

Atomic-scale understanding of oxide growth and dissolution kinetics of Ni-Cr alloys

Corresponding Author: Professor Penghao Xiao

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The manuscript reports a multiscale computation framework by combining DFT and KMC simulations to elucidate the microscopic processes leading to the corrosion/passivation of Ni-Cr alloys. The authors demonstrate the predictability capabilities of the computation approach by comparing the simulation results with experimental characterization. To the best knowledge of this reviewer, the work reported here represents the first of this kind to tackle the complex corrosion phenomena by taking into consideration of several key parameters including alloy composition, temperature, pH, and applied voltage. The authors are suggested to address a few important issues:

- 1) From simulations, the authors identify three distinct voltage regimes: oxide growth, dissolution, and competitive dissolution and deposition. However, the microscopic picture underlying the three regimes is not clearly described in the manuscript. For instance, there is no much discussion about why Ni and Cr are oxidized at similar rates, what are the key kinetic parameters controlling the oxidation rate of the two species, what drives the reprecipitation of Ni or Cr and what are the important kinetic parameters leading to the difference in the reprecipitation rates of the two metals?
- 2) Following the questions above, how do these key kinetic parameters vary with or depend on external corrosion/passivation conditions such as pH and applied voltage? If a clear correlation can be established from the simulations between the intrinsic kinetic processes and external conditions, this computation framework and the outcome of the simulations will be of high impact to the broad materials science community.
- 3) In reality, aqueous corrosion involves a large quantity of protons (or OH) that may easily penetrate into oxide lattice and significantly affect the atom mobility, kinetics, and microstructure evolution of the passivation oxide film, as shown in a recent paper (Nat Mater. 17, 514 (2018)). Any discussion or results of the simulations incorporating such a doping effect would strengthen the work for dealing with more realistic corrosion processes.
- 4) More simulations details will be helpful. For instance, how the oxide growth and dissolution is achieved in the simulations, is there a fixed size of O sublattice and the oxide growth/dissolution is judged by tracking the position/number of metal atoms in the O sublattice? How diffusion barriers of Ni and Cr atoms are calculated and how the diffusion barriers depend on the stoichiometry of the oxide? Similarly, what are the kinetic or energy criteria used to define oxide growth, dissolution and reprecipitation?

Reviewer #3

(Remarks to the Author)

Dear authors,

Thank you so much for attempting to create a model of a passive oxide film growth on Ni-Cr alloys. In case of the existence of a valid model that will match experimental data, it will have a huge impact in the field of aqueous corrosion. However, the current study does not provide sufficient information. Two main concerns which could not give me a possibility to recommend this article to be published are:

1. What was the main reason to use evaluated temperatures (363K, 400K, and even 500K) in modeling? Especially, to use different temperatures in one set of experiments (e.g. polarization at 363K, simulation at 400K, other experiments at room temperature)?
2. Most parts of the experiments were done on Alloy 22. Also, authors emphasized several times that they 'developed an

ab initio-based model capable of describing competing oxide growth and dissolution at the surface of a multicomponent alloy', mentioned alloys 80Ni-20Cr, Alloy 22, Inconel 600, 617, and Hastelloy 230, 276, 282. However, the model doesn't consider the presence of minor alloying elements such as Mo, Al, Fe, and W, which, as was reported a lot, play a huge role in passive film growth. All mentioned questions leave a lot of doubts about the model's validity. As minor concerns, I would like to mention a mixture of temperature units (K and C) throughout the text, even together in the same figure capture.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have addressed all my concerns and questions. I would suggest for acceptance.

Reviewer #3

(Remarks to the Author)

Dear Authors,

Thank you so much for your response and detailed explanations of the reasons for using Alloy 22 in the electrochemical tests instead of Ni20Cr. I absolutely agree that Ni20Cr is a difficult system to perform electrochemical testing on not only because it is susceptible to pitting but also crevice corrosion in acidic electrolytes mostly. However, it is misleading to use a system that is more corrosion resistant in electrochemical tests because of the presenting alloying elements (Mo, W, etc.) to prove the concept of formation of only Cr and Ni oxides on the surface of NiCr alloys. It is already proved by several research groups (P. Marcus and J. Scully for instance), that Mo plays a huge role in NiCr-based alloys' passivity. The role of Mo is still debated though, but it is known for sure, that Mo ions form mixed oxide layers with Cr and/or Ni. New data. Included in Supplementary, does show the difference, at least in the Ni signal. You can't tell about the same behavior of growth and precipitation without considering alloying elements, unfortunately. Thus, to create a good, valid model, I must suggest either using Alloy 22 as the main alloy system in the model taking into account Mo, W, Fe, etc., which is way too difficult, or doing everything on Ni20Cr. As a suggestion of how to avoid pitting – probably, you need to go to the lower NaCl concentration (1 M will give pitting for sure).

