SAND2008-0519C

U.S. Department of Energy
Office of Civilian Radioactive Waste Management

www.ocrwm.doe.gov

Effects of Cold Work on Alloy 22 Corrosion

Presented to:
Workshop on Cold Work In Iron and Nickel-Base Alloys Exposed to High Temperature Water Environments

Presented by:
Gerald Gordon
Consulting Scientist
Sandia National Laboratories, Yucca Mountain Project

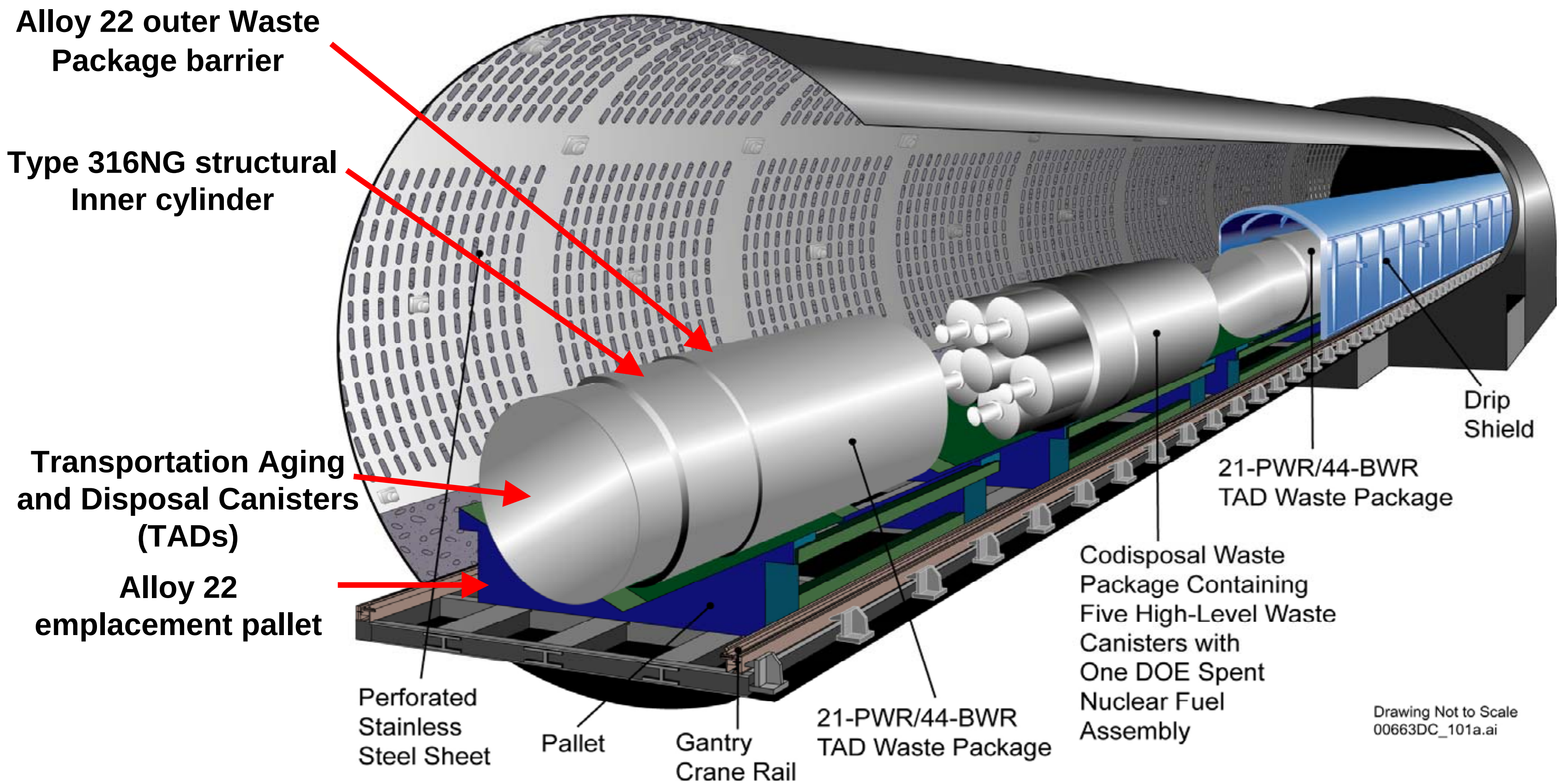
Contributors:
Peter Andresen, GE Global Research Center
Raul Rebak, Lawrence Livermore National Laboratory
Kevin Mon, AREVA NP, Inc.

June 4-8, 2007
Toronto, Canada

Outline

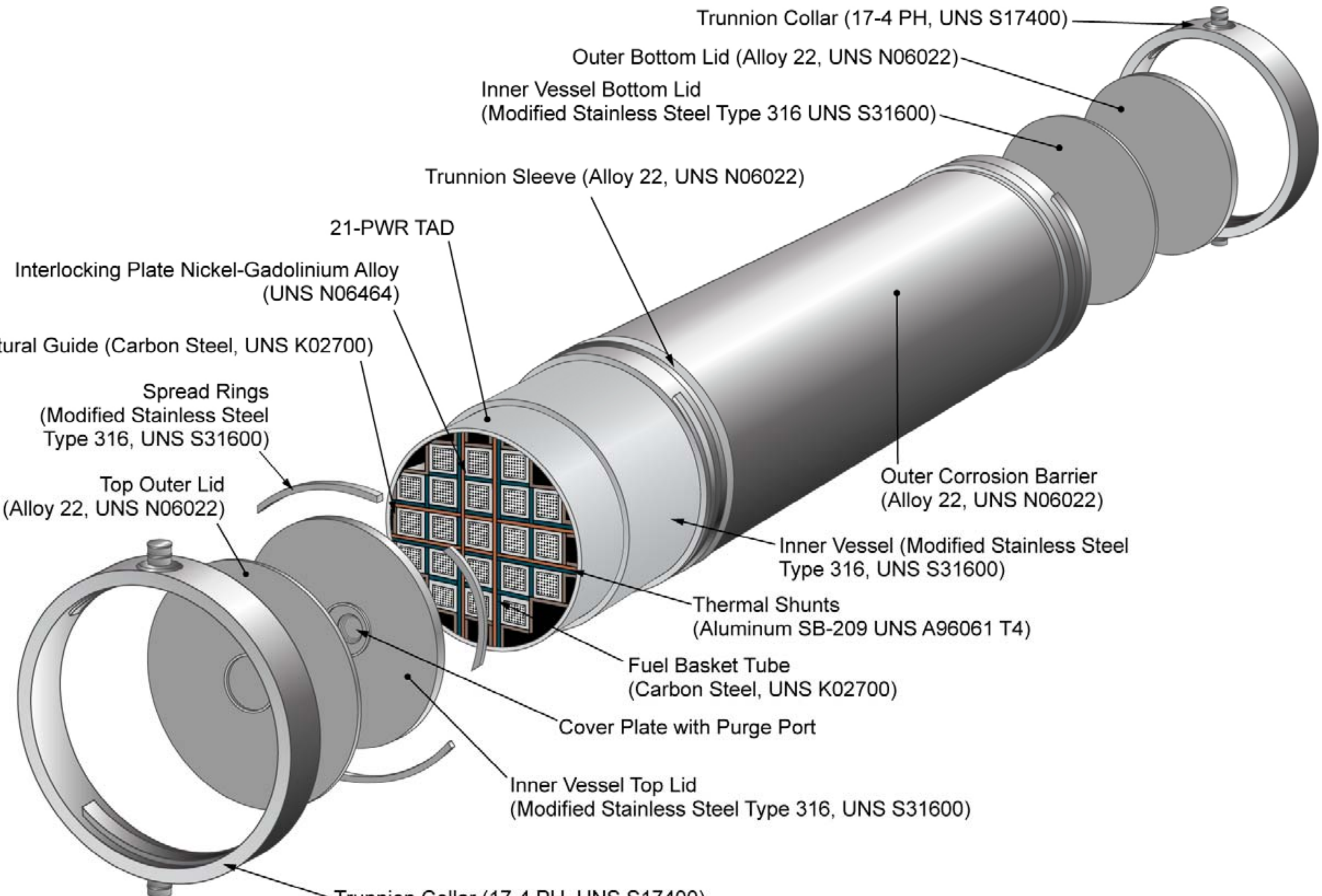
- Overview of Alloy 22 Waste Package application and exposure conditions in Yucca Mountain Repository
- Project Approach to Mitigate Cold Work and Weld Residual Stress Effects
- General and localized corrosion response of cold worked surfaces
- Effect of cold work on SCC susceptibility
- Conclusions

Emplacement Drifts and Waste Packages



Utilities load fuel into TADs which are shipped to YMP
TADs loaded into waste packages, minimizing handling of bare fuel.

Schematic of WP Outer and Inner Cylinders



Drawing Not To Scale
00688DC_020a.ai

Corrosion Resistant Materials

- **The external Alloy 22 wall of the Waste Package (WP) will be the Corrosion Resistant Layer**

Chemical Composition of Alloy 22 (UNS N06022)

UNS	Cr	Mo	Fe	W	Co	V	C	Mn	S	Si	P	Ni
N06022	20.0-22.5	12.5-14.5	2.0-6.0	2.5-3.5	2.5 max	0.35 max	0.015 max	0.50 max	0.02 max	0.08 max	0.02 max	Bal.

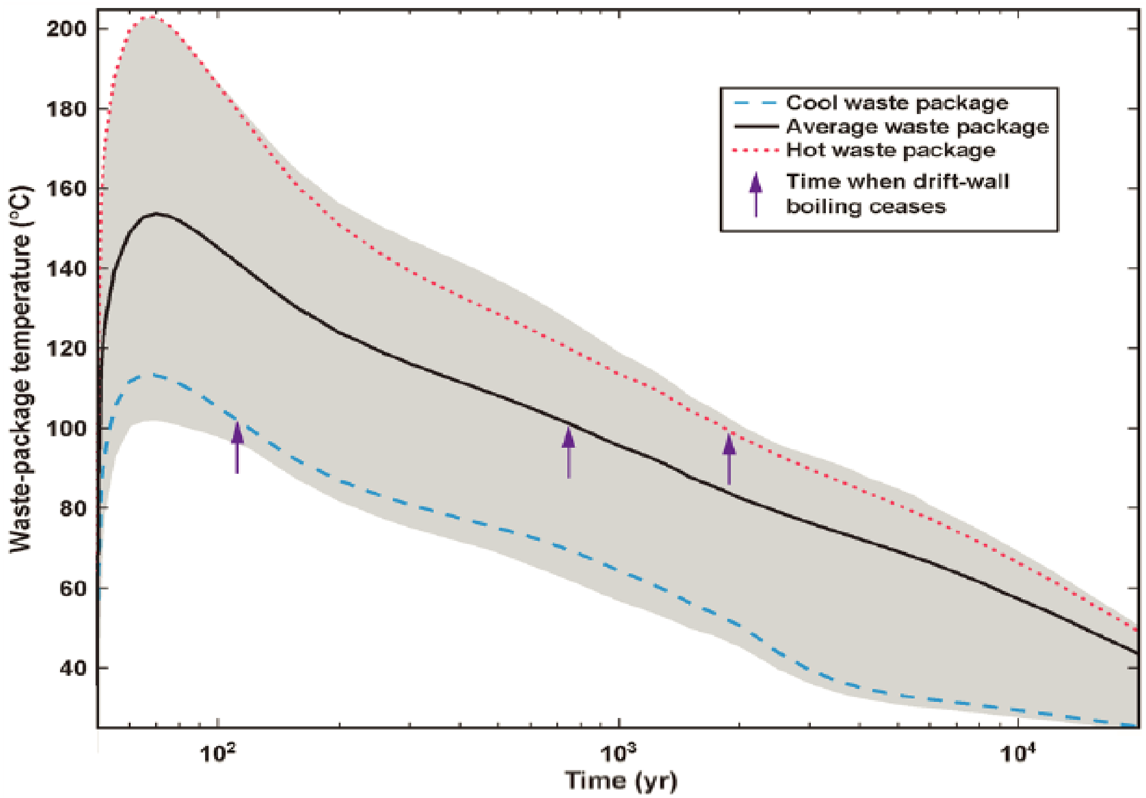
  - **Highly resistant to General Corrosion, Localized Corrosion, and Stress Corrosion Cracking**

- **WP remains on Alloy 22 pallet during handling and emplacement**
  - **Minimizes unplanned contact and potential for mechanical damage**

Environment

- The Yucca Mountain environment is basically dry
- Concentrated aerated multi-ionic solutions may contact the waste package surface
- These solutions may contact the waste package as a result of
  - Seepage
    - Requires failure of the overlying drip shield
  - Condensation
  - Deliquescence of salt or dust

Waste Package Temperature Versus Time



- **Seepage Possible after Drift Wall Cools Below Boiling**
  - **Typically after ~ 1000 years**
- **Above ~110°C, only Dust Deliquescent environments possible**

Overview of Project Approach to Mitigate Cold Work and Weld Residual Stress Effects

- **The Project will mitigate potential for SCC by removing near-surface residual tensile stresses by**
  - **Shop solution heat treatment plus quenching of as-fabricated containers prior to nuclear waste loading**
    - **Removes fabrication related cold work**
    - **Rapid quench rate minimizes precipitation**
  - **Waste packages (WP) damaged during shipment from shop to site will not be used**
  - **Following waste loading at site, final WP closure lid is remotely weld sealed**
  - **Low plasticity burnishing (LPB) of outer Alloy 22 final closure lid weld in hot cell to mitigate residual tensile surface stresses**
    - **Closure welding and LPB process optimization underway at Idaho National Laboratory**

