

Anodic Kinetics of NiCrMo Alloys During Localized Corrosion

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Presented by:
**Roger C. Newman, David X. He
University of Toronto
Department of Chemical
Engineering and Applied
Chemistry**

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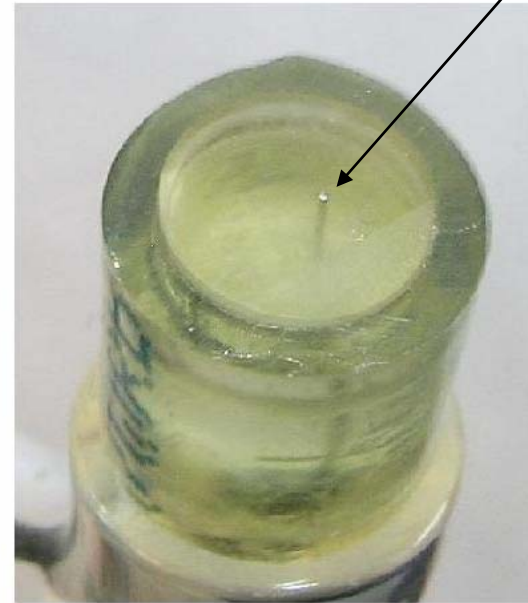
Aims of the research

- **-to acquire localized corrosion kinetic maps for a series of NiCrMo alloys that display current density versus potential and local chemistry (dissolved cation concentration and associated chloride concentration)**
- **-to understand the form of these maps and the underlying processes involved, including any similarities to or differences from stainless steels**
- **(in further work)**
 - to measure and understand the effect of adding nitrate ions.**

The main tool: The artificial pit technique



Working electrode is dissolved anodically to create an artificial pit [crevice] cavity



(shows room-temperature version of the mounting resin – high-temperature resin used for 90°C experiments)

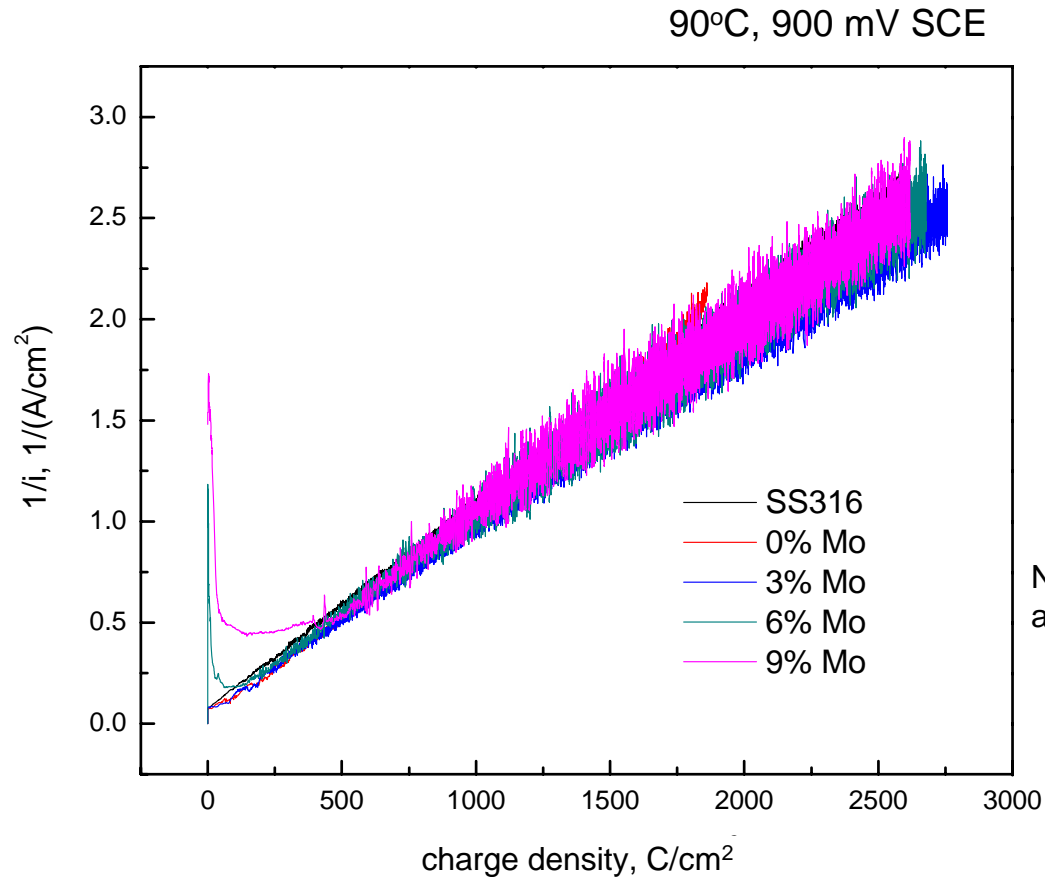
Merits of the artificial pit technique

- Simple coulometry gives the cavity depth (diffusion length).
- The cavity grows under anodic diffusion control at oxidizing potentials and in the active (film-free) state at lower potentials.
- The diffusion-controlled region gives the product $D \cdot c_{\text{sat}}$ directly for the dissolving cations, where c_{sat} is the solubility of the salt, such as NiCl_2 , that limits the current, and D the diffusivity of the dissolving cations.
- Unsteady-state experiments and associated modeling can give D separately, and thence i vs. c ($c < c_{\text{sat}}$) at various E : thus producing a complete kinetic map for a particular alloy system, *including the range of currents and potentials that are relevant to crevice corrosion in practice.*

