# Stress corrosion cracking (SCC) and Fatigue corrosion in welding



Collected by M. Azadi



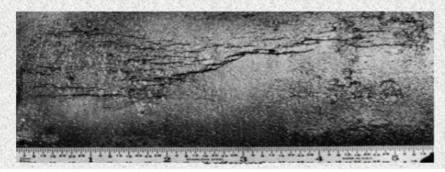


## References

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- 3. Stress-Corrosion Cracking: Materials Performance and Evaluation Hardcover, R. H. Jones (Editor) (1992)
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#### First SCC Inquiry

- 1985-1992 one company 5 SCC ruptures
- First Inquiry 1993
  - Considering current knowledge of SCC
  - Concluded that SCC managed properly



#### SCC Inquiry 1996

- Two ruptures in 1995
- Evidence SCC widespread on both gas and liquid pipelines
- Since 1977 22 failures
  - ♦ 12 ruptures, 10 leaks
- Provide a forum to share SCC knowledge
- Knowledge shared around world

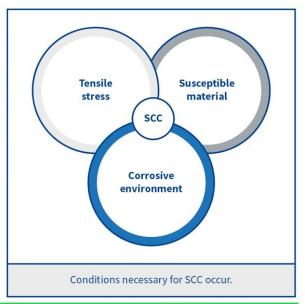
# Stress corrosion cracking (SCC)

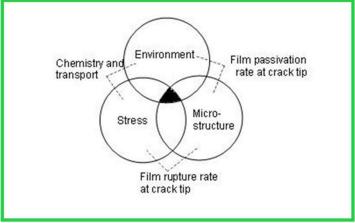
- SCC is a significant failure mechanism in materials science and engineering.
- SCC is the cracking induced by the combined influence of tensile stress and a corrosive environment.
- SCC is the propagation of often branched cracks in a material within a corrosive environment, potentially leading to the catastrophic failure of a component/structure, as the cracking appears brittle.
- SCC is the growth of crack formation in a susceptible material exposed to a corrosive environment while under tensile stress (either residual or applied). It leads to unexpected, sudden failure of normally ductile materials subjected to a static stress, well below the yield strength of the metal.

## **SCC** conditions

- Applied or residual stresses
- An aqueous corrosive medium
   (Chlorides and hydrogen sulphide are common),
- Elevated temperatures

Unlike many forms of corrosion, SCC may not be visible to the naked eye.





## Key Components for SCC to Occur

- **1.Susceptible Material:** The material must be chemically susceptible to the environment. Different material types (metals, polymers, ceramics) have specific environments that cause SCC.
- **2.Specific Corrosive Environment:** The environment must be one that specifically promotes SCC for the given material. Often, only trace amounts of a chemical are necessary to trigger the process.
- **3.Tensile Stress:** A static tensile stress must be present. This can be:
  - 1. Applied Stress: Stress from external loads during operation.
  - **2. Residual Stress:** Stress remaining in the material from manufacturing processes like welding, cold forming, machining, or heat treatment.

## Tensile Stress

- Common sources of tensile stresses are:
- 1: External stresses caused by
  - Centrifugal forces
  - Temperature variation
- 2: Residual stresses due to
  - Forming
  - Heat treatment
  - Welding
  - Machining
  - Grinding

#### 3-39 Stress Effects

Increasing the stress decreases the time before cracking occurs, as shown in Fig. 3-59. There is some conjecture concerning the minimum stress required to prevent cracking. This minimum stress depends on temperature, alloy composition and environment composition. In some cases it has been observed to be as low as about 10% of the yield stress. In other cases, cracking does not occur below about 70% of the yield stress.

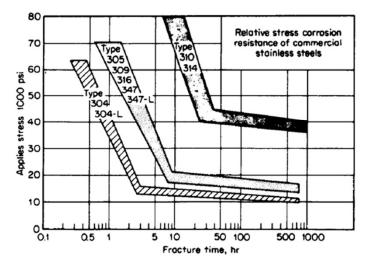


Figure 3-59 Composite curves illustrating the relative stress-corrosion-cracking resistance for commercial stainless steels in boiling 42% magnesium chloride.

# Susceptible Material

The two classic cases of stress-corrosion cracking are "season cracking" of brass, and the "caustic embrittlement" of steel. Both of these obsolete terms describe the environmental conditions present that led to stress-corrosion cracking. Season cracking refers to the stress-corrosion cracking failure of brass catridge cases. During periods of heavy rainfall, especially in the tropics, cracks were observed in the brass cartridge cases at the point where the case was crimped to the bullet. It was later found that the important environmental component in season cracking was ammonia, resulting from the decomposition of organic matter.

# Susceptible Material

Stainless steels crack in chloride environments but not in ammonia-containing environments, whereas brasses crack in ammonia-containing environments but not in chlorides. Further, the number of different environments in which a given alloy will crack is generally small. For example, stainless steels do not crack in sulfuric acid, nitric acid, acetic acid, or pure water, but they do crack in chloride and caustics.

## SCC examples-metals

- Certain <u>austenitic</u> <u>stainless steels</u> and <u>aluminum</u> <u>alloys</u> crack in the presence of <u>chlorides</u>. This limits the usefulness of austenitic stainless steel for <u>containing</u> water with higher than a few parts per million content of chlorides at temperatures above 50 °C;
- Mild <u>steel</u> cracks in the presence of <u>alkali</u> and <u>nitrates</u>;
- Copper alloys crack in <u>ammoniacal</u> solutions (<u>season cracking</u>);
- High-tensile steels have been known to crack in an unexpectedly brittle manner in a whole variety of aqueous (water/moist) environments, especially when chlorides are present.

# SCC examples

SCC examples Table 3-12 Environments that may cause stress corrosion of metals and alloys

Material	Environment	Material	Environment
Aluminum alloys	NaCl-H <sub>2</sub> O <sub>2</sub> solutions	Ordinary steels	NaOH solutions
	NaCl solutions		NaOH-Na <sub>2</sub> SiO <sub>2</sub> solutions
	Seawater		Calcium, ammonium, and
	Air, water vapor		sodium nitrate solutions
Copper alloys	Ammonia vapors and		Mixed acids
	solutions		$(H_2SO_4-HNO_3)$
	Amines		HCN solutions
	Water, water vapor		Acidic H <sub>2</sub> S solutions
Gold alloys	FeCl <sub>3</sub> solutions		Seawater
	Acetic acid-salt solutions		Molten Na-Pb alloys
Inconel	Caustic soda solutions	Stainless steels	Acid chloride solutions
Lead	Lead acetate solutions		such as MgCl <sub>2</sub> and
Magnesium alloys	NaCl-K <sub>2</sub> CrO <sub>4</sub> solutions		BaCl <sub>2</sub>
	Rural and coastal		NaCl-H <sub>2</sub> O <sub>2</sub> solutions
	atmospheres		Seawater
	Distilled water		H <sub>2</sub> S
Monel	Fused caustic soda		NaOH-H <sub>2</sub> S solutions
	Hydrofluoric acid		Condensing steam from
	Hydrofluosilicic acid		chloride waters
Nickel	Fused caustic soda	Titanium alloys	Red fuming nitric acid, scawater, N <sub>2</sub> O <sub>4</sub> , methanol-HCl

# SCC examples

#### Media that cause SCC in engines

Material type	Media that can cause SCC in engines	Characteristics of the SCC mechanism
Low-alloy steels	Nitrate and carbone solutions, chloride	Intergranular
Cr steels	Chloride	Intergranular
CrNi steels	Chloride ions, sulfite ions	Depending on the chloride content, pH value, stress levels, and temperature: transgranular SCC until the entire surface is attacked by pitting corosion. May be intergranular at Cr-depleted grain boundaries
Ni alloys	Sulfur	Mostly SCC-resistant with regard to watery electrolytes, but SCC may occur under the influence of sulfur in an airtight zone
Al alloys	Chlorine ions	Intergranular
Mg alloys	Chlorine ions	Intergranular
Ti alloys	Chloride	With smooth surfaces required temperature > 300°C     With notched or cracked parts, SCC can occur at room temperature (III. 5.4.2.1-8)
Be alloys	Halogen ions (e.g. Chloride) and sulfate ions	Pitting corrosion

## Is stainless steel immune to SCC?

The ferritic family of stainless steels, which includes grades such as type 430 and 444 is very resistant to chloride SCC.

The duplex stainless steel with its dual austenite/ferrite microstructures has a resistance that is between that of the austenite and ferrite grades.

## Features of SCC

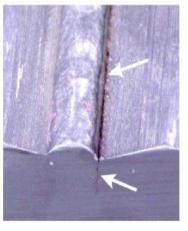
- Fracture Appearance: SCC typically results in a brittle fracture appearance, even in materials that are otherwise considered ductile.
- Cracking Morphology: Cracks can be transgranular (crossing the metal grains) or intergranular (following the grain boundaries), depending on the material and environment.
- Time-Dependent: SCC is not instantaneous; it is a time-dependent process that involves an **incubation period** followed by a period of slow crack growth.
  - During stress-corrosion cracking, the metal or alloy is virtually unattacked over most of its surface, while fine cracks progress through it.

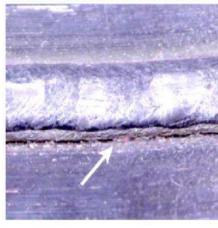
A 10:1 ratio of pit depth to width was suggested to be needed for a pit to initiate a crack.

# SCC



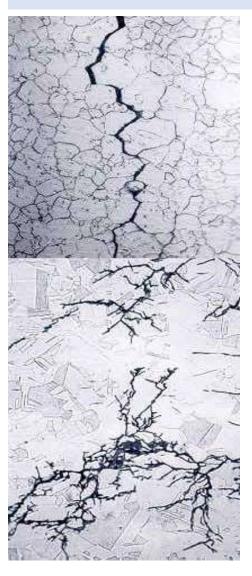








## SCC



The micrograph above (X500) illustrates intergranular SCC of an Inconel heat exchanger tube with the crack following the grain boundaries.

The micrograph below (X300) illustrates SCC in a 316 stainless steel chemical processing piping system. Chloride SCC in austenitic stainless steel is characterized by the multi-branched "lightning bolt" transgranular crack pattern.

Welded joints are particularly vulnerable due to their heterogeneous microstructure and the presence of stress concentrators. These conditions favor SCC crack initiation, which can lead to accelerated degradation in welded components if adequate preventive measures are not implemented.

- SCC is frequently observed in or near welds because the welding process simultaneously introduces two of the three necessary conditions for SCC: high tensile stress and a susceptible microstructure.
- Welding critically affects the two factors in the area surrounding the weld, known as the Heat-Affected Zone (HAZ).

#### 1. High Tensile Residual Stress

The primary reason for SCC near welds is the presence of **high tensile residual stress** generated during the welding thermal cycle.

**Mechanism:** Welding involves highly localized heating (melting) and subsequent rapid cooling. As the molten weld metal and the adjacent HAZ cool, they try to contract. This contraction is resisted by the surrounding, cooler, rigid material.

**Result:** This unequal expansion and contraction locks in high **residual tensile stresses** in the weld metal and the HAZ. These residual stresses can often be close to or even exceed the material's yield strength, easily meeting the stress threshold required to initiate SCC, even without any external operating load.

#### 2. Material Susceptibility (Microstructural Changes)

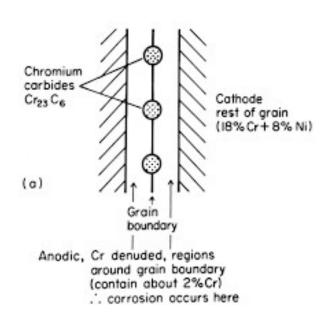
The intense heat from welding can alter the material's microstructure in the HAZ, making it more chemically susceptible to corrosion.

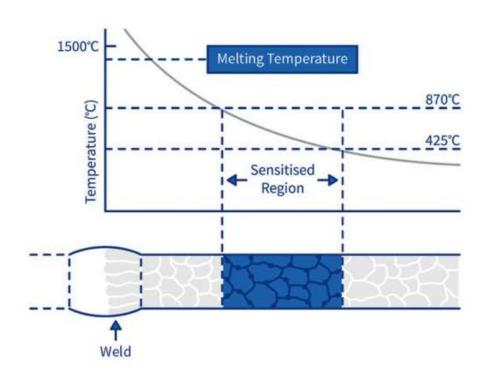
<u>Sensitization</u> in <u>Stainless Steel</u>: This is the most common example. When austenitic stainless steels (like Type 304 or 316) are heated into a critical temperature range (about 450 to 850 °C) during welding, chromium carbides precipitate (form) along the grain boundaries. This process depletes the adjacent metal of its chromium content, creating chromium-depleted zones (or an active zone) along the grain boundaries. Since chromium provides the alloy's corrosion resistance (by forming a protective passive film), the depleted grain boundaries become anodic (more active) relative to the bulk metal (cathode), creating a micro-galvanic cell that is highly vulnerable to selective dissolution and intergranular SCC.

<u>Contamination</u>: Welding fluxes and fumes can introduce highly aggressive chemicals, such as fluorine or chlorides, onto the surface of the weld and HAZ, locally increasing the concentration of corrosive species and promoting cracking.