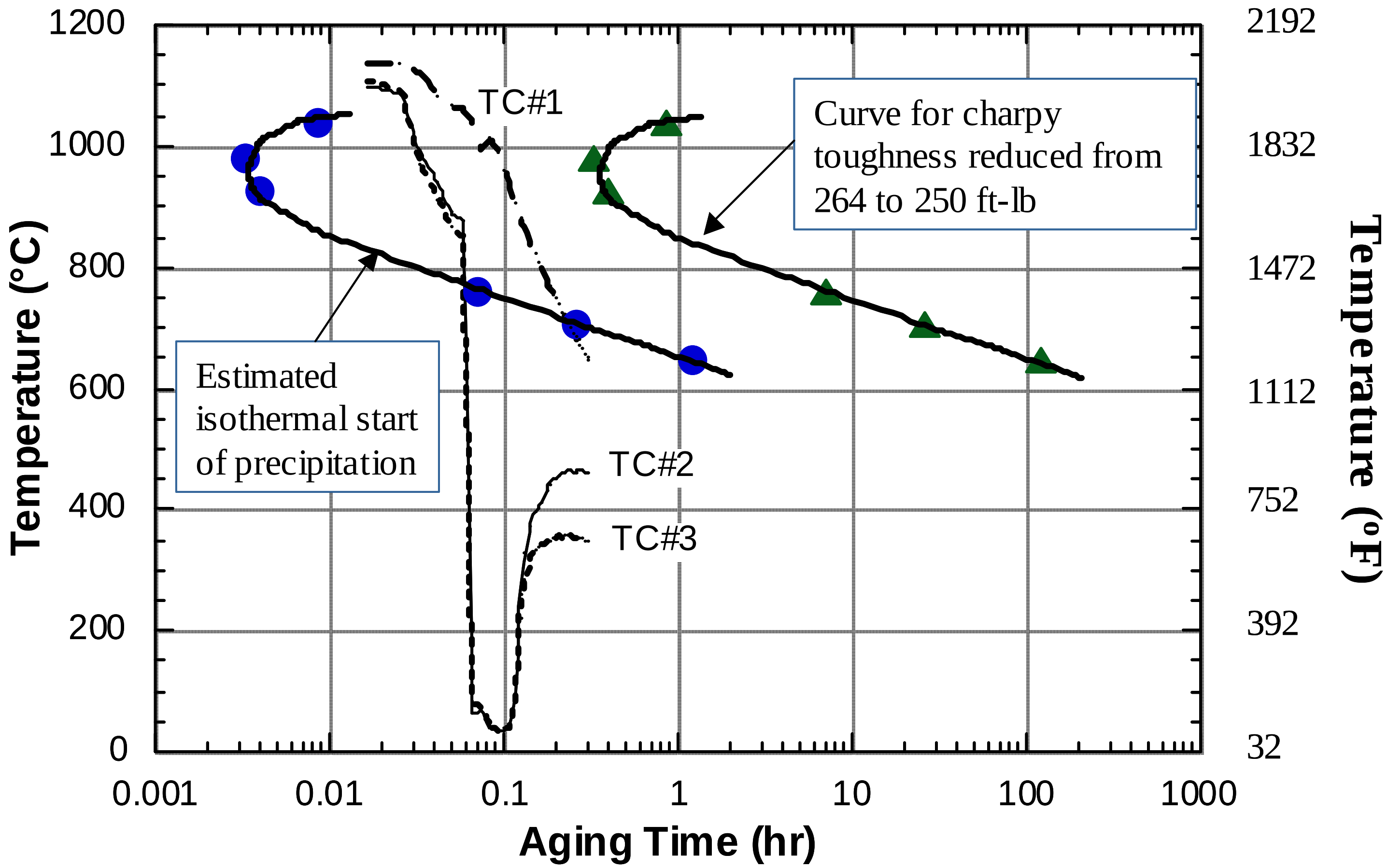
Solution Annealing

Solution Anneal and Water Quench
Alloy 22 Waste Package Mockup

- **Full-scale diameter, Quarter-scale Length**
- **Solution Anneal Temperature: 1150°C**
- **ANSYS model predictions consistent with measurement**
  - **Quenching from outer surface results in surface compressive layer**

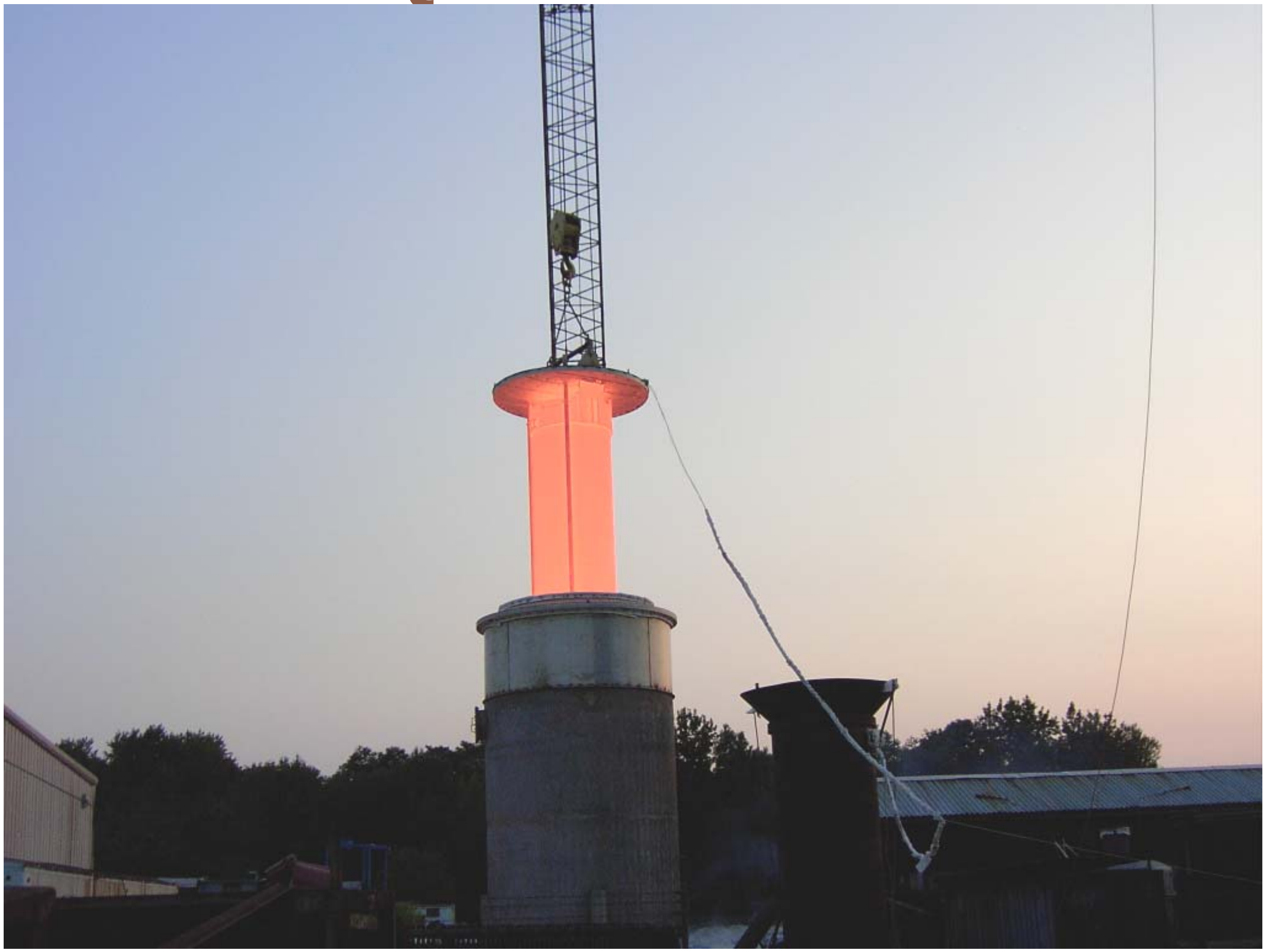
WP Mockup Cooling Response Relative to Alloy 22 TTT Curves

Water quenched with no water inside.
Container lifted out of water after 4.5 minutes and air cooled



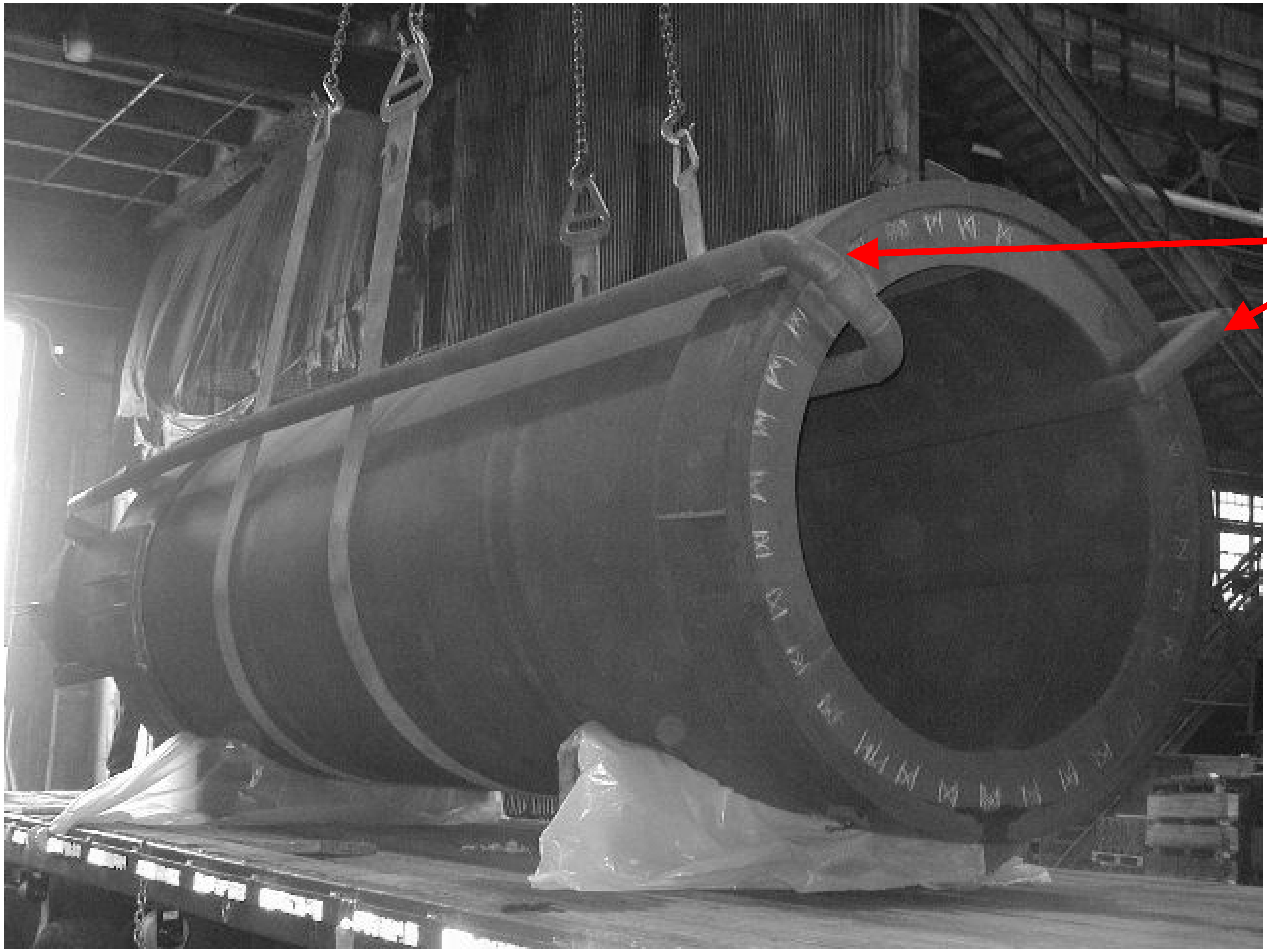
Single sided quench met specified cool down rate

Full Size Alloy 22 WP Prototype Above Quench Tank



Prototype quenched from both sides. Cooling rate met specification (150°C/minute from soak temperature to 370°C)

