Stress Assisted Corrosion

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Several figures used in the book have been taken from various sources who have been acknowledged wherever the source was known. If any has been missed, that is due to oversight.

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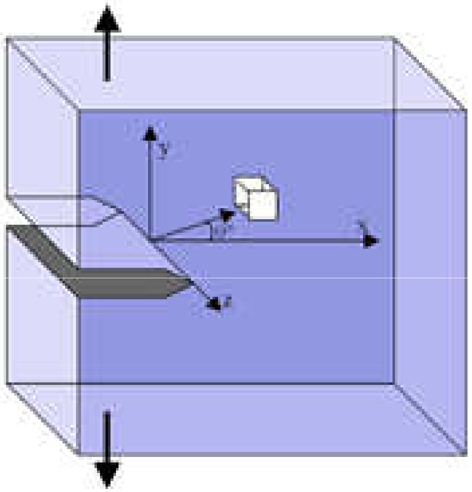

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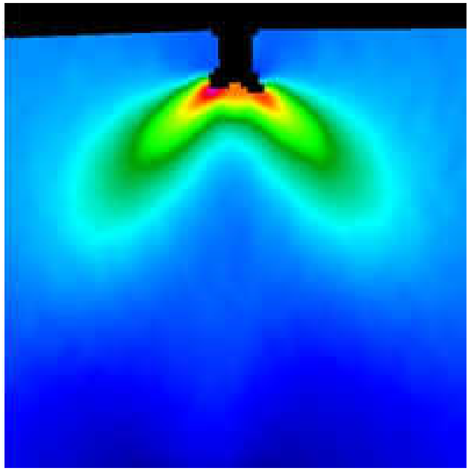

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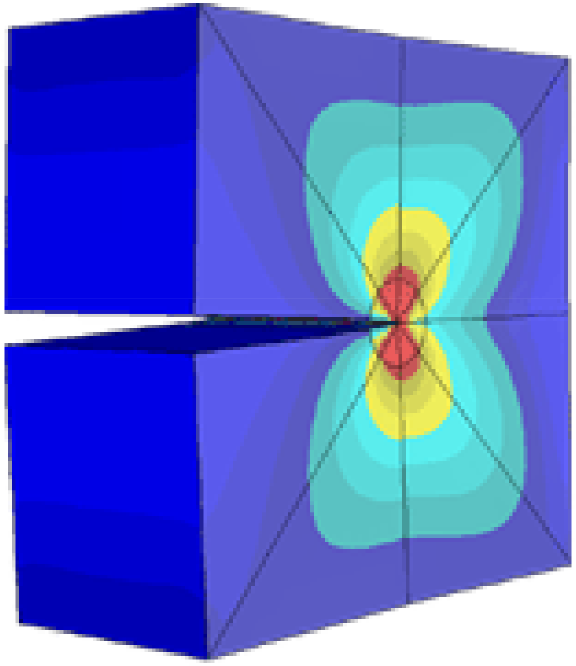


http://www.esrd.com/Images/Graphics/

A. A little bit of fracture mechanics

Questions of vital importance

Why does a material fracture?

Energy is the key : all processes tend to lower energies of systems. In fracture we consider two types of energy

i. The elastic energy due to stress – this is reduced as a crack occurs in a body

ii. The chemical energy of surfaces – this is increased as surfaces are created, that is, as cracking occurs

The energy concept was first used by Griffith to explain the conditions for Brittle Failures.
His theory was modified by Orowan to include ductile materials.

How does a metal fracture?

The fracture mode depends on loading mode, on the materials inherent plastic properties, on the grain boundary character

When does a material fracture?

When stress exceeds critical values, Temperature is conducive or Corrosion causes dissolution reducing the effective load bearing capacity. Time is also a factor (ageing).

How to prevent fracture?

After knowing the "How" and "When" a material fractures, the obvious prevention methodology is to eliminate or reduce the factors which accelerate fracture

A. A little bit of fracture mechanics

Defects

A perfect material without any defect would have theoretical strength of a few gigapascals – practically no testing machine could break it. But no material is perfect – they either have grain boundaries, or inclusions, or voids, or vacancies, or dislocations – therefore a material's strength is substantially lower- about ten to hundred times lower. In fact if the stress versus strain curve was drawn it would be like this (Fig.1). In practical, everyday materials, which do not have any other defects, dislocations are activated and start moving well below the theoretical strength, corresponding to the yield stress of the material. Dislocations are planes of atoms which are in non-crystallographic positions as shown below (Fig.2). These move when stress is applied as shown here.

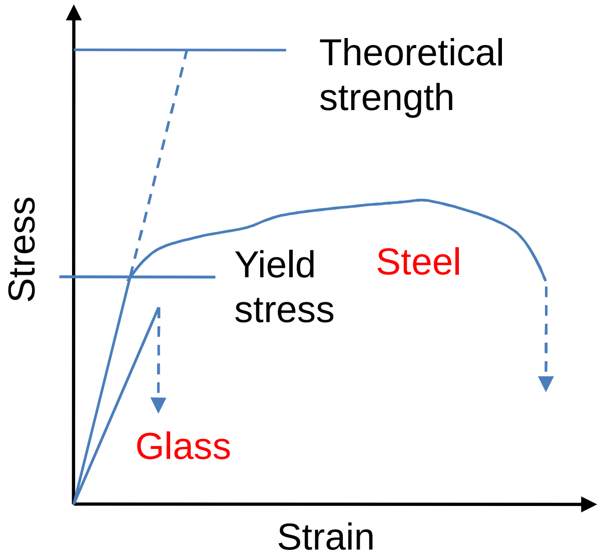


Fig. 1. Strength of materials

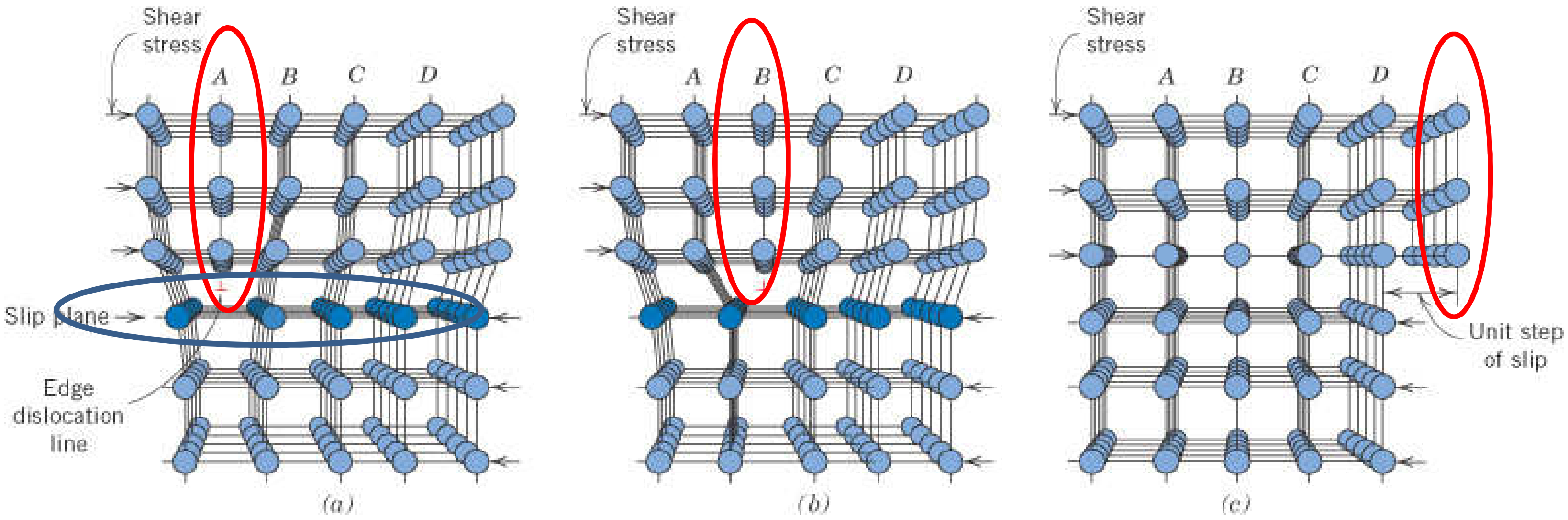


Fig. 2. Dislocations and their movement

www.csun.edu/~bavarian/Courses/MSE%20227/.../ch8_deformation.ppt

A. A little bit of fracture mechanics

(other than dislocations & grain boundaries)

How does a material, with no flaws, fracture?

As dislocations move and cause slip steps, the materials extends in the direction of the stress. Eventually a situation is reached when the cross section of the material is so small that the stress causes interatomic bond breaking. In very ductile material the fracture surface can reduce to a point. This is further evidence of the very high cohesive strength (interatomic bond strength) that a material possesses.

Additionally, and in most circumstances, the movement of dislocations and the presence of inclusions cause local decohesion of the material matrix from the inclusions and local voids are formed. These voids grow with increase in stress and cause local stresses to be very high and interatomic bond breaking occurs in the material adjacent to the voids. The fracture has microscopic semispherical dimples as shown in the photograph (Fig.3).

Sometimes a weaker grain boundary (compared to the matrix) will accelerate fracture by allowing the cracks to move through them.

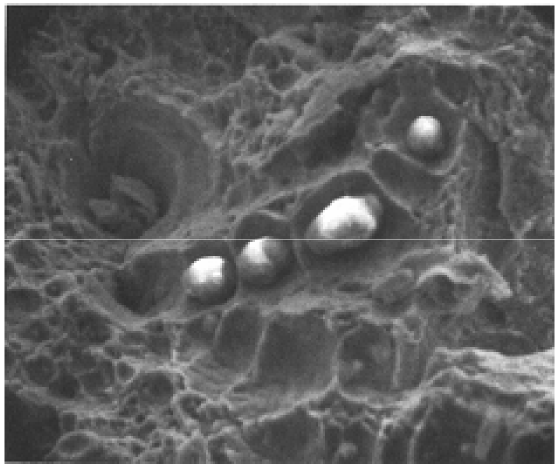


Fig. 3. Voids around inclusions

www.csun.edu/~bavarian/Courses/.../ch9_Failure_Mechanisms.ppt

What about materials which are not ductile and do not have dislocation activity? Should they not fail near the theoretical limit?

No, because they have flaws (internal cracks or inclusions). These inclusions cause local stress intensification and consequent failures. Griffith was the first to explain the lower fracture strength of brittle materials based on the concepts of internal cracks and energy considerations.

