2.37 Å was used for neutron
 630 measurements. A custom three-electrode electrochemical cell was employed for chemical and
 631 potential condition control.

632
 633 D3 uses a collimated neutron beam with a wavelength of 2.37 Å. The neutron beam
 634 travelled through the Si wafer before it reached the metal/electrolyte interface at a small grazing
 635 angle. The intensity of the specular reflected beam was recorded at different grazing angles and
 636 the reflectivity curves were plotted as a function of the scattering vector, Q_{beam} , whose magnitude
 637 is related to the incident beam angle, θ , and the neutron wavelength, λ , by the following
 638 expression^{57,58}:

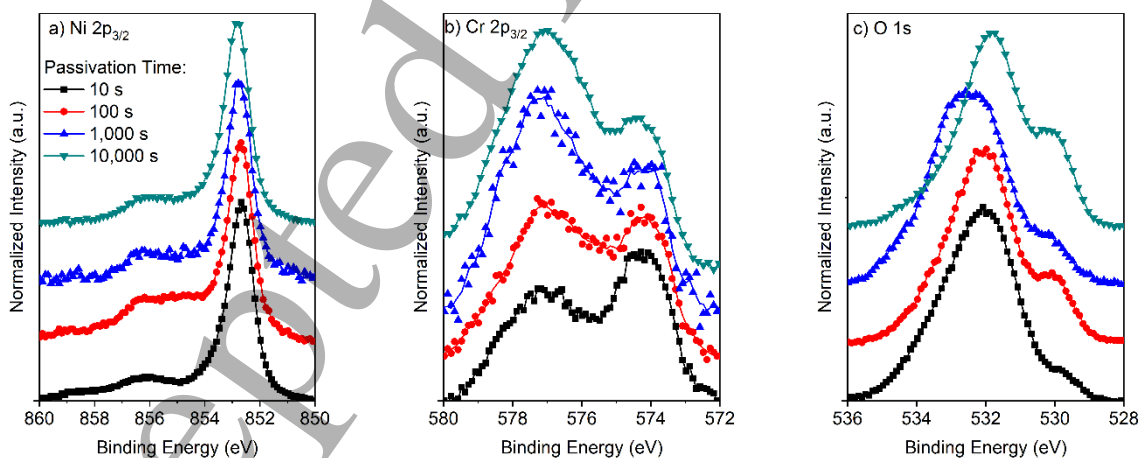
$$Q_{beam} = \frac{4\pi}{\lambda} \sin \theta \quad \text{Equation B1}$$

639 The thickness, roughness, and scattering length density (SLD) profile of the layers in the thin film
 640 sample were obtained by fitting the reflectivity curves to a thin film model using a least square fit
 641 algorithm which includes a recursion algorithm developed by Parratt^{55,57-59}.

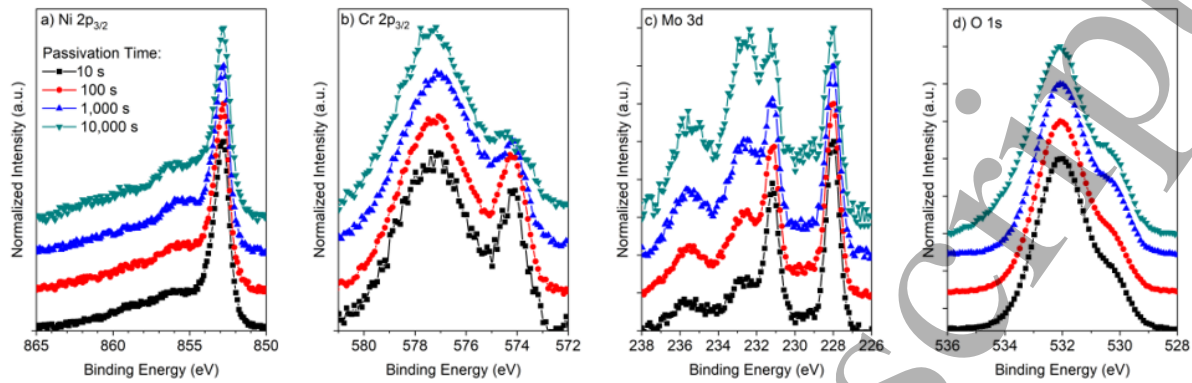


643
 644
 645 Figure B2. A schematic of the potential steps during *in situ* neutron reflectometry experiments.

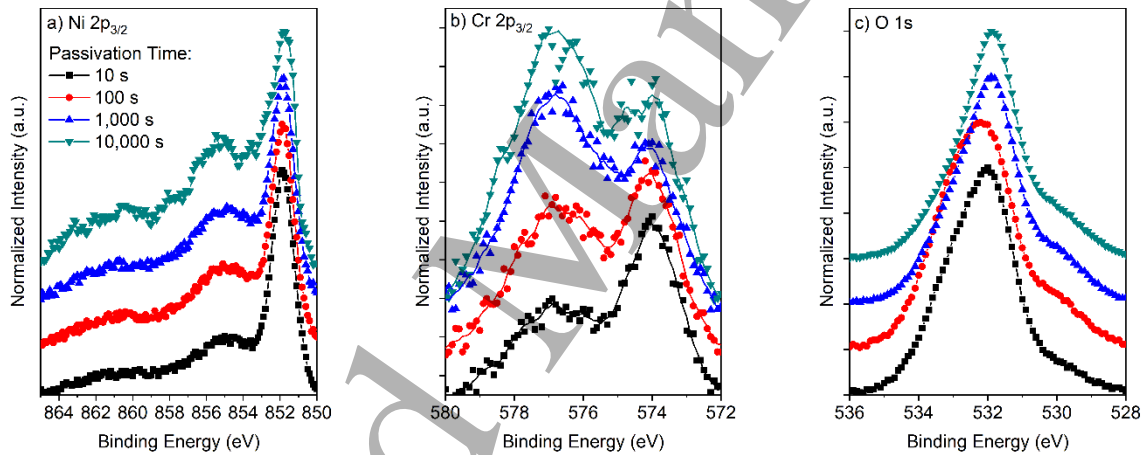
646
 647 **Appendix C – XPS analysis of the films formed on Ni-22Cr and Ni-22Cr-6Mo in both the**
 648 **acidic and alkaline environments during the passivation**



