Examination of Corrosion Products and the Alloy Surface after Crevice Corrosion of C-22 Alloy

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- The views, opinions, findings, and conclusions or recommendations of authors expressed herein do not necessarily state or reflect those of the DOE/OCRWM/OCS

Key Acronyms

- PTFE – Polytetrafluoroethylene
- SEM – Scanning Electro Microscopy
- EDS – Energy Dispersive X-ray Spectroscopy
- AES – Auger Electron Spectroscopy
- XPS – X-ray Photoelectron Spectroscopy
- XRD – X-ray Diffraction
- ASTM – American Society for Testing and Materials

Objective

- An overall objective is to determine the evolution of corrosion damage, i.e. the severity, shape, location/distribution and damage profile
- Study is part of a program to analyze the evolution of localized corrosion damage over long periods of time
  - A set of coordinated projects is under way, and this study focuses on the post initiation stages of crevice corrosion, i.e. crevice propagation, stifling and arrest processes
- Results are presented here on the composition of corrosion products and the composition of the metal surface after localized corrosion

Approach

- The approach is to force the initiation of crevice corrosion by applying anodic polarization to a multiple crevice assembly (MCA)
- Results are reported here for alloy C-22, a Ni-Cr-Mo alloy, exposed to a high temperature, concentrated chloride solution

Materials and Test Condition

- **Materials: alloy C-22**

Composition of alloy C-22, wt%

Cr	Mo	Fe	W	Co	Mn	V	Si	S	P	C	Ni
21	13.1	3.8	2.8	2.1	0.25	0.011	0.024	0.005	0.006	0.0052	BAL

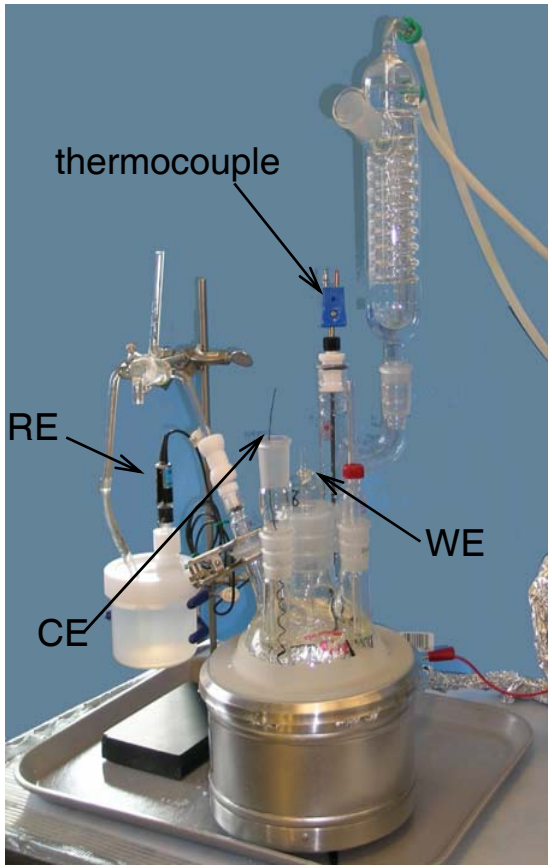
- **Test Conditions**
  - 4M NaCl, open to air, 100°C
  - Anodic polarization to E= -0.150 V-SCE, a potential above the repassivation potential of alloy C-22 for these test conditions
  - The metal specimen and crevice formers are wetted with test solution prior to tightening the test assemblies
  - PTFE tape covered ceramic was the crevice former

Experimental Methods

- Cyclic potentiodynamic polarization
  - with MCA specimens
- Crevice corrosion tests at constant potential
  - with MCA specimens
  - Polarize at potential more positive than the repassivation potential
  - Monitor corrosion by current vs. time measurement
- Post test exam-optical/macroscopic to 50x in binocular microscope
- Damage profile and 3-D reconstruction
  - InfiniteFocus microscope (IFM), an optical 3D measurement device
- Analyses of corroded alloy surfaces and corrosion products
  - SEM/EDS, AES, XPS, XRD
- Solution analysis
  - Inductively Coupled Plasma (ICP)