Waste Package Shell Following Annealing

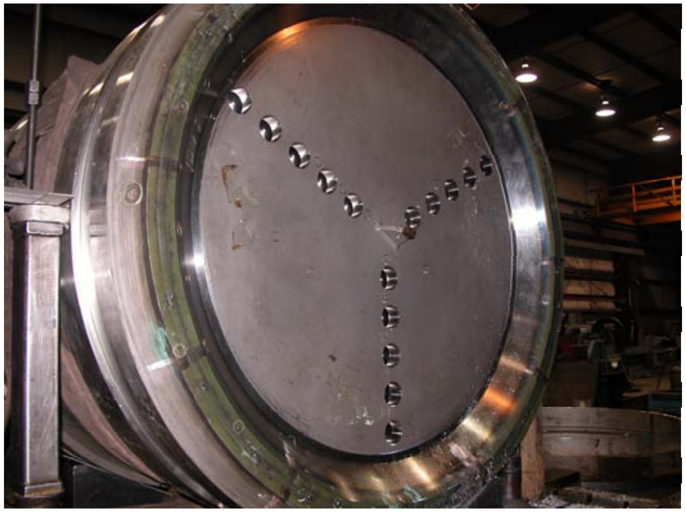


Air sparger purge pipes used only during quench

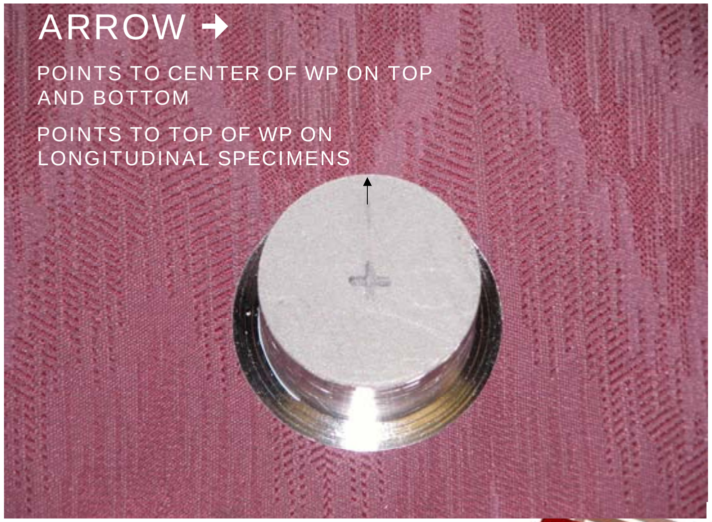
Post-annealed Alloy 22 WP Shell

Post-Anneal 'Hockey Puck' Corrosion Evaluation Specimens from WP Mockup

TOP – AFTER SPECIMENS REMOVED



SPECIMEN NOTATION

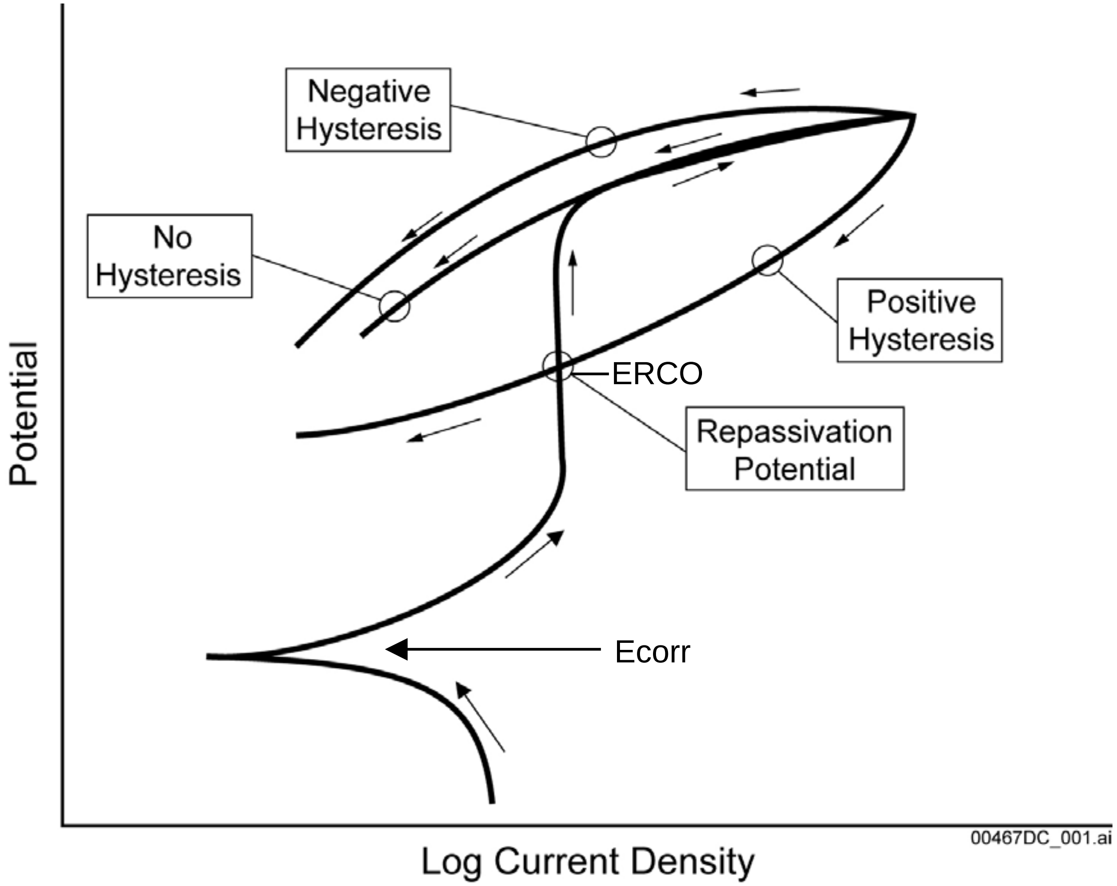


Post-Annealing Evaluation

- **Hockey Puck specimens cored from solution heat treated/quenched, full-diameter Alloy 22 WP outer shell**
  - **Weld seam and base metal specimens subjected to detailed evaluation including**
    - **Metallographic and TEM examination***
      - » **<0.05% Topologically Close Packed (TCP) phases remained in weld metal**
      - » **Less than ~0.1% present before solution anneal**
    - **Corrosion rate and localized corrosion measurements performed to confirm fabrication-related cold work effects were removed by annealing**

*** Torres, et al., Aging and Phase Stability of Alloy 22 Welds, UCRL-TR-217339, November 30, 2005**

Typical CPP Curve Showing Crevice Repassivation Potential, ERCO



Crevice Repassivation Potentials for Specimens from Annealed WP Mockup and Archive Materials

Material/ Data Source	ER1	ERCO	ER, CREV
1 M NaCl, 90°C			
Current PCA Mockup (Table 2)	-43 ± 1	-53 ± 1	NA
Archive MA MCA Ref. 4-5	-80 ± 19	-49 ± 16	-30 ± 8
Archive ASW MCA Ref. 4-5	NA	NA	-99 ± 9
5 M $CaCl_2$, 90°C			
Current PCA Mockup (Table 2)	-124 ± 43	-121 ± 68	NA
Archive MA MCA Ref. 5	-182 ± 7	-121 ± 63	NA
Archive ASW MCA Ref. 5	-175 ± 10	-174 ± 15	-130 ± 3
6 m NaCl + 0.9 m KNO_3, 100°C			
Current PCA Mockup (Table 2)	-43 ± 13	-75 ± 1	NA
Archive ASW MCA Ref. 6	-49 ± 27	-63 ± 23	NA

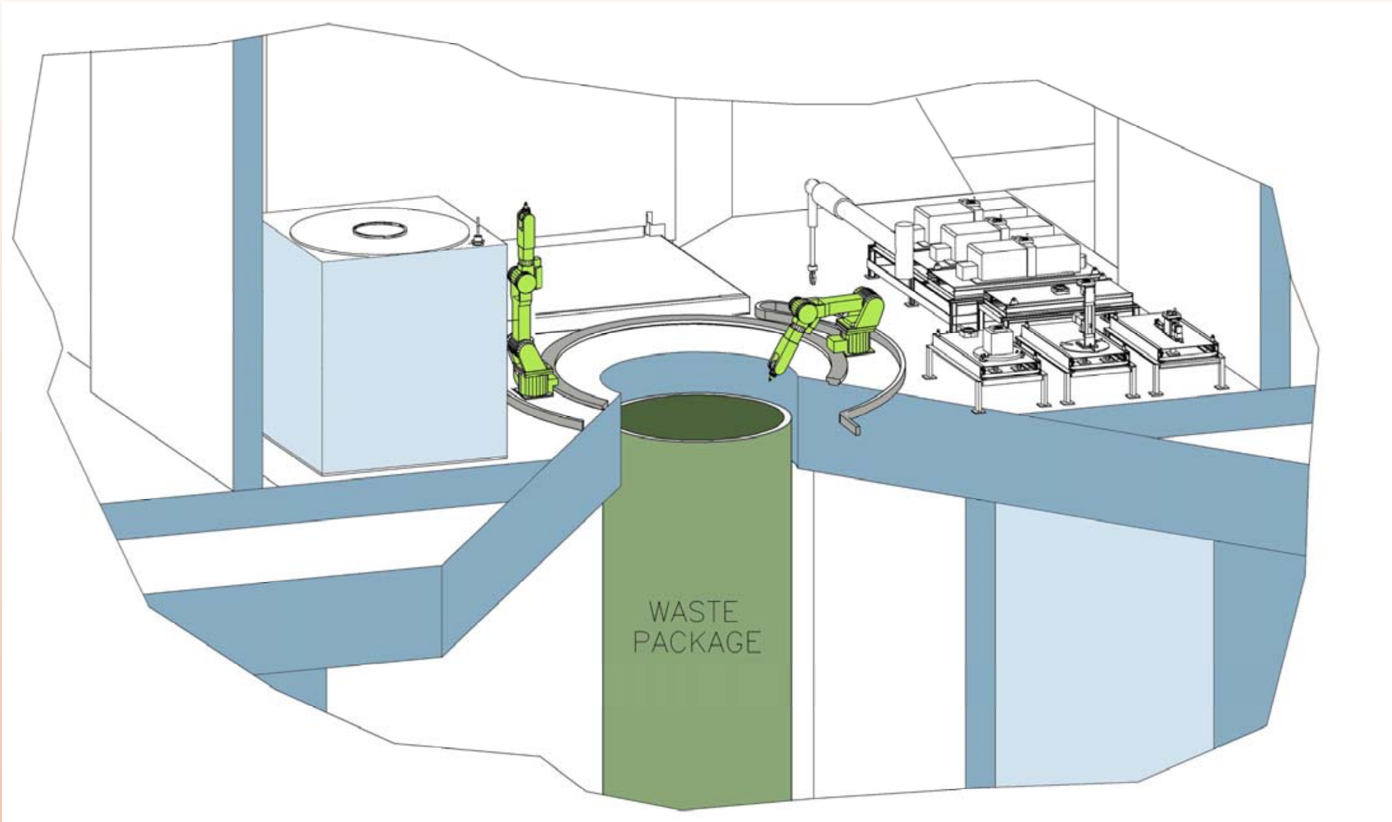
ER1 = Potential in reverse scan where current density is 1 μA/cm²
ERCRO = Potential where reverse scan crosses forward scan
ER, CREV obtained using Tsujikawa Hisamatsu electrochemical (THE) method
PCA = Prism crevice assembly
MA = Mill annealed
ASW = As-welded
MCA = Multiple crevice assembly

Crevice corrosion response unchanged by WP solution heat treatment

(Rebak, UCRL-TR-216918, September 2005)

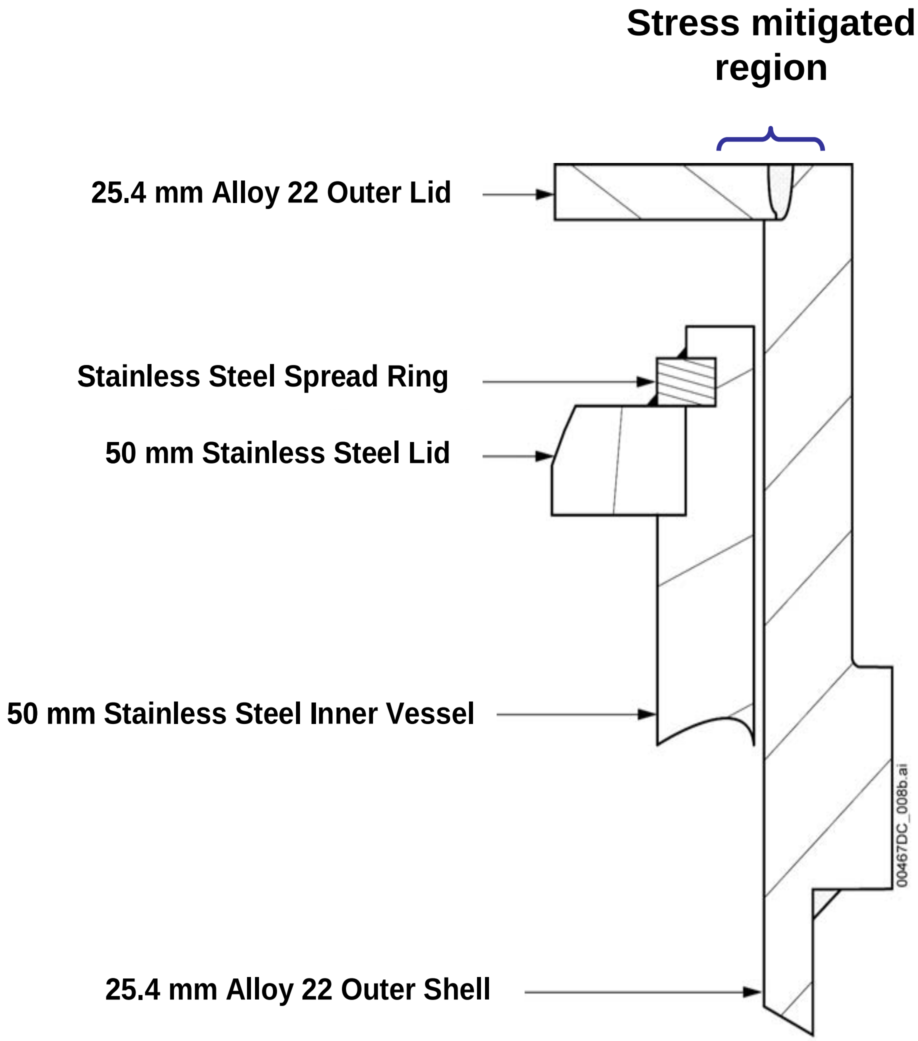
Site Hot Cell Closure Welding Concept

Welding

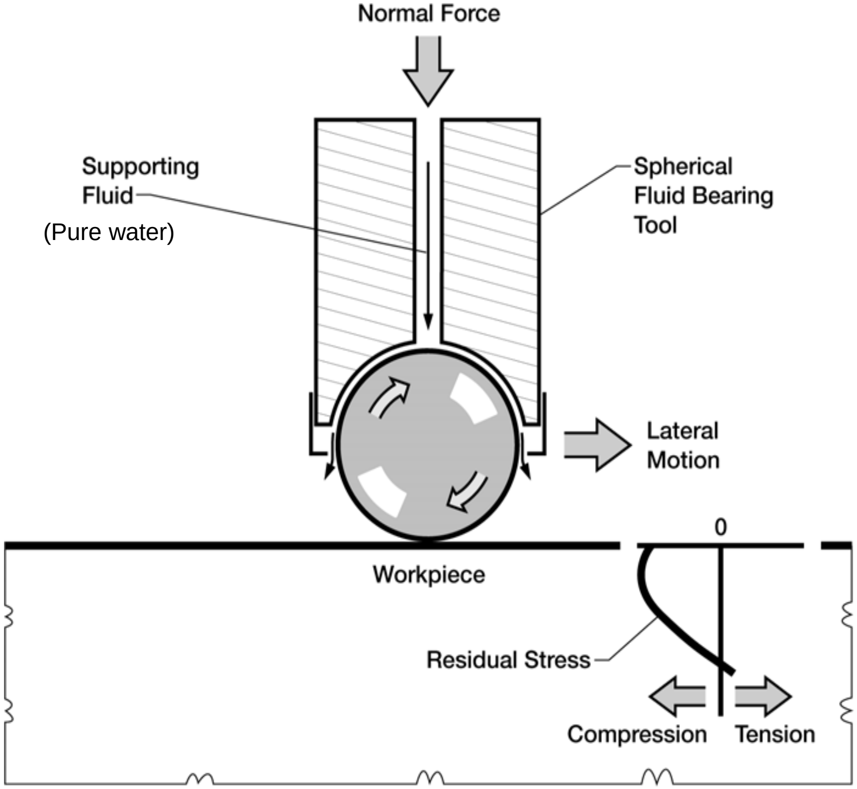


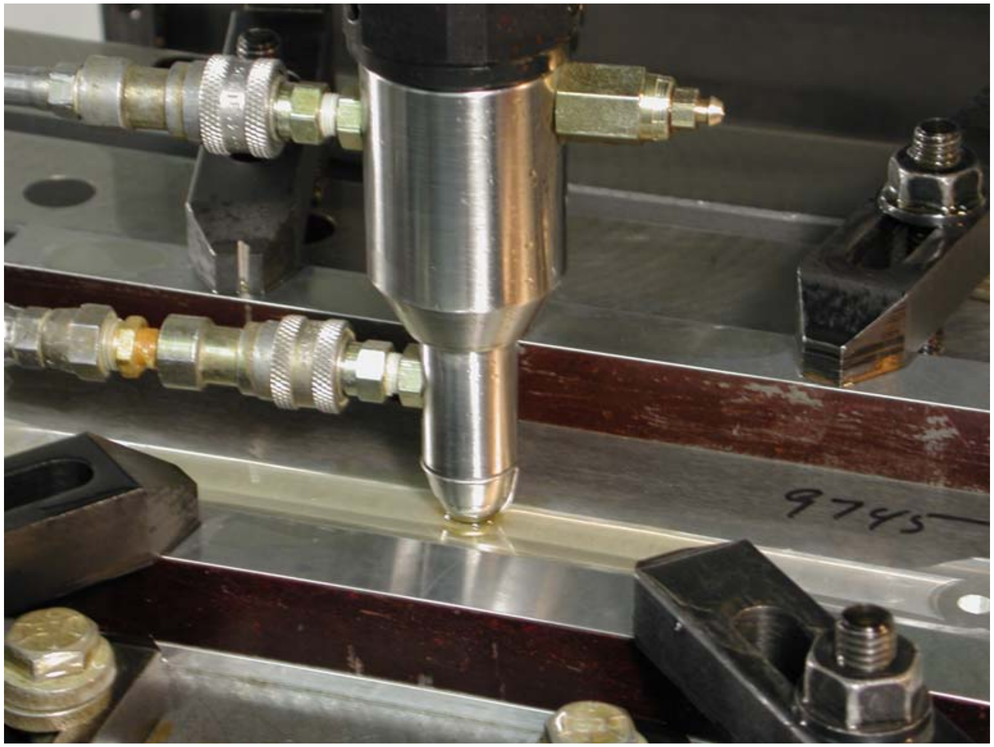
Alloy 22 (WP) Cross Section

- **After closure welding, WP outer lid stress mitigated by low plasticity burnishing**
  - **Delays onset of SCC**
- **No corrosion credit for 316NG stainless steel inner vessel**