Other minor comments:

1. Title of the section _ Three Regimes – is too general. Probably, Kinetics regimes (or just Regimes of...) of oxide formation and/or dissolution.
2. Same comment on the title Environmental Effects... What environment do you mean? In this paper and model, you are talking about only aqueous electrolytes (not air oxidation or molten salts). Furthermore, there is no effect of electrolyte composition considered, only pH. If so, title it as an influence of electrolyte or solution pH.
3. In addition to the previous comment, there is a significant influence on electrolyte composition. It is shown in Marcus' group works when chloride was added to sulfuric acid electrolytes, and as mentioned in your paper ICP-MS and XPS studies of Scully's group in chloride electrolytes and freshly published work utilized AESEC and XPS in sulfites. You got the point, that Cr enrichment occurs in acidic solution, but there is also a big difference between chloride and sulfate solutions. It is impossible to incorporate everything in the model, of course. So, in this case, what solution composition was tested and used to inform the model (in particular, chlorides) should be emphasized.
4. P. 24 'Cr trapped' change to 'Cr captured' as it is solid capture (not trapping).

Version 2:

Reviewer comments:

Reviewer #3

(Remarks to the Author)

In general, the authors addressed all my concerns and comments. I can recommend accepting this paper with a minor comment: the references are pretty much outdated. Please, add more references after 2020, especially in the last two years 2023-2024 there is none of them in the current manuscript version.

Open Access This Peer Review File is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

In cases where reviewers are anonymous, credit should be given to 'Anonymous Referee' and the source.

The images or other third party material in this Peer Review File are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

To view a copy of this license, visit <https://creativecommons.org/licenses/by/4.0/>

We thank the reviewers for all the comments. They helped us improve our manuscript. Below the reviewer comments are in black and our responses are given in blue.

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

The manuscript reports a multiscale computation framework by combining DFT and KMC simulations to elucidate the microscopic processes leading to the corrosion/passivation of Ni-Cr alloys. The authors demonstrate the predictability capabilities of the computation approach by comparing the simulation results with experimental characterization. To the best knowledge of this reviewer, the work reported here represents the first of this kind to tackle the complex corrosion phenomena by taking into consideration of several key parameters including alloy composition, temperature, pH, and applied voltage. The authors are suggested to address a few important issues:

1) From simulations, the authors identify three distinct voltage regimes: oxide growth, dissolution, and competitive dissolution and deposition. However, the microscopic picture underlying the three regimes is not clearly described in the manuscript. For instance, there is not much discussion about why Ni and Cr are oxidized at similar rates, what are the key kinetic parameters controlling the oxidation rate of the two species, what drives the reprecipitation of Ni or Cr and what are the important kinetic parameters leading to the difference in the reprecipitation rates of the two metals?

why Ni and Cr are oxidized at similar rates, what are the key kinetic parameters controlling the oxidation rate of the two species

We thank the reviewer for this question, which highlights the complexity of these competing processes. One key is that Ni-Cr exchange is much slower than vacancy diffusion, so Ni and Cr tend to migrate to the oxide/metal interface without rearranging their sequence. This was explained in the method section under “Other approximations... 5”. A new figure, S10, in the Supporting Information calculates the barriers for both processes to better illustrate this point. Macroscopically, the faster vacancy diffusion without species exchange means there is little selectivity between the oxidation of the two cations, leading to oxidation at similar rates. Hence, the oxide composition largely tracks the alloy composition (prior to dissolution).

The overall oxidation rate (i.e., oxide thickness) in Regime I is mainly determined by the cation vacancy diffusion rate within the oxide. In contrast, in Regime II, vacancy diffusion rates are largely inconsequential, as they are bypassed by the dissolution-reprecipitation process.

what drives the reprecipitation of Ni or Cr and what are the important kinetic parameters leading to the difference in the reprecipitation rates of the two metals?