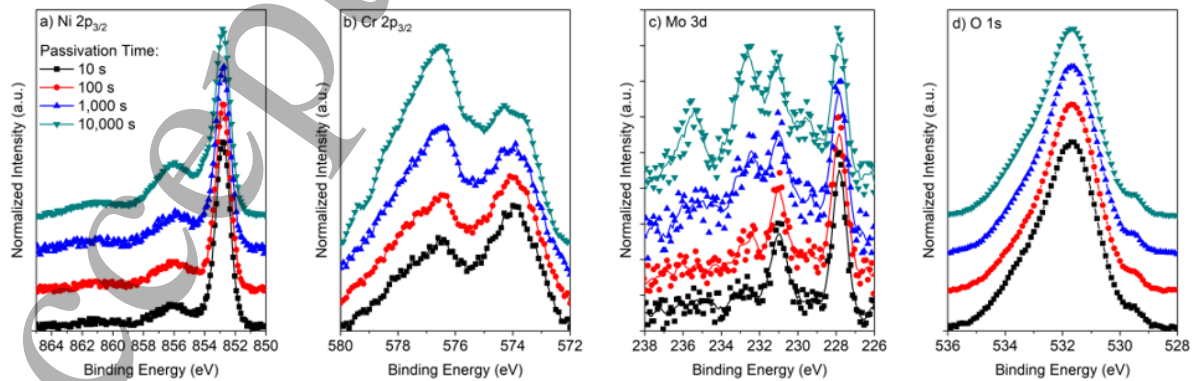
649
 650 Figure C1. a) Ni 2p_{3/2}, b) Cr 2p_{3/2}, and c) O 1s peaks normalized to the metal peaks for Ni-22Cr
 651 alloy passivated at +0.2 V_{SCE} for various times up to 10 ks in 0.1 M Na₂SO₄ pH 4.
 652



653
654 Figure C2. a) Ni $2p_{3/2}$, b) Cr $2p_{3/2}$, c) Mo 3d, and d) O 1s peaks normalized to the metal peaks for
655 Ni-22Cr-6Mo alloy passivated at $+0.2 V_{SCE}$ for various times up to 10 ks in 0.1 M Na_2SO_4 pH 4.
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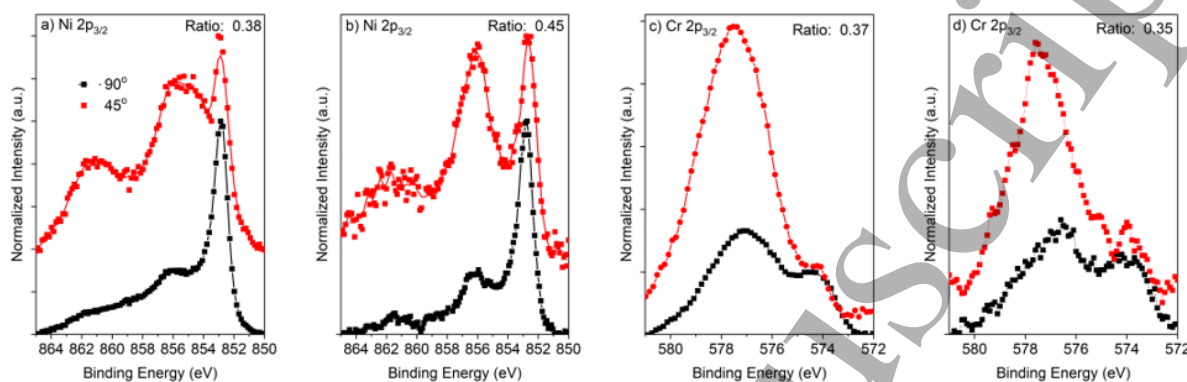


657
658 Figure C3. a) Ni $2p_{3/2}$, b) Cr $2p_{3/2}$, and c) O 1s peaks normalized to the metal peaks for Ni-22Cr
659 alloy passivated at $+0.2 V_{SCE}$ for various times up to 10 ks in 0.1 M Na_2SO_4 pH 10.
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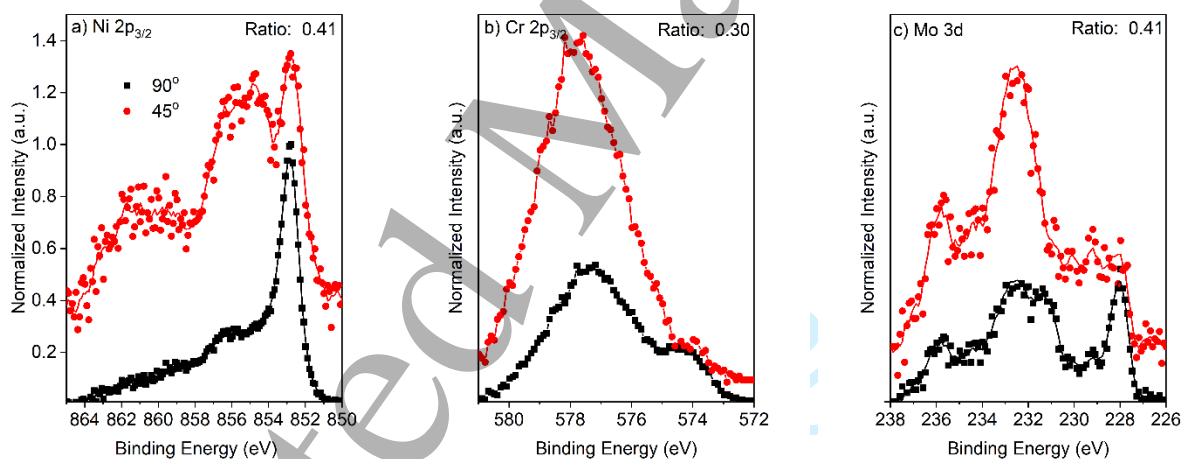


661
662 Figure C4. a) Ni $2p_{3/2}$, b) Cr $2p_{3/2}$, c) Mo 3d, and d) O 1s peaks normalized to the metal peaks for Ni-22Cr
663 alloy passivated at $+0.2 V_{SCE}$ for various times up to 10 ks in 0.1 M Na_2SO_4 pH 10.
664

662 Figure C4. a) Ni $2p_{3/2}$, b) Cr $2p_{3/2}$, c) Mo $3d$, and d) O $1s$ peaks normalized to the metal peaks for
 663 Ni-22Cr-6Mo alloy passivated at $+0.2 V_{SCE}$ for various times up to 10 ks in 0.1 M Na_2SO_4 pH
 664 10.