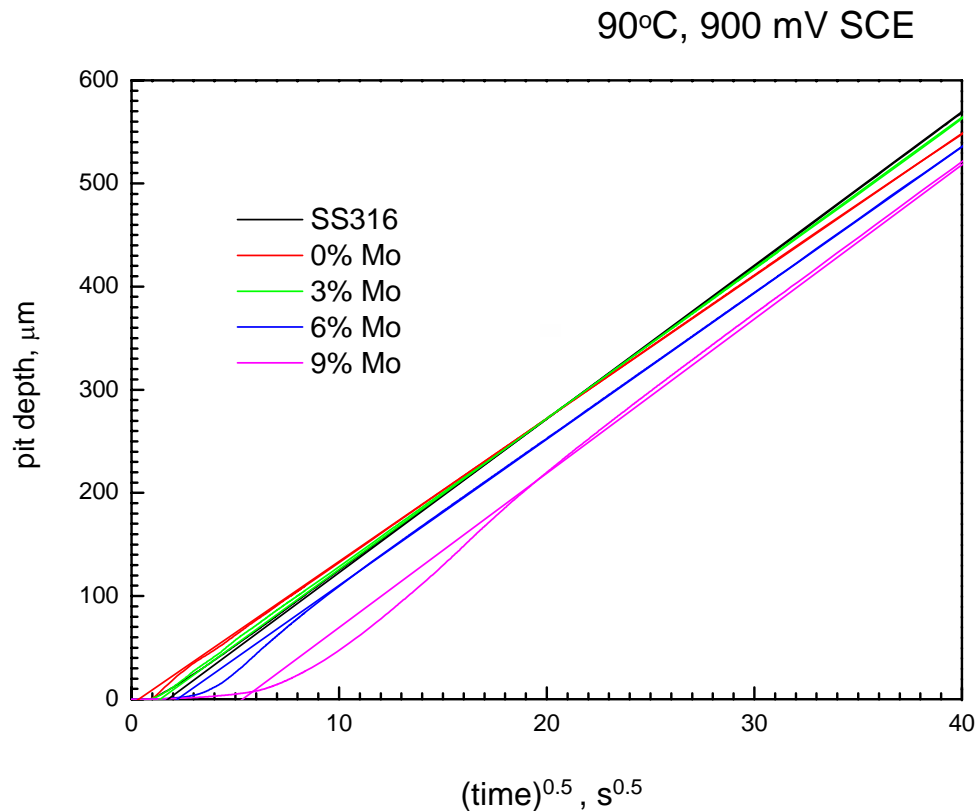
Materials used in this study

- **Ni-22Cr-xMo, swaged and drawn to 125 μm (typically) wire [DOE Ames Lab]**
- **x = 0, 3, 6, 9 and 13**
- **Other alloys with W addition to be studied later**
- **Electrolytes** **this talk – 1M NaCl only**
other ongoing work – NaCl + NaNO₃
bulk and thin-layer
90°C