Test Cell and Specimen

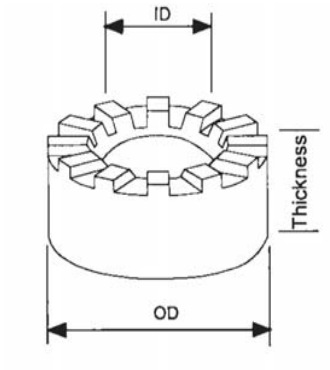
Test Cell

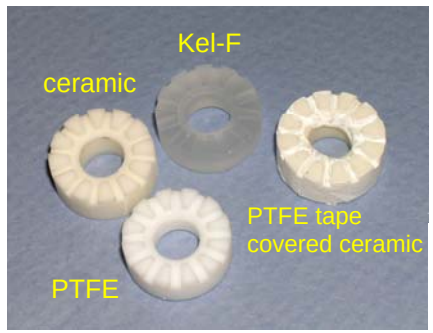


MCA

- Two segmented washers
- Grade 2 Ti bolt and nuts
- Applied Torque: 70 in-lb

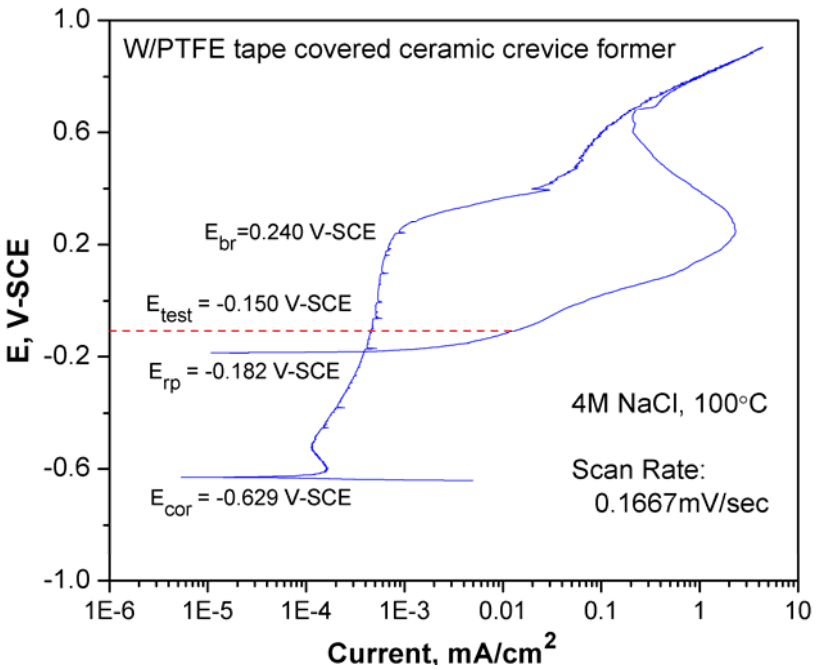
Crevice formers: after ASTM G48-03





- 12 contact plateaus (feet)
- ID: 9.9 mm OD: 15.9 mm Thickness: 6.3 mm
- Contact area: about 6 mm^2/foot

Cyclic Potentiodynamic Polarization

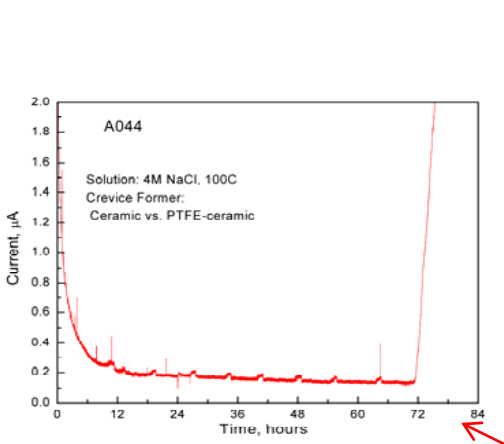


E_{rp}: the potential where the reverse scan of the polarization curve intersects the forward scan

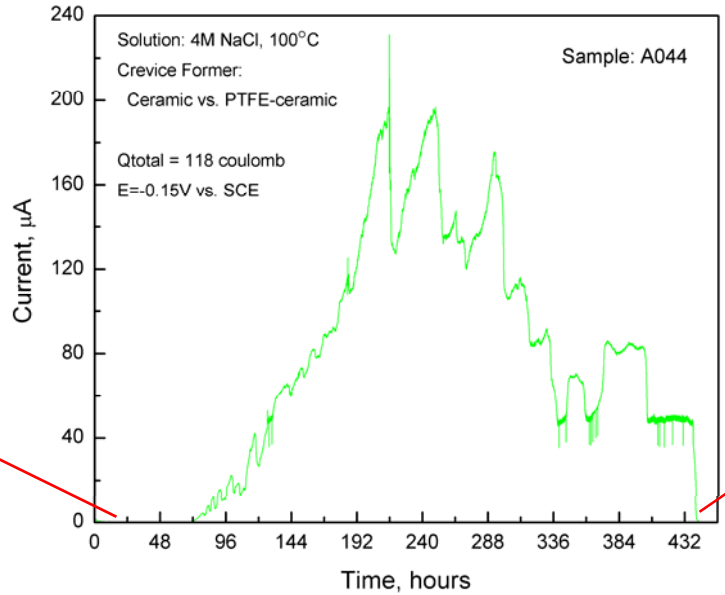
E_{br}: the potential at which a permanent rise in current density from the passive region is commenced

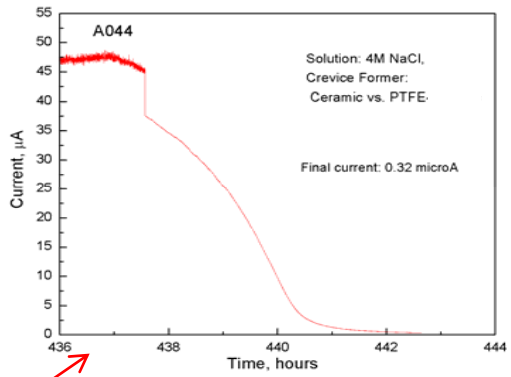
- **Used as basis for applied potential during crevice corrosion tests**
- **Aggressive corrosion solution**
  - 4M NaCl (20wt%)
  - 100°C
- **Severe crevice former**
  - PTFE tape covered ceramic
  - Create tight crevice, 70 in-lb
- **Select E_{test} at 30 to 50mV above E_{repass}**
  - $E_{re\text{-}pass}$ =-0.182 V-SCE
  - E_{test} = -0.150 V-SCE
- **Criteria for crevice corrosion during MCA test**
  - Hysteresis loop on reverse scan
  - Determination of repassivation potential
  - Visible damage under crevice former after test