665 Figure C5. a,b) Ni $2p_{3/2}$ and c,d) Cr $2p_{3/2}$ angle-resolved XPS spectra which were normalized to
 666 the metal peaks for Ni-22Cr alloy passivated at $+0.2 V_{SCE}$ for various times up to 10 ks in
 667 0.1 M Na_2SO_4 a,c) pH 4 and b,d) pH 10. The ratio of the oxide areas for each angle measurement
 668 is included for reference.
 669



670 Figure C6. a) Ni $2p_{3/2}$, b) Cr $2p_{3/2}$, and c) Mo $3d$ angle-resolved XPS spectra which were
 671 normalized to the metal peaks for Ni-22Cr-6Mo alloy passivated at $+0.2 V_{SCE}$ for various times
 672 up to 10 ks in 0.1 M Na_2SO_4 pH 4. The ratio of the oxide areas for each angle measurement is
 673 included for reference.
 674

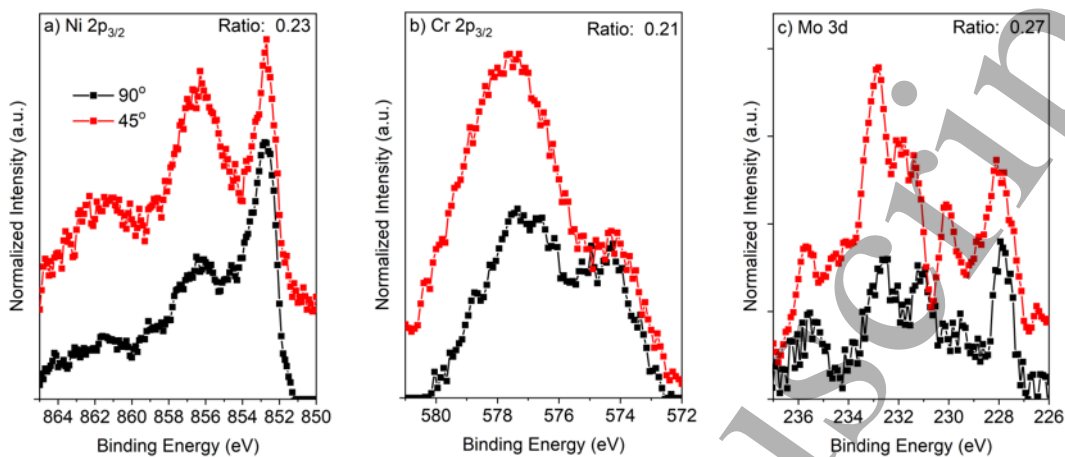


Figure C7. a) Ni $2p_{3/2}$, b) Cr $2p_{3/2}$, and c) Mo 3d angle-resolved XPS spectra which were normalized to the metal peaks for Ni-22Cr-6Mo alloy passivated at +0.2 V_{SCE} for various times up to 10 ks in 0.1 M Na₂SO₄ pH 10. The ratio of the oxide areas for each angle measurement is included for reference.

Figures

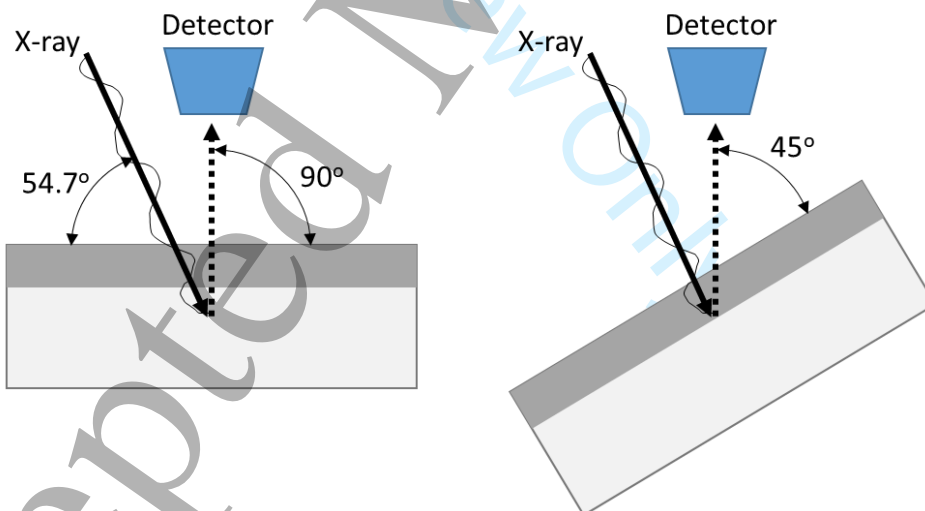
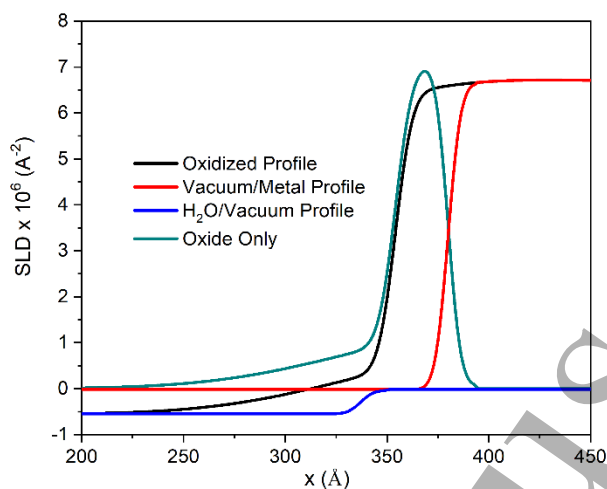
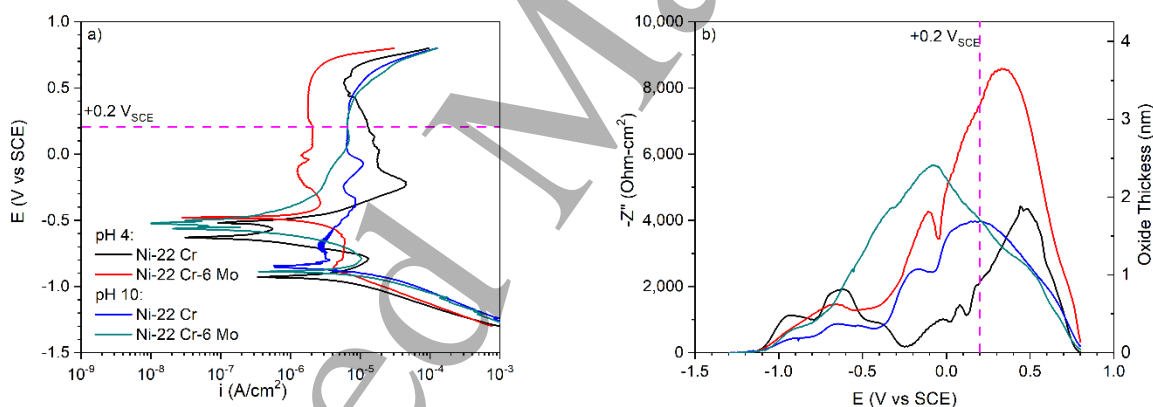