Diffusion controlled growth shows little or no effect of alloyed Mo

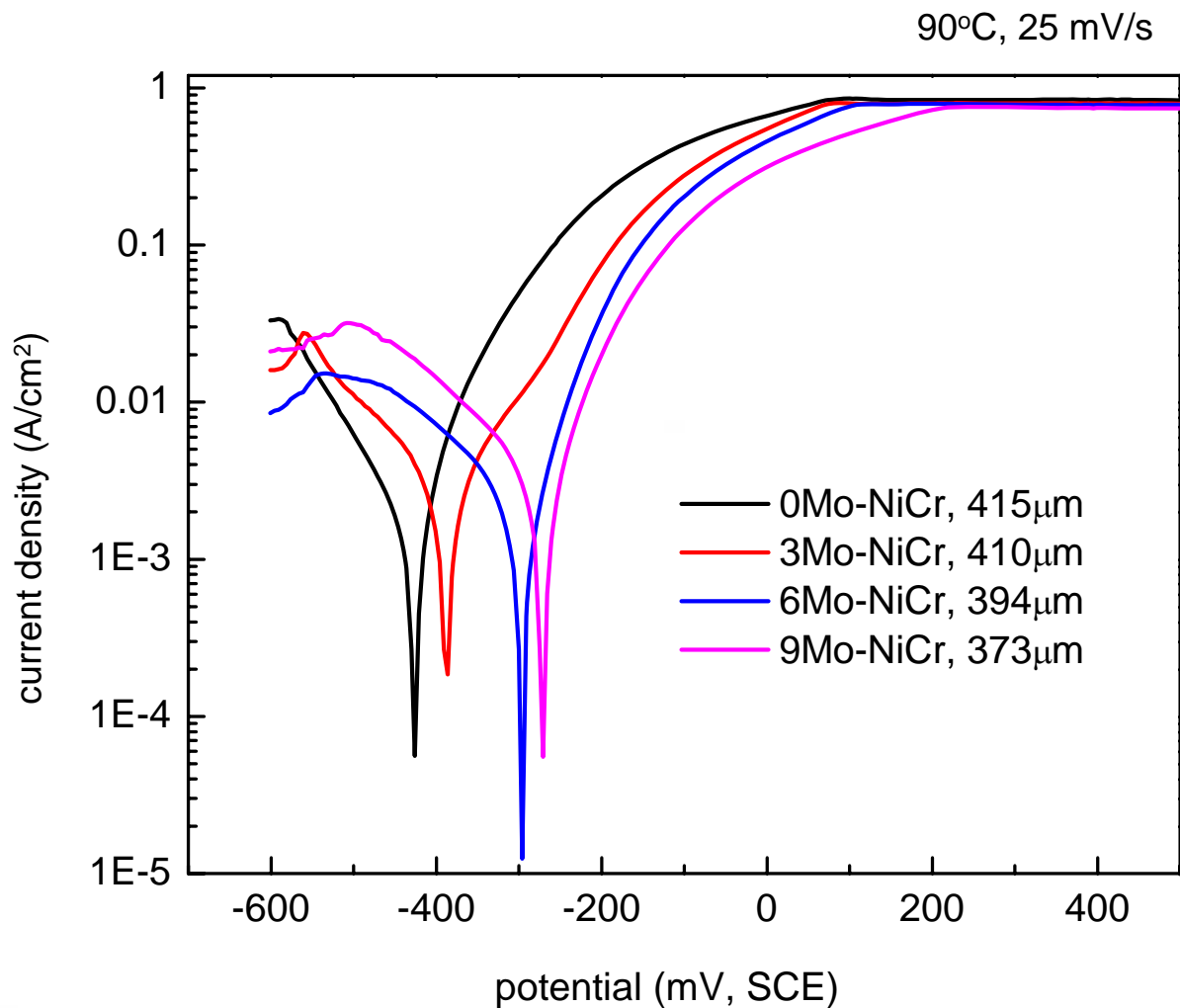


Diffusion-controlled growth (continued)