A. A little bit of fracture mechanics

Fracture Modes

The type of fracture can be classified based on the extent of ductility or on the granular morphology

I. Classification based on plasticity (Fig.4)

i. **Ductile fracture**: shows significant deformation, characterized by high strain to failure. This means that there is significant dislocation movement

ii. **Brittle fracture** :shows low strain to failure, separation is perpendicular to load direction. There is little dislocation activity

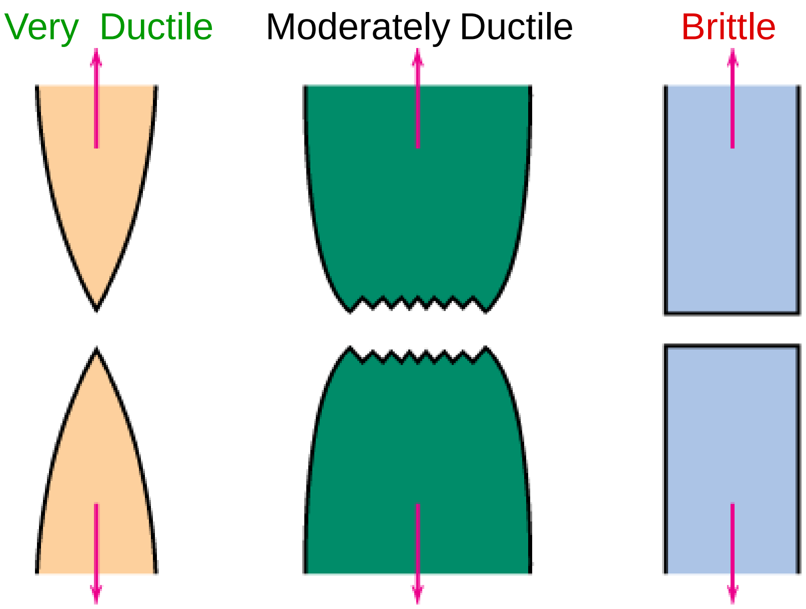
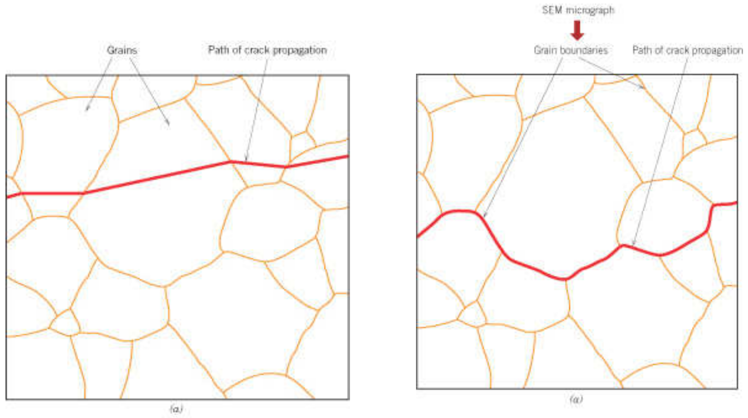


Fig. 4. Fracture classification based on plasticity

2. Classification based on crack propagation nature (Fig. 5)

i. **Transgranular fracture:** cracks tend to follow preferred crystal planes known as cleavage planes

ii. **Intergranular fracture:** crack tend to propagate along grain boundaries. This is often the case when the grain boundaries are weaker than the matrix due to precipitation or segregation of elements



Transgranular Fracture Intergranular Fracture

Fig. 5. Fracture classification based on crack propagation

Figs 4& 5 source :
www.csun.edu/~bavarian/Courses/.../ch9_Failure_ Mechanisms.ppt

A. A little bit of fracture mechanics

Why can we not predict fracture based on the stress-strain curve alone?

Yes, we can, when we are absolutely sure that there are no internal flaws. In such cases the safe limit for operation is fixed as a fraction of the yield stress. Many industrial components, especially those which have uniform cross sections, have stationary loading, and do not see corrosive environments, follow the threshold stress based design of components – they work fine as long as you include a safety factor.

Why flaw based fracture mechanics is necessary?

- Normal materials and especially components have flaws. These flaws are either internal or external (due to the component design).
- For brittle material stress-strain curves are irrelevant. Flaw based predictions are essential because local stresses near flaws are very different from the global stresses (Fig. 6)
- Using a stress-strain curve based design necessitates the use of a generous safety factor, to cater for the finite possibility of flaws.
- Acknowledging there are flaws and if possible measuring their dimensions, provides a more accurate estimate of the component safety limits.
- It is possible to estimate the local stresses accurately using a Flaw-based fracture mechanics concept. This provides a good understanding of local mechanisms near the crack tip.

***A Flaw** : anything that causes local stress concentration*

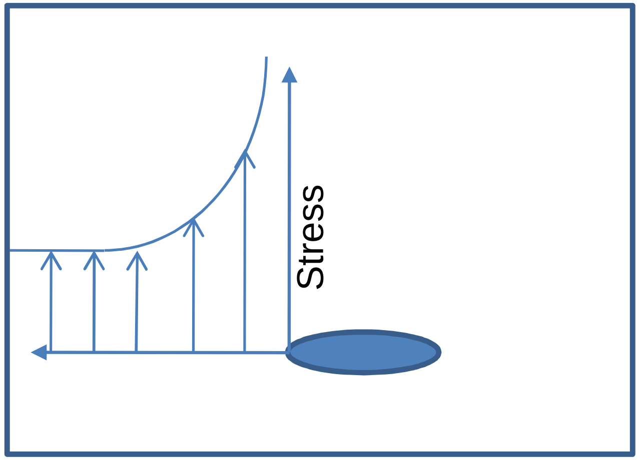


Fig. 6. Local stress pattern near a flaw

A. A little bit of fracture mechanics

Stress intensification at flaws

Reason

when a body is subjected to any load or stress, lines of force pass through the material, *a la* magnetic lines of force, as shown in the Fig. 7. The density of these lines at any point is a measure of the stress. These lines are equispaced at the two ends of the sample under stress. Near the crack, they are closely spaced, which is why stress intensification occurs near crack tips and the effect dies away with distance from the tip

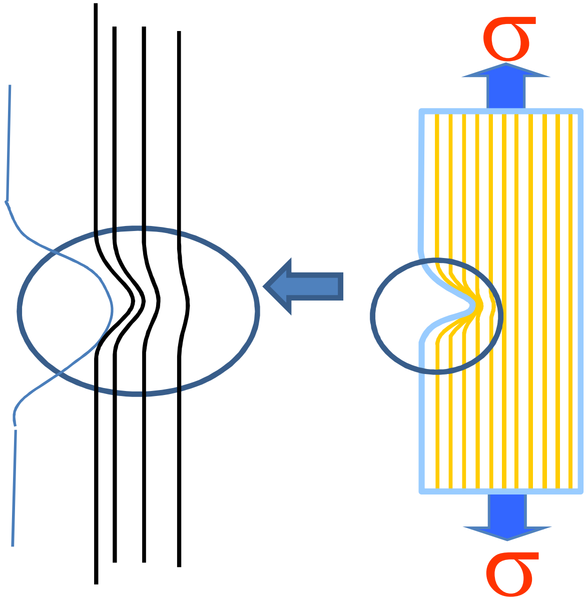


Fig.7. Stress intensification near cracks

Modes of fracture

Depending on the relative direction of loading and the direction of crack growth, there can be 3 types of fracture:

Mode I :The fracture plane is perpendicular to the normal force. e.g. tension tests of brittle materials.

Mode II fractures occur under the action of a shear stress, with the fracture propagating in the direction of shear. e.g. punching of hole in a metal plate.

Mode III fractures are also shear separations, but here the fracture propagates perpendicular to the direction of shear. e.g. cutting of paper with scissors.

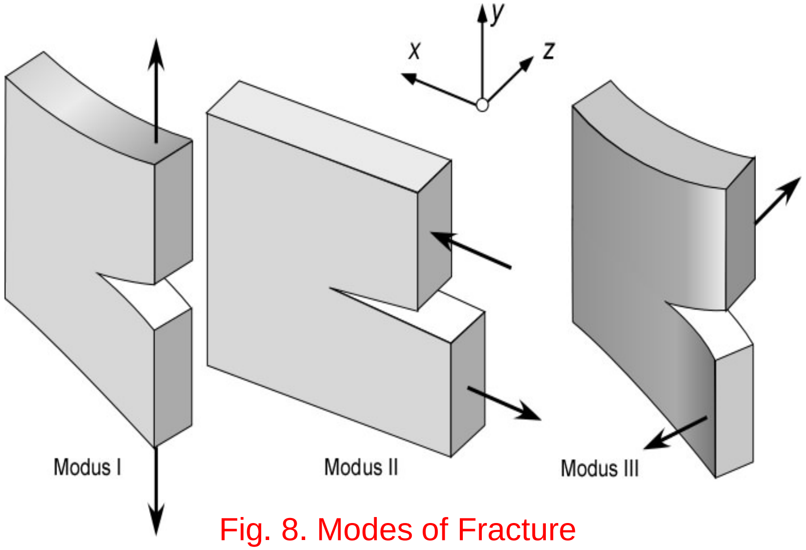


Fig. 8. Modes of Fracture

W. Brocks, 5 lectures at Politechnico di Milano, 2012

A. A little bit of fracture mechanics

Concept of Stress Intensity Factor, K

Irwin showed that the stress ahead of a crack as well as the displacements due to an applied load could be defined by a parameter K and the radial co-ordinates of any point (P) ahead of the crack (Fig. 9). That is, if the the radial co-ordinates of a point are (r, θ) with respect to a crack as shown below, then the stresses[σ_x, σ_y, σ_z] and the displacements [u,v,w] at that point are uniquely defined using K.

$$\sigma_{rr} = \frac{K_I}{\sqrt{2\pi r}} \cos\frac{\theta}{2}\left(1 + \sin^2\frac{\theta}{2}\right) \quad \text{……[A1]}$$

$$\sigma_{\theta\theta} = \frac{K_I}{\sqrt{2\pi r}} \cos^3\frac{\theta}{2} \quad \text{……[A2]}$$

$$\sigma_{r\theta} = \frac{K_I}{\sqrt{2\pi r}} \cos^2\frac{\theta}{2} \sin\frac{\theta}{2} \quad \text{……[A3]}$$

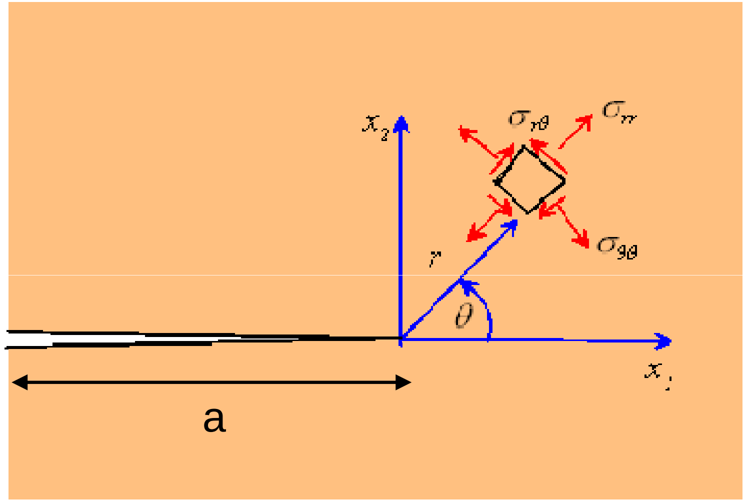


Fig. 9. K defined stress field ahead of a crack

N.B. None of the above equations needs to be memorized for this course

K is defined as follows

$$\mathbf{K = Y\sigma\sqrt{(\pi a)}} \quad \text{……[A4]}$$

Where **Y** = a geometrical constant , **σ** is the applied stress and "**a**" is the crack length. Please note that for an elliptical crack in the specimen center, "**2a**" is the crack length

A. A little bit of fracture mechanics

Concept of Crirical Stress Intensity Factor, K_c

It is evident from the earlier sections that in a flawed component or specimen, the local stresses near the crack tip is solely defined by the parameter K. This simplifies our life considerably, since now we can measure critical values of K and call it K_c, for the situation when fracture occurs, i.e

For fracture : $K > K_c$ ……..*[A5]*

Depending on the loading mode we can thus have $\mathbf{K_{IC}}$, $\mathbf{K_{IIC}}$ and $\mathbf{K_{IIIC}}$.
It should be clarified here that by fracture we do not mean a full failure of the specimen, rather an increase in the crack size from its stable stationery value. That is to say, we consider the fracture event to have started as soon as there is an increase in the flaw size.
It is noted that K_c values are quite often intrinsic material properties, especially if no deleterious environments are present.

