

The Combined Effect of Bicarbonate and Chloride Ions on the Stress Corrosion Cracking Susceptibility of Alloy 22

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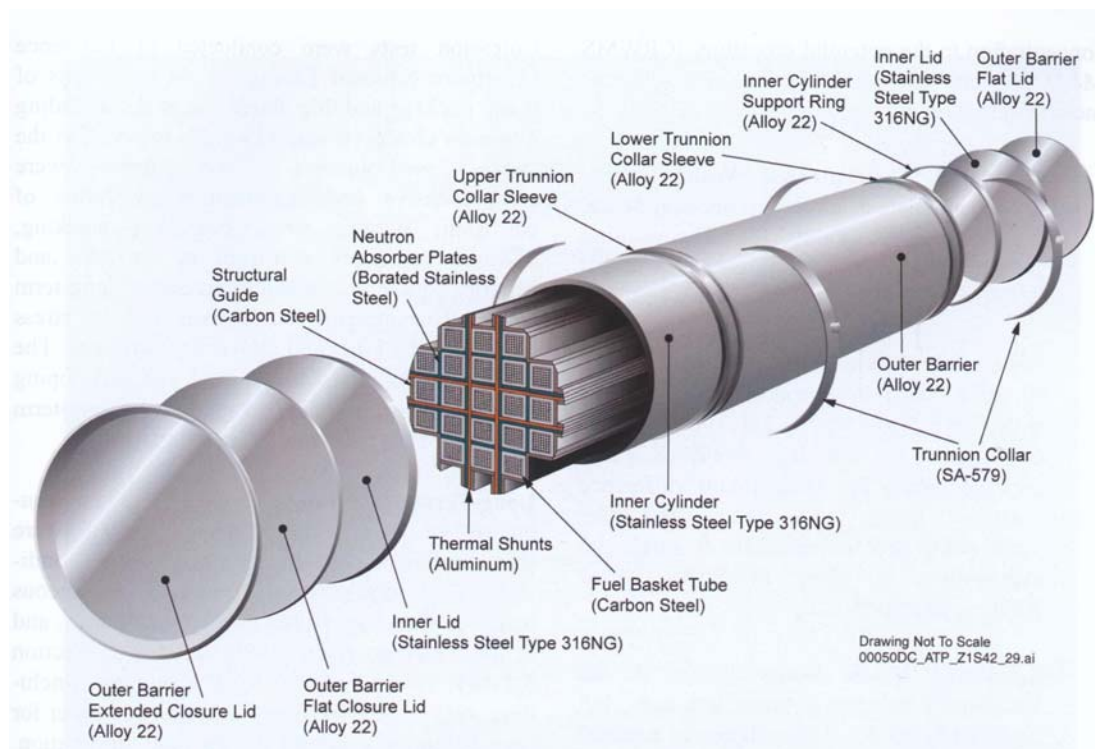
Corrosion 2006
San Diego, California
March 12–16, 2006
Paper No. 06506



Outline

- Introduction
- Stress Corrosion Cracking (SCC) of Alloy 22 in Solutions Containing Bicarbonate & Chloride Ions
- Effect of Electrochemical Potential
- Effect of Solution Temperature
- Summary & Conclusions

Potential Waste Package Design for High-Level Nuclear Waste Disposal



(DOE, 2001)

- Alloy 22 (Ni-22Cr-13Mo-4Fe-3W in weight %) Outer Barrier for Corrosion Resistance
- Stainless Steel (Type 316NG) Inner Cylinder for Structural Support
- Long Lifetime of Waste Package as Key Attribute for Performance of Potential Yucca Mountain Repository

Simulated Concentrated Water (SCW) for Alloy 22 Testing

Ion	K ⁺	Na ⁺	Mg ²⁺	Ca ²⁺	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	HCO ₃ ⁻
mg/L	3,400	40,900	<1	<1	1,400	6,700	6,400	16,700	70,000
mM	87	1,780	<0.041	<0.025	74	189	103	174	1,148

Reference: G.M. Gordon, "Corrosion Considerations Related to Permanent Disposal of High-Level Radioactive Waste", *Corrosion*, 58(10), p. 811, 2002.

- Estill, et al. (*Corrosion 2002*) Reported SCC in Slow Strain Rate Tests (SSRTs) in SCW at 73 °C [163 °F] and 400 mV_{SSC} [356 mV_{SCE}]
- Chiang, et al. (*Corrosion 2005*) Reported Bicarbonate Ions Are the Predominant Constituent in SCW that Promoted SCC at 95 °C [163 °F] and 400 mV_{SCE}

Objectives and Scope

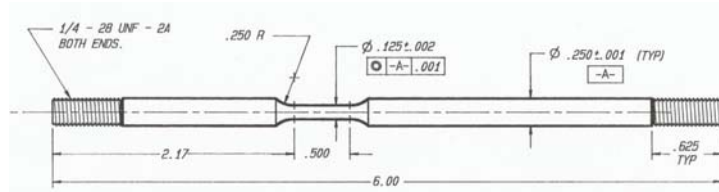
- ❑ Evaluate SCC Susceptibility of Alloy 22 in Solutions Containing a Combination of Chloride and Bicarbonate Ions Using SSRTs
- ❑ Determine the Effect of Electrochemical Potential on SCC Susceptibility
- ❑ Determine the Effect of Temperature on SCC Susceptibility
- ❑ Correlate SSRT Results with Potentiodynamic and Potentiostatic Anodic Polarization Tests