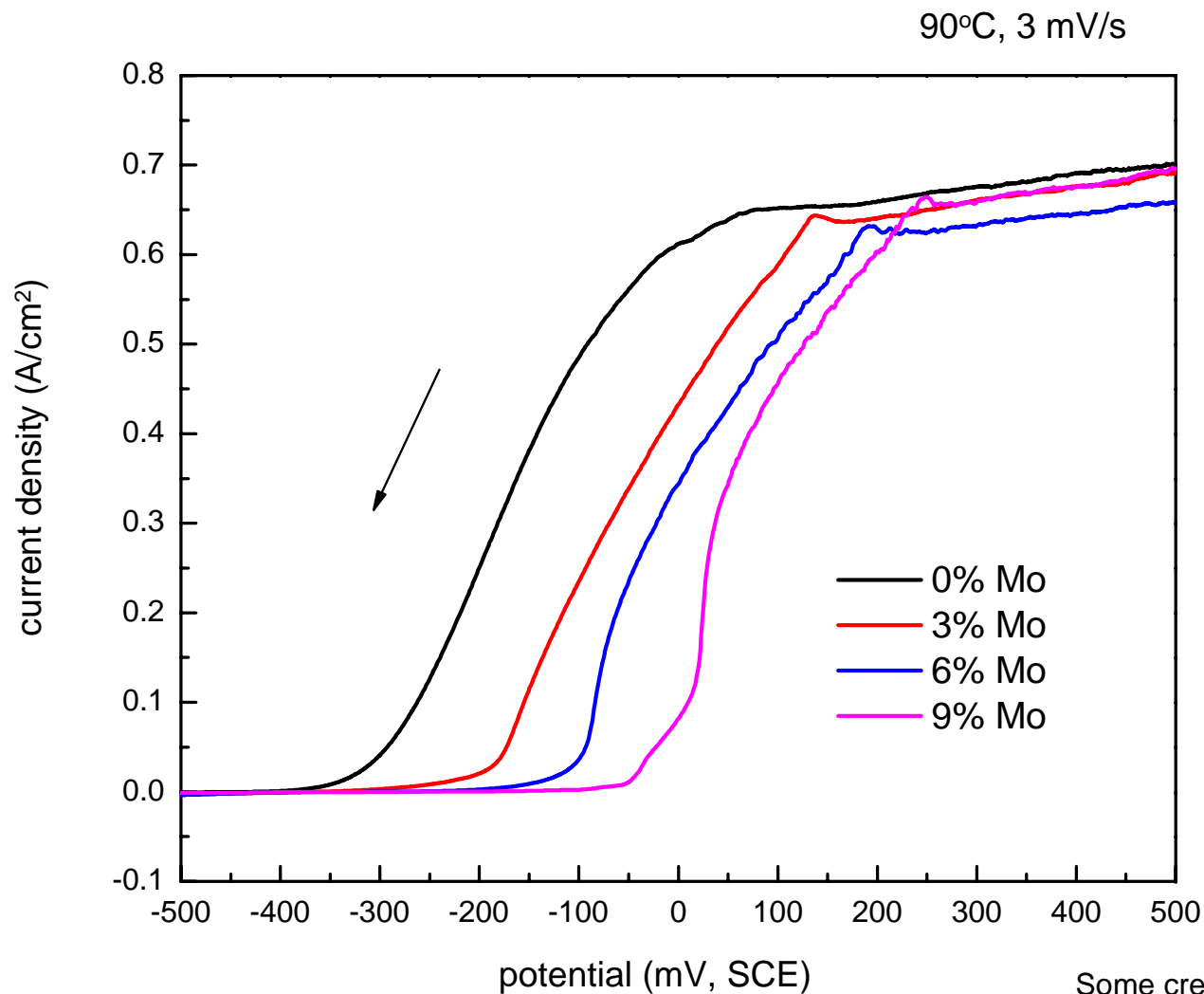


This and the previous slide are fully consistent with simple diffusion control – deviations are due to the varying pit coalescence period (longer for higher Mo)

Fast potentiodynamic backscans give the dissolution kinetics in a nearly saturated pit solution

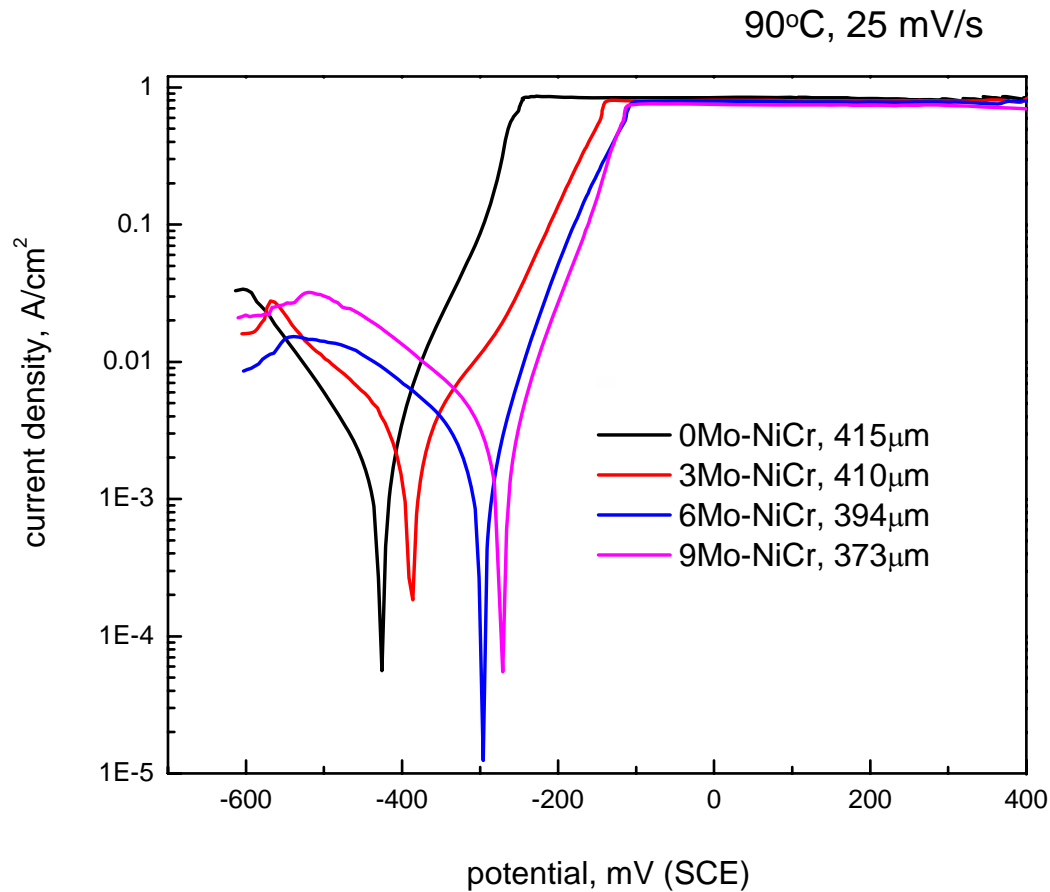


Slow backscans show repassivation at $i \approx 0.3-0.6 i_{lim}$ - allows pit surface chemistry to follow current