The advantage K_c gives us is that we now have a single parameter definition of fracture, and we can set safe operating limits based on K_c, we need not specify stress limits or flaw size limits separately.

Knowing the flaw size it is possible to define the safe operating stress, conversely, if the operating stress is known the tolerable flaw size can be defined. In fact defining a Critical Flaw Size for a component of a given material is more in vogue

Numerical example: A component with maximum flaw size of 9 mm fails at an applied stress of 100 Mpa. Find the failure stress for another component of similar design and made of the same material which has a maximum flaw size of 4 mm.

$$K = Y\sigma\sqrt{(\pi a)}$$

Note that Y will be the same for both component due to the same design. Thus $\sigma_1 \sqrt{(\pi a_1)} = \sigma_2 \sqrt{(\pi a_2)}$.
Substituting for σ_1 = 100 MPa, a_1 = 9mm and a_2 = 4mm, σ_2 is calculated as 150 Mpa.

A. A little bit of fracture mechanics

Defining thresholds for safe operation

Using Threshold Stress Concepts : I had stated earlier that a certain fraction of the yield stress could be specified as a threshold limit for safe operation. But this is a very conservative limit. It may be better to obtain a time to failure curve for different stress levels and then define the threshold for no fracture as shown in Fig. 10.

Using Threshold K_c concepts : Alternatively the threshold limit can be set by looking at crack growth rates as a function of *K*, the stress intensity factor, and setting the limit as the *K* value below which no crack growth occurs (Fig. 11).

Which is better?

The threshold stress concept does not factor in the possibility of cracks and flaws in the material and is therefore of limited practical use. It is also not indicative of the crack initiation event .

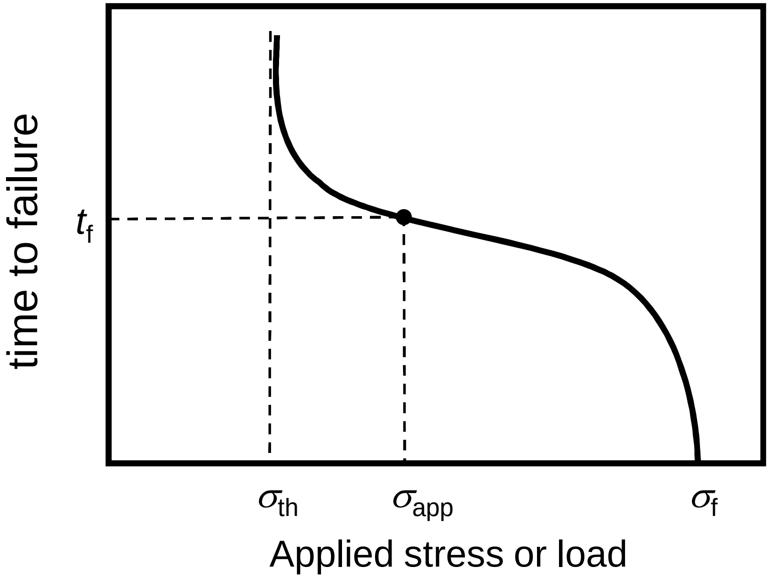


Fig. 10. Threshold stress for failure

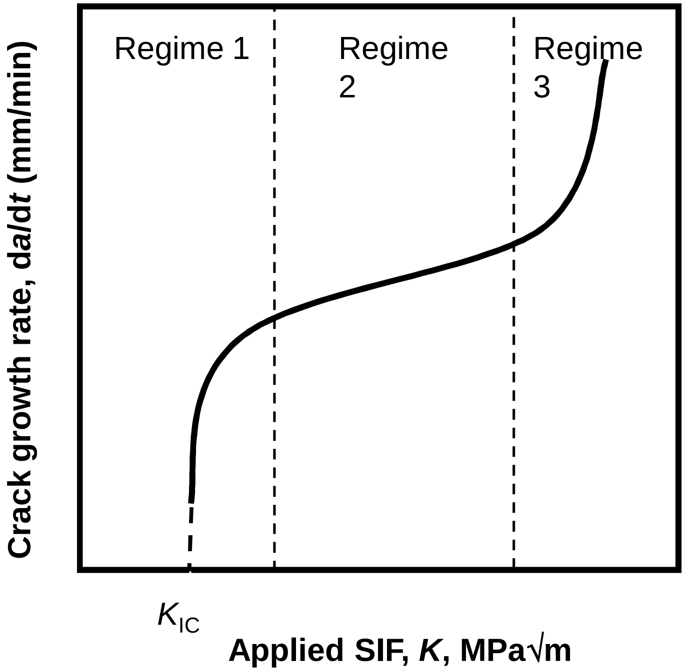


Fig. 11. Threshold stress intensity factor

A. A little bit of fracture mechanics

The special case of pressure vessels : *Design Concepts*

Pressure vessels like pipings, boilers, tubes, etc, which are subjected to operational pressure due to presence of a fluid inside them have very stringent fracture considerations as any unstable fracture will not only cause a loss of the costly component, but likely loss of human lives. The following concepts are used in material design for pressure vessels

A. Yield before break

This stipulates that the material should be such that it yields before it breaks. Yielding can also make the component unusable due to dimensional changes, but this is easily detectable. This means that the maximum flaw size in the component should be such that the yield stress required to fracture is more than the yield stress (σ_{YS}) of the material. So $\sigma_f > \sigma_{YS}$, *where* σ_f *is the critical fracture stress. Since* $\sigma_f = K_{IC}/Y\sqrt{(\pi a)}$, *this means that*

$$K_{IC}/Y\sqrt{(\pi a_c)} > \sigma_{YS} \qquad \text{or}$$

$$a_c < [1/Y^2\pi]\,[K_{IC}/\sigma_{YS}]^2 \qquad \text{………..} \ [A6]$$

The parameter $[K_{IC} / \sigma_{YS}]^2$ *is therefore a useful parameter for material selection. Please note that while* K_{IC} *is a measure of material toughness,* σ_{YS} *is a measure of material strength.*

B. Leak before break

In modern usage, this criterion states that a flaw should be detectable much before it reaches the critical size (a_c) when catastrophic fracture can occur. So, with this criteria, we first specify a maximum allowable flaw size (a_d) which can be detected by available techniques (NDT, etc.).

In the most conservative estimate, $a_c > t$, *the thickness of the pipe. Also the pipe should not yield under the operating pressure. The operating pressure p is given as*

$$p = 2\sigma t/r \qquad \text{……….}[A7]$$

where σ *is the hoop stress and r is the pipe radius. Setting* $\sigma = \sigma_{YS}$ *and using the definition of* $a_c = t = [1/Y^2\pi]\,[K_{IC} / \sigma]^2$ *, the maximum allowable pressure can be calculated*

$$p_{max} = [2/Y^2\pi]\,[K_{IC}^2/\sigma_{YS}] \ \text{……….}[A8]$$

Thus for maximising the operating pressure, the material selection is determined by the parameter $[K_{IC}^2/\sigma_{YS}]$

B. Stress Corrosion Cracking

B. Stress Corrosion Cracking

Importance of Stress in Corrosion

In many types of corrosion like atmospheric or galvanic (two metal) corrosion, stress has a minor and indirect bearing on the corrosive process. But there are a whole array of corrosion types which are accelerated by stress, especially tensile stresses. These are Stress Corrosion Cracking (SCC), Hydrogen Embrittlement (HE) and Corrosion Fatigue (CF). Additionally, pitting is often enhanced by the presence of stresses. The reverse is also true, that is, mechanical degradation is accentuated by corrosion. Thus the different thresholds of mechanical damage like fatigue threshold can be substantially reduced in corroding systems.

Origin of stress

Many components are designed to withstand stresses and in them the stresses are incidental. Thus compellers, load bearing members, gears, shafts, turbines, and a million others are supposed to work under stresses. Additionally residual stresses may be present due to heat treatment, joining processes, surface treatment and forming operations.

The nature and origin of the stresses can be of different types. Dead load, cyclic, frictional and hydrostatic are certain common stress forms in components. Thermal stresses and magnetostrictive stresses can also occur. Overloads due to human errors can accentuate the problem.

How does Stress accelerate Corrosion damage?

Stresses, especially tensile ones, rupture protective films on the component surface and thereby accelerate corrosion. Thus many passivating alloys which have strong corrosion resistance are found prone to SCC. This is also what happens in *Erosion Corrosion*. Even in the absence of protective films, stresses increase material corrosion possibly by changing the surface activity.

It works the other way round too. Fracture of a material occurs by the initiation and propagation of cracks. Corrosion can enhance the crack propagation by anodic dissolution at the crack sites, and even produce crack initiators, for example through pitting. The stresses prevent the build up of protective films and the corrosion effect at the crack tip is sustained.

B. Stress Corrosion Cracking

Damage mechanisms due to simultaneous presence of corroding environment and stress

The nature of stress, the mode of application of stress and the corrosion mechanism or the electrochemical regime, (that is, whether the component is behaving as a cathode or an anode) is the basis of classification of the different types of degradations due to the simultaneous presence of stress and corrosion, presented in the table below.

In certain synergisms, the corrosive phenomenon and the mechanical stressing may occur sequentially instead of concurrently, for e.g. pitting of airframe components can occur during idle conditions and fatigue can initiate from these pits during flight.

Classification of Stress & Corrosion assisted damage

Type	Stress	Electrochemical reaction
Stress Corrosion Cracking	Tensile, Monotonic or Static	Anodic dissolution
Hydrogen Embrittlement	Tensile, Monotonic or Static	Normally cathodic. Anodic if substantial H is produced during corrosion
Corrosion Fatigue	Cyclic	Anodic or cathodic
Erosion corrosion	Shear (due to fluid flow), impact	Anodic
Cavitation corrosion	High impact implosion	Anodic – breakdown of passivity
Fretting corrosion	Contact / frictional stresses	Generally no electrochemical reaction involved

B. Stress Corrosion Cracking

What is Stress Corrosion Cracking?

According to its nomenclature, Stress corrosion cracking should be a generic term to include all synergistic degradations which occur in the presence of stresses and corrosive environments. This would actually include all the degradations mechanisms included in the earlier table. However, in common usage, SCC refers to those degradations which occur under static or monotonically increasing stresses, with stresses generally acting normal to the component. The crack propagates perpendicular to the principal stress as shown here (Fig. 12).

Also in SCC there is either active dissolution of the material or the material is in the anodic regime. Thus SCC occurs when the three conditions of tensile stresses, susceptible material and corrosive environment are all present as shown in Fig. 13.