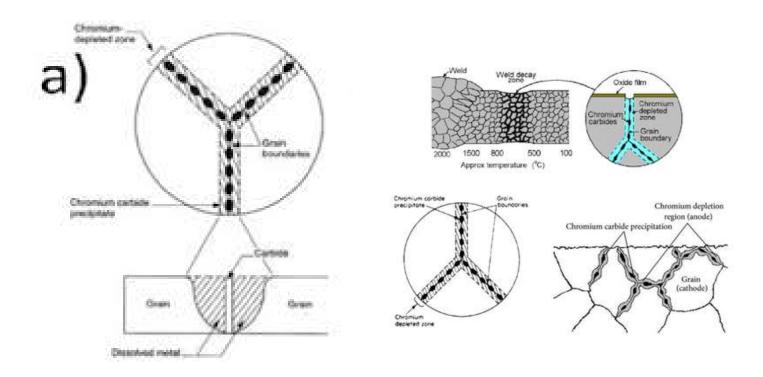
<u>Metallurgical Heterogeneity</u>: The weld metal, the heat-affected zone, and the base metal all have different microstructures and electrochemical properties, which can lead to variations in corrosion potential and contribute to localized corrosive attack.

# Weld decay or Sensitization





# Weld decay or Sensitization



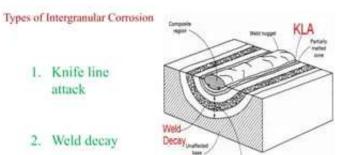
## Difference In Weld Decay And KLA

#### **KLA**

- \* KLA occur in narrow band in the parent metal immediately adjacent to the weld.
- \* KLA occurs in stabilized steel.

### Weld Decay

- \* Weld decay develops at the appreciable distance from the weld.
- \* Weld decay occurs in nonstabilized steels.



Welding induces complex residual stresses around the welded joint, both tensile and compressive, which can significantly influence SCC initiation sites and cracking paths.

The weld metal often contains different phases, segregation, or sensitization levels, which may increase susceptibility to localized corrosion and SCC.

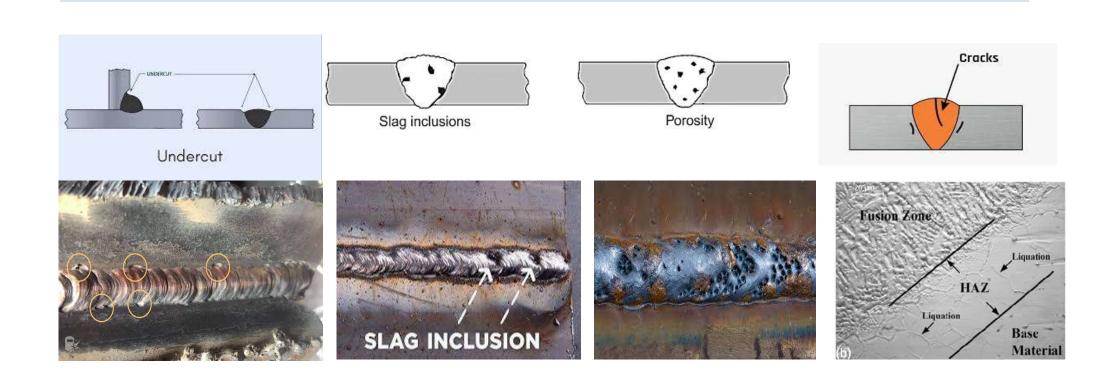
These factors combined produce a more vulnerable environment for SCC in the weld zone relative to the parent material.

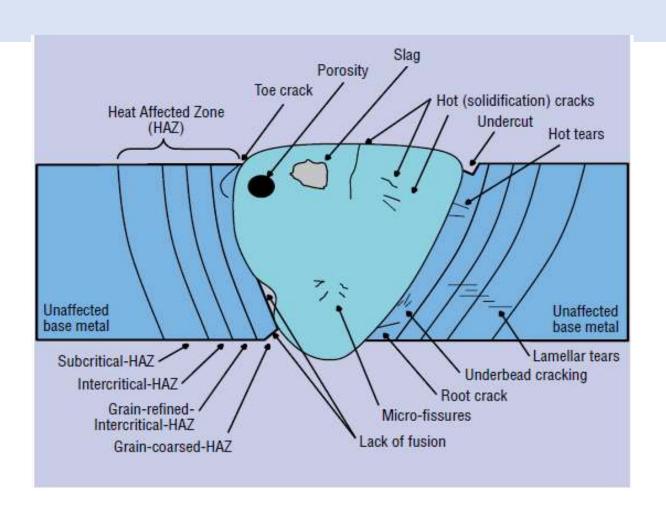
#### **Creating Geometric Stress Concentrations**

A weld is never perfectly smooth. It often has:

- •Undercut: A small groove melted into the base metal at the weld toe.
- •Slag Inclusions: Non-metallic particles trapped in the weld.
- •Porosity: Tiny holes or pores in the weld metal.
- •Microfissures: Very small cracks.

These features act as **stress concentrators**, significantly amplifying the local stress at a tiny point, making it easier for a crack to initiate.





**Factor** 

**Residual Stresses** 

**Microstructural Changes** 

**Chemical Inhomogeneity** 

**Surface Condition** 

**Welding Defects** 

Effect on SCC

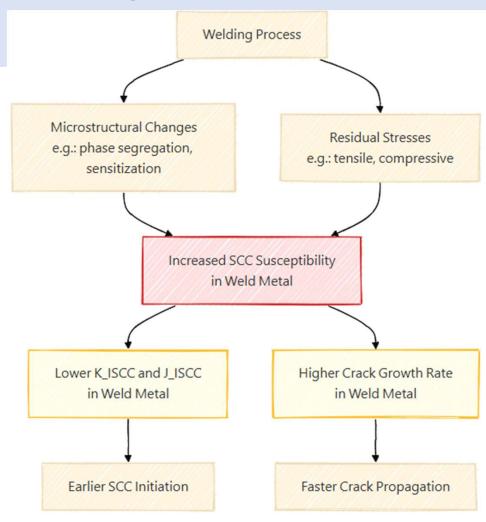
Welding introduces high tensile residual stresses in and near the weld zone due to uneven heating and cooling. These stresses can drive SCC even without external loads.

The weld metal and heat-affected zone (HAZ) can have microstructural variations (grain growth, sensitization, or precipitation) that make certain regions more prone to corrosion cracking.

Segregation of alloying elements or formation of chromium-depleted zones (in stainless steels) increases SCC susceptibility.

Oxide films, weld spatter, or rough surfaces after welding can act as initiation sites for cracks.

Porosity, undercuts, or microcracks from poor welding can initiate SCC under stress and corrosive conditions.



# SCC type

Many forms of SCC typically afflict pressure equipment in the oil refining, petrochemical, and other heavy processing industries, including but not limited to:

- Amine Stress Corrosion Cracking
- Ammonia Stress Corrosion Cracking
- Carbonate Stress Corrosion Cracking
- Caustic Stress Corrosion Cracking
- Chloride Stress Corrosion Cracking
- Polythionic Acid Stress Corrosion Cracking

## **Amine SCC**

often referred to as alkaline SCC or simply amine cracking, is a cracking mechanism caused by the combined effects of an aqueous alkanolamine solution (typically used to absorb H<sub>2</sub>S and/or CO<sub>2</sub> from gaseous or liquid hydrocarbon process streams) and the presence of either applied or residual tensile stress.

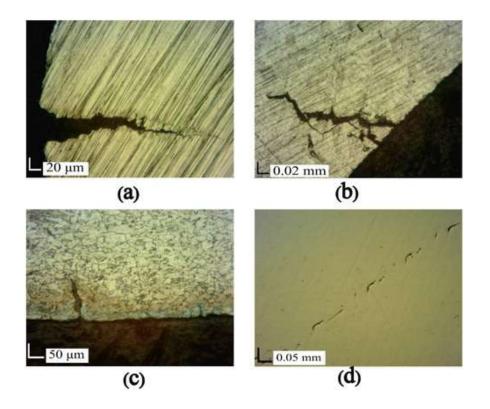
Amine SCC is typically branched and intergranular in nature, and usually occurs near welds in carbon and low-alloy steels, especially in equipment that was not subject to stress relief.

In general, amine unit equipment such as contactors, regenerators, absorbers, strippers, heat exchangers, filters, and piping should be routinely scrutinized and inspected for in-service amine SCC.

## **Amine SCC**

Alkanolamines are compounds containing both hydroxyl- and amino-functional groups on an alkane backbone.

Primary and <u>secondary</u> <u>amines</u> chemically react with acidic gases such as CO<sub>2</sub> and H<sub>2</sub>S in aqueous solution



Amine cracking of API 5L X52 carbon steel in the presence of hydrogen sulphide and carbon dioxide

## **Ammonia SCC**

is a cracking mechanism caused by the combined effects of an ammonia environment and the presence of stress.

Ammonia SCC is most prevalent in carbon steel (especially highstrength steel) equipment in anhydrous ammonia service or in copper-zinc alloys, such as admiralty brass or aluminum brass, in aqueous ammonia environments.

## **Ammonia SCC**

is usually either transgranular or intergranular in copper alloys, and more intergranular in nature for carbon steels.

In general, ammonia storage tanks, piping, and related components in ammonia refrigeration units are particularly susceptible to ammonia SCC damage.

Additionally, ammonia may be present in cooling water or steam condensate in boiler feedwater systems due to chemical treatments or be present in certain process streams either as a contaminant or an acid neutralizer, thereby introducing the risk for ammonia SCC.

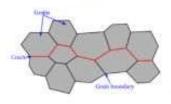
# **Ammonia SCC**

AMMONIA STRESS CORROSION CRACKING

#### Limits for SCC:

- 1. Anhydrous Ammonia (water < 0.2%)
- 2. Oxygen level > 1 ppm
- 3. Carbon Steel with Tensile Stress >= 70 Ksi
- Stresses (welds w/o PWHT, Cold working stresses, external or internal stresses)





#### **Case Studies**

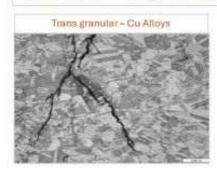


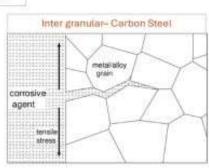
Catastrophic Failure of 500 ton Anhydrous Ammonia Tank. (Bangladesh, 2016)



Ammonia tank failure due to NH3 SCC, results in 22 fatalities. (South Africa, 1974)

#### Cracks Morphology





#### Susceptible Area:

Ammonia storage tanks, ammonia lines, ammoniacal water lines, refrigeration units.

#### Inspection Techniques:

WFMPI of welds and HAZ area. Angle beam (SRUT, PAUT).

## **Carbonate SCC**

often simply referred to as carbonate cracking, is a cracking mechanism caused by the combined effects of the presence of carbonates and tensile stress.

Carbonate SCC is a form of alkaline SCC that occurs in carbon and low-alloy steels in process environments containing a free water phase with carbonate ions and some amount of H<sub>2</sub>S.

## **Carbonate SCC**

Typical damage morphology of carbonate SCC involves surface breaking cracks, often characterized by small, spider-web type cracking that often initiates at weld defects.

Carbonate SCC typically occurs in oil refinery <u>fluid catalytic</u> <u>cracking units (FCCU)</u> and sour water stripper units.



## Caustic SCC

Sometimes referred to as caustic embrittlement (although it is not technically an embrittlement damage mechanism), is a form of degradation caused by the combined effects of a caustic environment and tensile stress.

Caustic SCC is characterized by surface-breaking crack-like flaws that most often occur adjacent to non-PWHT welds in pressure equipment exposed to caustic (e.g., caustic soda).

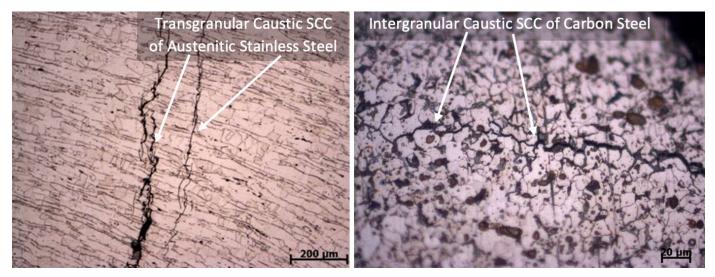
## Caustic SCC

Carbon, low-alloy, and 300 series stainless steels are particularly susceptible to caustic SCC, while nickel-base alloys are generally more resistant, although not entirely immune.

Cracking in carbon steels is usually intergranular, although in rare cases, it can be transgranular, and it tends to exhibit multiple, oxide-filled cracks.

In 300 series stainless steels, cracking is most often transgranular, and it can be difficult to distinguish from chloride SCC.

# **Caustic SCC**





# Chloride SCC

is a cracking mechanism caused by the combined effects of tensile stress, temperature, and an aqueous chloride environment. Brittle-looking surface cracks with many branches characterize Cl-SCC.

Cracking is usually transgranular, but in sensitized 300-series stainless steels, it can be intergranular.

