Backup Slides

Chemical Compositions (Weight %)

Alloy	Nickel	Chromium	Molybdenum	Iron	Other (maximum values)
22	56	22	13	3	2.5 Co, 3W, 0.35V,.015C
C-4	63	16	16	3	2.0 Co, 0.7Ti, .015C
C-276	59	15.5	16	5	2.5 Co, 4W, 0.35V, .02C
C	56	16.5	17	6	4.5W, 0.15C
625	60	22	9	5	4.0Nb, 0.4Ti, 0.4Al,.10C
825	40	22	3	32	2.2 Cu, 1.0Ti, 0.2Al,.05C
600	76	16	-	8	
690	62	29	-	9	

Legend:
Co - cobalt
W - tungsten
Ti - titanium
Nb - niobium
Al - aluminum
Cu - copper

Composition of Representative Yucca Mountain Waters

Constituent	J-13 Well Water (mg/l)	'Perched Water' (mg/l)	Pore Water (ESF-HD PERM-2) (mg/l)
Na^+	45.80	36.0	61
Si	28.5	37.0	66
Ca^{++}	13.0	25.0	106
K^+	5.04	1.7	7
Mg^{++}	2.01	2.2	16.6
F^-	2.18	0.7	
Cl^-	7.14	6.3	110
NO_3^-	8.78	4.0	3
$SO_4^=$	18.4	15.0	111
HCO_3^-	128.9	147.0	
pH	7.41	8.1	8.32

Concentration of 28 Minor Elements in J-13

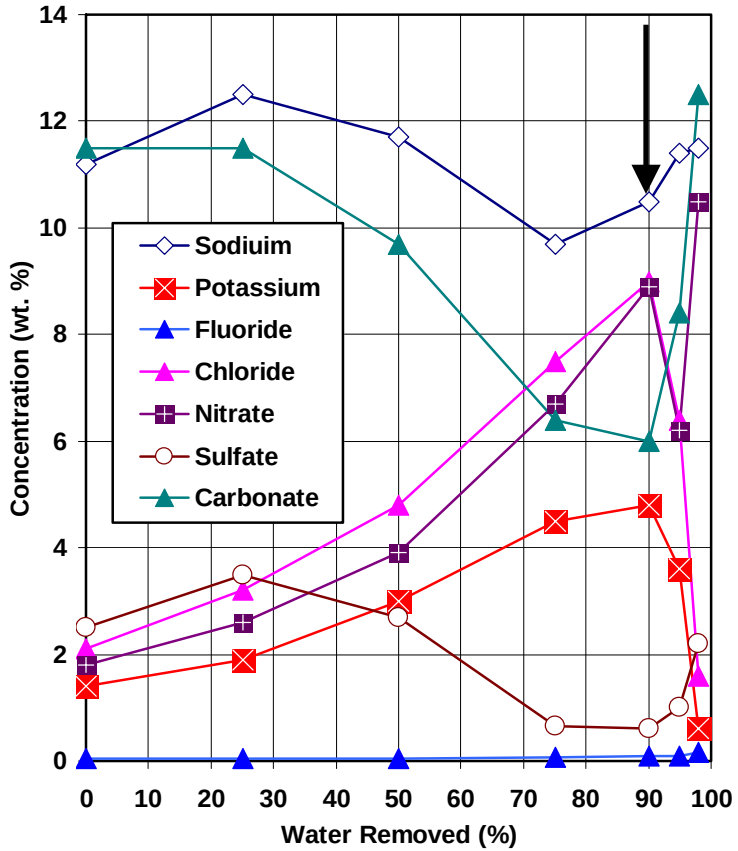
(Measured at Argonne National Laboratory)

Table 1. Concentrations of 28 elements in J13 well water and EJ13 simulated groundwater. Concentration are given in units of ng/mL solution.

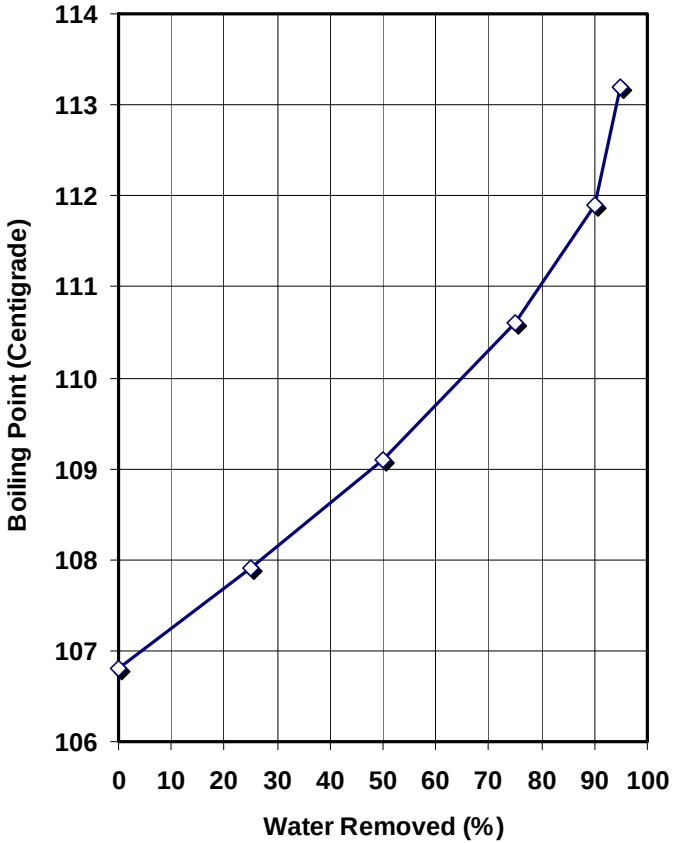
Element	J13 5/23/89	EJ13 7/8/98	EJ13 1/18/99	EJ13 4/17/98
Li	47.1	44.6	42.6	47.6
B	94.9	139	131	124
Na	44100	47500	40300	42100
Mg	1660	63	231	198
Al	4.17	664	531	673
Si	28700	42000	32900	32800
K	6590	7950	8650	9400
Ca	14000	7230	3380	8280
V	6.43	7.33	7.75	8.04
Cr	0.739	0.811	0.422	0.787
Mn	<0.59	0.717	6.6	1.14
Fe	<5.97	<5.97	<5.97	<5.97
Co	<0.06	<0.06	<0.06	<0.06
Ni	<2.35	<2.35	<2.35	<2.35
Cu	6.1	<2.17	<2.17	<2.17
Zn	19.3	7.66	19.1	7.76
Ga	<0.05	1.08	1.29	1.46
As	12.6	12.6	14.3	15.8
Se	<39.7	<39.7	<39.7	<39.7
Rb	10.3	19.6	18.7	24.5
Sr	39.7	27.2	17.2	43.3
Ag	<0.09	<0.09	<0.09	<0.09
Cd	<0.89	<0.89	<0.89	<0.89
Cs	1.77	1.58	0.945	1.56
Ba	1.26	0.439	0.408	1.12
Tl	<0.03	0.053	0.043	0.08
Pb	6.08	0.496	0.286	0.586
U	0.701	0.835	<0.03	0.969

Saturated J-13 (BSW) SCC Test Environment

Basis of Near-Saturation Test Media (BP ~ 112°C and pH ~13)