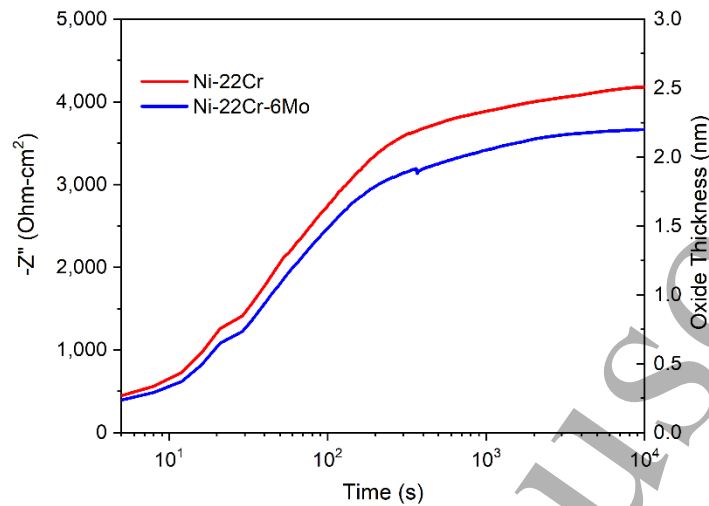
Figure 1. Schematic of the angle-resolved XPS set-up and effect of sample tilting on the probe depth.



687
688 Figure 2. Sample profile subtraction for passivated Ni-22Cr-6Mo, wt%, where SLD profiles for
689 the unoxidized metal and the H₂O were subtracted from the experimental data in order to isolate
690 the profile for the passive film. The same analysis method was applied for all alloys and
691 environments.

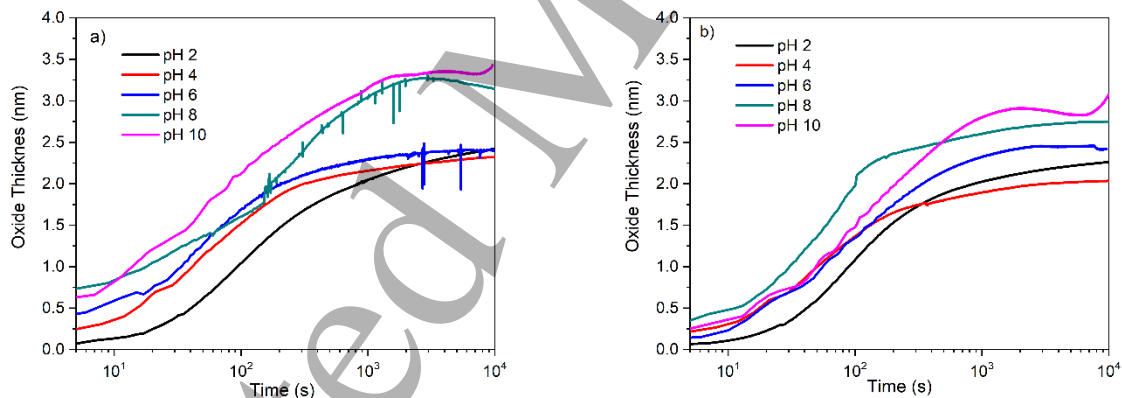


692
693
694 Figure 3. (a) DC current and (b) AC impedance variations during upward potentiodynamic
695 polarization of Ni-22Cr and Ni-22Cr-6Mo alloys in deaerated 0.1 M Na₂SO₄ at pH 4 and 10 with
696 the potential used in this study (+0.2 V_{SCE}) indicated by the dotted lines.
697



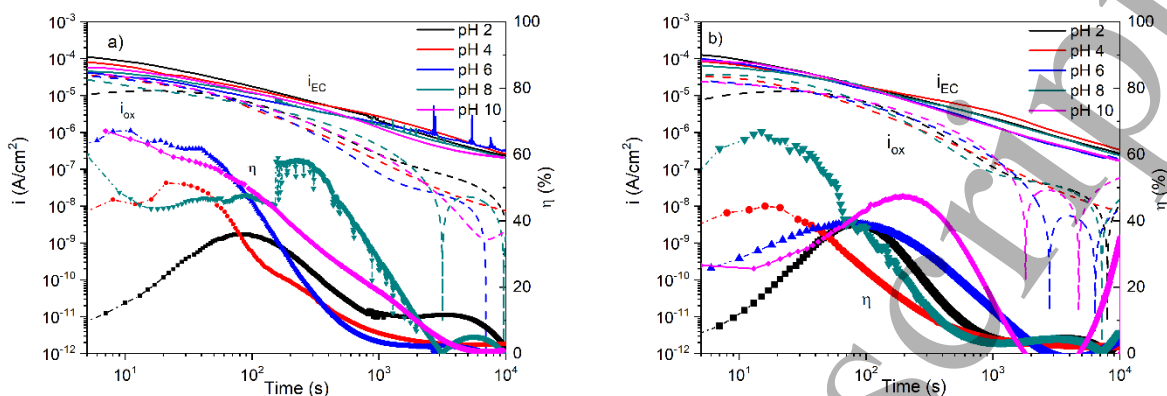
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Figure 4. Measured increase in $-Z''$ at 1 Hz during passivation of various Ni-based alloys at $+0.2 V_{SCE}$ in deaerated $0.1 M Na_2SO_4$ pH 4 solution for 10 ks with a subsequent full EIS spectrum obtained and fitted in order to compare l_{ox} for each method at the end of the passivation.