Fig. 12. Jacket around cooling pipe. Circumferential hoop stresses are responsible for cracking along the pipe length

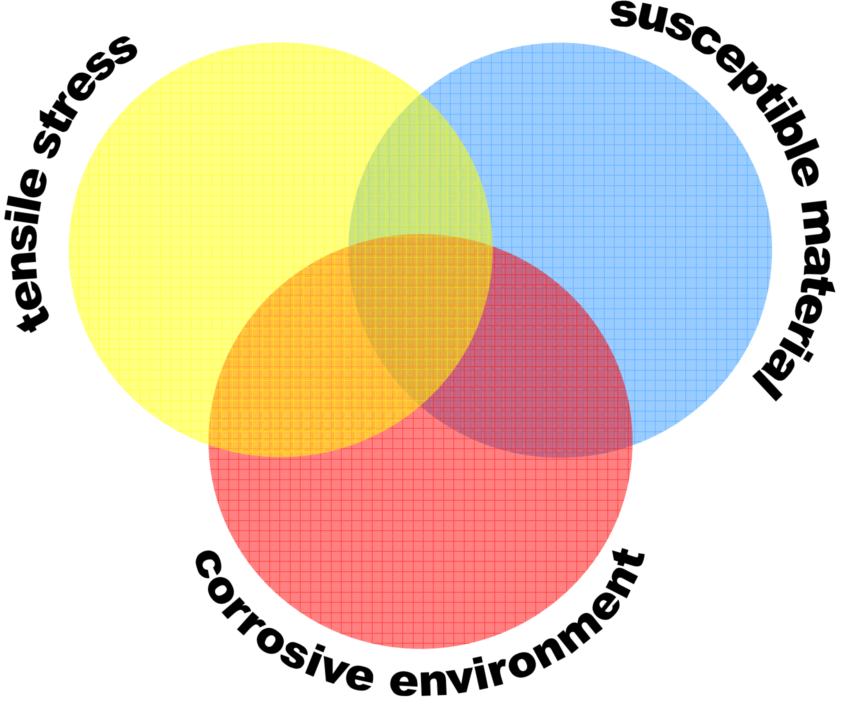


Fig. 13. Conditions necessary for SCC

B. Stress Corrosion Cracking

Mechanisms of Stress Corrosion Cracking

The two main mechanisms of SCC are :

1. **Active Path Dissolution**:
   In this process accelerated corrosion occurs along a path of high corrosion susceptibility. Grain boundaries with their diffuse atomic structure and abundance of segregated elements and precipitates are normally more electrochemically active than the rest of the matrix. In sensitized stainless steels, chromium carbide precipitates form at the grain boundaries with a resultant depletion of chromium which is required for passivation. Thus the grain boundaries are preferentially attacked as compared to the passive matrix. In the absence of stress, this results in intergranular corrosion. In the presence of stresses cracks initiate at the grain boundaries and propagate along them. Further propagation and the rate of crack growth is limited by the rate of corrosion of the metal at the crack tip, which limits the maximum crack growth rate to around 10^{-2} mm/s, while practically, crack growth rates are often much lower, about 10^{-8} mm/s. Active path dissolution produces intergranular cracking.

2. **Film induced cleavage :**
   Corrosion products may reside on the metal/alloy surface. These films are brittle and cracks may initiate in them and propagate some distance into the underlying ductile material causing an incipient crack in the material, before the crack growth is arrested (Fig. 14). The crack faces then get covered by the brittle film and the process repeats itself. The film-induced cleavage process would normally be expected to give a transgranular fracture.

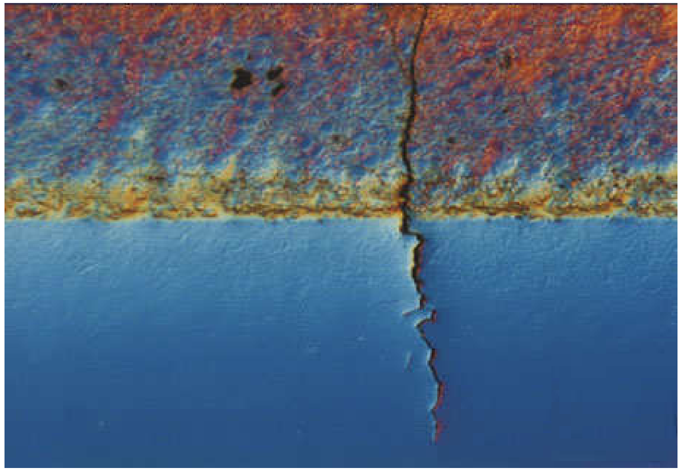


Fig. 14. A mechanical crack in overlay caused substrate cracking

http://hghouston.com/resources/corrosion-images/

B. Stress Corrosion Cracking

Mechanism of crack propagation

The basic process can be summarized as follows:

Incipient surface cracks are either present inherently in the material or are produced during stress application (Fig. 15). One way incipient cracks can be produced is by the emergence of slip steps at the surface during deformation. The cracks on the whole are less accessible than the surface. This may result in differential concentration cells being set up, or there may be acidification of the crack tip. The cracks become seats of relatively high anodic activity. As a result, the crack tip undergoes anodic dissolution and advances incrementally (Fig. 16). If the anodic processes are uninterrupted, the crack growth occurs continuously. If, however, the crack tip sees periods of inactivity, the crack grows in fits and spurts and the resultant fracture surface shows discontinuous cracking.

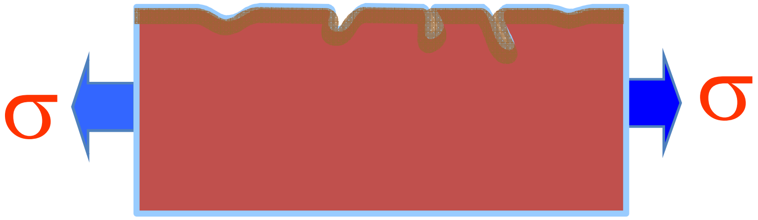


Fig. 15. Incipient cracks may be present or are produced during stressing

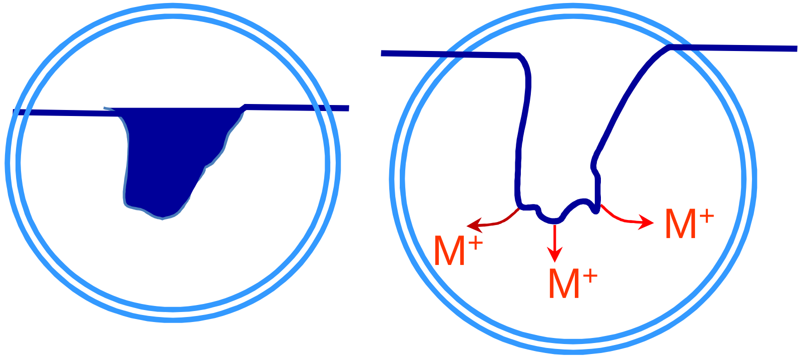


Fig. 16. Crack tip dissolution occurs in preference to crack face dissolution

[Courtesy: S. Sivaprasad]

B. Stress Corrosion Cracking

Critical stress intensity factor for Stress Corrosion Cracking [K_{ISCC}]

Let us recall the critical stress intensity factor (K_{IC}). In corroding media, the critical stress intensity factor below which no crack growth occurs is typically smaller and called $\boldsymbol{K_{ISCC}}$. This defines the safe limit for operation. Please note that the crack growth rates are faster at all *K*s in a corroding medium. The K_{ISCC} is determined experimentally (Fig. 17).

Calculation of safe limits of operation under SCC

1. K_{ISCC} is known or determined expermientally
2. The flaw size ("*a*") is known or determined by Non-destructive evaluation for components under operation or by microscopy for virgin components
3. Use $\boldsymbol{K = Y\sigma\sqrt{(\pi a)}}$ to determine the safe stress below which no stress corrosion will occur. Remember that "*Y*" is dependent on the crack geometry.

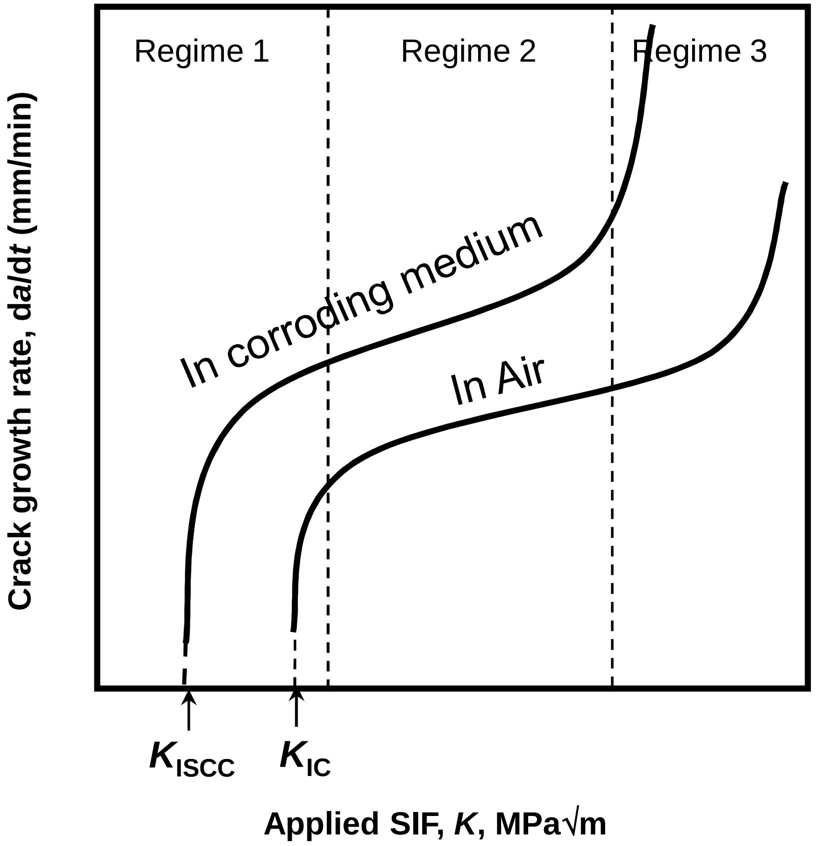


Fig. 17. Definition of K_{ISCC}

B. Stress Corrosion Cracking

“Environment specificity” in SCC

A specific environment and material combination is required for SCC. Not all corrosive environments promote the formation of stress corrosion cracks in all materials. Even if a material is known to corrode in a given environment, it may not cause SCC. In fact it is often observed that SCC occurs in environments which cause limited corrosion or even mild inhibition of corrosion, and alternatively, environments which cause widespread uniform corrosion in a material is least likely to cause SCC. The reason for this is that a crack has to remain sharp for it to experience the maximum crack driving force. Uniform corrosion tends to blunt the cracks and therefore crack driving forces decrease substantially.

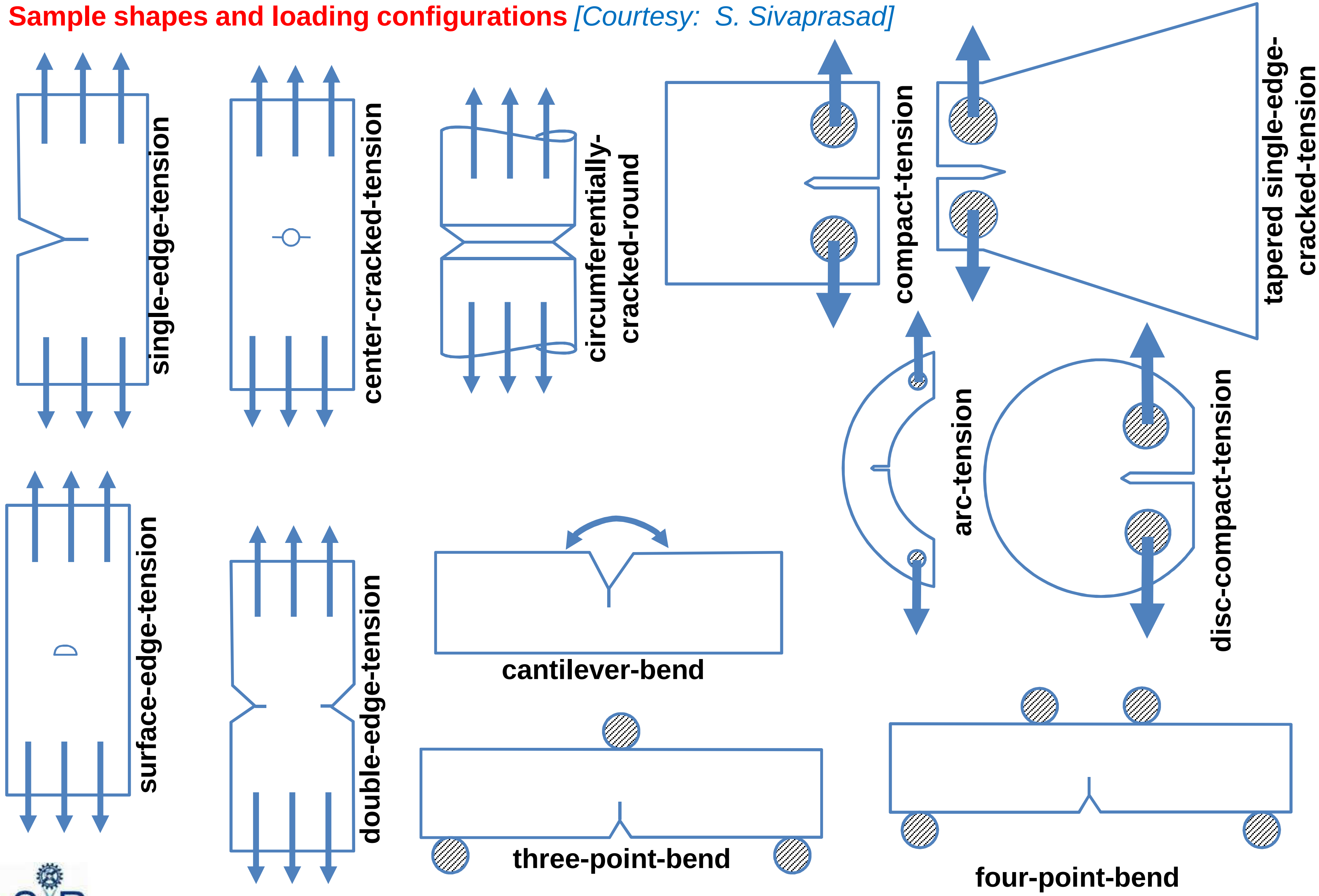
The environment-material specificity is highlighted in the adjacent Table

