STRESS CORROSION (“Stress Corrosion Cracking” - SCC)

Under tensile stress, and in a suitable environment, some metals and alloys crack . . . usually, SCC noted by absence of significant surface attack . . . occurs in “ductile” materials.

“Transgranular” SCC

Cross section of stress-corrosion crack in stainless steel.

"Intergranular" SCC ("IGSCC")

Two original "classic" examples of SCC

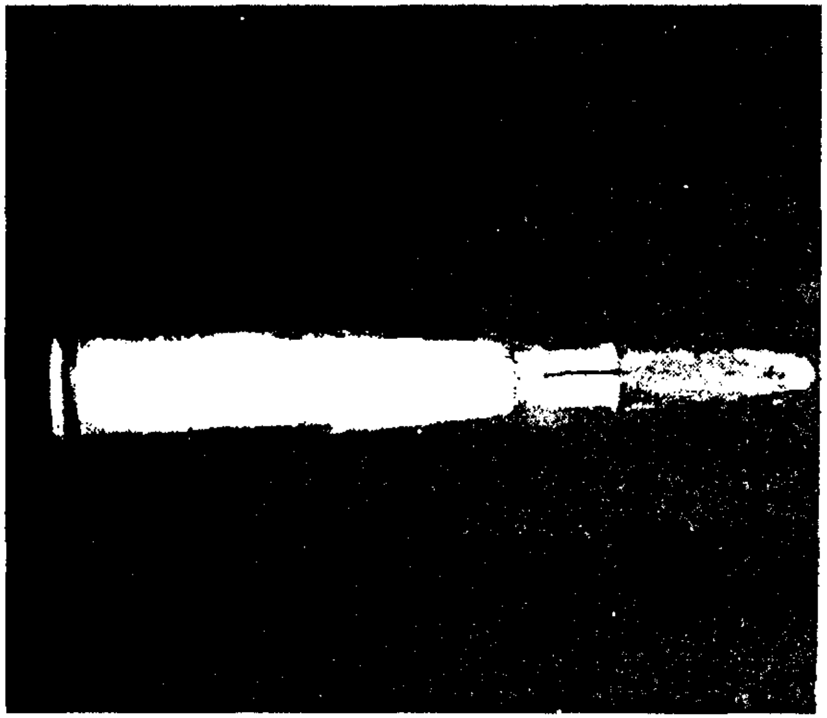
- **"season cracking" of brass;**
- **"caustic embrittlement" of CS;**

both terms obsolete.

Intergranular stress corrosion cracking of brass.

"Season Cracking"

SCC of brass cartridge cases.



Season cracking of German ammunition.

Occur where brass case is crimped onto bullet, i.e., in area of high residual stress.

Common in warm, wet environments (e.g., tropics).

Ammonia (from decomposition of organic matter, etc.) must be present.

"Caustic Embrittlement"

Early steam boilers (19th and early 20th century) of riveted carbon steel.

Both stationary and locomotive engines often exploded.

Examination showed:

- **cracks or "brittle" failures around rivet holes;**
- **areas susceptible were cold worked by riveting (i.e., had high residual stresses);**
- **whitish deposits in cracked regions were mostly "caustic" (i.e., sodium hydroxide from chemical treatment of boiler water); small leaks at rivets would concentrate NaOH and even dry out to solid.**

SCC revealed by dye penetrant.

Carbon steel plate from a caustic storage tank failed by caustic embrittlement.