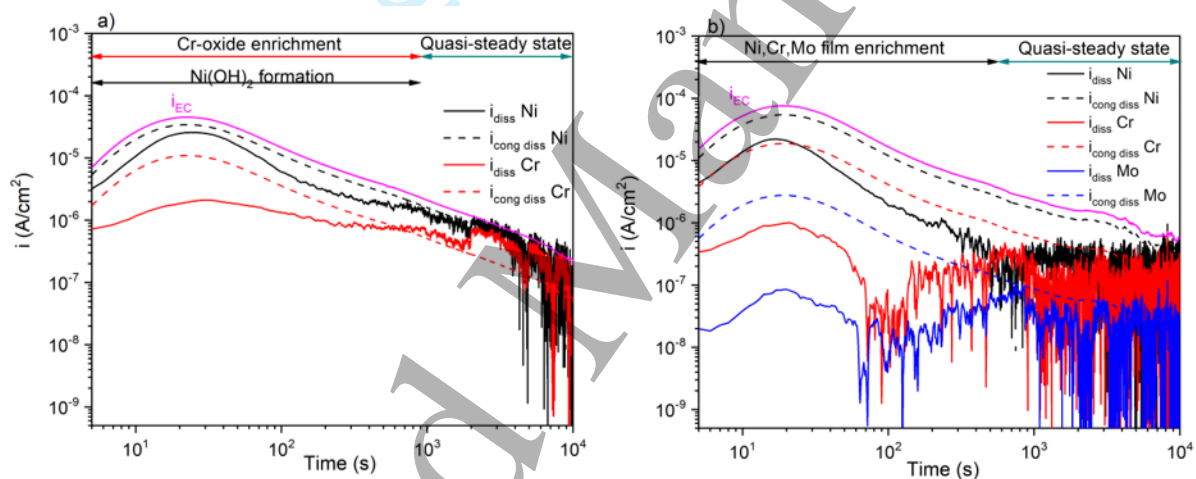


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Figure 5. Influence of electrolyte pH on the measured film thickness, l_{ox} , computed using Equation 1 for (a) Ni-22Cr alloy (b) Ni-22Cr-6Mo in $0.1 M Na_2SO_4$ solutions.



710
711
712 Figure 6. Influence of electrolyte pH on the measured i_{EC} and i_{ox} computed using the SF-EIS
713 results in Figure 5 and Equation 3, and the current efficiency, η , computed using Equation 4 for
714 the (a) Ni-22Cr alloy and, (b) Ni-22Cr-6Mo in 0.1 M Na_2SO_4 solutions.



715
716
717 Figure 7. Experimentally determined i_{EC} and experimental i_{diss} AESEC current densities for cation
718 emission versus total element specific current densities for congruent dissolution from the alloys
719 (a) Ni-22Cr and, (b) Ni-22Cr-6Mo held at +0.2 V_{SCE} in 0.1 M Na_2SO_4 pH 4 solution.

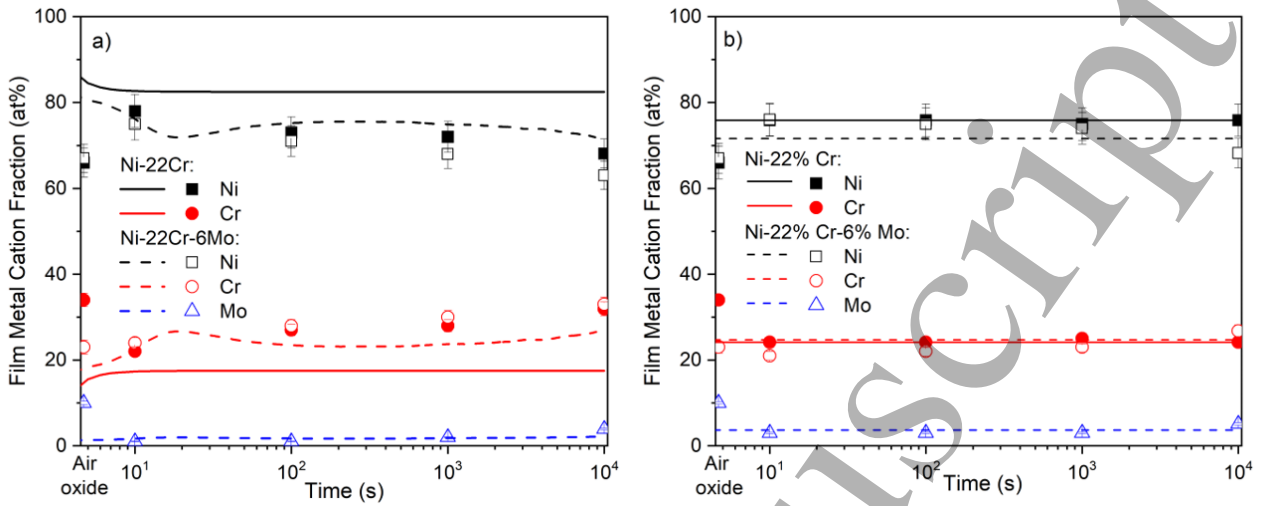


Figure 8. Relative accumulation of metal cations in the passive films during growth at +0.2 V_{SCE} according to AESEC (lines) and XPS (symbols) measurements on the Ni-22Cr and Ni-22Cr-6Mo alloys in 0.1 M Na₂SO₄ (a) pH 4 and, (b) pH 10 solution. Native (air-oxide) composition according to XPS marked at 0 time (symbols).