Chemical Composition & Tensile Properties of Alloy 22

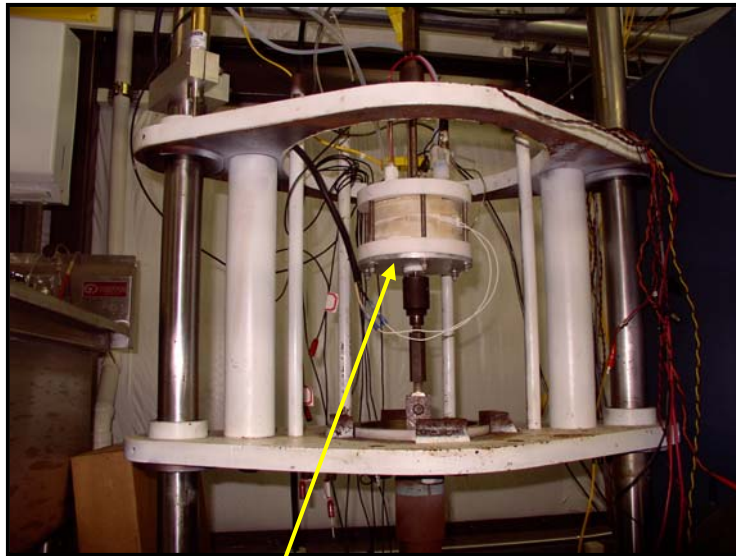
Material	Composition (wt%)											
	Ni	Cr	Mo	W	Fe	Co	Si	Mn	V	P	S	C
Alloy 22 Heat 2277-3-3266	Bal	21.40	13.30	2.81	3.75	1.19	0.03	0.23	0.14	0.008	0.004	0.005

Material	Tensile Strength MPa [ksi]	Yield Strength MPa [ksi]	Elongation (%)	Reduction in Area (%)	Modulus MPa [ksi]
Alloy 22 Heat 2277-3-3266	787 [114.2]	347 [50.3]	71	79	1.95×10^5 [2.83×10^4]

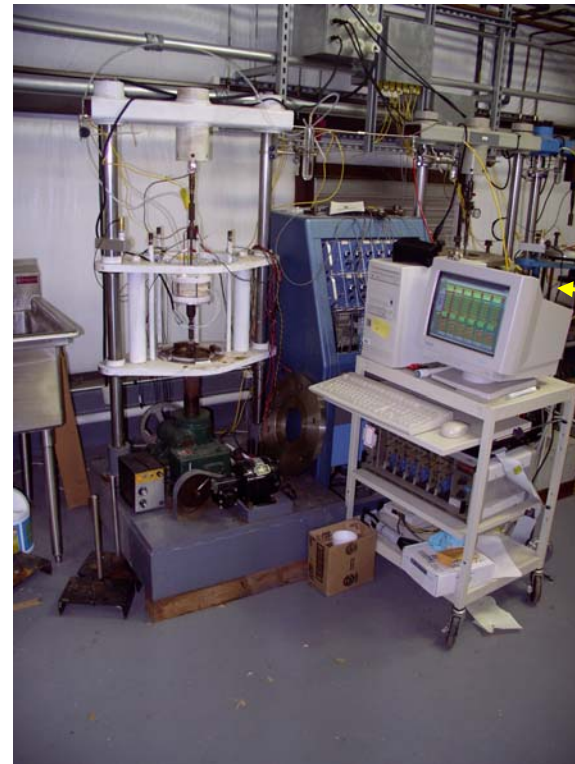
SSRT Experimental Setup



Specimen



Test Cell



Data Acquisition System

SCC Testing Conditions

□ SSRT

- ◆ SCW and electrolyte containing $[\text{Cl}^-]$ & $[\text{HCO}_3^-]$ ions
- ◆ Electrochemical potentials 100 to 400 mV_{SCE}
- ◆ Test temperatures 22 to 95 °C [72 °F to 203 °F]
- ◆ Strain rate $3.2 \times 10^{-6}/\text{s}$
- ◆ Air test at 22 °C [72 °F] as control

□ Potentiodynamic & Potentiostatic Anodic Polarization Tests

- ◆ Environment: Electrolyte containing $[\text{Cl}^-]$ & $[\text{HCO}_3^-]$ ions at 95 °C [203 °F]

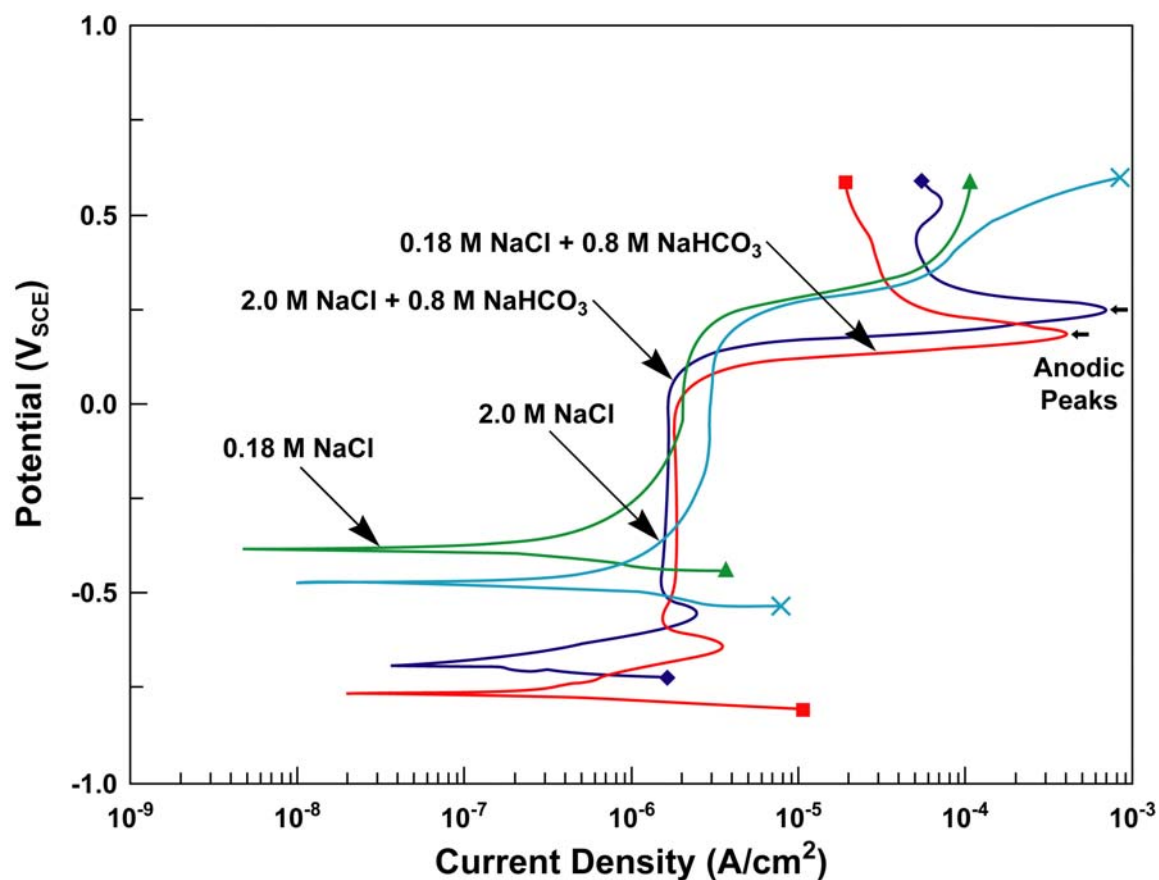
SSRT Conditions & Results for Alloy 22

(Strain Rate: $3.2 \times 10^{-6}/s$)