Initiation, Propagation and Arrest of Crevice Corrosion



Initiation



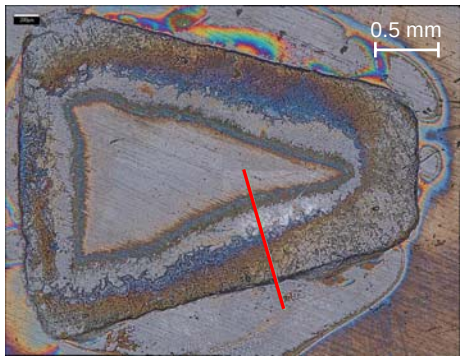


Repassivation

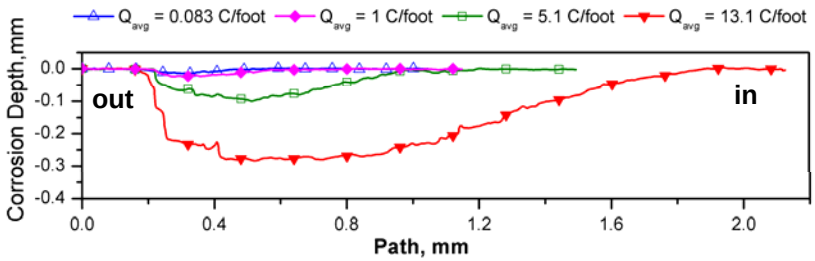
- 4M NaCl, 100°C, E=-0.150 V-SCE, PTFE tape covered ceramic
- Three stages: incubation, propagation, repassivation
  - Incubation, I ≈ 0.5 µA and less
  - Propagation, I increase up to 200 µA with many serrations (stifle/arrest events)
  - Repassivation, I ≈ 0.5 µA and less
- Multiple initiation sites beneath crevice feet
- Stifling/arrest events during propagation
- Repassivation of entire specimen

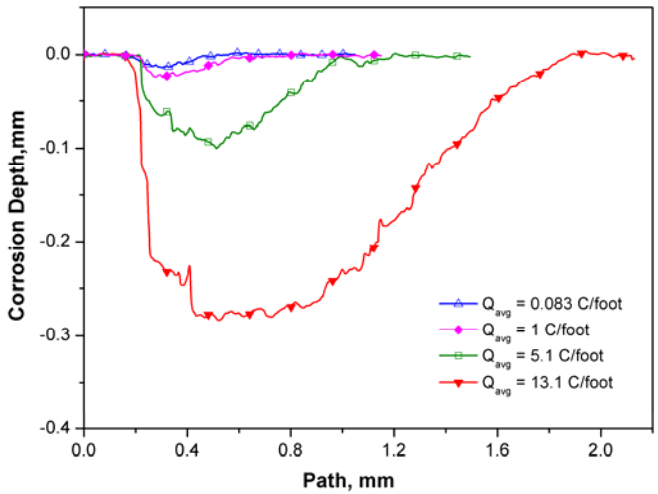
Corrosion Depth Profile

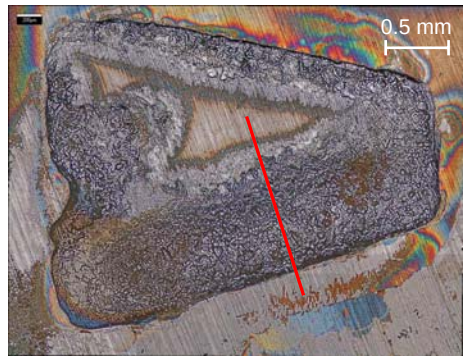
Q_{total} = 0.25 coulomb/3 feet



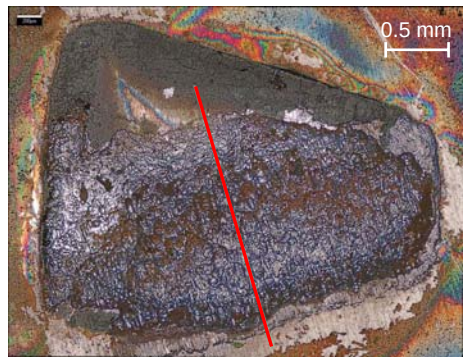
Q_{total} = 10 coulomb/10 feet







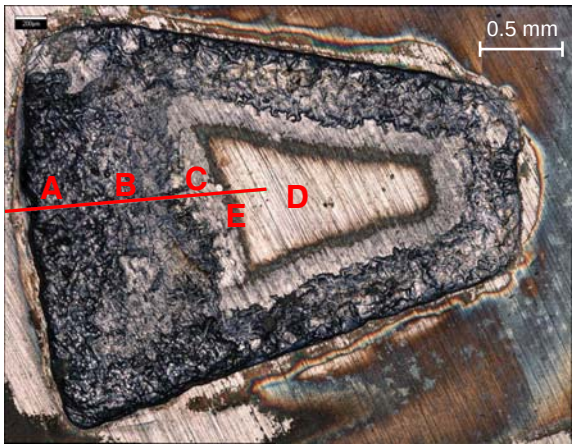
Q_{total} = 51 coulomb/10 feet

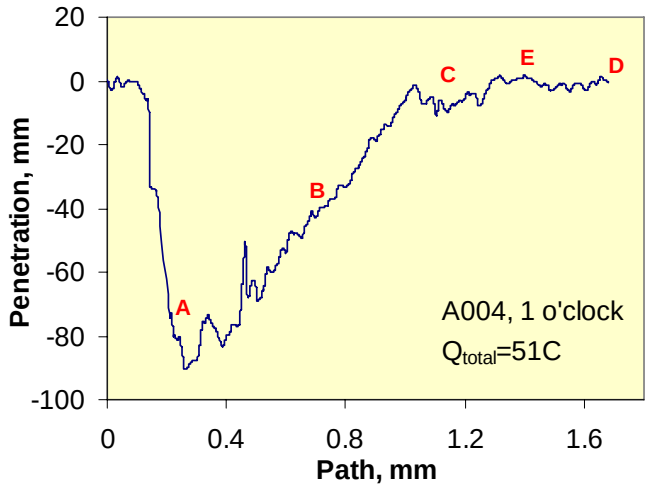


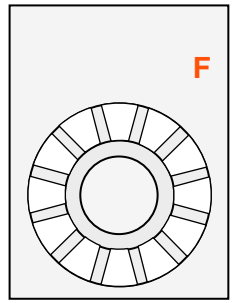
Q_{total} = 118 coulomb/9 feet

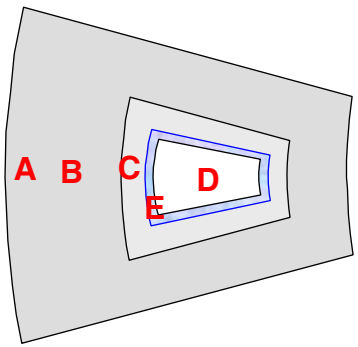
- With increasing amount of corrosion, the corrosion profile became wider and deeper
- Corrosion initiated near edges under crevice former
- Multiple initiation sites found under the crevice feet
- Corrosion products in crevice at corroded areas and outside the crevice on uncorroded surface