The dissolution process is driven by demixing enthalpy because the mixed oxide is a metastable state that is kinetically trapped due to limitations in cation diffusion rates within the oxide.

Once the ions are in solution, the kinetics of rearrangement become facile, and the thermodynamic preference for segregated pure oxides dominates upon reprecipitation.

In order to clarify these processes and the underlying governing physics, we have included an additional concluding summary, as well as a new Figure 6 in the main text that schematically depicts what drives the physics in the three different voltage regimes. We hope this will clarify the central message for the reader.

2) Following the questions above, how do these key kinetic parameters vary with or depend on external corrosion/passivation conditions such as pH and applied voltage? If a clear correlation can be established from the simulations between the intrinsic kinetic processes and external conditions, this computation framework and the outcome of the simulations will be of high impact to the broad materials science community.

The external potential controls the energy landscape for dissolution due to the requirement of charge transfer, with dissolution energy varying linearly with potential. This makes the decomposition of the mixed oxide more thermodynamically favorable and hence kinetically accessible. However, it simultaneously makes the reprecipitation process less thermodynamically favorable. If the voltage is low, the system remains in Regime I due to the inability to access dissolution. If the voltage is high, the system is pushed into Regime III because reprecipitation is thermodynamically inaccessible. Regime II represents the intermediate case where the behavior is determined by both processes, as reprecipitation is still favorable but the barrier for dissolution can be overcome.

The effect of pH mirrors the effect of potential. The pH adjusts the free energy of dissolution, with lower pH making dissolution more favorable and reprecipitation less likely. Higher temperature enhances all kinetic processes, leading to thicker oxide formation. In addition, temperature increases the driving force for dissolution due to stronger solution entropy contributions; like potential and pH impacts, this also makes reprecipitation more difficult.

These effects have now been summarized in the conclusion and depicted in the new Figure 6.

3) In reality, aqueous corrosion involves a large quantity of protons (or OH) that may easily penetrate into oxide lattice and significantly affect the atom mobility, kinetics, and microstructure evolution of the passivation oxide film, as shown in a recent paper (Nat Mater. 17, 514 (2018)). Any discussion or results of the simulations incorporating such a doping effect would strengthen the work for dealing with more realistic corrosion processes.

This is a fair point. Our primary intention was to successfully capture the qualitative underlying physics for the dissolution-reprecipitation process. However, inclusion of H effects could aid a more detailed quantitative comparison of general corrosion phenomena. We could in principle extend our methodology to incorporate H as another diffusing species within the oxygen lattice

(e.g., $\text{Ni}(\text{OH})_2$, which shares the same essential oxygen lattice structure). This would require significant additional DFT training data but could be a future direction for study based on the same essential simulation framework. We expect that the addition of H would impact the relative stability of the expressed oxide and hydroxides. It could also alter rates of cation diffusion within the oxide, as is suggested in Nat Mater. 17, 514 (2018).

We have added the following sentences in the concluding paragraph:

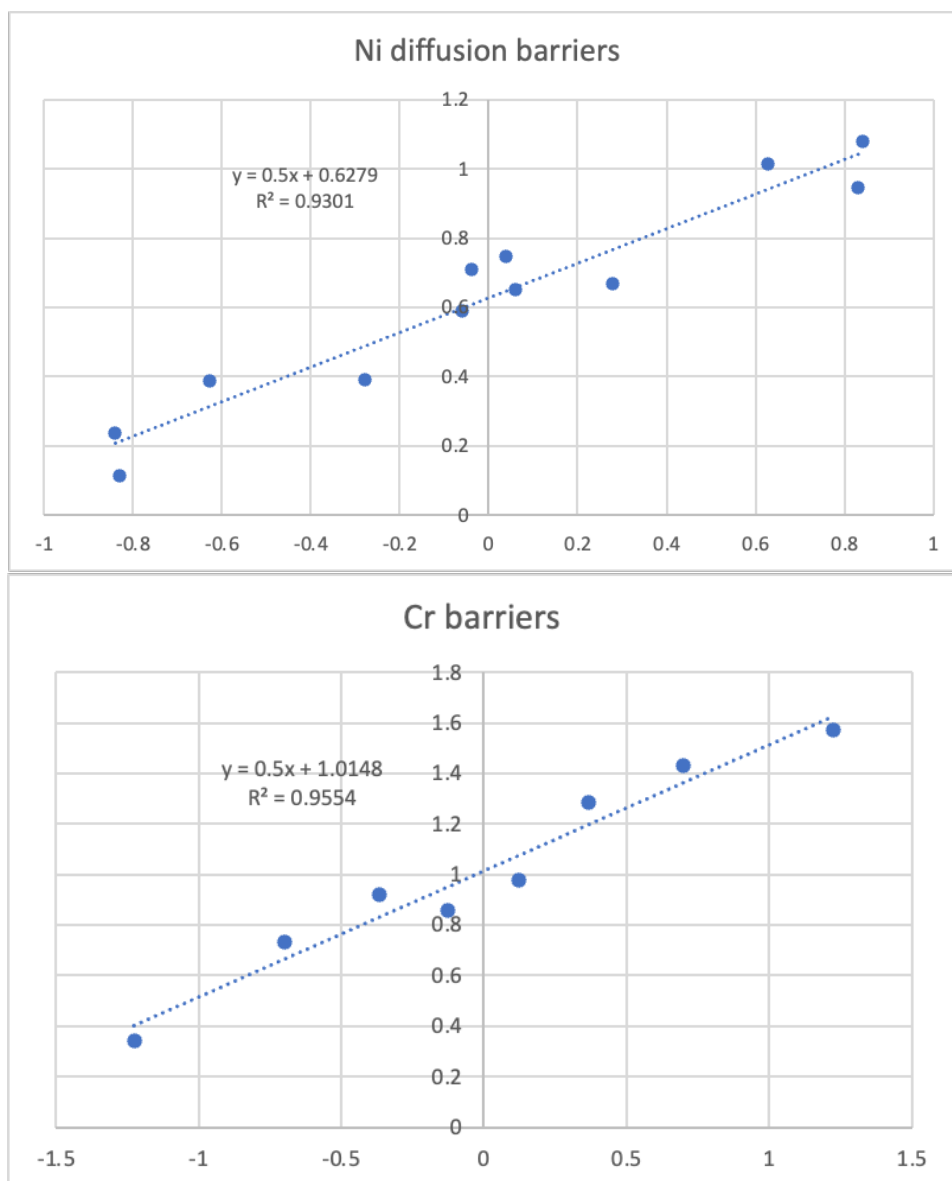
“Our simulation framework includes phase (meta)stability, defect-defect interactions and their interplay with ion diffusion. Based on the same framework but with more DFT training data, more species could be incorporated in the oxide lattice to study more general corrosion phenomena, such as effects of other minor elements from the alloy and H from the environment~\cite{luo2018atomic}”

4) More simulations details will be helpful. For instance, how the oxide growth and dissolution is achieved in the simulations, is there a fixed size of O sublattice and the oxide growth/dissolution is judged by tracking the position/number of metal atoms in the O sublattice? How diffusion barriers of Ni and Cr atoms are calculated and how the diffusion barriers depend on the stoichiometry of the oxide? Similarly, what are the kinetic or energy criteria used to define oxide growth, dissolution and reprecipitation?

The Reviewer is correct that the oxide thickness is determined by tracking the position of propagating metal atoms at the leading edge of the reaction front in the fixed, extended O sublattice. The_occupied O lattice was treated as O^{2-} , i.e., oxide, while the unoccupied O lattice was treated as having the energy of half of an O_2 gas molecule per O. An explicit statement to this effect has been added to the Methods.

To obtain the local environment-dependent diffusion barriers for Ni and Cr, we first parameterized the cluster expansion model for rapid evaluation of configuration-dependent energies of initial and final hopping states based on DFT calculations of ~1200 oxide configurations. Baseline diffusion barriers were computed for four or six reference configurations for each element (eight or twelve barriers considering forwards and backwards reactions), which were used to fit to a BEP relation to determine the dependence on local oxide environment/stoichiometry according to Eq. 6, as described in Methods.

Below we plot the diffusion barrier E_a versus energy change ΔE from DFT and NEB calculations. The environmentally independent diffusion barrier, E_{a0} , is determined by the intercept according to Equation 6.