Austenitic (e.g., 300 series) stainless steels are generally most prone to Cl-SCC. While duplex stainless steels and nickel-base alloys are typically more resistant, they are not strictly immune (nickel content of the alloy has a notable effect on overall resistance).

# Chloride SCC

Carbon steels, low alloy steels, and 400 series stainless steels are not susceptible to Cl-SCC.

Similar to other SCC damage mechanisms, non-PWHT weld regions are usually the most susceptible to Cl-SCC damage due to elevated tensile residual stresses, and cold-worked components, such as expansion bellows, are areas of concern due to residual plastic strains.

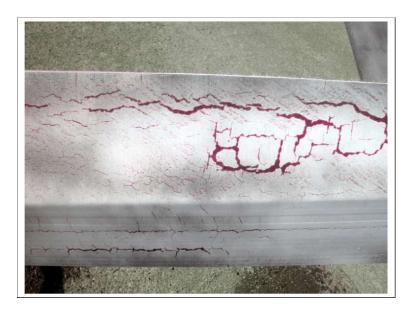
Other common locations that tend to exhibit Cl-SCC include water-cooled condensers and crude tower overhead condensers.

# **Chloride SCC**



Chloride SCC (Cl-SCC): Morphology of Damage & Mitigation Strategies





# Polythionic Acid SCC

<u>PASCC</u> is a form of intergranular stress corrosion cracking that usually occurs in sensitized austenitic stainless steels and some nickel-base alloys when sulfide scale on the steel surface is exposed to oxygen and moisture.

The most common source of oxygen is the ingress of air when process equipment is opened for cleaning, inspection, or maintenance activities during a planned unit outage.

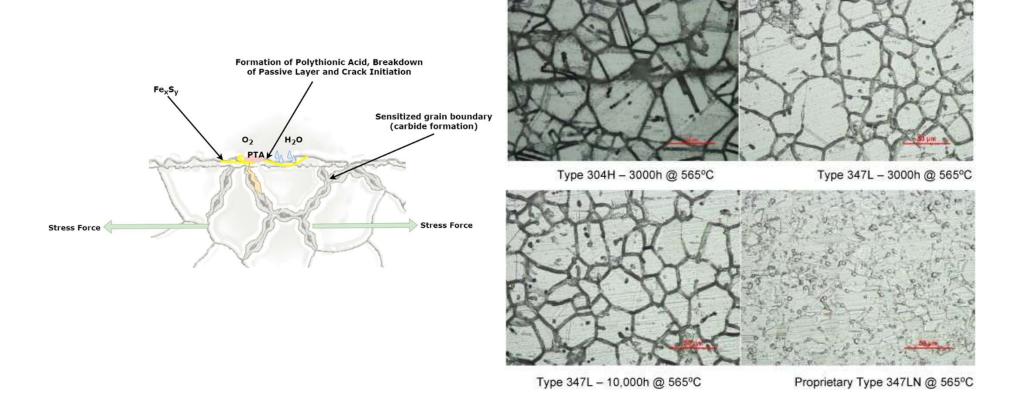
PASCC usually occurs during equipment start-ups or shutdowns, and cracking can propagate rapidly through-wall in a matter of hours under the right conditions.

# Polythionic Acid SCC

Equipment most susceptible to PASCC includes <u>fired</u> <u>heaters</u> burning oil, gas, coke, and most other sources of fuel (containing sulfur), heater tubes, hot feed/effluent exchanger tubes, and bellows in hydroprocessing units.

Crude/vacuum and coker unit piping have also exhibited PASCC, and severe cases have been found in FCC units (e.g., air rings, plenums, slide valves, cyclone components, expansion joint bellows, and piping).

# Polythionic Acid SCC



# Comparison Table

SCC Type	Environment / Chemicals	Susceptible Materials	Cracking Type	Typical Locations / Industries	Key Factors	Prevention
Amine SCC	Aqueous amine solutions	Carbon steel	Usually surface- breaking, branched cracking; can be intergranular	Gas sweetening units, amine absorbers, rich amine circuits	High temp, amine degradation products, tensile stress	Stress-relief, control contaminants, filtration, use Cr-Mo steels
Ammonia SCC	Moist ammonia + oxygen	Copper alloys (brass)	Intergranular cracking ("season cracking")	Fertilizer plants, refrigeration, ammonia storage/transfer	Oxygen contamination, residual stress	Avoid brass, remove O <sub>2</sub> , stress-relief
Carbonate SCC	Concentrated Na <sub>2</sub> CO <sub>3</sub> (sodium carbonate) solutions	Carbon steel	Intergranular cracking	Petroleum refining (e.g., reformer effluent systems, steam generators)	High pH, elevated temperature, high carbonate concentration	Stress relief, carbonate control, maintain protective scale, upgrade alloys
Caustic SCC	Concentrated caustic (NaOH) solutions	Carbon steel	Intergranular, starts at stress concentration points	Caustic wash systems, boilers, desalters	High caustic concentration, heat, local concentration under deposits	Control NaOH concentration, avoid crevices, stress-relief, use nickel alloys
Chloride SCC	Chloride-containing water or salts	Austenitic stainless steels (304/316)	Transgranular cracking	Refineries, chemical plants, cooling water services	Temp 50–150°C, tensile stress, oxygen, evaporation of chlorides	Reduce chlorides, lower temps, use duplex or high-Ni alloys, avoid stagnant areas
Polythionic Acid SCC	Polythionic acids formed from sulfur compounds + air + moisture during shutdown	Sensitized stainless steels	Intergranular cracking	Sulfur-containing units (hydrotreaters, FCC, reactors), especially during shutdowns	Sensitization of SS (chromium carbide formation), exposure to air	Use low-C or stabilized SS (316L, 347), avoid sensitization, nitrogen purge, alkaline wash

## How does surface finish affect SCC?

• Surface finishes influence the formation of oxide films, diffusion of metal ions, the corrosion rate and thus the SCC behavior.

# SCC Mechanism/step

No single mechanism explains all cases of SCC, but several wellestablished models exist. They generally share a common sequence of stages:

- **1.Initiation:** A local defect of the protective surface film (passive layer) occurs due to mechanical stress or local corrosion (like pitting).
- **2.Propagation:** A tiny crack propagates through the material via a specific mechanism (detailed below), driven by the combined action of stress and corrosion.
- **3.Final Fracture:** The crack grows to a critical size where the remaining ligament can no longer support the load, and the component fails by fast, mechanical fracture.

### Mechanism

The exact mechanism is complex and still debated, but common models include:

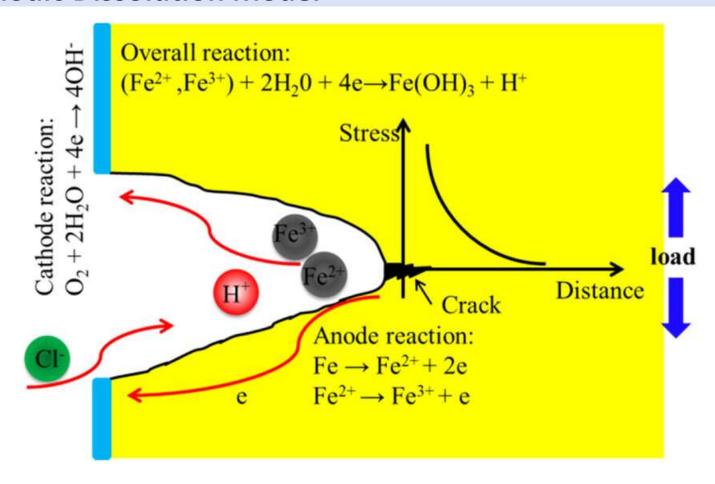
- **1.Anodic Dissolution:** The stress breaks the protective oxide layer at the crack tip, exposing the highly reactive bare metal. This metal dissolves rapidly (anodic dissolution) before the oxide layer can repassivate, allowing the crack to advance.
- **2.Hydrogen Embrittlement (HE):** In some systems (especially highstrength steels), the corrosion reaction produces hydrogen, which is absorbed into the metal. The hydrogen weakens the metal structure ahead of the crack tip, leading to brittle fracture.

- This is the most classic and widely applicable model, especially for systems where the metal forms a protective passive film (e.g., stainless steels, aluminum alloys in chlorides).
- Core Idea: The protective film is brittle and cannot deform with the metal underneath. Local plastic deformation at the crack tip causes the film to rupture.

#### Process:

- At the sharp crack tip, stress concentration causes localized plastic deformation (slip steps).
- This slip shears and ruptures the brittle passive film, exposing fresh, highly reactive bare metal.
- The exposed bare metal acts as a **local anode** and dissolves rapidly (anodic dissolution).
- This dissolution sharpens and advances the crack a tiny distance.
- The passive film then **repassivates** (re-heals) over the freshly exposed surface.

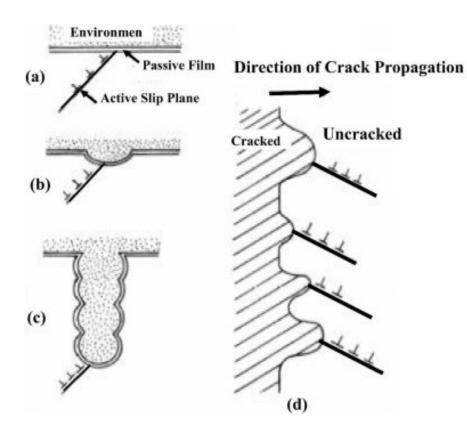
### **The Anodic Dissolution Model**

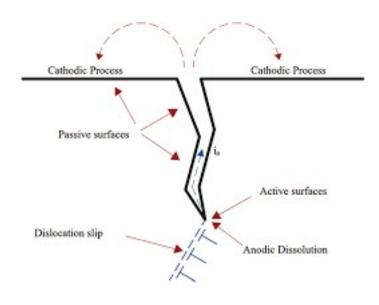


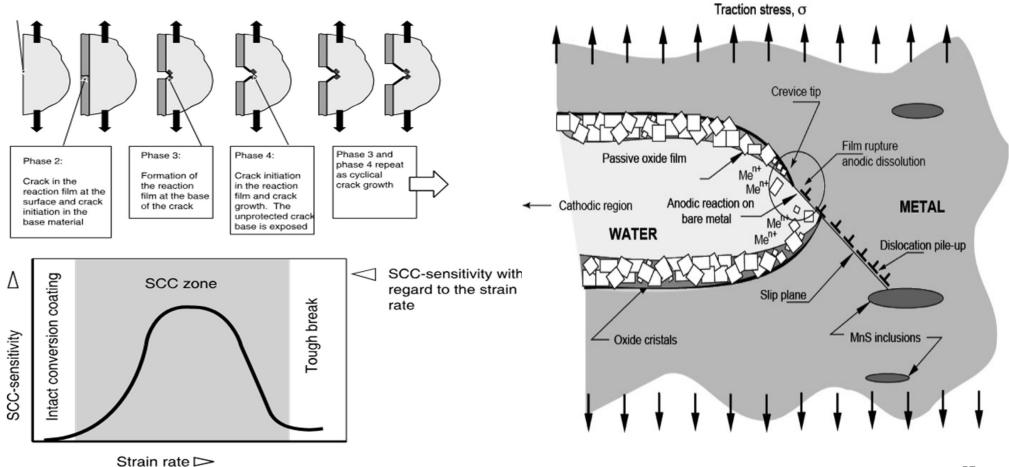
### Driving Force:

The crack advances by repeated cycles of **film rupture** → **rapid dissolution** → **repassivation**. The rate is controlled by how quickly the metal dissolves before the film re-forms.

• Analogy: It's like taking two steps forward (dissolution) and one step back (repassivation), but the net result is forward crack growth.







### The Hydrogen Embrittlement Mechanism

This mechanism is dominant in high-strength steels, titanium alloys, and some aluminum alloys, typically in environments that produce hydrogen (e.g., aqueous solutions, H<sub>2</sub>S in "sour" oil and gas).

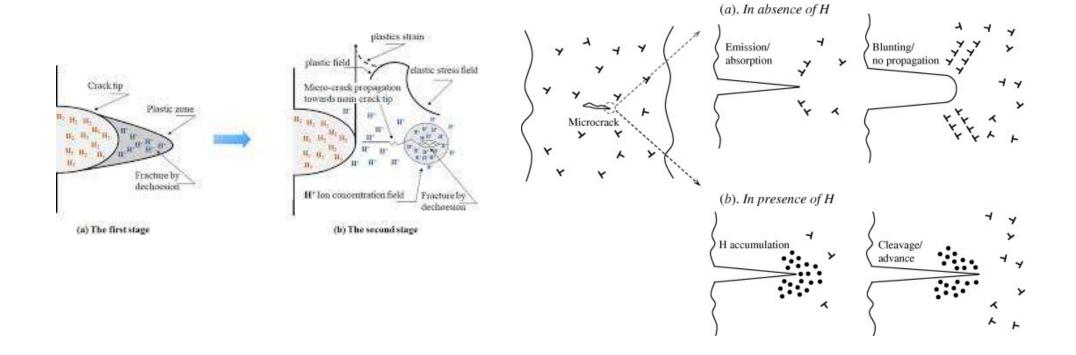
•Core Idea: Corrosion reactions at the crack tip (or on the surface) generate atomic hydrogen (H), which enters the metal and embrittles it.