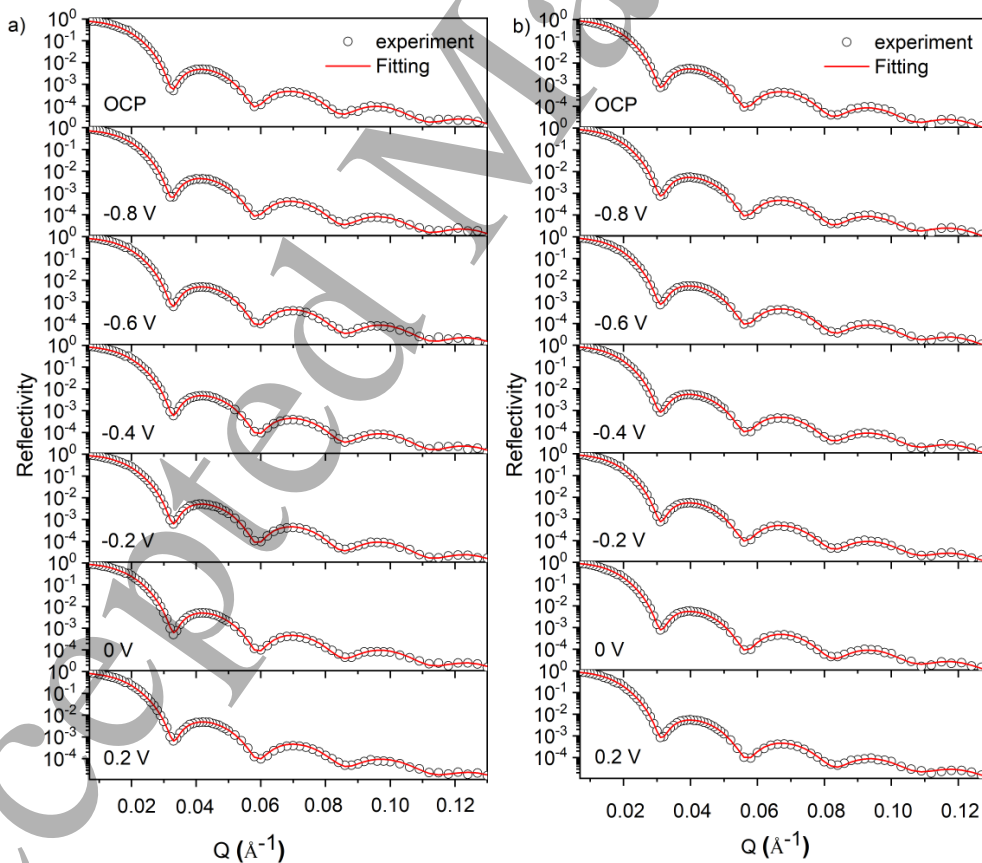
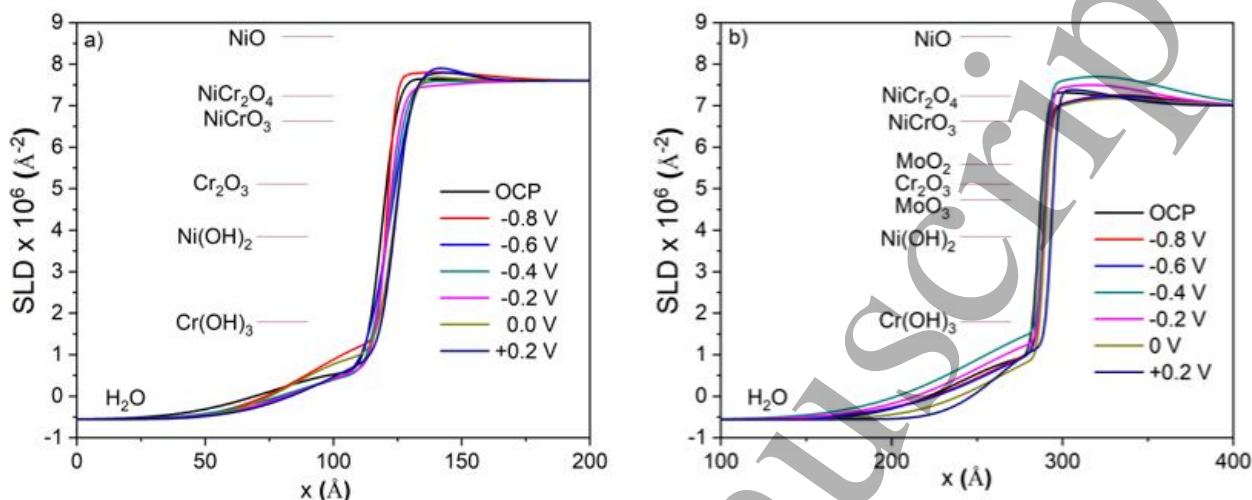
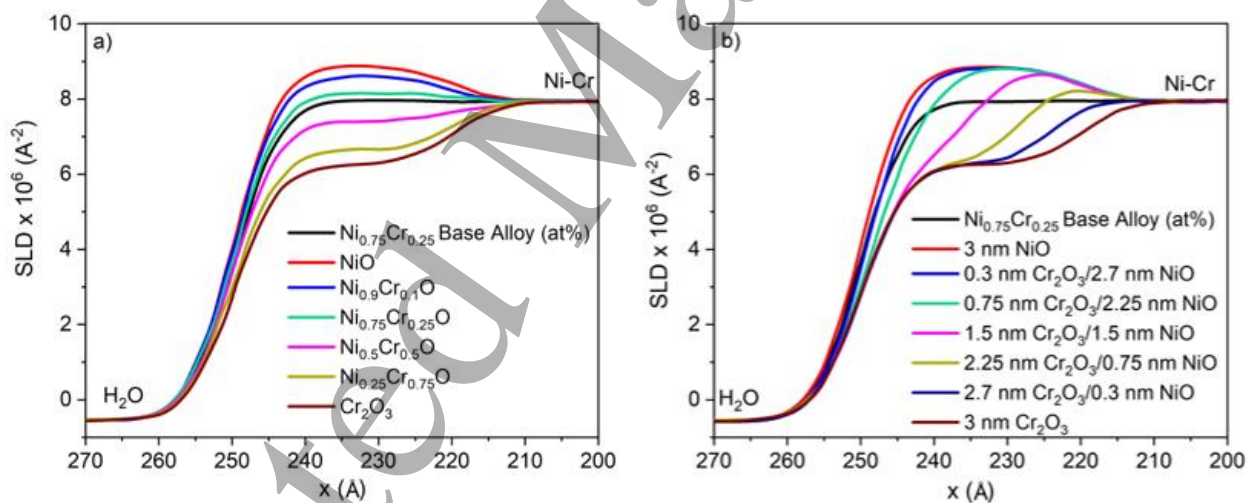


