

SURFACE ANALYSES OF ALLOY 22 UNDER CONDITIONS THAT PROMOTE STRESS CORROSION CRACKING

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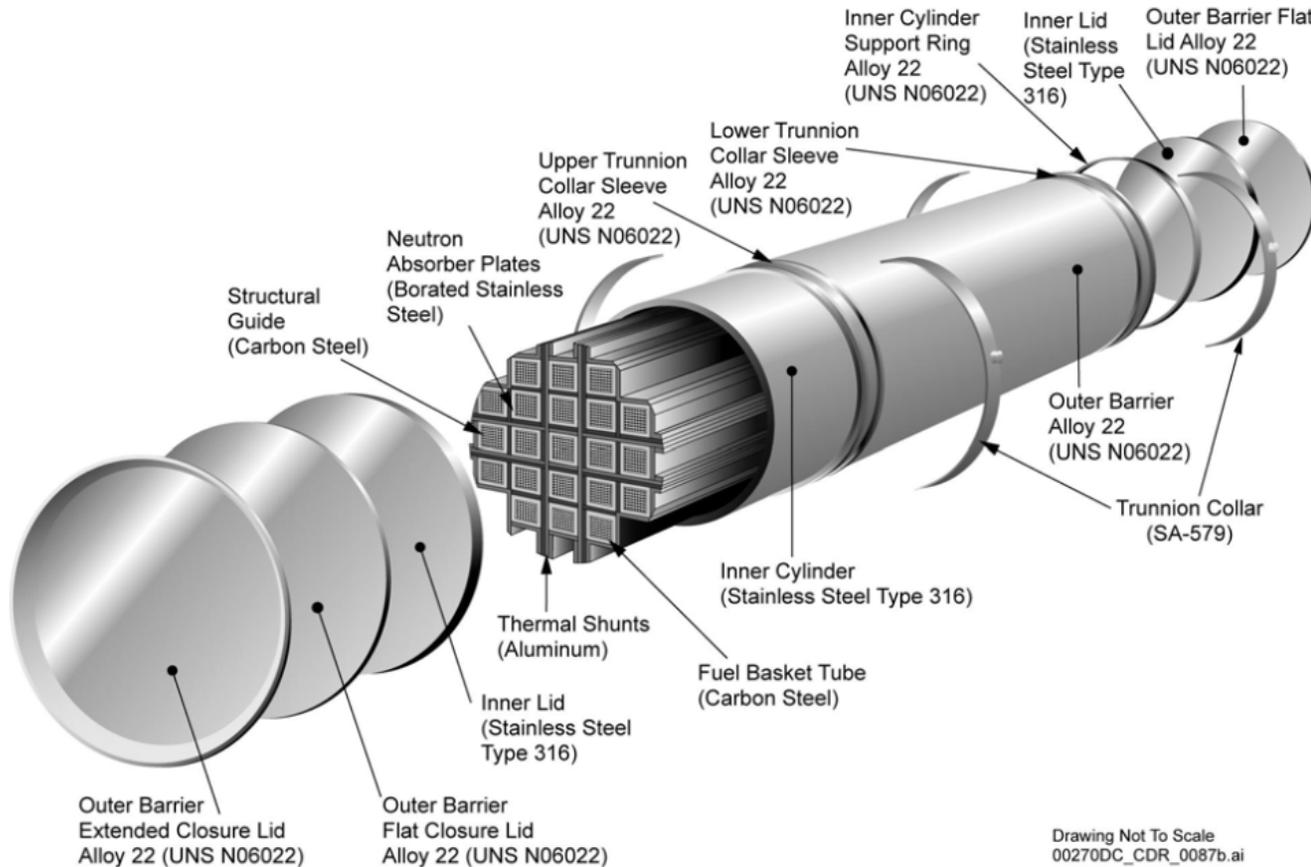
San Antonio, Texas 78238-5166