Starting Solution ~ 5000X J-13



Saturated J-13 solution selected for testing (BSW) contains highest chloride content, a boiling point of ~112°C and a bounding pH value of ~13

Bounding Water Compositions Added to LTCTF

- Codes: BSW = basic saturated water; SSW= simulated saturated water
- These waters simulate the concentrated salt solutions that are formed on a warm metal surface by repeated wet-dry cycles from water drips
- The waters are high in chloride and nitrate (most soluble ions)
- BSW water is strongly alkaline and contains saturated levels of other anions
- SSW water contains only near saturation levels of chloride and nitrate and is slightly acidic
- Composition of these waters:

	BSW	SSW
Cl^-	130,830 mg/L	154,000 mg/L
NO_3^-	139,650	1,576,000
SO_4^{-2}	14,700	
F^-	1470	
Na^+	105,840	584,000
K^+	67,620	170,000
pH	~ 13	~6

Long Term Corrosion Test Facility (LTCTF)

Media	Temp.	pH	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	Si	SO_4^{2-}	Cl^{-}	NO_3^{-}	F^{-}	HCO_3^{-}	Equiv. NaCl
	°C		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
SDW	60	9.5	3.5	1.2	36	430	17	170	68	62	14	720	112
SDW	90	9.9	3.4	ND	38	460	16	180	74	64	15	700	122
SCW	60	9.2	16	29	4600	36000	18	13000	7400	7000	330	44000	12199
SCW	90	9.2	15	3.4	4500	44000	58	13000	7500	7200	1400	51000	12363
SAW	60	2.7	58	52	4300	43000	30	41000	28000	23000	0	0	46157
SAW	90	2.7	58	53	4300	43000	50	40000	27000	24000	0	0	44508
SCMW	60	7.8	400	4	85	10	10	1200	11	10	< 0.1	< 1	18

SDW: Simulated Dilute Well Water (10X J-13)
SCW: Simulated Concentrated Well Water (1000X J-13)
SAW: Simulated Acidified Well Water
SCMW: Simulated Cement-Modified Water

General Corrosion Path Forward

- **Adding new 'bounding' test environments to long term corrosion tests**
  - **Basic Saturated Water [BSW] at 110°C and Simulated Saturated Water [SSW] at 120°C**
  - **Testing in all environments continues (5 and 10 years) with additional very long term testing planned for Performance Confirmation**
- **Since very low measured corrosion rates lie within estimated range of measurement uncertainty (~0.04 microns/yr at one standard deviation)**
  - **Installing more sensitive larger surface area coupons**
  - **Installing high sensitivity corrosion probes of Alloy 22**
  - **Continuing Atomic Force Microscope (AFM) studies on polished specimens with masked areas**
    - **quantifies rates and reveals how 'uniform' attack is (nanometer scale)**

General Corrosion Path Forward

- Using electrochemical impedance spectroscopy and linear polarization (LP) as other test methods to corroborate very small corrosion rates
  - corroborate weight loss data from long term tests
  - evaluate effects of films formed during container fabrication and welding and from long term thermal exposure in repository

Localized Corrosion Path Forward

- **Perform focused tests to increase confidence that crevice corrosion susceptibility will not develop over long times**
  - **Measure E_{corr} on 0-3 year exposed corrosion specimens to demonstrate E_{corr} does not approach film breakdown or repassivation potentials with time**
  - **Develop and benchmark passive film model to gain further confidence in film stability over time**
- **Separate effects of ionic mix of species in full range of relevant YM waters on critical potentials and margin between E_{corr} and E_{crit}**
  - **Separate damaging species (chloride, fluoride) from beneficial species (nitrate, carbonate, silicate etc.)**
    - **pore water, perched water, and ground waters have somewhat different ionic ratios**

Localized Corrosion Path Forward

- **Determine critical crevice potentials in environments containing relevant heavy metal concentrations e.g. Pb, Hg, As**

Waste Package Environment Path Forward

- **Confirm all potentially bounding waste package surface environments have been identified including pore waters, perched waters, ground waters and waters evolving from potential introduced materials**
- **Determine expected maximum concentrations and chemical forms of heavy metals (Pb, Hg, etc.) and other potentially deleterious minor elements (e.g. As) in relevant repository environments**
- **Experimentally confirm temperature/relative humidity window of corrosion susceptibility for range of deposits that could be present on waste package surface under drip shield**

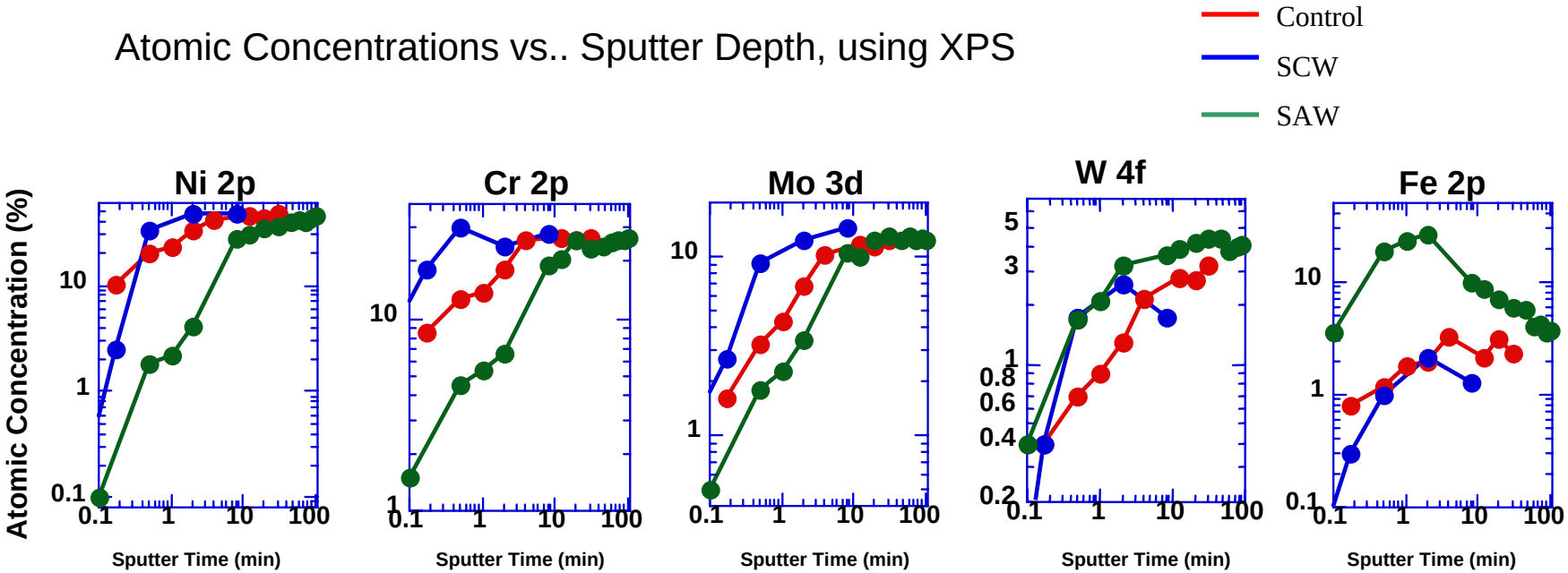
Characterization of Alloy 22 Passive Film

- **Evaluations of passive film have been conducted utilizing Atomic Force Microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) to understand the nature of the film**
  - **Initial XPS analyses indicate elemental composition varies across layers as expected for diffusion controlled processes**

Characterization of Alloy 22 Passive Films (One Year Exposure in LTCTF)

Weight-Loss Coupons from LTCTF: 90°, 1 yr.

