Comparison of Elemental Resolved non-confined and restricted electrochemical degradation of Nickel Base Alloys

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Passive film properties of nickel base alloys (NBAs) have been studied extensively, yet elemental resolved dissolution currents under corrosive conditions are less well studied. Here, we compare elemental dissolution currents during anodic polarisation and repassivation under crevice and freely-exposed conditions for various NBAs using an ICP-MS flow-cell approach. With a new sample design we can track communication of a crevice environment with the electrolyte, providing insight into crevice solution chemistry and solubility of passive film-forming elements. Data indicates Mo can only form stable precipitate layers under openly corroding conditions. Local elemental depletion was further examined by XPS and nanometer resolved XRF.

Keywords: nickel base alloys, ICP-MS, restricted (confined) corrosion, localized corrosion, oxide breakdown, synchrotron-XRF

INTRODUCTION

Compared to stainless steels nickel base alloys (NBAs) are considerably more corrosion resistant making them a preferred industrial choice in demanding environments, including chemical and food processing, aerospace as well as energy applications.1–4 NBAs are typically alloyed with >10% chromium and 1-5% molybdenum which are key alloying elements for providing an excellent corrosion resistance in extreme environments.5–8 The pronounced corrosion resistance in anodic and acidic environments suggests the formation of a very stable and well adhering passivating thin film, which is formed and/or stabilized mainly by these alloying elements.9–11 It has been suggested that molybdenum and chromium may segregate to the alloy surface.8,11–13

The thickness of the passive films is estimated at about 2 nm,6,14 and the chromium content is known to strongly influence the breakdown of the passive film. This suggests a key role of chromium in the passive film chemistry, formation kinetics and stability.9,14 The mechanism of molybdenum inhibition is less well understood. Increasing molybdenum content results in lower passive currents, and it was suggested that MoO42− ions (molybdates) accumulate at the outer interface of the passive film.12 This may stabilize the passive film against chloride ingress and hence dissolution, resulting in lower corrosive currents.6,15

It was further suggested that molybdenum forms insoluble molybdate species after anodic dissolution from the matrix, building up passivating precipitate films which in turn lowers anodic dissolution rates.13

Jakupi et al.16 suggested that molybdenum may accumulate at defect sites, which may also trigger lower anodic dissolution rates at defect sites.

While passive films and passivity have been studied extensively for NBAs, the elemental resolved dissolution during and after breakdown of the oxide, specifically under crevice and pitting conditions, is less well studied. Material dissolution is a central aspect of an ongoing localized corrosion, and industrial cleaning procedures involve pickling, where a complete oxide breakdown is desired, which is particularly demanding for NBAs.17

Recent studies by Ogle et al.13 investigated the transpassive dissolution in high salt environments, and NBA passivation in acidic solutions18 using spectroelectrochemistry in flow-cells coupled to ICP-OES analysis.

![Flow Cell Diagram](image)

FIG. 1. a) Schematic of the flow cell used. A PTFE cylinder is used for establishing laminar flow across the working electrode. The counter electrode (Pt) is placed up-stream and the reference electrode (Ag|AgCl) is placed downstream to avoid contamination of the WE. Standard HPLC fittings are used for all tubings. Corrosion patterns for different types of experiments are shown schematically and as microscope pictures for b) crevice corrosion and c) embedded samples, as well as a finite element method simulation (see methods) of the concentration distribution after 1.5 sec of material release at the electrode surface.

Here, we use a similar approach in a newly designed ICP-MS flow cell19,20 shown in Figure 1a. This cell allows us to measure and compare elemental dissolution rates and faradic currents under crevice and pitting conditions (see Figure 1b/c), depending on the sample design respectively. Similar to classic flow-cell designs a crevice is formed with the sealing O-ring, if a bulk sample (type 1) is mounted. Figure 1b also shows a finite element simulated concentration profile of corroding species in the flowing electrolyte, demonstrating significant dissolution in the crevice region under the

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O-ring. In contrast, as shown in Figure 1c, an embedded sample (type 2) can be mounted without crevice formation under the O-ring. The well adhering glue limits crevice formation at the embedded glue/sample edge during experimental duration, as demonstrated by comparison of the visual corrosive damage after experiments (Figure 1c). Also, finite element simulations, shown as insets, indicate that the dissolving species originate from the exposed area. The flow is also guided well into the exit for both sample settings, ensuring limited convective broadening of the ICP-MS signal. This is ensured by the design of the flow channels, which enter and exit as circular openings between and O-ring and a PTFE stamp. This ensures a stable channel height and laminar flow.

| Alloy composition | abbreviation | Ni | Cr | Fe | Mo | minor components |
|-------------------|--------------|----|----|----|----|------------------|
| Ni₈₆Cr₅Fe₉         | Cr5          | 86 | 5  | 9  | -  | -                |
| Ni₇₅Cr₁₆Fe₉        | 600          | 72 | 15.5 | 8 | Mn(1) Si(0.5) |
| Ni₇₄Cr₁₆Fe₉Mo      | Mo1          | 74 | 16 | 9  | 1  | -                |

Using this setup, we study the elemental dissolution behaviour of a series of commercial and model NBAs under crevice and non-crevice conditions. The alloy compositions and abbreviations used in this work are given in Table I. The compositions were selected for evaluating the influence of the total chromium content (5% and 16% Cr) and the impact of trace/minor amounts of molybdenum (1% Mo) on initial corrosion and subsequent repassivation.