We have made some slight changes to the description in Methods to include the barrier error bars:

“For ion diffusion, we further simplify the expression by assuming the curvatures of the two parabolic surfaces are identical, in which case the BEP relation becomes:

$$E_a = (4E_{a0} + \Delta E)^2 / 16E_{a0}$$

$$\approx E_{a0} + 0.5 \cdot \Delta E$$

where E_a is the activation energy, and ΔE is the energy difference between initial and final states, and E_{a0} is the intercept when $\Delta E = 0$. The only parameter E_{a0} was fitted from ΔE and E_a , calculated with the climbing-image nudged elastic band (CI-NEB) method by averaging over five independent reference configurations, which yielded values of 0.63 (+/-0.08) eV for Ni and 1.01 (+/-0.08) eV for Cr. Physically, E_{a0} is related to the curvature of the local energy wells, which is largely determined by the interaction between the hopping cation with the immediate nearest-neighbor oxygen anions; hence, E_{a0} should be mostly independent of the specific cation distribution.”

The criteria for growth, dissolution, and reprecipitation are determined only by tracking the change in the number of metal atoms in the oxide and solution rather than by invoking any specific kinetic or energy criterion. The boundaries for Regimes I, II, and III are merely qualitative, based on an ensemble averaged thickness and compositions as shown in Figure 2(c).

Reviewer #3 (Remarks to the Author):

Dear authors,

Thank you so much for attempting to create a model of a passive oxide film growth on Ni-Cr alloys. In case of the existence of a valid model that will match experimental data, it will have a huge impact in the field of aqueous corrosion.

We thank the reviewer for the positive endorsement of the potential impact of our study.

However, the current study does not provide sufficient information. Two main concerns which could not give me a possibility to recommend this article to be published are:
What was the main reason to use evaluated temperatures (363K, 400K, and even 500K) in modeling? Especially, to use different temperatures in one set of experiments (e.g. polarization at 363K, simulation at 400K, other experiments at room temperature)?

We understand that the different temperatures can cause some confusion. The chosen elevated simulation temperatures are for convenience of accelerating the computations. This is commonly done to improve statistics within reasonable run times. As shown in Fig. 4a (simulation) and 4c (experiments on Alloy 22), the primary impact of temperature is to shift the exact voltage thresholds for transitioning among the different kinetic regimes. Because we are interested primarily in reproducing the correct trends rather than quantitative voltages, the modest temperature discrepancy should not be a concern. It is also worth noting that our simulation setup deliberately neglects water evaporation or other temperature-sensitive water-related side reactions, which ensures that the same governing chemistry is retained even at elevated temperatures. These points have been added to the Methods section for clarification.

Regarding the use of different experimental temperatures: the electrochemical testing was performed between 298 and 363 K where the maximum experimental temperature was constrained by the boiling point of water. We use the simulations at 300K and 400K to bound these datasets and the simulation at 500K to simulate a higher degree of acceleration than can be accessed readily by experiment. XAS of Ni₇₀Cr₃₀ data is only available for films grown at 298K. This is for technical reasons; we were attempting in situ EC XAS which did not have a heating stage and these data were used as our control. We have added new XPS data for Ni₈₀Cr₂₀ at 363K in the passive region (See Figure S1). The same essential passive oxide behavior is shown, validating our choice.

2. Most parts of the experiments were done on Alloy 22. Also, authors emphasized several times that they 'developed an ab initio-based model capable of describing competing oxide growth and dissolution at the surface of a multicomponent alloy', mentioned alloys 80Ni-20Cr, Alloy 22, Inconel 600, 617, and Hastelloy 230, 276, 282. However, the model doesn't consider the presence of minor alloying elements such as Mo, Al, Fe, and W, which, as was reported a lot, play a huge role in passive film growth.

We acknowledge the reviewer's comment that the minor elements play a crucial role in determining the behavior and corrosion resistance of Alloy 22. We have added an additional paragraph to the Model Setup section and a supplemental figure to the Supporting Information (S1) to justify why we use Alloy 22 experimental data to compare with our binary model.

As for modeling, we opted for Ni80Cr20 due to its simplicity and ability to demonstrate competing dissolution-precipitation phenomena, which dictates the qualitative corrosion behavior and is the primary focus of our study. We agree that this binary model alloy is not standardly referred to as "multicomponent", and we have dialed down that language in the description of the model. In terms of experimental validation, we selected Alloy 22 because it does not pit, resulting in a more uniform surface response and current-voltage curves that more accurately represent the homogeneous dissolution-precipitation reaction. Note that pitting is not included explicitly in our model (it arises from imperfections that are neglected in our uniform corrosion setup). We elaborate below.