### The Hydrogen Embrittlement Mechanism

#### •Process:

- 1.A cathodic corrosion reaction (e.g.,  $2H^+ + 2e^- \rightarrow 2H$ ) occurs at the metal surface inside the crack.
- 2.The generated atomic hydrogen (H), rather than forming H<sub>2</sub> gas, is **adsorbed** onto the fresh metal at the crack tip and **absorbs** into the lattice.
- 3. These hydrogen atoms diffuse through the metal lattice, assisted by the high stress field at the crack tip.
- 4. The hydrogen accumulates in regions of high tri-axial stress (just ahead of the crack tip), where it reduces the metal's cohesive strength.
- 5. This leads to a brittle, sub-critical crack advance, often by decohesion along grain boundaries or by facilitating void formation.
- **Driving Force:** The reduction in atomic bonding strength due to concentrated hydrogen, leading to crack propagation under an applied stress that would otherwise be safe.

# The Hydrogen Embrittlement Mechanism



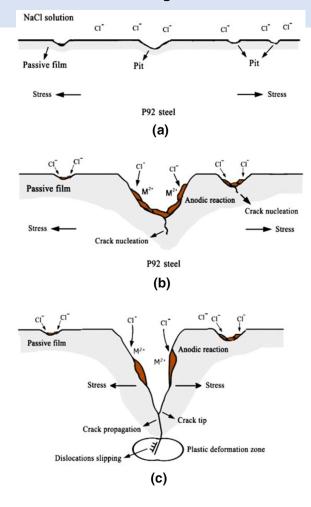
# **The Adsorption Model**

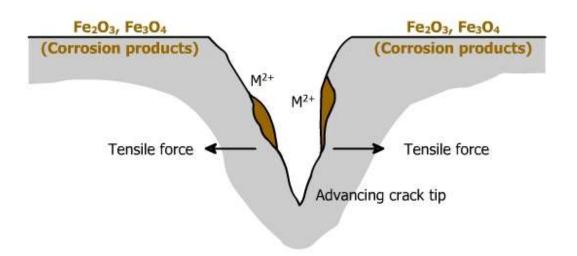
- This is a more controversial model that sits between the purely dissolution and purely embritlement models.
- Core Idea: Specific corrosive species (like Cl<sup>-</sup> ions) are adsorbed onto the metal surface at the crack tip. This adsorption itself reduces the metallic bond strength at the crack tip.

#### Process:

- Aggressive ions from the environment are attracted to the highly stressed region at the crack tip.
- These ions adsorb onto the metal atoms at the very apex of the crack.
- The adsorption process effectively lowers the energy required for bond rupture (the "surface energy").
- This weakening allows brittle crack propagation at stress levels far below the material's normal yield strength, even in the absence of significant dissolution or hydrogen ingress.
- Driving Force: The reduction in surface energy due to the adsorption of specific chemical species.

# **The Adsorption Model**



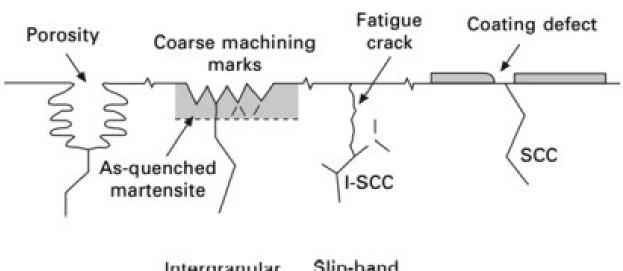


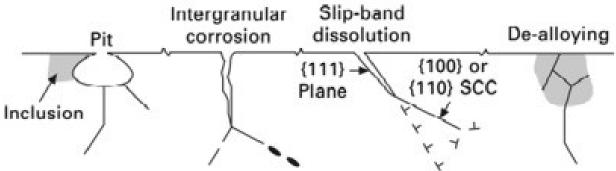
Schematic of stress corrosion cracking.

### **How to Distinguish the Mechanisms Visually and Experimentally**

Feature	Anodic Dissolution (Film-Rupture)	Hydrogen Embrittlement	
Fracture Path	Often intergranular (along grain boundaries) but can be transgranular.	Often intergranular or quasi- cleavage.	
Crack Appearance	Frequently shows branching.	May be straighter, with less branching.	
Effect of Potential	Worse at anodic potentials (which promote dissolution).	Worse at cathodic potentials (which hydrogen production).	
Strain Rate Effect	Maximum susceptibility at intermediate strain rates (allows time for dissolution between film ruptures).	Susceptibility increases with decreasing strain rate (allows more time for hydrogen to diffuse).	
Temperature Effect	Often has a maximum susceptibility at a specific temperature.	Severity typically decreases as temperature increases (hydrogen diffuses away faster).	

## SCC mechanism





#### **Common SCC Mechanisms examples by Material and Environment**

Environment/Material	Primary Mechanism	Role of Welding	Crack Path & Features	Examples
Chloride (Cl <sup>-</sup> ) in Austenitic SS (e.g., 304L/316L)	Slip-dissolution or corrosion- enhanced plasticity: Passive film ruptures under stress, exposing metal to anodic dissolution; repassivation fails in Cl <sup>-</sup> , leading to localized attack. Adsorption of Cl <sup>-</sup> weakens bonds.	Sensitization in HAZ (500-800°C exposure forms $Cr_{23}C_6$ ); residual stress + $\delta$ -ferrite dissolution; pits in WM/HAZ initiate cracks.	Often TGSCC (zig-zag on {111} planes); branched, brittle fractography. IGSCC if sensitized. Rates: ~10 <sup>-11</sup> to 10 <sup>-9</sup> m/s at 50-100°C.	Boiling MgCl <sub>2</sub> tests; marine atmospheres; refinery overheads. Threshold: >1-10 ppm Cl <sup>-</sup> , T>50°C, O <sub>2</sub> present.
Sulfide (H₂S) in Carbon/Low Alloy Steels	Hydrogen embrittlement (cathodic): H₂S poisons H recombination, allowing atomic H diffusion into steel; H traps at inclusions/GBs, reducing cohesion.	Hard HAZ (>22 HRC) from rapid cooling; slag/inclusions trap H; residuals drive blistering/cracking.	IGSCC or stepwise (HIC linking); SOHIC in high-stress welds. Brittle, no ductility loss visible.	Sour oil/gas (NACE TM0177); pH<5, H₂S>0.05 psi partial pressure, RT max susceptibility.

# How to stop stress corrosion cracking?

They may also suggest various heat treatments to reduce residual stresses.

Other means of controlling SCC include using corrosion inhibitors during cleaning operations, employing a closed system to control the environment, and coating the material to isolate it from the environment

### Preventive measures against stress corrosion cracking



### Best practices in material selection

Choosing materials with high resistance to SCC can mitigate risks in environments exposed to stress.



# **Corrosion inhibitors for prevention**

Utilizing corrosion inhibitors in specific environments can effectively reduce the risk of stress corrosion cracking.

0



## Monitoring stress levels continuously

Implementing continuous stress monitoring systems can help in identifying critical conditions that lead to SCC.

# Prevention and Mitigation

SCC is notoriously difficult to predict, so prevention is key:

**1.Material Selection:** Choose materials that are known to be resistant to the operating environment (e.g., using low-carbon stainless steels or nickel alloys instead of susceptible grades).

#### 2. Environmental Control:

- **1. Deaeration:** Removing oxygen (a common cathodic reactant) from the environment.
- **2. Inhibitors:** Adding chemical species that reduce the corrosivity of the medium.
- **3. Deionization:** Removing aggressive ions like chlorides.

# Prevention and Mitigation

- 3- Stress Reduction:
- •Design Modification: Designing components to reduce applied tensile stress.
- •Post-Weld Heat Treatment (PWHT): A heat treatment process to relieve residual stresses induced by welding.
- •Surface Treatment: Applying compressive residual stresses to the surface (where SCC usually initiates) using methods like **shot peening** or **burnishing**. **Compressive stress** on the surface is a very effective countermeasure, as SCC requires tensile stress.
- **4- Cathodic Protection:** Applying a small negative electrical potential to make the component the cathode in an electrochemical cell, which can stop the anodic dissolution process. (Note: Caution is required, as this can sometimes increase the risk of hydrogen embrittlement).

# Prevention and Mitigation

**1. Post-Weld Heat Treatment (PWHT / Stress Relieving):** This is the most effective method. The welded component is heated to a specific temperature and held for a time, allowing the residual stresses to relax through creep. This removes the "tensile stress" leg of the SCC triangle.

#### 2. Material Selection:

- 1. Using "L-Grade" stainless steels (e.g., 304L, 316L) with low carbon content to prevent sensitization.
- 2. Using stabilized grades (e.g., 321, 347) with Titanium or Niobium that preferentially form carbides, preventing chromium depletion.
- 3. Selecting alloys that are inherently more resistant to SCC in the specific service environment.
- 4. Proper filler materials compatible with base metal.

#### 3. Improved Welding Techniques:

- 1. Using proper welding parameters to minimize the width of the susceptible HAZ.
- 2. Ensuring a smooth weld profile to reduce stress concentrations.
- **4. Environmental Control:** If possible, controlling the service environment by removing chlorides, controlling temperature, or adjusting pH can be effective.

# How to study SCC in the laboratory?

• Slow Strain Rate Testing (SSRT): A dynamic method where specimens are strained at low rates (e.g.,  $10^{-6}~\rm s^{-1}$ ) in corrosive environments to accelerate cracking and measure ductility loss.

Standardized as ASTM G129.

 Boiling Magnesium Chloride Test: An accelerated qualitative test using U-bend or tensile specimens in boiling 42% MgCl₂ (155°C) to rank chloride SCC susceptibility in stainless steels.

Standardized as ASTM G36.

• Constant Load Testing: Applies sustained tensile stress (e.g., via deadweight) in corrosive media; used for threshold stress determination.

Part of NACE TM0177 (Method A) for sulfide SCC in H₂S environments.

# How to study SCC in the laboratory?

- Rising Step Load (RSL) Testing: Incrementally increases load to rapidly determine SCC thresholds like K\_ISCC; faster than constant load methods.
- U-Bend Test: Bends specimens into a U-shape for constant strain exposure; simple qualitative screening. Standardized as ASTM G39.
- Breaking Load Method: Measures residual strength after environmental exposure to quantify SCC resistance in aluminum alloys.

Standardized as ASTM G139.

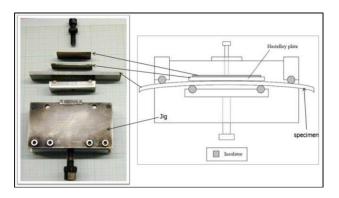
• Fracture Mechanics-Based Tests: Use pre-cracked specimens (e.g., compact tension) to plot crack velocity vs. stress intensity; includes rising load/displacement per ISO 7539-9.

# 1- Constant Load/Deflection Tests (Most Common for Screening)

#### a) Bent Beam Tests

- These are simple, low-cost tests ideal for screening a large number of material samples in a flat, sheet form.
- **Principle:** A flat specimen is elastically bent into a fixed jig and exposed to the corrosive environment.
- **Stress:** The outer surface is in tension, and the stress is calculated from the bend radius and material elasticity.
- Common Standards: ASTM G39
- **Pros:** Simple, many samples can be tested at once.
- **Cons:** Stress state is not uniform, and the stress can relax if the crack propagates.

#### **Bent Beam Tests**









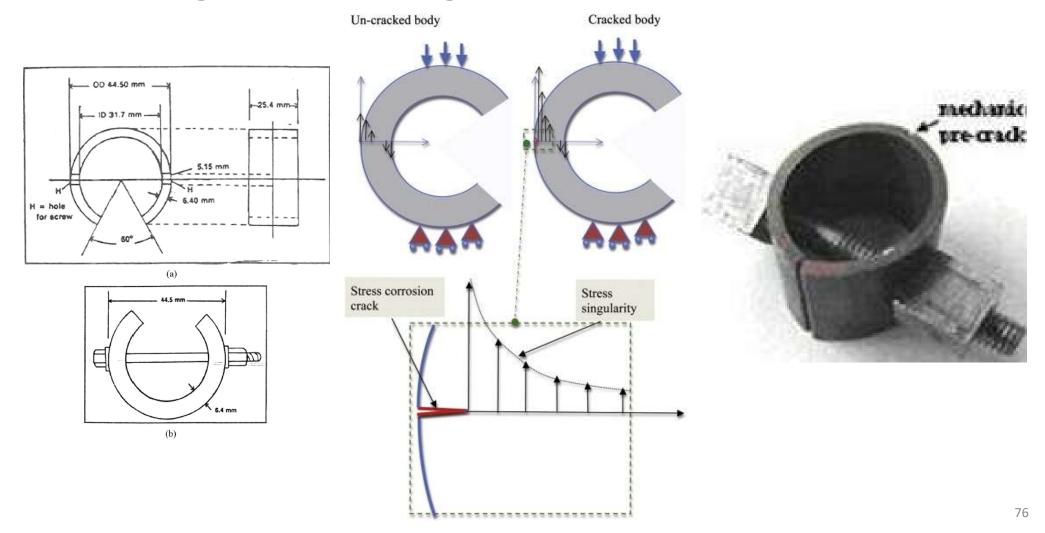


### 1-Constant Load/Deflection Tests

#### b) C-Ring and O-Ring Tests

- These are used for tubular products, rods, and fasteners.
- **Principle:** A ring-shaped specimen is stressed by tightening a bolt to deflect it a measured amount. The stress is concentrated on the outer surface of the C-Ring.
- Common Standards: ASTM G38 (Standard Practice for Making and Using C-Ring Stress-Corrosion Test Specimens)
- Pros: Excellent for testing the SCC susceptibility of pipes, tubes, and curved components.

