

SCC of Fixed Climbing Protection in Thailand



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Outline

- Introduction
- Corrosion resistance of 316 stainless
- Thailand SCC Case Study
- Uster, Switzerland SCC Case Study
- Titanium
- Other Materials

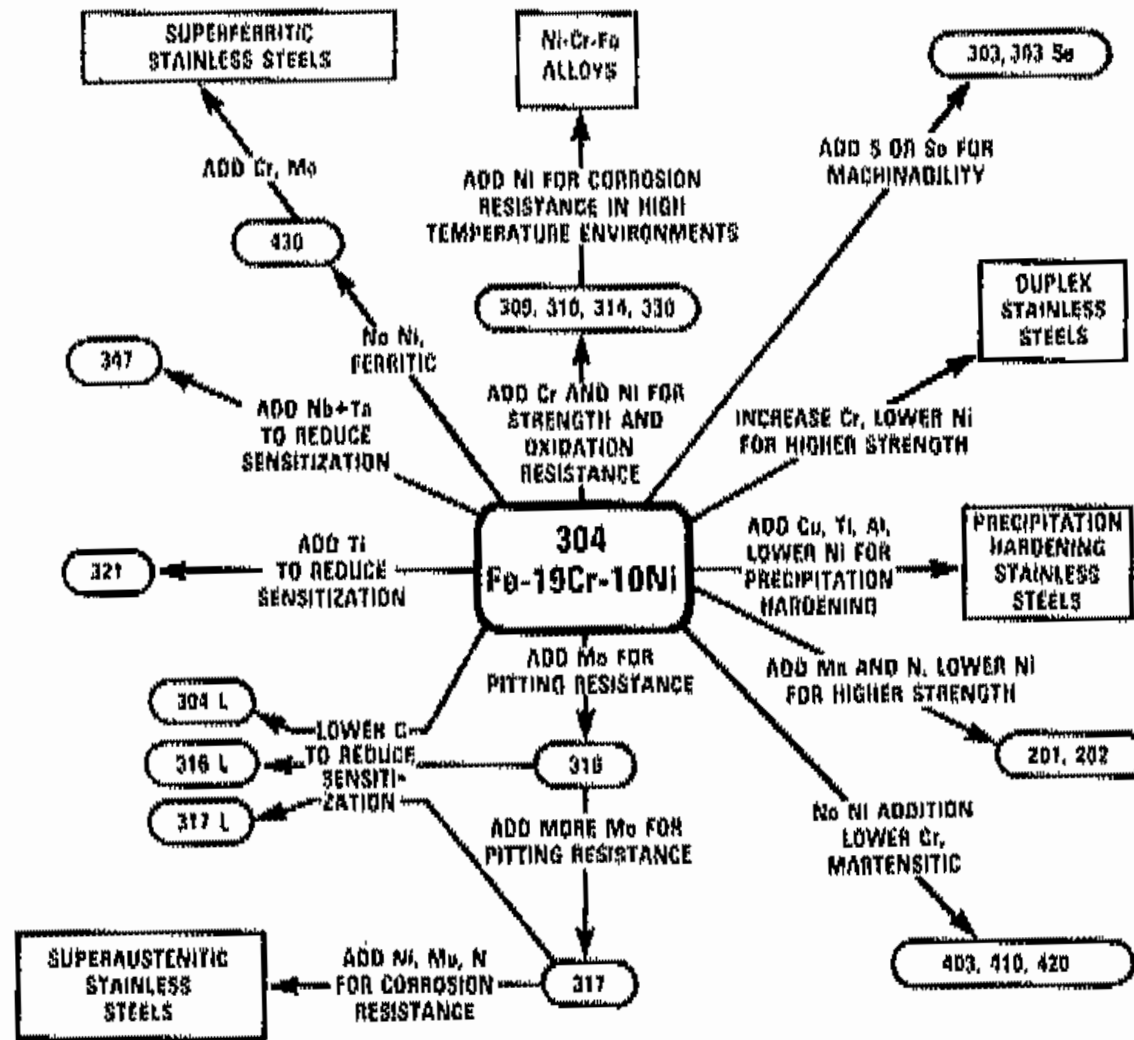
Stainless Steels

- Large family of corrosion-resistant steels
- Minimum of 12% chromium

Table II: Metallurgical Characteristics

Austenitic	Non-magnetic Non-hardenable by heat treatment Single phase from 0° (K) to melting point Crystallographic form – face centered cubic Very easy to weld
Ferritic	Magnetic Non-hardenable by heat treatment Crystallographic form – body centered cubic Low carbon grades easy to weld
Duplex	Magnetic Non-hardenable by heat treatment Contains both austenite and ferrite Easy to weld
Martensitic	Magnetic Heat treatable to high hardness levels Crystallographic form – distorted tetragonal Hard to impossible to weld
Precipitation Hardening	Magnetic Crystallographic form – martensitic with microprecipitates Heat treatable to high strength levels Weldable