RESULTS

Here, we first quantify elemental dissolution currents $i_{MS}$ during polarisation at different anodic polarisation for crevice and non-crevice type samples in the ICP-MS (see again Figure 1). We characterize extended corrosive dissolution and the subsequent repassivation of the materials, to obtain insight into the crevice chemistry. As a side note, in this work we do not study freely corroding crevices under OCP conditions, we rather accelerate the degradation reaction by application of anodic potentials, in the transpassive regime. We then further characterize the surface chemistry of corroded and repassivated alloys with X-ray photo-electron spectroscopy (XPS) and discuss the passivating film chemistry and structure before and after corrosive dissolution. Finally, high-resolution X-ray fluorescence spectroscopy was performed on corroded samples, to further visualize local elemental surface depletion at corroding sites. Anodic polarisation and elemental resolved dissolution. Figure 2 displays representative data of elemental dissolution currents $i_{MS}$ recorded during 40 minute active corrosion with a type 1 (electrochemically triggered degradation under confined conditions) and type 2 (open area electrochemical degradation) samples at $\phi_p = 1.0$ V for, Ni₈₆Cr₅Fe₉ (Cr5), Alloy 600, and Ni₇₄Cr₁₆Fe₉Mo in aerated 1 mM NaCl solution at unbuffered pH of 7, respectively.

First, based on absolute dissolution currents, these three samples indicate increasing corrosion resistance from Cr5 < Mo1 ~ Alloy 600 for the electrochemically triggered degradation under confined conditions (CC), and Cr5 < Alloy 600 < Mo1 for open area corrosion.

Second, under crevice condition Figure 2a-c, stepping from 0.2 V to 1.0 V, i.e. results in an immediate and steep increase of nickel dissolution rates over more than one order of magnitude for all alloys. Alloys 600 and Mo1 further indicate a peak dissolution of nickel after 30 seconds, followed by a steady decay of the dissolution rate during ongoing corrosion at 1.0 V. In contrast, for the Cr5 alloy Cr dissolution shortly plateaus after 30 seconds, and after 90 seconds the dissolution rate of all elements increases further. Figure 2a also shows that for Cr5 the second increase of $i_{MS(Ni)}$ after 90 seconds is accompanied by a steep increase of the iron dissolution rate over more than one order of magnitude. The dissolution ratios ($D_R$) after 40 minutes active corrosion shown in Figure 3 indicate that Cr5 reaches close to bulk dissolution ratios, while Alloy 600 and Mo1 exhibit comparatively higher Cr, as well as considerably enhanced Mo dissolution ratios, respectively, with a clearly retarded Fe dissolution under crevice conditions.

Under openly corroding conditions of embedded samples Figure 2d-f, stepping from 0.2 V to 1.0 V, i.e. indicates a similar pattern with a very steep increase of Ni-dissolution. In contrast to the CC type and shown in Figure 3, open corrosion establishes a near bulk-ratio dissolution after 40 minutes, with moderately higher Ni, and hence lower Fe and Cr dissolution rates, compared to the bulk composition. For the open corrosion we also see that the electrochemical current (EC) is lower compared to measured dissolution current for Cr5 and Alloy 600. In contrast, Mo1 shows a generally very low corrosion rate, with a second increase of rates after an initial 2-3 minutes of anodic corrosion.

Repassivation. Figure 4 compares elemental dissolution currents for all alloys and sample types during repassivation after 5 and 40 minutes of corrosive polarisation, respectively. Due to diffusion broadening, all samples show that the dissolution currents for all alloys drop to a lower base level within 60-100 seconds after stepping into the repassivating region at $\phi_i = 0.2$ V. This results from the retention time of the dissolved material in the tubes between the electrochemical cell and the detection in the ICP-MS.

Type 1 samples: Figure 4a-c shows type 1 samples, indicating that the base level for the Cr5 alloy is almost half an order of magnitude higher compared to alloys 600 and Mo1. This is in line with the polarisation curves, shown in Figure S1. For Cr5 the passive current level also depends on the transpassive polarisation time. After 5 minutes of the resulting passive dissolution the current of all elements is about...
FIG. 2. Comparison of anodic dissolution at bulk pH = 7 in 1 mM NaCl of Cr5, alloy 600 and Mo1. Multiple repetitive measurements provided similar quantitative results. Rates are normalized to the electrode area, which is estimated at the circumference and width of the observed crevice for type 1, and the embedded area for type 2 samples.

20-30% higher compared to longer polarisation times. In contrast, both alloy 600 and alloy Mo1 show no pronounced difference of dissolution currents after 5 or 40 minute anodic corrosion followed by repassivation.

During repassivation the iron dissolution remains negligible for alloys 600 and Mo1, and remains at a significantly higher level for the Cr5 alloys.

In contrast to the Cr5 alloy both, alloys 600 and Mo1, indicate a significant initial peak of the dissolution rate of Cr and Mo during repassivation (marked by arrow), which increases with the time of preceding anodic polarisation. The dissolution rates for Cr and Mo peaks are considerably above the value measured during corrosive dissolution, indicating a significant material release during repassivation.

