Corrosion Research at the Center for Nuclear Waste Regulatory Analyses

Presented by

Gustavo A. Cragnolino

Center for Nuclear Waste Regulatory Analyses (CNWRA)
Southwest Research Institute

San Antonio, Texas

Nuclear Waste Technical Review Board

Spring Meeting

May 13-14, 2003

CNWRA
A center of excellence
in earth sciences
and engineering

SwRI ®

Acknowledgement

Contributors

D. S. Dunn, Y.M. Pan, O. Pensado, L. Yang, and V. Jain

Work performed for the U.S. Nuclear Regulatory Commission under Contract No. NRC-02-02-012

Overall Approach

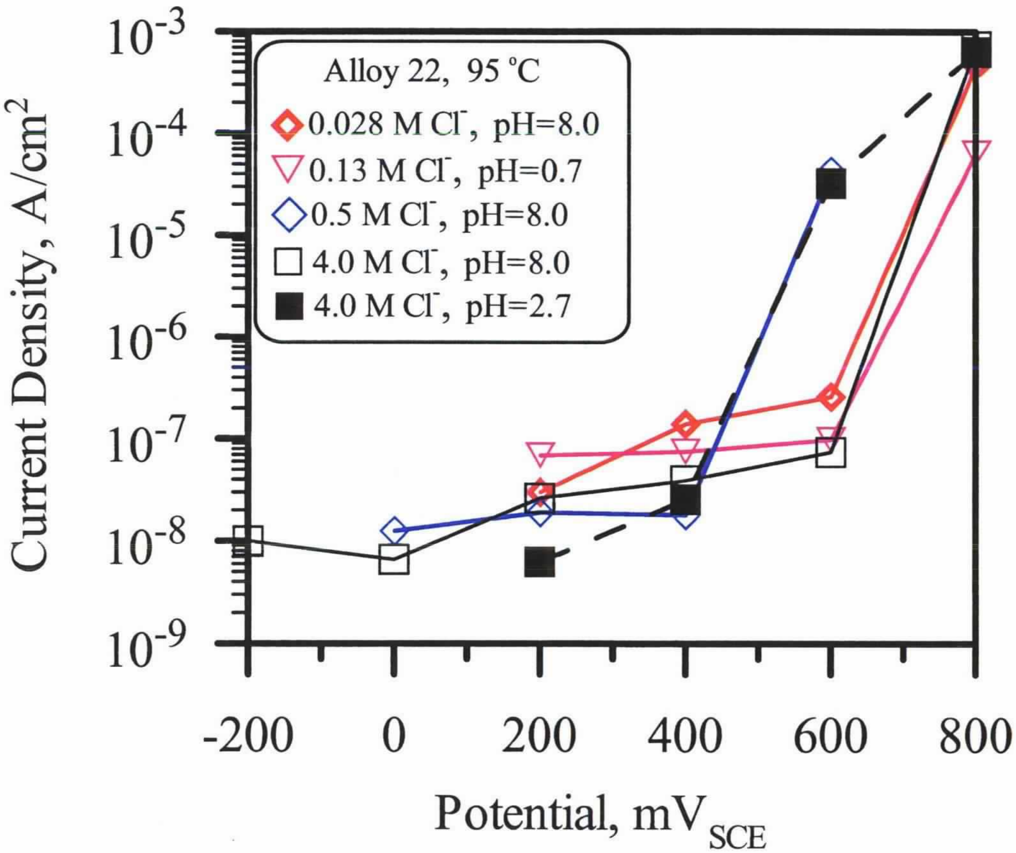
- Identify risk significance of different corrosion processes
- Provide input to performance assessment models and codes
- Increase confidence in conceptual and abstracted models by evaluating classes of materials (e.g., Ni-Cr-Mo alloys) through experimental research and modeling
- Evaluate natural, archeological, and industrial metal analogs to support technical basis for performance assessment models
- Assess the adequacy of DOE models, data and analyses for the predominant corrosion processes

Presentation will be focused on experiments and modeling on the corrosion behavior of Alloy 22

Outline

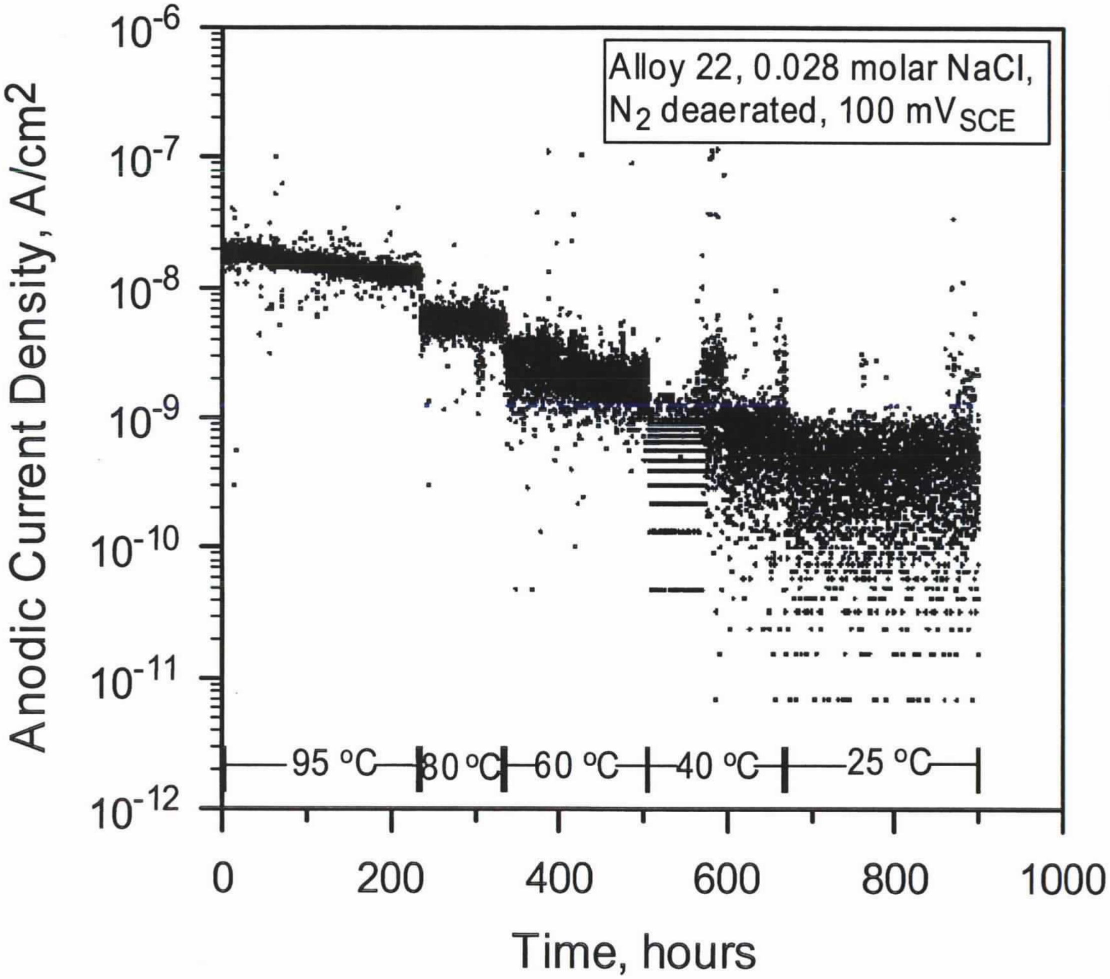
- Uniform passive corrosion
  - Experimental results
  - Mechanistic modeling
- Localized corrosion
  - Corrosion potential
  - Crevice corrosion repassivation potential
- Effects of welding and manufacturing processes
  - Microstructural alteration
  - Localized corrosion susceptibility
- Stress corrosion cracking