Stainless Steels- General



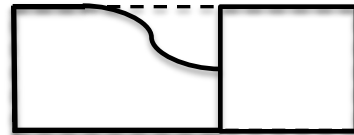
Corrosion Types- A Partial List



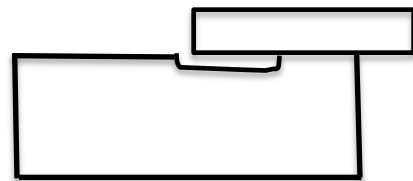
General



Pitting



Galvanic

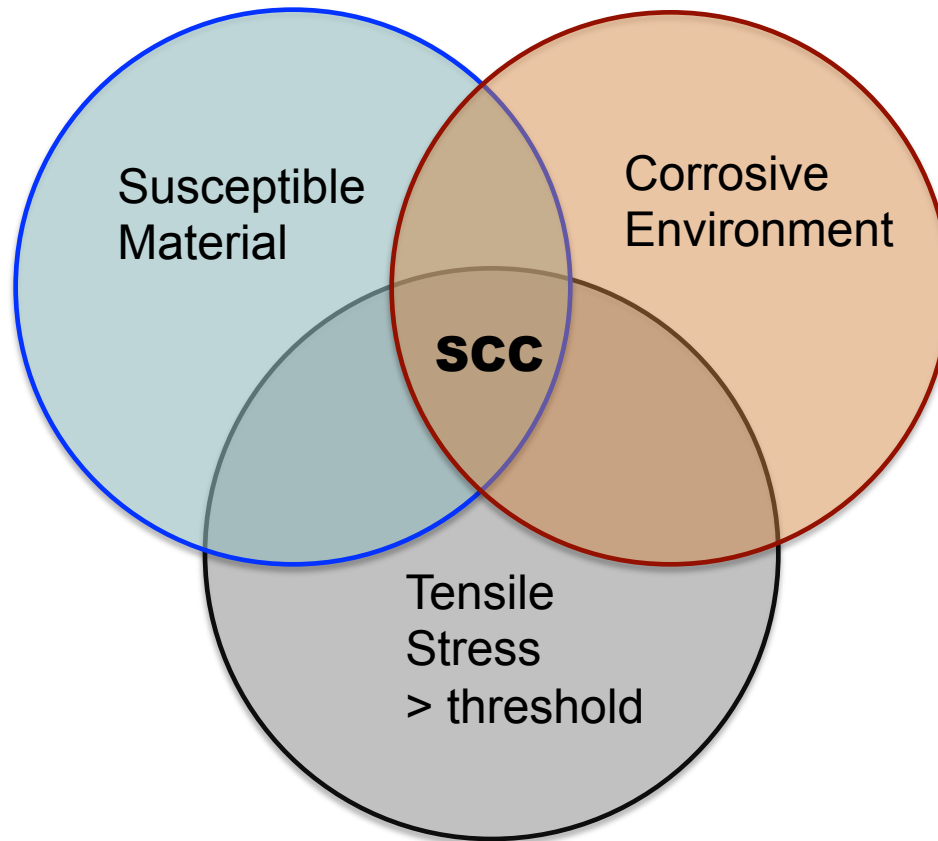


Crevice



Stress Corrosion Cracking

Stress Corrosion Cracking-101



SCC Corrosion Resistance of 316 Stainless

- Seaside Tests
- Boiling NaCl, CaCl₂, MgCl₂
- Chloride Films



Test Rack for Stainless Steels

Kure Beach, NC

- 5-15y duration



Material	Annealed	Welded	Cold worked	Sensitized, 650°C 1.5h
316	No Failure	No Failure	No Failure	Intergranular attack

The traditional engineering viewpoint is that chloride SCC does not occur in non-sensitized austenitic stainless steels at temperatures below 60°C (140°F) in near-neutral chloride solutions.

Accelerated SCC Testing

Boiling 26% NaCl, U-Bend

pH	Material	Time to Failure, Weeks	
		Min	Max
6	316	NC	NC

NC = No cracking after 30 weeks

Accelerated SCC Testing

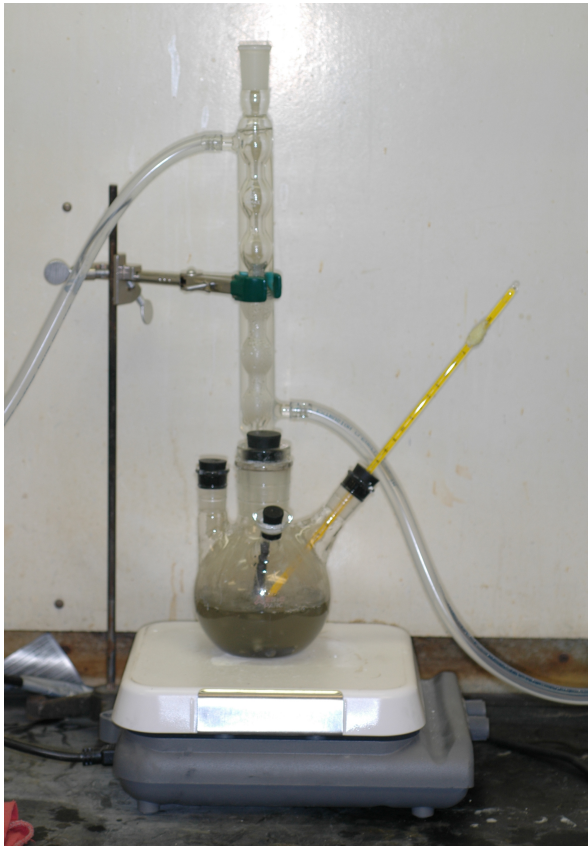
Boiling 26% NaCl, U-Bend, 316

**Time to Failure,
Weeks**

pH	Min	Max
2	1.0	5.0
4	1.0	16.0
6	NC	NC

NC = No cracking after 30 weeks

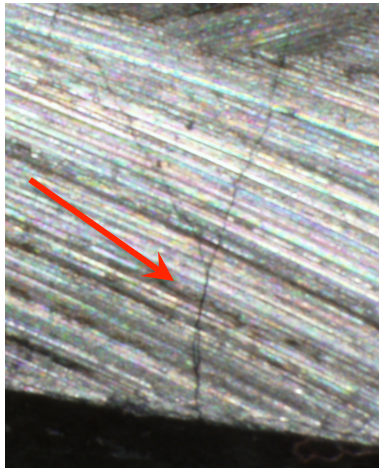
Boiling MgCl_2 Test Extremely Aggressive



*ASTM G36-94, Standard Practice
for Evaluating Stress-Corrosion-
Cracking Resistance of Metals
and Alloys in a Boiling Magnesium
Chloride Solution*