Atomic Concentrations vs.. Sputter Depth, using XPS



- **Control specimen has as-machined surface with air formed film, probably a single layer**
- **In simulated concentrated water (SCW), [1000X J-13]; film enriched in Cr and Mo and depleted in Fe near metal interface (inner layer)**
- **In simulated acidic water (SAW) at pH = 2.7; film enriched in W and Fe and contains less Ni,Cr and Mo than air formed film on control**

Long Term Passive Film Stability Path Forward

- **Specific elements of the path forward program include:**
  - **Growing thicker oxide films at higher temperatures (90-175°C) using autoclaves, humid air and/or electrochemical techniques (anoxic polarization) to accelerate growth for compositional/structural studies**
  - **Resolving kinetics of film growth and metal loss:**
    - **logarithmic, parabolic or higher order?**
    - **does film growth become linear as it thickens?**
    - **does film become mechanically brittle and spall off?**
    - **what are film dissolution kinetics?**

Long Term Passive Film Stability Path Forward

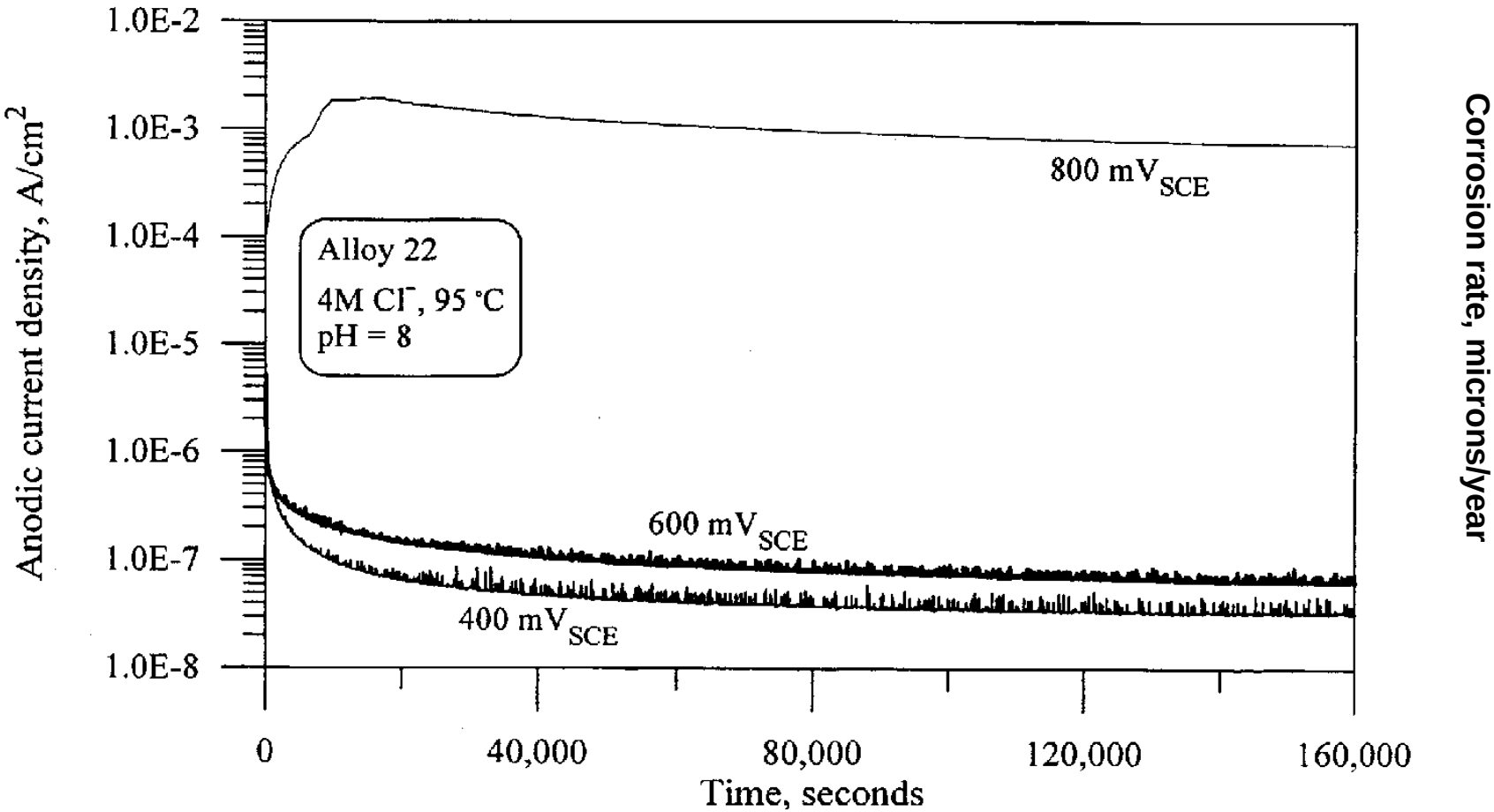
- Calculating Pourbaix diagram to establish expected thermodynamically stable phases in surface film
- Determining chemical, structural, and mechanical properties of films, including thickened films using 'battery' of surface analytical techniques
  - need multiple techniques to resolve ambiguities where spectral lines coincide or when different morphological forms of the oxide film exist
- Correlating changes in E_{corr} measured in LTCTF with compositional changes in passive film over time
- Determining changes in film structure/ properties on high defect concentration cold-worked materials

Long Term Passive Film Stability Path Forward

(Continued)