Uniform Passive Corrosion of Alloy 22



- Current densities < 10^{-7} A/cm^2 up to 400 mV_{SCE} indicate passive corrosion
- Passive current densities are almost independent of potential, [Cl^-], and pH
- Transpassive dissolution occurs at potentials ranging from 400 to 600 mV_{SCE}
- No pitting corrosion is observed

Effect of Temperature on Passive Current Density



- Passive current density exhibits Arrhenius dependence on temperature

  $I = I_0 \exp[-E_a/RT]$

  with

  $I_0 = 0.023$ A/cm^2

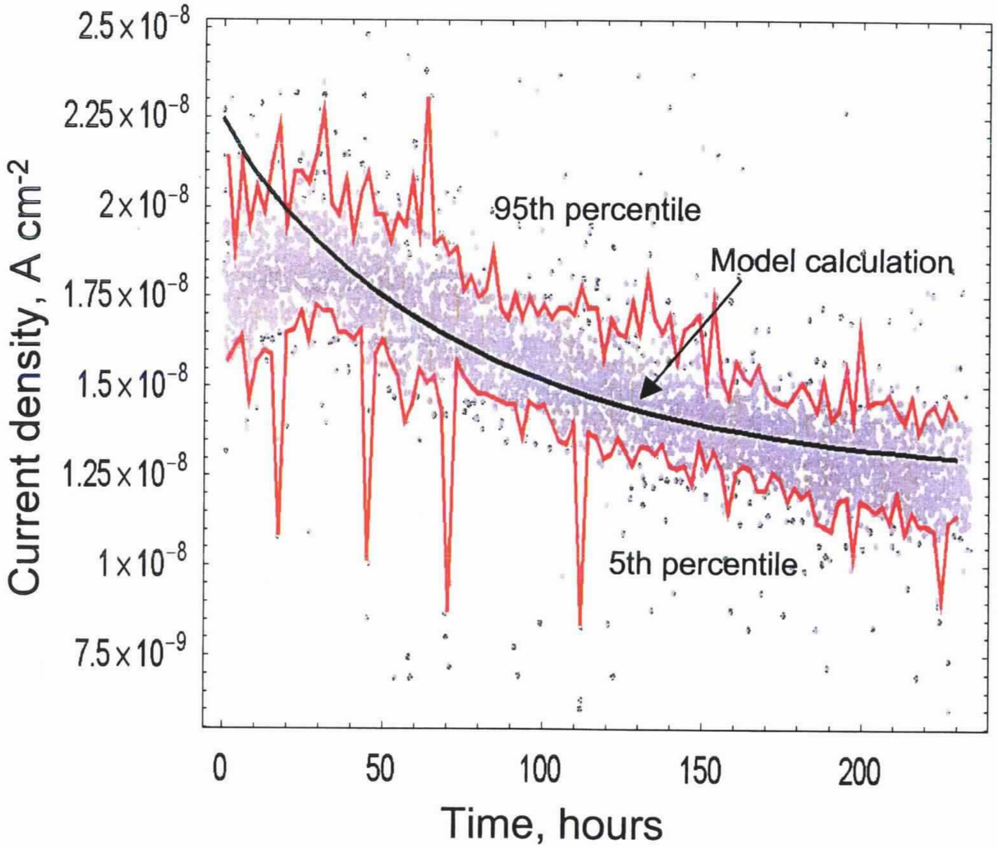
  and

  $E_a = 44.7 \pm 5.5$ kJ/mol

Long-Term Extrapolation of Passive Corrosion

- Assumptions
  - Dissolution is stoichiometric and planar
  - Corrosion rate does not change with time if variables such as temperature remain constant
- Modeling of long-term passive corrosion
  - Extension of Point Defect Model for ternary Ni-Cr-Mo alloys
  - Based on Cr_2O_3-rich passive film with Ni, Cr, and Mo (interstitial cations) as predominant charge carriers
  - Vacancies created by alloy dissolution and accumulated at the metal-film interface as a result of their very low diffusivities in the metal lattice
- Processes to consider
  - Periodic spalling of the passive film
  - Roughening of the corroding surface
  - Enhancement of corrosion rates by transient transpassivity

Passive Corrosion Model for Ni-Cr-Mo Alloys



0.028 M NaCl at 95 °C and 100 mV_{SCE}

- Computed decrease in current density due to vacancy accumulation at interface
- The passive current density decreases with time until steady state passive dissolution is reached at a critical value of vacancy accumulation
- The corrosion rate is estimated using Faraday's laws

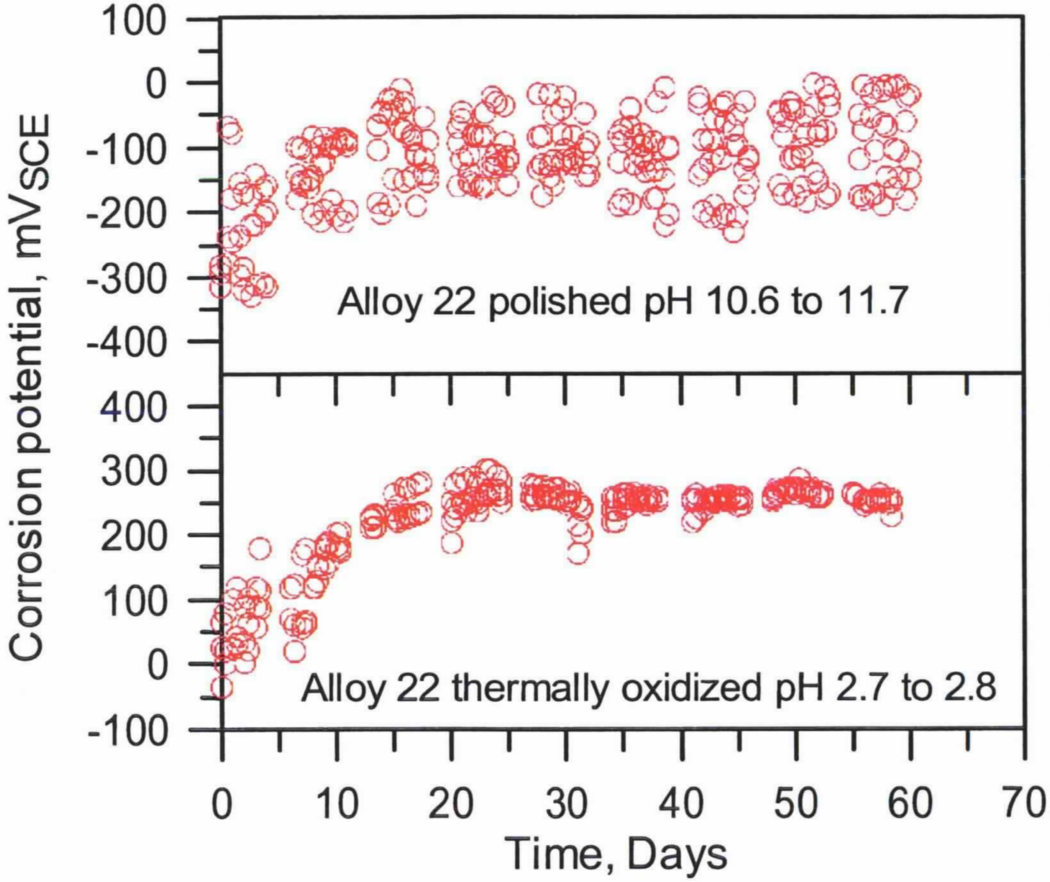
$$CorrosionRate = \frac{i_{pass}\, EW}{F\, \rho}$$