AES Analysis Locations on Alloy C-22 Surface





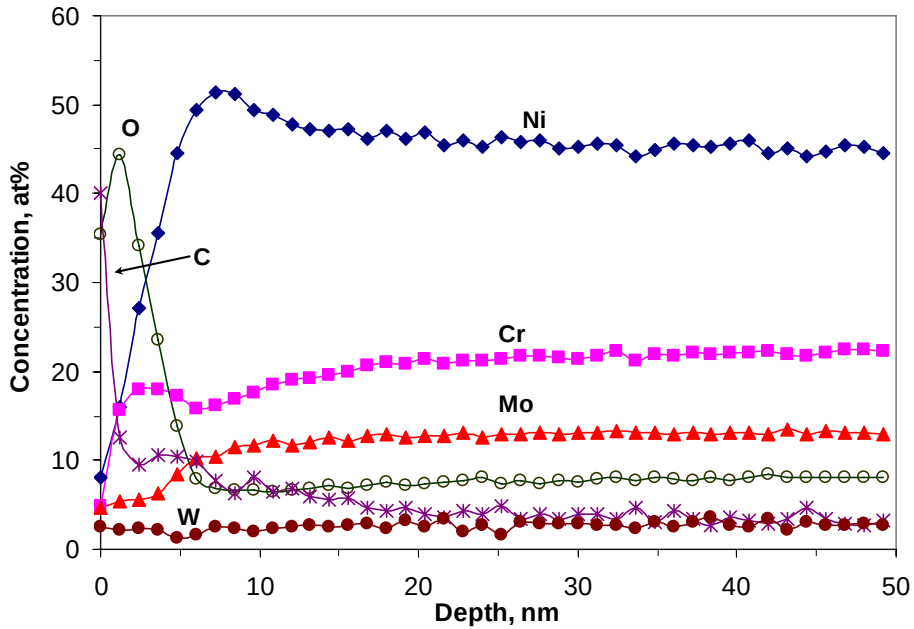


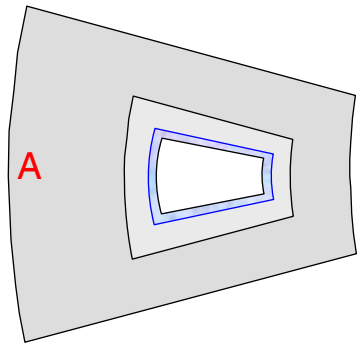


Tested for 268.3 hours, total flow of charge 51 coulomb, 5.1 coulomb/foot on average

Position	Description
A	80 μm penetration
B	30 μm penetration
C	10 μm penetration
D	on the island, no corrosion
E	stained area, border of corroded region
F	area exposed to test solution

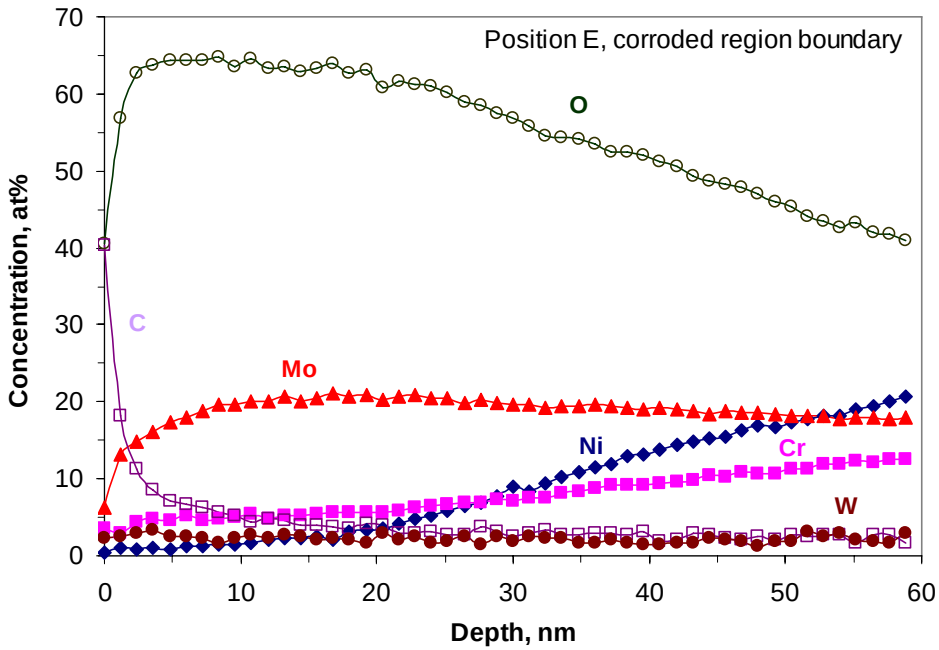
AES Depth Profile in Deeper Corrosion Region

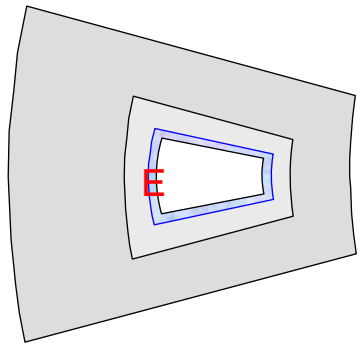




- Crevice corrosion penetration is about 80μm at position A
- Sample was ultrasonically cleaned with methanol before measurement
- AES depth profile of metal surface after loose corrosion products removed; shiny, metallic metal surface
- Passive film on the alloy surface (chromium-rich oxide) of approximately 2 - 8 nm
- Overall congruent dissolution of the alloy in active regions within the crevice
  - No preferential dissolution of elements on microscopic/macroscopic scale
  - Formation of soluble and insoluble corrosion products
  - On nanoscale, Ni enrichment and Cr depletion at metal surface beneath the passive film