Low Plasticity Burnishing (LPB)





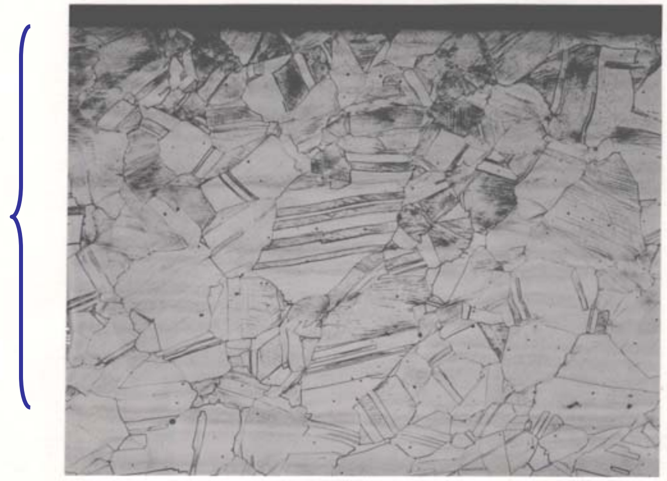
- Automated
- Forces Controlled By Patented Methodology
- Movement Controlled By Numerical Controller

Welded Plate being LPB Processed

Prevéy et al., Lambda Research High Cycle Fatigue Conf.,March 2001

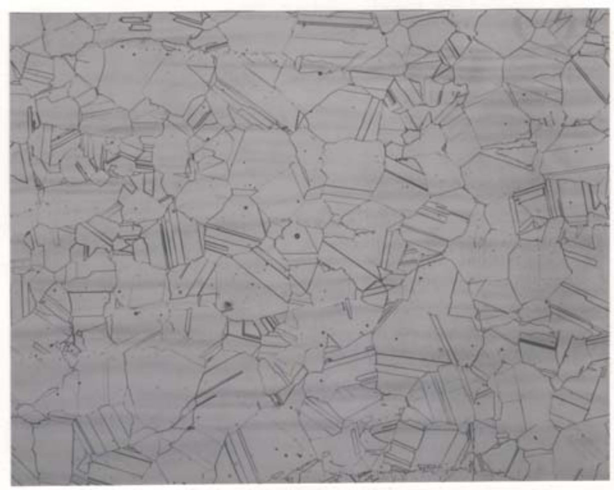
Surface Cold Work from LPB Processed Alloy 22

Surface cold work



At Surface, 100X

Burnished surface region

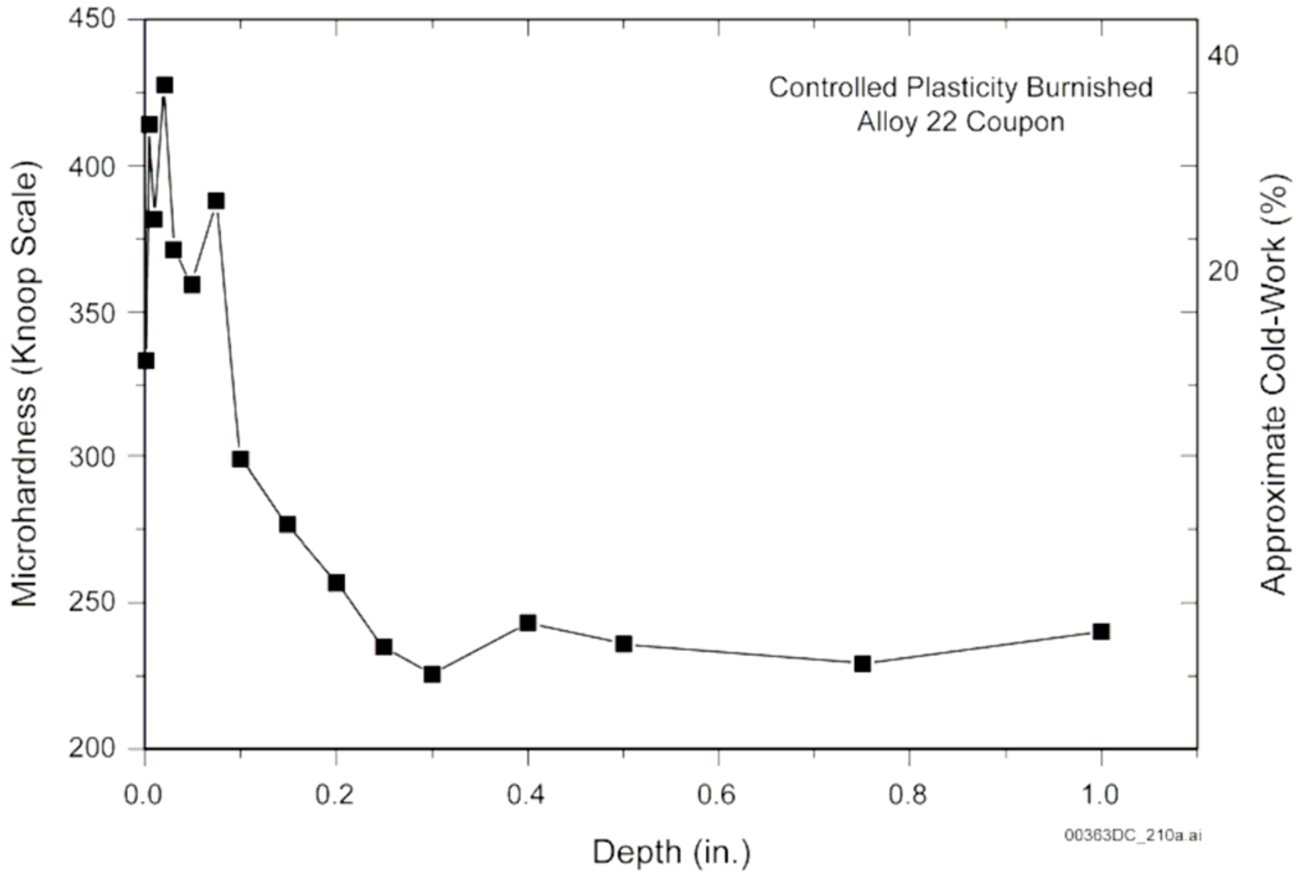


Remote from Surface, 100X

Below burnished region

Bunishing results in surface cold-worked layer

Microhardness Measurements for Burnished Alloy 22 Plate



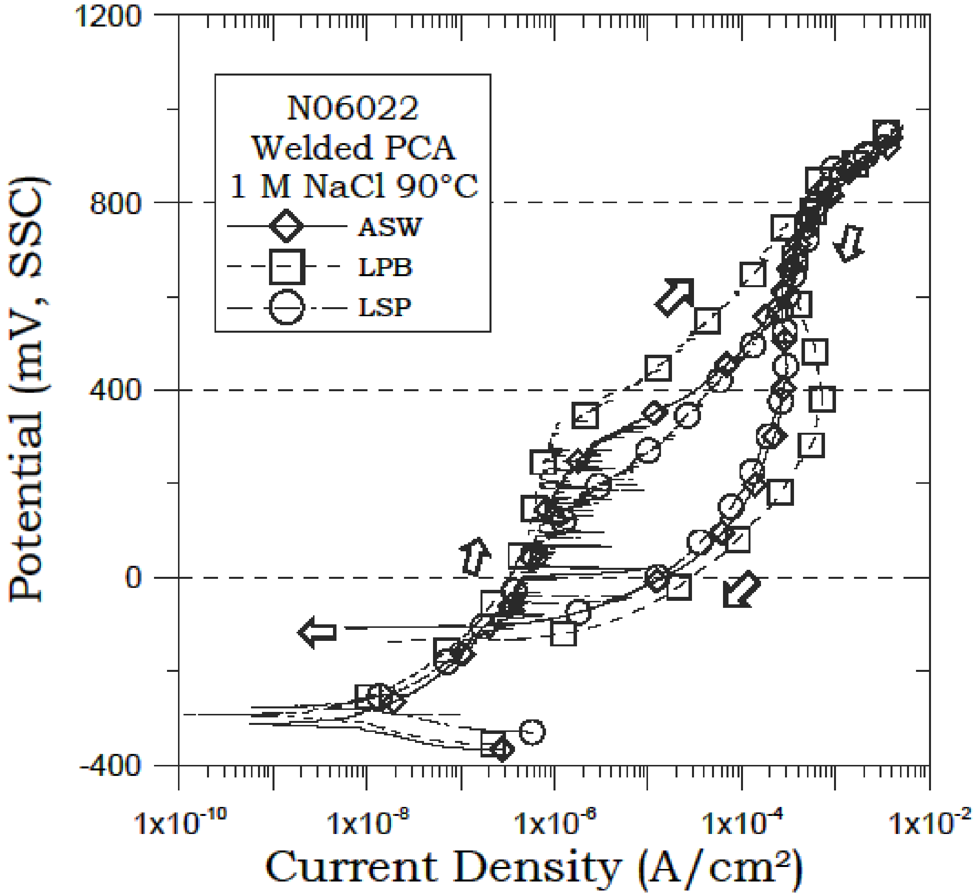
NOTE: 1.0 in. = 25.4 mm.

Microhardness (Knoop Scale) versus Depth from Outer Surface for Controlled Plasticity Burnished Alloy 22 Plate Material

Outermost surface region contains ~20-35% cold work

Haynes International 1997. Hastelloy C-22 Alloy. Kokomo, Indiana: Haynes International. [DIRS 100896], TIC: 238121; BSC 2004b, Lambda Research Microhardness Distribution. Procurement Document No.TA004667. Las Vegas, Nevada: Bechtel SAIC Company. ACC: ENG.20040420.0016.

Comparison of As-welded with Peened or Burnished Cold Worked Alloy 22 Surfaces



Similar CPP behavior for as-welded (ASW), laser shot peened (LSP) and low plasticity burnished (LPB) surfaces

(Rebak, UCRL-TR-216918, September 2005)

Corrosion Response of Cold Worked Surfaces

Characteristic Potentials (mV, SSC) and Corrosion Rates (µm/year)
of Alloy 22 in deaerated 1 M NaCl solution at 90°C

ID	Material	E_{corr} 24 h	Corrosion Rate	E20	E200	ER10	ER1	ERCO
W6	ASW	-286	0.22, 0.27, 0.21	374	567	-17	-88	-104
W7	ASW	-198	0.19, 0.15, 0.21	356	547	-17	-79	-91
Ave ± SD	ASW	-242 ± 44	0.208 ± 0.039	365 ± 9	557 ± 10	-17 ± 0	-84 ± 5	-98 ± 7
B3	LPB	-260	0.18, 0.15, 0.20,	480	706	-59	-123	-134
B4	LPB	-258	0.20, 0.21, 0.19	383	623	-10	-95	-111
Ave ± SD	LPB	-259 ± 1	0.188 ± 0.021	432 ± 49	665 ± 42	-35 ± 25	-109 ± 14	-123 ± 12
P2	LSP	-244	0.41, 0.51, 0.38	319	544	-14	-86	-104
P5	LSP	-195	0.22, 0.23, 0.23	381	575	-22	-100	-114
Ave ± SD	LSP	-220 ± 25	0.330 ± 0.121	350 ± 31	560 ± 16	-18 ± 4	-93 ± 7	-109 ± 5

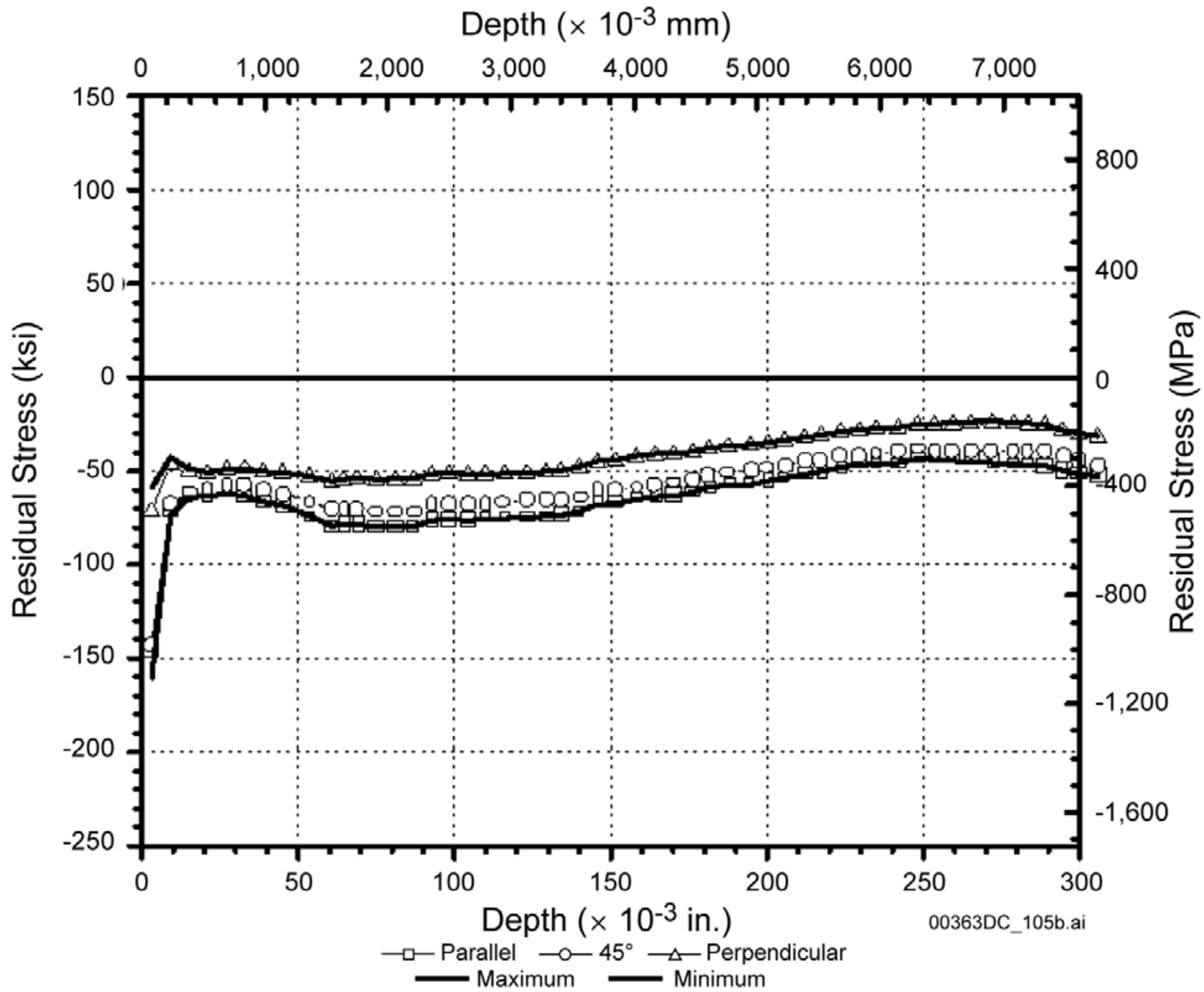
ASW = As-welded
LSP = laser shot peened
LPB = low plasticity burnished

