

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

K.T. Chiang<sup>2</sup>, D.S. Dunn<sup>2</sup>, and G.A. Cragolino<sup>1,2</sup>

<sup>1</sup>Center for Nuclear Waste Regulatory Analyses

<sup>2</sup>Southwest Research Institute<sup>®</sup>

San Antonio, Texas, U.S.A.

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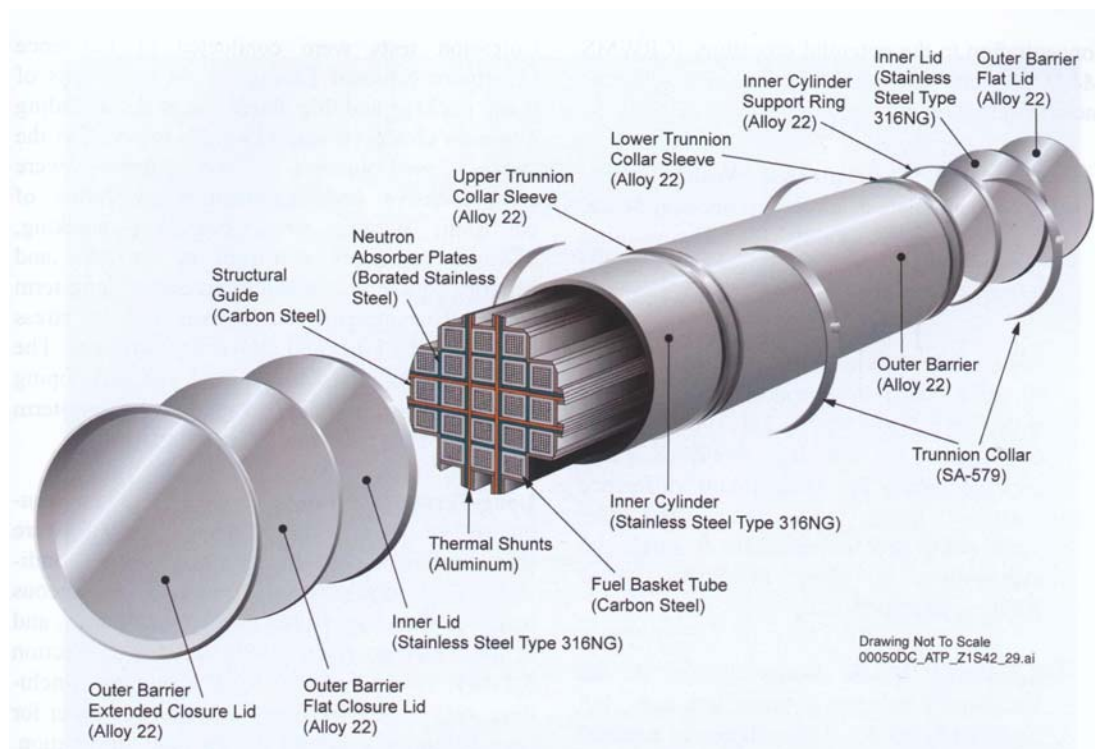


# Outline

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- 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 <sup>+</sup>	Na <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	F <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>
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<sub>SSC</sub> [356 mV<sub>SCE</sub>]
- 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<sub>SCE</sub>

# Objectives and Scope

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- ❑ 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

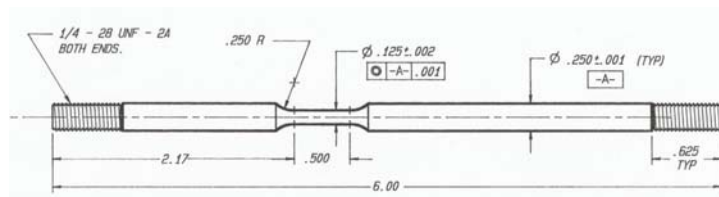
# Chemical Composition & Tensile Properties of Alloy 22

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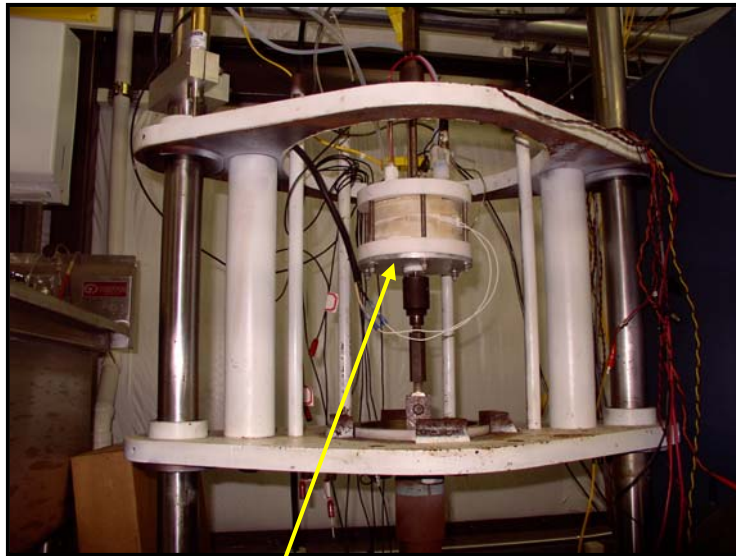
Material	Composition (wt%)											
	Ni	Cr	Mo	W	Fe	Co	Si	Mn	V	P	S	C
<b>Alloy 22 Heat 2277-3-3266</b>	Bal	21.40	13.30	2.81	3.75	1.19	0.03	0.23	0.14	0.008	0.004	0.005

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

# SSRT Experimental Setup



Specimen



Test Cell



Data Acquisition System

# SCC Testing Conditions

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## □ SSRT

- ◆ SCW and electrolyte containing  $[\text{Cl}^-]$  &  $[\text{HCO}_3^-]$  ions
- ◆ Electrochemical potentials 100 to 400 mV<sub>SCE</sub>
- ◆ 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]