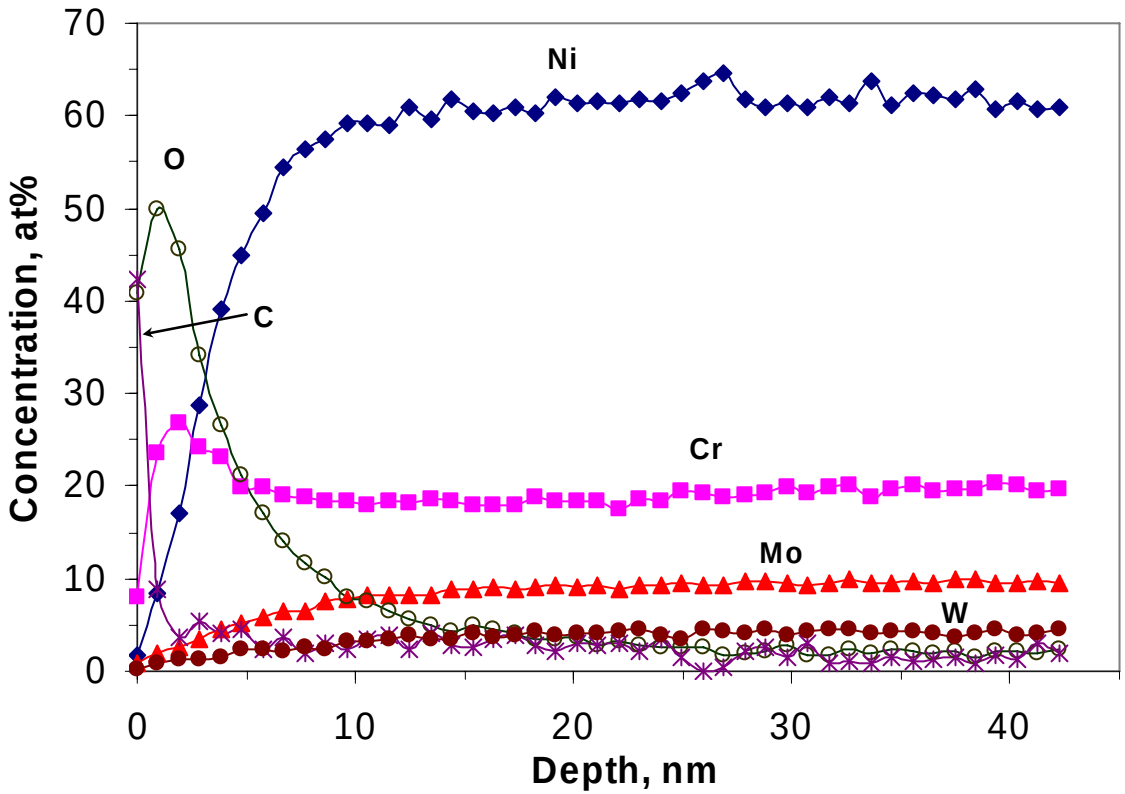
AES Depth Profile of Transition Area between Corroded and Uncorroded Regions

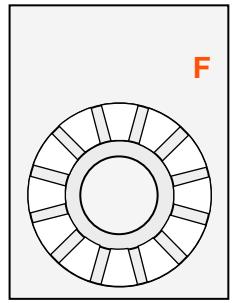




- At transition zone, a thin layer of corrosion products remained on surface
- Corrosion products contain high amounts of Mo and O and are depleted in Ni and Cr
- Ratio of Mo:O is approximately 1:3 (MoO_3)
- Composition is in agreement with the composition of corrosion products in the crevice measured by EDS

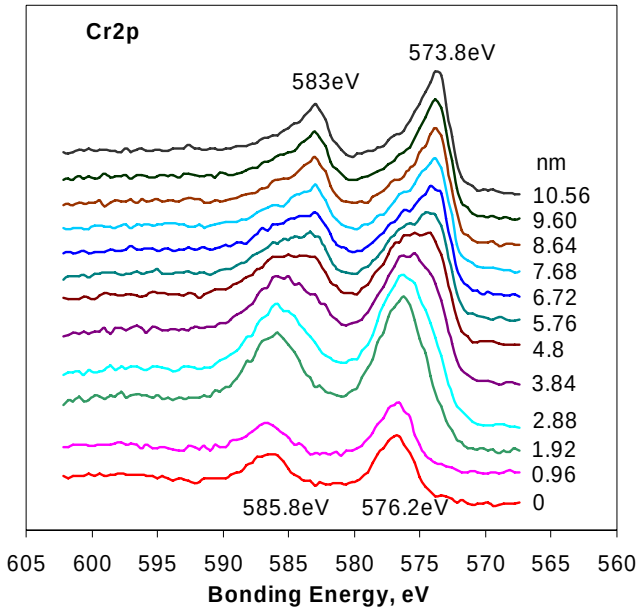
XPS Depth Profile of Freely Exposed Surface

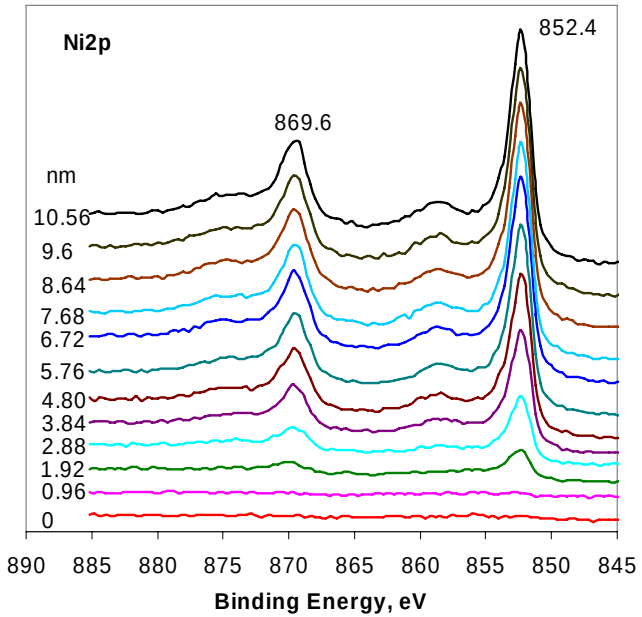




- Measured on freely exposed area, position F
- Passive film on metal surface
- The depth profile is in agreement with the result measured by AES