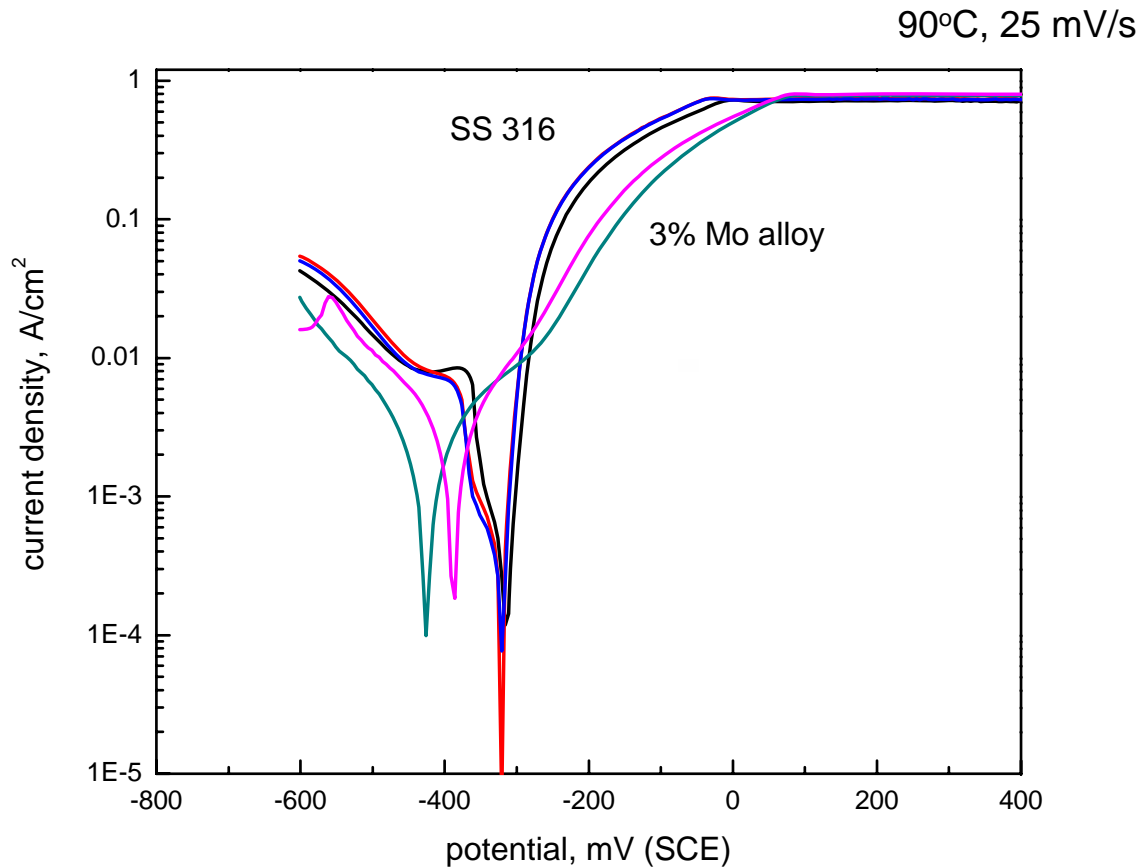


Some crevice corrosion issues here

Impedance measurement allows IR correction of the fast backscans, showing Tafel behavior