E_{corr}, ERCO and corrosion rates for ASW surfaces comparable to cold-worked LSP and LPB surfaces

(Rebak, UCRL-TR-216918, September 2005)

Low Plasticity Burnishing (LPB) Process

Measured Stress (Using 1-in Ring-Core Method) versus Depth
for Alloy 22 Plasticity-Burnished 1-in-thick Gas Tungsten Arc Welding Welded Plate



Several mm deep compressive layer in cold-worked region will mitigate SCC potential

In-Drift Chemistry vs. Corrosion Testing Environments

Chemical Compositions of Principal Laboratory Testing Media

	Basic Sat'd Water		Simulated Dilute Water		Simulated Concen'd Water		Simulated Acidified Water		Simulated Saturated Water	
	<110°C		60 and 90°C		60 and 90°C		60 and 90°C		60 and 90°C	
Ion	mM	mg/L	mg/L	mM	mg/L	mM	mg/L	mM	mg/L	mM
K^+	2320	90,846	34	0.87	3,400	87	3,400	87	142,000	3,632
Na^+	10,059	231,224	40	17.8	40,900	1,780	37,690	1,780	487,000	21,182
Mg^{2+}	-	0	1	0.04	<1	20.04	1,000	41	0	0
Ca^{2+}	-	0	0.5	0.01	<1	20.01	1,000	25	0	0
F^-	85	1616	14	0.74	1,400	74	0	0	0	0
Cl^-	5,000	177,695	67	1.89	6,700	189	24,250	684	128,000	3,610
NO_3^-	2,860	177,168	64	1.03	6,400	103	23,000	371	1,313,000	21,175
SO_4^-	176	16,907	167	1.74	16,700	174	38,600	396	0	0
HCO_3^-	1,786	107,171	947	15.52	70,000	1,148	0	0	0	0
Si(aq)	~251	7,059	27-49		27-49		27-49		27-49	
pH^-	12-13		9.8-10.2		9.8-10.2		2.7		5-5.7	
NO_3^-/Cl^-	0.572		0.545		0.545		0.542		5.87	

Mg/l for test media from DTN:LL040803112251.117

- **Significant testing also performed in a broader range of seepage, pore water and deliquescent brine environments at temperatures to 220°C**

Cold Work Effects on SCC Initiation Response

Alloy 22 Stress Corrosion Cracking (SCC)

- **Alloy 22 extremely resistant to SCC initiation**
  - **Only observed in**
    - **Bicarbonate containing brines under slow strain rate testing, and only on anodically polarized ($E_{app} > E_{corr}$) specimens***
    - **one U-bend specimen exposed to ~250ºC, highly acidic, Pb containing brine (pH 0.4)****
    - **Hydrofluoric acid (20% HF at 93ºC)****
  - **No initiation observed in broad range of repository relevant brines at open circuit potential**

***Shukla, et all., Paper No. 06502, Corrosion 2006, NACE**

****King, et al., Paper No. 04548, Corrosion 2004, NACE, Fix et al., Paper 04549, Corrosion 2004, NACE**

Cold Work Effects on SCC Initiation

U-bend and Constant Load Test Results

Long-Term Corrosion Test Facility (LTCTF)

Lawrence Livermore National Laboratory

Test facility tanks

Test specimen rack

- **Evaluation of General, Localized, Galvanic and Stress Corrosion**
- **Over 20,000 specimens on test at 60^{O}C and 90^{O}C in aerated SAW, SCW and SDW in liquid phase, vapor phase and water line**

Long Term Exposure of Alloy 22 U-bends

- U-bend specimens examined after LTCTF exposure to a range of environments for 5 years* (some up to 9.3 years**)
- Double U-bends exposed in 105^{O}C BSW brine for over 6 years***
- Apex strain in single and double U-bends equivalent to ~12% cold work

Figure 6. Alloy 22 U-Bend specimen tested for 9.3 years in SCW at 90°C. No cracking

No SCC initiation observed in any annealed or as-welded Alloy 22 U-bend specimens

***Stuart et al., Paper No. PVP200726163, 2007 ASME Pressure Vessel and Piping Division Conference, July 22-26, 2007; Fix, et al., **NACE Paper No. 04549, Corrosion 2004; Fix et al., **The Long-Term Corrosion Test Facility at the Lawrence Livermore National Laboratory Final Report, UCRL-PROC-229377, May 24, 2007.

Alloy 22 U-bend Tests in 160ºC SCW at GE GRC

Exposed single U-bend

Exposed double U-bend

18 single U-bends fabricated from welded Alloy 22 plate and 10 double U-bends from annealed plate exposed to 160°C SCW brine for 15,000 hours without SCC initiation

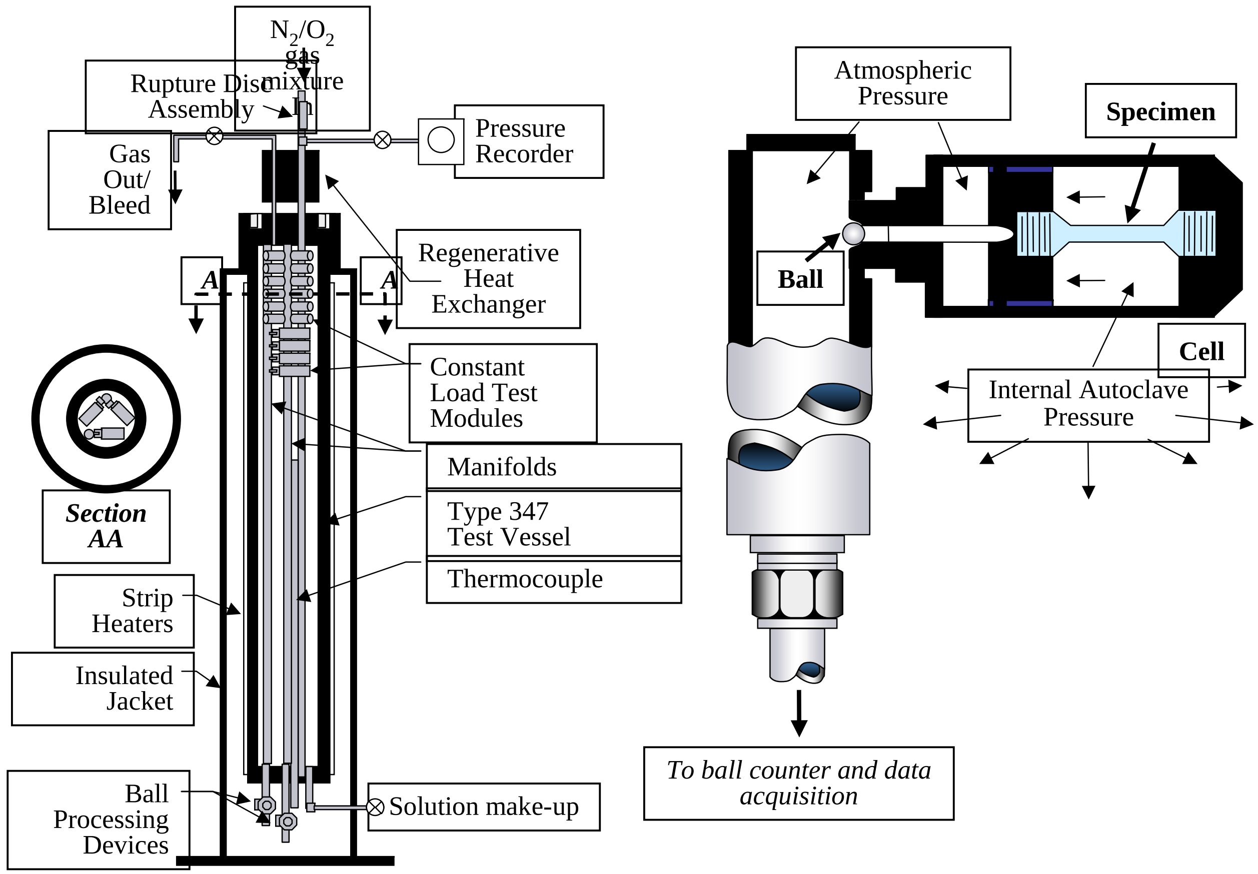
- Specimen arms periodically tightened to reduce stress relaxation
- Typically weld HAZ contains ~10-20% plastic strain
- In addition, U-bend apex region contains ~12% plastic strain

*U-bend tests performed at GE Global Research Center, P.L. Andresen and G.M. Gordon , "SCC Initiation and Growth in Alloy 22 and Titanium Alloys in Concentrated Groundwater", Proceedings, 12th International Conference on Environmental Degradation of Materials in Nuclear Systems-Water Reactors, Salt Lake City, UT, August 2005

Alloy 22 U-bend Tests in 160^{o}C Brine

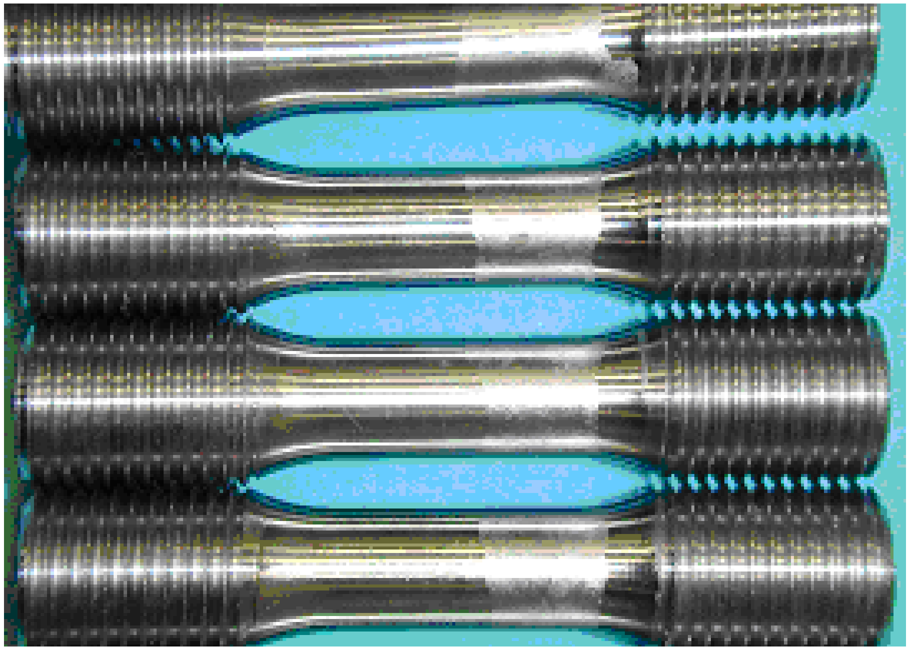
- Typical exposed U-bend apex region after 15,000 hours brine exposure
  - No SCC initiation

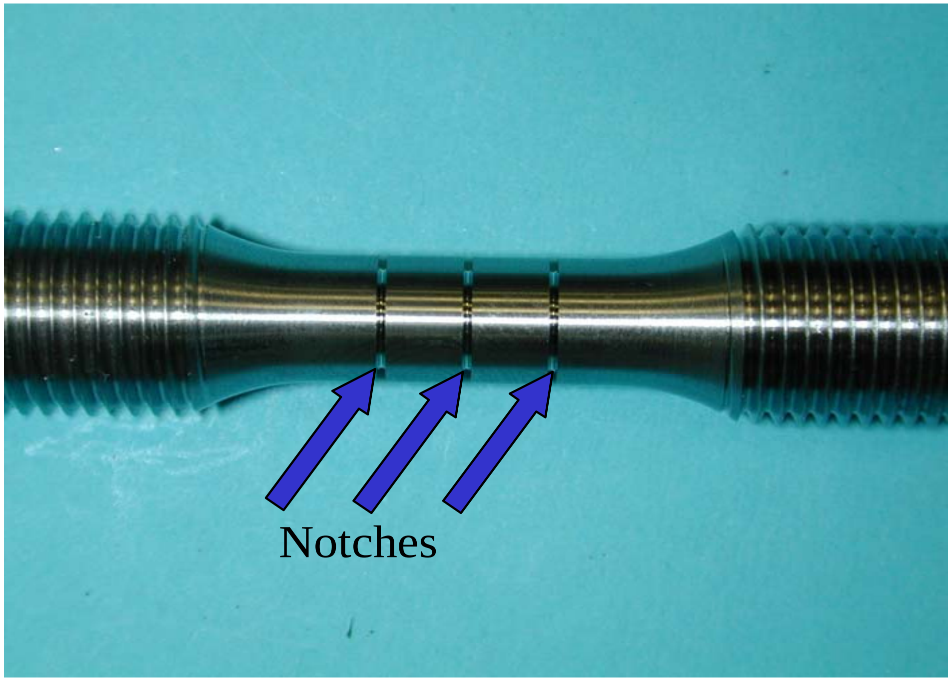
GE GRC Constant Load SCC System



- **Alloy 22 tested in 105ºC, aerated 15% BSW brine for 3.7 years at stresses up to 96% UTS.**
- **Conditions include mill annealed, as-welded, 20% cold worked and cold work + long range ordering (LRO) [creviced and uncreviced]**