CORROSION/2006

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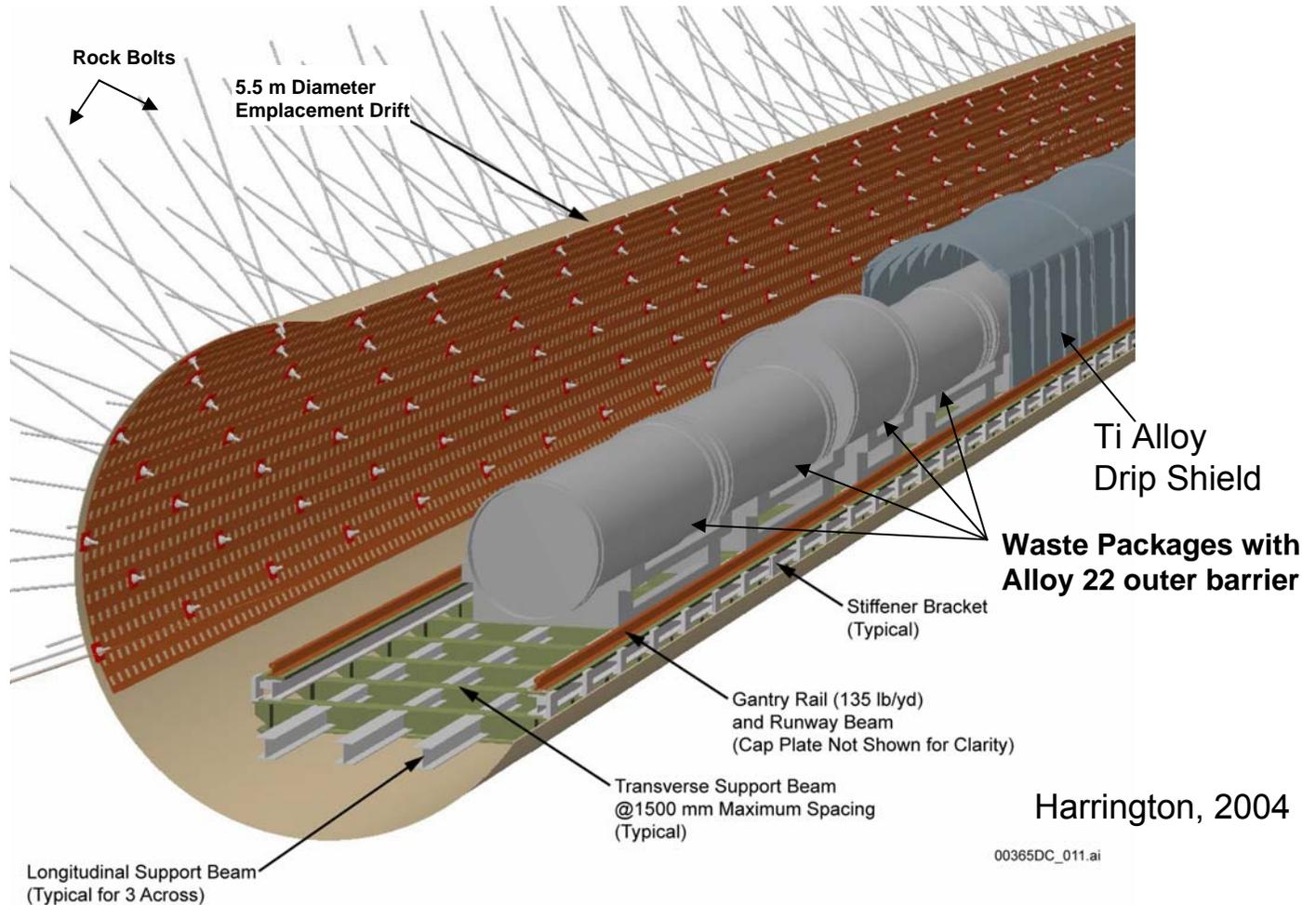
Potential Waste Package Design



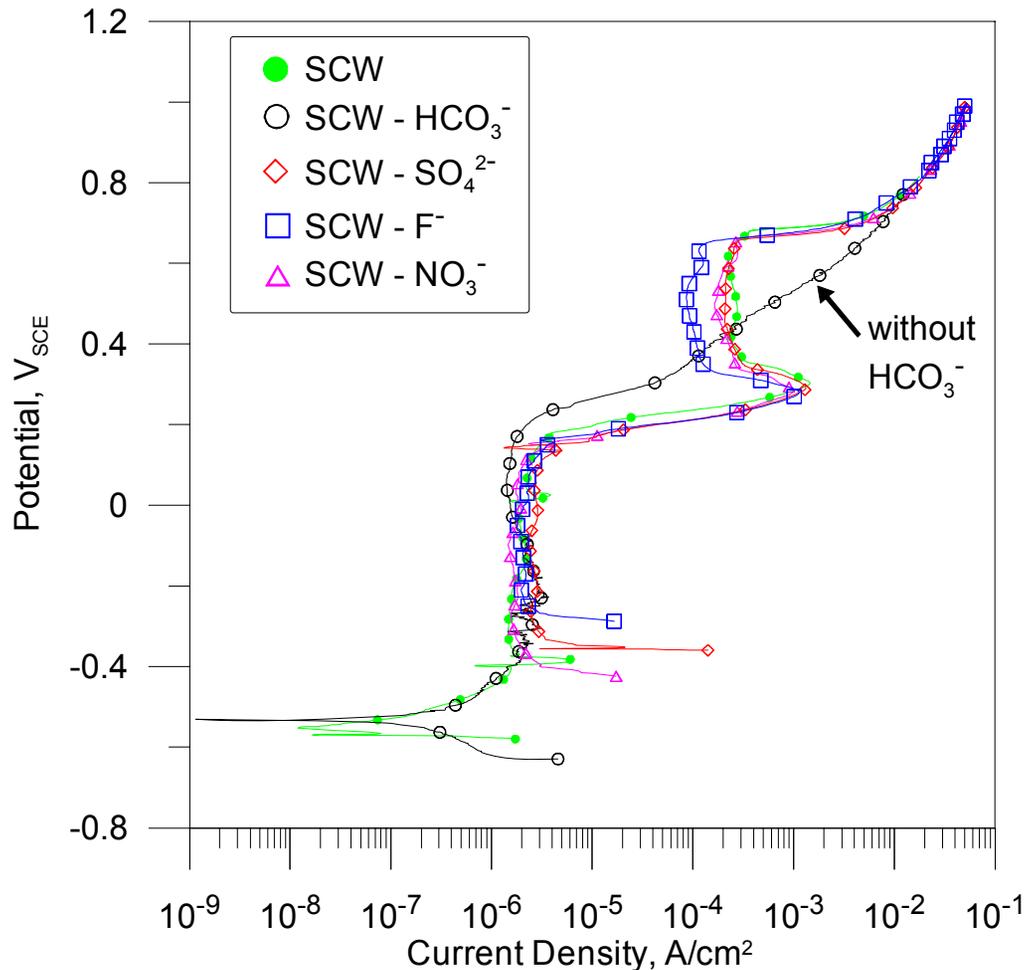
- Alloy 22 Outer Container
- Type 316 Nuclear Grade Stainless Steel Inner Container