Figure 9. Measured reflectivity curves for a) Ni-20Cr and b) Ni-20Cr-10Mo films oxidized in 0.1 M Na₂SO₄ pH 4 solution at various potential steps (Figure B2, Appendix B). The NR

731 measurements started 1 hr after the applied potential was switched to the set value and each
732 measurement took approximately 90 minutes to complete



733
734 Figure 10. Full SLD profiles for a) the Ni-20Cr film and b) the Ni-20Cr-10Mo film oxidized in
735 0.1 M Na_2SO_4 pH 4 solution at various potential steps. The theoretical SLD values for differrent
736 materials are indicated by horizontal lines.
737



738
739 Figure 11. Simulated SLD profiles for a) a non-stoichiometric oxide, $\text{Ni}_{1-x}\text{Cr}_x\text{O}$, containing
740 varying % Cr^{3+} and b) a bilayer oxide comprised of Cr_2O_3 and NiO with varying thickness of
741 each conformal layer. An interfacial roughness of 5 \AA was used to replicate the experimental
742 parameter.
743

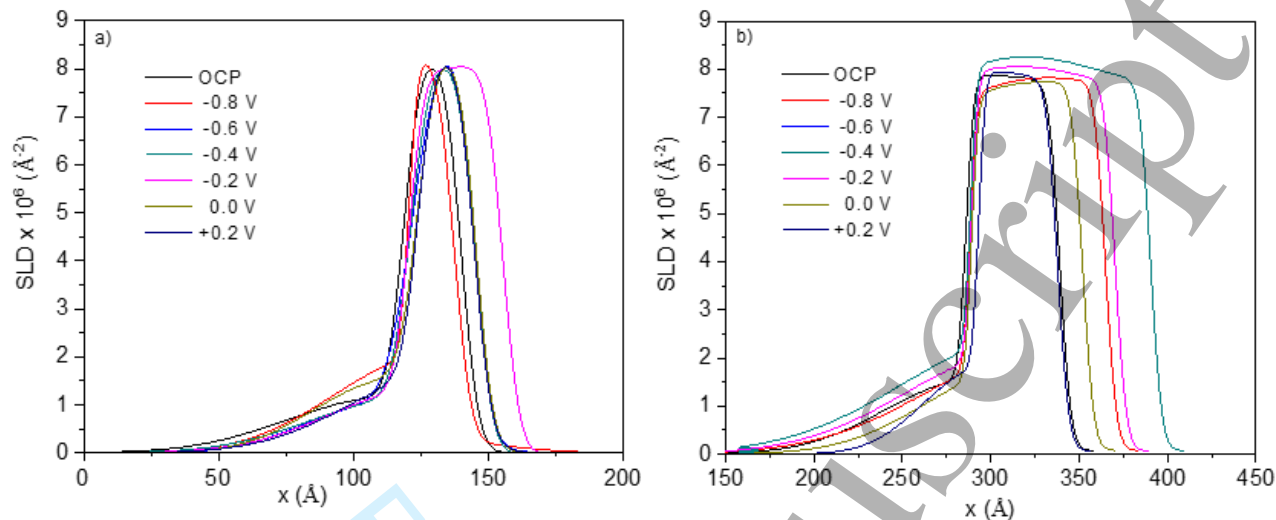


Figure 12. Analysis of the NR profiles given in Figure 10 where a sample profile for the base metal exposed to water on a SiO₂ substrate was simulated and subtracted from the overall reflectometry curve in order to obtain that of just the passive film for a) Ni-20Cr alloy and b) Ni-20Cr-10Mo alloy in 0.1 M Na₂SO₄ pH 4 where the peak SLD correlates to the Cr³⁺ cation fraction and the approximate l_{ox} is indicated by the peak width

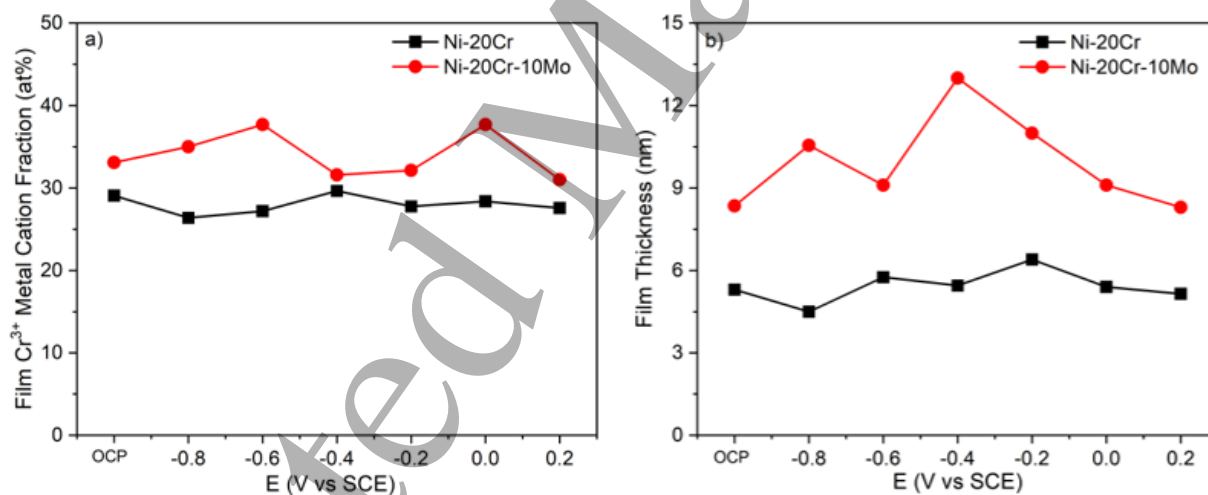


Figure 13. (a) Metal cation fraction and (b) passive film thickness computed from the peak SLD in Figure 12 for Ni-20Cr and Ni-20Cr-10Mo alloys in 0.1 M Na₂SO₄ pH 4 oxidized at varying potentials.