- Breakdown of passivity or enhanced dissolution for extended periods is unlikely

Localized Corrosion of Alloy 22

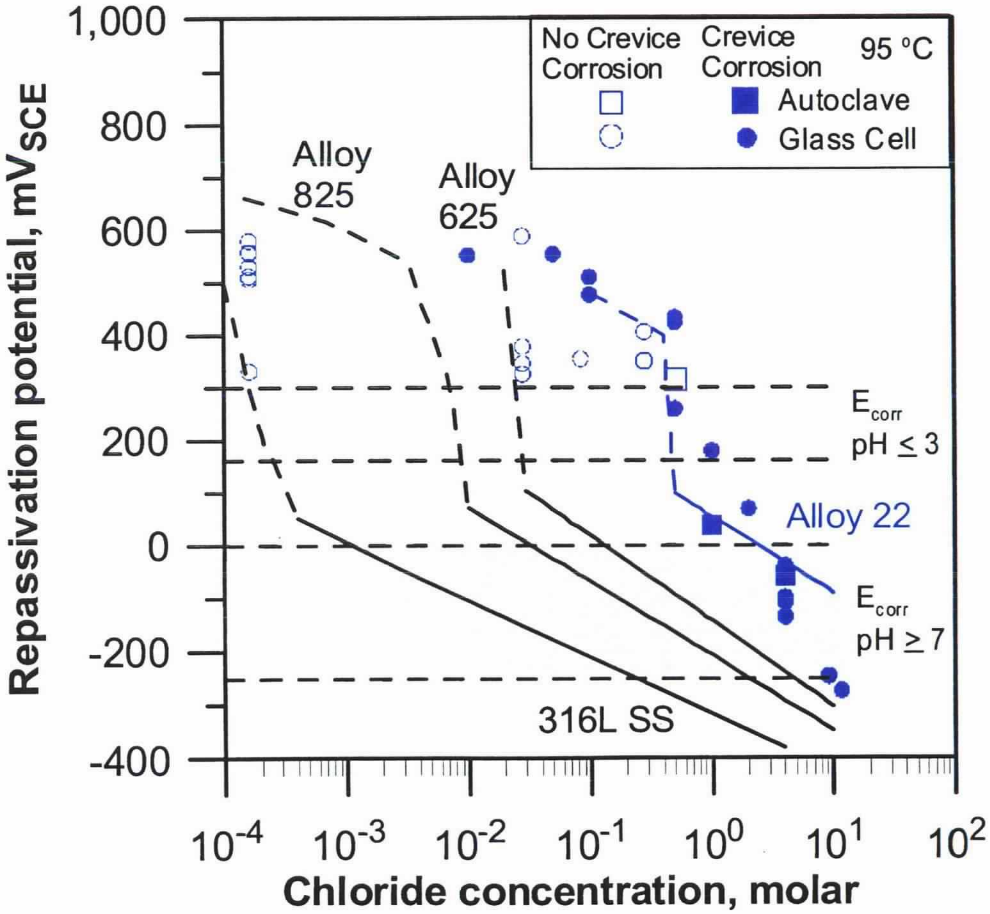
- Localized corrosion resistance of Alloy 22 is the result of additions of Cr, Mo, and W as alloying elements
- Crevice corrosion repassivation potential measured in short-term tests is the threshold potential for long-term initiation of localized corrosion
- Localized corrosion testing of Alloy 22
  - Crevice corrosion repassivation potential (E_{rcrev})
  - Corrosion potential (E_{corr})
- Localized corrosion can occur if $E_{corr} > E_{rcrev}$

Corrosion Potential



- Corrosion potential measured in air saturated solutions
- Smooth specimens with no crevice
- Corrosion potential is strongly dependent on solution pH but slightly dependent on [Cl^-]