Anderson et al. 2003

Drift Emplacement



Anodic Polarization Test Results



- Slow Strain Rate Tests Show Bicarbonate Necessary for Stress Corrosion Cracking
- Similar Results in All Solutions Except in the Absence of Bicarbonate

Objectives

- Analyze the Composition of the Oxide Films on Alloy 22 Specimens as a Function of Solution Chemistry and Electrochemical Conditions
- Compare Oxide Film Compositions Formed Under Conditions that Are Known to Promote Stress Corrosion Cracking with Oxides Formed Under Benign Conditions

Material

Alloy 22 Composition

| Material | Ni | Cr | Mo | W | Fe | Co | Si | Mn | V | P | S | C |
|-------------------------|------|-------|-------|------|------|------|-------|------|------|-------|-------|-------|
| Alloy 22 2277-3-3266 | 57.8 | 21.40 | 13.60 | 3.00 | 3.80 | 0.09 | 0.030 | 0.12 | 0.15 | 0.008 | 0.002 | 0.004 |

- Alloy 22 Test Specimens 19 × 13 × 4 mm [0.75 × 0.51 × 0.15 in] Machined From a 12.7-mm [0.5-in] Plate
- Specimens Were Polished to a 2,000 Grit Finish and Ultrasonically Cleaned in Acetone and Deionized Water

Approach

Specimen Preparation

- Alloy 22 specimens placed in standard electrochemical test cells
- Test solutions maintained at 95 °C [203 °F]
- Specimens potentiostatically polarized
- Solutions contained ratios of chloride and bicarbonate, which are known to be significant for stress corrosion cracking based on slow strain rate tests