# **C-Ring and O-Ring Tests**

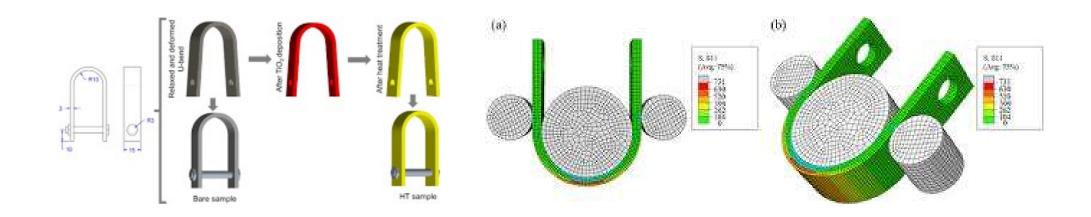


### 1- Constant Load/Deflection Tests

#### c) U-Bend Tests

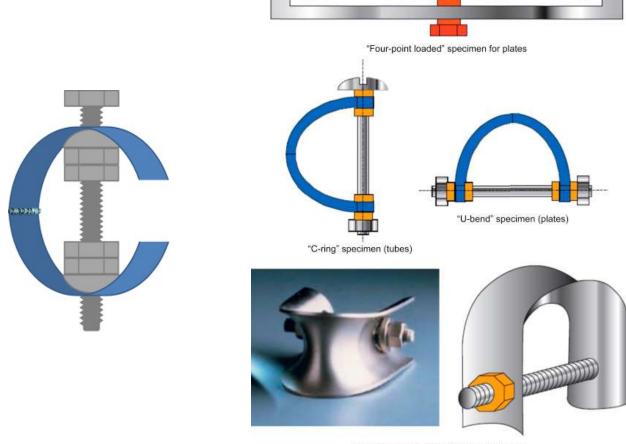
- This is one of the most severe tests, often used for highly resistant materials or for a "go/no-go" qualification.
- **Principle:** A flat strip is bent 180° into a "U" shape and often secured with a bolt, plastically deforming the specimen.
- **Stress:** The outer surface experiences stresses at or above the yield strength.
- Common Standards: ASTM G30 (Standard Practice for Making and Using U-Bend Stress-Corrosion Test Specimens)
- Pros: Very high stress, quick results for susceptible materials.
- Cons: The stress is poorly defined and non-uniform.

#### **U-Bend Tests**



ASTM G58 (weldment specimen practices)

#### Tests



Reverse U-bend (RUB) specimen for tubes

### 1- Constant Load/Deflection Tests

#### d) Direct Tension Test

- This is the most fundamental and quantitatively accurate constant load test.
- **Principle:** A tensile specimen is subjected to a constant load (usually a percentage of its yield strength) while immersed in the corrosive environment.
- **Stress:** The applied stress is known precisely and is uniform across the cross-section.
- Common Standards: ASTM G49 (Standard Practice for Preparation and Use of Direct Tension Stress-Corrosion Test Specimens)
- **Pros:** Well-defined, constant, and uniform stress. Excellent for generating quantitative data like time-to-failure.
- Cons: More complex and expensive equipment (creep frames or dead-weight loaders) is required.

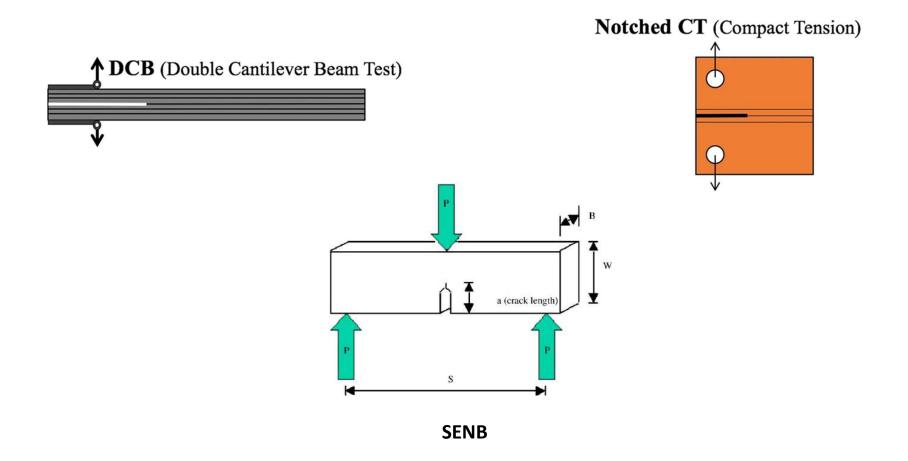
# 2. Pre-cracked Specimen Tests (Fracture Mechanics Approach)

- These tests are used when a component is known to contain flaws or cracks (as most real-world structures do). They measure the material's resistance to the growth of an existing crack.
- **Principle:** A sharp pre-crack (via fatigue cycling) is introduced into a specimen. It is then subjected to a constant load or displacement in a corrosive environment.
- **Key Parameter:** The goal is to determine **K**<sub>ISCC</sub>, the **Threshold Stress Intensity Factor for SCC**. This is the value below which a pre-existing crack will not propagate due to SCC.
- Common Specimen Types:
  - Compact Tension (C(T))
  - Double Cantilever Beam (DCB)
  - Single Edge Notched Bend (SENB)
- Common Standards: ASTM E1681 (Standard Test Method for Determining a Threshold Stress Intensity Factor for Environment-Assisted Cracking of Metallic Materials)
- **Pros:** Provides data for fracture mechanics-based design; models real-world flaws.
- Cons: More complex and expensive; requires precise machining and pre-cracking.

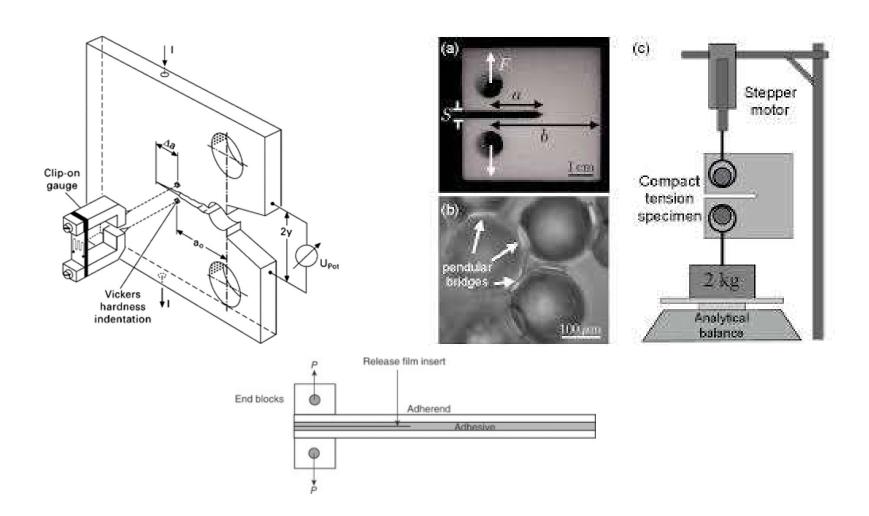
### 2. Pre-cracked Specimen Tests

Specimen	Loading Mode	Primary Use	Strengths
C(T) Compact Tension	Tension (Mode I)	Fracture toughness, SCC crack growth, fatigue	Compact, standardized, widely used
<b>DCB</b> Double Cantilever Beam	Tensile opening (Mode I)	SCC crack growth, adhesive fracture	Stable crack growth, ideal for long-duration SCC
<b>SENB</b> Single Edge Notched Bend	Bending	Fracture toughness, R-curves	Simple geometry, easy to prepare

### 2. Pre-cracked Specimen Tests



### 2. Pre-cracked Specimen Tests



# Test on statically loaded pre-cracked

Derive a graph of crack growth rate as a function of stress intensity factor.

The time of exposure needed to cause SCC failure depends on the stress intensity at any pre-existing or developed crack tip. K<sub>1</sub> determines the growth rate of SCC cracks.

Modern measurement of SCC is based on fracture mechanics principles to produce a value of K<sub>1SCC</sub>.

$$\frac{da}{dt} = AK^m$$

where: da is the crack growth,

dt is the time interval,

A and m are material constants which

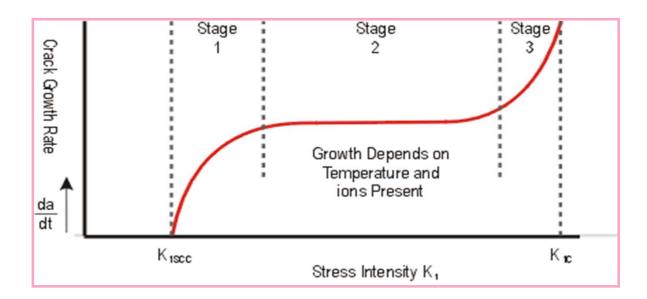
are dependent on the environment.

#### **Pre-cracked Specimen Tests**

Below a threshold value of K<sub>1</sub>, called K<sub>1</sub>scc, growth of a crack by SCC is not expected.

Stage 1: The initial SCC growth rate increases with increasing K<sub>1</sub>. Crack velocity is highly sensitive to applied k.

stage 2: The crack growth rate is independent of K1 and depends instead on the corrosive environment and temperature. (steady state)

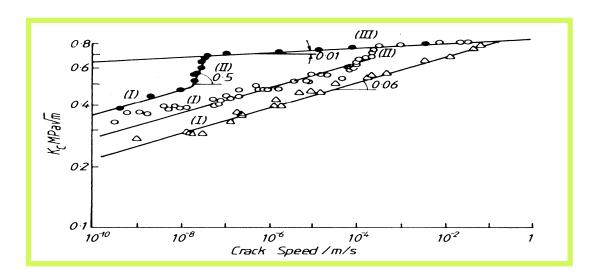


#### **Pre-cracked Specimen Tests**

Fracture mechanics tests are used to:

- 1- Characterize crack velocity in SCC
- 2- Find the threshold for stress corrosion crack growth(*K*1scc)

As the applied load is constant in SCC, it is more useful to talk about crack velocity and plot these against applied stress intensity level to give what are termed  $\nu$ -K curves.



#### **Pre-cracked Specimen Tests**

It should be appreciated that Kisco is not an invariant material property, and will be affected by all of the material and environmental factors.





Alloy	Klc	SCC	Klscc
	( <i>MN</i> / <i>m</i> 3 /	environme	( <i>MN</i> / <i>m</i> 3 /
	2)	nt	2)
13Cr steel	60	3% NaCl	12
18Cr- 8Ni	200	42% MgCl2	10
Cu- 30Zn	200	NH4OH, pH7	1

Material	K≀c MPa (√m)
Aluminum alloy	٣٦
Steel alloy	٥,
Titanium alloy	77-88
Aluminum oxide	YA-1 £

### 3. Slow Strain Rate Test (SSRT)

- SSRT involves applying a slow, constant strain rate to a specimen immersed in a corrosive environment while monitoring stress and elongation responses.
- It is used to study hydrogen-assisted SCC and other environmentally sensitive cracking phenomena by allowing hydrogen diffusion and interaction with the metal matrix, as seen in pipeline steel

### 3. Slow Strain Rate Test (SSRT)

- This is an accelerated test used for rapid ranking of materials or for environments where SCC is difficult to initiate.
- **Principle:** A tensile specimen is pulled to failure at a very slow, constant strain rate (e.g., 10 e-6 to 10 e-7 1/s) while immersed in the corrosive environment.
- **Mechanism:** The slow straining continuously ruptures the protective surface film, exposing fresh, reactive metal to the environment and promoting crack initiation and propagation.
- Analysis: Results are compared to a test done in an inert environment. Key metrics include:
  - Reduction in time-to-failure
  - Reduction in percent elongation and reduction in area
  - · Loss of tensile strength
  - Examination of fracture surface for brittle SCC features.
- Common Standards: ASTM G129 (Standard Practice for Slow Strain Rate Testing to Evaluate the Susceptibility of Metallic Materials to Environmentally Assisted Cracking)
- Pros: Very rapid results (typically days); highly sensitive for detecting SCC susceptibility.
- Cons: The severe conditions may cause failures that would not occur in service; results are qualitative for ranking, not for direct design.

## 4. Crack growth measurements:

1-POTENTIAL DROP measurement for crack-growth studies.

These measurement modes are based on resistance change caused by crack growth. The computer program calculates crack length from these measurements using Johnson function.