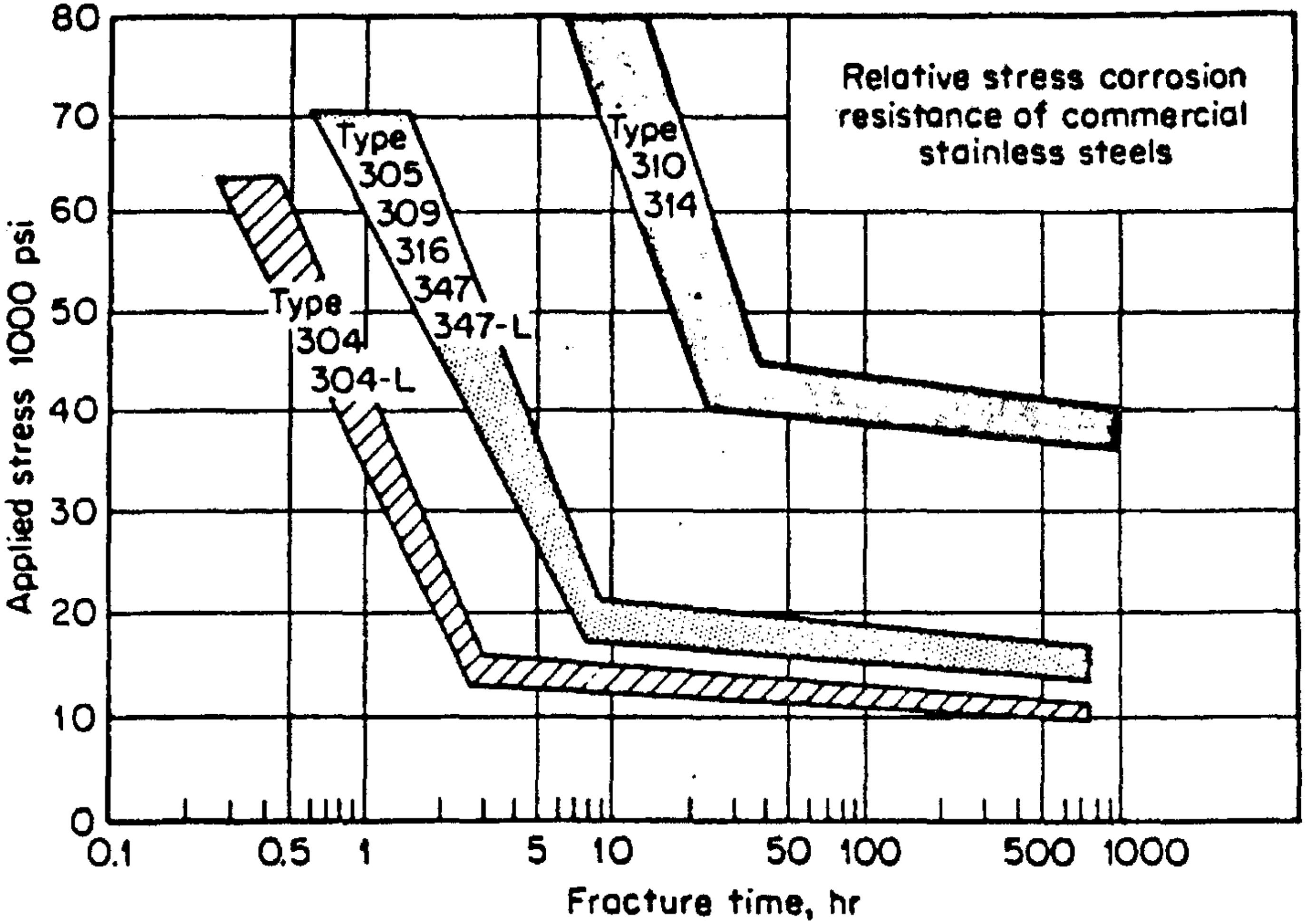
Factors important in SCC:

- environmental composition;
- stress;
- temperature;
- metal composition;
- metal microstructure;

e.g., brasses crack in NH_3, not in Cl^-;
SSs crack in Cl^-, not in NH_3;
SSs crack in caustic, not in H_2SO_4, HNO_3, CH_3COOH, . . . etc.

STRESS

The greater the stress on the material, the quicker it will crack. (N.B. in fabricated components, there are usually RESIDUAL STRESSES from cold working, welding, surface treatment such as grinding or shot peening, etc., as well as APPLIED STRESSES from the service, such as hydrostatic, vapour pressure of contents, bending loads, etc.).



DISCUSS:
how would you obtain such a curve and what does it mean?

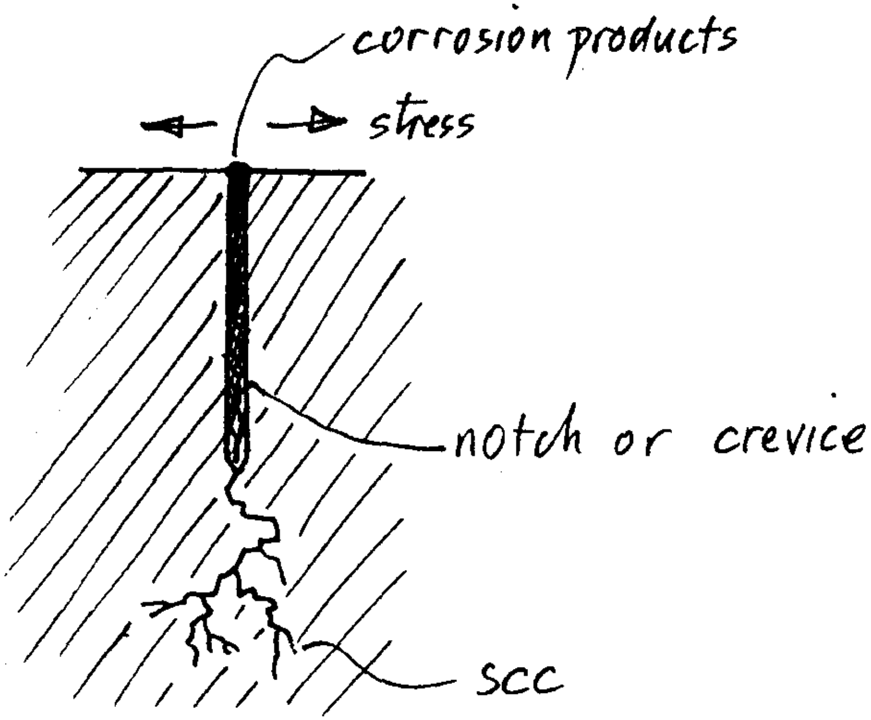
Composite curves illustrating the relative stress corrosion-cracking resistance for commercial stainless steels in boiling 42% magnesium chloride.

The MAXIMUM stress you can apply before SCC is formed (c.f. MINIMUM stress to be applied compressively to prevent SCC) depends on alloy (composition and structure), temperature, and environment composition.

Such "THRESHOLD" stresses may be between 10% & 70% of the yield stress - <u>Q.V.</u>

<u>N.B</u>. residual stresses from welding steel can be close to the yield point.