Typical Welded Constant Load Specimens

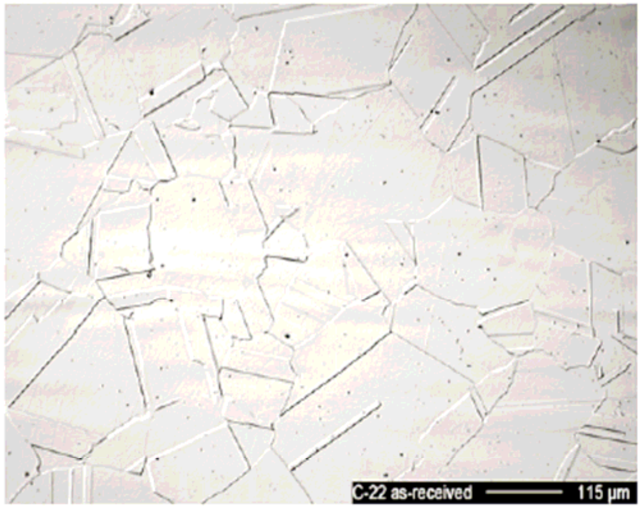




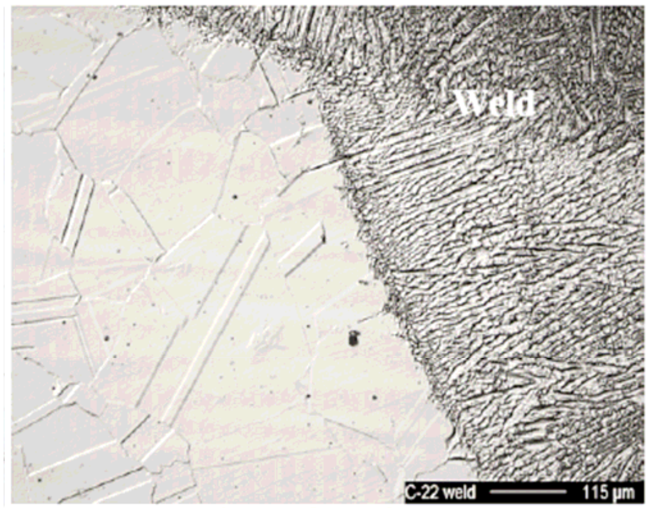
Example of Notched Keno Specimen (Welded C22)

For notched specimens, notches located in base metal, HAZ and weld metal

Some Alloy 22 Microstructures Tested for SCC

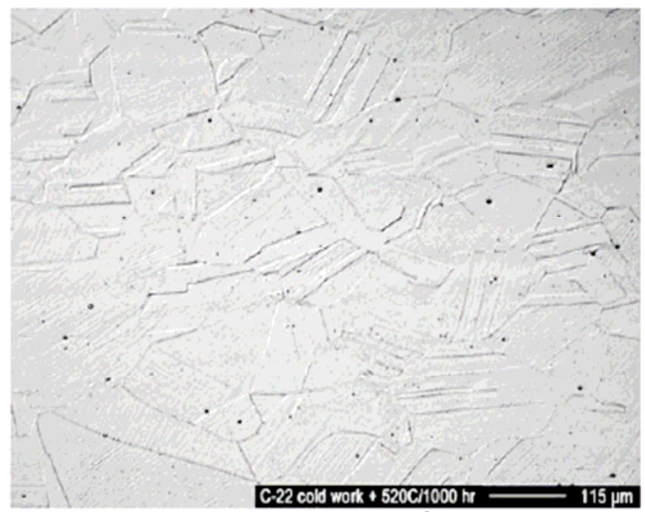


As-received (AR)



AR Weld Fusion Region

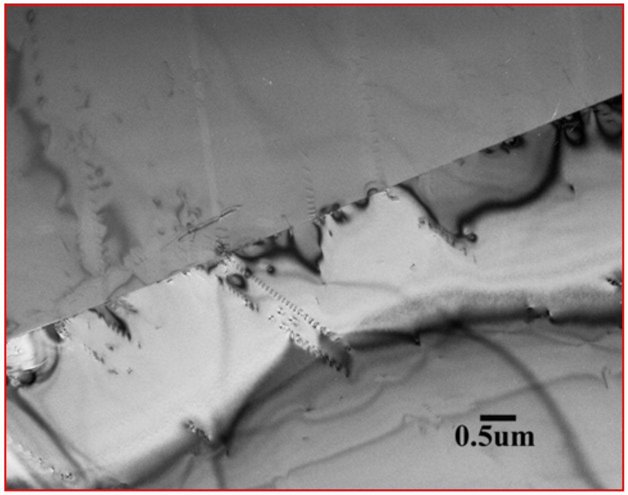
AR + HT2 (520°C/1000hr)



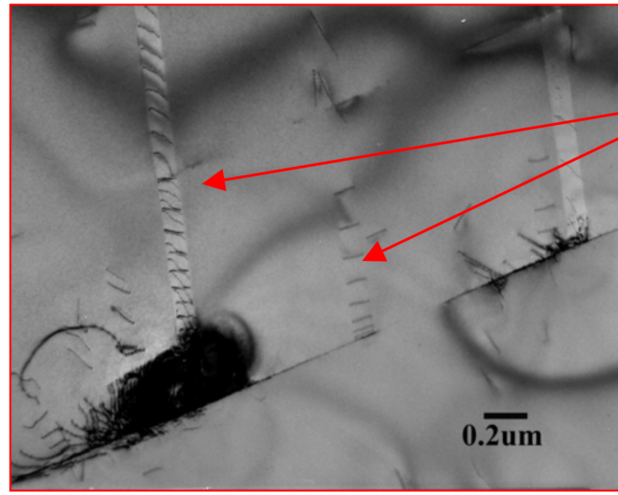
AR + 20% cold work + HT2 (520°C/1000 hr)

Young, L.M.; Catlin, G.M.; Andresen, P.L.; and Gordon, G.M. 2003. "Constant Load SCC of Proposed Waste Package Materials in Mixed Salt Solutions." Eleventh International Conference on Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors, August 10-14, 2003, Stevenson, Washington. Pages 267-279. La Grange Park, Illinois: American Nuclear Society. TIC: 255512, [DIRS 167011]

TEM Comparison of Alloy 22 Structures Tested at GE GRC in Constant Load Tests

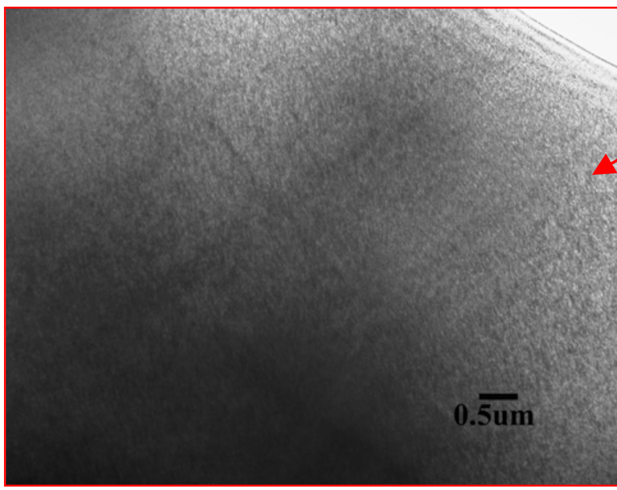


Annealed



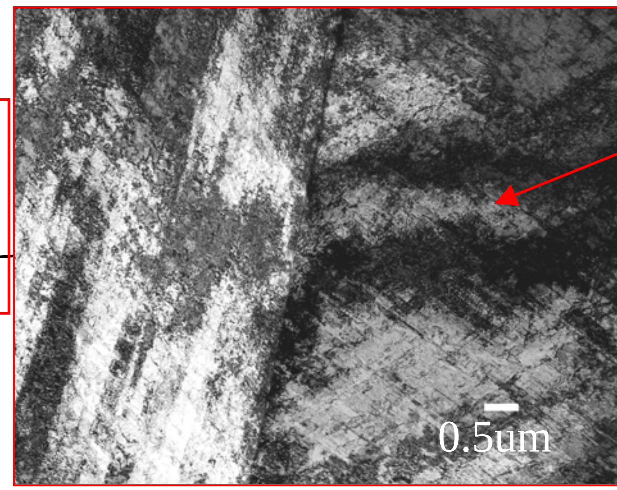
Annealed

Low dislocation density



Annealed + 520^{o}C/1000hr

High density of fine, coherent $Ni_2(Cr,Mo)$ ordered phase



20% Cold Work + 520^{o}C/1000hr

High dislocation density

Long Range Ordering (LRO) and/or cold work leads to hardening

Mechanical Properties of Constant Load Specimens

Tensile Properties in Air at 125°C

Material/Condition	Yield Strength (MPa)	Ultimate Tensile Strength (MPa)	~Cold Work Level (%) Equivalent to Measured Strength*
Alloy-22 As-received	324	717	0
Alloy-22 As-received + 20% CW	862	917	20
Alloy-22 As-received + HT2 (520°C/1000 h)	483*	1027*	15
Alloy-22 20% CW + HT2 (520°C/1000 h)	917*	1234*	20-30

*Determined at 105°C

LRO increases strength by coherent precipitation

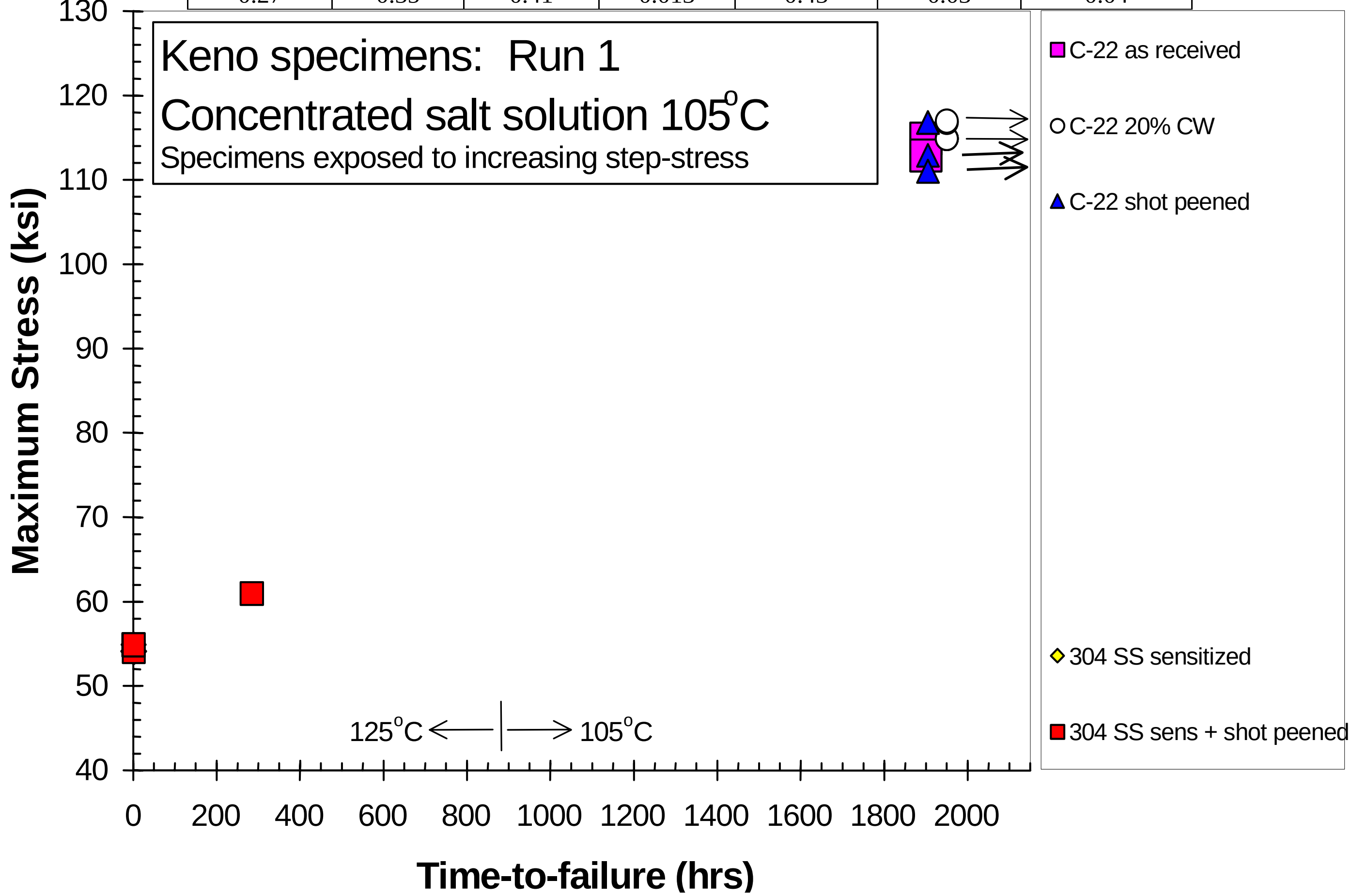
LRO produces strength levels similar to cold-working

*Haynes International 1997. Hastelloy C-22 Alloy. Kokomo, Indiana: Haynes International. [DIRS 100896], TIC: 238121

Initial Constant Load Test Results

Calculated Molar Composition of Keno Solution (M)

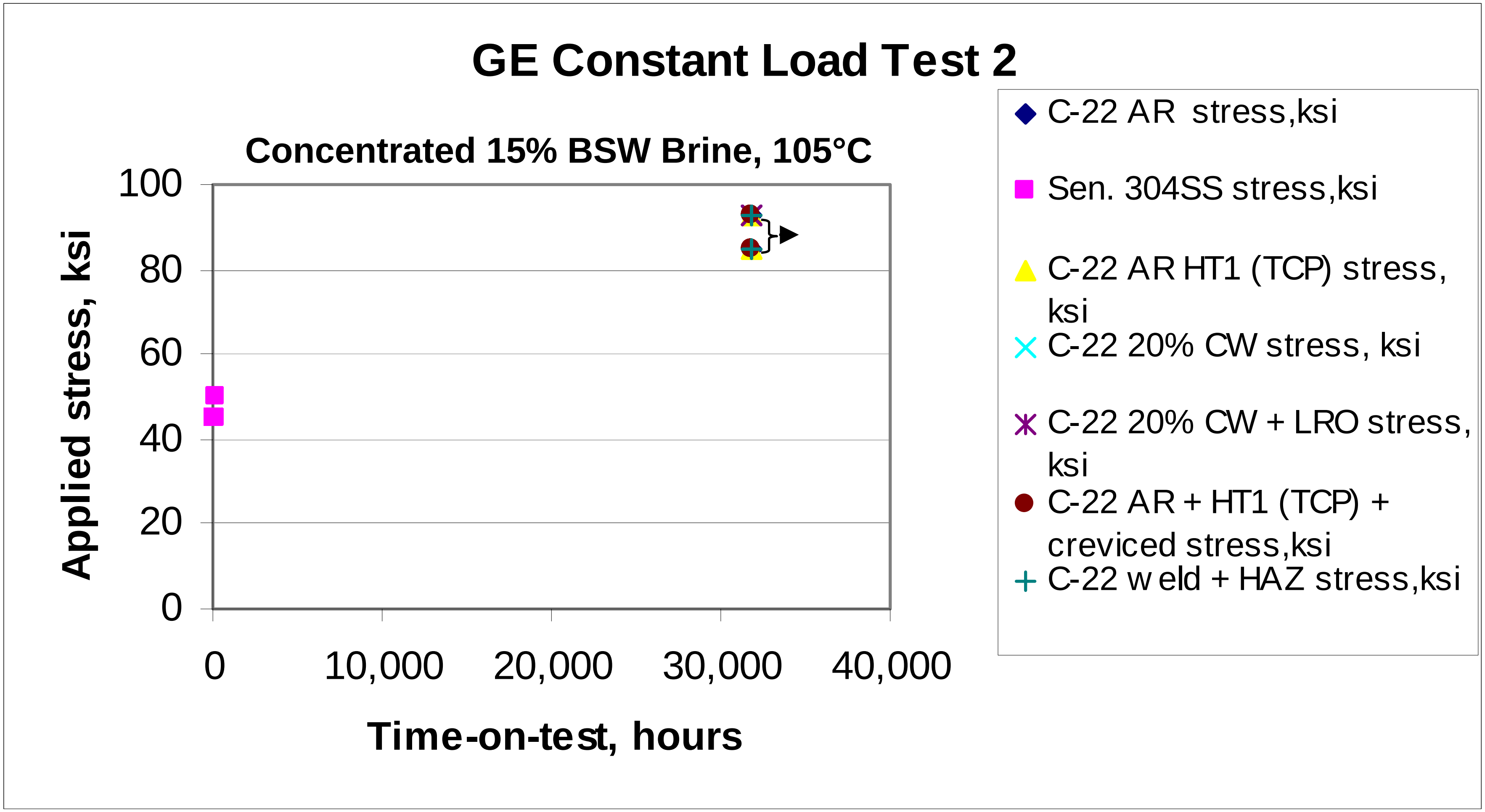
Na_2CO_3	KCl	NaCl	NaF	$NaNO_3$	Na_2SO_4	$Na_2SiO_3.9H_2O$
0.27	0.35	0.41	0.013	0.43	0.03	0.04