Localized Corrosion of Mill-Annealed Alloy 22

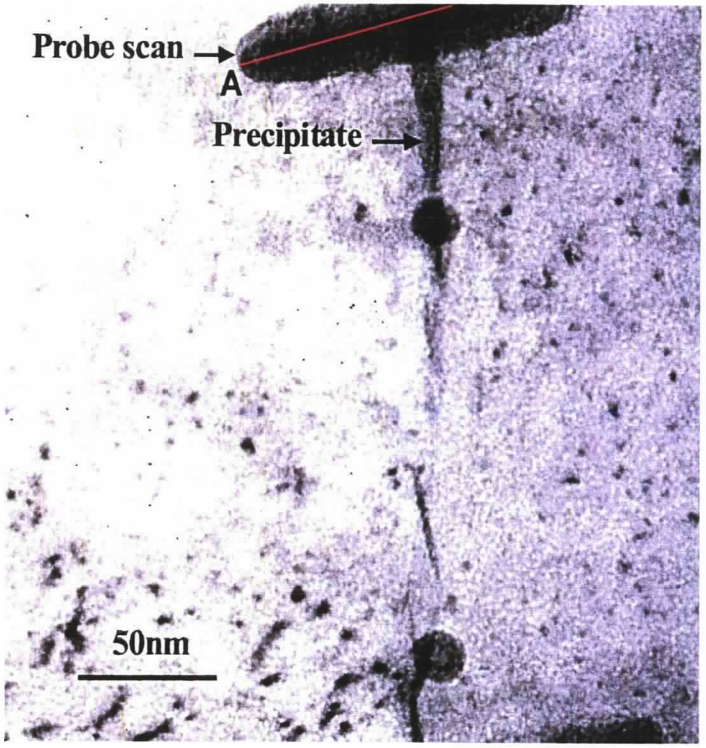


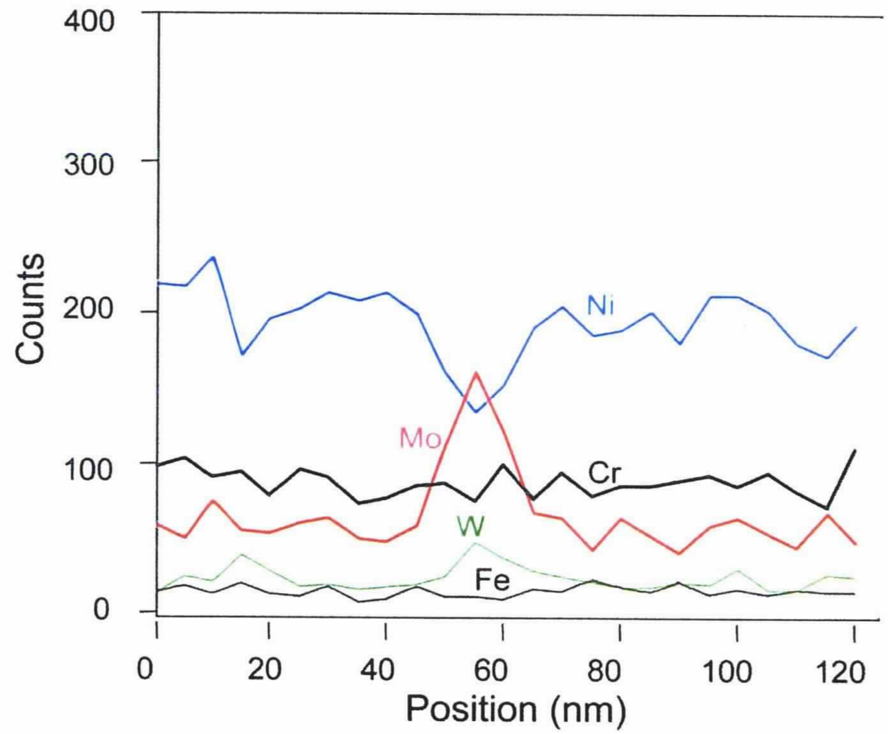
- ❑ Alloy 22 in the mill annealed condition is quite resistant to localized corrosion in chloride solutions
- ❑ Increased resistance with respect to other Ni-Cr-Mo alloys is due to the high Mo (and W) content of Alloy 22

Effect of Welding and Fabrication Processes

- Topologically close packed (TCP) phase precipitates are formed at grain boundaries in a few minutes at 800 to 900 °C
- Interdendritic regions in welds become rich in Mo and W and depleted in Ni
- As-welded material contains TCP phases in the interdendritic regions
- Precipitates have high concentrations of Mo (and W)
- Cold work from forming and machining may increase precipitation kinetics

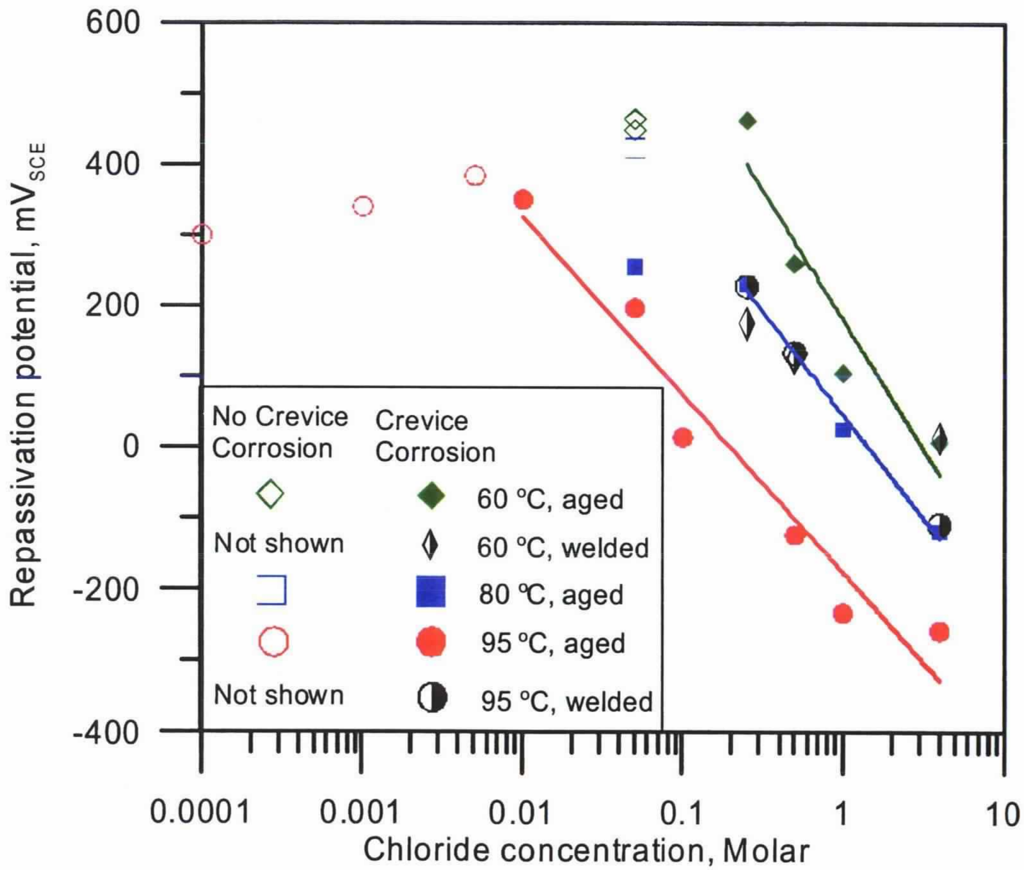
Grain-Boundary Microstructure and Chemistry (5 minutes at 870°C)





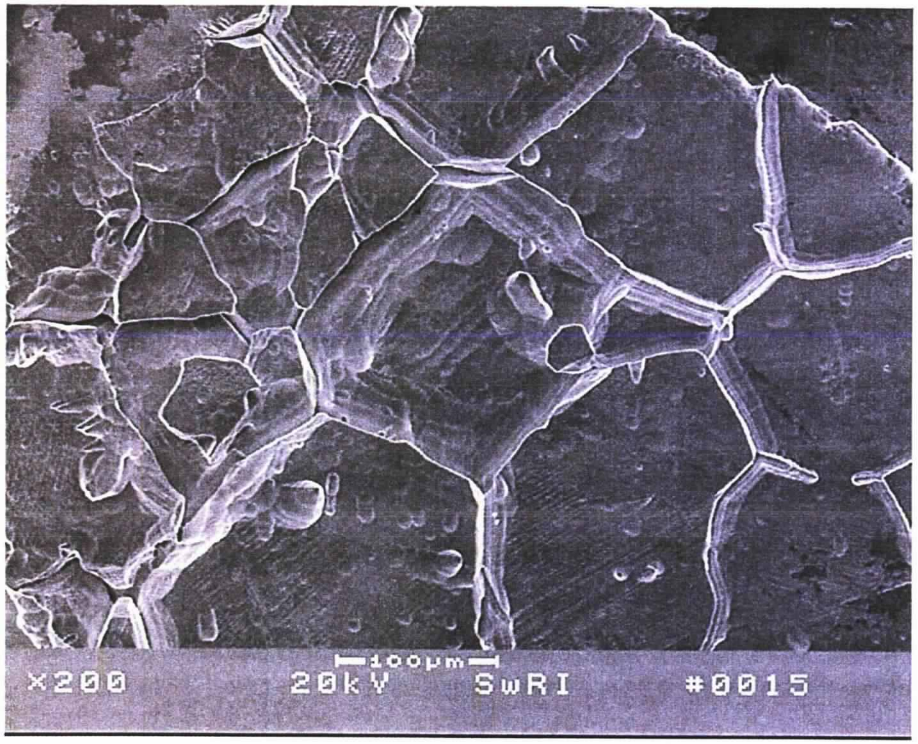
- Aging at 870°C for 5 minutes produced thin-film type, Mo- and W-rich precipitates at grain boundaries
- No detectable depletion of Mo, W, or Cr across grain boundaries