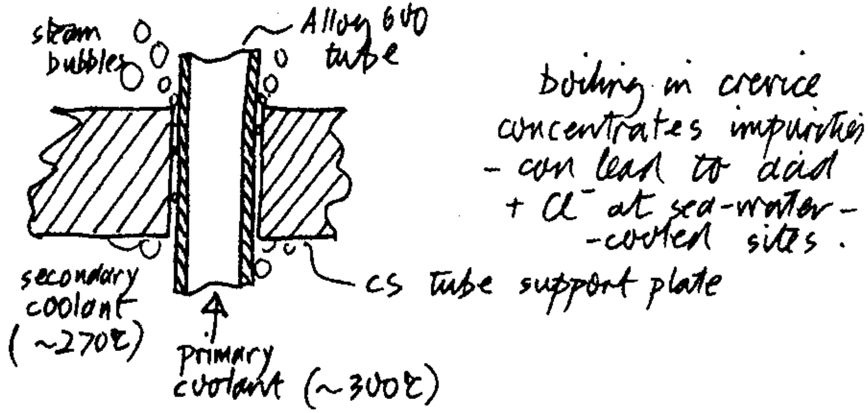
<u>N.B</u>. corrosion products can induce large stresses by "wedging".



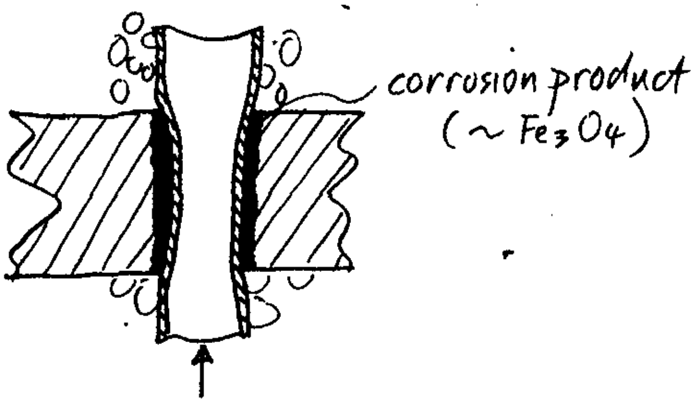
N.B. small-radius notch tip and even smaller-radius crack tip are STRESS RAISERS

A "wedging action" by corrosion products of ~ 10 ksi (10,000 psi) can induce → ~ 300 ksi (300,000 psi) at the crack tip.

Corrosion product wedging → “denting” of S.G. tubes in some PWRs . . .



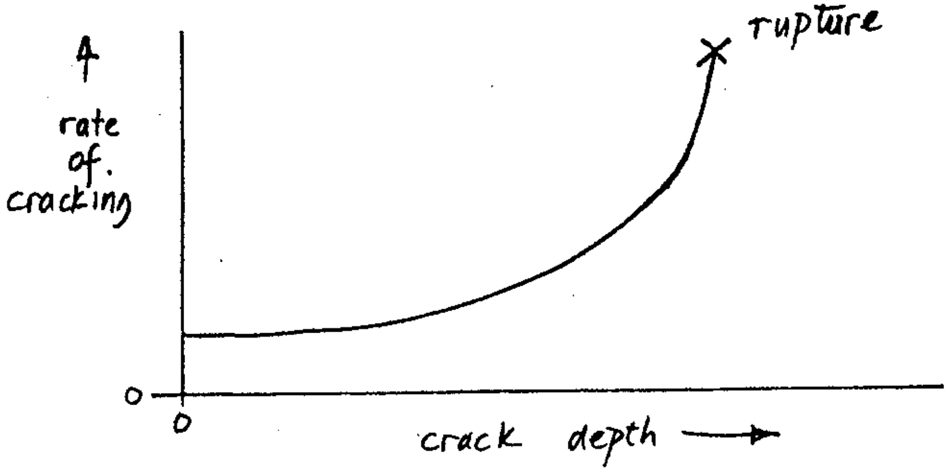
boiling in crevice concentrates impurities - can lead to acid + Cl⁻ at seawater- cooled sites.

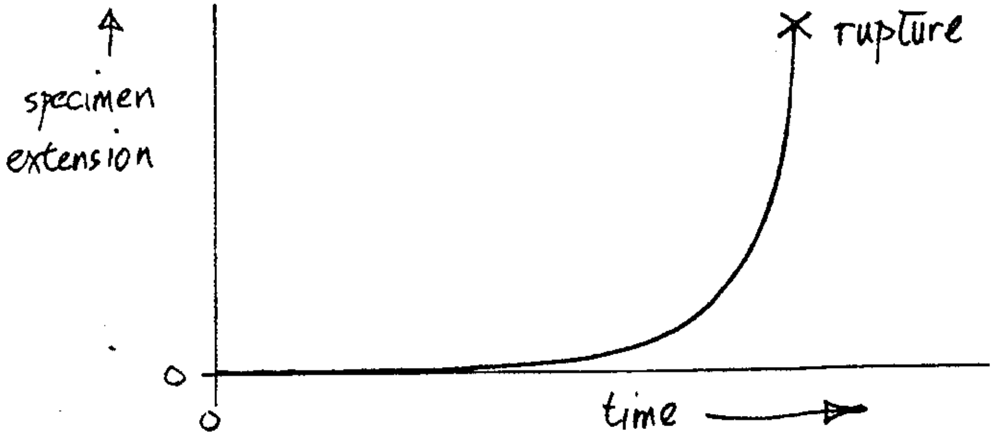


“Hour-glassing” of Alloy- 600 tubes led to severe straining and cracking of tubes. Surrey PWR in U.S. was first to replace S.Gs. because of denting.