- *35-43% MgCl_2*
- *125-155°C*

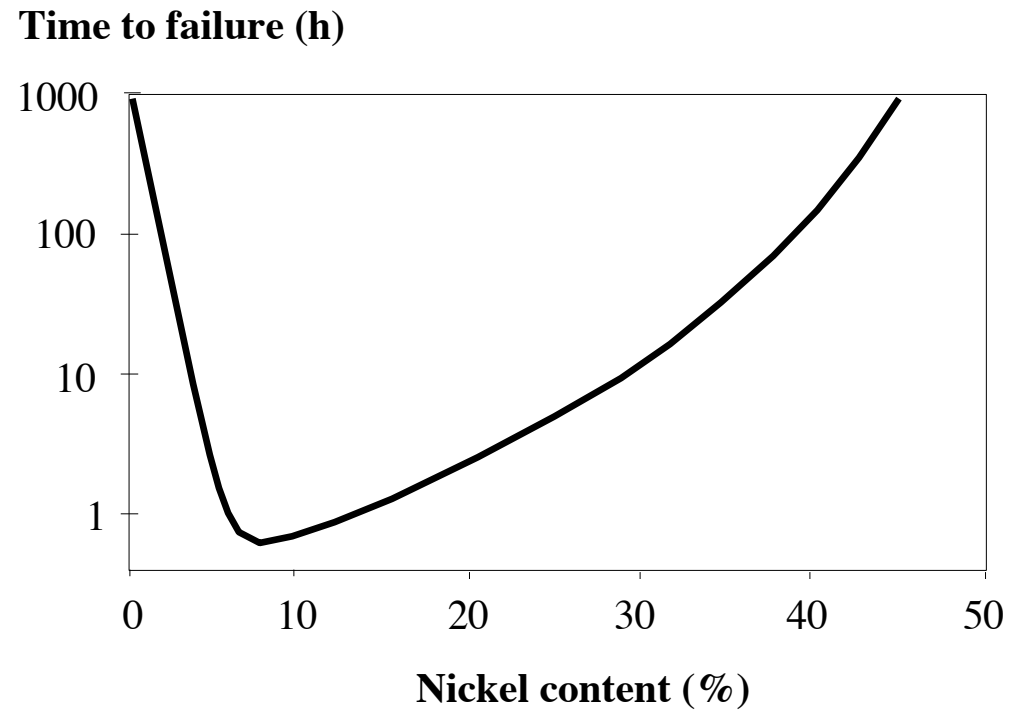
ASTM G36 Boiling MgCl₂ Tests



Petzl Hanger

Unloaded Hanger	MgCl ₂ % (T, °C)	Time to Crack, h
316L	43, (155)	<4.5
	35, (125)	<26

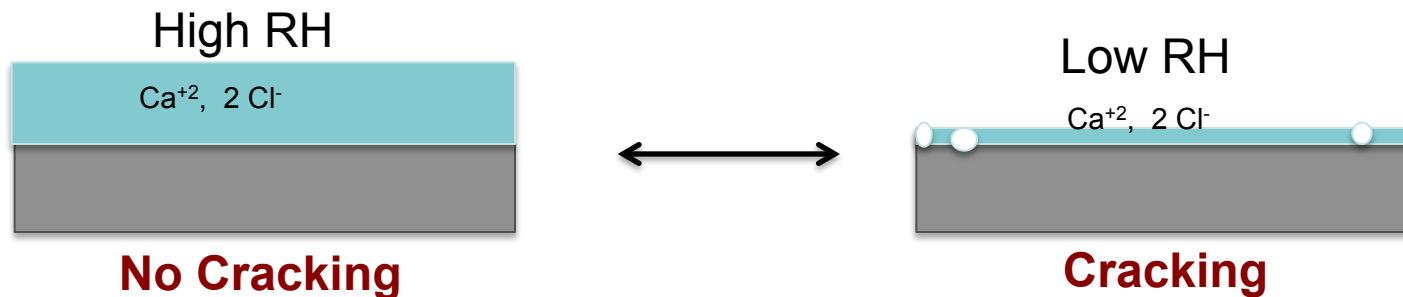
Boiling MgCl_2 Tests



Stress corrosion cracking susceptibility in boiling MgCl_2 as a function of nickel content (4).

Chloride Film SCC Tests Ambient Temperature

Shoji, 1989



- Tests conducted on U-bend specimens 304L, 316L containing salt deposits: NaCl, MgCl₂, CaCl₂, ZnCl₂
 - Tests designed for films of maximum chloride concentration
 - Test duration: 2 years, ambient temperature
- **Cracking occurred with maximum concentrations for Mg, Ca, Zn chloride salts BUT NOT NaCl.**

Saturated Chloride Films

Importance of Humidity

Salt	Saturated concentration, wt% as Cl	Relative Humidity required for saturated Cl solutions (%)
NaCl NO FAILURE	16	75
MgCl₂ FAILURE	27	33
CaCl₂ FAILURE	29	31
ZnCl₂ FAILURE	42	10

Low humidity required for Mg, Ca, Zn chloride salts to cause SCC on austenitic stainless steels.

Thailand SCC Case Study

Hanger Fragment



Available Fragment



Example Hanger and Bolt

- Used at Railay Beach
- Installed 1994, 15m from cliff base contacting ocean at high tide
- Hanger broke in 2004 when tested by hand.