The primary objective of this paper was to address the dissolution of the mixed oxide and reprecipitation of the pure phase. Much of the experimental characterization was performed some time ago but was held because we did not understand why the nickel oxide would first dissolve and then reprecipitate under the same driving force. What the modeling work shows with clarity is that the mixed oxide is a metastable phase which would prefer to phase segregate. At sufficient overpotential, Ni can preferentially dissolve and then reprecipitate as a pure phase. In short, dissolution mediates phase separation.

To model the dissolution-precipitation phenomenon, we utilized Ni80Cr20, which is a simpler and more manageable alloy compared to the 5-component Alloy 22. Even with only two components, we still needed to calculate DFT energetics of over 1000 metal-oxygen-vacancy configurations to parameterize the energy landscape. Multicomponent formulations will require additional computational advances to handle the higher complexity, which we are currently pursuing. Nevertheless, to the best of our knowledge, this work is the most comprehensive attempt to date, and represents a first step towards studying other alloys.

Likely the bigger question in the reviewer's mind is why we chose to validate the model using the more complex Alloy 22 rather than a simple binary alloy. Unlike Ni80Cr20, Alloy 22 does not exhibit pitting, providing a more accurate representation of the dissolution-precipitation behavior without the complications of spatially varying local chemistry caused by pitting. Nonintuitively, it is our view that the more complex alloy is able to illustrate the simpler

dissolution-precipitation behavior due to the presence of minor elements that mitigate pitting, resulting in a more homogeneous surface reaction. Nevertheless, it is important to confirm that Alloy 22 and a simpler Ni80Cr20 alloy have the same dissolution-precipitation behavior. This is confirmed in a new study inserted in the Supporting Information, showing the same formation of a porous overlayer in both cases. In addition, we have found that the Ni and Cr composition of the passive films formed on both alloys in pH 3 and 8 solutions are similar, as evidenced by X-ray photoelectron spectroscopy (XPS) spectra, which are also included in the supplementary figure.

Notably, the fact that Ni80Cr20 is prone to pitting can be visually observed. This leads to a significant difference in the current-voltage response curve between the two alloys because the current response is a mixture of general metal dissolution from the oxide (the focus of this study) and highly localized (but large) currents from occasional pits. For these reasons, we chose Alloy 22 as the demonstration material for the observed trends.

All mentioned questions leave a lot of doubts about the model's validity.

As minor concerns, I would like to mention a mixture of temperature units (K and C) throughout the text, even together in the same figure capture.

Thank you for point this out. We have corrected the figure caption. In the main text where we are comparing model and experiments, we use only K. We include temperature in both C and K within the experimental section.

Below the reviewer comments are in black and our responses are given in blue.

Reviewer #1 (Remarks to the Author):

The authors have addressed all my concerns and questions. I would suggest for acceptance.

Reviewer #3 (Remarks to the Author):

Dear Authors,

Thank you so much for your response and detailed explanations of the reasons for using Alloy 22 in the electrochemical tests instead of Ni20Cr. I absolutely agree that Ni20Cr is a difficult system to perform electrochemical testing on not only because it is susceptible to pitting but also crevice corrosion in acidic electrolytes mostly. However, it is misleading to use a system that is more corrosion resistant in electrochemical tests because of the presenting alloying elements (Mo, W, etc.) to prove the concept of formation of only Cr and Ni oxides on the surface of NiCr alloys. It is already proved by several research groups (P. Marcus and J. Scully for instance), that Mo plays a huge role in NiCr-based alloys' passivity. The role of Mo is still debated though, but it is known for sure, that Mo ions form mixed oxide layers with Cr and/or Ni. New data. Included in Supplementary, does show the difference, at least in the Ni signal. You can't tell about the same behavior of growth and precipitation without considering alloying elements, unfortunately. Thus, to create a good, valid model, I must suggest either using Alloy 22 as the main alloy system in the model taking into account Mo, W, Fe, etc., which is way too difficult, or doing everything on Ni20Cr. As a suggestion of how to avoid pitting – probably, you need to go to the lower NaCl concentration (1 M will give pitting for sure).