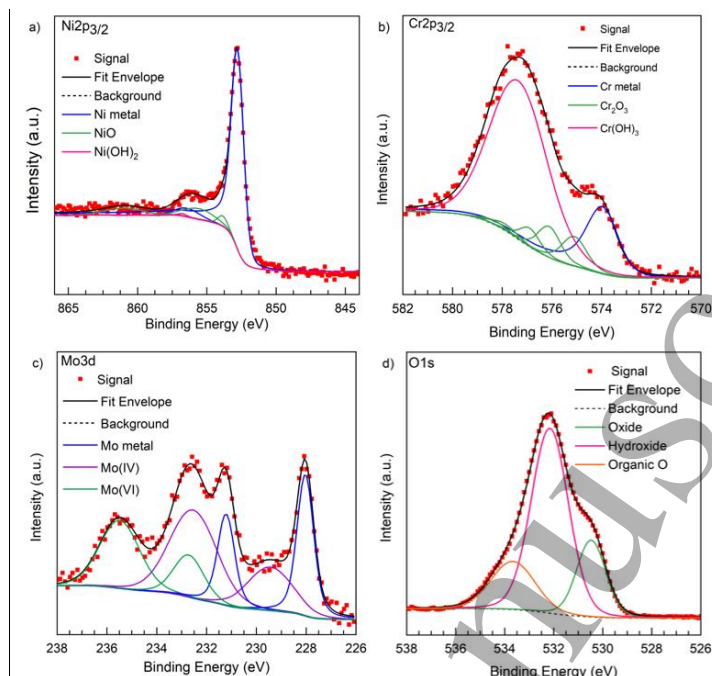


Figure 14. Focused, deconvoluted XPS spectra for a) Ni $2p_{3/2}$, b) Cr $3p_{3/2}$, c) Mo $3d$, and d) O $1s$ bands collected on Ni-22Cr-6Mo alloy passivated at $+0.2 V_{SCE}$ for 10,000 s in 0.1 M Na_2SO_4 pH 4 where the solid black and magenta lines indicate the Shirley background and overall fit to the spectra, respectively.

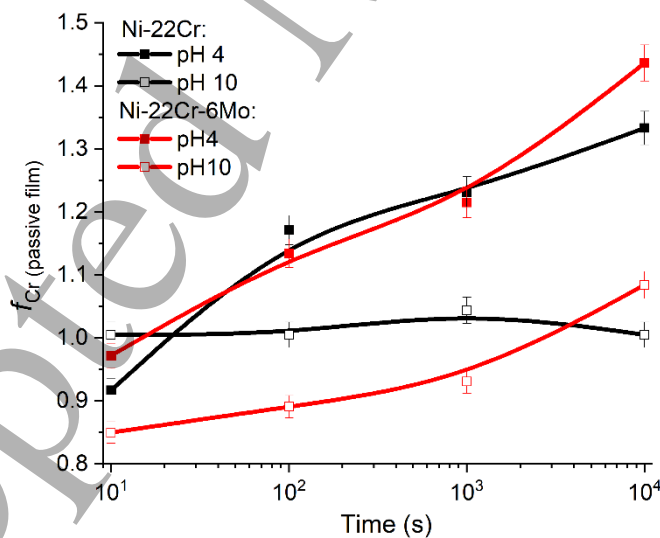


Figure 15. Passive film Cr(III) enrichment/depletion factor $f_{Cr(III)}$ calculated by using Equation 13 for Ni-22Cr and Ni-22Cr-6Mo alloys following 10s to 10 ks of potentiostatic passivation at $+0.2 V_{SCE}$ in 0.1 M Na_2SO_4 at pH 4 and 10

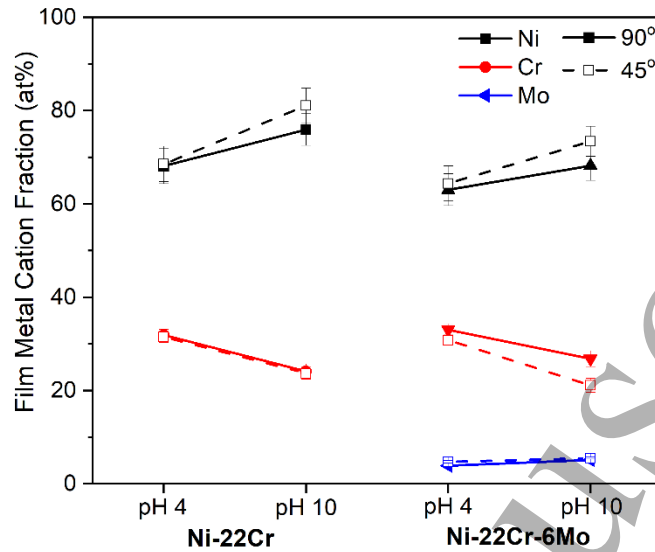


Figure 16. Film cation fraction according to angle-resolved XPS measurements at 90° and 45° on Ni-22Cr and Ni-22Cr-6Mo alloys surfaces following 10 ks of potentiostatic passivation at +0.2 V_{SCE} in 0.1 M Na₂SO₄ at pH 4 and 10.

Table 1. Cation and elemental fractions detected by XPS after 10 min of cathodic reduction at -1.3V_{SCE} in 0.1 M Na₂SO₄ pH 4 and pH 10 N₂(g) deaerated solution

Alloy	Take-off Angle	Passive Film Cation Fraction			Metal/Film Interface Elemental Fraction		
		Ni	Cr	Mo	Ni	Cr	Mo
Ni-22Cr (pH 4)	90°	0.44	0.56	–	0.78	0.22	–
	45°	0.29	0.71	–	0.81	0.19	–
Ni-22Cr (pH 10)	90°	0.15	0.85	–	0.78	0.22	–
	45°	0.11	0.89	–	0.86	0.14	–
Ni-22Cr-6Mo (pH 4)	90°	0.32	0.57	0.11	0.78	0.17	0.04
	45°	0.28	0.58	0.14	0.81	0.14	0.05
Ni-22Cr-6Mo (pH 10)	90°	0.73	0.18	0.09	0.61	0.25	0.14
	45°	0.69	0.15	0.15	0.58	0.21	0.21