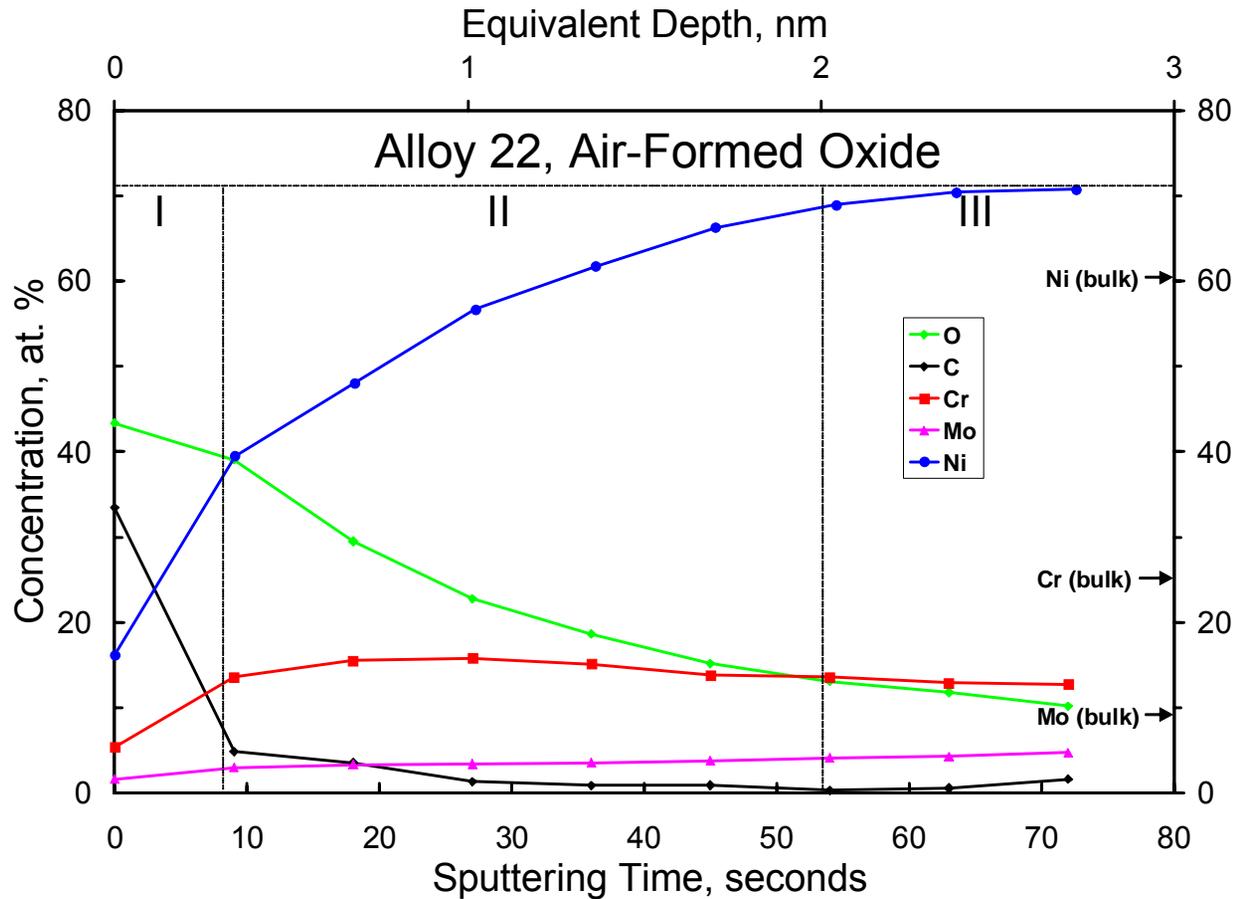
Surface Analyses

- Oxide films analyzed using X-ray photoelectron spectroscopy
- The sputtering rate was 2.27 nm/min [8.94×10^{-5} mil/min], obtained by sputtering an SiO₂ film

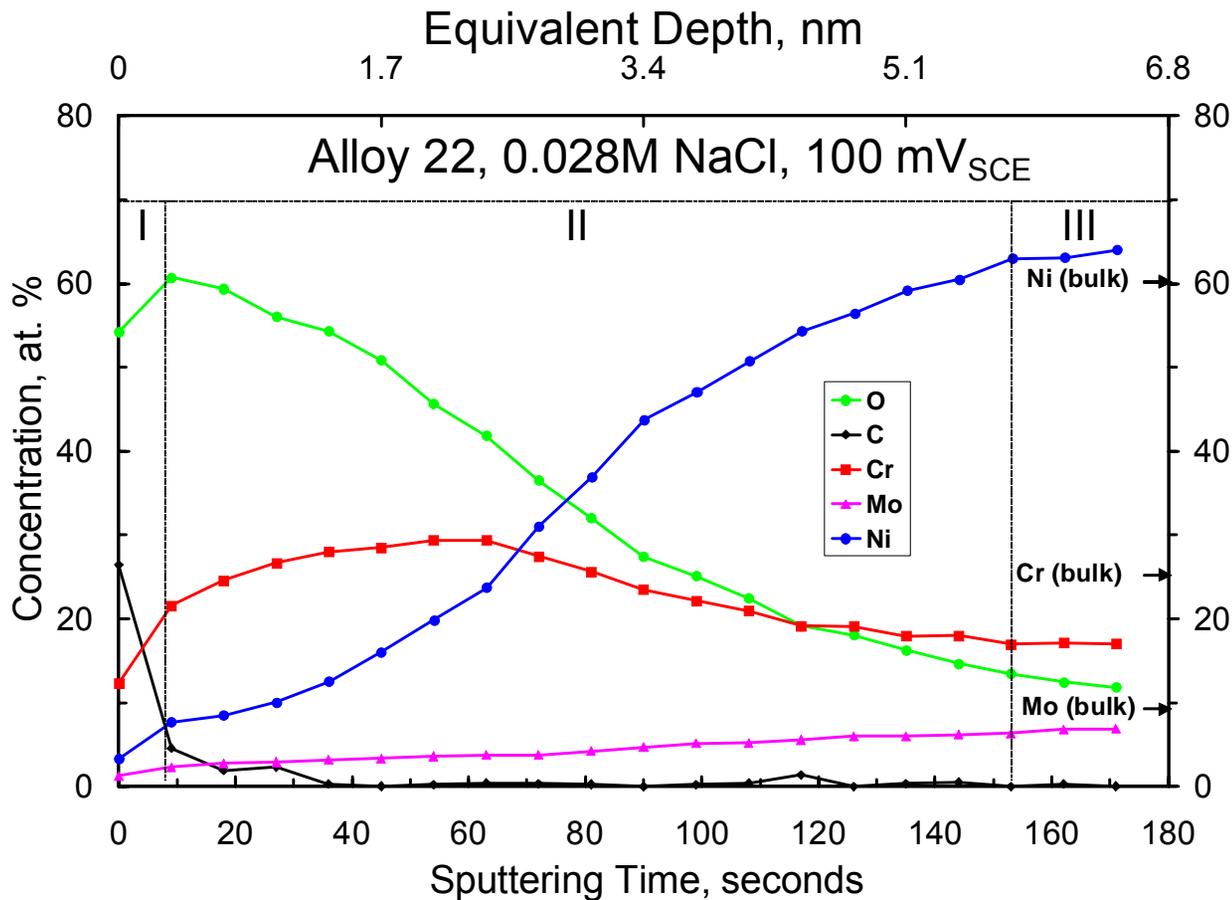
Composition of Simulated Concentrated Water (SCW)

| Ion | K ⁺ | Na ⁺ | Mg ²⁺ | Ca ²⁺ | F ⁻ | Cl ⁻ | NO ₃ ⁻ | SO ₄ ²⁻ | HCO ₃ ⁻ |
|-----------------------|----------------|-----------------|------------------|------------------|----------------|-----------------|------------------------------|-------------------------------|-------------------------------|
| Concentration (Molar) | 0.09 | 1.78 | <0.0004 | <0.0003 | 0.074 | 0.19 | 0.10 | 0.17 | 1.14 |