Figure S2 compares the integrated amount of dissolved chromium and molybdenum during repassivation as a function of the transpassive polarisation time. Data indicates a saturation after about 20 minutes of transpassive polarisation. Furthermore, comparing the integrated Cr and Mo dissolution currents for alloys Mo1 and 600 (Figure S2) during repassivation indicates that the Mo content in Mo1 results in a smaller dissolution current for the Cr during repassivation for up to 20 minutes of corrosive polarisation. During this initial period a considerably larger amount of Mo peak dissolution occurs during repassivation, while only limited chromium dissolution emerges. After 20 minutes of corrosive dissolution the dissolved amount of chromium is again similar compared to alloy 600 that is polarised at 1.0 V.

Type 2 samples: For type 2 samples shown in Figure 4d-f no such peaks were observed, and for Cr5 and Alloy 600 a decay of the dissolution currents consistent with diffusion broadening was observed. In contrast, Mo1 shows a prolonged dissolution time for all elements during repassivation.

Surface characterization - XPS. XPS was further used to compare passive films formed during passivation and after corrosion and repassivation. Therefore spectra were collected...
at openly corroded and at crevice corroded regions, using a small spot XPS. For these XPS measurements the surfaces were pulled out from the electrolyte at the given potential and they were washed afterwards with minute amounts of Milli-Q water, to avoid significant changes of the surface chemistry due to washing (see experimental details for more information). We want to emphasize, that this procedure allows us to closely resemble, or "freeze", the conditions in the electrolyte. But clearly, ex-situ XPS is only an approximation for the state during active aqueous degradation. In future work, one may expect further insight from high pressure XPS.\textsuperscript{23,24}

The full set of core level spectra for all alloys and elements are shown in the supporting information for all materials studied for openly corroded areas (\textbf{Figures S3-S5}), and crevice corroded areas (\textbf{Figures S6-S7}) respectively. Peak fitting was applied as shown in the spectra, and resulting XPS surface ratios for metallic and oxide components of fitted compounds are summarized in \textbf{Figure 5a}.

Survey spectra indicated no further elements other than atmospheric carbon. We first summarize the results of the spectra for the major elements, while Mo is discussed separately, as it indicates most pronounced differences.

\textbf{Cr, Fe, Ni spectra after non-crevice passivation.} After 40 minutes of open crevice free passive polarisation at 0.2 V 600 and Mo1 indicate a Cr\textsubscript{2}O\textsubscript{3} and Fe(III) enriched passive film, while oxidized Ni appears to be insignificant, and mostly metallic Ni is observed. In contrast, Cr5 shows a considerably more Ni-rich (60\%) and the Cr content in the passive film is still two-fold above bulk level concentration.

\textbf{Cr, Fe, Ni spectra after open corrosion.} XPS spectra recorded after corrosion (\textbf{Figures S3-S5}) indicate significant differ-
FIG. 5. a) Surface composition of the alloys according to XPS analysis. Type 1 and 2 were polarised at 1.0 V for 40 min, pass indicates passivation at 0.2 V for 40 min. Type 1 is measured at the area of the crevice, type 2 represents the data taken from spots in the inner part of the metal sample. b) Molybdenum 3p core level spectra after 40 minutes of polarisation in the (bottom) passive regime at 0.2V, and (top) the anodic regime at 1.0 V for type 1 and type 2 polarisation. (c.f. text for details).

ences of the passive film content. First, the Ni-signal indicates a more pronounced oxide/hydroxide component after reprecipitation, which is in line with a reprecipitated outer layer of nickel oxide/hydroxide. Also, the metallic signals for both alloy 600 and Cr5 show a considerably lower intensity of metallic Cr and Fe relative to the oxidized species, indicating a thicker passive film.

Cr, Fe, Ni spectra after crevice corrosion. Spectra under crevice condition (Figures S6-S7) clearly indicate a thinner oxide in the crevice corrosion. Specifically, relative comparison of the metallic and the oxide peaks indicates a relatively higher metal signal for all alloys. Further, Ni(II) shows no hydroxide signals for all alloys.

Comparison of Mo spectra. As shown in Figure 5b, for Mo1 the elemental ratios of the Mo oxides strongly differ for the openly exposed, crevice and passive film surface chemistry.

First for open non-crevice corrosion (type 2), after passivation molybdenum at 0.2 V is chemically present as Mo(VI) and lower oxidized species Mo(<VI). Also, metallic Mo is clearly detectable indicating a thin passive film.

Second, and in contrast, Mo core level spectra in Figure 5 after corrosion at 1.0 V and repassivation indicate a fully oxidized and highly enriched Mo(VI) species in the passive film. The data indicates a nearly exclusive Mo(VI) content, with a minor (~ 6 %) possibly defect (e.g. oxygen interstitial) related peak at even higher binding energies after transpassive dissolution and subsequent repassivation. This small peak is shifted to very high binding energies, which in our view supports an interpretation of an interstitial site, which is highly coordinated by lattice oxygen (defect). Other secondary effects such as shake ups are unlikely in this case, as the highly oxidized form is expected to be diamagnetic. The total Mo content in this passive film is at 7-8%, which is considerably above the 1% bulk concentration. This indicates a thick molybdate precipitate overlayer, which is also consistent with the disappearance of the metallic Mo peak, and significantly weaker metallic peaks in all other elemental spectra (Figure S4).

Finally, the spectra in the crevice corroded area (type 1, 1.0 V) indicate fully oxidized species, and only minor lower oxidation states (in the noise limit). In general, the considerably smaller signal levels again indicate a lower film thickness, in particular considering that the metallic Mo signal is still visible.