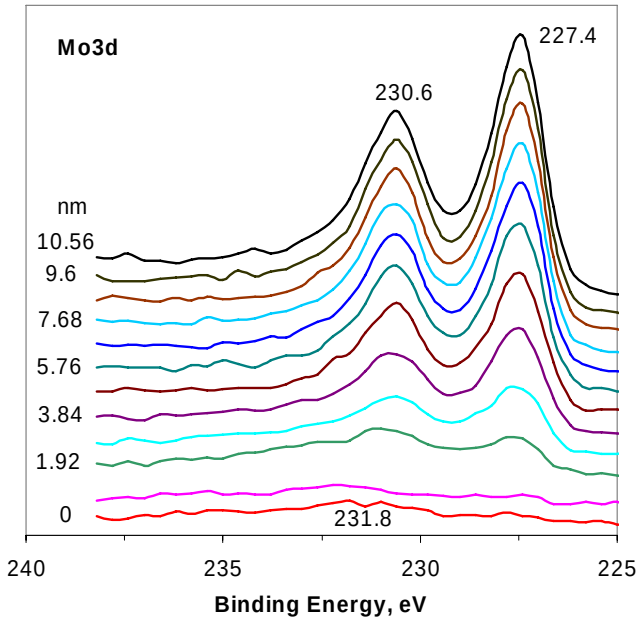
XPS Depth Profile of Freely Exposed Surface

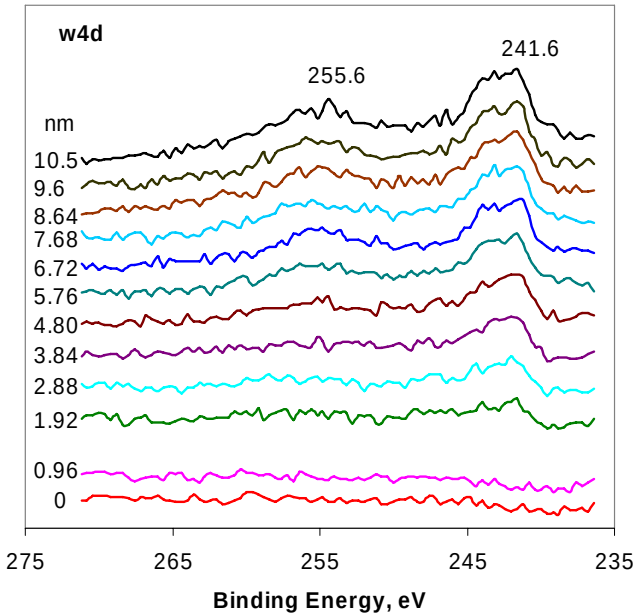




- For the top several nm, Cr exists as oxides
  - $Cr2p^{3/2}$ 576.2 eV, $Cr2p^{1/2}$ 585.8 eV, (Cr_2O_3)
- After about 10nm, Cr exists as metallic Cr
  - $Cr2p^{3/2}$ 573.8 eV, $Cr2p^{1/2}$ 583 eV, metallic Cr
- The amount of Ni on the surface is very small
- Except the top several nm, the binding energy of Ni does not change with depth,
  - $Ni2p^{1/2}$ 869.6eV, $Ni2p^{3/2}$ 852.4 eV, metallic Ni

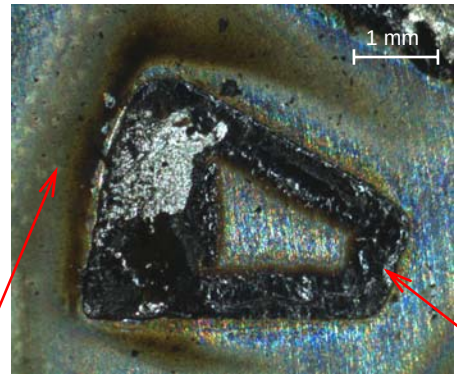
XPS Depth Profile of Freely Exposed Surface





- Small amount of Mo exits on the top surface as oxide
  - $Mo3d^{5/2}$ 231.8 eV
- Mo exists as metallic when depth is more than 10nm
  - $Mo3d^{5/2}$ 230.6 eV, $Mo3d^{3/2}$ 227.4 eV
- No W found on the top surface
- W exists as metallic when depth is more than 10nm
  - $W4d^{5/2}$ 255.6 eV, $W4d^{3/2}$ 241.6 eV