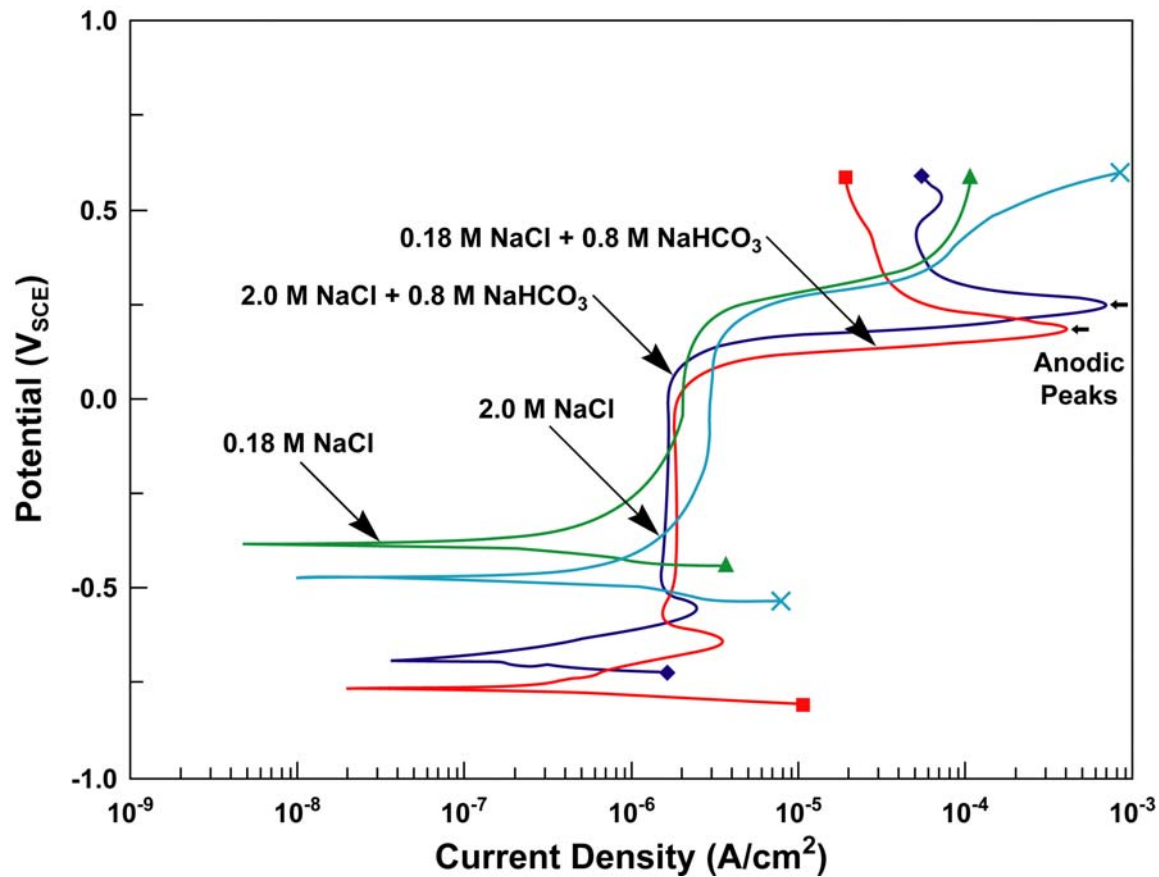
# SSRT Conditions & Results for Alloy 22

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

Environment	T(°C) [°F]	E <sub>Applied</sub> (mV <sub>SCE</sub> )	t <sub>f</sub> /t <sub>f</sub> <sup>air</sup>	P <sub>max</sub> / P <sub>max</sub> <sup>air</sup>	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 <sup>-</sup>	95 [203]	400	1.02	1.09	N
1.1 m HCO <sub>3</sub> <sup>-</sup> + 4.2 m Cl <sup>-</sup>	95 [203]	400	0.51	0.70	Y
1.1 m HCO <sub>3</sub> <sup>-</sup> + 7.2 m Cl <sup>-</sup>	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 <sub>3</sub> <sup>-</sup> + 2.2 m Cl <sup>-</sup>	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