Time to Failure

Major damage during SCC occurs in late stages as cracks progress, cross-sectional area decreases, stress increases until final failure occurs by mechanical rupture.





Environmental Factors

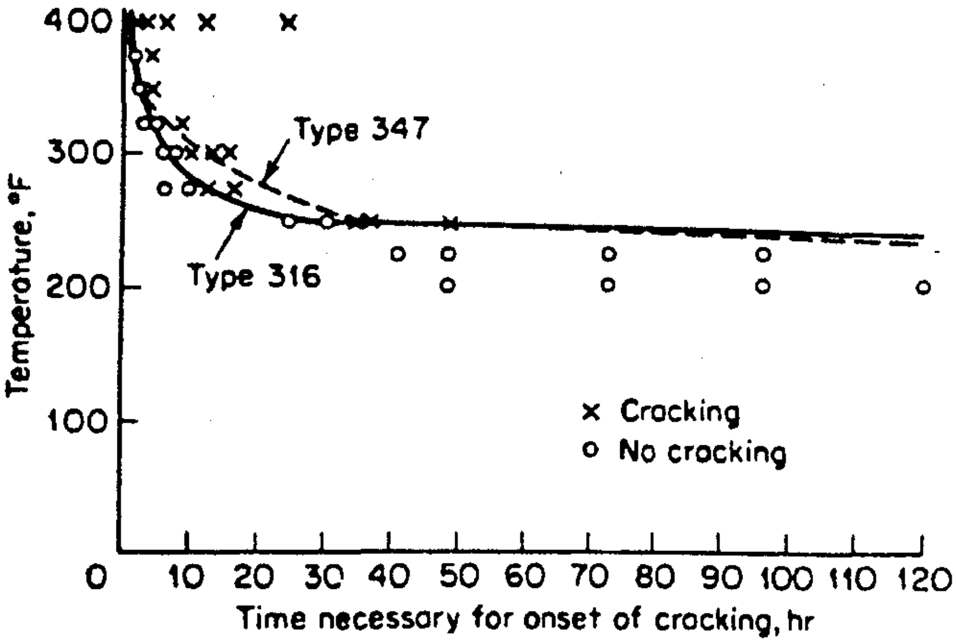
No general pattern, SCC common in aqueous solutions, liquid metals; also found in fused salts, nonaqueous inorganic liquids . . .

Environments that may cause stress corrosion of metals and alloys

Material	Environment	Material	Environment
Aluminum alloys	NaCl-H_2O_2 solutions	Ordinary steels	NAOH solutions
	NaCl solutions		NaOH-Na_2SiO_2 solutions
	Seawater		Calcium, ammonium, and sodium nitrate solutions
	Air, water vapor		
Copper alloys	Ammonia vapors and solutions		Mixed acids (H_2SO_4-HNO_3)
	Amines		HCN solutions
	Water, water vapor		Acidic H_2S solutions
Gold alloys	$FeCl_3$ solutions		Seawater
	Acetic acid-salt solutions		Molten Na-Pb alloys
Inconel	Caustic soda solutions	Stainless steels	Acid chloride solutions such as $MgCl_2$ and $BaCl_2$
Lead	Lead acetate solutions		
Magnesium alloys	NaCl-K_2CrO_4 solutions		
	Rural and coastal atmospheres		NaCl-H_2O_2 solutions
			Seawater
	Distilled water		H_2S
Monel	Fused caustic soda		NaOH-H_2S solutions
	Hydrofluoric acid		Condensing steam from chloride waters
	Hydrofluosilicic acid		
Nickel	Fused caustic soda	Titanium alloys	Red fuming nitric acid, seawater, N_2O_4, methanol-HCl