No SCC initiation in Alloy 22 (annealed or 20% cold worked) at stress levels very near UTS

Young, L.M.; Catlin, G.M.; Andresen, P.L.; and Gordon, G.M. 2003. "Constant Load SCC of Proposed Waste Package Materials in Mixed Salt Solutions." Eleventh International Conference on Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors, August 10-14, 2003, Stevenson, Washington. Pages 267-279. La Grange Park, Illinois: American Nuclear Society. TIC: 255512, [DIRS 167011]

Constant Load Test Results



Annealed, as-welded, 20% cold worked (CW), and 20% CW + LRO specimens on test for 3.7 years without SCC initiation

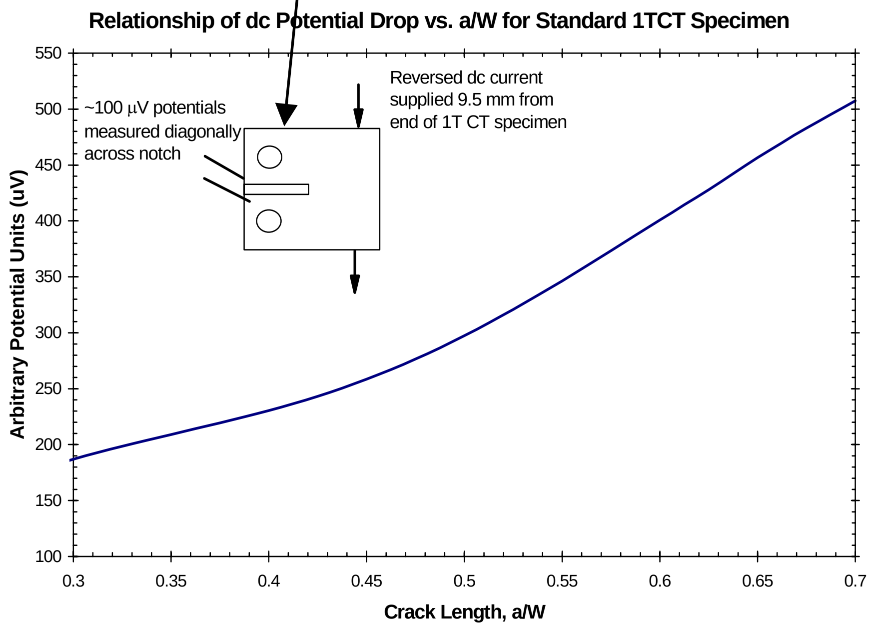
Updated from P.L. Andresen and G.M. Gordon , "SCC Initiation and Growth in Alloy 22 and Titanium Alloys in Concentrated Groundwater", Proceedings, 12th International Conference on Environmental Degradation of Materials in Nuclear Systems-Water Reactors, Salt Lake City, UT, August 2005

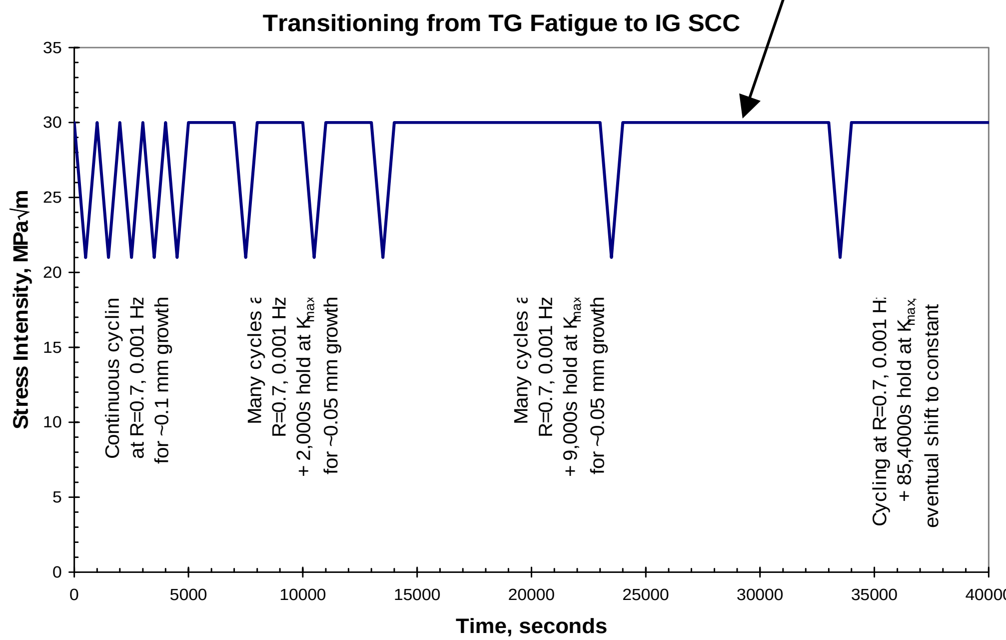
Cold Work Effects on SCC Growth Rates

SCC Crack Growth Load Cycle Approach

1T Compact Tension (CT) Specimen

Hold time

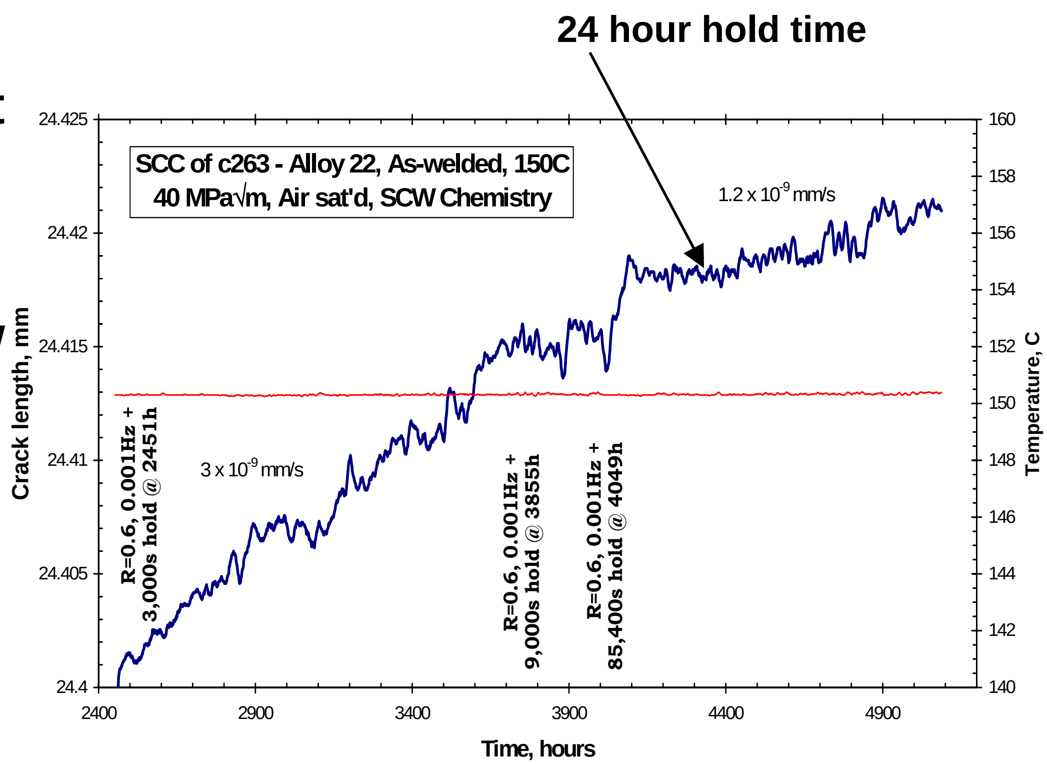




Fatigue pre-cracked instrumented CT specimens tested in autoclave loops with increasing hold time at maximum load

Alloy 22 SCC Growth

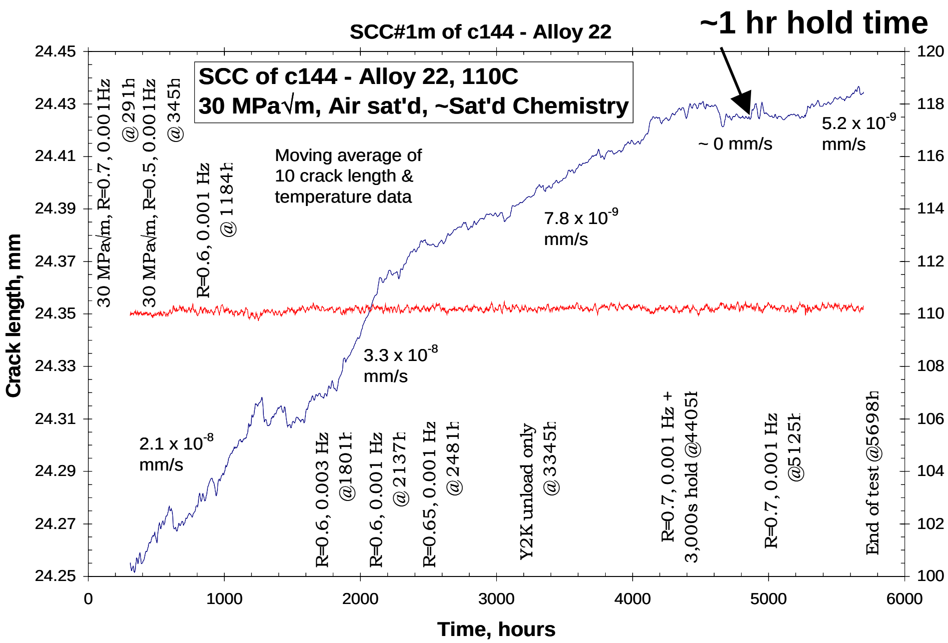
- **Alloy 22 extremely resistant to SCC initiation**
- **However, if initiated under cyclic conditions, very slow crack growth can occur under sustained load**
- **Therefore, residual stress mitigation planned for closure welds.**

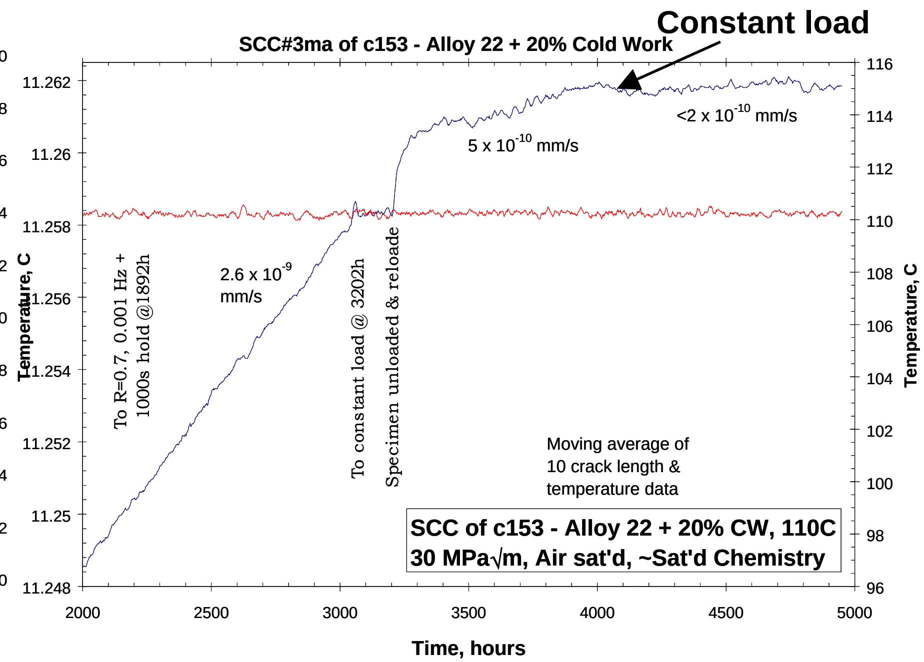


As-welded Alloy 22 compact tension specimen exposed to 150°C SCW

P.L. Andresen and G.M. Gordon , "SCC Initiation and Growth in Alloy 22 and Titanium Alloys in Concentrated Groundwater", Proceedings, 12th International Conference on Environmental Degradation of Materials in Nuclear Systems-Water Reactors, Salt Lake City, UT, August 2005