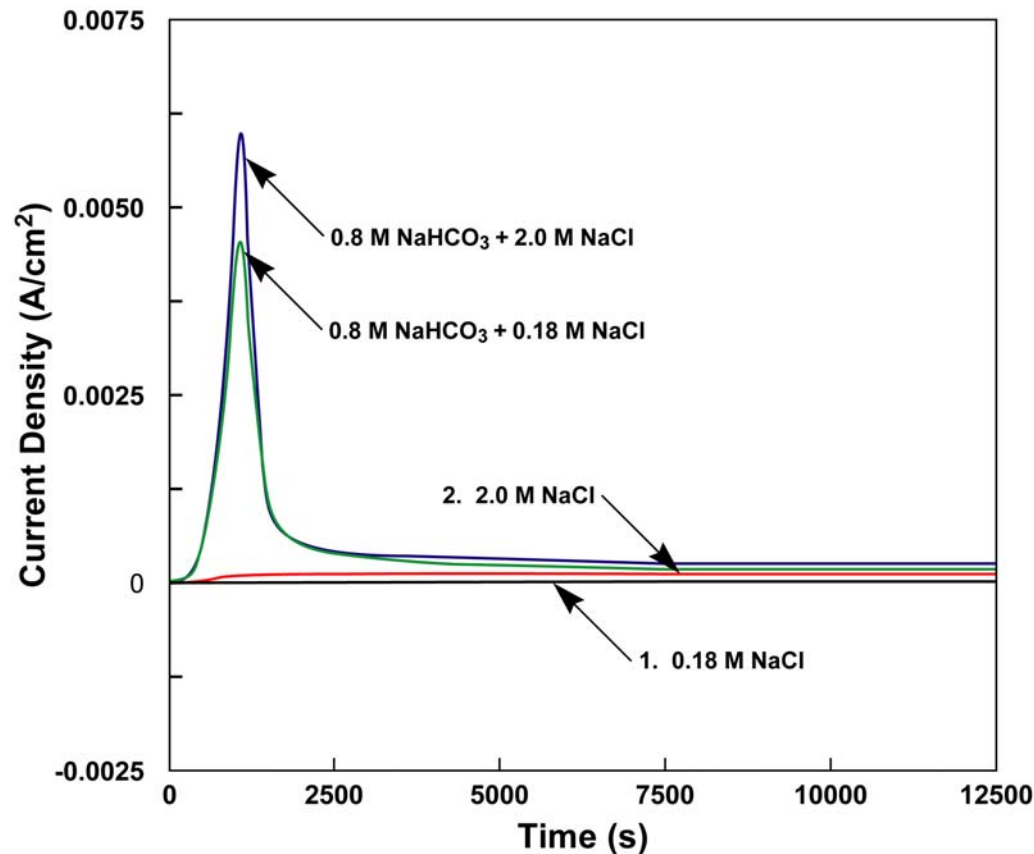
Mill-Annealed Alloy 22 at 95°C [203 °F]  
Deaerated NaHCO<sub>3</sub> + NaCl Solution



- Anodic Peaks Were Observed in NaHCO<sub>3</sub> + NaCl Solutions
- No Anodic Peak in NaCl-Only Solutions

# Anodic Current Density Versus Time Behavior

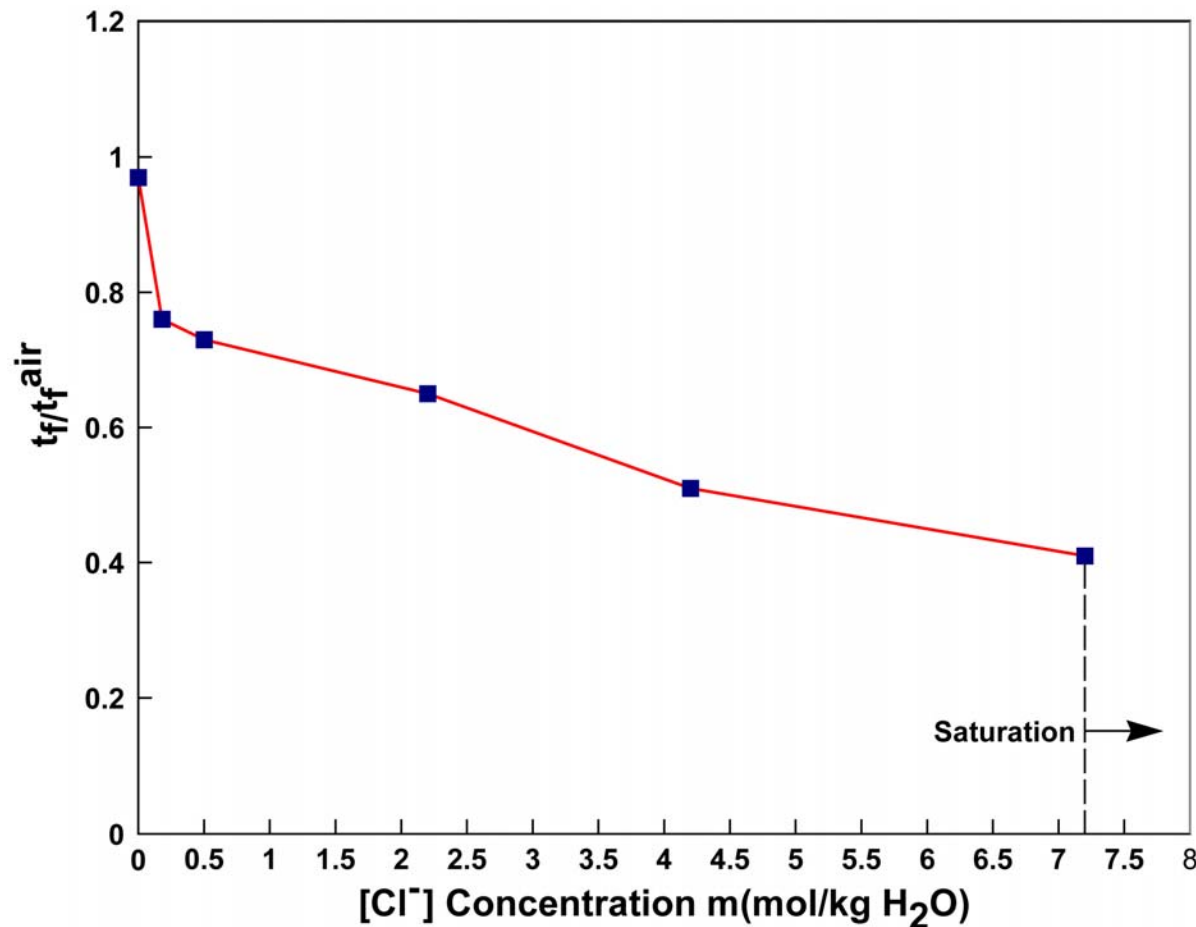
Mill-Annealed Alloy 22 at 95°C [203 °F] and 400 mV<sub>SCE</sub>  
Deaerated NaHCO<sub>3</sub> + NaCl Solution



- No Peak Exists in NaCl-Only Solutions
- Pronounced Current Peaks Observed in NaHCO<sub>3</sub> + NaCl Solutions