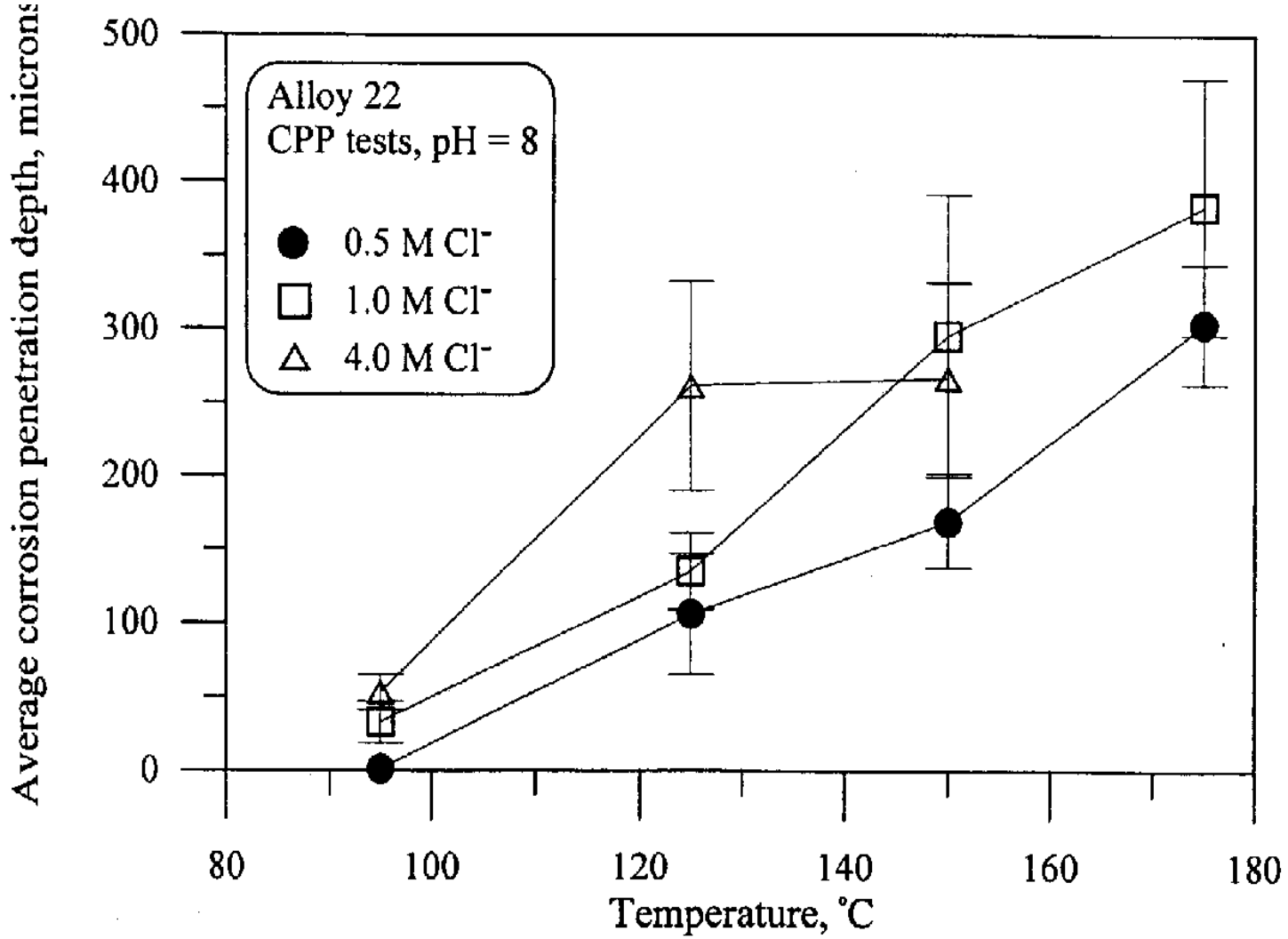
- Assessing film defect structures, diffusing species and film/solution interface reactions
  - AC impedance
  - cyclic polarization
  - contact electrical resistance
- Continuing examination of films formed on naturally occurring Josephinite as received and after exposing to selected LTCTF environments and comparing to respective Alloy 22 films
- Comparing films formed on Alloy 22 with other similar passive film alloys with longer industrial experience such as Alloys C, C-4, C-276 and 625

Alloy 22 Potentionstatic Corrosion Rates in NaCl



Corrosion rates obtained from potentiostatically controlled tests in 4M NaCl, pH 8.0 at 95°C (from CNWRA 99-004)

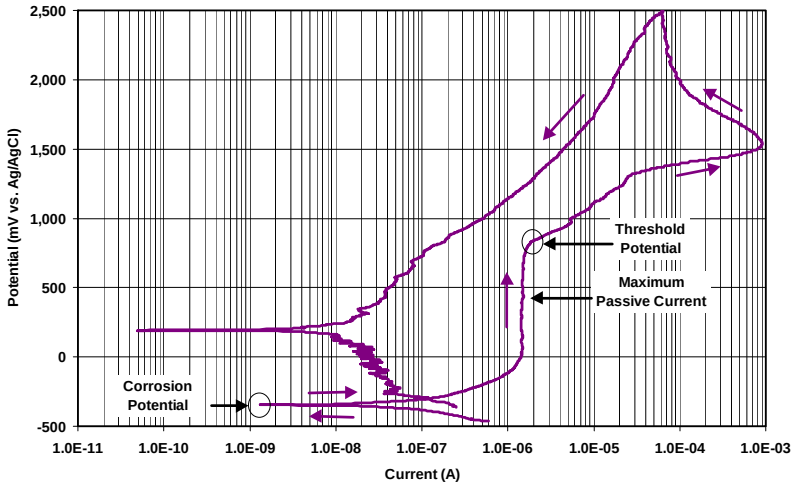
Alloy 22 Crevice Penetration vs. Temperature
(After Cyclic Polarization Testing in NaCl Solutions)



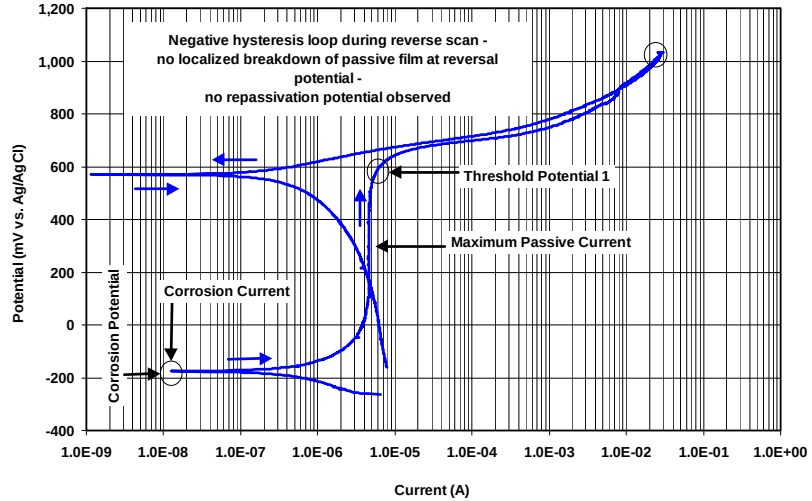
Crevice corrosion severity drops rapidly with temperature
(Data from USNRC CNWRA 99-004)

Drip Shield & WP Resistant to Localized Corrosion

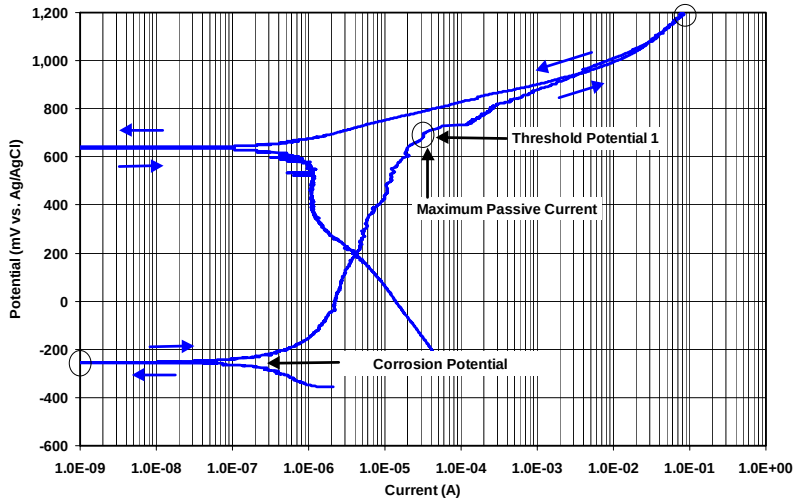
Ti Gr 7 in SSW at 120 C (NEA031s)