Material	Environments
Al alloys	Chlorides, moist air
Mg alloys	Chloride-chromate mixtures, moist air
	Nitric acid, fluorides.
	Sodium hydroxide
Cu alloys	Ammonia, moist air, moist sulfur dioxide
C steels	Nitrates, hydroxides, carbonates
	Anhydrous ammonia
Austenitic steels	Chlorides, sulfur acid
High strength steels	Moist air, water, chlorides, sulfates, sulfides
Ni alloys	Hydroxides
Ti alloys	Halides, methanol

http://www.corrosion-doctors.org/Forms-SCC/scc- environments.htm

B. Stress Corrosion Cracking

Sample shapes and loading configurations *[Courtesy: S. Sivaprasad]*



B. Stress Corrosion Cracking

Essential conditions

1. Suitable environment – it should not cause general corrosion of the material
2. Material specificity – the materials should be susceptible to SCC in the given environment
3. Presence of externally imposed or inherent tensile stresses

Conditions met in season cracking (Fig.18)

1. ***Environment : Moist air + ammonia.***
2. ***Material : Cu present in brass reacts to form soluble cuproammonium $(Cu(NH_4)_2$ ions***
3. ***Tensile stress : Residual stresses due to crimping of the bullets***

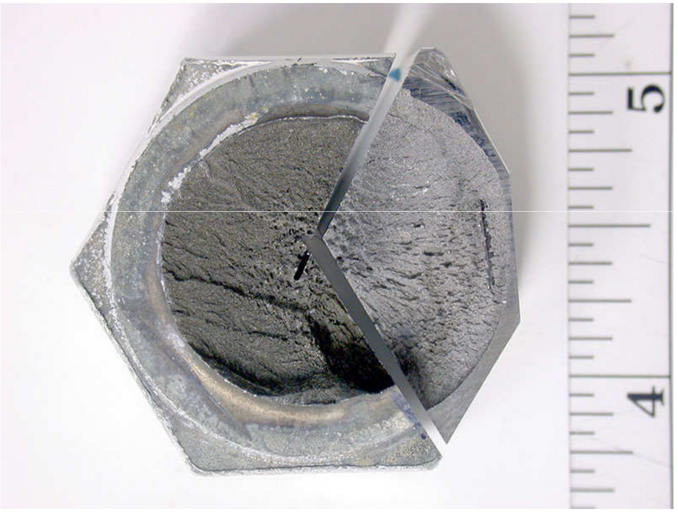
Fig.18. Classic example of season cracking
http://en.wikipedia.org/wiki/Season_cracking

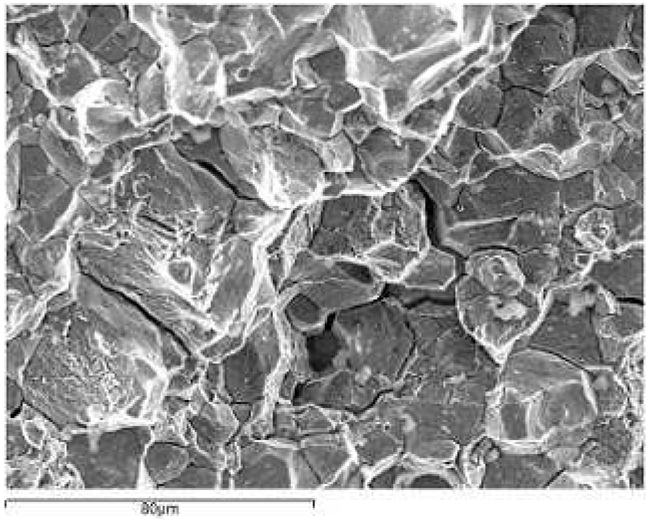
Prevention of Stress Corrosion Cracking

It is obvious that removal of any one or more of the above essential conditions will reduce or eliminate SCC. Let us look at each in turn.

1. Environmental :
   - a. Modify environment : add inhibitors, scavengers
   - b. Employ anodic or cathodic protection
   - c. Modify temperature of operation
2. Material :
   - a. Change alloy composition : use material selection principles
   - b. Change alloy microstructure
   - c. Use surface treatment - coatings, deposits, cladding
3. Stress :
   - a. Select correct operating stress
   - b. Relieve any fabrication/joining induced residual stresses
   - c. Impose surface compressive stresses : shot peening, sand blasting
   - d. avoid stress concentrators in design

C. Hydrogen & Stress Assisted Degradations





C.1. Hydrogen entry and distribution

Peculiarities of hydrogen diffusion

A. Hydrogen is one of the smallest atom in size with consequent high mobility. Please note that C and N are equivalent in atomic size, but are much heavier.

B. Hydrogen is absorbed as an atom (not as ion or molecule). It responds to both a concentration gradient as well as to a stress gradient, i.e.

$J_H = D\ \delta C_H / \delta x$ ………………. [C1] *[Fick's First Law]*

$J_H = f\ (\delta\sigma_{hydro} / \delta x\ )$ ……………………[C2]

Where J_H is the hydrogen flux, C_H is the hydrogen concentration and σ_{hydro} is the hydrostatic stress . In a stressed component, the hydrostatic stress gradient reaches a maximum a little ahead of the crack tip. The reason hydrogen responds positively to tensile hydrostatic stress gradients is that it normally has a positive molar volume for most metallic materials. Which means that hydrogen entry would cause an expansion in the metallic lattice. Therefore if there is already an expanded lattice due to stress applied, H has easy entry.

This means the following

1.A tensile stress (resulting in a tensile hydrostatic stress) will pull hydrogen ahead of the crack tip

2.The total hydrogen entry is far greater than what is calculated using normal diffusion when there is a tensile stress present

3.The effective diffusivity of hydrogen is significantly enhanced in the presence of a stress

4.Compressive stresses (e.g. shot peening) will reduce hydrogen entry

C. The hydrogen atoms which resides in the normal interstitial positions in an atomic lattice are the diffusible hydrogen. Hydrogen gets trapped at microstructural discontinuities. There are either reversible traps or irreversible traps. Dislocation cores are reversible traps, while certain precipitates and inclusions like MnS, carbides, etc., are irreversible traps.

C.1. Hydrogen entry and distribution

Hydrogen entry Scheme

Hydrogen enters the material from any of the following sources

1. Corrosion reactions
2. Processing environments (sour crude, oil & gas, chemical processing, etc.)
3. Cathodic protection systems
4. Anodic coatings or plating, sacrificial anodes or imposed voltages during processes
5. During fabrication (welding, etc.)

Hydrogen from external sources enters the material by first adsorbing onto the surface, followed by absorption into the material and then diffusion through the matrix. A part of the hydrogen exists as a solute in the normal positions of the lattice, while a part of it resides at "hydrogen traps" which have a high affinity for hydrogen. In linepipe steels, for example, MnS inclusions can act as hydrogen traps. The lattice decohesion can start at these trapped sites fuelled by hydrogen.

The hydrogen entry and distribution is shown schematically in the adjacent figure (Fig. 19).

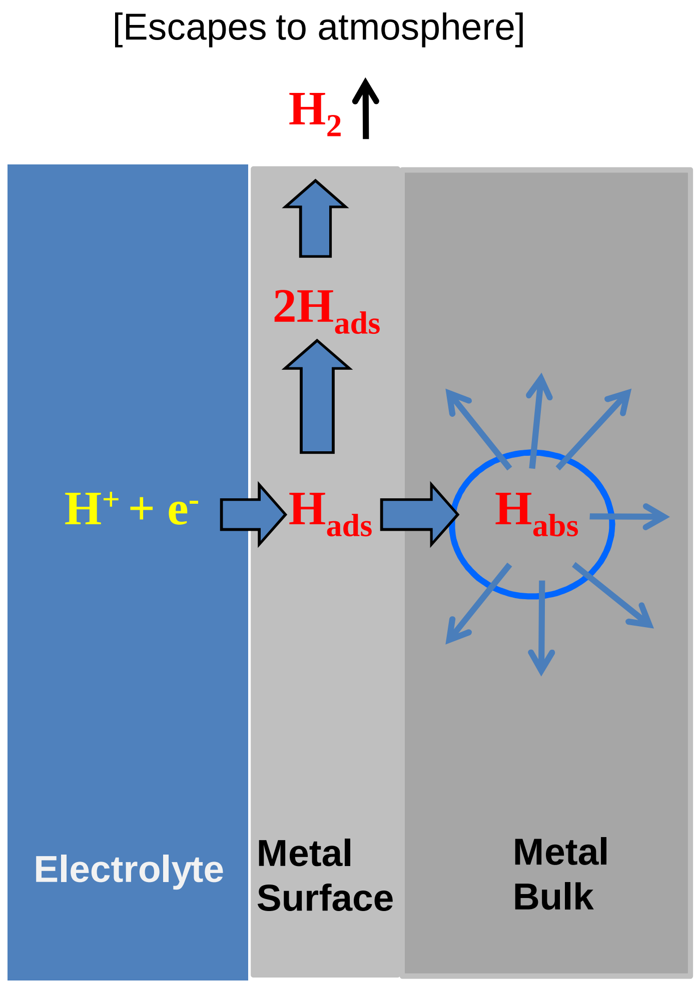


Fig. 19. Schematic of hydrogen entry into materials

C.1. Hydrogen entry and distribution

Hydrogen transport within the metallic lattice

- The fast diffusing hydrogen either travels through interstitial spaces or is trapped at trapping sites (Fig. 20). If the trapping is reversible, small application of load can free it.
- If dislocations trap hydrogen, they carry them as they move during plastic deformation.