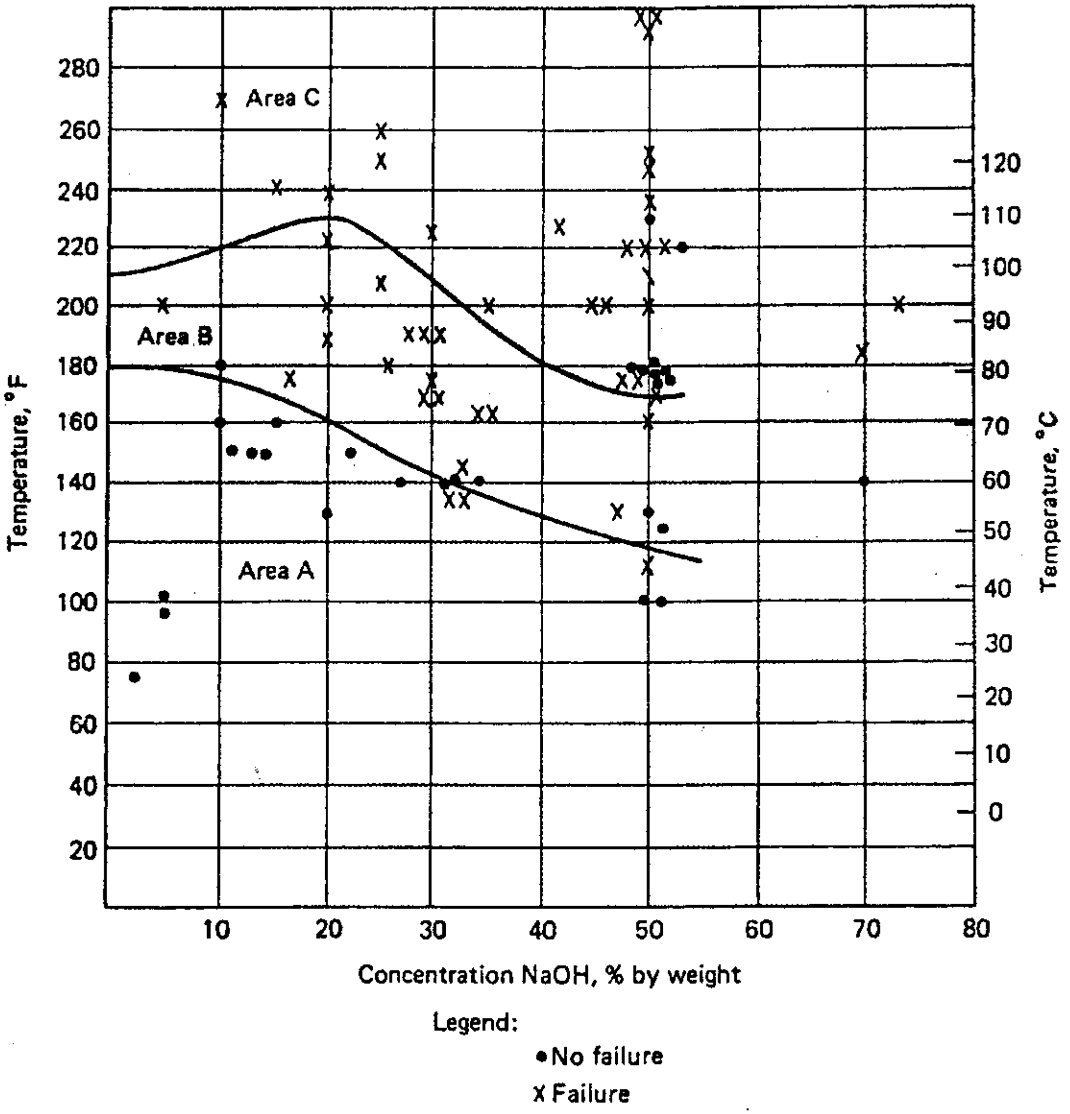
N.B. Coriou (France) cracked Inconel-600 in pure water at ~300°C in 1959!!!

Increasing temperature accelerates SCC:



Effect of temperature on time for crack initiation in types 316 and 347 stainless steels in water containing 875 ppm NaCl.

Most susceptible alloys crack ~ < 100°C; Mg alloys crack at room temperature. Alternate wetting and drying may aggravate SCC - accelerate crack growth (possibly because of increasing concentration of corrosive component as dryness is approached).



NACE caustic soda chart superimposed over the data on which it is based.

Area A:
Carbon steel, no stress relief necessary; stress relieve welded steam-traced lines;

Area B:
Carbon steel; stress relieve welds and bends;

Area C:
Application of nickel alloys to be considered in this area; nickel alloy trim for valves in areas B and C.

Metallurgical Factors in IGSCC

In austenitic SS and Ni alloys, sensitization is of major importance in determining susceptibility to IGSCC . . . depletion of grain boundaries in Cr because of carbide precipitation makes them vulnerable to attack.

e.g., IGSCC of recirculation piping in BWRs (type 304 SS) induced by ~ 200 ppb dissolved oxygen in the otherwise pure H_2O coolant resulted in a major replacement problem. Plants using L-grade experienced very much less SCC.

Al alloys (e.g., with Mg and Zn) are also susceptible to IGSCC because of precipitation within grain boundaries . . . Mg-rich precipitates can denude the grain boundaries of Mg, make them susceptible to attack in aqueous media.

N.B. In grain-boundary- precipitate mechanisms for inducing IGSCC, very local galvanic effects between precipitates and matrix are important:

- **some precipitates are ANODIC;**
- **some precipitates are CATHODIC.**

Grain boundary segregation of alloy constituents or impurities (without precipitation of separate phases) can also induce IGSCC.

e.g., Mg enrichment of grain boundaries in Al alloys is a factor in IGSCC

- **promotes local dissolution and hydrogen entry (maybe to form hydride, MgH);**
- **also . . . grain boundary enrichment of impurities and/or C in Fe-base alloys, Ni-base alloys and austenitic stainless steels can contribute to IGSCC;**
- **segregation of P, Si, S, N. B reported; only clear link with IGSCC reported for P in austenitic SS in oxidizing aqueous solutions, for P in ferritic alloys in nitrate and caustic solutions.**

Transgranular SCC

Lattice structure in metal/alloy matrix important: dislocation emergence, movement along slip planes under stress, and similar factors that can disrupt passivating films, will promote dissolution of metal at highly localized and strained areas.

Irradiation-Assisted SCC (IASCC).

Since ~ 1987, some in-reactor components have cracked in LWRs . . . generally in core-support structures at the top of the vessel (austenitic SS, Ni alloys). More widespread in BWRs than PWRs . . . radiolytic chemical species (especially oxidizing radicals) seem to be the cause.