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

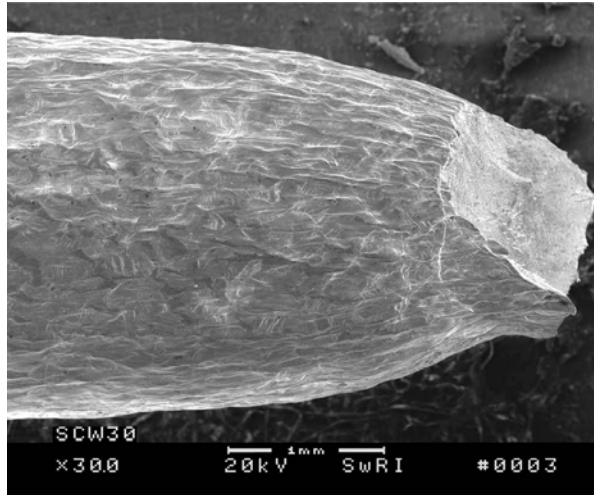
Mill-Annealed Alloy 22 at 400 mV<sub>SCE</sub> and 95°C [203 °F], SSRTs at  $3.2 \times 10^{-6}$ /s



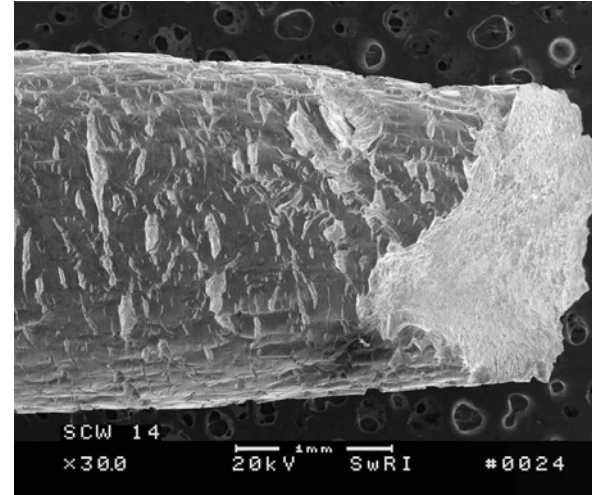
- At a Constant Bicarbonate Level (1.1 m), Susceptibility of Alloy 22 to SCC Increases with Increasing Chloride Ion Concentrations