Environment	T(°C) [°F]	E _{Applied} (mV _{SCE})	t _f /t _f ^{air}	P _{max} / P _{max} ^{air}	SCC
Air	22 [72]	N/A	—	—	N
SCW	95 [203]	400	0.77	0.79	Y
SCW	95 [203]	200	1.0	1.0	N
7.2 m Cl ⁻	95 [203]	400	1.02	1.09	N
1.1 m HCO ₃ ⁻ + 4.2 m Cl ⁻	95 [203]	400	0.51	0.70	Y
1.1 m HCO ₃ ⁻ + 7.2 m Cl ⁻	95 [203]	400	0.41	0.64	Y
	95 [203]	300	0.62	0.78	Y
	95 [203]	200	0.91	0.91	Y
	95 [203]	100	1.03	0.92	N
1.1 m HCO ₃ ⁻ + 2.2 m Cl ⁻	95 [203]	400	0.65	0.77	Y
	75 [167]	400	0.73	0.92	Y
	55 [131]	400	0.91	0.98	Y§
	22 [72]	400	0.92	1.05	N
§ Minor transgranular cracking, mostly on side surfaces					

Anodic Polarization Behavior

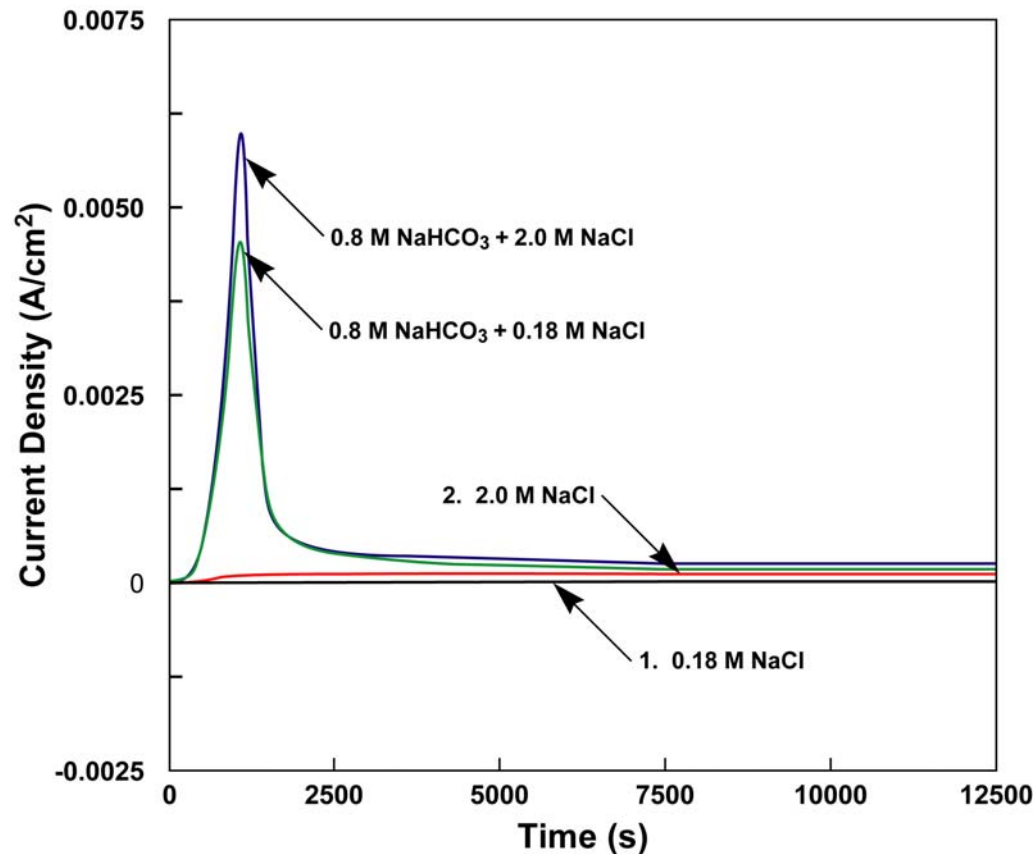
Mill-Annealed Alloy 22 at 95°C [203 °F]
Deaerated NaHCO₃ + NaCl Solution



- Anodic Peaks Were Observed in NaHCO₃ + NaCl Solutions
- No Anodic Peak in NaCl-Only Solutions