Air-Formed Oxide on Alloy 22

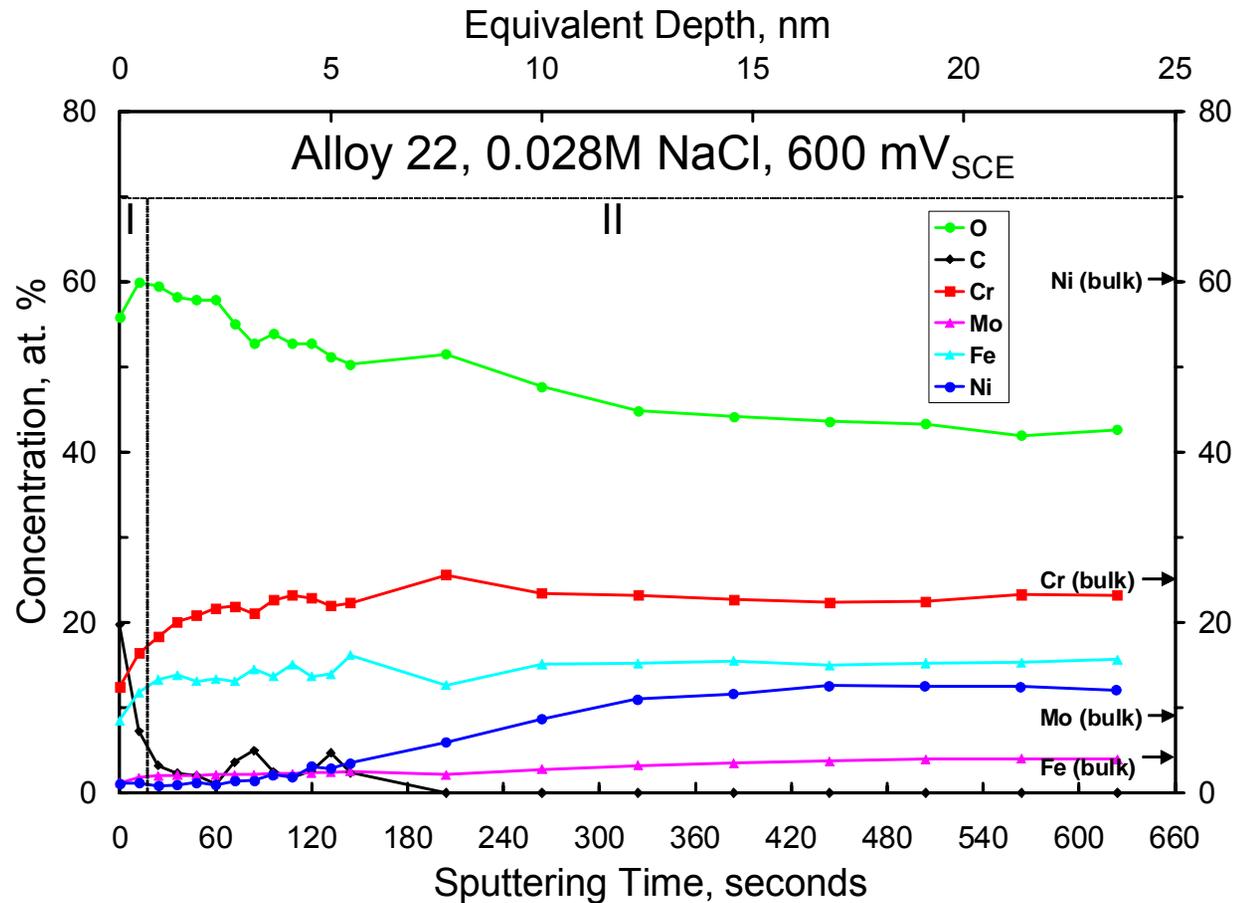


Passive Oxide Film



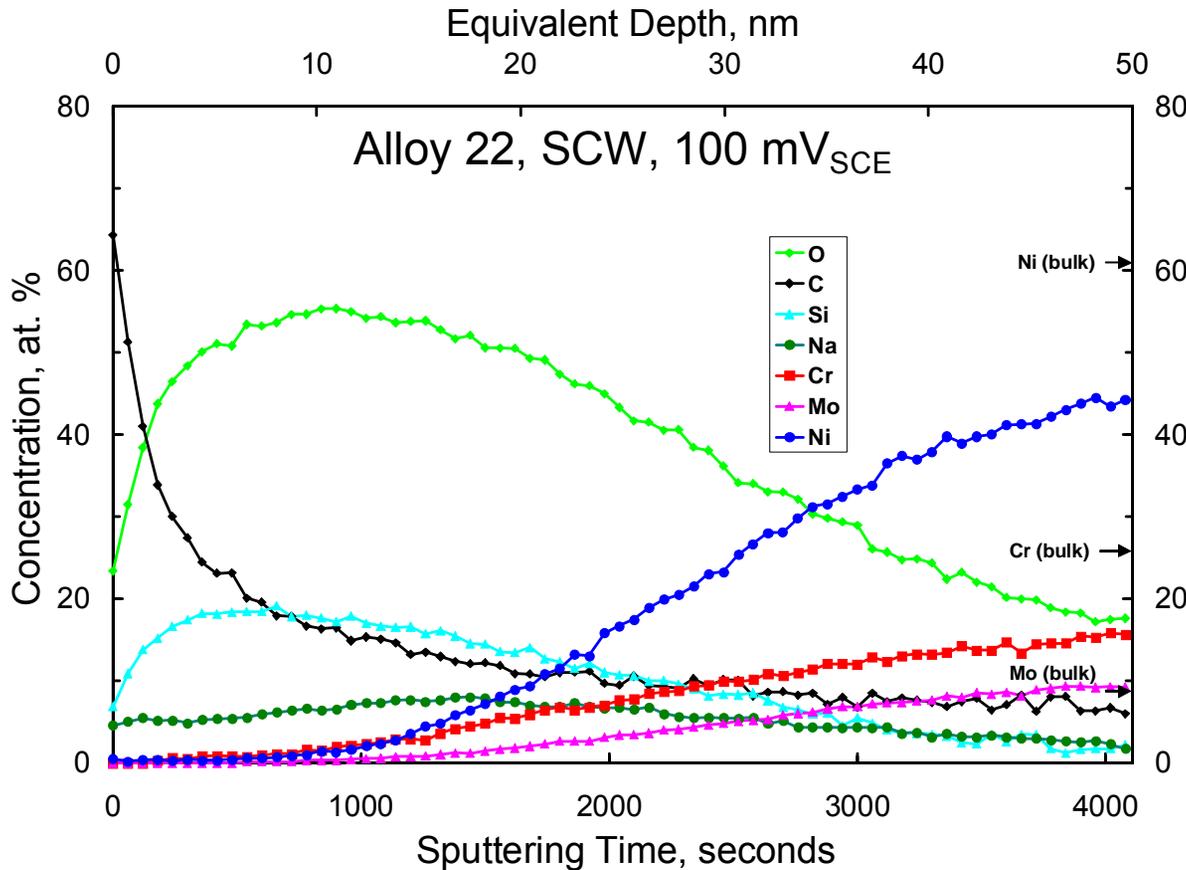
- Oxide Formed at 100 mV_{SCE} in 0.028 M NaCl