Corrosion Products of Alloy C-22

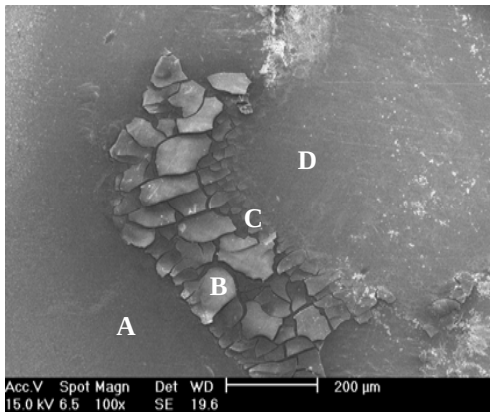


corrosion products on uncorroded metal surface

corrosion products with crevice

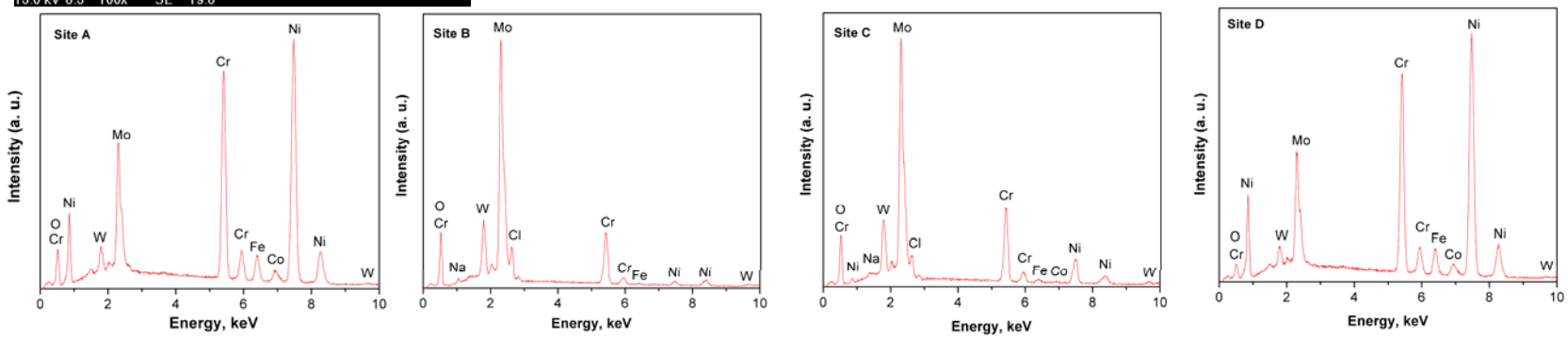
- 4M NaCl, 100°C, E=-0.150 V-SCE, PTFE tape covered ceramic crevice former
- Loose, black corrosion products were found in the crevice after test
- Green corrosion products were found around the crevice on the uncorroded metal after test
- Green corrosion precipitation was found in test solution after test
- Solution color changed to light green during test

EDS Analysis of Alloy C-22 Crevice Corrosion



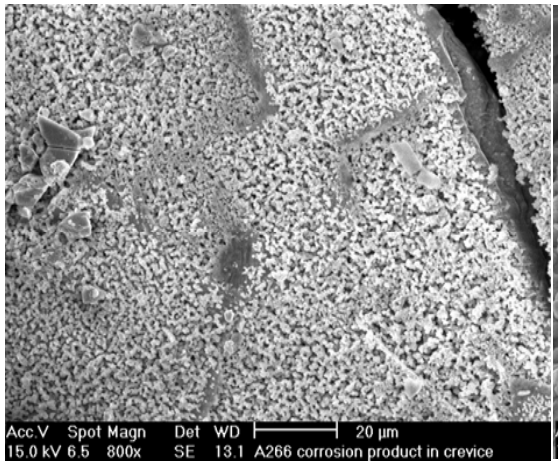
Composition at different locations, at%

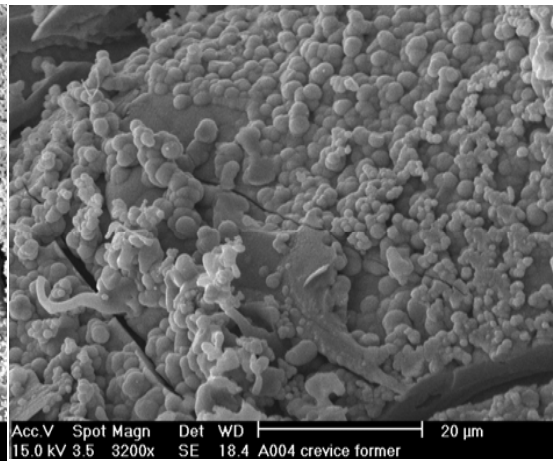
Location	O	Cr	Fe	Ni	Co	Mo	W	Na	Cl	Ni/Cr	Mo/Cr	W/Cr
A	21.4	20.7	3.4	43.9	1.8	7.0	1.0	0.5	0.3	2.1	0.3	0.05
B	67.9	7.8	0.2	0.9	0.03	16.2	1.8	1.0	3.7	0.1	2.1	0.2
C	60.1	11.0	0.6	6.2	0.3	16.5	1.6	0	2.4	0.6	1.5	0.15
D	11.7	22.7	3.8	51.1	2.3	7.4	0.7	0	0.3	2.3	0.3	0.03

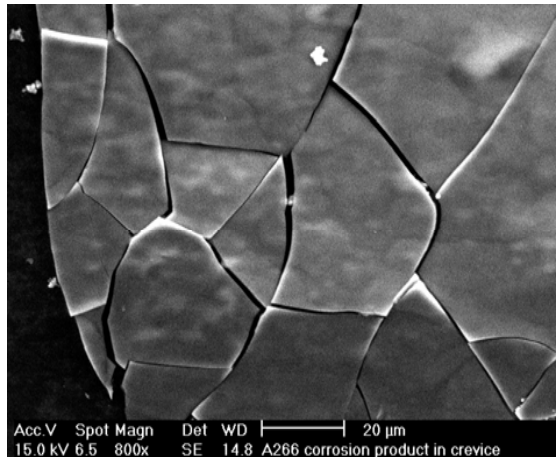


- 4M NaCl, 100°C, E=-0.150 V-SCE, PTFE tape covered ceramic crevice former
- Tested for 251.6 hours, total flow of charge 59.8 coulomb to the whole specimen
- Loose, black corrosion products found under the crevice former after test
- Compare thick corrosion products layer (B) with composition of alloy C-22
  - Corrosion products are high in O
  - Depleted in Ni, Cr and Fe, and enriched in Mo and W