Effect of Fabrication Processes on Localized Corrosion



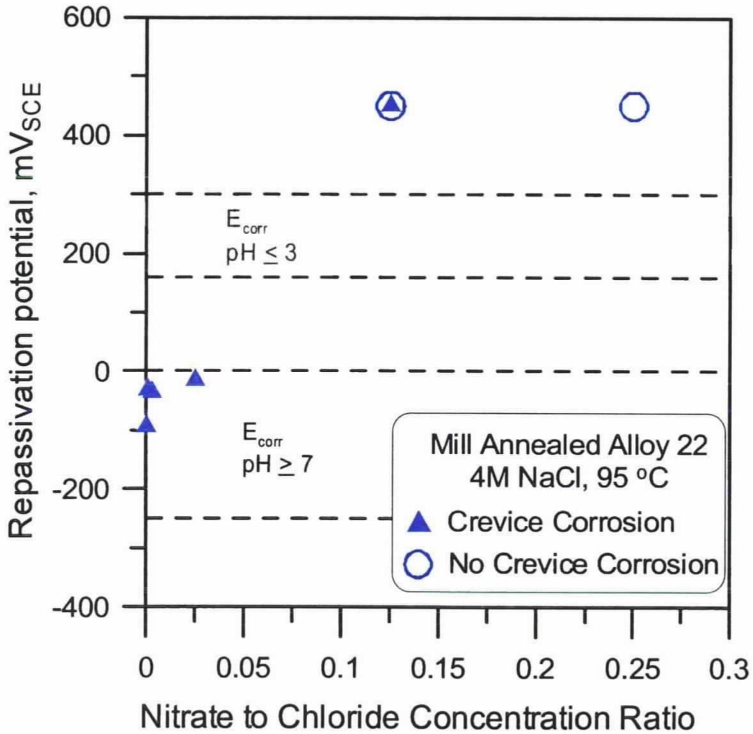
- Welding and short-term thermal aging increase localized corrosion susceptibility
- Localized corrosion observed at lower [Cl^-] and lower temperatures compared to the mill annealed condition

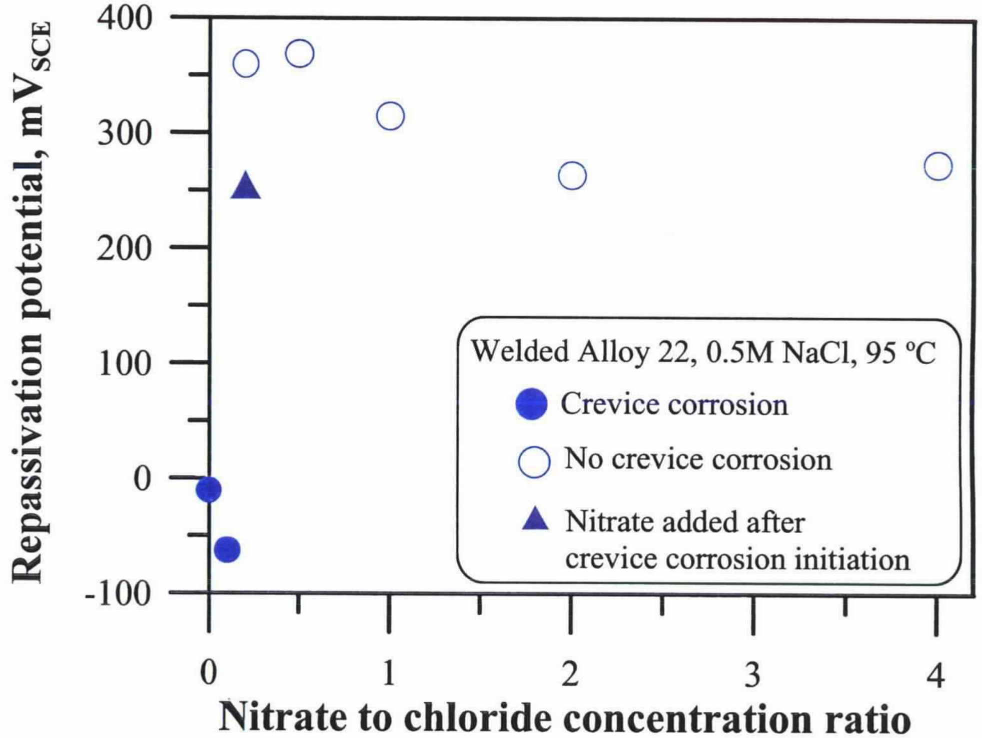
Effect of Thermal Aging on Localized Corrosion of Alloy 22



- Thermally treated at 870 °C for 5 min and tested in 0.01 M NaCl at 95 °C
- E_{rcrev} is 350 mV_{SCE} and 3 of 24 crevice sites exhibited this intergranular attack ,
- No attack was observed in 0.001 M NaCl after 1 hr treatment at 870 °C
- The attack is related to TCP precipitation at grain boundaries

Effect of Nitrate on Localized Corrosion of Alloy 22





- Nitrate is an efficient inhibitor of localized corrosion induced by chloride
- Critical nitrate to chloride molar concentration ratio is 1.2 for mill-annealed material and 0.2 for welded material