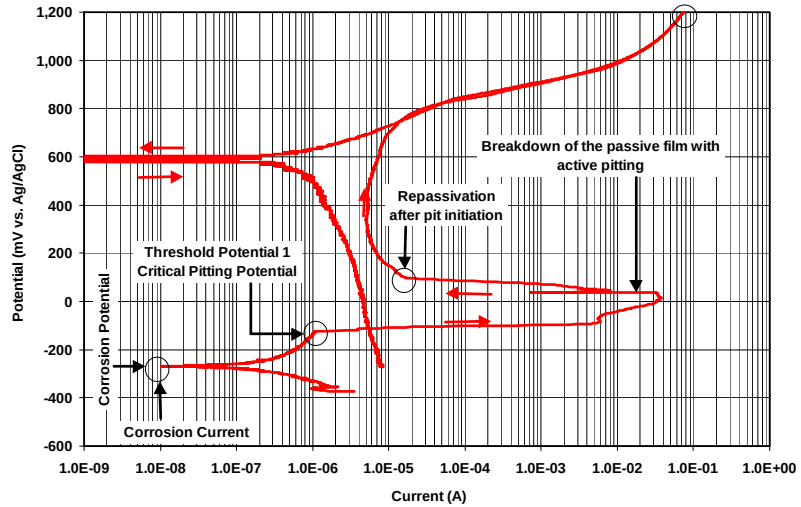
Alloy 22 in SAW at 90 C (DEA002)



Alloy 22 in SSW at 120 C (DEA033)



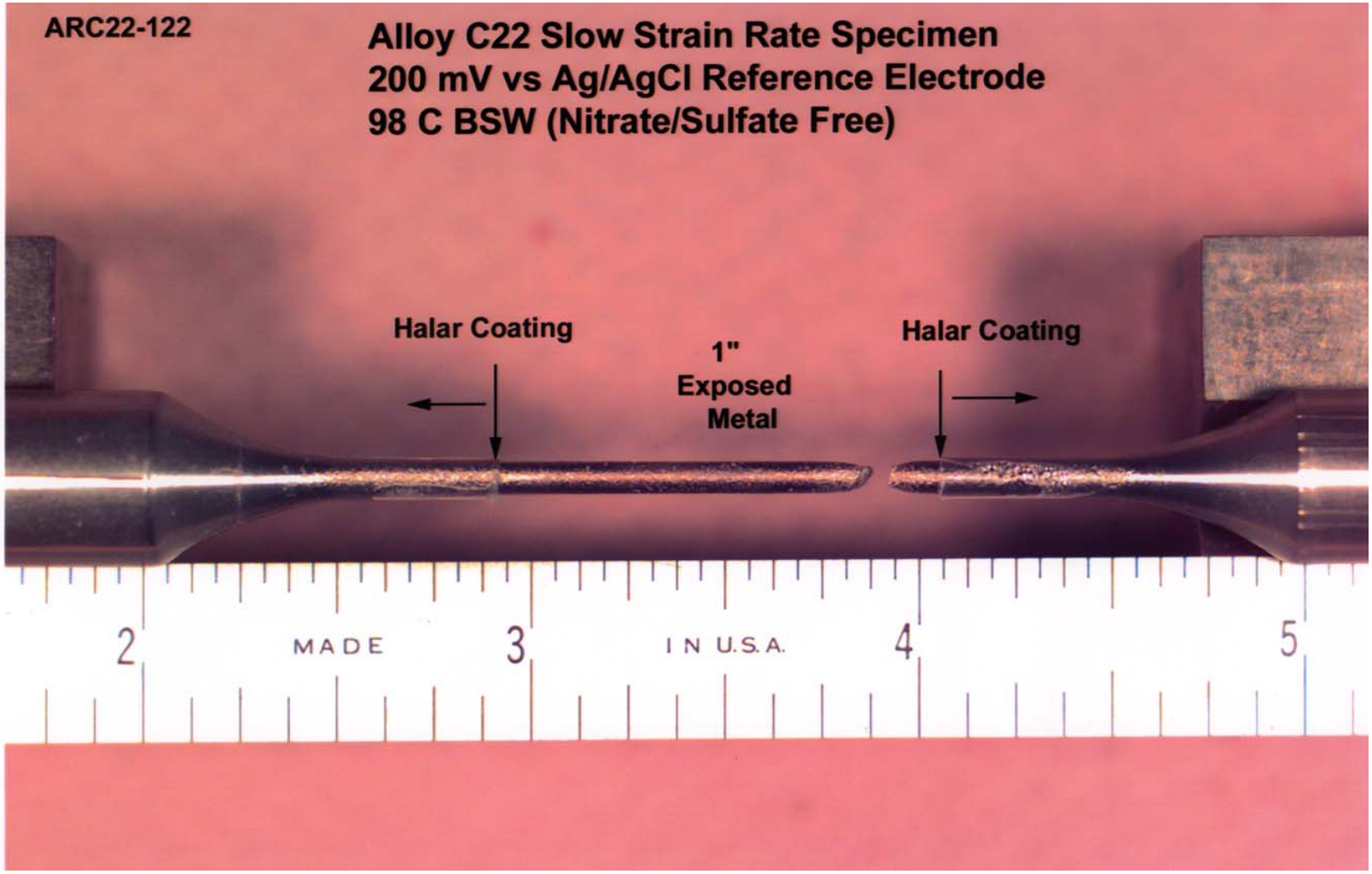
316L in SSW in SSW at 100 C (PEA016)



The DS & WP materials appear to have exceptional resistance to localized corrosion

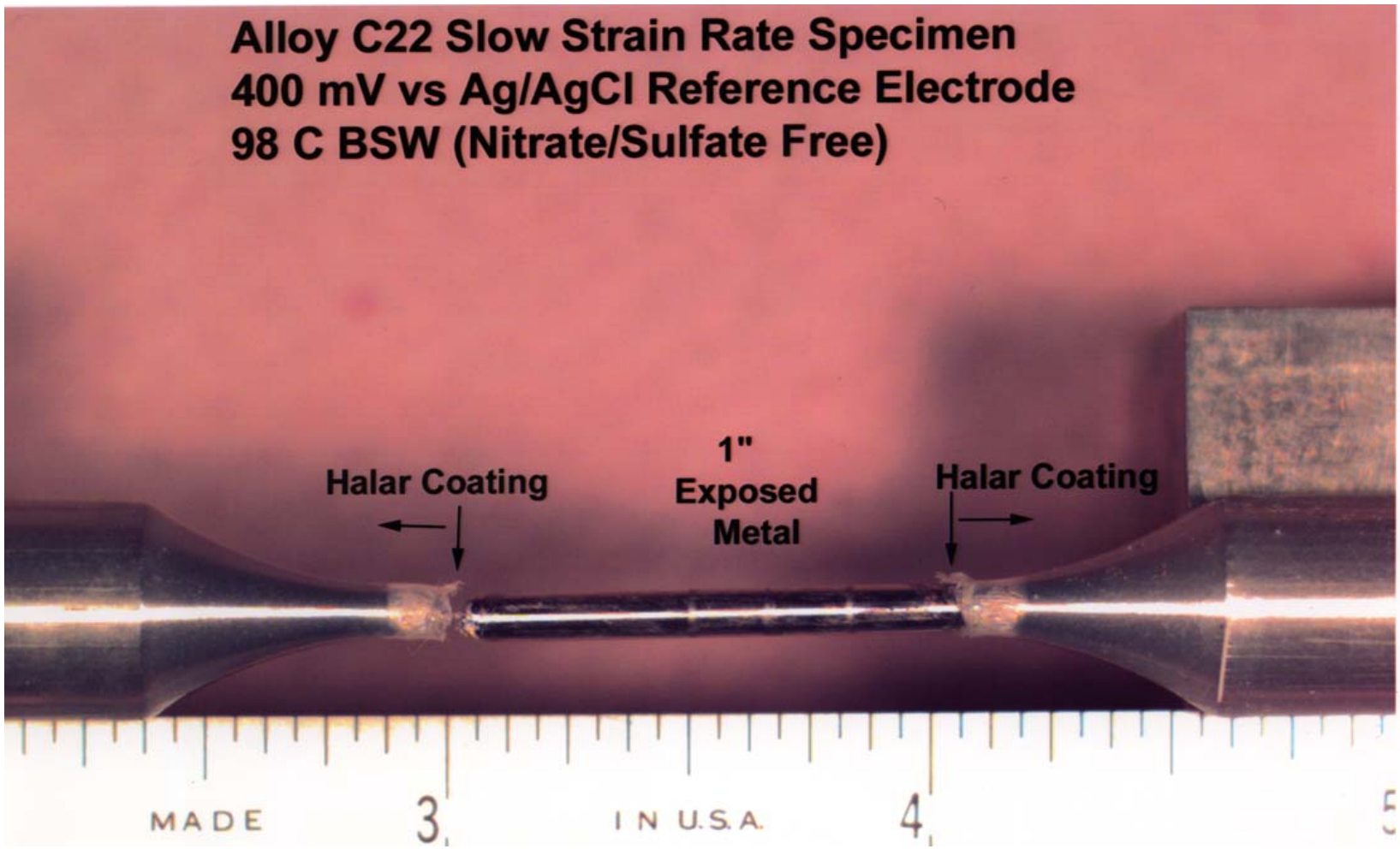
Stainless steel is to serve primarily as a structural material