Corollary : Plastic deformation enhances hydrogen effects

- H, in turn enhances dislocation mobility, so a synergistic relation is built with dislocations.
- The hydrogen which are irreversibly trapped can accumulate at those sites (sulphide/ carbide inclusions). As a result local voids near these traps are created

The activities of hydrogen within the metal lattice

A. In a hydride forming metal or alloys (Zr, V, Ti, etc.)

1. Forms a brittle metallic hydride
2. The hydride formation is often stress assisted
3. Changes phase transformation temperatures

B. In a non-hydride forming metal or alloy (Fe, Al, etc.)

1. Causes phase transformation (e.g. formation of ε-martensite)
2. Interacts with metal atoms by donating electrons to the d-orbitals of the metals. This reduces the atomic bonding strength.
3. Causes void formation and crack initiation at irreversible trapping sites
4. Changes slip system activities, favors planar slip

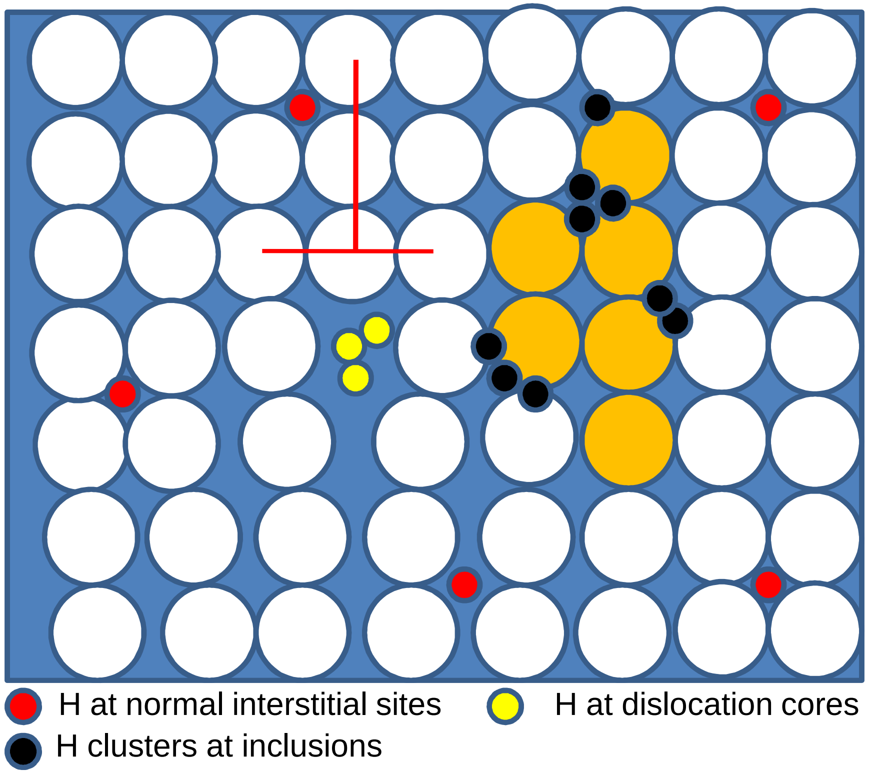


Fig. 20. Residence of hydrogen in metal lattice

C.2. Hydrogen degradations

Types of Hydrogen Degradation of materials

The various hydrogen enhanced material degradation mechanisms are loosely termed hydrogen embrittlement (HE). However, HE is only one specific form of hydrogen degradation. The classification of the different hydrogen degradations can be done based on the temperature of occurrence, environment severity (H fugacity) and presence of external stresses; and there are, broadly, three different types of hydrogen degradations:

1. **Hydrogen attack (HA)**
2. **Hydrogen induced cracking (HIC)**
3. **Hydrogen embrittlement (HE)**

The distinction between the three are made in the table below. Strictly speaking, Hydrogen attack and Hydrogen induced cracking do not qualify as SCC as there is no externally impressed or internal residual stresses required for their occurrence. But, in both, the hydrogen is responsible for generating significant stresses leading to cracking. They are included here for the sake of completeness.

Type of degradation	Hydrogen Fugacity	Temperature	Stress requirement	Common occurrence
Hydrogen attack [HA]	Medium to high	Higher than ambient	No external stress required	Condensers, tubings, etc exposed to high H fugacity at high temperatures
Hydrogen induced cracking [HIC]	High	Ambient	No external stress required	Sour crude transportation pipeline
Hydrogen embrittlement [HE]	Low	Ambient	External or residual stress required	Numerous components

C.2.1. Hydrogen Embrittlement

Definition

Hydrogen embrittlement (HE) is often thought of as a form of SCC. However there are important differences with SCC for HE to merit separate identity.

Hydrogen embrittlement is, as the name suggests, the embrittlement of materials due to the presence of hydrogen. HE does not necessarily manifest in classical brittle cracking (intergranualr or cleavage) but always results in a loss in ductility .

HE requires the presence of externally applied or internal residual stress. HE is a low fugacity phenomenon and often a few ppm to tens of ppm of H can cause HE. The insidious nature of cracking, the easy availability of Hydrogen through electrochemical reactions in aqueous systems, high diffusivity of H through solids, all make HE a big threat for numerous materials and components (Fig. 21). Hydrogen is produced at the cathode in most corrosion processes. If cathodic protection is applied to a component, hydrogen is again produced in the vicinity of the component. So irrespective of the electrochemical potential of the component, HE remains a threat.

Fig. 21. HE can result in extremely brittle cracking as shown here for a screw which has failed within a nut

http://metassoc.com/site/2013/07/hydrogen-embrittlement-high-strength-steels-achilles-heel-part-4/

C.2.1. Hydrogen Embrittlement

Cracking Mechanism

In HE there is either no corrosion product or passive film on the surface of the component as well as on the incipient crack faces or it is not substantial to retard hydrogen entry. In comparison with SCC therefore H diffusion occurs unimpeded and the existence of high stresses ahead of the crack tips help hydrogen diffusion. The crack is not allowed to blunt (Fig. 22) as hydrogen generally favors planar fracture. Thus a high stress intensity is maintained at the crack tip.

HE can initiate as well as propagate from multiple locations (Fig. 23). They tend to merge and may move as one or many crack fronts. Eventually the remaining ligament of the component fractures due to overload, which is generally through void coalescence. The extent of the brittle zone is decided by the amount of hydrogen, the material properties and the stress applied.

As the crack grows into the material, the stress increases for a constant load situation. Consequently, the hydrogen entry also increases due to stress aided diffusion and catastrophic failures may occur.

The hydrostatic stress maximum normally occurs a finite distance from the crack tip. Thus in HE the cracking may occur slightly ahead of the existing crack and then joining of the two causes crack growth. This may give the appearance of discontinuous cracking.

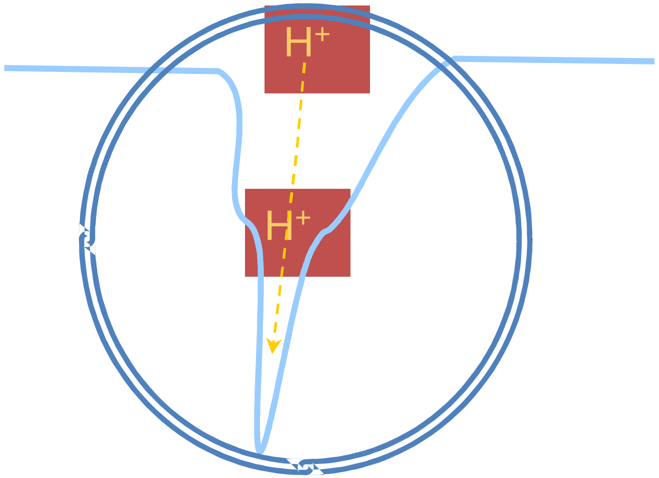


Fig. 22. Crack tip processes in HE

[Courtesy: S. Sivaprasad]

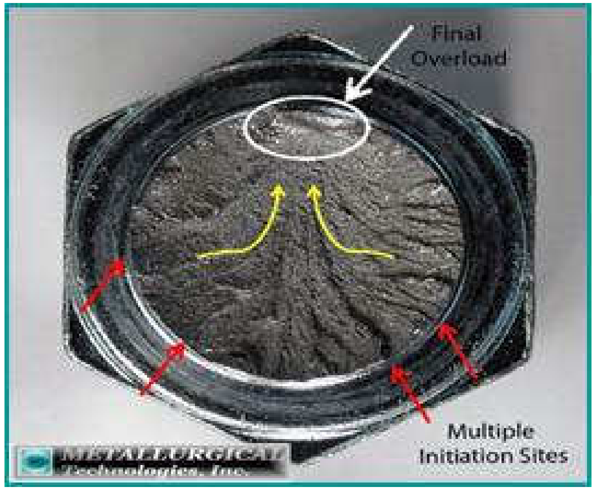


Fig. 23. Multiple site HE crack initiation

http://met-tech.com/Hydrogen_Embrittlement.html

C.2.1. Hydrogen Embrittlement

Cold Cracking of welds

Cold Cracking or Delayed Cracking is the appearance of cracks near and along welds within a finite time interval after welding and is caused by hydrogen generated during welding (Fig. 24). It can occur within a few minutes to up to a few days after welding (hence called "Delayed Cracking") . The susceptibility is most near ambient and decreases both at lower as well as higher temperatures (hence "Cold cracking").

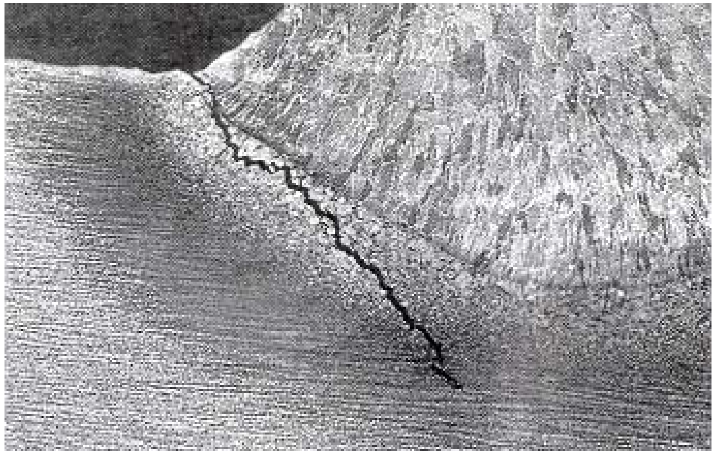


Fig. 24. Cold cracking near a weld
http://www.twi.co.uk/technical-knowledge/job-knowledge/defects-hydrogen-cracks-in-steels-identification-045/

Why are welds and near welds so susceptible to HE?

There are a number of reasons:

1. Different microstructures are produced near the weld including "Widmanstatten phases", which are hard phases and therefore increase susceptibility to HE. Additionally the higher cooling rates of the near weld region ensures martensite formation in these regions in steels.
2. H is often introduced during welding either from the atmosphere or from the electrode. An inert atmosphere and /or a low H electrode reduce this problem.
3. Welding also introduces residual stresses concentrated near the weld, as a result of differential cooling rates and/or volume changes brought about by new phase formation.

Thus proper choice of electrodes, preheating the job, using post-weld heat treatment, are all effective in reducing hydrogen related failures near weld

C.2.1. Hydrogen Embrittlement

How is SCC different from HE?

- ❑SCC is an anodic process as opposed to HE where the significant reaction is cathodic (production of H). Although SCC occurs in relatively benign environments, there is material loss brought on by active path dissolution, while HE proceeds with no material loss.

- ❑SCC can be controlled by cathodic protection, while HE would be accelerated by the same.

- ❑SCC does not occur in aggressive environments, and normally requires the formation of protective films. Thus there is a material-environment specificity in SCC. HE can occur for any material-environment combination as long as there is a source of H and stresses are sufficient.