Thank you for the observation—you are certainly correct that there could be mitigating factors arising from the minority elements. After some wrestling with how to properly address this, we ultimately took the reviewer's suggestion to carefully redo the measurements on Ni20Cr. In particular, we repeated most of electrochemical tests and necessary characterization (AFM, XPS, XAS) on Ni20Cr in a NaCl-free solution. Although this took quite some time to complete, we are now quite satisfied with the qualitative agreement between Ni20Cr and Alloy 22 and hope that the reviewer will agree. The same basic dissolution-reprecipitation mechanism is observed experimentally, both in terms of the polarization curve behavior and the essential composition and morphology trends. In both cases, a thick porous Ni oxide forms in the transpassive voltage region before general dissolution starts in near-neutral solution (pH~8); such Ni oxide is replaced by a thin Cr-rich oxide in the same voltage region until general dissolution occurs in acidic solution (pH~3). We note that the actual voltages associated with the three regimes shift (as the reviewer notes, this is expected based on the known role of Mo and possibly other elements in enhancing passivity), but the transitions are still observable, and the essential conclusions of our manuscript remain robust.

We have now restructured the paper partially around the comparison between Alloy 22 and Ni20Cr, as we believe that the qualitative similarity emphasizes the generality of the predictions. Figures 2, 3, and 5 in particular have been reformulated to show the comparisons.

In addition to showing similar behavior, the findings actually help to exclude a possible role of Mo in terms of the dissolution-precipitation mechanism. Instead, we can conclude that Mo adjusts the rates of dissolution but does not qualitatively change the mechanism. Note, however, that we are focused on general corrosion rather than pitting, so any conclusions regarding the role of Mo should be limited to this mode. Still, we believe that the new understanding of the morphological and compositional changes may also lay the foundation for better understanding of pitting and the role of Mo in the future.

We sincerely thank the reviewer for encouraging us to do this. Although it was a substantial lift, the results speak for themselves as a testament to value of the peer review process. The paper is truly improved, and the model can now be claimed as more generally describing Ni-Cr alloys.

The added contents in the main text are summarized in the following:

1. Figure 2 (a): potentiodynamic scan for the 80%Ni-20%Cr model alloy.
2. Figure 3: AFM and XPS for 80%Ni-20%Cr in regime (I) and (II).
3. Figure 5(b, c): potentiodynamic scan and XPS for 80%Ni-20%Cr at low pH.
4. A discussion on the comparison between 80%Ni-20%Cr and Alloy 22 on page 11, “Hence, the primary porous oxide compositions for 80%Ni-20%Cr and Alloy 22 show remarkable consistency (at least within the outermost surface region). Notably, the spectral and morphological similarities between the two alloys in regime (II) demonstrates that the appearance of this transition is not strongly influenced by the presence of the other alloying elements in Alloy 22 (Mo, W, and Fe), despite the known impact of these elements in promoting corrosion resistance.^{29–33} We can therefore conclude that in the context of general corrosion (as opposed to pitting), these secondary elements shift the onset potentials for the different regimes but do not qualitatively change the associated mechanisms.”

Other minor comments:

1. Title of the section _ Three Regimes – is too general. Probably, Kinetics regimes (or just Regimes of...) of oxide formation and/or dissolution.

This has been retitled “Voltage-dependent Kinetic Regimes for Surface Oxide Evolution”.

2. Same comment on the title Environmental Effects... What environment do you mean? In this paper and model, you are talking about only aqueous electrolytes (not air oxidation or molten salts). Furthermore, there is no effect of electrolyte composition considered, only pH. If so, title it as an influence of electrolyte or solution pH.

This has been retitled “pH and Temperature Effects”.

3. In addition to the previous comment, there is a significant influence on electrolyte composition. It is shown in Marcus’ group works when chloride was added to sulfuric acid electrolytes, and as mentioned in your paper ICP-MS and XPS studies of Scully’s group in chloride electrolytes and freshly published work utilized AESEC and XPS in sulfites. You got the point, that Cr enrichment occurs in acidic solution, but there is also a big difference between

chloride and sulfate solutions. It is impossible to incorporate everything in the model, of course. So, in this case, what solution composition was tested and used to inform the model (in particular, chlorides) should be emphasized.

We have done our best to detail the solution compositions in each case. Table 2 on page 35 in the Methods section has the exact solution compositions, as well as pHs for each measurement. Tables S4 and S5 in the SI summarize all the electrochemical processing parameters for each figure.

4. P. 24 'Cr trapped' change to 'Cr captured' as it is solid capture (not trapping).

This has been fixed.