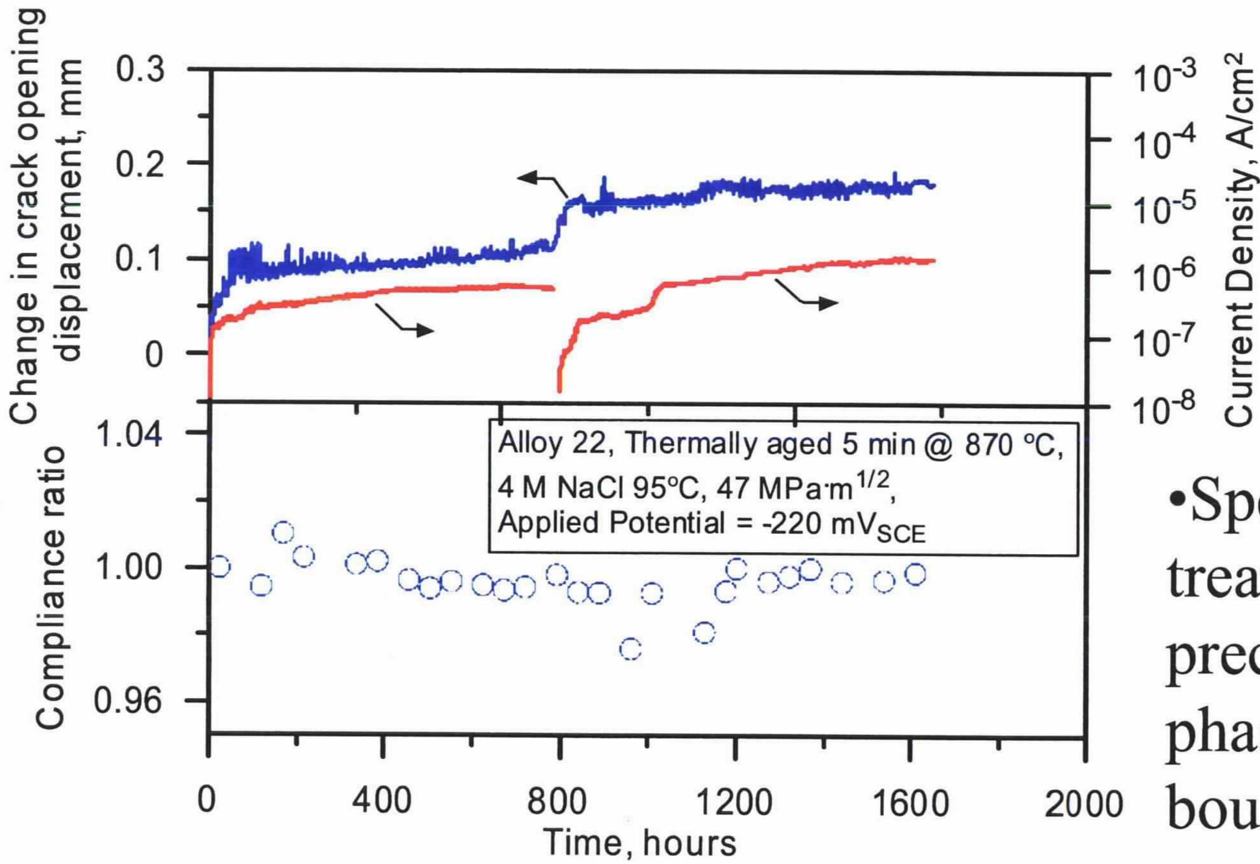
Stress Corrosion Cracking Testing of Alloy 22

Results of tests using precracked compact tension (CT) specimens

Alloy 22	Solution	T (°C)	E_{app} (mV_{SCE})	R	Time (hr)	Crack growth
Mill-annealed	9.1 m LiCl	95	−250	1.0	3,300	No
Mill-annealed	9.1 m LiCl	95	−200 to −245	1.0	3,400	No
Mill-annealed	9.1 m LiCl	95	−220 to −250	0.7	3,600	No
Mill-annealed	SCW	73	380	0.7	800	No
Mill-annealed	SCW	95	380	1.0	500	No
Mill-annealed	SCW	95	380	0.7	600	No
Thermally aged	4 M NaCl	95	−220	1.0	1,600	No

- Constant ($R = K_{Imin}/K_{Imax} = 1$) or cyclic ($R = 0.7$ and 0.001 Hz) loading
- $K_{Imax} = 47\ MPa{\cdot}m^{1/2}$
- *In-situ* monitoring of crack growth using compliance measurements

Thermally Treated Alloy 22 in Concentrated NaCl Solution



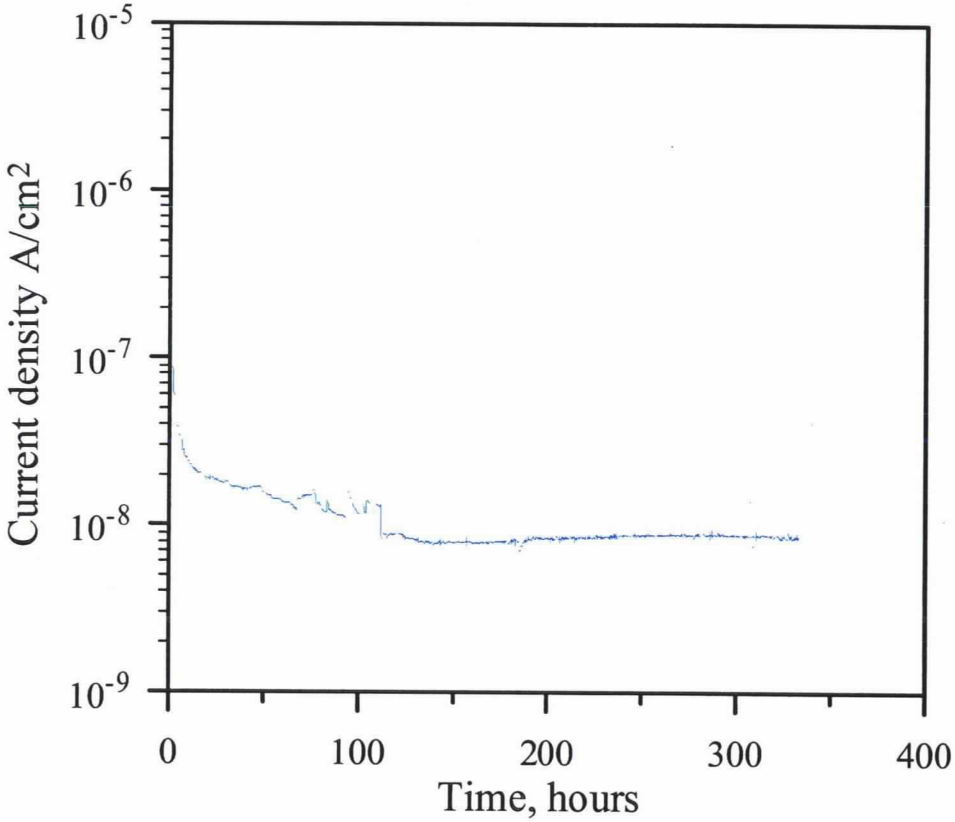
- Specimen thermally treated to induce precipitation of TCP phases at grain boundaries; only IG attack was observed

Summary

- Measured passive corrosion rates, with the support of mechanistic modeling, lead to estimates of container life well beyond the 10,000-yr regulatory period
- Alloy 22 is very resistant to pitting corrosion but is susceptible to crevice corrosion in chloride-containing solutions at temperatures above 60 °C when $E_{corr} > E_{rcrev}$
- Chloride concentration, temperature, and nitrate-to-chloride concentration ratio are important factors in localized corrosion susceptibility
- Fabrication processes such as welding and annealing treatments could significantly decrease localized corrosion resistance
- No SCC of mill annealed Alloy 22 has been observed over a wide range of environmental conditions