2-Crack growth behavior of SCC at the initial stage is detected by using acoustic emission (AE) techniques.

3-Tape method

## 4. Crack growth measurements:

#### **Ultrasonic and Imaging Techniques for Crack Detection**

- •Novel non-destructive evaluation (NDE) methods such as subharmonic phased array ultrasonic imaging have been developed to measure crack depths, including closed cracks that are difficult to detect by conventional ultrasonic methods.
- •This method enables precise 3D visualization of SCC cracks and their complex branching patterns, improving the understanding of crack morphology and propagation.

### 5. Microscopic and Fractographic Analysis

- Optical microscopy, scanning electron microscopy (SEM), and Auger electron spectroscopy are used post-testing to characterize crack surfaces, identify crack initiation sites, and crack growth modes (e.g., transgranular vs intergranular).
- These analyses confirm crack path morphology and mechanism, aiding in understanding the role of metallurgical factors and environmental interactions

#### 6- Pit-to-Crack Transition Studies

- Advanced 3D imaging like X-ray computed tomography combined with finite-element analysis has been employed to study how corrosion pits evolve into cracks, a critical stage for stress corrosion cracking initiation and propagation.
- These studies provide new conceptual understanding of local plastic strain development around pits leading to crack nucleation

#### Common SCC Test Methods for Welds

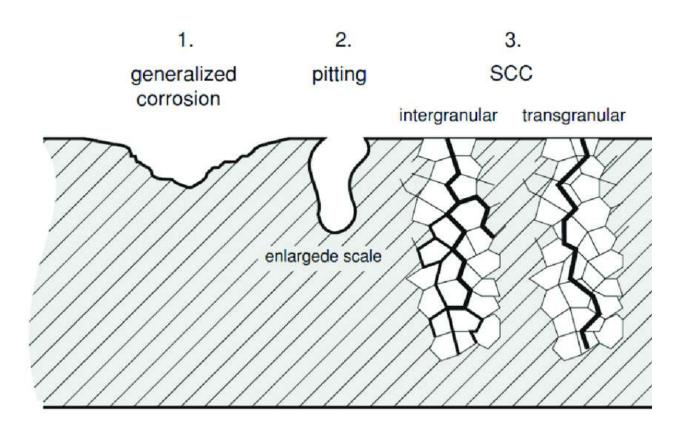
Method	Standard	Specimen Type	Application to Welds	Key Details
Constant Load Tensile	NACE TM0177 Method A (also ANSI/NACE)	Uniaxial tensile (weld transverse)	Sulfide SCC (SSC) in H₂S for carbon steels, CRA welds	720-hour exposure; stress ≥72% SMYS (specified minimum yield strength); pH 2.7-5. H₂S-saturated NaCl + acetic acid. Welded samples qualify via hardness (≤22 HRC) or direct testing.
Bent-Beam	NACE TM0177 Method B; ASTM G39 (U-bend)	Bent-beam or U-bend (weld in tension zone)	Qualitative screening for stainless welds in chlorides/H₂S	Deflection to induce strain; expose 720+ hours. U-bend: Weld centered on apex for max HAZ stress.
C-Ring	NACE TM0177 Method C	Bolted C-ring (from pipe welds)	Circumferential welds in pipes	Stress via bolt torque; ideal for girth welds under hoop stress.
Boiling MgCl <sub>2</sub>	ASTM G36	U-bend or tensile (welded)	Chloride SCC in austenitic stainless welds	42% MgCl <sub>2</sub> at 155°C; 100-1000 hours. Detects sensitization in HAZ.
Acidified NaCl	ASTM G123	Bent or tensile (welded)	Chloride SCC ranking for Ni- bearing stainless welds	Boiling 25% NaCl + H <sub>2</sub> SO <sub>4</sub> ; varies exposure for threshold Ni content.
Four-Point Bend	NACE TM0316 (aligned with TM0177)	Bent-beam (weld in bend)	Sour service CRA welds (e.g., duplex SS)	Stress to 90-100% yield; HPHT autoclaves possible.
Pre-Cracked Fracture Mechanics	ISO 7539-9; ASTM G129 (SSRT variant)	Compact tension (CT) or double-cantilever beam (DCB) with weld/notch in HAZ	Quantitative K_ISCC or da/dt for welds	Rising load/displacement; precrack at weld. For thick products/joined parts.

### **Key Factors to Control in Any SCC Test**

- Stress Level: Must be known and controlled.
- **Environment:** Composition, temperature, pH, and concentration are critical.
- Material Condition: Heat treatment, microstructure, and grain direction must be documented.
- Specimen Preparation: Surface finish and the absence of unintended cold work are vital.

#### What is the risk classification of SCC?

SCC can be classified into low risk, high risk, or very high risk lesions, determined by (amongst others) their size, thickness, and location.



# **Corrosion Fatigue**



### What is Corrosion Fatigue?

- **Definition:** The progressive, simultaneous action of cyclic stress and a corrosive environment.
- It is **not** simply fatigue + corrosion. It is a **synergistic** process where the combined effect is far worse than the sum of the individual effects.
- Leads to catastrophic failure at stress levels **much lower** than the fatigue limit in air and in a **shorter time**.

#### The Synergy Explained:

"The corrosive environment attacks the material, creating pits and cracks. Cyclic stress opens these cracks, allowing the corrosive agent to penetrate further, accelerating the failure."

#### 3-47 Corrosion Fatigue

Fatigue is defined as the tendency of a metal to fracture under repeated cyclic stressing. Usually, fatigue failures occur at stress levels below the yield point and after many cyclic applications of this stress. A schematic illustration of a typical fatigue fracture in a cylindrical bar is shown in Fig. 3-73. Characteristically, fatigue failures show a large smooth area and a smaller area which has a roughened and somewhat crystalline appearance. Studies have shown that during the propagation of a fatigue crack through a metal, the frequent cyclic stressing tends to hammer or pound the fractured surface smooth. A crack propagates until the cross-sectional area of the metal is reduced to the point where the ultimate strength is exceeded and rapid brittle fracture occurs. The surface of a brittle fracture usually has a roughened appearance. The unusual appearance of fatigue fractures has led to the common misstatement which attributes such failures to metal "crystallization." This is obviously incorrect, since all metals are crystalline, and the roughened surface which appears on the roughened fracture is the result of brittle fracture and not crystallization.

Fatigue tests are conducted by subjecting a metal to cyclic stresses of various magnitudes and measuring the time to fracture. Results of such tests

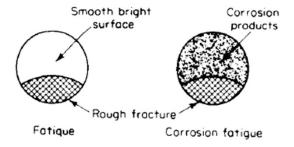
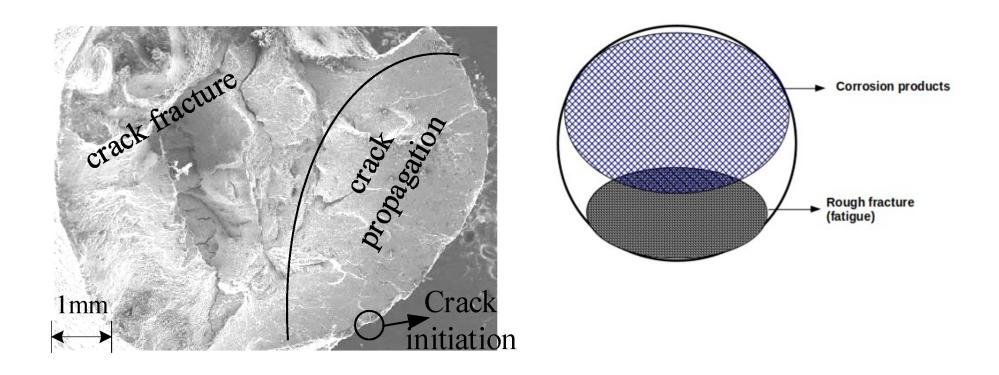


Figure 3-73 Schematic illustration of fatigue and corrosion-fatigue failures.

# **Corrosion Fatigue**



#### **Environment factor**

Corrosion fatigue is also influenced by the corrosive to which the metal is exposed. Oxygen content, temperature, pH, and solution composition influence corrosion fatigue. For example, iron, steel, stainless steels, and aluminum bronzes possess good corrosion fatigue resistance in water. In seawater, aluminum bronzes and austenitic stainless steels retain only about 70 to 80% of their normal fatigue resistance. High-chromium alloys retain only about 30 to 40% of their normal fatigue resistance in contact with seawater. It is apparent that corrosion fatigue must be defined in terms of the metal and its environment.

Bogar and Crooker\* tested alloys of steel, aluminum, and chromium in natural seawater, ASTM seawater, and a 3% sodium chloride solution. They conclude "that solution composition seldom has a large or a consistent effect on marine corrosion fatigue test results." Davis, Vassilaros, and Gudas† tested metal matrix composites.

### Why is it a Critical Problem?

- "Silent" Failure: Components can fail without significant plastic deformation or obvious warning.
- Reduced Life: Dramatically shortens the service life of structures and components.
- **High Cost:** Causes billions in annual losses for industries like aerospace, marine, energy, and civil infrastructure.
- Safety Hazard: Poses significant risks to public safety (e.g., aircraft, bridges, pipelines).

#### The Mechanism: A Step-by-Step Process

- **1.Pit Initiation:** The corrosive environment attacks the metal surface, creating microscopic pits at sites of local chemistry or microstructure variation.
- **2.Stress Concentration:** These pits act as stress concentrators, amplifying the local stress under cyclic loading.
- **3.Crack Nucleation:** A fatigue crack initiates at the base of the pit.
- **4.Crack Propagation:** The corrosive agent attacks the freshly exposed metal at the crack tip, weakening it and accelerating crack growth with each stress cycle.
- **5.Final Fracture:** The crack grows to a critical size, resulting in sudden, brittle fracture.

### **Key Characteristics & S-N Curve Comparison**

- No Fatigue Limit: Unlike fatigue in air, corrosion fatigue typically shows no endurance limit. Failure can occur at any stress level if given enough cycles.
- Frequency Dependence: Crack growth rate is highly dependent on the loading frequency. At lower frequencies, the environment has more time to act at the crack tip, leading to faster failure.
- Strong Environmental Influence: The type of corrosive agent (e.g., saltwater, acids, H<sub>2</sub>S) drastically affects the severity.

Corrosion fatigue is probably a special case of stress-corrosion cracking. However, the mode of fracture and the preventive measures differ and it is justifiable to consider it separately.

Renewed attention has been given to corrosion fatigue because of potential catastrophic failures in aerospace, nuclear, and marine (offshore platforms, submarines) structures. Extensive testing and detailed theoretical studies have been conducted. Although the mechanism (or mechanisms) of this type of corrosion remains unclear, it is known that crack initiation and crack growth respond differently to environmental factors.

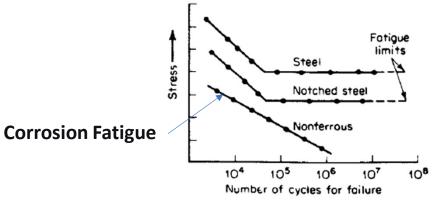


Figure 3-74 Schematic illustration of the fatigue behavior of ferrous and nonferrous alloys.

#### Real-World Applications & Case Studies

- Aerospace: Aircraft wings and fuselages (cyclic pressurization + atmosphere).
- Marine & Offshore: Ship hulls, oil platform legs, propellers (seawater + waves).
- **Power Generation:** Turbine blades, heat exchanger tubes (steam/water + vibration).
- Civil Engineering: Bridges, cables, and reinforced concrete (weather + traffic loads).

# Relationship Between Corrosion Fatigue and Welded Parts

- Welding introduces **heterogeneous microstructures** with varying grain sizes, phases, and sometimes segregation or sensitization in the heat-affected zone (HAZ) and weld metal. These regions can act as preferential sites for crack initiation due to local electrochemical differences and mechanical properties mismatch.
- Moreover, residual tensile stresses develop in the weld and adjoining zones from thermal expansion and contraction, which can significantly accelerate fatigue crack initiation and growth under cyclic loading.

The altered metallurgical state, combined with residual stresses, increases the **susceptibility of welded joints to corrosion fatigue** compared to the base metal.

# Relationship Between Corrosion Fatigue and Welded Parts

- Similar to stress corrosion cracking (SCC), welded metal often exhibits lower threshold stress intensities and faster crack growth rates during corrosion fatigue.
- The weld zone acts as a site where corrosion pits or microcracks more readily form and coalesce due to the combined effects of mechanical cyclic stress, corrosive attack, and residual stresses.

# Why Welds are the "Achilles' Heel"

Welded joints are inherent hotspots for corrosion fatigue due to a "perfect storm" of local conditions:

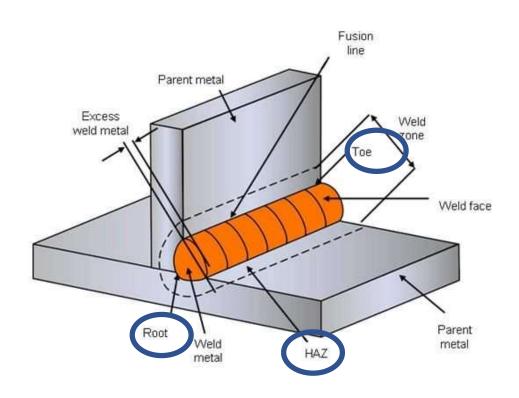
- **Geometric Stress Concentrations:** The weld profile (reinforcement, toe) creates natural notches.
- Metallurgical Inhomogeneity: The weld metal, Heat-Affected Zone (HAZ), and base metal have different structures and properties.
- Residual Stresses: High tensile residual stresses from the welding thermal cycle can approach the material's yield strength.
- **Potential Defects:** Voids, slag inclusions, or micro-cracks can act as pre-existing crack initiation sites.