Petzl Hanger

Chemistry & Hardness

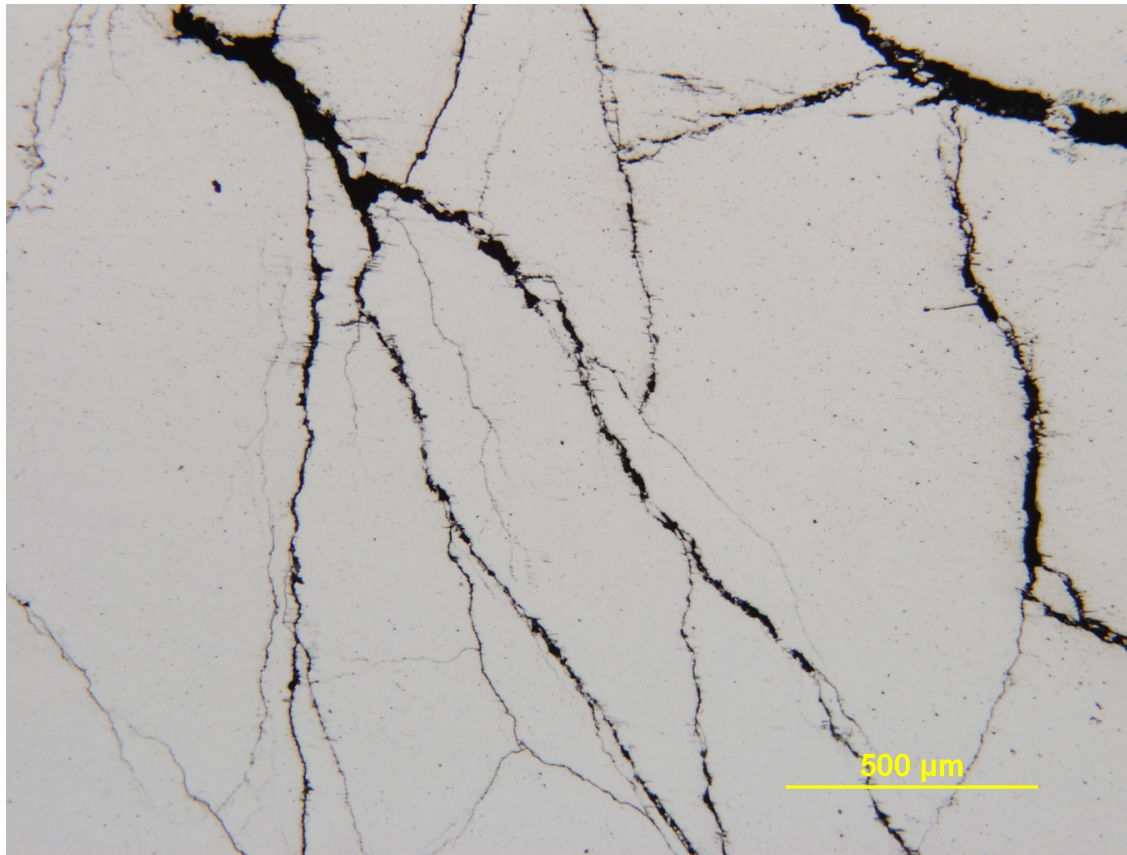


- Hanger
 - 316L, 0.14 in thickness, rated 25 kN
- Intact hanger: 350 Hv hardness
 - Typical Annealed 316L is 230 Hv

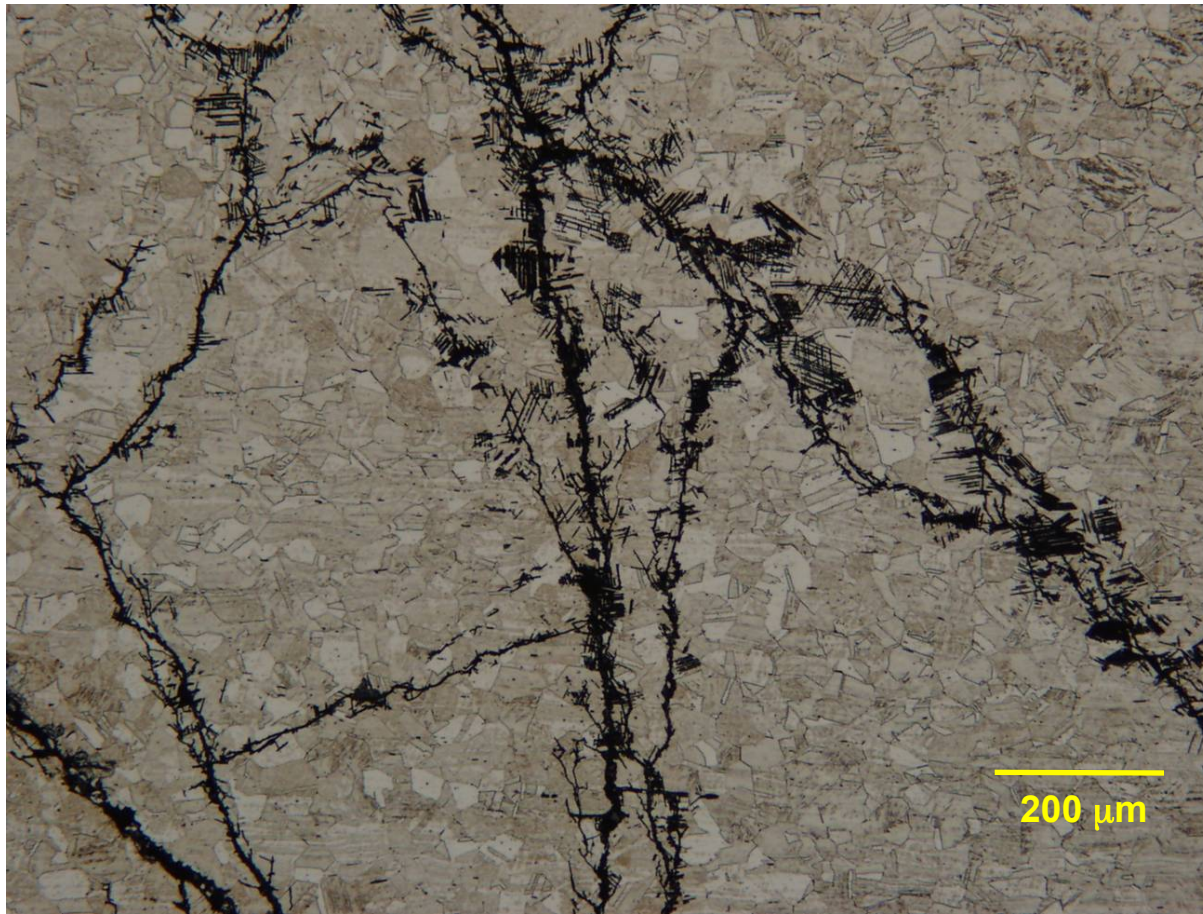
Chemical Analysis (wt pct):

C	Cr	Ni	Mn	Mo	P	Si	S
0.018	16.5	10.2	1.8	2.1	0.024	0.61	<0.005

Optical Microscopy Unetched Surface, A-A'

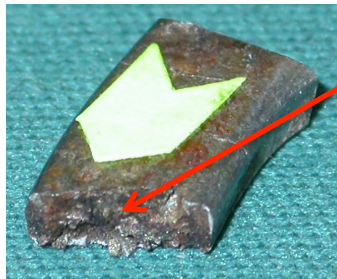


Optical Microscopy- Etched Microstructure, A-A'



Analysis of Corrosion Product

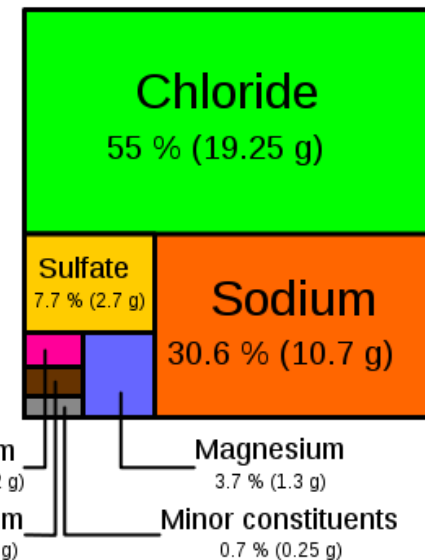
XPS/ESCA



Fe, Si, Cr, Ni, Cl, Na, Ca, S,
O, Mg, Al detected in solid.