# Synergistic Effect of $[\text{Cl}^-]$ and $[\text{HCO}_3^-]$ in Causing SCC of Alloy 22 at 400 mV<sub>SCE</sub>

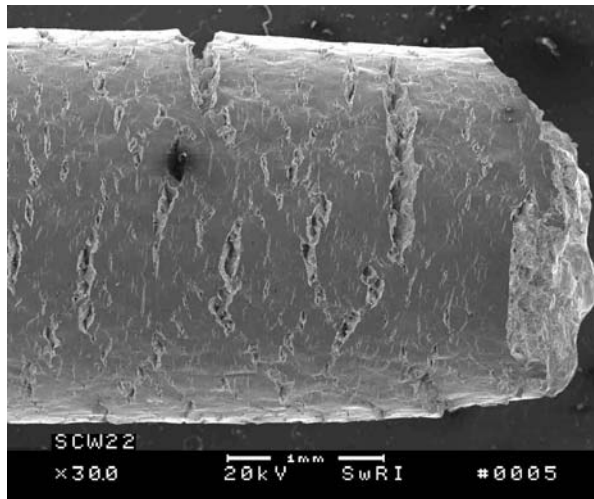
7.2 m  
 $\text{Cl}^-$  only



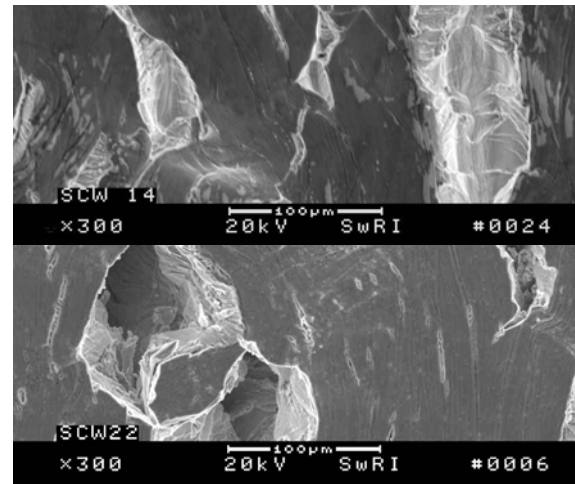
1.1 m  
 $\text{HCO}_3^-$   
only



1.1 m  
 $\text{HCO}_3^-$  +  
4.2 m  $\text{Cl}^-$



1.1 m  
 $\text{HCO}_3^-$   
only

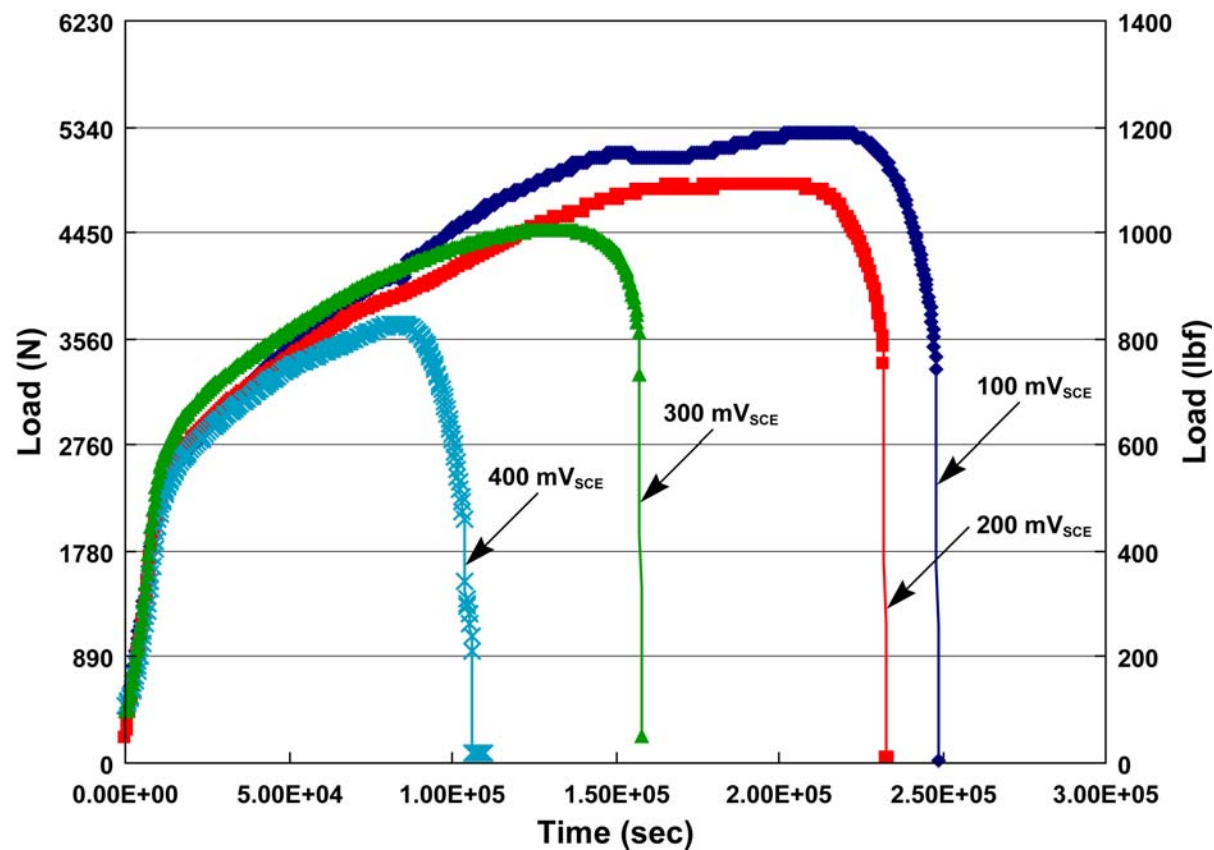


1.1 m  
 $\text{HCO}_3^-$  +  
4.2 m  $\text{Cl}^-$



# Effect of Electrochemical Potential

Mill-Annealed Alloy 22 at 95°C [203 °F], SSRTs at  $3.2 \times 10^{-6}/s$   
1.1 m  $\text{HCO}_3^-$  and 7.2 m  $\text{Cl}^-$  Solution

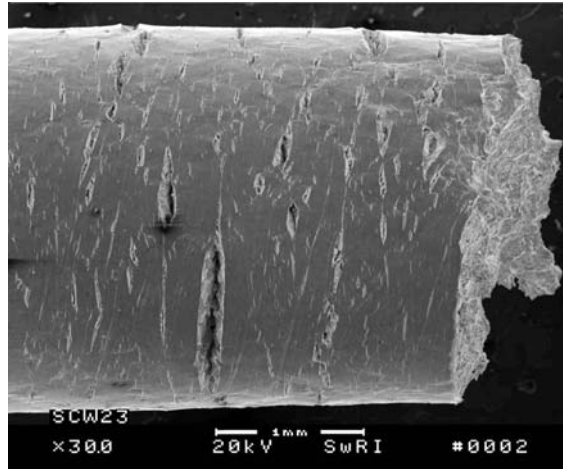


- Susceptibility of Alloy 22 to SCC Decreased with Decreasing Electrochemical Potential

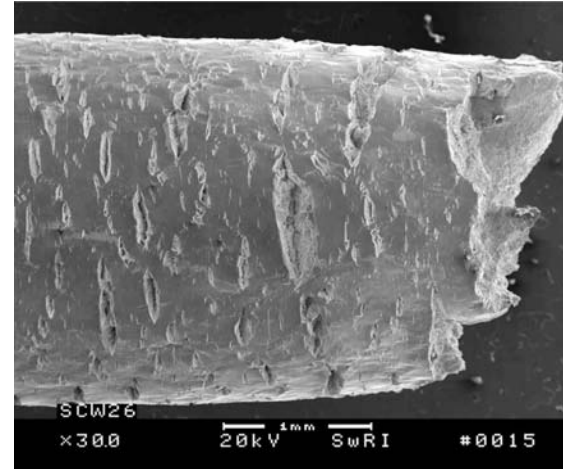


# Fracture End of Alloy 22 in 1.1 m $\text{HCO}_3^-$ and 7.2 m $\text{Cl}^-$ Solution at Various Electrochemical Potentials