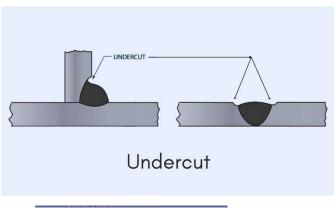
### **Critical Locations for Initiation**

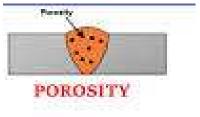
Cracks almost always start at stress concentrators. The most common sites are:

- **1.The Weld Toe:** The most common origin point due to the sharp geometric discontinuity and microstructural changes.
- **2.The Weld Root:** In partial penetration welds, the root is a severe internal stress concentrator.
- **3.Undercuts:** A welding imperfection that creates a very sharp, pre-existing notch.
- **4.Slag Inclusions & Porosity:** Internal defects that act as initiation points within the weld.

### **Critical Locations for Initiation**









### The Mechanism: A "Worst-Case" Scenario

The process is accelerated in welds:

- **1.Localized Corrosion:** The corrosive environment attacks the less-resistant HAZ or the anodic weld metal, often forming pits at the weld toe.
- **2.Residual Stress Amplification:** The welding residual stress acts as a constant mean stress, dramatically increasing the effective stress ratio (R-ratio) of the cyclic load.
- **3.Rapid Crack Initiation:** Pits form easily at the stress concentration of the weld toe.
- **4.Accelerated Propagation:** The crack grows through a susceptible microstructure (e.g., coarse-grained HAZ) under the combined action of cyclic stress and corrosion.

# **Key Factors Influencing Severity**

#### Welding Process & Procedure:

- Heat Input (affects HAZ size and microstructure)
- Welding Sequence (influences residual stress pattern)

#### Weld Geometry:

- Weld Toe Angle & Radius (sharp vs. smooth)
- Reinforcement Height (excessive reinforcement is detrimental)

#### Post-Weld Treatment (PWT):

• The single most important factor for improving fatigue life.

#### Material & Environment:

- Steel grade (e.g., susceptibility to HAZ hardening)
- Aggressiveness of the environment (e.g., seawater, H₂S)

## The Power of Post-Weld Treatment (PWT)

- Grinding: Removes the weld toe notch, improving geometry. (Good Improvement)
- **TIG Dressing:** Remelts the weld toe to create a smoother transition and a finer microstructure. (Better Improvement)
- Shot Peening / Hammer Peening: Induces beneficial compressive residual stresses at the surface to counteract tensile stresses and resist crack initiation. (Excellent Improvement)
- Stress Relief Annealing: Reduces global residual stresses (effective but often impractical for large structures).

## **Design for Corrosion Fatigue Resistance**

- 1.. Reducing fatigue by minimizing vibration and pressure fluctuation.
- 2.. Reducing the corrosion by using high-performance alloys resistant to corrosion fatigue.
- 3.. Reducing the corrosion by using coatings and inhibitors to delay the initiation of corrosion fatigue cracks.

# **How to Prevent & Control Corrosion Fatigue**

#### 1. Material Selection:

- \* Use more corrosion-resistant alloys (e.g., stainless steels, nickel alloys, titanium).
- \* Select materials with high intrinsic fatigue strength.

#### 2. Environmental Control:

- \* Use coatings (paints, platings), inhibitors, or cathodic protection. \* Control the chemistry of the environment (e.g., de-aerate water).

#### • 3. Design & Stress Management:

- \* Avoid stress concentrators (sharp corners, notches).
  \* Use generous radii and smooth surface finishes.
  \* Lower the operating stress levels.

#### 4. Surface Treatments:

\* Introduce compressive residual stresses via shot peening or surface rolling. This helps to resist crack initiation.

# **Design for Corrosion Fatigue Resistance**

Prevention starts at the drawing board.

#### Detail Design:

- Use full penetration welds instead of fillet welds where possible.
- Locate welds in areas of lower stress.
- Avoid complex, highly constrained joints.

#### • Fabrication Control:

- Enforce strict welding procedures to minimize defects and undercut.
- Specify and enforce Post-Weld Treatment requirements for critical joints.

#### Protection:

 Apply high-performance protective coatings carefully, ensuring full coverage at weld toes.

# **Inspection & Monitoring Challenges**

• **Difficult to Detect:** Cracks initiate at a microscopic scale at the weld toe, often hidden under coatings or surface debris.

#### NDT Methods:

- Magnetic Particle Inspection (MPI) / Dye Penetrant Inspection (DPI): Good for surface-breaking cracks at the toe.
- Ultrasonic Testing (UT): Essential for detecting subsurface cracks and monitoring crack growth.
- Criticality: Regular, scheduled inspection of critical welds is mandatory for ensuring structural integrity.

# **Purpose of Corrosion Fatigue Testing**

- Fundamental Understanding: To study the synergistic mechanism between cyclic stress and a corrosive environment.
- Generate Design Data: To create S-N (Wöhler) curves and crack growth rate (da/dN) data for specific material-environment combinations.
- Material Selection & Comparison: To rank materials, coatings, and post-treatment processes for specific applications.
- Lifetime Prediction: To develop models for predicting the safe operating life of components.
- Failure Analysis Reproduction: To replicate service failures in the lab to confirm the root cause.

# **Key Testing Variables**

- A test is defined by controlling these parameters: **Mechanical Parameters:** 
  - Stress Amplitude (Δσ) & Mean Stress (σ<sub>m</sub>)
  - Stress Ratio (R =  $\sigma_{min} / \sigma_{max}$ )
  - Loading Frequency (f)
  - Waveform (e.g., sinusoidal)
- Environmental Parameters:
  - Solution Chemistry (e.g., 3.5% NaCl, simulated seawater)
  - Temperature
  - pH Level
  - Dissolved Oxygen Content
  - Flow Rate
- Material Condition:
  - As-received, welded, heat-treated, etc.

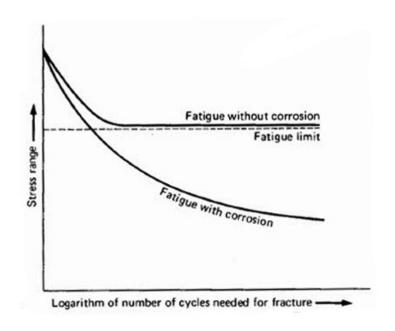
# **Test Method 1: S-N Curve Approach**

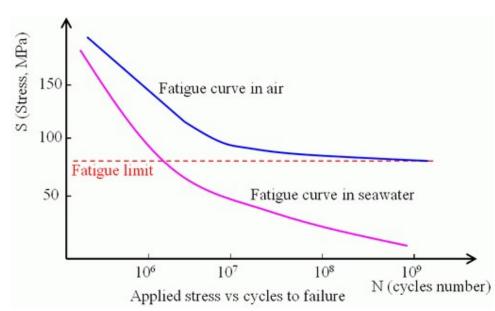
- **Objective:** Determine the number of cycles to failure (N\_f) at different stress amplitudes.
- **Specimen Type:** Smooth, polished specimens to simulate crack *initiation* life.

#### • Procedure:

- Immerse a series of specimens in the corrosive environment.
- Apply cyclic stress at a constant amplitude.
- Record the number of cycles until failure.
- Plot stress (S) vs. cycles to failure (N) on a log-log scale.
- Outcome: An S-N curve that shows the significant reduction in fatigue life compared to air, and the absence of a fatigue limit.

# **Test Method 1: S-N Curve Approach**





### **Test Method 2: Fracture Mechanics Approach**

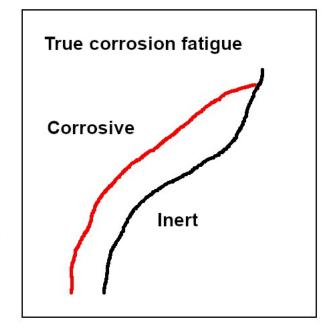
- Objective: Measure the crack *growth rate* (da/dN) as a function of the stress intensity factor range ( $\Delta K$ ).
- **Specimen Type:** Pre-cracked specimens (e.g., Compact Tension (CT), Single Edge Notched Bend (SENB)).
- Procedure:
  - Start with a pre-crack.
  - Apply cyclic loading in the corrosive environment.
  - Monitor crack length ('a') vs. number of cycles ('N').
  - Calculate da/dN and the corresponding ΔK.
- Outcome: A da/dN vs. ΔK plot, which shows a "plateau" (Region II) where crack growth is strongly influenced by the environment.

# **Test Method 2: Fracture Mechanics Approach**

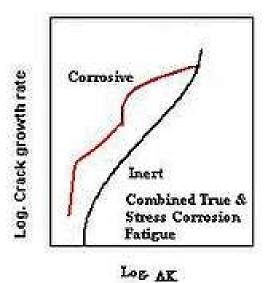
Region	Description	Behavior	
I	Near-threshold region	Crack growth rate is very low; corrosion can reduce the threshold (ΔK_th)	Region I Region II
11	Paris (steady- state) region	Linear on log— log scale; follows Paris law	m da/dN=C(ΔK) <sup>m</sup> Region III
III	Fast fracture region	Rapid crack growth approaching failure; accelerated by corrosion	$Log \Delta K$

# Fracture Mechanics Approach

Log crack growth rate



Log ΔK Sub critical crack growth in fatigue



Sub critical crack growth in fatigue

# **Critical Testing Equipment**

- Servo-Hydraulic or Electro-Mechanical Test Frame: For applying controlled cyclic loads.
- Environmental Chamber or Cell: To contain the corrosive environment around the specimen.
  - Simple Chamber: For immersion tests.
  - Self-Loading Cell: A pressurized cell that fits inside the test frame.

#### Instrumentation:

- Load Cell & Extensometer
- Potentiostat\* for electrochemical control.
- Crack Growth Measurement: (e.g., DCPD Direct Current Potential Drop, compliance method).

### The Role of Electrochemical Control

- Testing can be performed under different electrochemical conditions to simulate real-world scenarios:
- Free Corrosion Potential (E\_corr): The specimen corrodes freely without external current.
- Anodic Polarization: Applying a potential to make the specimen more susceptible to corrosion (accelerating the process).
- Cathodic Protection: Applying a potential to make the specimen a cathode, suppressing corrosion (e.g., simulating a protected pipeline).

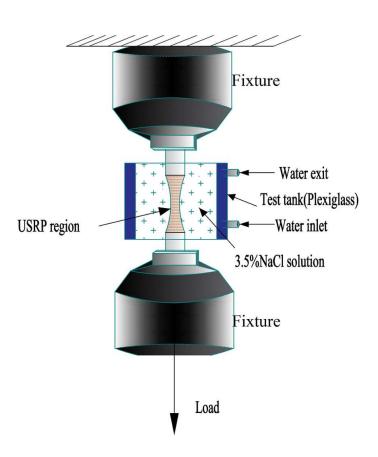
# **Challenges in Testing & Data Scatter**

- Frequency Sensitivity: Low frequencies give the environment more time to act, leading to faster crack growth. This makes tests time-consuming and expensive.
- **Solution Maintenance:** Keeping the solution chemistry (pH, O<sub>2</sub>) constant throughout a long test is difficult.
- **Specimen Preparation:** Surface finish and residual stresses must be carefully controlled.
- **Data Scatter:** Inherent in corrosion fatigue due to the stochastic nature of pit initiation and local chemical variations. Requires testing multiple replicates.

### **Standard Test Methods**

Standardization ensures consistent and comparable results.

- **ASTM E466:** Standard Practice for Conducting Force Controlled Constant Amplitude Axial Fatigue Tests of Metallic Materials.
- **ASTM E647:** Standard Test Method for Measurement of Fatigue Crack Growth Rates. (Includes guidelines for environmental testing).
- ISO 11782-1: Corrosion fatigue testing Part 1: Cycles to failure testing.
- ISO 11782-2: Corrosion fatigue testing Part 2: Crack propagation testing.
- ASTM G109: Standard Test Method for Determining the Effects of Chemical Admixtures on the Corrosion of Embedded Steel Reinforcement in Concrete.



# **Factors Influencing Corrosion Fatigue**

#### Environmental Factors:

- Corrosive Medium (e.g., saltwater is highly aggressive)
- Temperature
- pH Level
- Presence of Oxidizers

#### Metallurgical Factors:

- Alloy Composition
- Microstructure
- Heat Treatment

#### Mechanical & Stress Factors:

- Stress Amplitude (Δσ)
- Mean Stress
- Loading Frequency
- Stress Ratio (R-ratio)

# Corrosion Fatigue vs. Stress Corrosion Cracking (SCC)

eature

**Stress Type** 

**Material/Environment** 

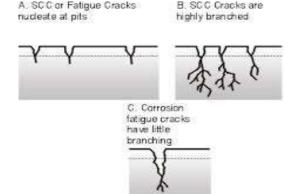
**Crack Path** 

**Corrosion Fatigue** 

**Cyclic** (fluctuating)

Occurs in virtually **all** metal/environment combinations.