- ❑One of the most important difference between SCC and HE is their response to strain rate during monotonic loading. The two are compared in Fig. 25 where reduction in area is used as the ductility measure. This difference in strain rate sensitivity lies in the difference in their mechanisms. SCC requires make and break of the protective surface film. At very high strain rates passive film regeneration is not possible; while, at very low strain rates, the rate of repassivation is faster than the rate of passive film rupture, so that the material remains passive with very little corrosion. Thus, it is only in intermediate strain rates, that one encounters SCC. HE has an inverse relationship with strain rate.

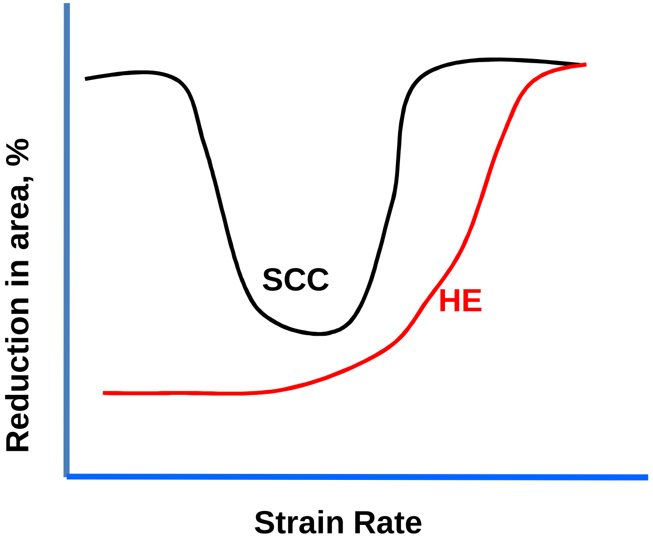


Fig. 25. Strain rate sensitivity of HE and SCC

C. 2.2. Hydrogen Attack *(Also called "Hot hydrogen Attack")*

Hydrogen attack (HA) is normally observed in steel components used for higher temperature and high H pressure service, such as condensers and pipings and the resultant fracture can be a splitting open of the component as shown in Fig. 26.

At high temperatures (200 – 600 ºC) and high hydrogen pressures, the H reacts with C present in the steel to produce methane gas.

$$Fe_3C + 2H_2 = 3Fe + CH_4$$

If the methanation occurs in the component interior, it tends to accumulate at grain boundaries and being unable to escape generates substantial pressure which may cause fracture. A side effect of this attack is that the steel tends to be decarburized as the carbides are used up. So loss of mechanical property occurs due to both reasons.

The pressure generated by hydrogen should increase with decrease of temperature as the above reaction is exothermic. However a diffusion of H to the carbides is required which is favoured by high temperature. Thus an optimum range of temperature for HA to occur exists.

The susceptibility of an alloy to hydrogen attack is given by the Nelson curves (Fig. 27).

Fig.26. H Attack in a condenser pipe
http://sirius.mtm.kuleuven.be/Research/corr-o-scope/hcindex2/tutor21.htm

What are the remedial measures ?

HA involves reaction of carbides with H. Hence addition of strong carbide formers, such as Ti and Nb as alloying elements, reduce HA susceptibility. High alloy steels are more resistant to HA. Special care should be taken during welding as the weld zone including the Heat affected zone (HAZ) is very susceptible. Post weld heat treatment as well as preheating of the material to be welded can reduce HA susceptibility. Therefore a proper choice of material and fabrication routes are essential to avoid or reduce susceptibility to HA.

C. 2.2. Hydrogen Attack

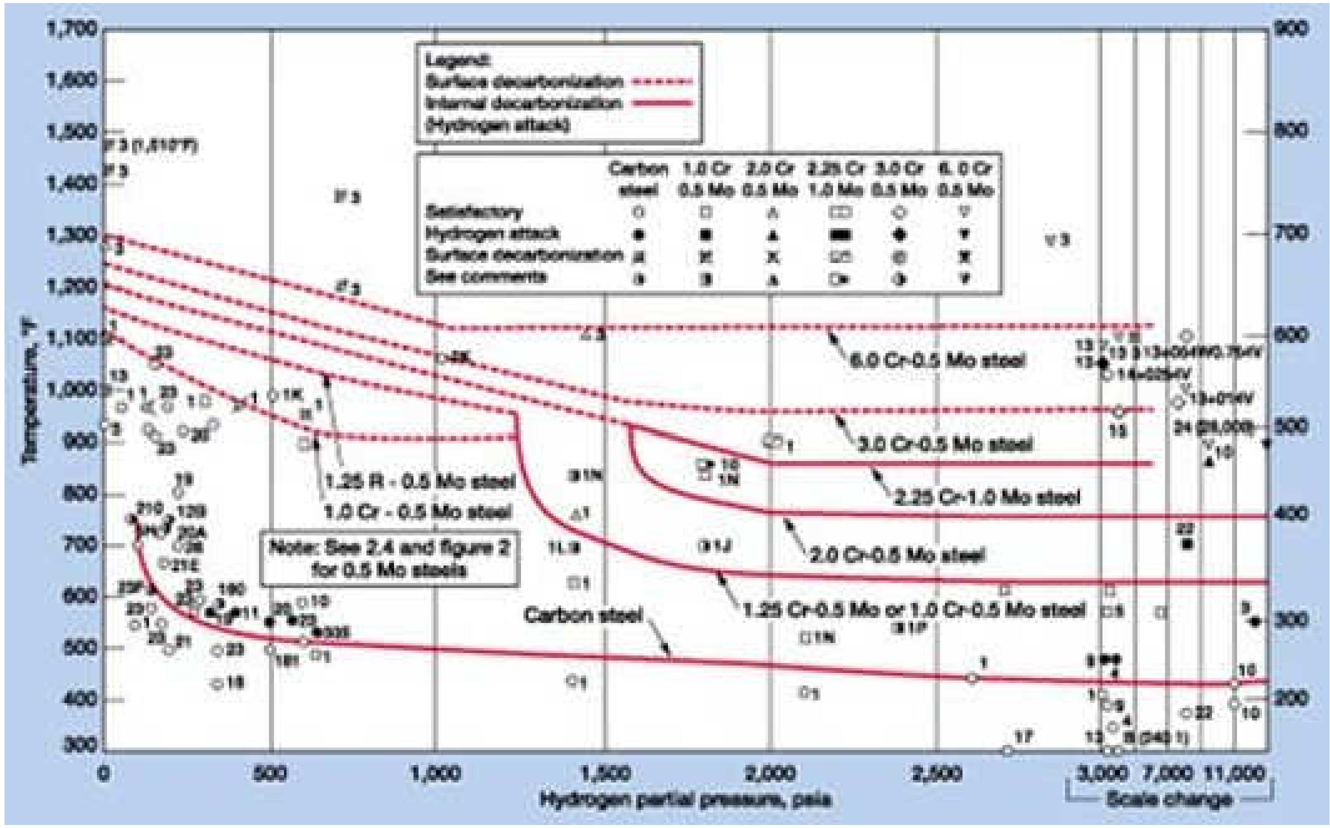


Fig. 27. Nelson curves show safe operating limits of temperature and hydrogen partial pressure for steels. Empirical curves drawn from actual experience

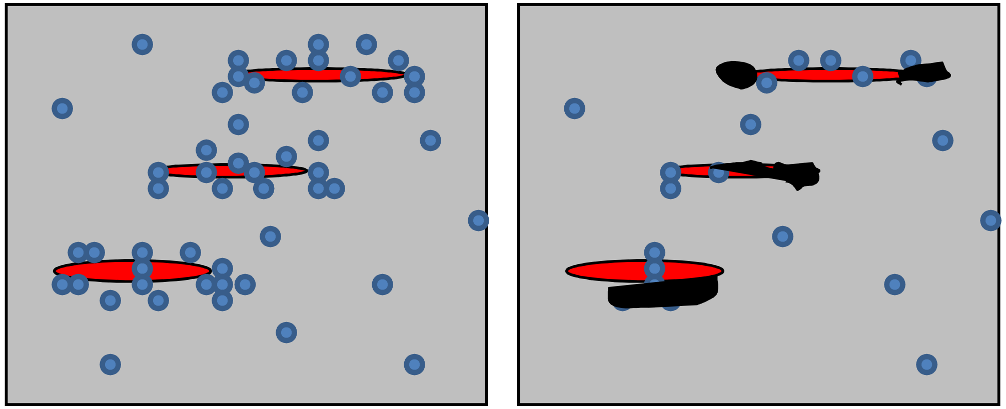
Namboodhiri, Hydrogen damage of metallic materials.

C. 2.3. Hydrogen Induced Cracking

Hydrogen induced cracking is typically a problem of the oil sector. Sour crude pipelines, linepipes and associated components are most affected by it. The presence of H_2S in sour crudes catalyzes the ingress of high H into the material. The high fugacity hydrogen causes HIC in the following sequence

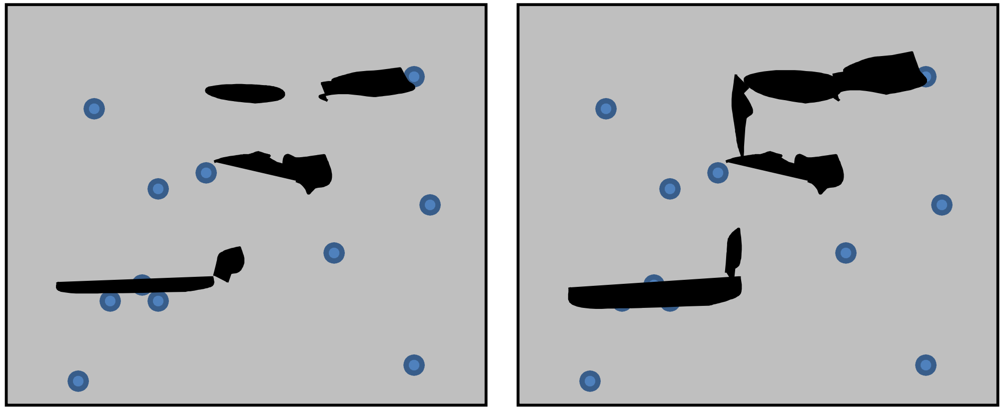
1. Hydrogen diffusion to preferential sites like MnS inclusions/ carbides
2. H accumulates at these sites causing lattice decohesion and creation of voids
3. These voids tend to follow the contour of the inclusions, so that if the inclusions are stringers, the voids tend to be linear
4. Nearby voids from different planes join together to produce a step-wise appearance. Hence HIC is also known as “Step-wise cracking”

The above sequence is schematically shown in the adjacent figure (Fig.28) and an actual photograph of HIC affected matrix is provided in Fig. 29.



1. H diffusion to inclusions

2. Void formation



3. Void Growth

4. Void Linkage

Fig. 28. Schematic of sequence of steps in HIC:

C. 2.3. Hydrogen Induced Cracking

The role of sour environments in HIC

Sour environments contain H_2S. This dissociates as follows:

$H_2S = HS^- + H^+$ The HS^- reacts with the metal
$HS^- + Fe^+ = FeS + H$
Thus hydrogen is produced in addition to whatever is available from the aqueous medium. Secondly H_2S retards the recombination of H atoms to form molecules and escape from the system. The test procedure for HIC uses an artificial sour environment (Fig. 30).