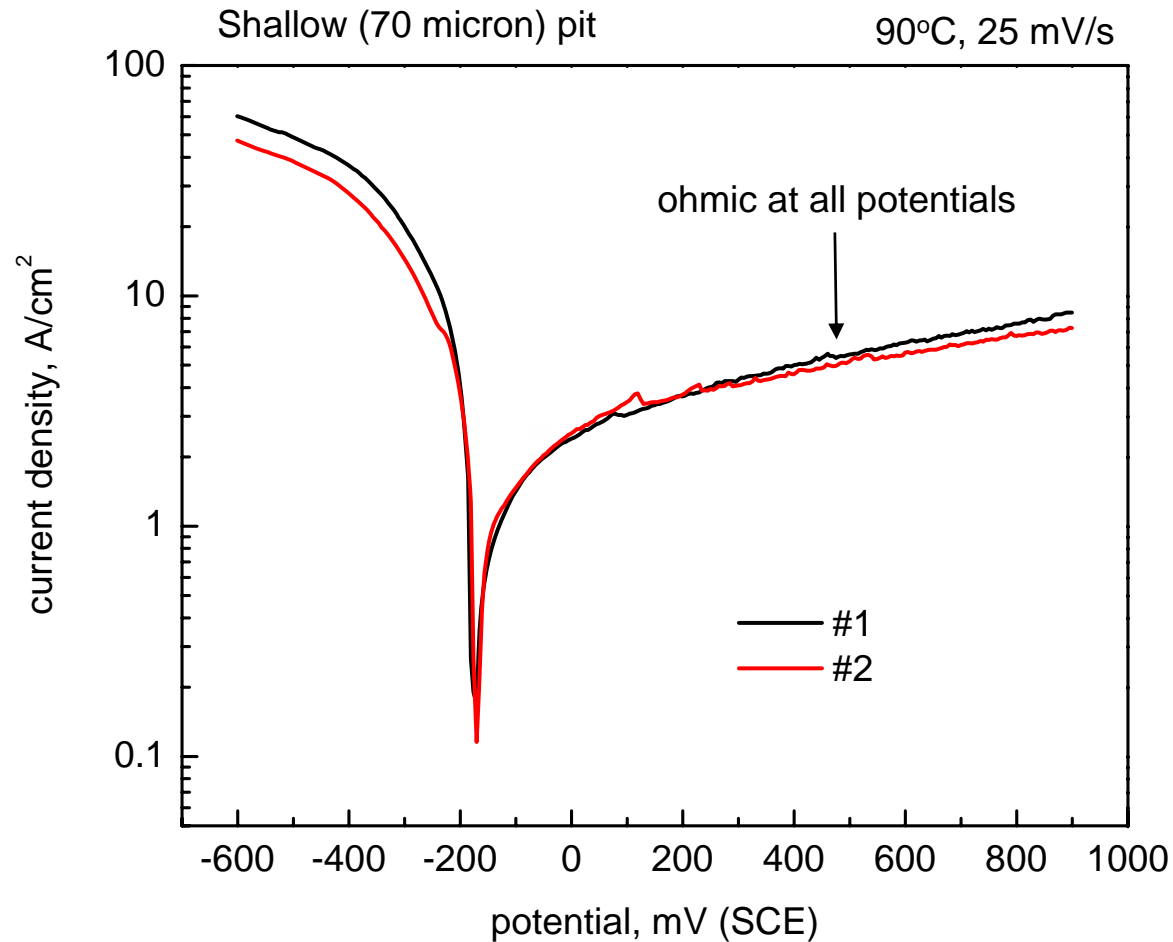


Comparison of Ni-22Cr-3Mo and 316SS in fast backscan experiments



High E_{corr} for 316SS probably due to low levels of alloyed Cu that dissolves during pit growth then replates - note reduction peak

Limited data for the 13Mo alloy indicate that its behavior may be subtly different



Conclusions from the basic electrochemical kinetic study

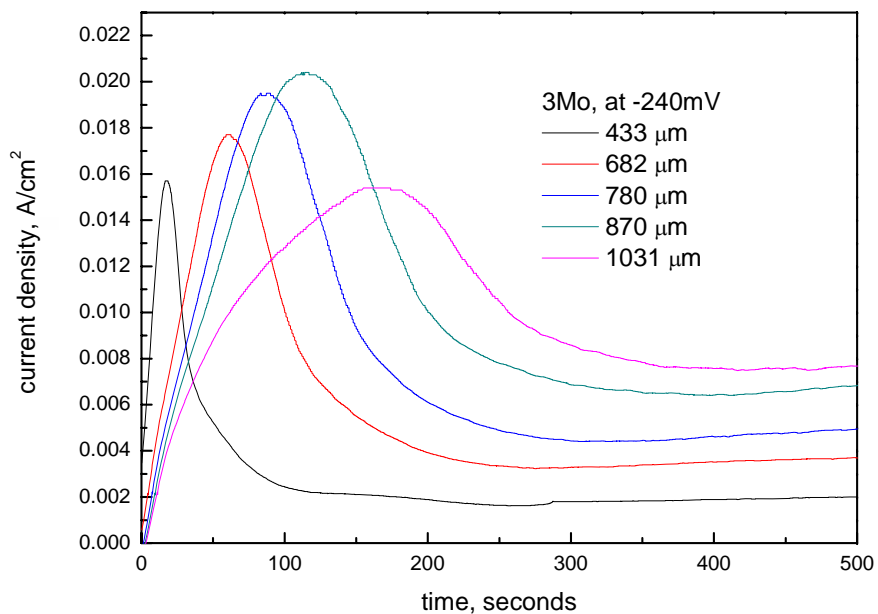
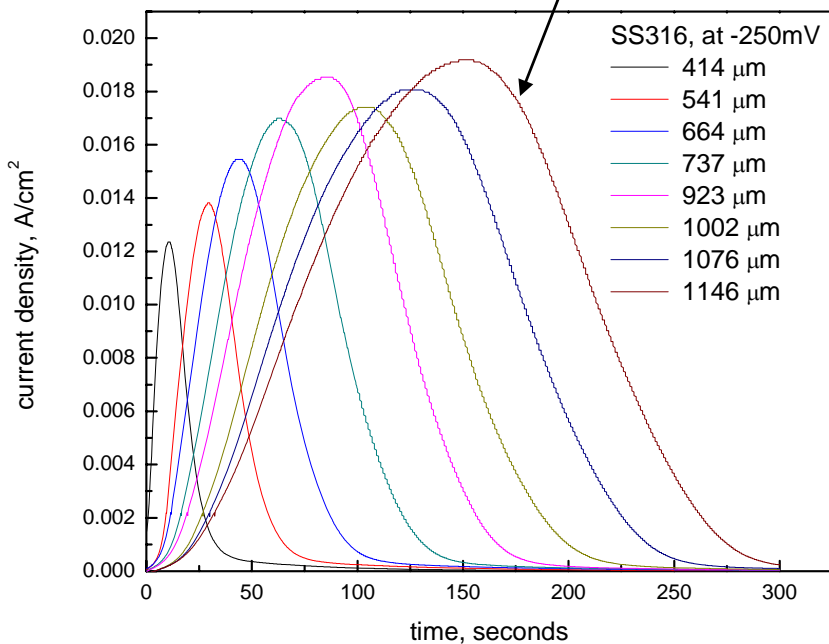
- Mo ennobles anodic dissolution of Ni-22Cr similarly to its effect in stainless steels.
- There are detailed differences in dissolution kinetics.
- Creating an active cavity is much more difficult at 13Mo than at 9Mo – there are indications that the 13Mo alloy forms a resistive porous corrosion product - but more work is required on this topic.