Anodic Current Density Versus Time Behavior

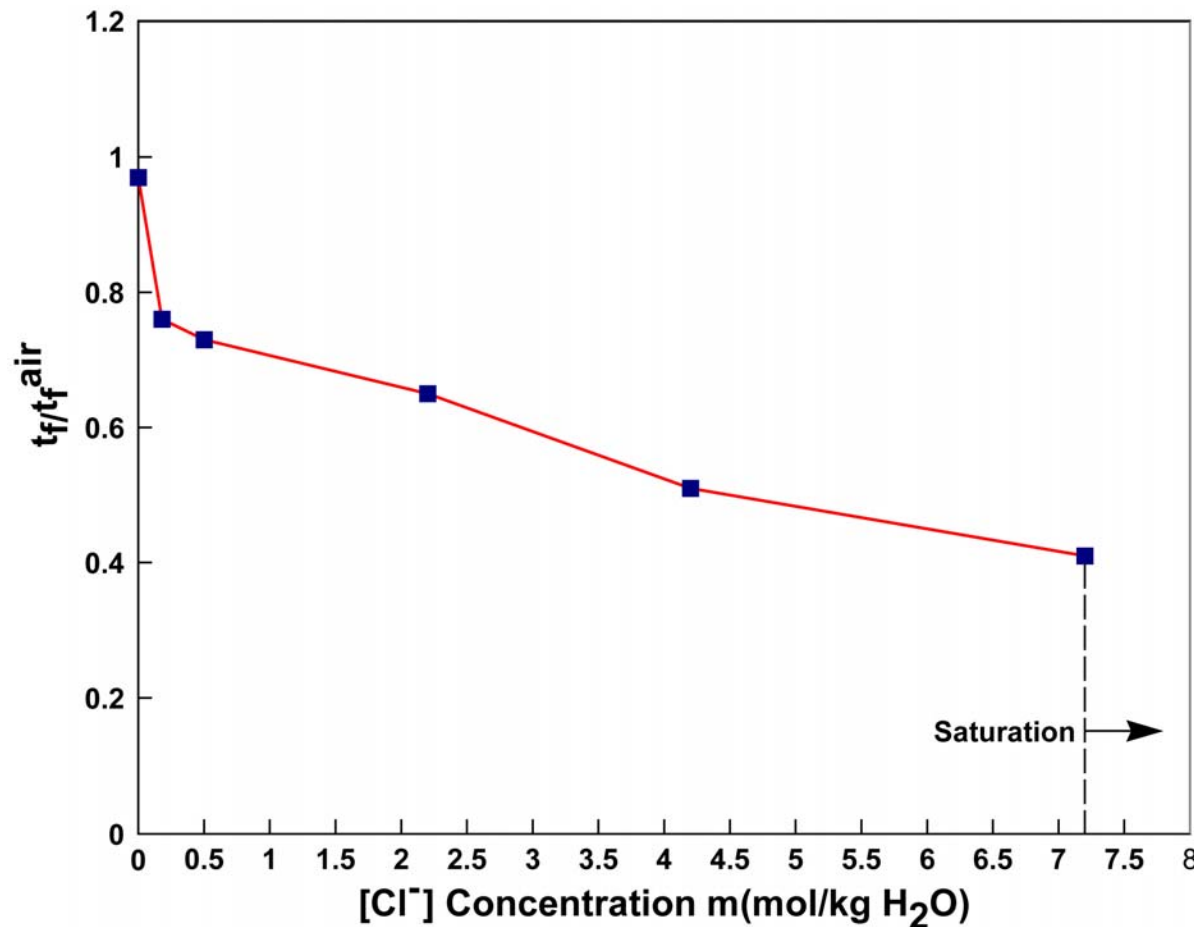
Mill-Annealed Alloy 22 at 95°C [203 °F] and 400 mV_{SCE}
Deaerated NaHCO₃ + NaCl Solution



- No Peak Exists in NaCl-Only Solutions
- Pronounced Current Peaks Observed in NaHCO₃ + NaCl Solutions

Effect of $[\text{Cl}^-]$ and $[\text{HCO}_3^-]$ on Time-to-Failure of Alloy 22 in SSRTs

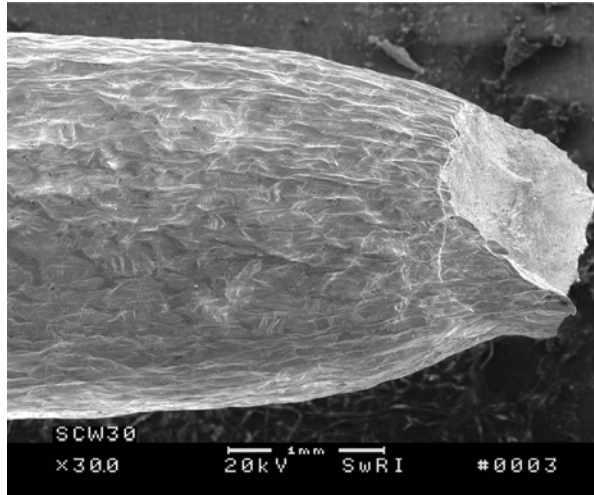
Mill-Annealed Alloy 22 at 400 mV_{SCE} and 95°C [203 °F], SSRTs at 3.2×10^{-6} /s



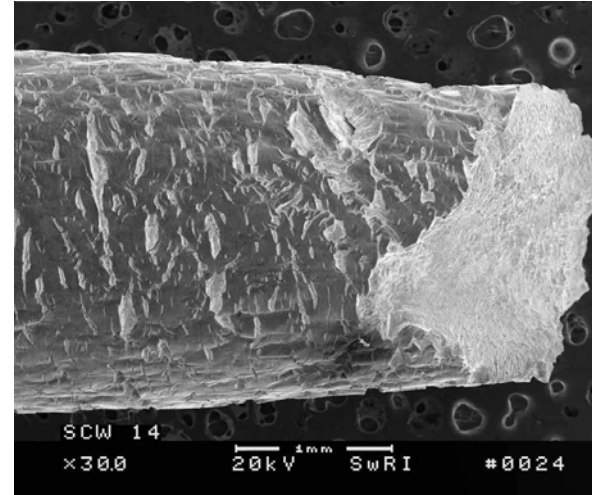
- At a Constant Bicarbonate Level (1.1 m), Susceptibility of Alloy 22 to SCC Increases with Increasing Chloride Ion Concentrations

Synergistic Effect of $[\text{Cl}^-]$ and $[\text{HCO}_3^-]$ in Causing SCC of Alloy 22 at 400 mV_{SCE}