Cation Ratio	Sea Salt Ratio	Failed Hanger Ratio
Na / Ca	25.5 / 1	1 / 1
Na / Mg	8.3 / 1	1 / 6.4

Sea salts



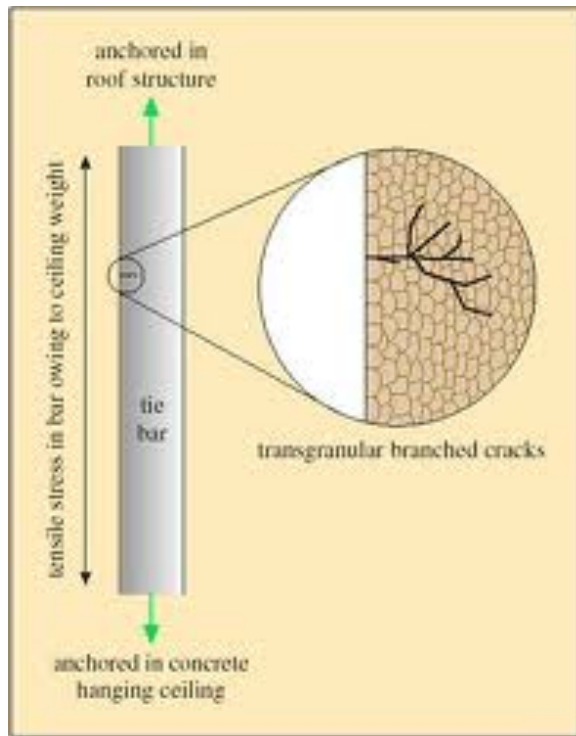
Solids on hanger NOT consistent with sea salt exposure
Very high levels of Mg, Ca

Tower Karst Geology 101



- Thailand tower karst undergoes tropical erosion
- Lush vegetation leads to very acidic soil waters
- Limestone normally dissolved by CO₂-containing water
 - Rainwater pH~5.6
 - Soil water in tropics as low as pH~3, much more aggressive in dissolving limestone
- Hot tropical sun evaporates water films, re-precipitates Ca, Mg minerals, results in features such as stalactites

Another Case Study: Indoor Swimming Pool Roof Failure Ambient SCC of Austenitic SS



- Uster, Switzerland indoor swimming pool roof collapsed in 1985 killing 12 people.
- Roof was suspended by 0.25” diameter 304 stainless rods in tension
 - Failed by TGSCC.
 - Failure does not occur on SS immersed in pool water.
 - Analysis of samples showed high levels of Cl and Mg, Zn, thought to be from construction materials.

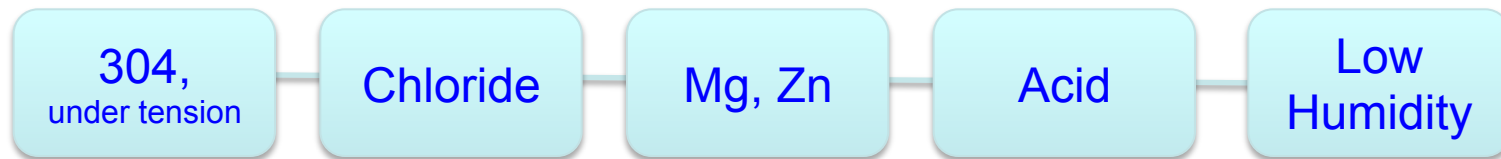
Indoor Pool Atmospheres

Olsted, 1991

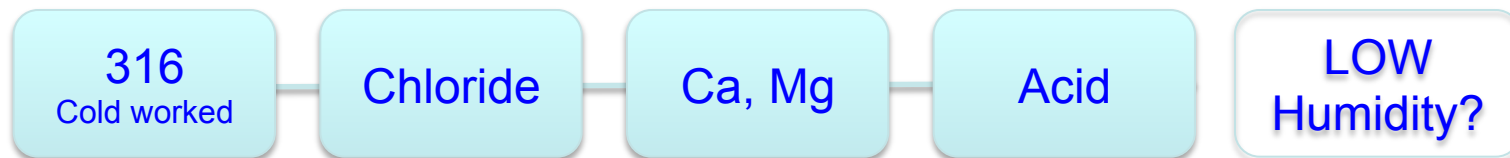
- Fountains produce aerosols of pool water that contain some chloramines
 - These aerosols thought to degrade to HCl
- Relative humidity low, 50-60%; RH lower in roof area
- Temperature range 26-28°C
- Mg, Zn from construction materials
- Conclusion: Combination of high chloride concentration, low pH and low humidity necessary for CI TGSCC.
 - High Cl/low RH unique to indoor swimming pool atmospheres??