Corrosion Products in Crevice





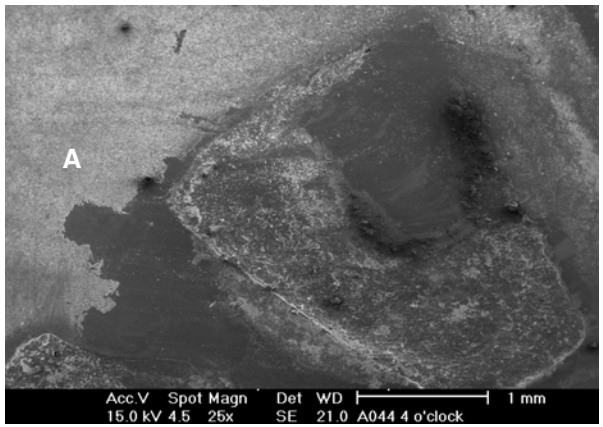


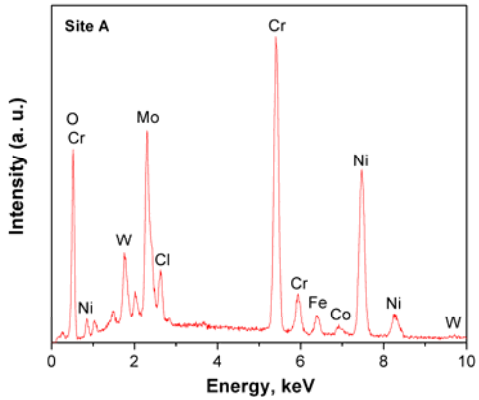
corroded metal side **crevice former side**

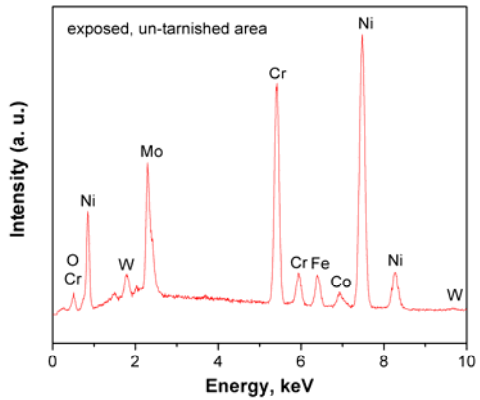
	O	Cr	Fe	Ni	Co	Mo	W
corroded metal side, at%	69.6	4.5	0.2	0.3	0	20.7	4.0
crevice former side, at%	70.0	3.4	0.1	0.3	0	21.6	3.6

- 4M NaCl, 100°C, E=-0.150 V-SCE, PTFE tape covered ceramic crevice former
- The corrosion products in the crevice show different morphologies on the side contacting the crevice former and on the side contacting the metal
  - Smooth surface on the crevice former side
  - Surface with fine micro structures were found on the side contacting the corroded metal
- EDS results show no composition difference between the two morphologies

EDS Analysis of Alloy C-22 Corrosion Products outside of Crevice on Uncorroded Metal







sample	O	Cr	Fe	Ni	Mo	W	Co
Site A, at%	52.3	16.7	1.4	17	5.5	0.5	0.6
exposed un-tarnished area, at%	10.8	22.5	4	51.8	7.2	0.9	1.8

- 4M NaCl, 100°C, E=-0.15V-SCE, PTFE tape covered ceramic crevice former
- Corrosion products deposited on uncorroded metal outside of crevice
- Tested for 462.7 hours, total flow of charge 118 coulomb, 13.1 coulomb/foot on average
- Green corrosion products found outside the crevice former after test
- Corrosion products contain high amount of oxygen
- High in Cr/Ni, Mo/Ni ratio compared to alloy C-22

XRD Results on Corrosion Products

- **XRD on the black corrosion products in the crevices**
  - **Only NaCl and C-22 was identified**
  - **Work in process**
- **XRD on green precipitation in solution**
  - **Only NaCl was identified**
  - **Others peaks were broadened**
  - **Work in process**

Solution Composition after Crevice Test

Sample	Q, coulomb	Ni	Cr	Mo	W	Fe	Co
A265 solution	94.2	10.8	0.117 (**92**)	0.456 (**24**)	ND	0.13 (**83**)	0.374 (**29**)
		10.4	0.137 (**76**)	0.434 (**24**)	ND	0.127 (**82**)	0.361(**29**)
A266 solution	59.8	4.18	ND	0.739 (**5.7**)	ND	ND	0.12 (**35**)
		4.28	ND	0.722 (**5.9**)	ND	ND	0.110 (**39**)
4M NaCl	n/a	ND	ND	0.06	ND	ND	ND
C-22	n/a	57	21 (**2.7**)	13.1 (**4.4**)	2.8 (**20**)	3.8 (**15**)	2.1 (**27**)

Note:

1. The numbers in parenthesis are the ratio of nickel to the element: Ni:Metal
2. Concentration for A265, A266 solution is mg/L, for C-22 is wt%

- 4M NaCl, 100°C, E=-0.150 V-SCE, PTFE tape covered ceramic crevice former
- Inductively Coupled Plasma (ICP) method
- Ni is the main element dissolved into the solution
  - Ni > Co > Mo > Fe > Cr >W
- Preliminary results, work in progress

Conclusion

- Loose, black corrosion products found under the crevice former after test
  - Depleted in Ni, Cr and Fe,
  - Enriched in Mo and W
  - Contains high amount of oxygen
- Passive film (chromium oxide) formed on the alloy surface in the repassivated crevice corrosion region
- After 10's µm of crevice corrosion penetration, a thin (several nm) zone of Ni enrichment and Cr depletion within the metal was observed; however, on the micro/macro scales, the alloy dissolution occurred by a uniform, non-selective dissolution
- Corrosion products outside the crevice on uncorroded metal has high Cr/Ni, Mo/Ni ratio and high amounts of oxygen
- Analysis of the test solution shows Ni as the main species (Ni^{++})