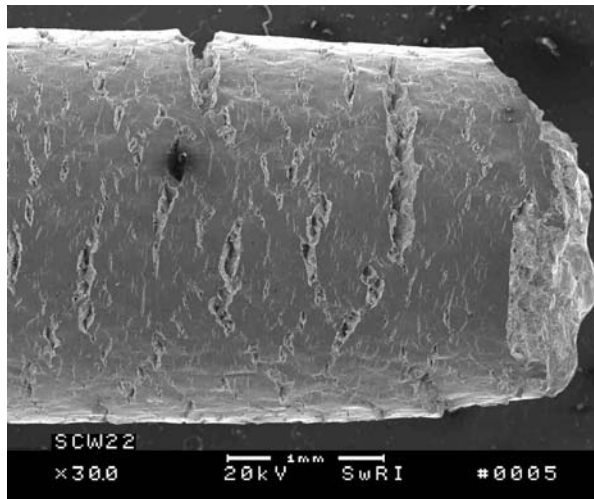
7.2 m
 Cl^- only



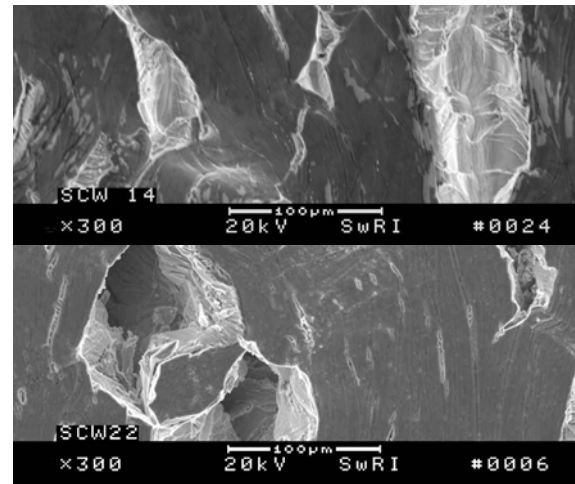
1.1 m
 HCO_3^-
only



1.1 m
 HCO_3^- +
4.2 m Cl^-



1.1 m
 HCO_3^-
only

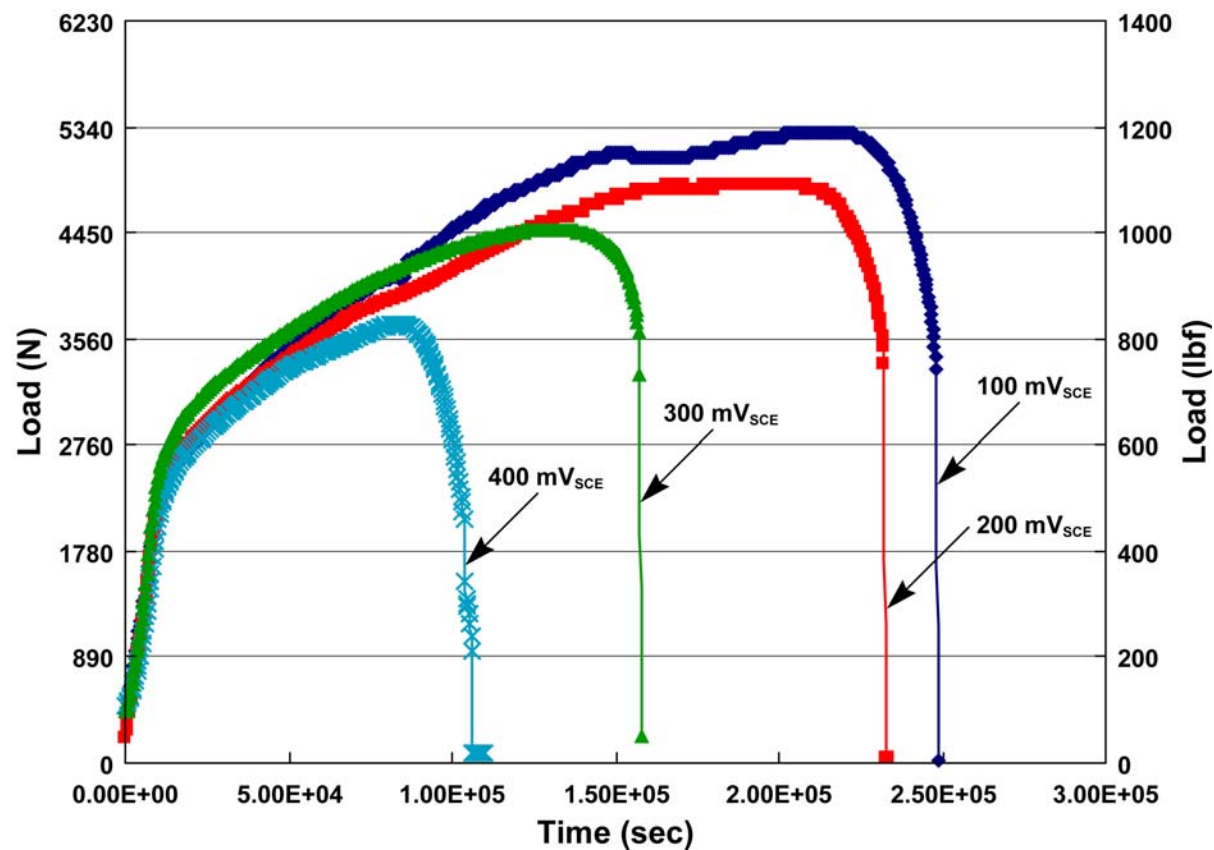


1.1 m
 HCO_3^- +
4.2 m Cl^-



Effect of Electrochemical Potential

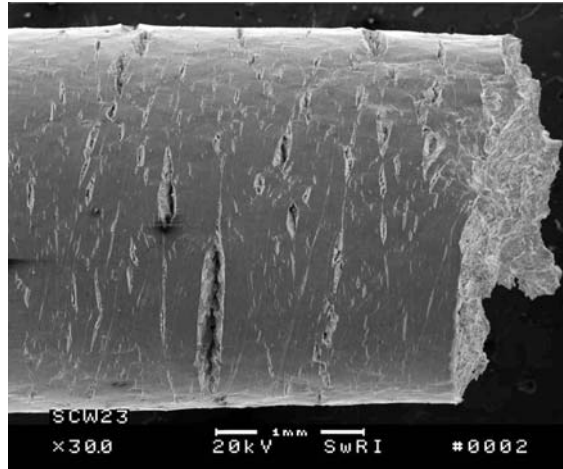
Mill-Annealed Alloy 22 at 95°C [203 °F], SSRTs at $3.2 \times 10^{-6}/s$
1.1 m HCO_3^- and 7.2 m Cl^- Solution



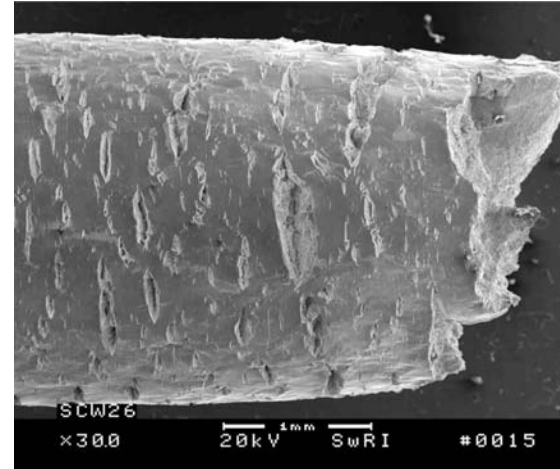
- Susceptibility of Alloy 22 to SCC Decreased with Decreasing Electrochemical Potential