Conditions Necessary for Atmospheric TGSCC The Perfect Storm

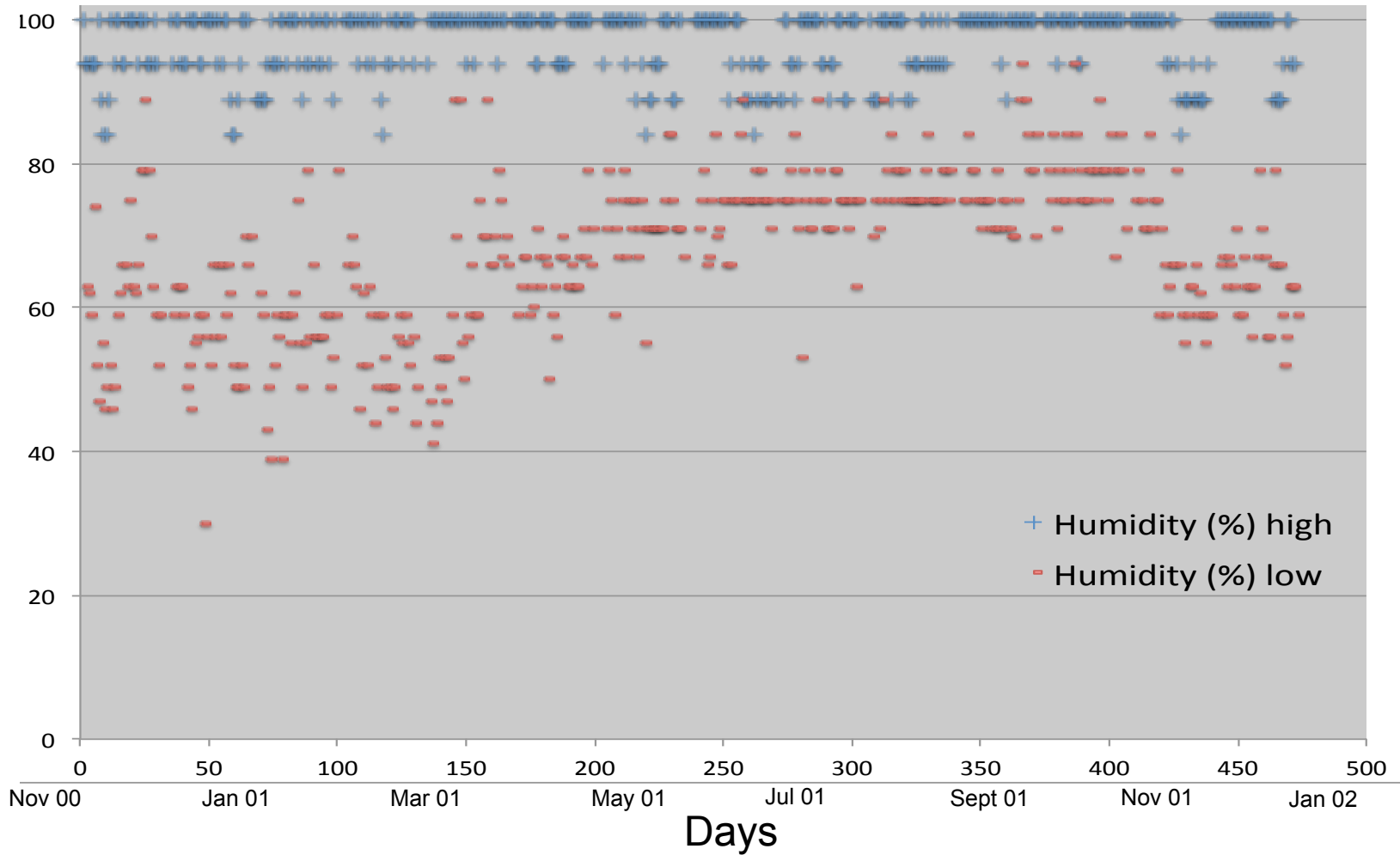
- Indoor swimming pool roof collapse



- Thailand bolt failures



Daily Relative Humidity Phuket, Thailand



→ RH frequently 50-60%

Source: *The Weather Underground*

Conclusions



- Cold-worked, austenitic stainless steel climbing anchors on tower karst formations in southern Thailand fail by ambient temperature, Cl-induced TGSCC
- Acidic soil waters associated with the high limestone dissolution-precipitation rates in tower karst allow for high concentrations of CaCl_2 and MgCl_2 to accumulate
- Humidity levels on the coast are within the range necessary for ambient temperature TGSCC to occur

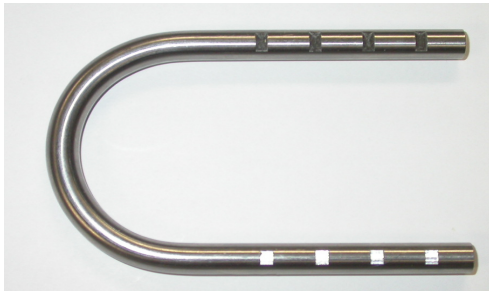
Titanium Replacement Anchors



Ushba Tortuga
Unalloyed Ti (Grade 2)

- Extremely corrosion resistant, virtually immune to chloride attack at any stress level
- Survived 28 days in boiling MgCl_2 , no cracking observed including weld area
- Can withstand hydrochloric acid to high concentrations
- Tough material
- Weldable

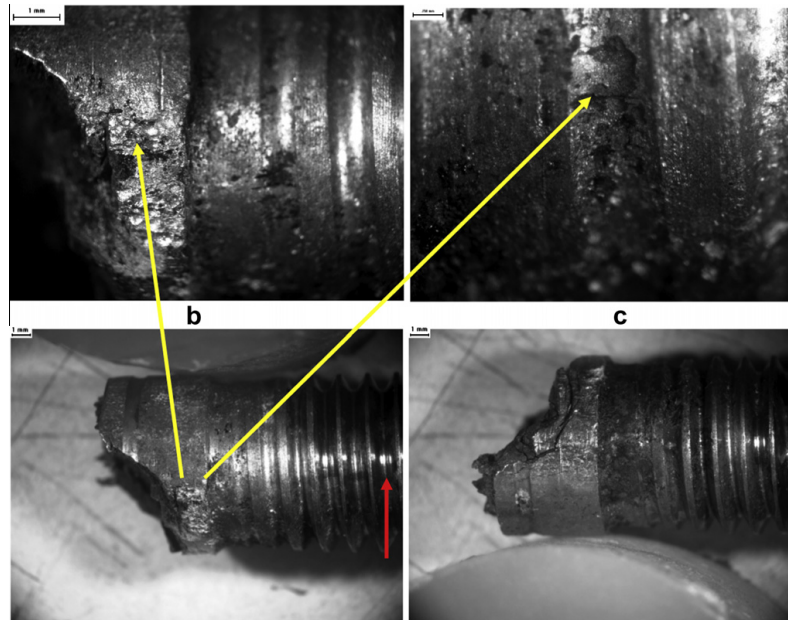
Titanium Replacement Anchors



Ti-6Al-4V
Grade 5

- Survived 28 days in boiling MgCl_2 , no cracking observed
- Ti-6Al-4V highly SCC resistant but not completely supported by manufacturers in aqueous chloride environments unless it's Grade 23 (extra low interstitials)
- Much stronger than Ti Grade 2

Stainless Steel Failure Varasova, Greece



- Climbing bolt 303 stainless
- Both pitting and SCC observed
- Many pits turned into cracks

Acknowledgments

- Josh Lyons, Thaitanium project
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- John Byrnes, Mike Shelton
- Exponent Failure Analysis Associates, Larry Eiselstein

TMI Slides

Root Cause Analysis

- What environmental conditions are responsible for the extensive TGSCC of austenitic stainless in Thailand?