Creviced Specimen Polarized to 200 mV and Strained to Failure without Crevice Corrosion



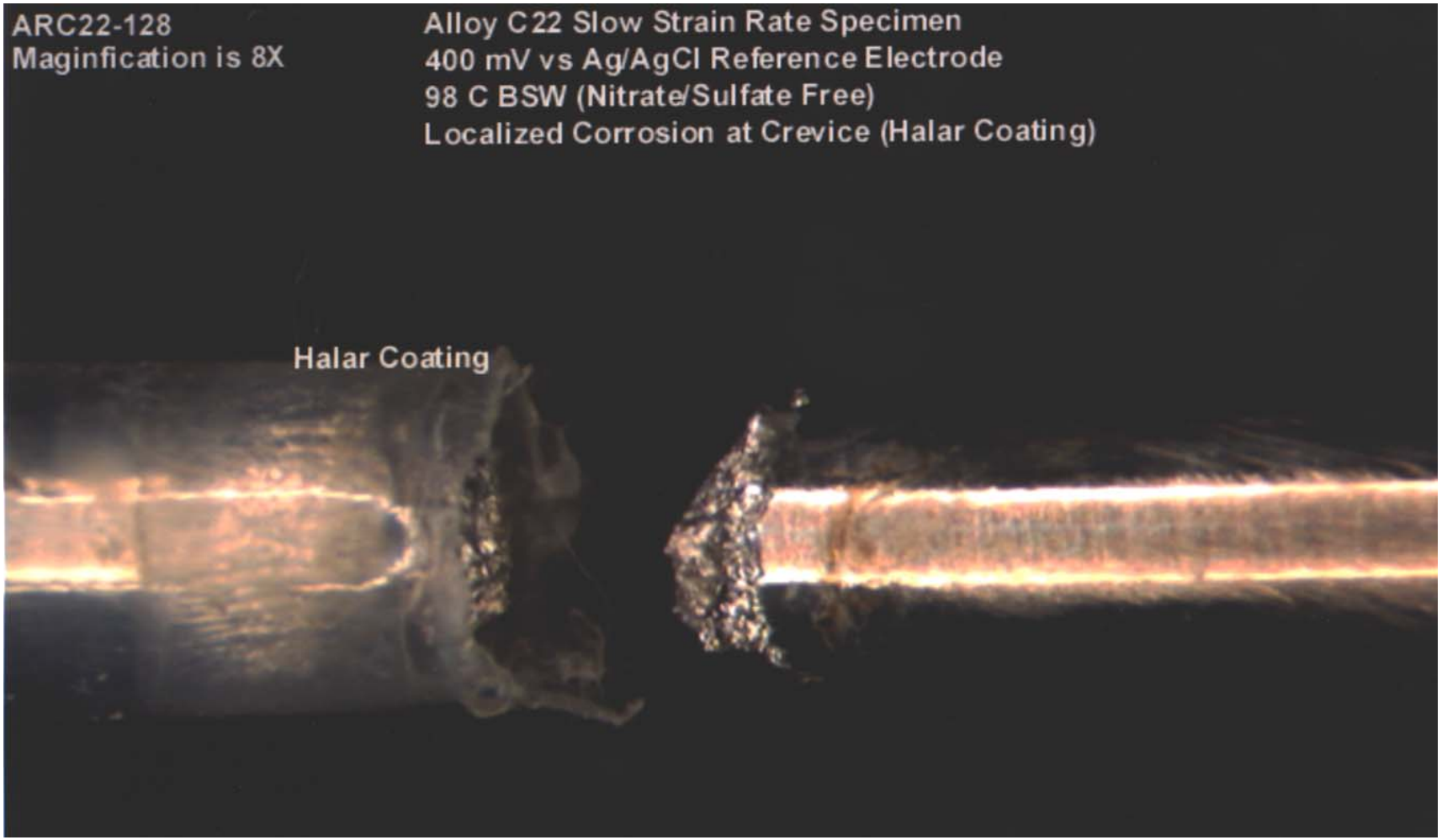
No crevice corrosion observed at 200 mV without buffers

Crevice Corrosion in Slow Strain Rate Specimen Tested at 400 mV in BSW without Inhibitor Ions