- High Cr and Mo Concentrations in the Oxide

Transpassive Conditions



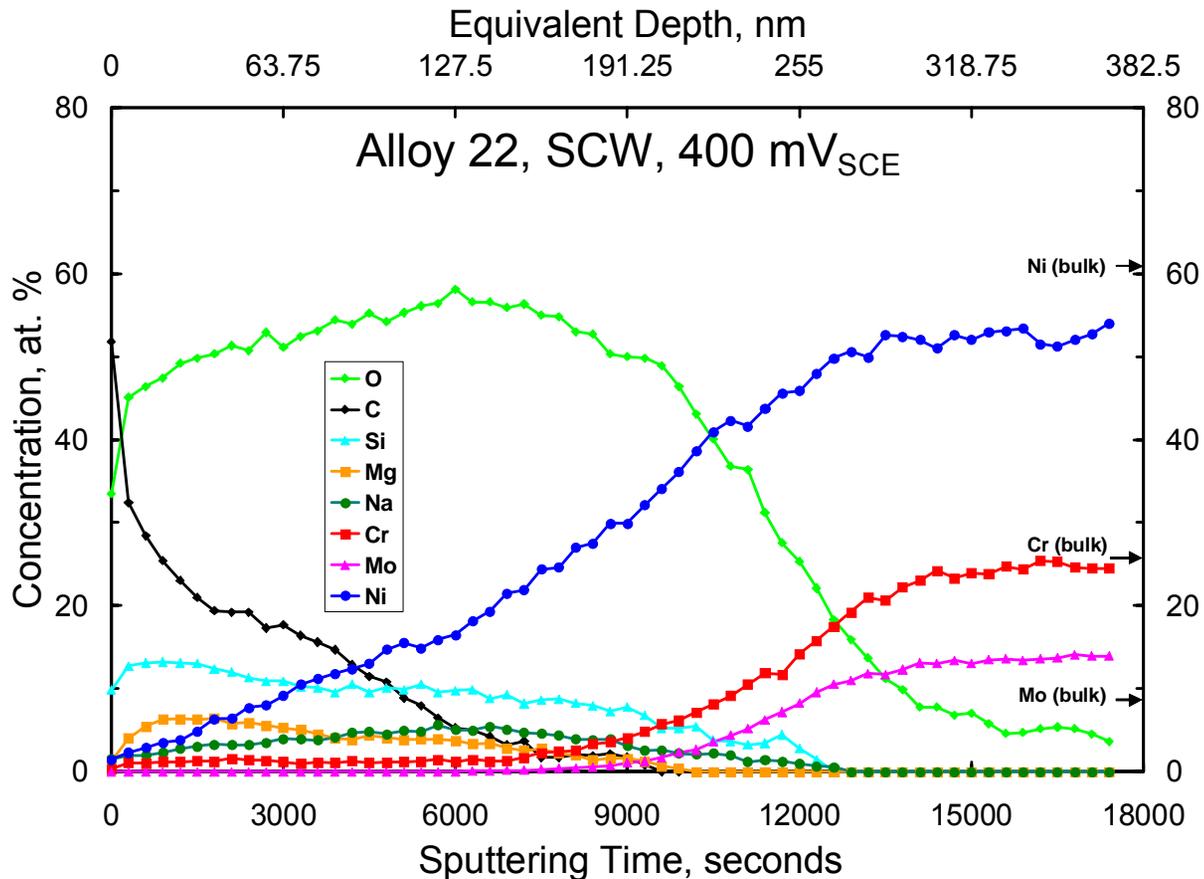
- Oxide Formed at 600 mV_{SCE} in 0.028 M NaCl
- High Cr and Mo Concentrations in the Oxide