Factors	Environmental Condition
Chloride (sea water)	Necessary but not sufficient
High Humidity	Should help prevent corrosion by diluting chloride films
Warm Temperatures	Generally below 60°C is considered safe unless exposed to very corrosive conditions
Acidic Soil Waters	Much more aggressive when combined with chloride
Dissolved Limestone	Chloride salts are much more aggressive as CaCl₂ or MgCl₂
Low Humidity Intervals	Makes CaCl₂, MgCl₂ salts extremely corrosive

Ferritic Stainless Steels

- Generally very resistant to chloride SCC because low nickel content
- Not strengthened by cold work or heat treatment
- Mechanical properties tradeoff compared to austenitic stainless
 - Much lower toughness
 - Generally limited to thin sections (3mm)
 - As section size increases, ductility decreases
 - Ductile-to-brittle transition phase can be room temperature for some specimen sizes
- Variable chloride pitting corrosion resistance

Stainless Steels

Pitting Corrosion Resistance

- A high Pitting Resistance Equivalence Number (PREN) is desired

$$\text{PREN} = \%Cr + 3.3(\%Mo) + 16(\%N)$$

A PREN of 32 is considered the minimum for seawater pitting resistance.

Metallurgical Category	Alloy	PREN
Austenitic	Type 304, 304L	18.0
	Type 304N, 304LN	19.6
	Type 316, 316L	22.6
	Type 316N, 316LN	24.2
	Type 317, 317L	27.9
	Type 317LMN	31.8
	AL-6XN	42.7
	Alloy 625	46.4
	Alloy C-276	73.9
	20Cb-3	25.6
Duplex	Alloy 2205	30.5
	7-MoPLUS	31.7
Ferritic	SEA-CURE Stainless	49.5
	Type 430	16.0
	Type 439	17.0
	Type 444	23.3

Duplex Stainless Steels

Boiling CaCl₂ Tests

Summary of test results for concentrated calcium chloride

Table 7

Material UNS No.	Exposure time [h]	Number of specimens			
		U-bend		4-PB	
		Tested	Failed due to SCC	Tested	Failed due to SCC
S30400	96	6	6	–	–
	340	–	–	4	4
S32101	500	6	0	2	0
S32304	500	6	0	2	0
S32205	500	6	0	2	0
S32750	500	–	–	2	0

Duplex Stainless Steels Boiling MgCl₂ Tests

Summary of test results for concentrated magnesium chloride

Table 8

Material UNS No.	Exposure time [h]	Number of specimens	
		Tested	Failed due to SCC
S30400	24	3	3
S32101	24	3	3
S32304	24	3	3
S32205	24	3	3

SCC Susceptibility

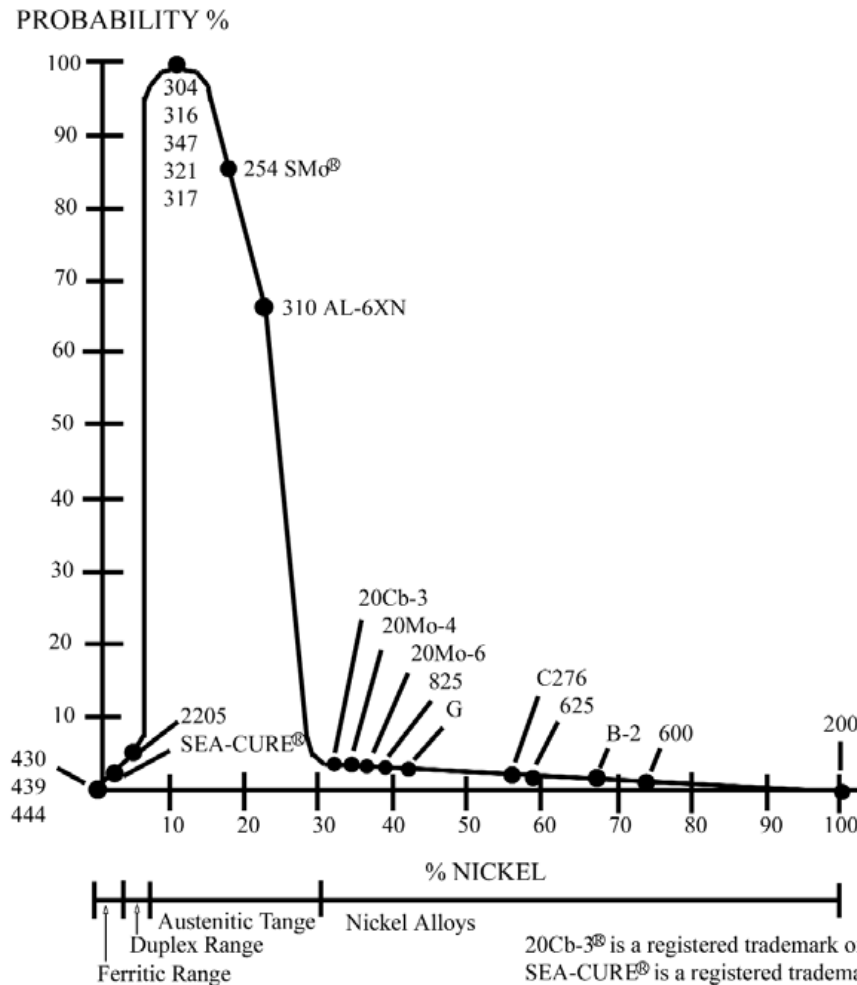


Figure 7: Probability of chloride stress corrosion cracking occurring as a function of the nickel content of the alloy. Cracking will not occur below the stress corrosion cracking threshold temperature, but will above.