Nano-XRF/SEM characterization of corroded areas. Figure 6 shows electron microscopy images and corresponding high resolution (500 nm spatial resolution) XRF elemental mappings for representative areas showing corrosive damage after polarisation in the ICP-MS cell. The elemental mappings show a relative distribution of elements over the probed location (see methods for details), and indicate that nickel depletes locally, while iron and chromium maps indicate a local enrichment compared to bulk level at corroded sites, which is consistent with XPS data. For Mo1 it was not possible to achieve sufficient signal intensity for mapping local changes.

DISCUSSION AND INTERPRETATION

Comparison of anodic corrosion and elemental dissolution under restricted and non-restricted conditions. Our data indicates that we can follow both a freely exposed corrosion
of an embedded sample, or preferential confined condition-type degradation (CC) underneath the O-ring using targeted ICP-MS flow cell/sample design concepts. CC establishes a direct communication of the crevice electrolyte with the bulk electrolyte flowing through the ICP-MS flow cell.

First, the open corrosion of type 2 samples results in a preferential dissolution of Ni, while Cr as well as Fe dissolve at ratios below bulk level metal concentrations at both passivating and anodic corrosion conditions. Under passive conditions, at 0.2 V, the Ni-hydroxide and oxide peaks in XPS almost disappear, which is in line with the observed dissolution behaviour in ICP-MS. This suggests, Ni dissolves through an intact chromium oxide layer, and any initially present oxidized Ni species dissolve as well, as expected for a high field mechanism. I.e. the potential gradient drives the Nickel dissolution through the formed passive layer. At 1.0 V anodic corrosion we see a preferential and also localized dissolution (see also Figure 1c photograph after corrosion), which is further evident from the XRF data, which shows depletion of Ni and enrichment of the other alloying elements locally. Localized corrosion is likely triggered by the local breakdown of the passive film. Further, for Mo1 repassivation leads to the formation of an expected passivating Mo(VI)-rich precipitate. This interpretation is consistent with previous work, and suggests high oxidation states in the Mo-precipitate formed at 1.0 V. This precipitate dissolves slowly after repassivation, as evidenced by the slow transient ICP-MS dissolution profile of Mo in Figure 3f. Based on the XPS data, the Mo content of the passive film increases 7-fold compared to the bulk concentration, and the film thickness is above 3-4 nm, but below 10 nm, based on the relative intensities of the metallic signals from underneath the passive film. Under different conditions e.g. Ogle et al. found a similar enrichment of Mo at the interface, as it is also known for Mo-containing stainless steels.

For crevice type samples the ICP-MS repassivation data show two interesting aspects: First, and as discussed above we see clear and time dependent peaks of the Cr and Cr/Mo dissolution, for alloy 600 and Mo1 respectively. These peaks were only found for type 1 samples. Hence, these are clearly related to the communication of the crevice solution with the flowing electrolyte. Upon lowering of the potential, the crevice environment, which established over the extended degradation period, dissipates by peaking, i.e. injecting, the crevice solution into the flowing electrolyte. Hence, the crevice solution at pH 7 base-level unbuffered pH is highly enriched in Cr and Mo containing soluble species, while Fe remains largely insoluble within the crevice. Based on the time dependent evolution of this dissolution peak, shown in Figure S2, the crevice environment reaches saturation after 20 minutes of constant polarisation under the applied conditions. The here studied approach deviates from realistic crevice corrosion since an external potential is applied, that likely results in an overestimation of the exchanged currents. Nevertheless the processes taking place in the crevice environment are comparable. The here reported enrichment in soluble species in the crevice is also found for crevice corrosion. Interestingly, for Mo1 data indicates a delayed Cr dissolution, while Mo preferentially dissolves initially. After 20 minutes, similarly, a saturation level is reached.

Furthermore the observed Fe retardation for both alloys indicates that the crevice is enriched with iron oxide, while Cr-oxide and Mo have lower effective protection levels in the crevice. The resulting oxide/transient protection layer is non-well adhering and does not passivate the active crevice surface well. This is consistent with 1) the observed current spikes in the Fe signal. The observed spikes indicate nano- to micro level Fe-oxide detachment from the repassivating areas, and 2) XPS of the crevice region also indicates Fe enrichment, and overall thinner oxide.

When comparing the surface composition of non-confined with the crevice corrodes samples, data clearly suggests and acidification of the crevice area, which drives localized corrosion, while inhibiting passive film formation. For the openly corroding samples, a similar breakdown of the oxides appears locally, as can be seen from the visual corrosive damage, which showed localized attacks. The fact that the dissolution current of Cr5 and alloy 600 was consistently higher in Cr and Mo containing soluble species, while Fe remains largely insoluble within the crevice. Based on the time dependent evolution of this dissolution peak, shown in Figure S2, the crevice environment reaches saturation after 20 minutes of constant polarisation under the applied conditions. The here studied approach deviates from realistic crevice corrosion since an external potential is applied, that likely results in an overestimation of the exchanged currents. Nevertheless the processes taking place in the crevice environment are comparable. The here reported enrichment in soluble species in the crevice is also found for crevice corrosion. Interestingly, for Mo1 data indicates a delayed Cr dissolution, while Mo preferentially dissolves initially. After 20 minutes, similarly, a saturation level is reached.