Mechanism of SCC

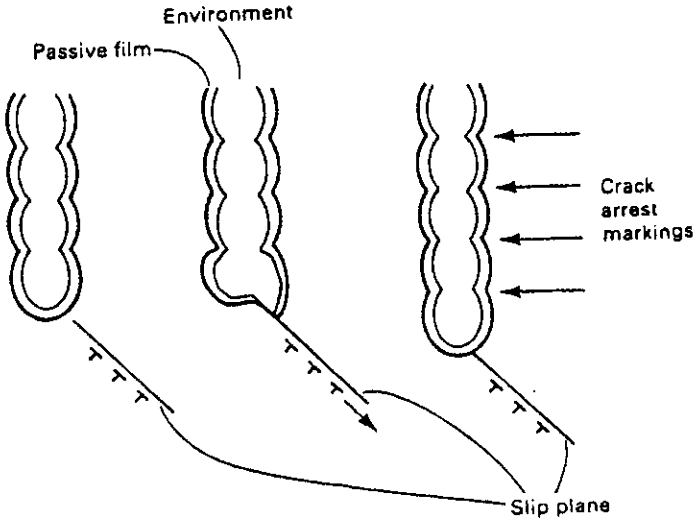
SCC is very complex; probably no single mechanism, but several operating at the same time.
Models (scientific descriptions) of mechanisms of two types:

- dissolution;
- mechanical fracture.

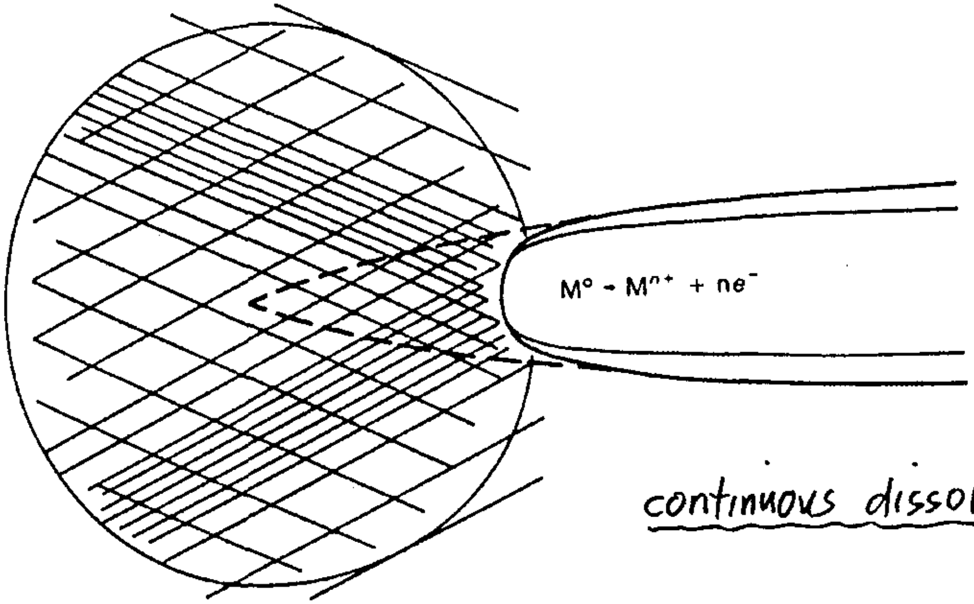
Dissolution Models of Crack Propagation.

Major model is based on Film Rupture . . . ("slip-dissolution") . . . high stresses at crack tip create local area of plastic deformation - ruptures passive films, exposed metal dissolves rapidly . . . some say periodic dissolution and re-passivation, some say crack tip always bare.

periodic rupture



Schematic representation of crack propagation by the film rupture model.