Often transgranular



**Stress Corrosion Cracking (SCC)** 

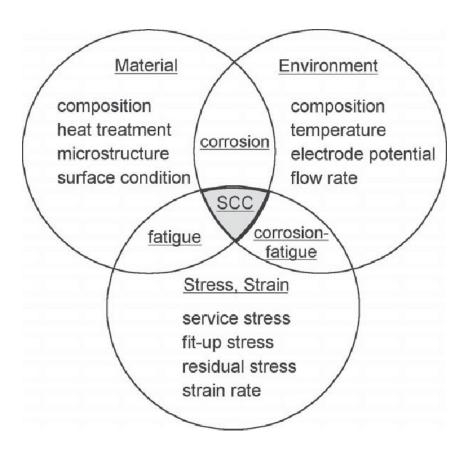
**Static** (constant tensile stress)

Requires a **specific** combination of metal and corrosive environment.

Can

be intergranular or transgranular.

## **Corrosion Fatigue vs. SCC**



Hydrogen damage

#### 3-48 Characteristics

Hydrogen damage is a general term which refers to mechanical damage of a metal caused by the presence of, or interaction with, hydrogen. Hydrogen damage may be classified into four distinct types:

- 1. Hydrogen blistering
- 2. Hydrogen embrittlement
- 3. Decarburization
- 4. Hydrogen attack

Hydrogen blistering results from the penetration of hydrogen into a metal. An example of blistering is shown in Fig. 3-75. The result is local deformation and, in extreme cases, complete destruction of the vessel wall. Hydrogen embrittlement also is caused by penetration of hydrogen into a metal, which results in a loss of ductility and tensile strength. Decarburization, or the removal of carbon from steel, is often produced by moist hydrogen at high temperatures. Decarburization lowers the tensile strength of steel. Hydrogen attack refers to the interaction between hydrogen and a component of an alloy at high temperatures. A typical example of hydrogen attack is the disintegration of oxygen-containing copper in the presence of hydrogen. Decarburization and hydrogen attack are high-temperature processes; they are discussed in detail in Chap. 11.

Hydrogen blistering and hydrogen embrittlement may occur during exposure to petroleum, in chemical process streams, during pickling and welding operations, or as a result of corrosion. Since both of these effects



### **Hydrogen Sources and Diffusion Pathways**

- Hydrogen can enter the welded areas during welding (e.g., from moisture, contaminants, fluxes) or service exposure to hydrogen-containing environments (e.g., corrosion, cathodic protection).
- Weld metal and HAZ, due to their microstructural complexity and defect concentrations (such as dislocations, grain boundaries), often serve as **preferential diffusion paths and trapping sites** for hydrogen.
- This localized hydrogen accumulation promotes embrittlement and facilitates crack nucleation especially in susceptible phases or weakened boundaries.

### **Hydrogen Sources**

#### 1. Moisture (Water Vapor)

This is the *most common* hydrogen source.

Moisture on the base metal surface

Moisture absorbed in electrodes, fluxes, and flux-cored wires

Humidity in the shielding gas system

Water ( $H_2O$ ) decomposes in the welding arc  $\rightarrow$  releases hydrogen.

#### 2. Hydrocarbons (Oils, Grease, Paint, Dirt)

Any organic contamination on:

The plate surface

Filler metals

Welding consumables

These contain hydrogen-bearing compounds that break down in the arc.

### **Hydrogen Sources**

#### 3. Moisture in Shielding Gas or Gas Supply System

Improper gas purity

Leaks pulling in humid air

Condensation in gas lines

Even small H<sub>2</sub>O levels can introduce hydrogen.

#### **4. Cellulosic Electrode Coatings**

E6010, E6011, and other cellulosic electrodes produce hydrogen as part of their decomposition—this makes them naturally "high hydrogen" processes.

### **Hydrogen Sources**

#### 5. Hydrogen in the Welding Environment

Damp work area

Condensation forming on cold plates before welding

#### **6. Welding Processes That Generate More Hydrogen**

Some processes inherently introduce more hydrogen:

SMAW (especially with non-low-hydrogen electrodes)

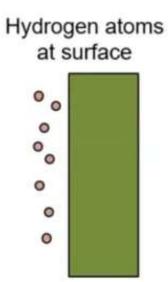
FCAW (flux-cored) with moisture in flux

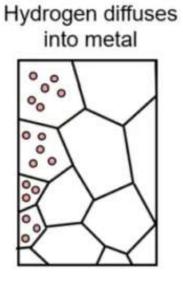
GMAW with contaminated wire

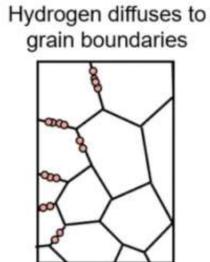
# Mechanisms of Hydrogen Embrittlement in Welded Zones

- Hydrogen embrittlement (HE) in welded zones is a dangerous phenomenon where atomic hydrogen (H), introduced during the welding process, diffuses into the heat-affected zone (HAZ) and the weld metal, making them susceptible to brittle cracking.
- This occurs under the influence of residual stresses, often leading to catastrophic failure without significant plastic deformation. It is also commonly known as Hydrogen-Induced Cracking (HIC) or Cold Cracking.

#### How embrittlement occurs







### HE

- For hydrogen embrittlement to occur in a weld, three factors must be present simultaneously:
- **1.Sufficient Hydrogen:** Introduced from the welding process (e.g., moisture, hydrocarbons, humidity).
- **2.Susceptible Microstructure:** A hard, brittle phase in the HAZ, typically martensite.
- **3.High Tensile Stress:** Residual stresses from welding and/or applied service loads.
- If any one of these three elements is eliminated, hydrogen cracking will not occur.

# Sources of Hydrogen in Welding

Hydrogen is introduced into the weld pool in its **atomic (H)** form from various sources:

- Moisture: The primary source. Found in electrode flux (e.g., in SMAW "stick" electrodes), submerged arc fluxes, shielding gas impurities, and humidity in the air.
- **Hydrocarbons:** Oil, grease, and rust (which contains hydrated oxides) on the base metal or filler wire.
- Shielding Gas: Impurities or leaks in systems using gases like CO<sub>2</sub> or argon-CO<sub>2</sub> mixes.
- The high temperatures of the welding arc (>>5000°C) dissociate water vapor (H₂O) and hydrocarbons into atomic hydrogen, which is extremely small and soluble in the molten steel.

•

### **Mechanisms of Embrittlement**

As the weld cools, the solubility of hydrogen in steel drops dramatically. The trapped atomic hydrogen seeks to escape or recombine, leading to several interacting embrittlement mechanisms. The three most accepted theories are:

- A. Hydrogen-Enhanced Decohesion (HEDE)
- B. Hydrogen-Enhanced Localized Plasticity (HELP)
- C. Hydride Formation (Primarily in Specific Alloys)

# A. Hydrogen-Enhanced Decohesion (HEDE)

This is the most widely accepted theory for high-strength steels.

- Concept: Atomic hydrogen diffuses to regions of high tri-axial stress (e.g., crack tips, notch roots, grain boundaries).
- Action: The presence of hydrogen reduces the metallic bond strength between iron atoms. It "weakens the glue" that holds the metal lattice together.
- **Result:** Under applied stress, the material fractures in a brittle manner at a stress level far below its normal yield strength because the atomic bonds separate more easily.

### B. Hydrogen-Enhanced Localized Plasticity (HELP)

- Concept: Atomic hydrogen facilitates the movement of dislocations (defects in the crystal lattice responsible for plastic deformation).
- Action: Hydrogen atmospheres "shield" dislocations, making it easier for them to move and multiply in localized regions (e.g., ahead of a crack tip).

Hydrogen lowers the stress field energy around dislocations. This reduces dislocation—dislocation repulsion, allowing dislocations to move more easily and in closer proximity.

• **Result:** This localized, intense plasticity leads to the formation of micro-voids and their coalescence, causing highly localized ductile failure that appears macroscopically brittle.

# C. Hydride Formation (Primarily in Specific Alloys)

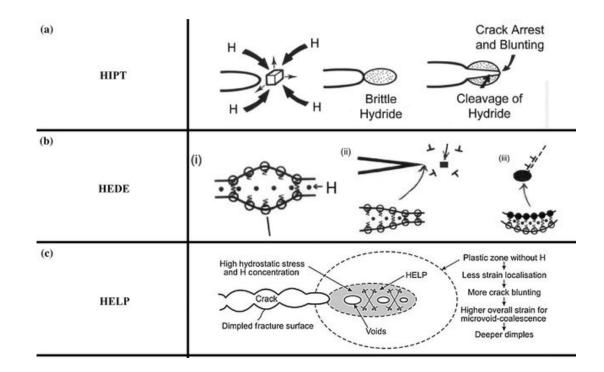
- Concept: In metals like titanium, zirconium, and their alloys, hydrogen has high solubility and can chemically combine to form brittle hydride phases.
- Action: These brittle hydride platelets precipitate, especially at grain boundaries or crack tips.
- **Result:** The crack propagates easily by fracturing the brittle hydrides or the hydride/matrix interface. **This is less common in carbon steels.**
- In welded carbon and low-alloy steels, **HEDE and HELP are the** dominant, often synergistic, mechanisms.

# Schematic diagrams of HE mechanisms

a HIPT-hydrogen induced phase transformation theory; or hydride formation

b HEDE- hydrogenenhanced decohesion mechanism;

c HELP -hydrogenenhanced localized plasticity mechanism



# Why the Heat-Affected Zone (HAZ) is the Most Vulnerable

#### 1. Microstructural Susceptibility:

- 1. The HAZ is heated to a temperature where the steel transforms to austenite. Upon rapid cooling (quenching by the surrounding cold base metal), this austenite can transform into a hard, brittle microstructure called **martensite**.
- 2. Martensite is highly susceptible to hydrogen embrittlement because its strained lattice provides numerous trapping sites for hydrogen and is inherently brittle.

#### 2. Hydrogen Concentration:

- 1. During welding, hydrogen is dissolved in the weld pool.
- 2. As the weld metal solidifies and cools, hydrogen diffuses outwards. The cooler HAZ, which is still a solid solution, acts as a sink for this diffusing hydrogen.
- 3. Hydrogen accumulates in the HAZ, particularly at the coarse-grained region closest to the fusion line.

# Why the Heat-Affected Zone (HAZ) is the Most Vulnerable

#### 1. High Residual Stresses:

- 1. The non-uniform heating and cooling during welding create significant tensile residual stresses that can approach the yield strength of the material.
- 2. These stresses are highest in the HAZ and are perpendicular to the weld bead, providing the driving force for crack initiation and propagation.
- A typical **underbead crack** is a clear example: it forms in the HAZ, just below the weld bead, often not visible from the surface.

# **Prevention and Control Strategies**

#### 1.Control Hydrogen Sources (Reduce Hydrogen):

- 1. Use **low-hydrogen welding processes** (e.g., TIG, MIG/MAG with clean gas).
- 2. Properly bake and store low-hydrogen electrodes (SMAW, FCAW) according to manufacturer specifications.
- 3. Thoroughly clean base metal and filler wire of all rust, oil, and moisture.
- 4. Ensure shielding gases are dry and of high purity.

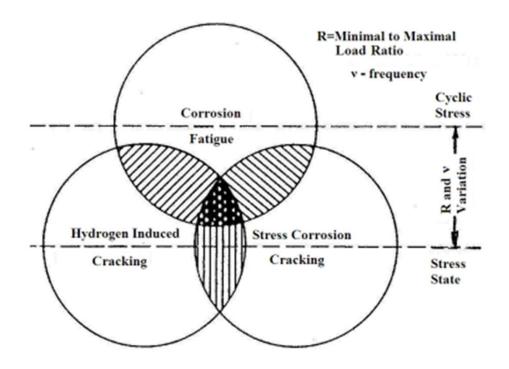
#### 2. Modify the Microstructure (Reduce Susceptibility):

- **1. Preheat:** The single most effective method. Preheating slows the cooling rate, allowing the austenite to transform into softer, more ductile microstructures (e.g., bainite, ferrite-pearlite) instead of martensite. It also provides time for hydrogen to diffuse away from the HAZ.
- **2. Post-Weld Heat Treatment (PWHT):** Stress-relief annealing reduces residual stresses and allows trapped hydrogen to diffuse out of the assembly.

# **Prevention and Control Strategies**

#### 1. Manage Stresses (Reduce Stress):

- 1. Use proper weld sequencing to minimize residual stresses.
- 2. Design joints to minimize restraint.
- 3. Use balanced welding to avoid high stress concentrations.



**Figure 1.** Diagram showing the relationship between SCC, CF, and HIC. When the frequency  $\mathbf{v}$  is less than 0.1Hz, SCC and HIC are possible; above this value it is CF. Adapted from [4].