Backup Slides

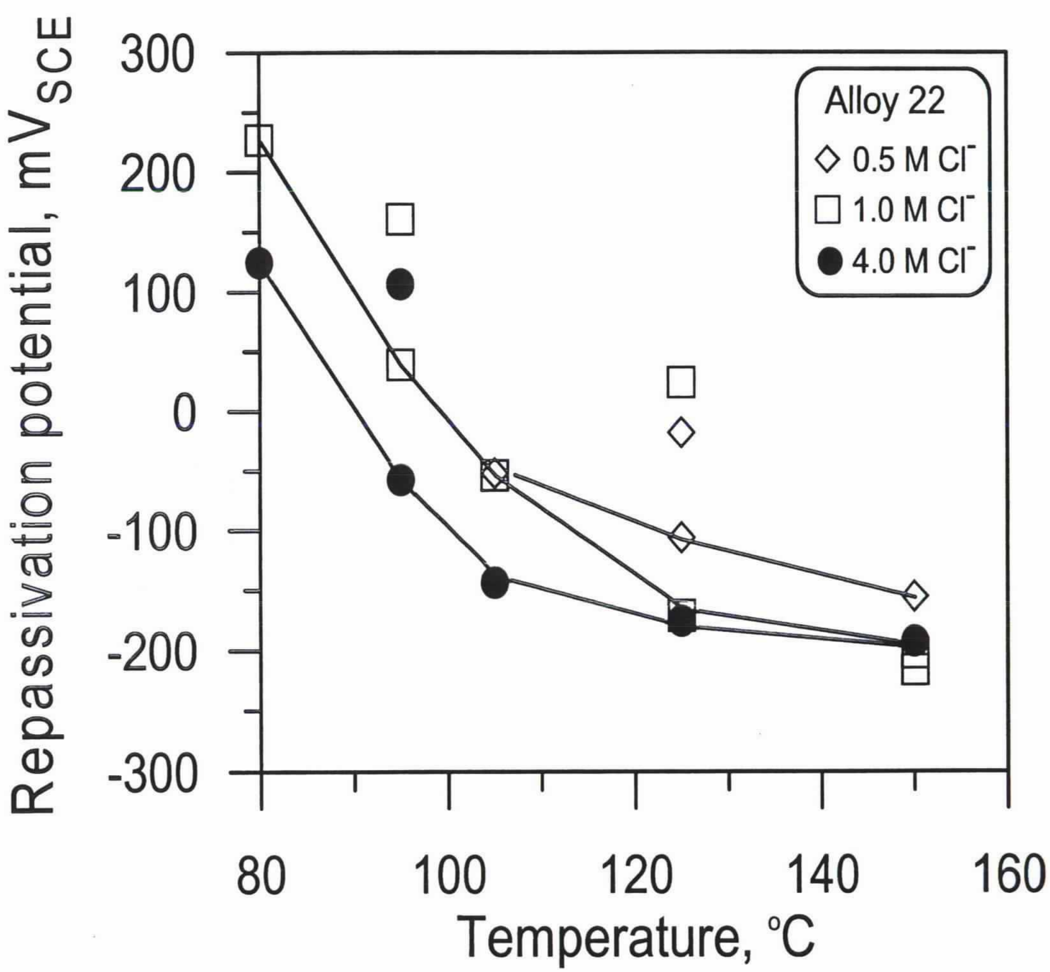
Uniform Passive Dissolution of Alloy 22



$$Corrosion\ Rate = \frac{i_{pass}\ EW}{F\ \rho}$$

- A steady-steady passive current density of 8×10^{-9} A/cm^2, corresponding to a corrosion rate of 8×10^{-5} mm/yr, was measured in 0.028 M Cl^- at 95 °C in a 15-day test at 0.1 V_{SCE}
- A container lifetime of ~100,000 yr can be estimated using an adjustment factor of 0.5 to account for surface roughness and other uncertainties
- This estimate does not consider defect generation or other metastable events that may alter the behavior of the passive film and lead to higher corrosion rates at longer times

Effect of Temperature on Localized Corrosion



- E_{rcrev} measured using creviced specimens in autoclave systems
- Significant decrease of E_{rcrev} with increasing temperature from 80 to 105 °C
- At higher temperatures E_{rcrev} values tend to level off

Crevice Corrosion Repassivation Potential

Alloy 22 Heat 2277-8-3175	T (°C)	$[Cl^-]_{crit}$ (M)	A_1 (mV_{SCE})	A_2 (mV/°C)	B_1 (mV)	B_2 (mV/°C)
Mill annealed	80 to 125 °C	0.5	1,300	–13.1	–362.7	2.3
Thermally Aged 5 minutes at 870°C	60 to 95 °C	0.01 to 0.25	800	–10.0	–584.2	3.7

$$E_{rcrev} = E^0_{rcrev}(T) + B(T)\log[Cl^-]$$

$$E^0_{rcrev}(T) = A_1 + A_2 T$$

$$B(T) = B_1 + B_2 T$$

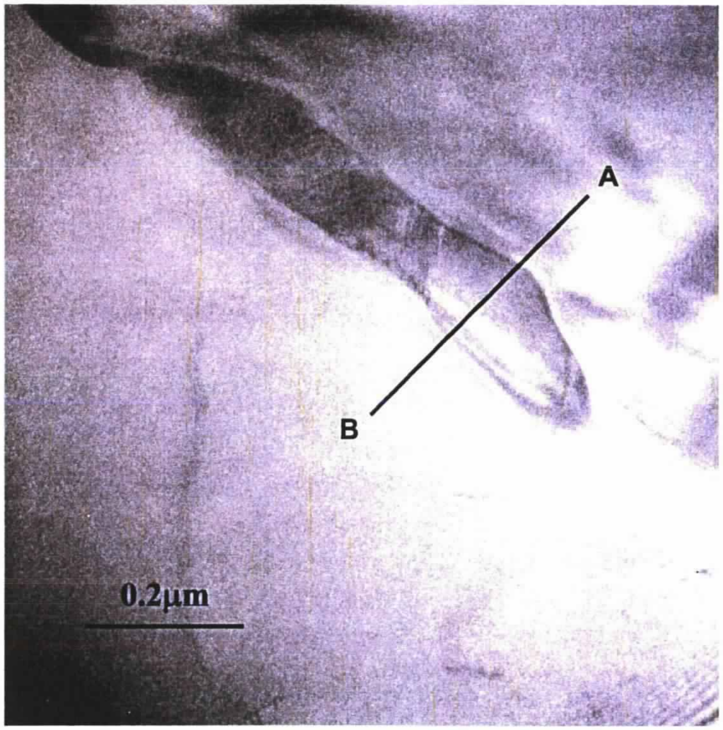
Waste Package Fabrication and Closure Processes