Fracture End of Alloy 22 in 1.1 m HCO_3^- and 7.2 m Cl^- Solution at Various Electrochemical Potentials

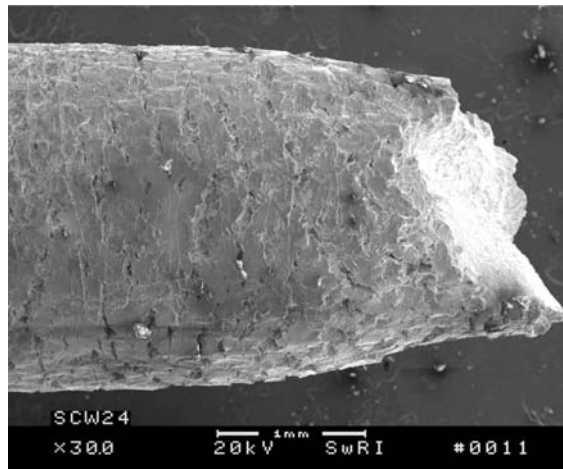
400
 mV_{SCE}



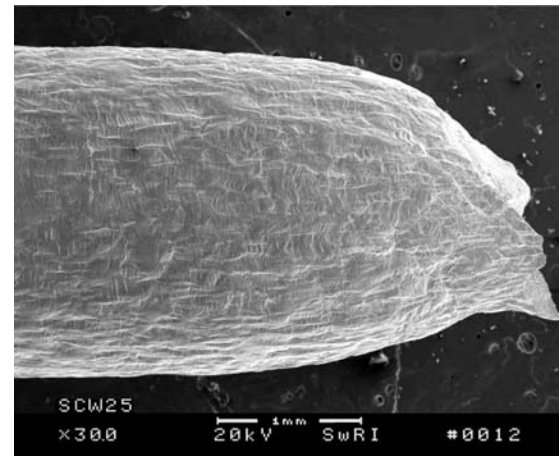
300
 mV_{SCE}



200
 mV_{SCE}

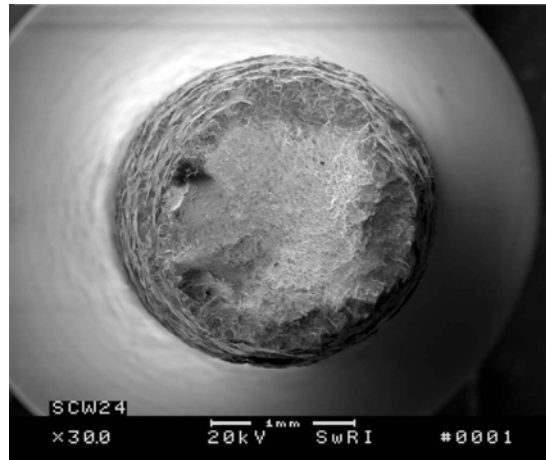


100
 mV_{SCE}

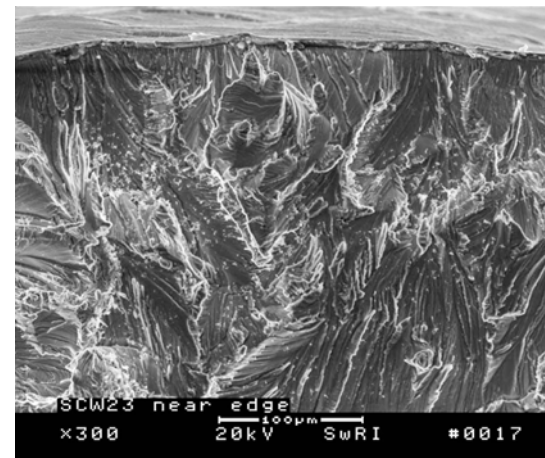
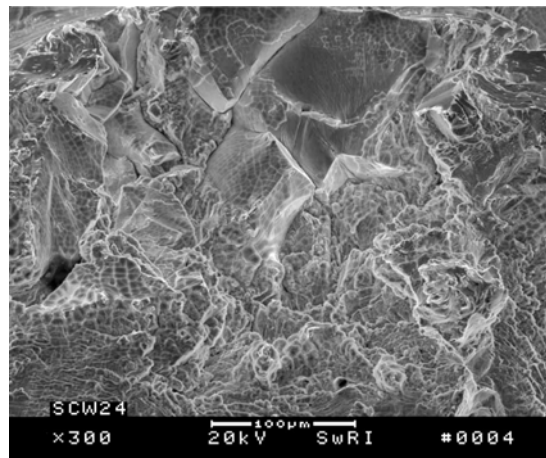
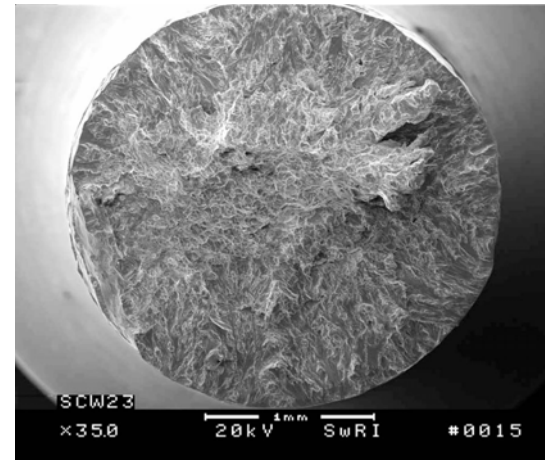