Kinetics in diluted cavity solutions

- The use of thin wires and shallow cavities formerly precluded measurements on artificial pit electrodes at corrosion rates relevant to crevice corrosion.
- Now modern low-noise potentiostats enable kinetics to be determined over 5 orders of magnitude in anodic current density and in very short experiments.
- These measurements are conducted in an unsteady state: (1) obtain the diffusion-controlled condition at high potential; (2) drop the potential to the crevice corrosion range; (3) measure current density versus time as the electrode first dissolves actively, then passivates.
- A finite difference diffusion model is used to obtain anodic current density (i) as a function of concentration of dissolving cations (c) - the separate determination of cation diffusivity D will not be discussed here.

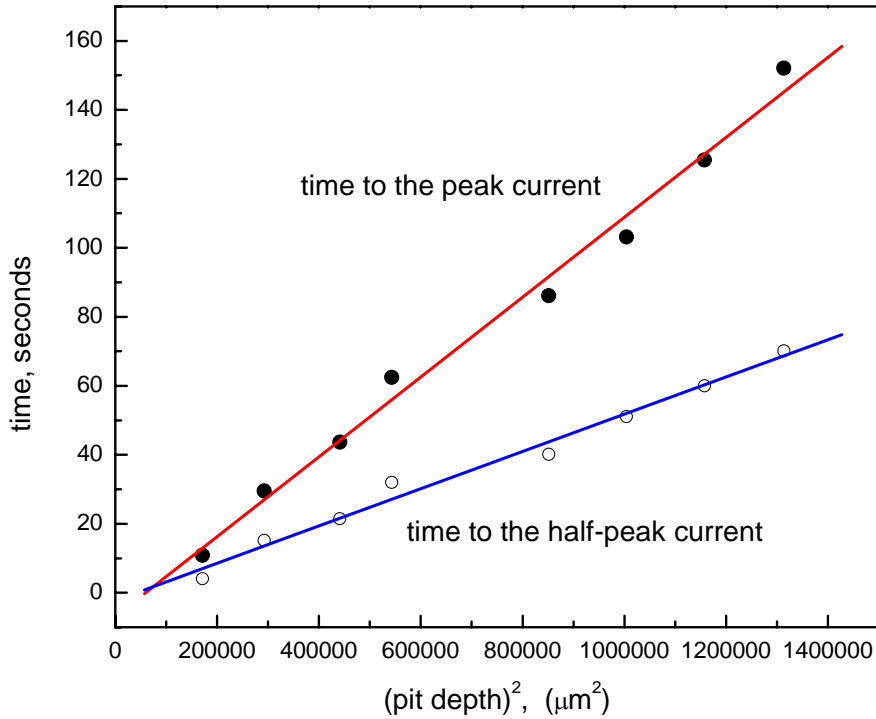
Current transients for pits of different depths after stepping the potential down from the limiting current region

Note that the falling part of these curves is not 'real' – passivation has started and dissolution undercuts the surface