continuous dissolution

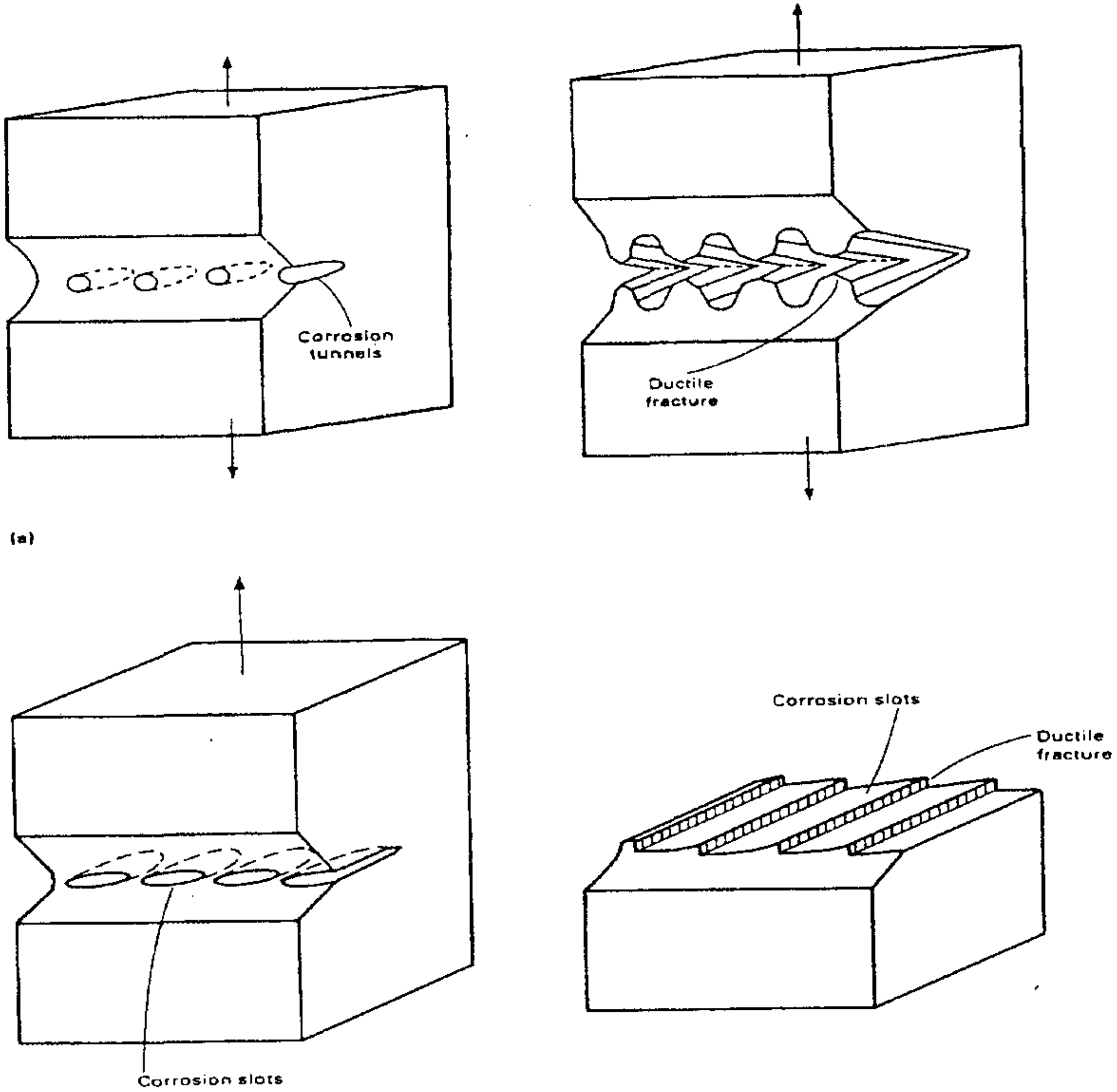
Mechanical Fracture Models of Crack Propagation

- **Corrosion Tunnel;**

Corrosion tunnel models.

(a) Schematic of tunnel model showing the initiation of a crack by the formation of corrosion tunnels at slip steps and ductile deformation and fracture of the remaining ligaments.

(b) Schematic diagram of the tunnel mechanism of SSC and flat slot formation.



- **Adsorption of impurities at the crack tip promotes the nucleation of dislocations**
    - **lead to shear-like fracture (seemingly brittle);**
- **Tarnish Rupture;**

  Cracks propagate by alternate film growth and (brittle) film fracture, followed by rapid film formation over exposed metal,
- **Film-Induced Cleavage;**
    - **Thin film forms;**
    - **Brittle crack initiates in layer;**
    - **Crack moves from film into matrix;**
    - **Crack continues through ductile matrix until it blunts and stops;**
    - **Process repeats;**
- **Adsorption-Induced Brittle Fracture;**

  Species adsorbing at crack tip alter inter-atomic bond strengths, lower stress required for fracture; propagation should be continuous;
- **Hydrogen Embrittlement;**

  Cathodic processes involving hydrogen-ion reduction can inject H into matrix . . . this can embrittle metal, promote cracking . . . most likely in ferritic steels also possible in Ni-base, Ti and Al alloys.

Prevention of SCC

1. ***Lowering the stress*** **below the threshold value if one exists. This may be done by annealing in the case of residual stresses, thickening the section, or reducing the load. Plain carbon steels may be stress-relief annealed at 1100 to 1200°F, and the austenitic stainless steels are frequently stress-relieved at temperatures ranging from 1500 to 1700°F.**
2. ***Eliminating the critical environmental species*** **by, for example, de-gasification, demineralization, or distillation.**
3. ***Changing the alloy*** **is one possible recourse if neither the environment nor stress can be changed. For example, it is common practice to use Inconel (raising the nickel content) when type 304 stainless steel is not satisfactory. Although carbon steel is less resistant to general corrosion, it is more resistant to stress-corrosion cracking than are the stainless steels. Thus, under conditions which tend to produce stress-corrosion cracking, carbon steels are often found to be more satisfactory than the stainless steels. For example, heat exchangers used in contact with seawater or brackish waters are often constructed of ordinary mild steel.**
4. ***Applying cathodic protection*** **to the structure with an external power supply or consumable anodes. Cathodic protection should only be used to protect installations where it is positively known that stress-corrosion cracking is the cause of fracture, since hydrogen embrittlement effects are accelerated by impressed cathodic currents.**

5. ***Adding inhibitors*** **to the system if feasible. Phosphates and other inorganic and organic corrosion inhibitors have been used successfully to reduce stress-corrosion cracking effects in mildly corrosive mediums. As in all inhibitor applications, sufficient inhibitor should be added to prevent the possibility of localized corrosion and pitting.**
6. ***Coatings*** **are sometimes used, and they depend on keeping the environment away from the metal - for example, coating vessels and pipes that are covered with insulation. In general, however, this procedure may be risky for bare metal.**
7. ***Shot-peening*** **(also known as shot-blasting) produces residual compressive stresses in the surface of the metal. Woelful and Mulhall* show very substantial improvement in resistance to stress corrosion as a result of peening with glass beads. Type 410 stainless was exposed to 3% NaCl at room temperature; type 304 to 42% $MgCl_2$ at 150°C; and aluminum alloy 7075-T6 to a water solution of $K_2Cr_2O_7$-CrO_3-NaCl at room temperature.**