Fracture Surface of Alloy 22 Strained in 1.1 m HCO_3^- and 7.2 m Cl^- Solution

200
 mV_{SCE}

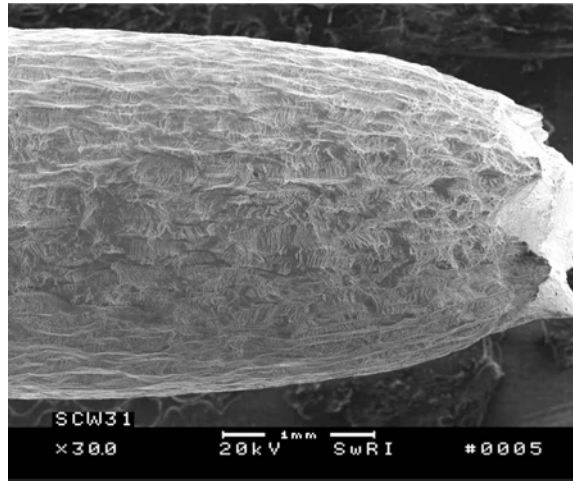


400
 mV_{SCE}

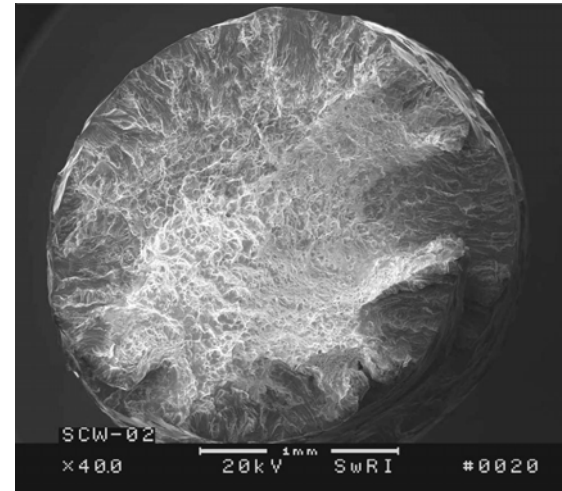
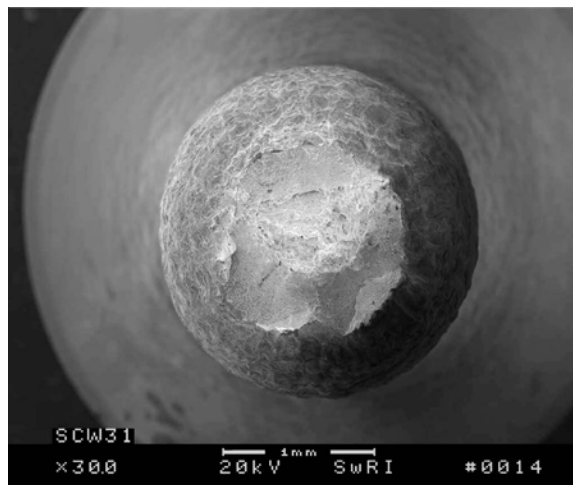
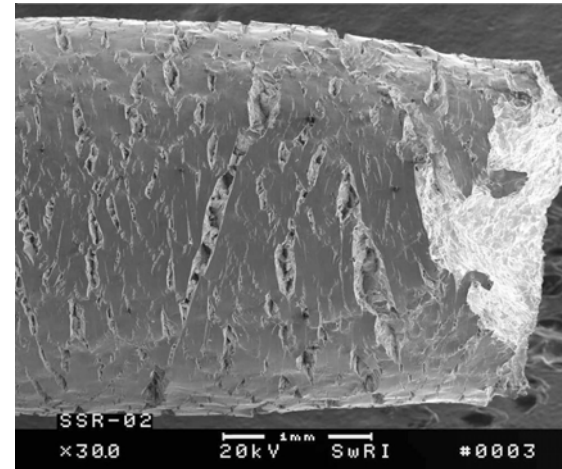