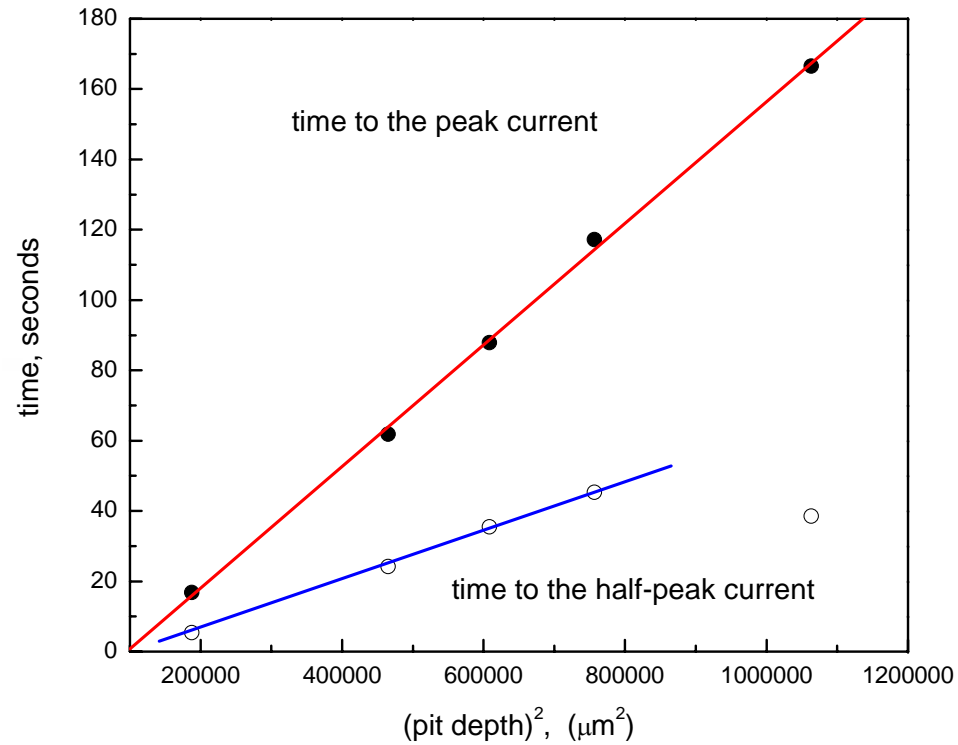


Differences in peak height reflect mildly time-dependent dissolution kinetics. Not clear whether the apparent easier passivation of 316SS is a real effect.

Time to peak current versus (depth)²

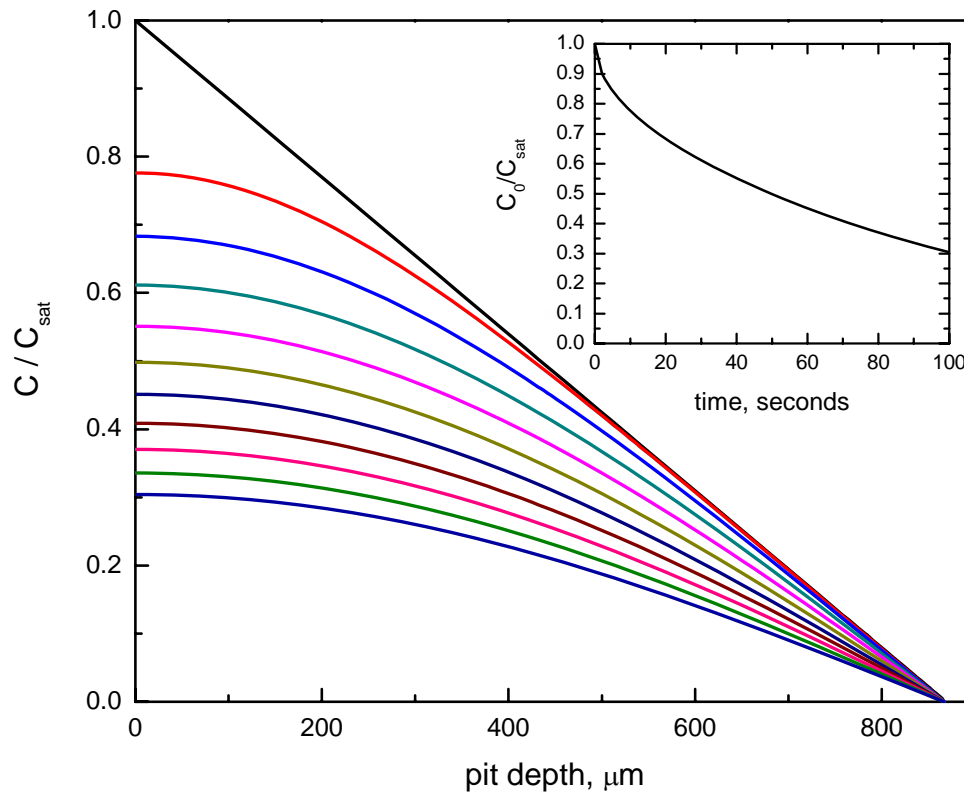


316SS



Ni-22Cr-3Mo

Approach to the determination of i vs c using the finite difference model (separate determination of D not discussed)



The example shown is for negligible i compared with i_{lim} .
The program accommodates the actual variation of i with t .

Conclusions

- **The effect of alloyed Mo on localized dissolution kinetics is broadly similar for NiCrMo alloys and stainless steels, but with differences in electrochemical quantities such as corrosion potential, corrosion current density and ease of repassivation.**
- **Between 9 and 13% Mo an unusual ohmic behavior appears that may be due to solids in the cavity, but this requires further work.**
- **A transient technique has been developed that enables rapid determination of a complete ‘localized dissolution kinetics’ map.**
- **Time-dependent dissolution kinetics require more research, but are also well revealed by the artificial pit technique. At present these effects appear to be mild (less than a factor of 3). The 13Mo alloy may have a more important degree of time-dependent behavior than the other NiCrMo alloys.**
- **The artificial pit technique has been extended to the range of crevice corrosion conditions that pertain for NiCrMo alloys in high temperature chloride solutions.**