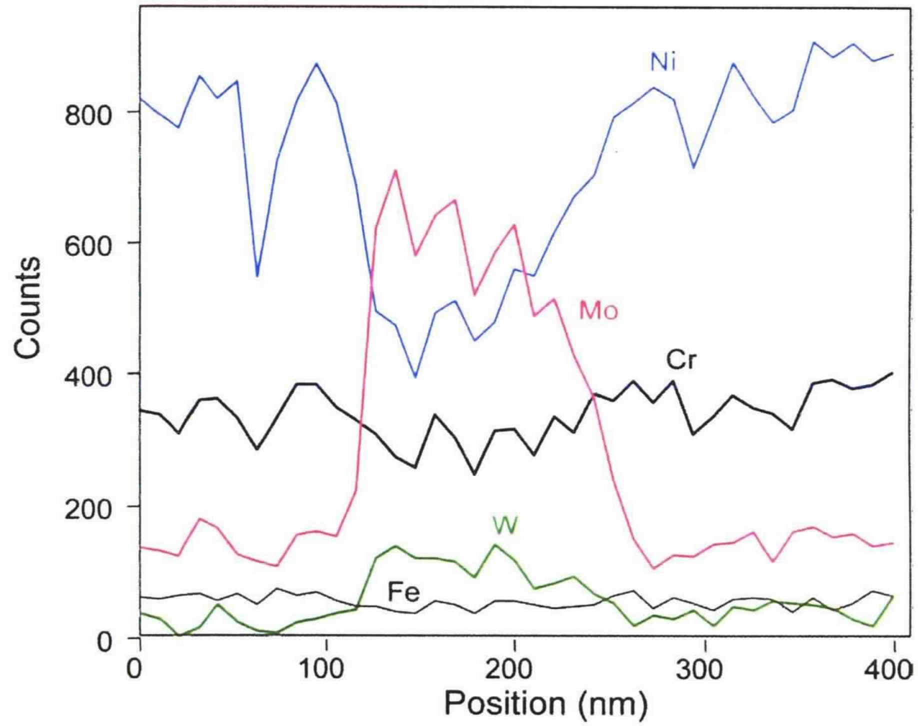
- Fabrication will require cold forming operations including rolling and machining
- Longitudinal and circumferential welding will be used to construct the disposal container
- Solution annealing is proposed for the disposal container after welding and prior to machining
- Dual closure lids will be installed using remote welding operations
- Residual stress mitigation of closure welds may include laser peening, low plasticity burnishing, and induction annealing

Alloy 22 Phase Stability

- Mill-annealed microstructure is single-phase face-centered cubic
- Long range ordering $Ni_2(Cr,Mo,W)$ occurs after hundreds of hours at temperatures below 600 °C
- Topologically close packed (TCP) phase precipitates after exposures at temperatures above 600 °C

Grain-Boundary Microstructure and Chemistry (30 minutes at 870°C)





- Substantial increase in precipitate size after aging for 30 minutes
- No detectable depletion of Mo, W, or Cr across matrix-precipitate interface

Composition of Precipitates

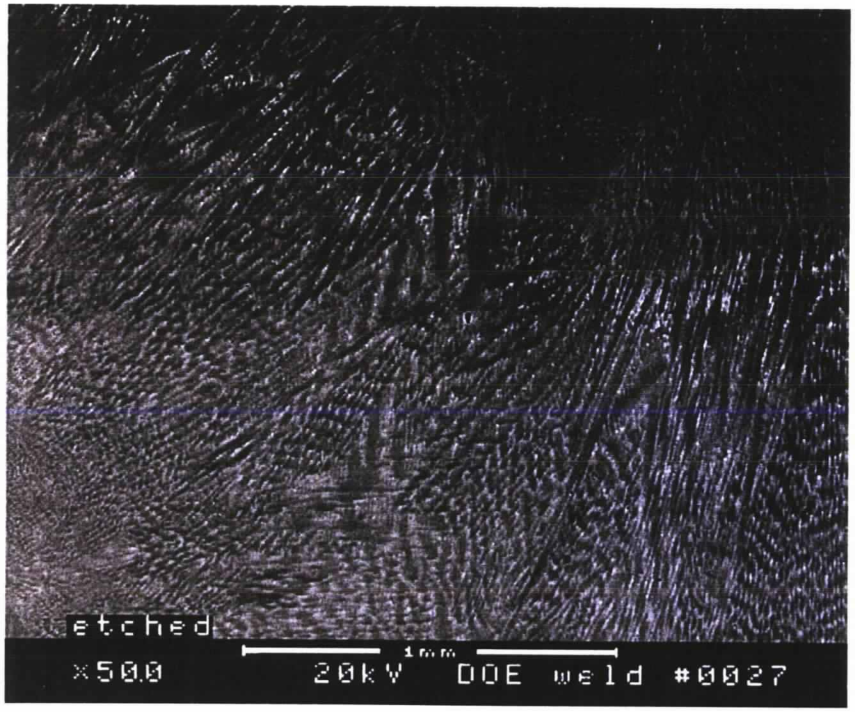
Chemical Composition of Grain Boundary Precipitates and the Vicinity (wt%)

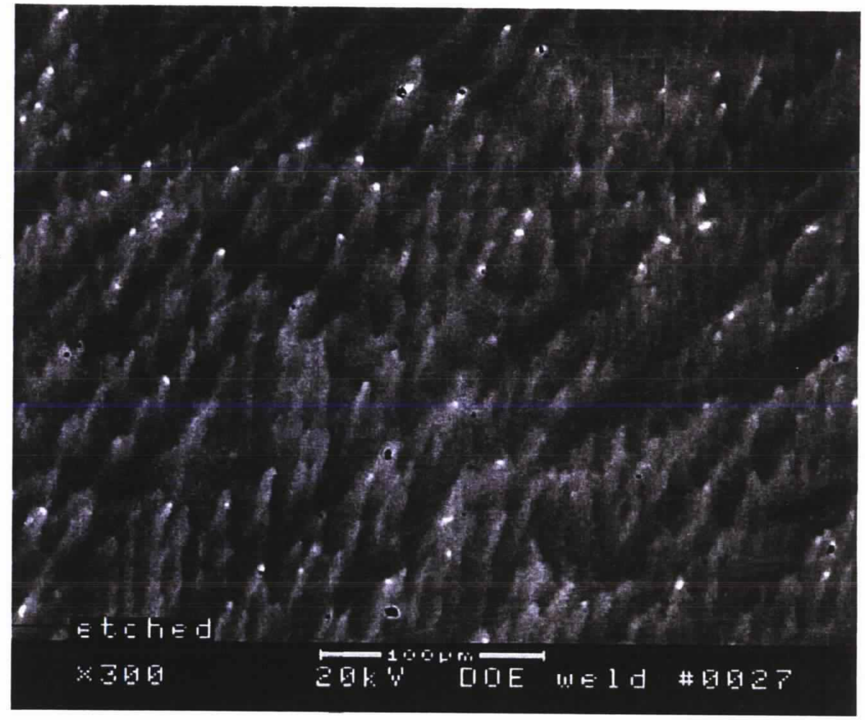
Probe Location	Ni	Cr	Mo	W	Fe
Precipitate	26.53 ± 3.00	17.81 ± 3.81	44.33 ± 2.66	8.88 ± 1.17	2.34 ± 0.27
Adjacent to Precipitate	58.42 ± 0.15	22.43 ± 0.25	11.75 ± 0.38	2.54 ± 0.70	4.46 ± 0.15
Bulk Composition	57.8	21.40	13.60	3.00	3.08

Calculated phase compositions at 870 °C

Phase	Amount		Chemical Content (wt%)							
	wt%	mole%	Ni	Cr	Mo	W	Fe	Co	Si	C
γ	88.88	90.83	62.60	21.69	10.34	1.85	3.39	0.095	0.034	0.001
P	11.01	9.07	28.47	19.10	39.50	12.29	0.59	0.045	—	—
M_6C	0.11	0.10	25.08	14.47	52.12	4.80	0.93	0.016	0.001	2.58

Microstructure of the Weld





- Alloy 22 Gas Tungsten Arc Weld (GTAW)
- Mo-rich precipitates in the as-welded condition