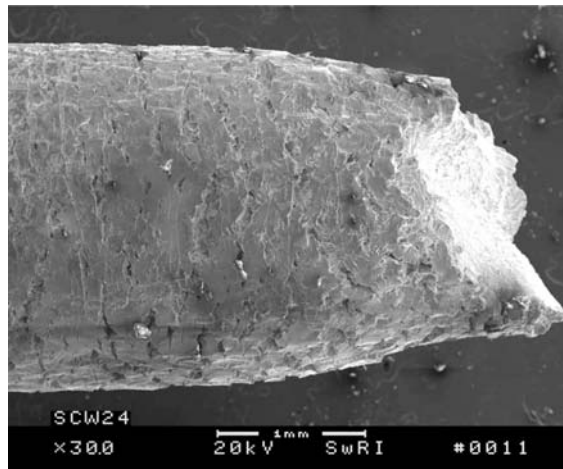
400  
 $\text{mV}_{\text{SCE}}$



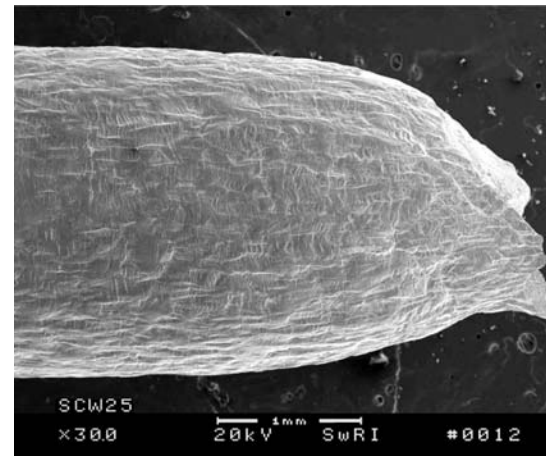
300  
 $\text{mV}_{\text{SCE}}$



200  
 $\text{mV}_{\text{SCE}}$

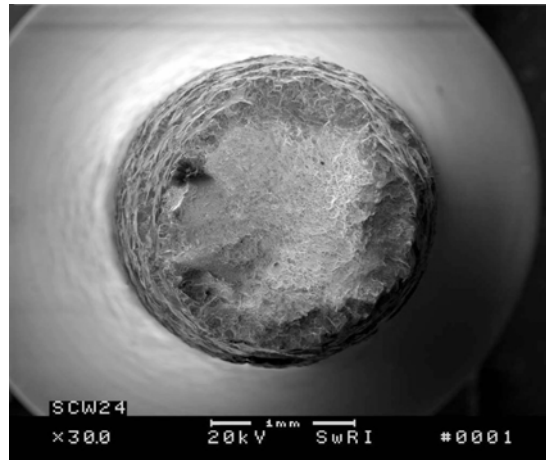


100  
 $\text{mV}_{\text{SCE}}$

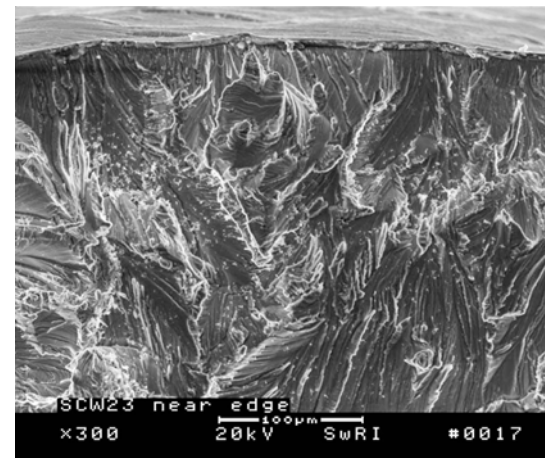
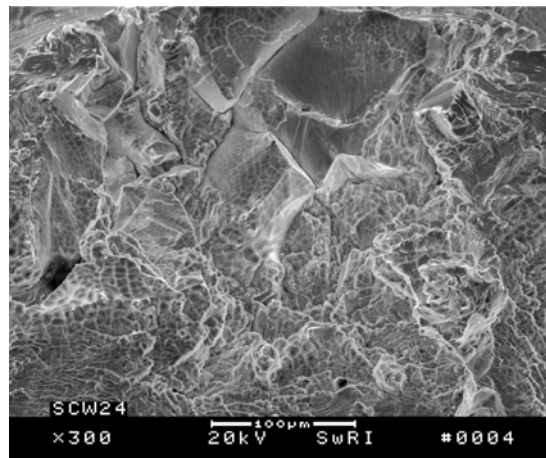
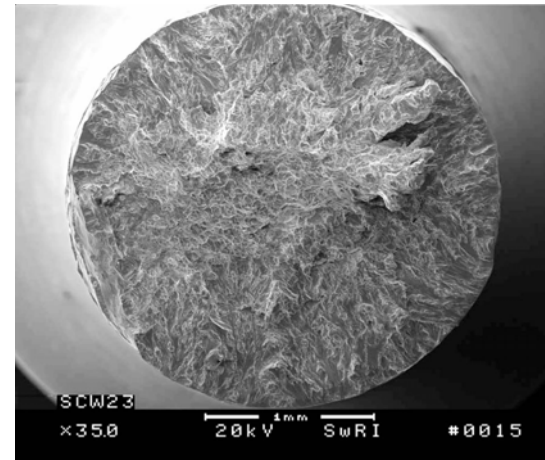