Alloy 22 Crack Growth in Annealed versus 20% Cold Worked Alloy 22





Annealed 20% Cold Worked

Annealed rate <1x10^{-11} mm/s (lower measurement limit) with ~1 hour hold time

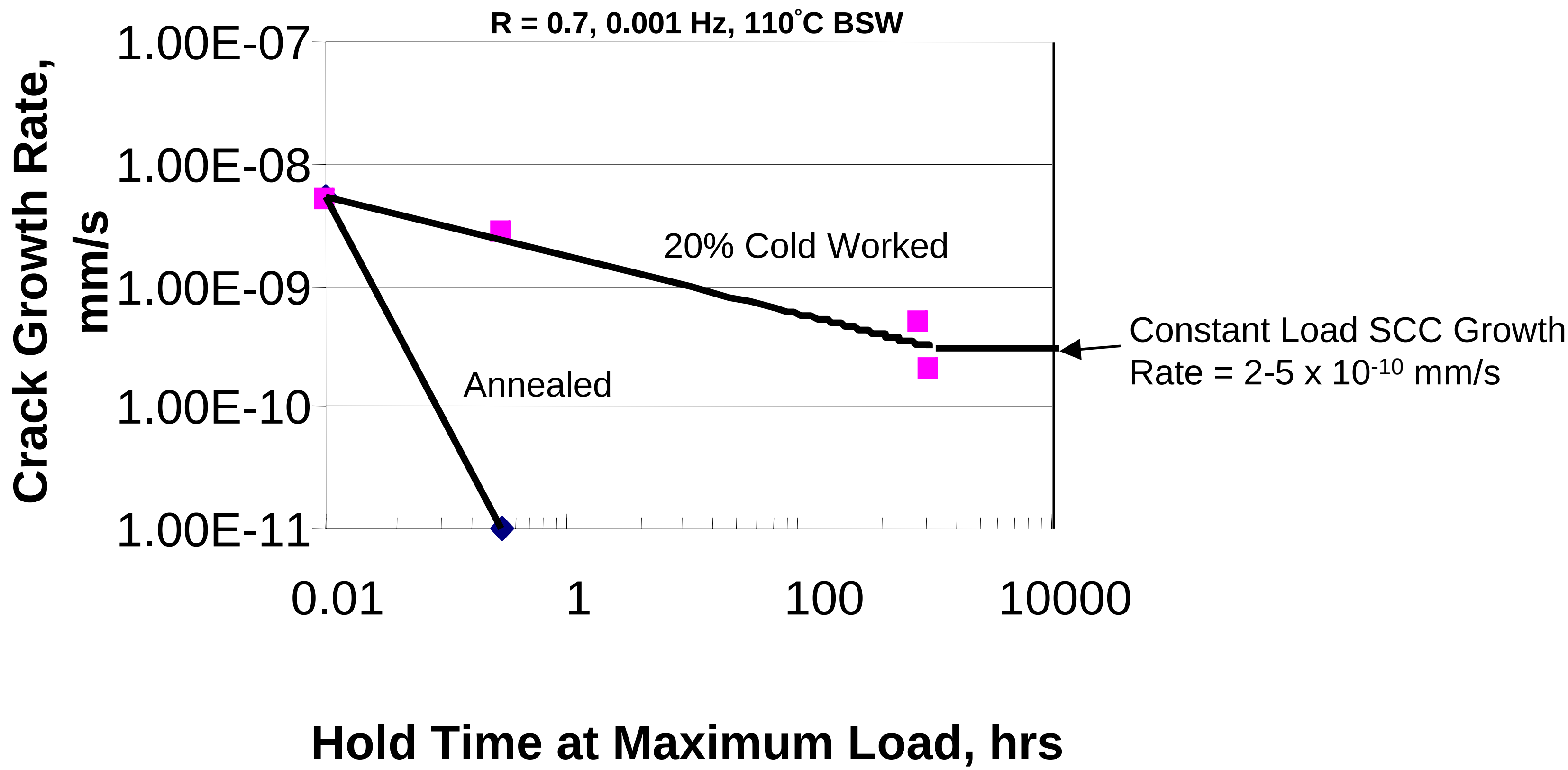
20% cold worked rate = 2-5 x 10^{-10} mm/s under constant load

Higher crack growth rate in cold worked material

P.L. Andresen and G.M. Gordon , "SCC Initiation and Growth in Alloy 22 and Titanium Alloys in Concentrated Groundwater", Proceedings, 12th International Conference on Environmental Degradation of Materials in Nuclear Systems-Water Reactors, Salt Lake City, UT, August 2005

Alloy 22 SCC Growth Rates vs Hold Time

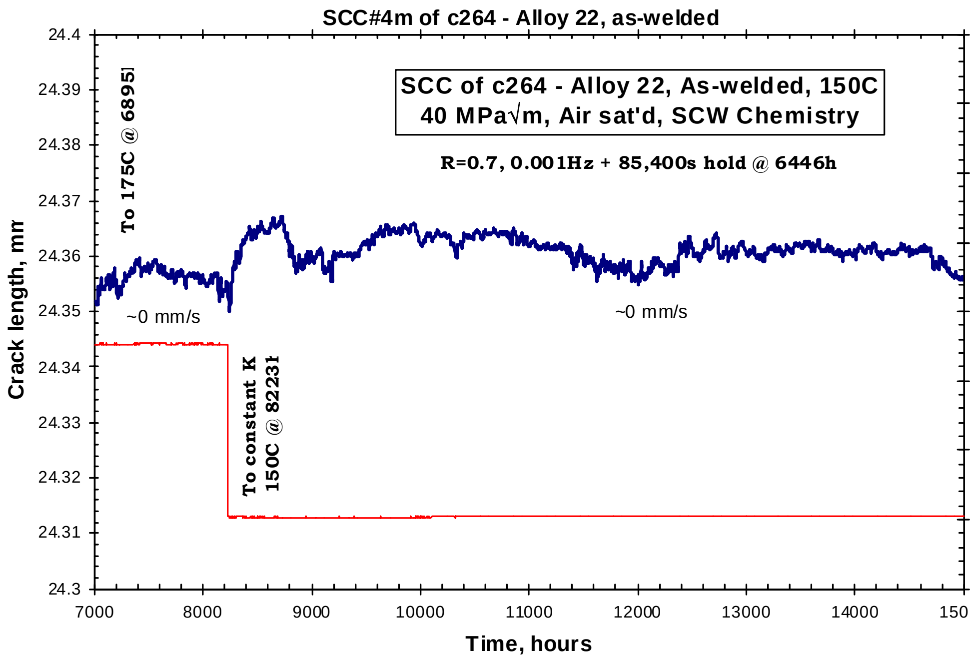
Cold Worked vs Annealed Crack Growth Rates at 30 MPa/m in Air Saturated BSW Brine

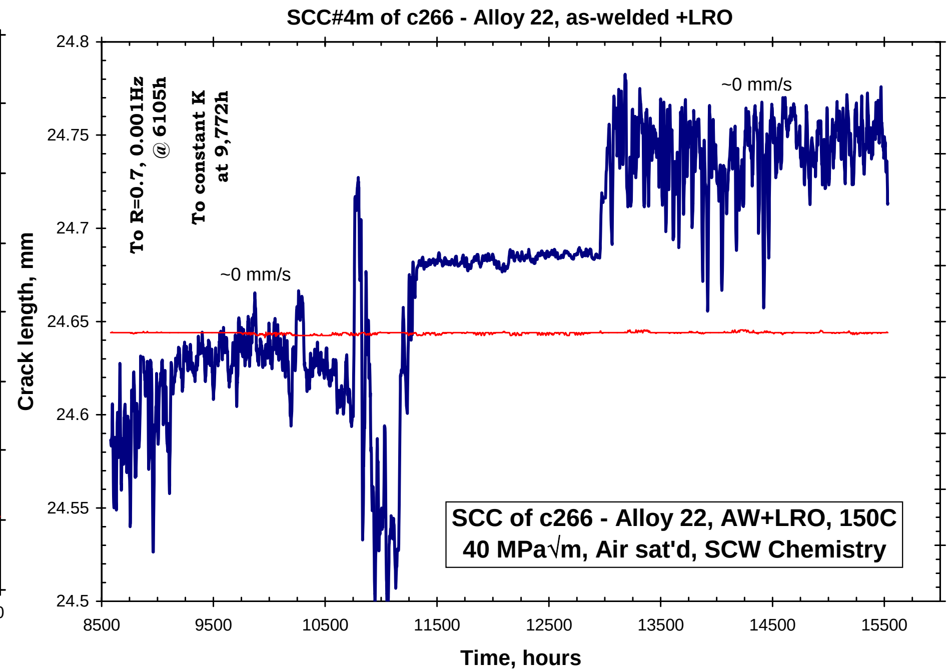


Sustained load rates extremely low but higher for cold worked material

P.L. Andresen and G.M. Gordon , "SCC Initiation and Growth in Alloy 22 and Titanium Alloys in Concentrated Groundwater", Proceedings, 12th International Conference on Environmental Degradation of Materials in Nuclear Systems-Water Reactors, Salt Lake City, UT, August 2005

Effect of Ordering (Hardening) on Crack Growth Rate of As-Welded Alloy 22 in 150ºC SCW Brine



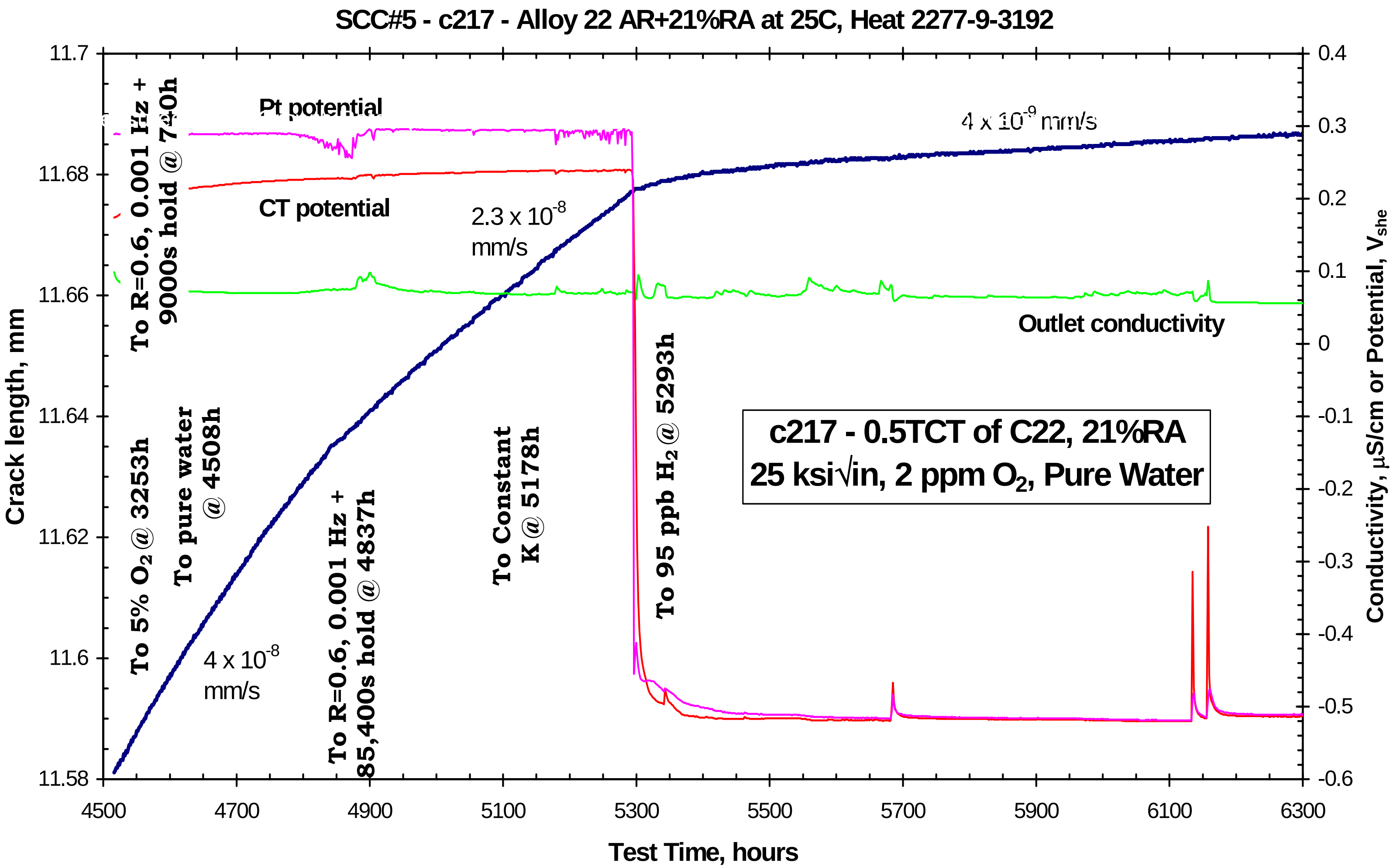


As-welded **As-welded + LRO**

Hardening from LRO had no measurable effect on SCC growth rate (< 1 x 10-11 mm/s (detection limit)) in welded Alloy 22

Andresen, P.L.; Kim, Y.J.; Emigh, P.W.; Catlin, G.M.; and Martiniano, P.J. 2005. Stress Corrosion Crack Initiation & Growth Measurements in Environments Relevant to High Level Nuclear Waste Packages. Report Number: GE-GRC-Bechtel-2005-1. [Niskayuna, New York]: General Electric Global Research Center. ACC: MOL.20060112.0042, [DIRS 176653]

Cold-worked (~20%) Alloy 22 in 288 °C Pure Water



Crack growth rate higher in pure oxygenated 288°C water (2.3×10^{-8} mm/s) than in 110°C BSW brine (~3×10^{-10} mm/s)

From Andresen, P.L.; Kim, Y.J.; Emigh, P.W.; Catlin, G.M.; and Martiniano, P.J. 2005. Stress Corrosion Crack Initiation & Growth Measurements in Environments Relevant to High Level Nuclear Waste Packages. Report Number: GE-GRC-Bechtel-2005-1. [Niskayuna, New York]: General Electric Global Research Center. ACC: MOL.20060112.0042.

Constant K_I Crack Growth Rates in Un-sensitized ~20% Cold Worked Alloys in 288°C Pure Water

Alloy	Stress Intensity Factor, MPa√m	Corrosion Potential ~+0.2 V_{SHE}	Corrosion Potential ~-0.5 V_{SHE}	Reference
Alloy 22	27.5	2.3×10^{-8} mm/s	4.0×10^{-9} mm/s	Andresen et al.,2005, [DIRS 176653], Fig. A3
Alloy 600	31.1	2.1×10^{-7} mm/s	3.2×10^{-8} mm/s	Andresen et al.,2005, [DIRS 176653], Fig. A7
Type 316L stainless steel	27.5	2.7×10^{-7} mm/s	1.9×10^{-8} mm/s	Andresen et al., [DIRS 176653], 2005, Fig. A4
Nitronic 50	27.5	3.3×10^{7} mm/s	4.7×10^{-8} mm/s	Andresen et al., 2005, [DIRS 176653], Fig. A6

Alloy 22 crack growth rate ~10X lower than for other alloys

Andresen, P.L.; Kim, Y.J.; Emigh, P.W.; Catlin, G.M.; and Martiniano, P.J. 2005. Stress Corrosion Crack Initiation & Growth Measurements in Environments Relevant to High Level Nuclear Waste Packages. Report Number: GE-GRC-Bechtel-2005-1. [Niskayuna, New York]: General Electric Global Research Center. ACC: MOL.20060112.0042; Andresen et al., NACE Paper 02510, Corrosion 2002.

Conclusions

- **Cold worked surfaces produced by low plasticity burnishing (LPB) or laser shock peening do not affect the general or localized corrosion resistance of Alloy 22 as indicated by:**
  - **Electrochemical tests such as CPP or LP that show the anodic behavior of as-welded and cold worked surfaces are equivalent**
  - **The crevice repassivation potentials in chloride solutions are the same**
- **Cold work (~12 to 20%) or hardening from LRO does not accelerate SCC initiation for test times up to at least 5 years**
- **SCC growth rates in 20% cold worked Alloy 22 are extremely low but higher than in mill annealed material**
- **Cold worked Alloy 22 SCC growth rates in 288°C pure water are about 10X lower than for other stainless steel and nickel alloys tested**