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Mo. Precipitation of molybdates passivates the surface for an openly corroding system.\textsuperscript{13,36,37}

However, under crevice conditions, we clearly see a lower protective effect, and no pronounced precipitation of molybdates. XPS and ICP-MS data for crevice type samples, indicate a lower oxide thickness and soluble molybdate species. Within the crevice region no highly oxidized molybdate based passive film can hence form, probably resulting from the acidification in the crevice and therefore increased solubility of the molybdates.\textsuperscript{13}

**CONCLUSIONS**

In conclusion, we can show that our sample design allows a comparative study of open and crevice type corrosion within the same ICP-MS flow cell. The communication of a crevice environment with the bulk electrolyte can be reproducibly tracked, providing insight into the crevice chemistry. Together with modelling, backtracking the exact chemistry and pH may become possible in the future.

Regarding the characterized systems, our findings are in line with the current understanding of NBA corrosion behaviour, and can be summarized as follows:

- During passivation the passive films are mainly consisting of Fe and Cr oxides, while Ni establishes a passive current by dissolution across the intact passive film.

- Under open corrosion we see a clear preferential dealloying of Ni at localized corroding areas.

- Consistent with ICP-MS dissolution currents, nanometer resolved XRF was utilized to confirm localized selective dissolution of Ni, and enrichment of the other alloying elements.

- The formation of a passive film with >7-8 \% MoO\textsubscript{3} confirmed a selective enrichment of Mo after corrosive dissolution and consequent repassivation for Mo1.

- In the crevice region oxides are thinner, and iron oxide enriches significantly, while the other alloying elements, including Cr, dissolve at higher rates and above bulk level concentration in the crevice.

- Under crevice condition Mo(VI) can hence not precipitate an effective protective layer, likely due to the low pH level that establishes in the crevice environment.

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**COMPETING INTERESTS**

The Authors declare no Competing Financial or Non-Financial Interests.

**METHODS AND MATERIALS**

\textbf{a. Chemicals and Materials} Sodium chloride (Carl Roth, p.a.), \(\text{HNO}_3\) (VWR Chemicals, Normatom), Milli-Q water (resistivity >18 M\ Ω cm, total organic carbon < 4 ppb) was used for making electrolyte solutions. Alloy 600 was obtained from VDM-Metals, and Cr5 and Mo1 were provided by Hauke Springer (MPI f. Eisenforschung, Düsseldorf). For embedded samples a 2 mm diameter cylinder was turned. The removed material was replaced with EPON 1009F epoxy resin (Hexion). The metal blocks were ground with sand paper of decreasing grain size (from P80 to P2500), then polished with diamond paste down to 0.05 \(\mu\)m. Prior to electrochemical transcritical dissolution at \(\phi_{TP}=1.0\) V the metals were preconditioned in-situ in the ICP-MS flow cell by (1) 5 minutes potentiostatic polarisation at \(-0.2\) V vs OCP, (2) followed by stepping into the passive regime at \(\phi_1=0.2\) V for another 5 minutes. We also compared results after preconditioning at \(-1.0\) V and subsequent oxidation in the passive regime at 0.2 V and found no quantitative differences.

\textbf{b. Inductively Coupled Plasma Mass Spectrometry (ICP-MS)} Measurements were performed using a Agilent 7900 ICP-MS from Agilent Technologies. Calibration was performed with multi-element standard solutions provided by Agilent and Inorganic Ventures. The ICP-MS uses a collision cell with 5 mL/min flow of helium as cell gas. Downstream of the electrochemical cell the analyte was mixed with standard solution. Cobalt was chosen as internal standard due to its similar mass with most of the alloy components. Electrochemical experiments were performed using a home-built flow cell out of PEEK and PTFE inspired by the Ogle- and Mayrhofer designs.\textsuperscript{19–21} In the cell design used particular attention was given to the flow profile, so that laminar flow is achieved (confirmed by flow simulations). The exposed electrode area is circular with an sealed with a 3 mm diameter O-ring. Figure 1 shows the flow-cell ICP-MS coupling used in this work. Pressurized nitrogen was used for pumping to establish a stable and pulsation free laminar flow of the electrolyte. Flow was checked both by an in-flow pressure sensor and by weighing the collected waste electrolyte after ICP-MS. The flow is set to 6 ± 0.2 mg of solution per second. Before each experiment the electrolyte was purged with compressed and filtered air for at least 30 minutes to guarantee the same.
concentration of dissolved oxygen. All electrochemical experiments were done using a Ag/AgCl-Electrode as reference and presented data is referenced to that potential.

c. Optical Microscopy Optical Microscope images were taken using a µsurf explorer (Nanofocus AG) and analyzed with µsoft metrology software. A 20x magnifying lens was used.

d. Scanning Electron microscopy (SEM) SEM imaging was performed at the USTEM facility at Vienna University of Technology, working on a FEI Quanta 250 FEG with a beam energy of 5 keV.

e. X-ray Photoelectron Spectroscopy (XPS) XPS Chemical composition and chemical states of the surface were determined using the Axis Supra (Kratos Analytical) spectrometer. No charge neutralization was used. XPS spectra were shifted with respect to adventitious carbon at 284.8 eV. Spectra were taken with a resolution of 0.1 eV and a pass-energy of 160 eV. All spectra were fitted using reference compounds from the NIST database (Ni, Fe, Cr, Mo). No positional shifts of the components were necessary to fit the measured spectra well, except for an 0.2 eV shift for Ni(OH)₂ and 0.5 eV shift for NiO reference components. Elements with unpaired electrons (Cr, Fe) were fitted with fixed multi-peak envelopes. Samples were during active potential application pulled out of electrolyte to 'freeze' the electric double layer. Afterwards they were dried in a N₂ stream.