# Fracture Surface of Alloy 22 Strained in 1.1 m $\text{HCO}_3^-$ and 7.2 m $\text{Cl}^-$ Solution

200  
 $\text{mV}_{\text{SCE}}$



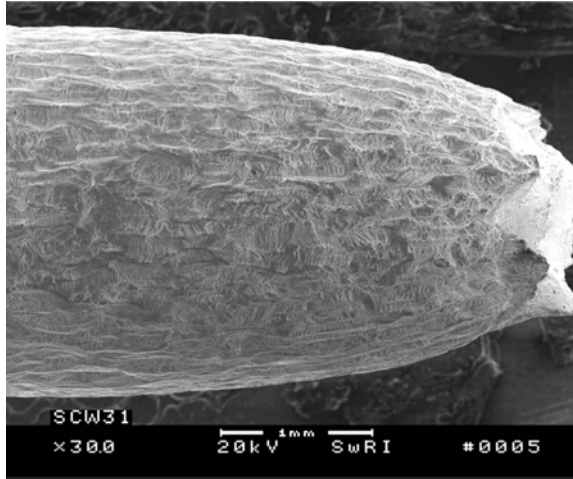
400  
 $\text{mV}_{\text{SCE}}$



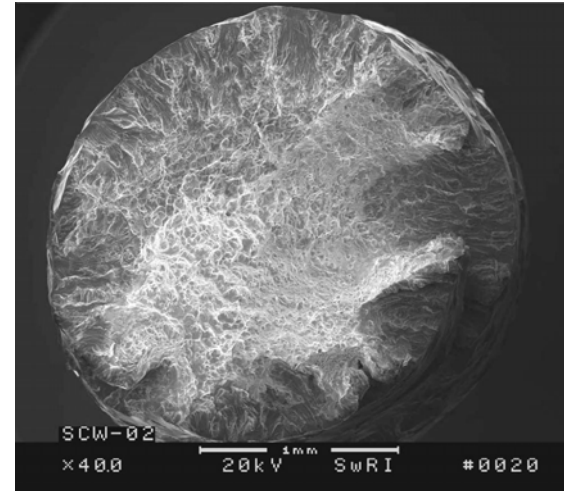
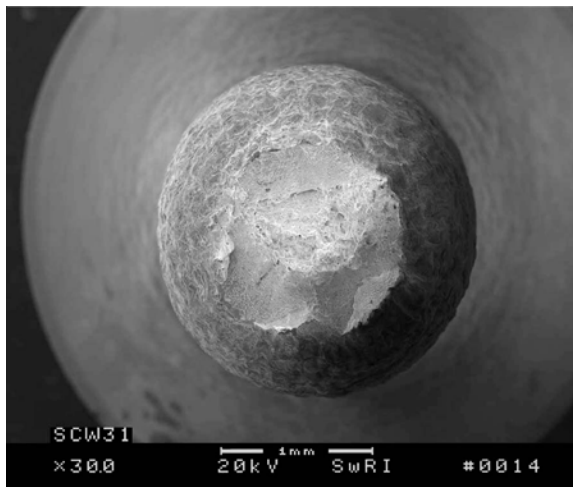
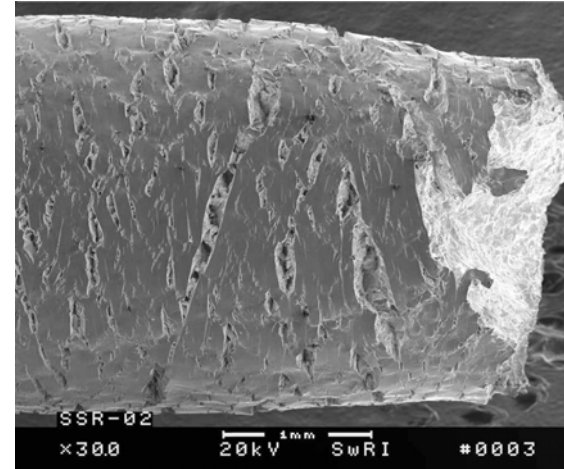