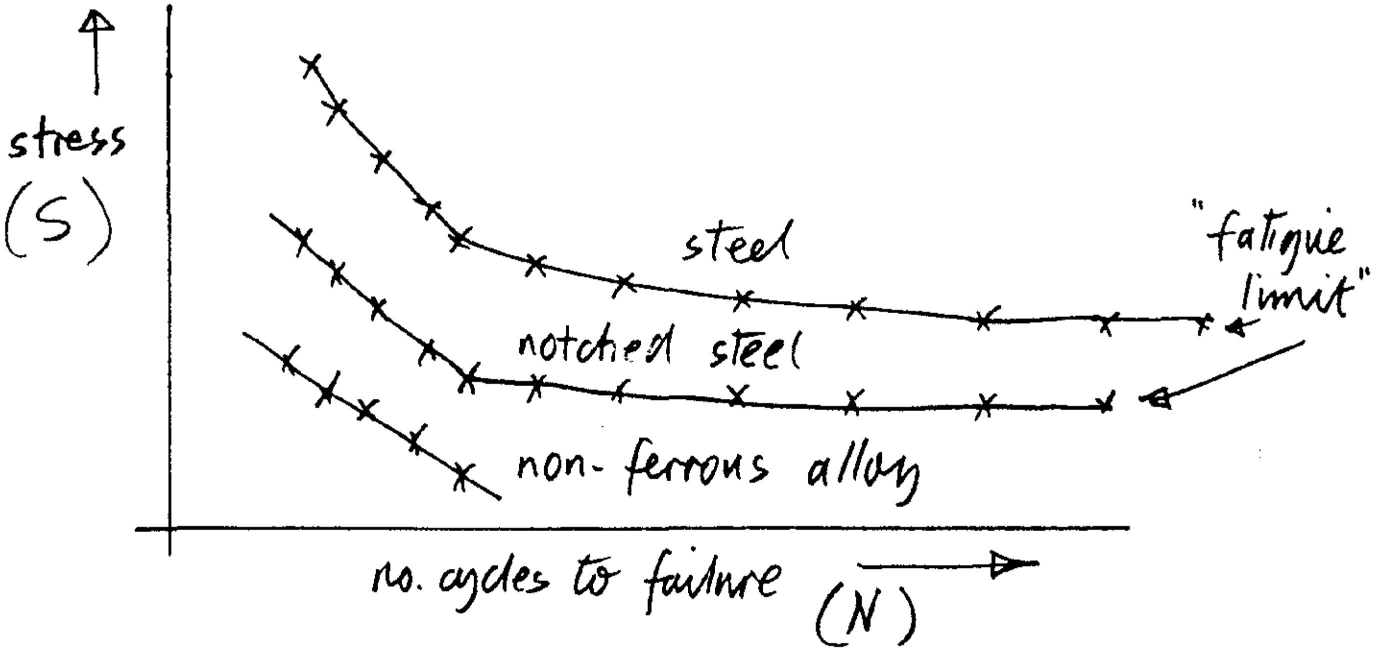
*M. Woelful and R. Mulhall, Glass Bead Impact Testing, *Meta Progr.* 57-59 (Sept. 1982).

Corrosion Fatigue

The fatigue fracture of a metal aggravated by a corrosive environment or the stress corrosion cracking of a metal aggravated by cyclic stress.

N.B. Fatigue fracture usually occurs at stresses below the yield point but after many cyclic applications of the stress.

Typical "S-N" curves:



Fatigue-fractured material often shows most of the fracture face shiny metallic, with the final area to fracture mechanically (by brittle fracture of a reduced cross-section) having a rough crystalline appearance . . .

fatigue cracks would have started here, cyclic stresses would have "hammered" surfaces together

brittle fracture

If corrosion-fatigue occurs, the "shiny-metallic" area might be covered with corrosion products; BUT <u>normal</u> fatigue fractures may also develop corrosion products - depends on environment, stress pattern, etc.

N.B. In normal fatigue, the frequency of the stress cycles is not important. (can do accelerated fatigue tests at high frequency - the total number of cycles determines fatigue).

BUT in corrosion fatigue, "low-cycle" stresses are more damaging than high-frequency stresses.

Environment is important.

e.g., in seawater:

- **Al bronzes and type 300 series SS lose 20-30% of normal fatigue resistance.**
- **high Cr alloys lose 60-70% resistance.**

N.B. Cyclic loads mean lower allowable stresses, this must be designed into components; if there is also a corrosive environment, the allowable stresses are EVEN LOWER.

Prevention of Corrosion Fatigue

- Change design so as to reduce stress and/or cycling;
- Reduce stress by heat treatment (for residual stress), shot peening (to change surface residual stresses to COMPRESSIVE);
- Use corrosion inhibitor with care!
- Use coatings . . . electrodeposited
    - Zn;
    - Cr;
    - Ni;
    - Cu;

and

- nitrided layers (heating of steels in contact with N-containing material e.g., NH_3, NaCN, etc.).