f. X-ray fluorescence High resolution X-ray fluorescence (XRF) experiments were performed at the Taiwan Photon Source (TPS) Beamline 21A at the National Synchrotron Radiation Research Center (NSRRC), Taiwan. This beamline is dedicated to white-light nano Laue diffraction for structural analysis and high spatial resolution fluorescence imaging. The spatial resolution can regularly reach 80 × 80 nm at this beamline. In XRF application, the beamline utilizes a pre-shaped Kirkpatrick-Baez mirror pair to focus the Monochromatic X-ray beam with energies 9.6 keV to generate fluorescence signal. XRF was collected by an in-plane detector with an take-off angle of 7 degree to increase the sensitivity to the surface fluorescence signal. Due to the fact that absolute XRF signal intensity is also influenced by the surface morphology, we normalize the fluorescence imaging and analyze intensity ratio between individual elemental signals as following, revealing relative local variation of elemental ratio on the surface:

\[
P_{\text{Me}}(\%) = I_{\text{Me}}/(I_{\text{Ni}} + I_{\text{Cr}} + I_{\text{Fe}}) \cdot 100\%
\]

The sampling depth of XRF technique is related to the photon energy of fluorescence, which is characteristic for individual elements. A rough estimation of the sampling depth from the XRF energies for Ni, Cr and Fe suggests 2.36, 0.96 and 1.53 μm sampling depths in this sampling geometry.

g. Finite Elements Methods Simulations Simulations for the concentration profiles shown in Fig. 1 b) and c) were conducted with COMSOL Multiphysics. The initial material release is set to be evenly distributed over the whole WE area. Electrolyte mass flow was set to 3 mg/s as measured for the experiments conducted.

DATA AVAILABILITY

The raw and processed data required to reproduce these findings are available from the corresponding author via www.repositum.tuwien.ac.at upon reasonable request.

REFERENCES

1. S. J. Rosenberg, Nickel and its alloys. Washington: National Bureau of Standards, 1968.
2. A. F. Rowcliffe, L. K. Mansur, D. T. Hoelzer, and R. K. Nanstad, “Perspectives on radiation effects in nickel-base alloys for applications in advanced reactors,” Journal of Nuclear Materials, vol. 392, no. 2, pp. 341–352, 2009.
3. M. B. Henderson, D. Arrell, R. Larsson, M. Heobel, and G. Marchant, “Nickel based superalloy welding practices for industrial gas turbine applications,” Science and Technology of Welding and Joining, vol. 9, no. 1, pp. 13–21, 2004.
4. S. Y. Persaud, B. Langelier, A. Korinek, S. Ramamurthy, G. A. Botton, and R. C. Newman, “Characterization of initial intergranular oxidation processes in alloy 600 at a sub-nanometer scale,” Corrosion Science, vol. 133, pp. 36–47, 2018.
5. J. R. Hayes, J. J. Gray, A. W. Szmodis, and C. A. Orme, “Influence of Chromium and Molybdenum on the Corrosion of Nickel-Based Alloys,” CORROSION, vol. 62, no. 6, pp. 491–500, 2006.
6. A. C. Lloyd, J. J. Noël, S. McIntyre, and D. W. Shosseh, “Cr, Mo and W alloying additions in Ni and their effect on passivity,” Electrochimica Acta, vol. 49, no. 17-18, pp. 3015–3027, 2004.
7. N. Ebrahimi, P. Jakupi, J. J. Noël, and D. W. Shosseh, “The Role of Alloying Elements on the Crevice Corrosion Behavior of Ni-Cr-Mo Alloys,” CORROSION, vol. 71, no. 12, pp. 1441–1451, 2015.
8. S. Y. Persaud and R. C. Newman, “A Review of Oxidation Phenomena in Ni Alloys Exposed to Hydrogenated Steam Below 500°C,” CORROSION, vol. 72, no. 7, pp. 881–896, 2016.
9. N. Ebrahimi, M. C. Biesinger, D. W. Shosseh, and J. J. Noël, “The influence of chromium and molybdenum on the repassivation of nickel-chromium-molybdenum alloys in saline solutions: Influence of Cr and Mo on the Repassivation of Ni-Cr-Mo Alloys,” Surface and Interface Analysis, vol. 49, no. 13, pp. 1339–1365, 2017.
10. H.-H. Huang, “Effect of chemical composition on the corrosion behavior of Ni-Cr-Mo dental casting alloys,” Journal of Biomedical Materials Research, vol. 60, no. 3, pp. 458–465, 2002.
11. J. Zhang, Y. Chen, and M. A. Brook, “Facile functionalization of PDMS elastomer surfaces using thiol-ene click chemistry,” Langmuir, vol. 29, no. 40, pp. 12432–12442, 2013.
12. N. Ebrahimi, J. J. Noël, M. A. Rodriguez, and D. W. Shosseh, “The self-sustaining propagation of crevice corrosion on the hybrid BC1 Ni-Cr-Mo alloy in hot saline solutions,” Corrosion Science, vol. 105, pp. 58–67, 2016.
13. D. Henderson, X. Li, D. W. Shosseh, J. J. Noël, and K. Ogle, “Molybdenum surface enrichment and release during transpassive dissolution of Ni-based alloys,” Corrosion Science, vol. 147, pp. 32–40, 2019.
14. S. Voyshnis, A. Seyeux, S. Zanna, B. Martin-Cabanas, T. Couvant, and P. Marcus, “Oxide layer growth on nickel-base alloy surfaces in high temperature water and in O₂ studied by ToF-SIMS with isotopic tracers,” Corrosion Science, vol. 145, pp. 212–219, 2018.
15. A. C. Lloyd, J. J. Noel, D. W. Shoesmith, and N. S. McIntyre, “The open-circuit ennoblement of alloy C-22 and other Ni-Cr-Mo alloys,” JOM, vol. 57, no. 1, pp. 31–35, 2005.