# Fracture Surface of Alloy 22 Strained in Simulated Concentrated Water

200  
 $\text{mV}_{\text{SCE}}$

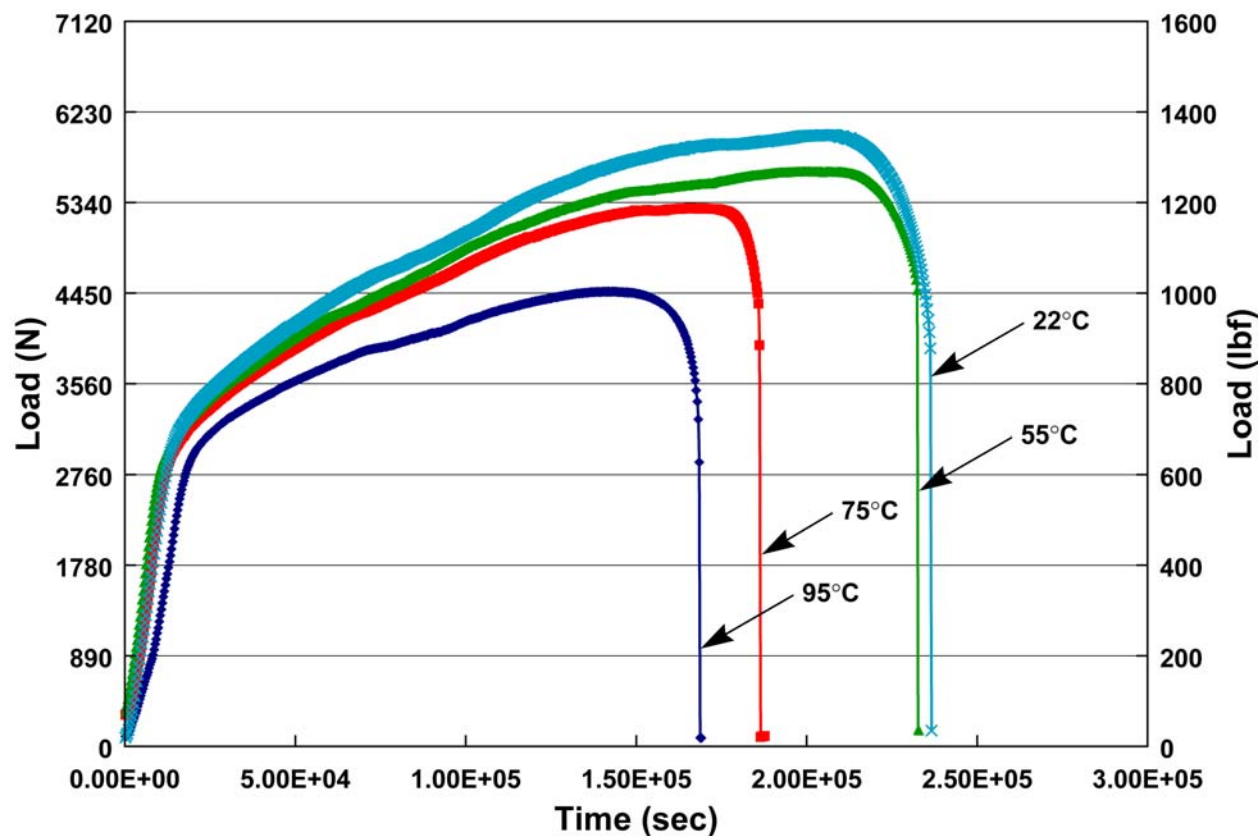


400  
 $\text{mV}_{\text{SCE}}$



# Effect of Solution Temperature

Mill-Annealed Alloy 22 at 400 mV<sub>SCE</sub>, SSRT at  $3.2 \times 10^{-6}$ /s  
1.1 m HCO<sub>3</sub><sup>-</sup> and 2.2 m Cl<sup>-</sup> Solution

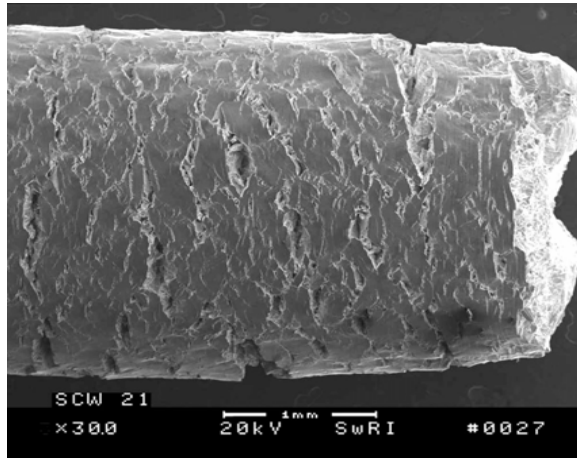


- Susceptibility of Alloy 22 to SCC Decreased with Decreasing Temperature

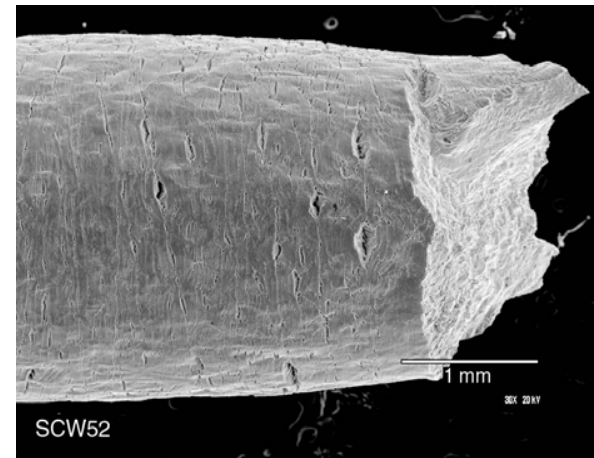
# Fracture End of Alloy 22 in 1.1 m $\text{HCO}_3^-$ Solution Containing 2.2 m $\text{Cl}^-$ at Various Temperatures

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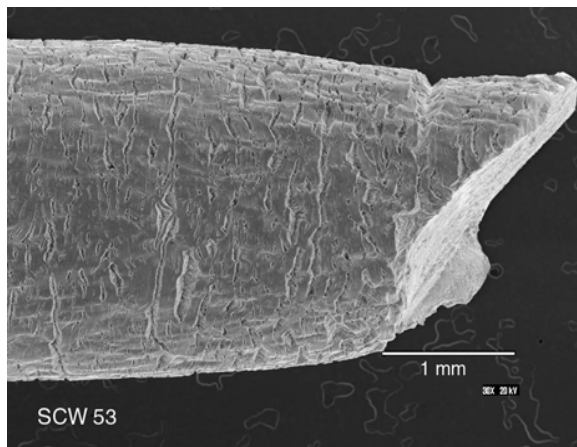
95°C  
[203°F]



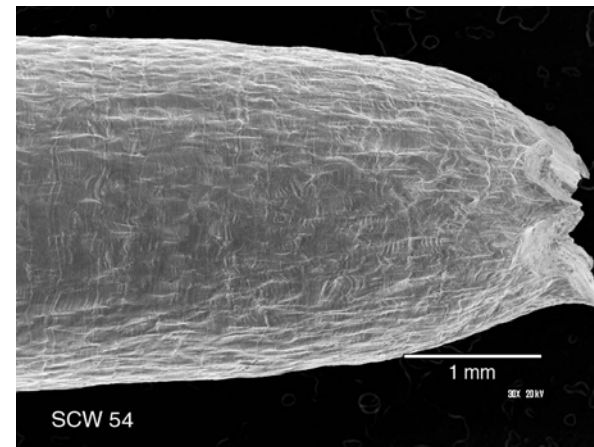
75°C  
[167°F]



55°C  
[131°F]



22°C  
[72°F]



# Summary and Conclusions

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- 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<sub>SCE</sub> Using SSRTs
- Two Major Anionic Constituents of SCW, HCO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> Ions Act Synergistically to Promote SCC in SCW
- For SCW and Its Variations Containing HCO<sub>3</sub><sup>-</sup>, and Cl<sup>-</sup> 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<sub>SCE</sub>
  - ◆ For a 1.1 m HCO<sub>3</sub><sup>-</sup> and 7.2 m Cl<sup>-</sup> solution, the transition occurs between 100 and 200 mV<sub>SCE</sub>
- At an Applied Potential of 400 mV<sub>SCE</sub>, the Susceptibility of Alloy 22 to SCC in HCO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> Solutions Decreases as Temperature Decreases, and No SCC Was Observed at Room Temperature

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