Simulated Concentrated Water



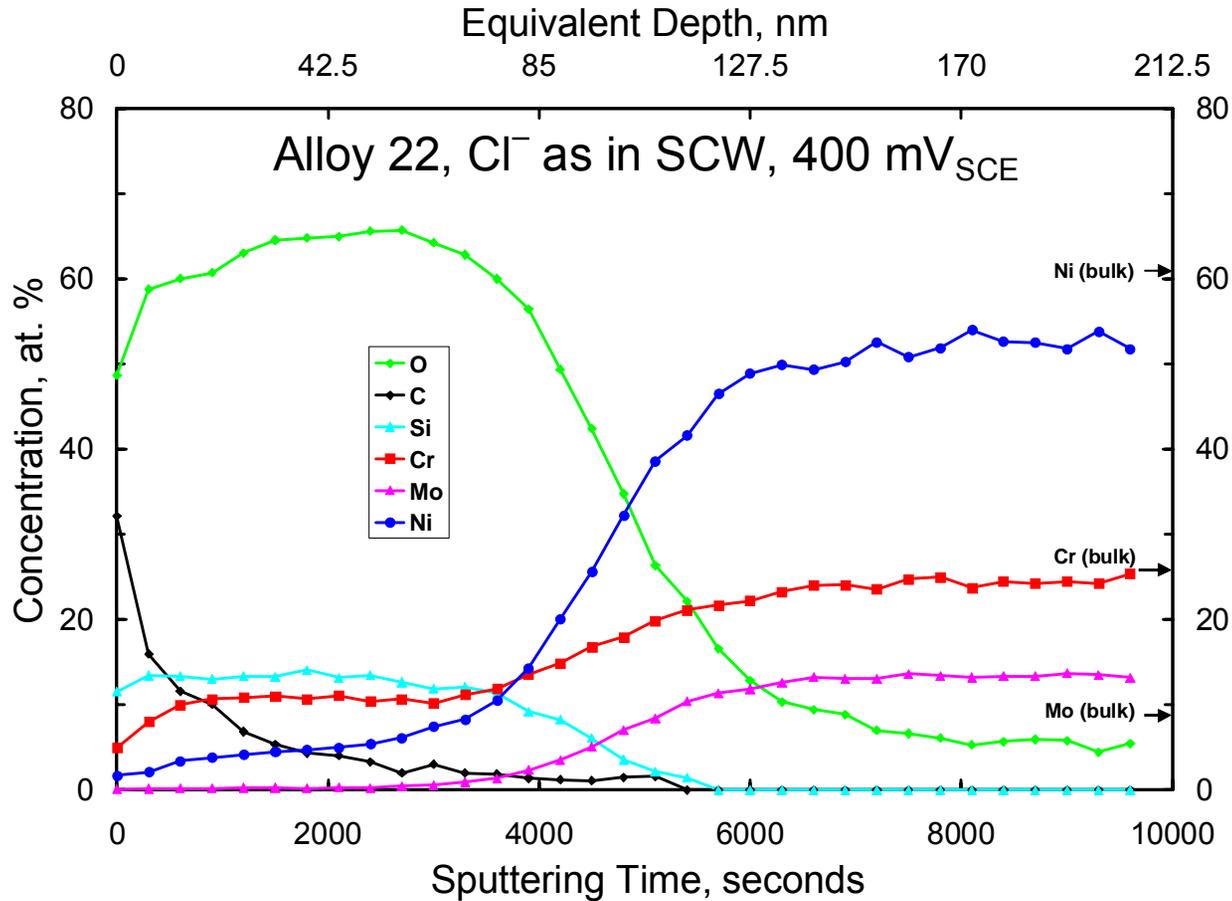
- Oxide Formed at 100 mV_{SCE} in Simulated Concentrated Water
- Low Cr and Mo Concentrations in the Oxide
- No Stress Corrosion Cracking Observed in Slow Strain Rate Tests

Simulated Concentrated Water (Continued)