16. P. Jakupi, J. J. Noel, and D. W. Shoesmith, “The evolution of crevice corrosion damage on the Ni-Cr-Mo–W alloy C-22 determined by confocal laser scanning microscopy,” Corrosion Science, vol. 54, pp. 260–269, 2012.

17. G. Pajonk and H. Bubert, “Influence of Pickling High Alloyed CrNi-Steels and Nickel Base Alloys with Citric Acid on the Composition of their Tarnish OXides,” Microchim Acta, vol. 133, no. 1-4, pp. 289–293, 2000.

18. X. Li and K. Ogle, “The Passivation of Ni-Cr-Mo Alloys: TiMe Resolved Enrichment and Dissolution of Cr and Mo during Passive-Active Cycles,” Journal of The Electrochemical Society, vol. 166, no. 11, pp. C3179–C3185, 2019.

19. S. O. Klemm, A. A. Topalov, C. A. Laska, and K. J. Mayrhofer, “Coupling of a high throughput microelectrochemical cell with online multielemental trace analysis by ICP-MS,” Electrochemistry Communications, vol. 13, no. 12, pp. 1533–1535, 2011.

20. A. K. Schuppert, A. A. Topalov, I. Katsounaros, S. O. Klemm, and K. J. Mayrhofer, “A Scanning Flow Cell System for Fully Automated Screening of Electrocatalyst Materials,” Journal of The Electrochemical Society, vol. 159, no. 11, pp. F670–F675, 2012.

21. K. Ogle and S. Weber, “Anodic Dissolution of 304 Stainless Steel Using Atomic Emission Spectroelectrochemistry,” Journal of The Electrochemical Society, vol. 147, no. 5, pp. 1770–1780, 2000.

22. M. Volmer, M. Stratmann, and H. Viehaus, “Electrochemical and electron spectroscopic investigations of iron surfaces modified with thiols,” Surface and Interface Analysis, vol. 16, no. 1-2, pp. 278–282, 1990.

23. J.-J. Velasco-Vélez, L. J. Falling, D. Bernsmier, M. J. Sean, P. C. J. Clark, T.-S. Chan, E. Stotz, M. Havercker, R. Kraehnert, A. Knop-Gericke, C.-H. Chuang, D. E. Starr, M. Favaro, and R. V. Mom, “A comparative study of electrochemical cells for in situ x-ray spectroscopies in the soft and tender x-ray range,” Journal of Physics D: Applied Physics, vol. 54, no. 12, p. 124003, 2021.

24. S. Pletinex, S. Abrahami, J. Mol, T. Hauffman, and H. Terryn, “Advanced (In Situ) Surface Analysis of Organic Coating/Metal Oxide Interactions for Corrosion Protection of Passivated Metals,” in Encyclopedia of interfacial chemistry, pp. 1–17, San Diego: Elsevier Science, 2018.

25. M. A. Khilla, H. Mkhia, A. Abu-El Soud, and Z. M. Hanafi, “Magnetic susceptibility of molybdenum trioxide, dioxide and some suboxides,” Czechoslovak Journal of Physics, vol. 30, no. 9, pp. 1039–1045, 1980.

26. N. Cabrera and N. F. Mott, “Theory of the oxidation of metals,” Progress in Physics, vol. 14, no. 1, pp. 163–184, 1949.

27. L. F. Lin, C. Y. Chao, and D. D. Macdonald, “A Point Defect Model for Anodic Passive Films: II. Chemical Breakdown and Pit Initiation,” Journal of The Electrochemical Society, vol. 128, no. 6, pp. 1194–1198, 1981.

28. L. Zha, H. Li, and N. Wang, “In Situ Electrochemical Study of the Growth Kinetics of Passive Film on TC11 Alloy in Sulfate Solution at 300 °C/10 MPa,” Materials, vol. 13, no. 5, 2020.

29. Z. Wang, E.-M. Paschalidou, A. Seyeux, S. Zanna, V. Maurice, and P. Marquay, “Mechanisms of Cr and Mo Enrichments in the Passive Oxide Film on 316L Austenitic Stainless Steel,” Frontiers in Materials, vol. 6, 2019.

30. R. G. Kelly and J. S. Lee, “Localized Corrosion: Crevice Corrosion,” in Encyclopedia of interfacial chemistry, pp. 291–301, San Diego: Elsevier Science, 2018.

31. M. Nie, J. A. Wharton, A. Cranny, N. R. Harris, R. J. K. Wood, and K. R. Stokes, “Characterisation of Crevice and Pit Solution Chemistries Using Capillary Electrophoresis with Contactless Conductivity Detector,” Materials, vol. 6, no. 10, pp. 4345–4360, 2013.