Fracture Surface of Alloy 22 Strained in Simulated Concentrated Water

200
 mV_{SCE}

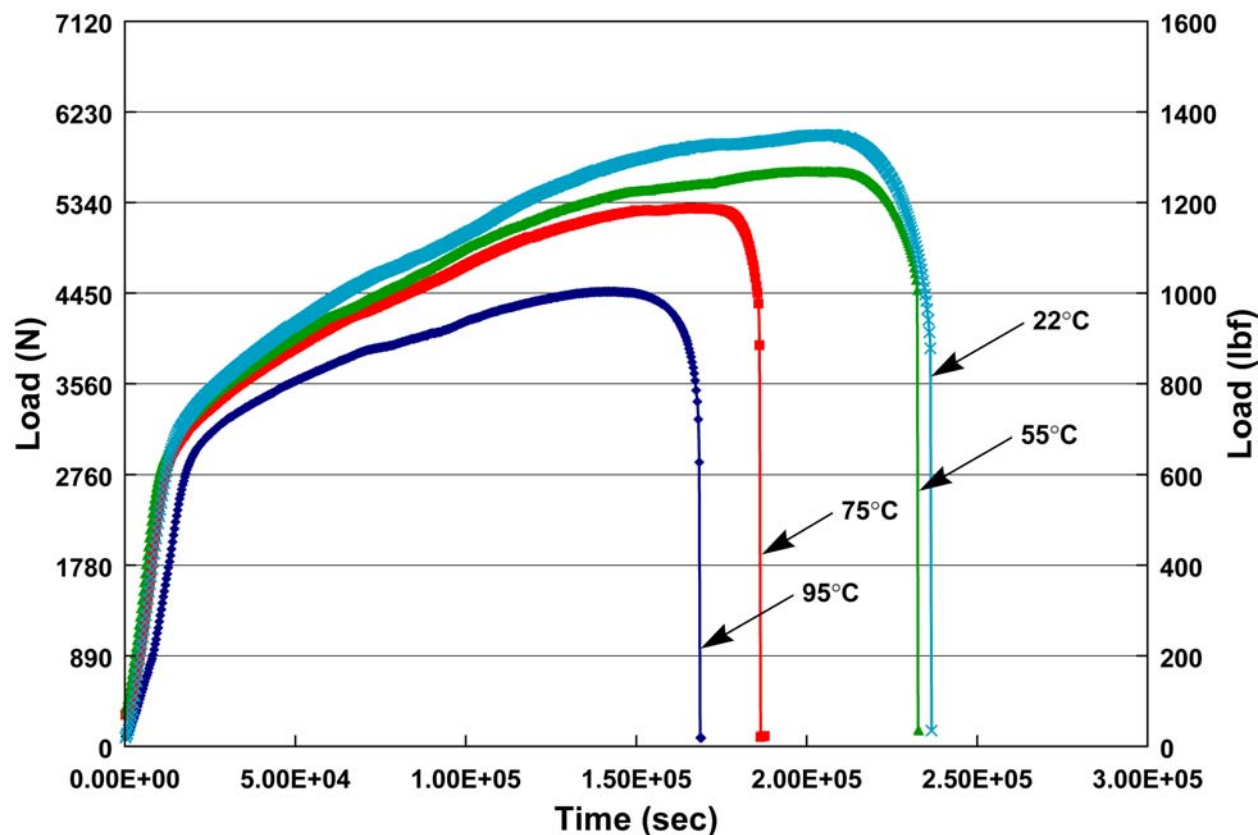


400
 mV_{SCE}



Effect of Solution Temperature

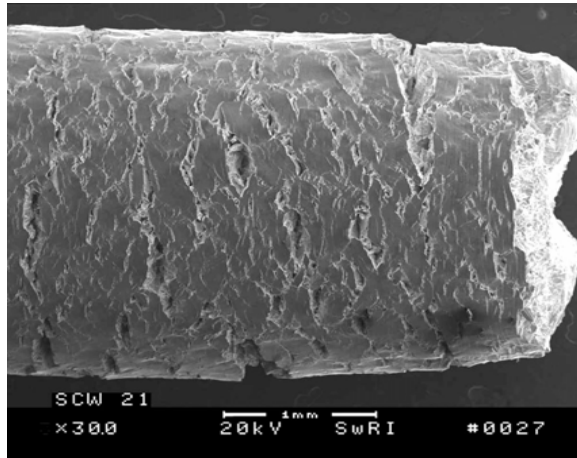
Mill-Annealed Alloy 22 at 400 mV_{SCE}, SSRT at 3.2×10^{-6} /s
1.1 m HCO₃⁻ and 2.2 m Cl⁻ Solution



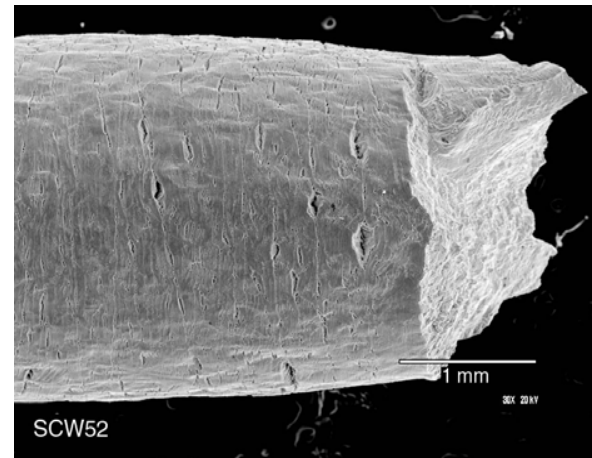
- Susceptibility of Alloy 22 to SCC Decreased with Decreasing Temperature

Fracture End of Alloy 22 in 1.1 m HCO_3^- Solution Containing 2.2 m Cl^- at Various Temperatures

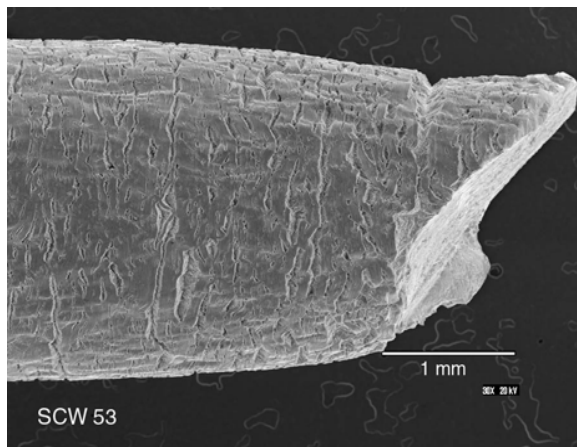
95°C
[203°F]



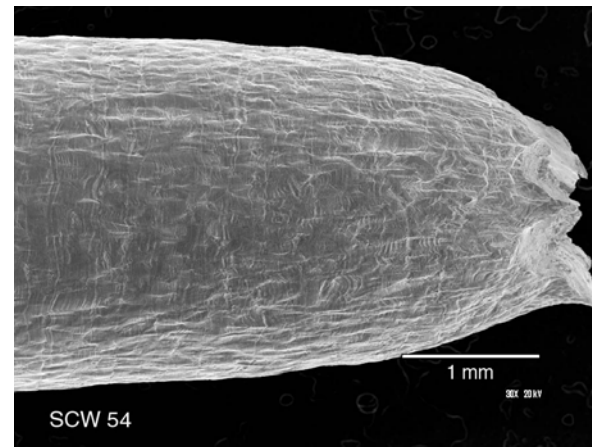
75°C
[167°F]



55°C
[131°F]



22°C
[72°F]



Summary and Conclusions

- Transgranular SCC of Alloy 22 Was Observed in SCW and Its Variations at 95°C [203°F] and a High Anodic Potential of 400 mV_{SCE} Using SSRTs
- Two Major Anionic Constituents of SCW, HCO₃⁻ and Cl⁻ Ions Act Synergistically to Promote SCC in SCW
- For SCW and Its Variations Containing HCO₃⁻, and Cl⁻ Ions, the SCC Susceptibility of Alloy 22 Is Strongly Dependent Upon Applied Electrochemical Potentials
 - ◆ For SCW, the transition from no cracking to transgranular SCC occurs between 200 and 400 mV_{SCE}
 - ◆ For a 1.1 m HCO₃⁻ and 7.2 m Cl⁻ solution, the transition occurs between 100 and 200 mV_{SCE}
- At an Applied Potential of 400 mV_{SCE}, the Susceptibility of Alloy 22 to SCC in HCO₃⁻ and Cl⁻ Solutions Decreases as Temperature Decreases, and No SCC Was Observed at Room Temperature

Acknowledgments

- The authors gratefully acknowledge the contributions of Lietai Yang, Walter Machowski, Brian Derby, and James Spencer
- This work was performed by the Center for Nuclear Waste Regulatory Analyses (CNWRA) for the U.S. Nuclear Regulatory Commission (NRC) under Contract No. NRC-02-02-012 on behalf of the NRC Office of Nuclear Material Safety and Safeguards, Division of High-Level Waste Repository Safety
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