Boiling MgCl₂ Tests

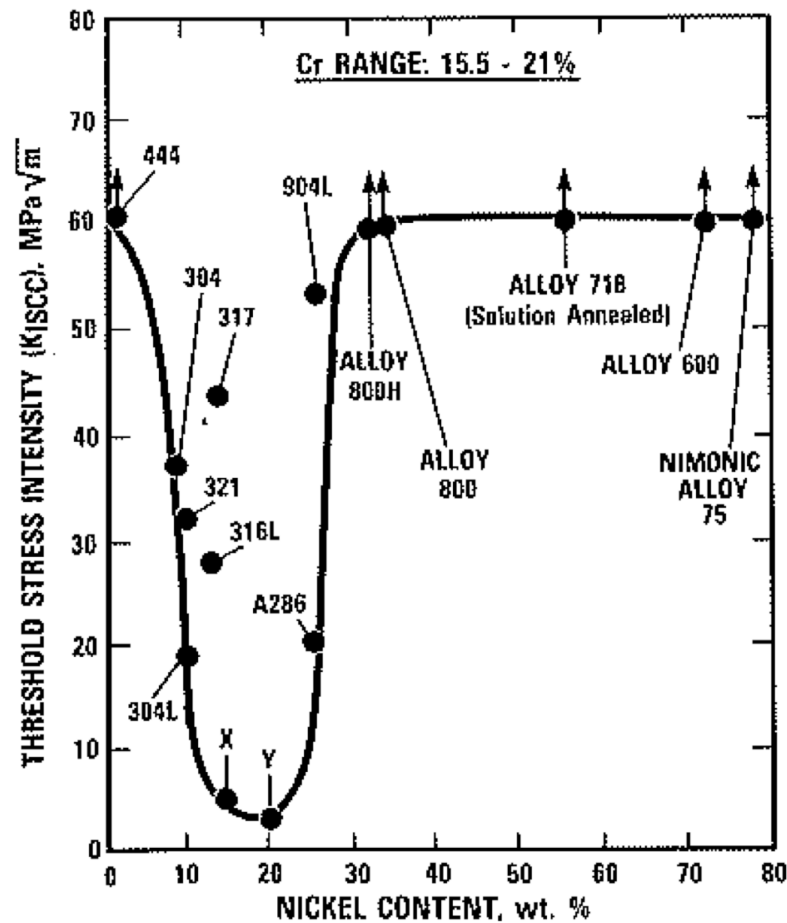
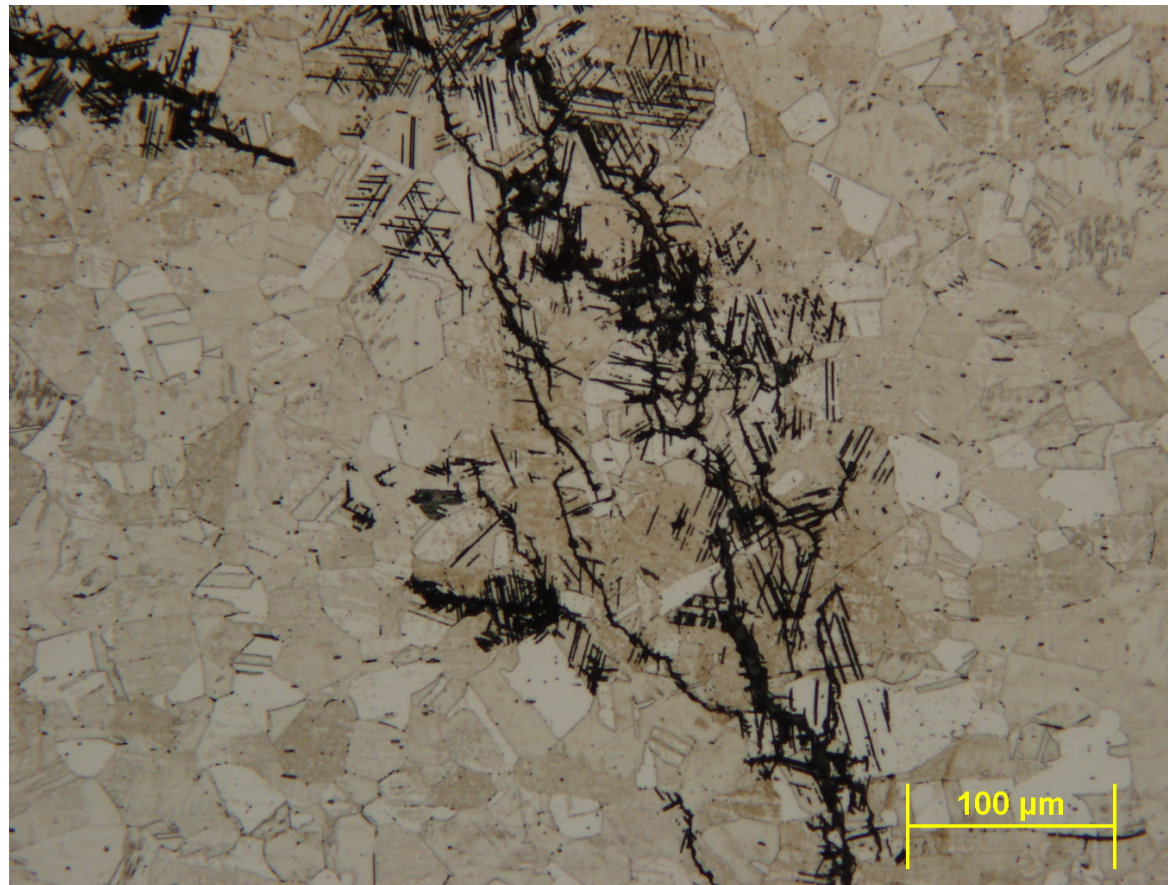


Fig. 8 Effect of nickel content on the stress-corrosion threshold stress intensity of various alloys in an aerated aqueous 22% NaCl solution at 105 °C (220 °F). Alloys X and Y are German heat-resistant grades. After Ref 27

Industry Tests Relevant to Climbing Hardware in Marine Environments

- Boiling MgCl_2 and CaCl_2 tests
 - Expect >1000h without cracking
- Acid Salt Spray Test
 - Use aggressive salts

Optical Microscopy- Etched Microstructure, A-A'



Boiling NaCl Tests High Temperature

		Test Temperature (Degrees C)					
		121	175		232		
		Chloride Content (ppm)					
Alloy	Ni %	1,000	10,000	100	1,000	100	1,000
S31603	11.0	Pass	Pass	Cracked	Cracked	Cracked	nt

Boiling NaCl Tests High Temperature

		Test Temperature (Degrees C)					
		121		175		232	
		Chloride Content (ppm)					
Alloy	Ni %	1,000	10,000	100	1,000	100	1,000
S43035	0.4	nt	nt	nt	Pass	Pass	Pass
S44660	2.0	nt	nt	nt	Pass	Pass	Cracked
S31803	5.0	nt	nt	nt	Pass	Cracked	nt
S30403	8.0	nt	Cracked	Cracked	Cracked	Cracked	Cracked
S31603	11.0	Pass	Pass	Cracked	Cracked	Cracked	nt
S31254	18.0	nt	nt	nt	Pass	Cracked	Cracked
N08367	25.0	nt	nt	nt	Pass	Cracked	Cracked

nt = Not Tested Pass = No cracks in 28 days