32. T. Kaji, T. Sekiai, I. Muto, Y. Sugawara, and N. Hara, “Visualization of Solution Chemistry inside Crevice by pH and pCl Sensing Plates,” ECS Transactions, vol. 41, no. 25, pp. 205–216, 2019.

33. N. J. Laycock, J. Stewart, and R. C. Newman, “The initiation of crevice corrosion in stainless steels,” Corrosion Science, vol. 39, no. 10-11, pp. 1791–1809, 1997.

34. C. Merola, H.-W. Cheng, D. Dworschak, C.-S. Ku, C.-Y. Chiang, F. U. Renner, and M. Valtiner, “Nanometer Resolved Time Visualization of AdSorption and Material Breakdown in Confinement,” Advanced Materials Interfaces, vol. 6, no. 10, p. 1802069, 2019.

35. N. Sriddhar, “Local Corrosion Chemistry—A Review,” CORROSION, vol. 73, no. 1, pp. 18–30, 2017.
SUPPORTING INFORMATION

Spectroelectrochemical Comparison of Elemental Resolved non-confined and Crevice Corrosion of Nickel Base Alloys

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FIG. S1. Polarization curves recorded for all alloys used in 1 mM NaCl solution at 1 mV/s. During repassivation, at 0.2V which was used for ICP-MS studies as repassivation/preconditioning potential, all alloys are repassivated, with Cr5 showing the highest passive current. At transpassive conditions at 1V Cr5 shows the highest corrosion current, followed by Mo1 and alloy 600, which is in line with ICP-MS data (see main manuscript for details).
FIG. S2. Integrated mass release during repassivation as a function of increasing time during transpassive dissolution. The data is corrected for diffusion broadening, and sums up material release during repassivation at 0.2V after 40 minutes of transpassive corrosion for alloy 600 (squares) and alloy Mo1 (points), respectively.
FIG. S3. XPS core level spectra of alloy 600 after passivation and repassivation. The data can be well fit using standard tabulated peak positions of reference materials (NIST database) and multiplet splitting as indicated and described in the methods section. Please note that spectra are shown in arbitrary units to enhance visibility of fittings, the quantitative peak analysis is summarized in the main part. (Left) Ni 2p, Fe 2p and Cr 2p spectra are shown after 40 minutes polarization under passive conditions at 0.2V. The nickel spectra show almost exclusively metallic signal, and only very small amounts of hydroxide and oxide were found. The iron spectrum indicates FeO(OH) and minor amounts of Fe2O3, and the chromium spectrum can be fit well with a metallic and a single component Cr2O3 component. (Right) Ni 2p, Fe 2p and Cr 2p spectra are shown after 40 minutes polarization under transpassive conditions at 1V. The nickel spectra indicate more hydroxide and oxide with respect to the metallic peak. The iron spectrum indicates FeO(OH) and minor amounts of Fe2O3, and the chromium spectrum can be fit well with a metallic and a single Cr2O3 component.
FIG. S4. XPS core level spectra of alloy Mo1 after passivation and repassivation. The data can be well fit using standard tabulated peak positions of reference materials (NIST database) and multiplet splitting as indicated and described in the methods section. Please note that spectra are shown in arbitrary units to enhance visibility of fittings, the quantitative peak analysis is summarized in the main part. (Left) Ni 2p, Fe 2p, Cr 2p and Mo 3d spectra are shown after 40 minutes polarization under passive conditions at 0.2 V. The nickel spectra show a strong metallic signal, and only very small amounts of hydroxide and oxide were found. The iron spectrum indicates FeO(OH) and minor amounts of Fe₂O₃, and the chromium spectrum can be fit well with a metallic and a single component Cr₂O₃ component. Molybdenum spectra indicate a metallic, a Mo(IV) and a Mo(VI) component. (Right) Ni 2p, Fe 2p, Cr 2p and Mo 3d spectra are shown after 40 minutes polarization under transpassive conditions at 1 V. The nickel spectra show a very weak metallic signal, and hydroxide and oxides were found. The iron spectrum indicates FeO(OH) and minor amounts of Fe₂O₃, and the chromium spectrum can be fit well with a weak metallic and a single Cr₂O₃ component. Molybdenum spectra indicate a strong Mo(VI) component and minor amounts of Mo at higher binding energies, which may correlate with molybdates.
FIG. S5. XPS core level spectra of alloy Cr5 after passivation and repassivation. The data can be well fit using standard tabulated peak positions of reference materials (NIST database) and multiplet splitting as indicated and described in the methods section. Please note that spectra are shown in arbitrary units to enhance visibility of fittings, the quantitative peak analysis is summarized in the main part. (Left) Ni 2p, Fe 2p and Cr 2p spectra are shown after 40 minutes polarization under passive conditions at 0.2V. (Right) Ni 2p, Fe 2p and Cr 2p spectra are shown after 40 minutes of polarization under transpassive conditions at 1V.
FIG. S6. XPS core level spectra of alloy 600 after 40 min of polarisation at 1.0 V vs Ag/AgCl. Comparison of the open area (left) and the crevice region (right).
FIG. S7. XPS core level spectra of alloy Mo1 after 40 min of polarisation at 1.0 V vs Ag/AgCl. Comparison of the open area (left) and the crevice region (right).