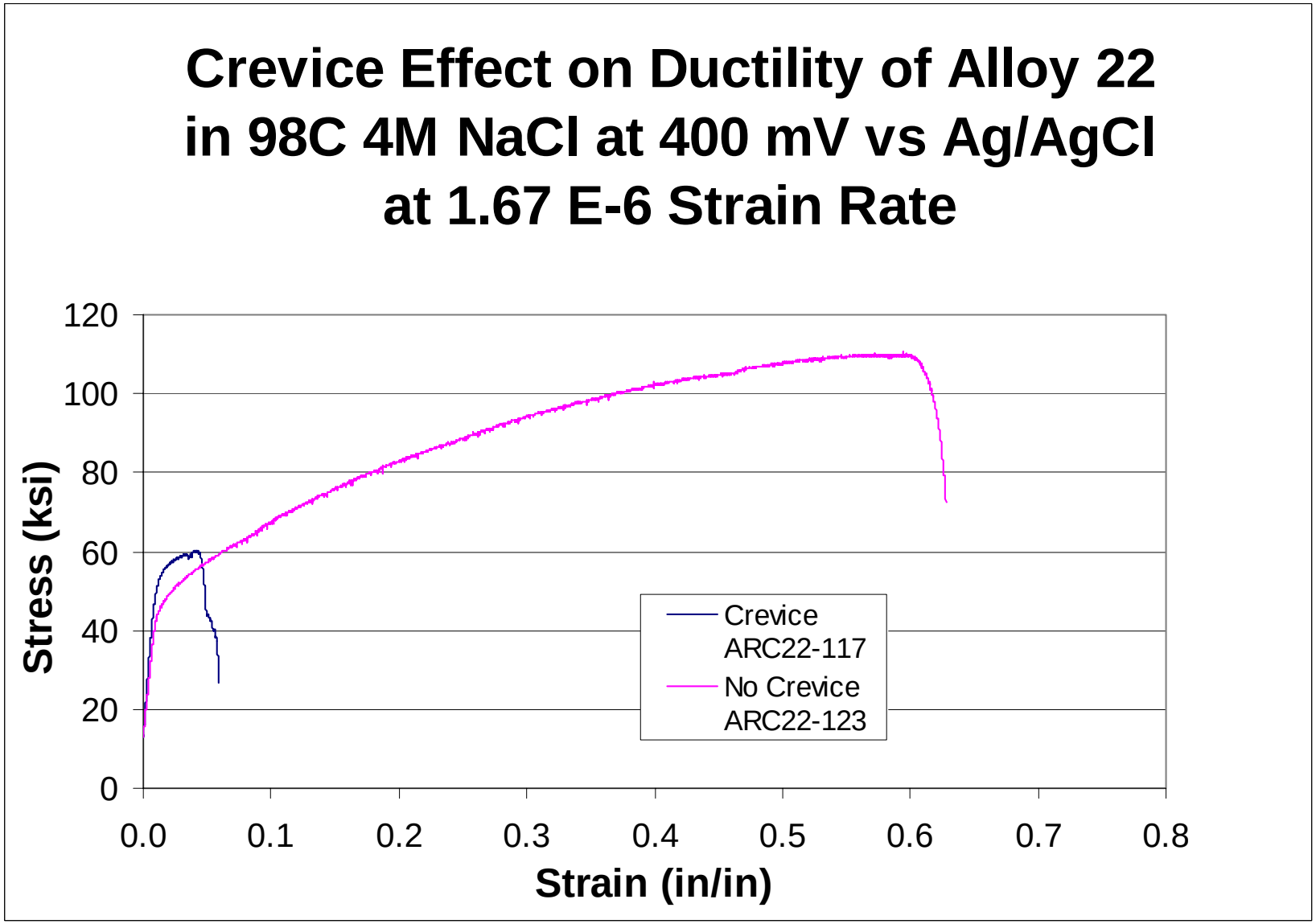


Crevice corrosion observed at 400 mV without buffers

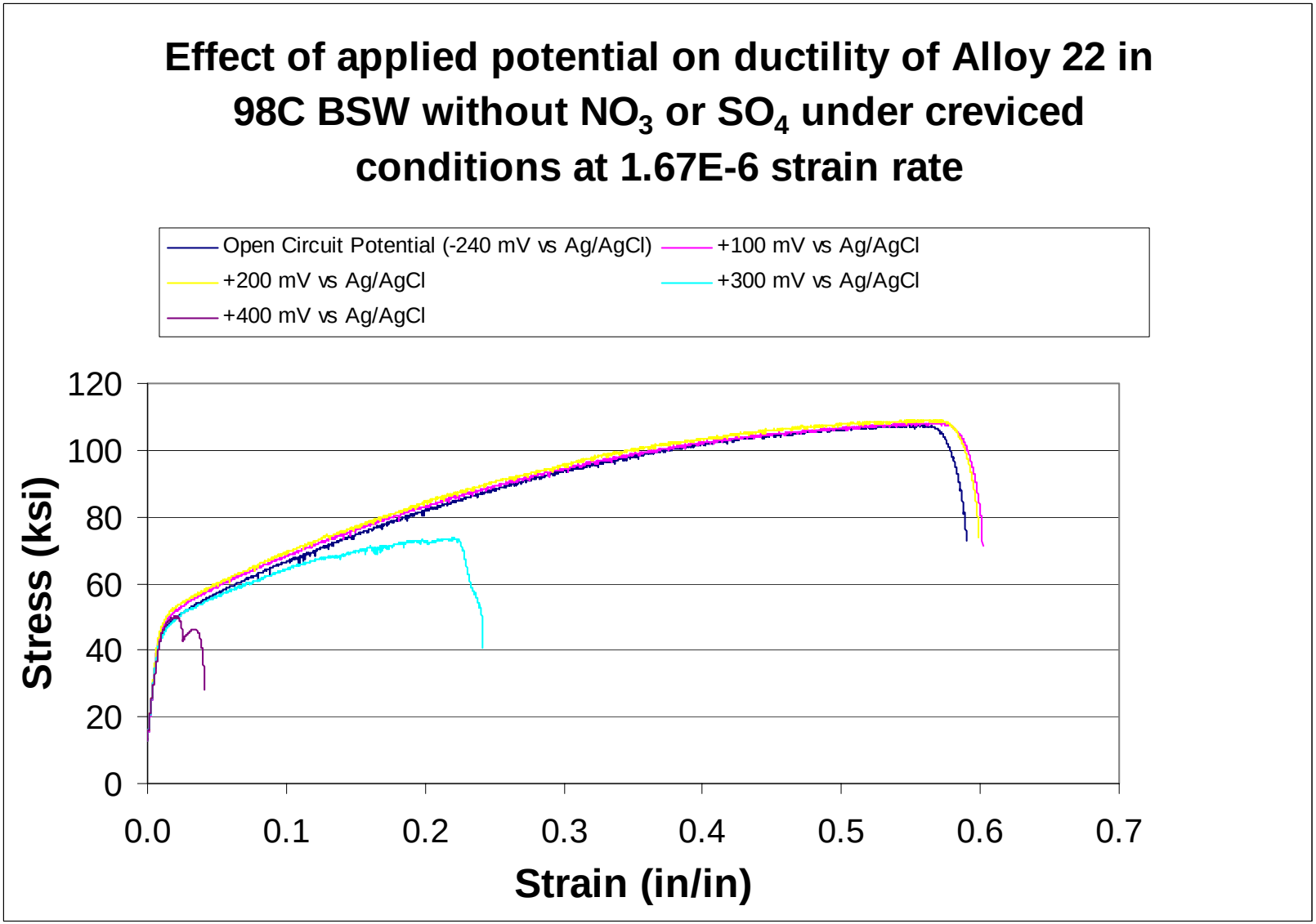
Crevice Corrosion Under Halar Crevice at 400 mV