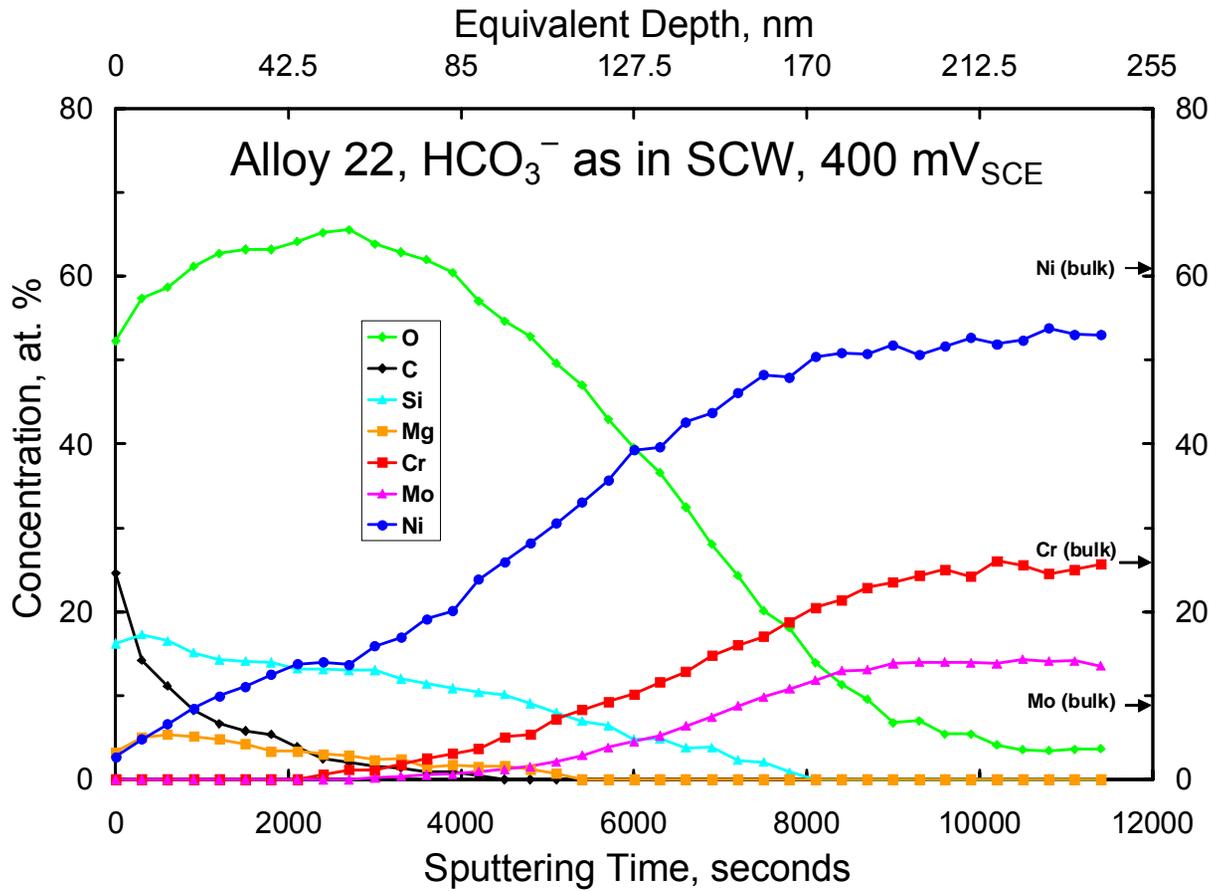
- Oxide Formed at 400 mV_{SCE} in Simulated Concentrated Water
- Low Cr and Mo Concentrations in the Oxide
- Stress Corrosion Cracking Observed in Slow Strain Rate Tests

Chloride Solution



- Oxide Formed at 400 mV_{SCE} in Solution with a Chloride Concentration the Same as in Simulated Concentrated Water
- Significant Cr Concentration in the Oxide
- No Stress Corrosion Cracking Observed in Slow Strain Rate Tests

Bicarbonate Solution



- Oxide Formed at $400 \text{ mV}_{\text{SCE}}$ in a Bicarbonate Solution with the Same Concentration as Simulated Concentrated Water
- Reduced Cr and Mo Concentrations in the Oxide
- No Stress Corrosion Cracking Observed in Slow Strain Rate Tests

Results Summary

| Solution | Potential, mV_{SCE} | SCC Expected? | Observations |
|---------------------------------|--|--------------------------|---|
| None (Air-Formed Oxide) | None | No | Thin oxide with Cr, Ni, and Mo |
| 0.028 M NaCl | 100 | No | Thin oxide with Cr, Ni, and Mo |
| | 600 | No | Oxide with Cr, Ni, and Mo |
| Simulated Concentrated Water | 100 | No | Thick oxide with reduced Cr concentration |
| | 400 | Yes | Very thick oxide with reduced Cr and Mo concentrations |
| 0.19 M NaCl | 400 | No | Oxide with Cr, Ni, and Mo |
| 1.14 M NaHCO ₃ | 400 | No | Thick oxide with reduced Cr and Mo concentrations |

Conclusions

- The Air-Formed Oxide on Alloy 22 Is a Thin Compact Layer That Contains Ni, Cr, and Mo in Similar Proportion to the Base Alloy
- In Aqueous Solutions, the Alloy 22 Oxide Layer Thickness and Composition are Dependent on Applied Potential and Solution Chemistry
- Oxide Films Formed Under Conditions that Promote SCC Are Significantly Thicker and Have Reduced Cr Concentrations Compared to the Air-Formed Oxide Film
- Oxide Films Formed at Anodic Potentials in Solutions With HCO_3^- Ions Have Reduced Concentrations of Cr
- At Anodic Potentials in Solutions Containing Only Cl^- , No SCC of Alloy 22 Is Observed, and the Oxide Films Produced Under These Conditions Have Significant Cr Concentrations

Future Considerations

- Time Dependent Changes in Oxide Film Composition
- Spatial Variation of Oxide Film Composition
- Electrochemical Characterization of the Oxides Formed Under Similar Conditions
- Analyses of Eh-pH Calculations for Alloy 22 in Chloride and Bicarbonate Containing Solutions
- Evaluation of Other Ni-Cr and Ni-Cr-Mo Alloys

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