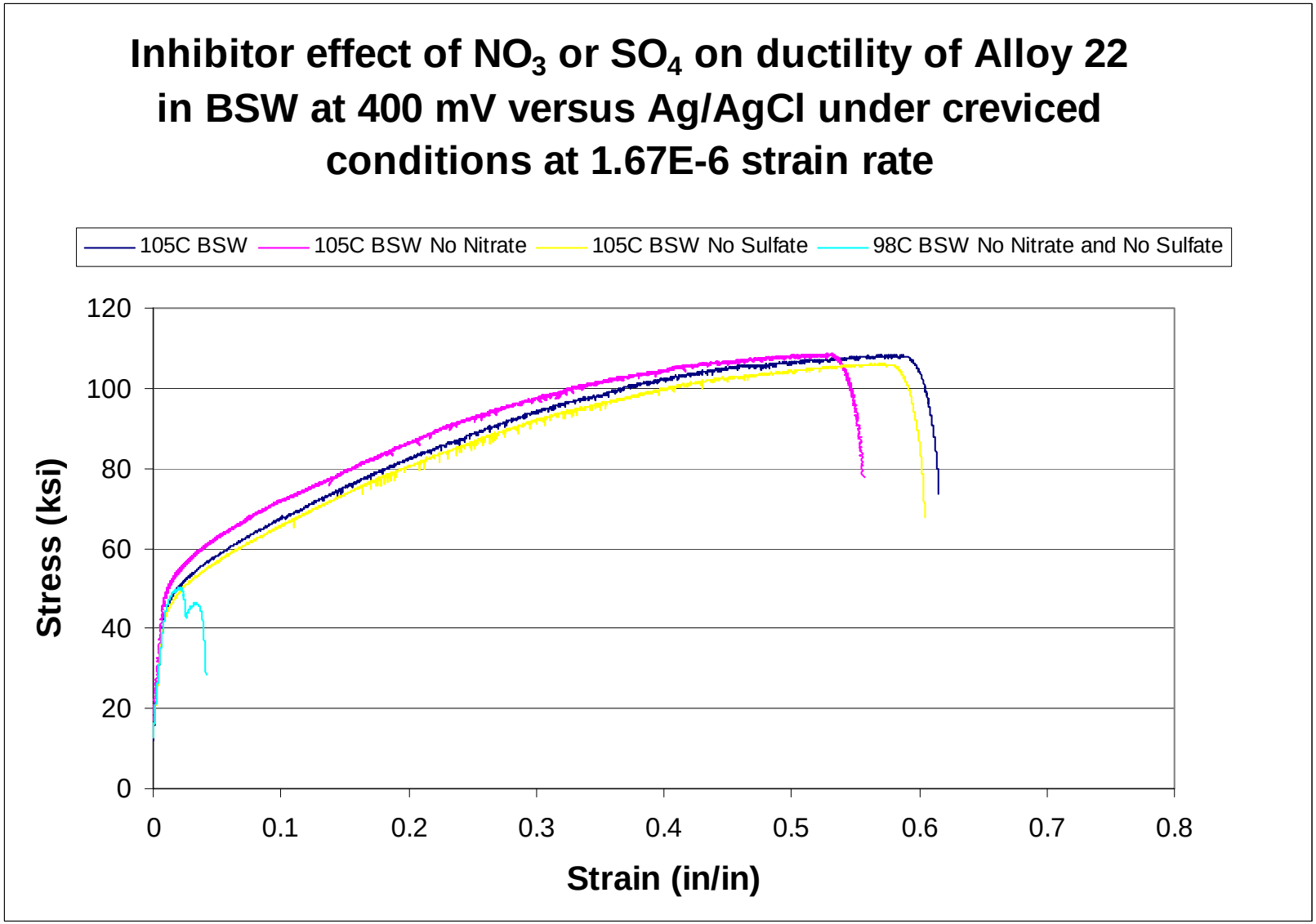
Alloy 22 Crevice Corrosion Under Slow Straining



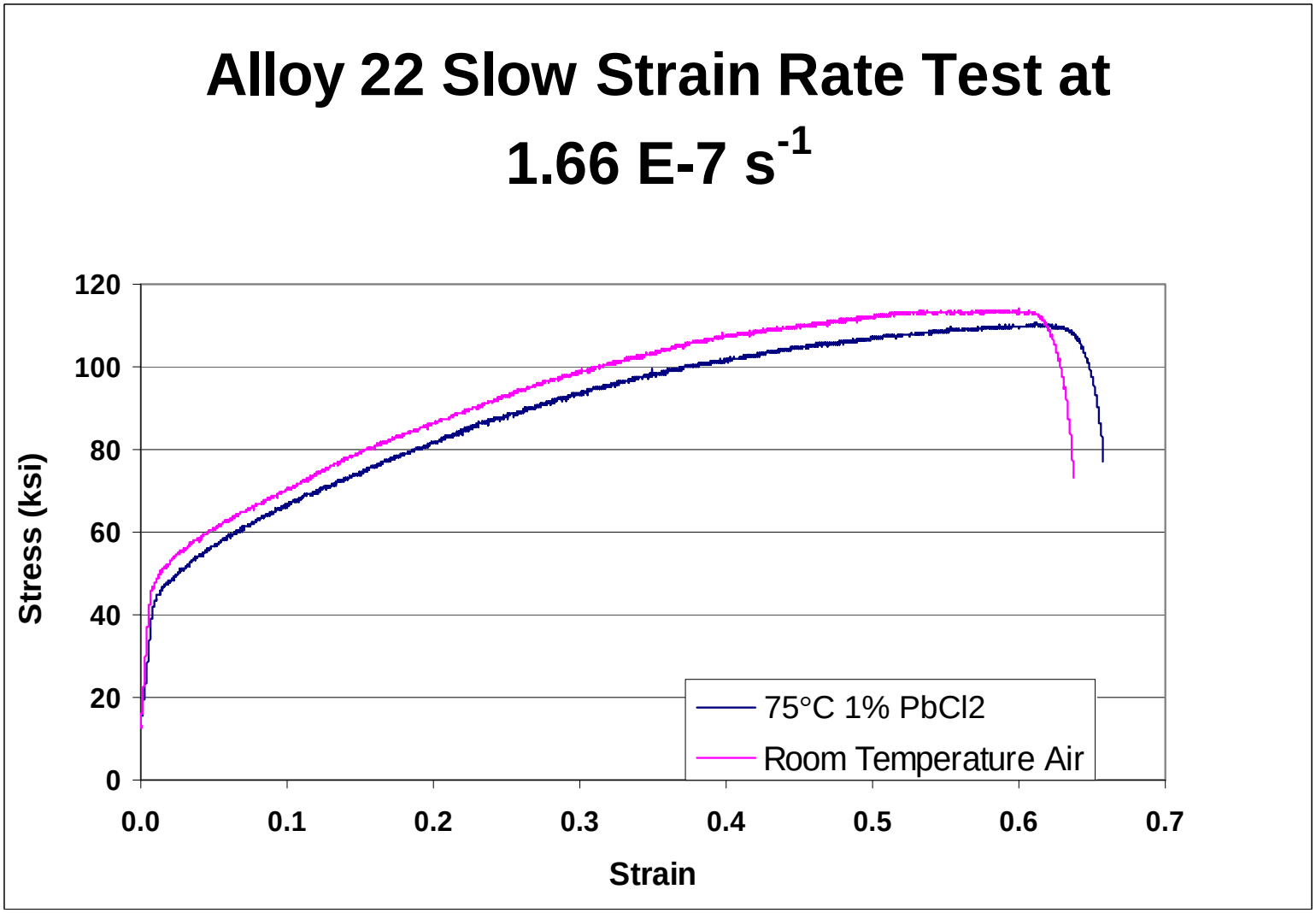
Alloy 22 Crevice Corrosion Under Slow Straining



Alloy 22 Crevice Corrosion Under Slow Straining



Alloy 22 Evaluation for Lead Effects



No deleterious effect of 1% $PbCl_2$ on stress corrosion or localized corrosion