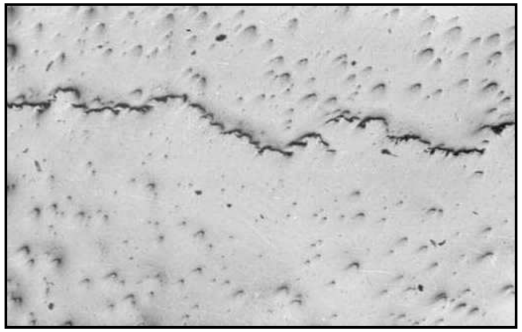


Fig. 29. HIC has a step-like appearance

The role of MnS stringers

H accumulates at MnS inclusions as they act like traps. The more stringer like the inclusions, the greater the surface area available for H adsorption. Additionally any stress concentration would happen at the stringer tips leading to enhanced H accumulation

Necessary conditions for HIC

1. High fugacity hydrogen (as is found in sour crude oils)
2. Stress is not necessary although it will aid HIC
3. Existence of large number of hydrogen traps (MnS inclusions)

Preventive Measures

Since MnS inclusions especially in long stringer forms and other inclusions are very detrimental, a very clean steel is desired. This requires sulfur control as well as addition of elements which globularize the inclusions or render the S harmless.

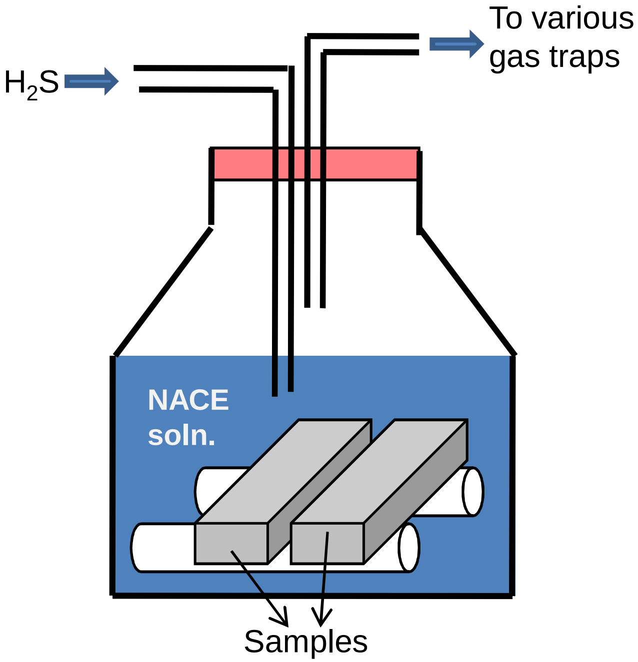


Fig. 30. Test set-up for HIC susceptibility measurement

C. 3. Mechanisms of Hydrogen degradation

Theories of Hydrogen Degradation

Many theories have been proposed to explain Hydrogen embrittlement in particular and Hydrogen degradation in general. Although there is still some debate, a few of these theories are now accepted for different types of hydrogen degradations. The more popular ones are as follows:

1. Brittle hydride formation
2. Pressure generation
3. Decohesion
4. Surface energy reduction
5. Hydrogen enhanced localized plasticity

1. Brittle hydride formation

This is one of the theories which is widely accepted for hydride forming metals and alloys (Zr, Ti, etc.). Hydrides formed by hydrogen are generally brittle and often the hydride formation is assisted by stress (Fig. 31).

The hydrogen diffuses from the matrix hydrides located far away from the influence of the crack tip stress field, to the tip of the crack, resulting in crack tip hydride. This hydride is brittle and cracks easily and the process is repeated. What needs to be realized here is that the hydrogen diffusion is stress aided and not due concentration gradient. The high hydrostatic stress near the crack pulls in hydrogen from the matrix hydrides as well as the lattice hydrogen.

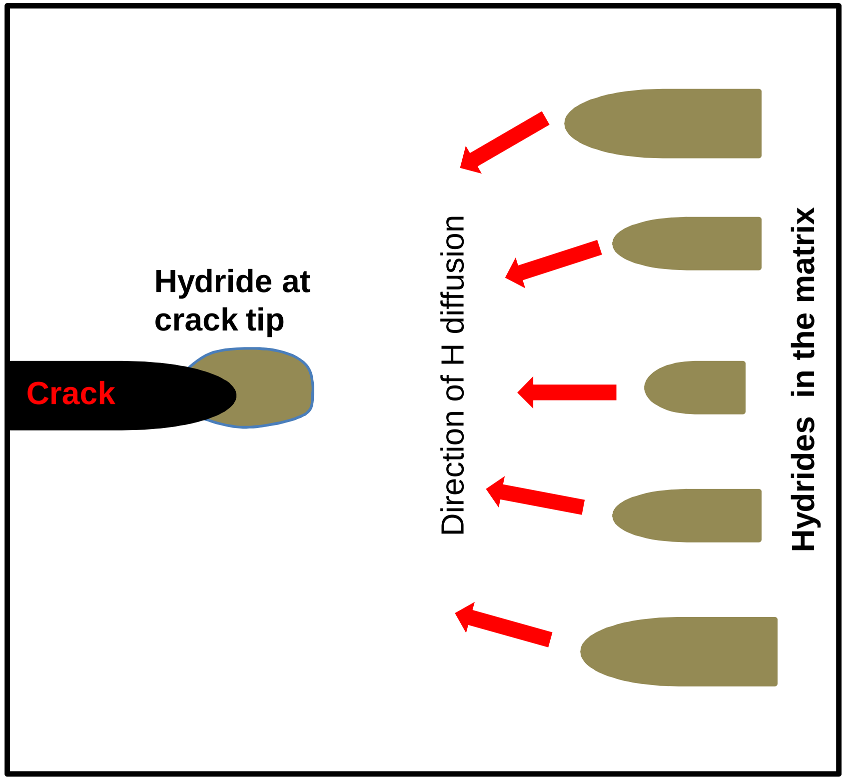


Fig. 31. Hydride formation at crack tip according to Dutton & Puls

C. 3. Mechanisms of Hydrogen degradation

Theories of Hydrogen Degradation

2. Pressure generation

In the pressure theories, hydrogen accumulation within the material especially at so called “traps” can cause considerable pressure creation. The basis of this theory lies in the Sieverts’s Law which relates the pressure developed to the hydrogen concentration. The schematics for HIC shown earlier (Fig.28) is the mechanism of pressure build-up.

The theory is acceptable for high fugacity hydrogen environments as is encountered during hydrogen Induced cracking or hydrogen attack, but it cannot explain low fugacity hydrogen embrittlement.

3. Decohesion Theory

This theory proposes that inter-atomic bonds of the material would be weakened by hydrogen (Fig. 20). It is said that hydrogen donates its electron to the base material thereby altering the interatomic forces. The evidence in favor of this theory are :

1. Atomistic calculations show that H can reduce the cohesive force of atoms.
2. Crack tip sharpness increase with H concentration

The criticism of this theory is that certain fractographic features like the absence of total cleavage in embrittled samples cannot be explained by this theory.

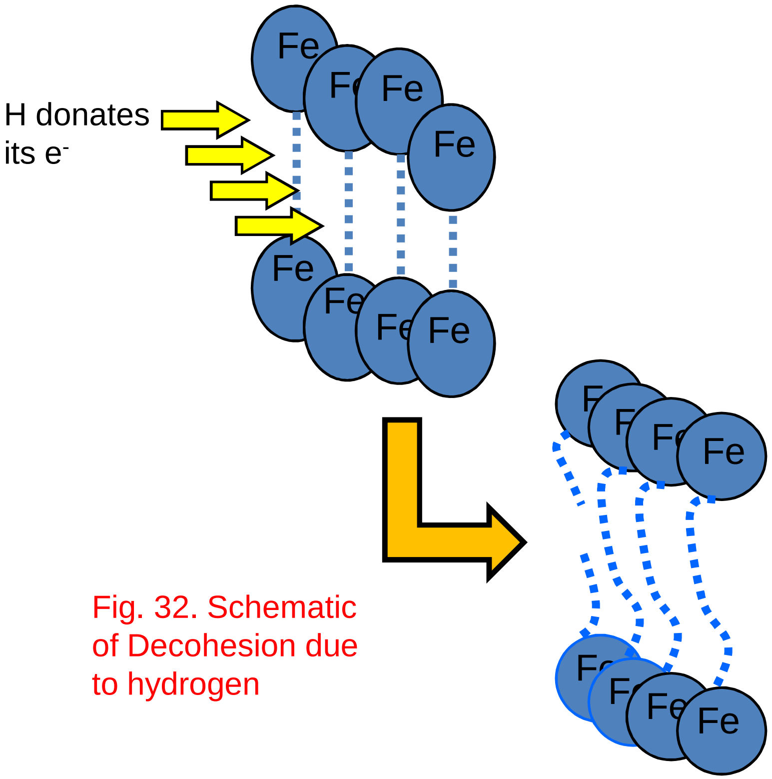


Fig. 32. Schematic of Decohesion due to hydrogen

C. 3. Mechanisms of Hydrogen degradation

4. Surface energy reduction

The basic postulate of this theory is that the presence of H reduces thermodynamic work of fracture by reducing the crack face surface energy (Fig. 33). This is a variant of the decohesion theory in that it also states that H interacts with atomic bonding. The genesis of this theory is from the phenomenon of liquid embrittlement, in which, the presence of liquid metal is known to cause embrittlement of the materials (e.g. Aluminium alloys by mercury).

There are two variants of this theory. The brittle fracture theory proposed that the adsorption of the hydrogen at the crack tip weakened inter-atomic bonds and propagated the crack. The ductile failure model proposed that adsorption of the hydrogen led to weakening of atomic bonds and nucleation of dislocations which moved under stress, leading to dislocation pile-up and thereby work hardened the solid.

The main criticism of this theory is that it cannot explain why other adsorbed atoms (e.g.O_2) which also should cause reduction of the surface energy, do not cause embrittlement.

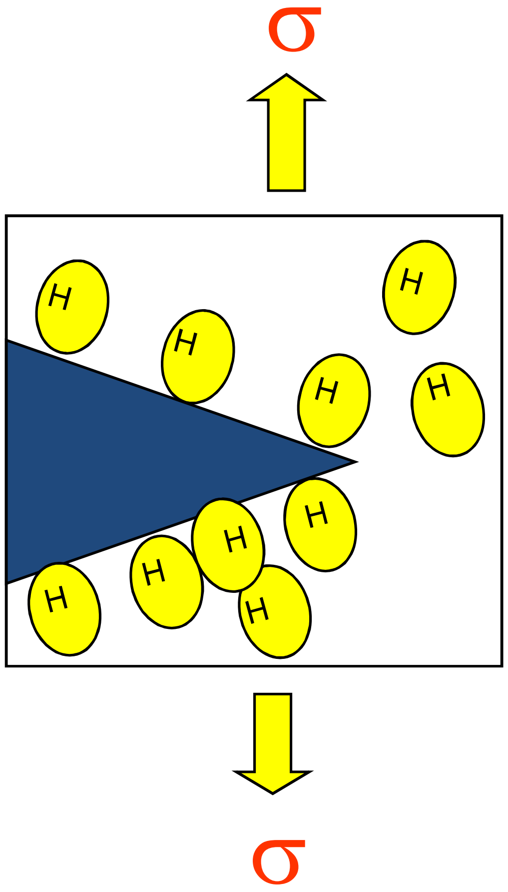


Fig. 33. Schematic of surface energy reduction theory

C. 3. Mechanisms of Hydrogen degradation

5. Hydrogen enhanced localised plasticity (HELP)

This theory states that H accelerates plastic deformation processes locally causing local micro-fractures. In-situ TEM studies with hydrogen charging has shown dislocation generation as well as increased mobility of dislocations. The counter argument to this theory is that such studies were carried out on thin foils which can lead to a number of artifacts including image forces. H either increases dislocation generation or dislocation mobility locally (Fig.34).

Isn't HELP a contradiction?

It does sound like one. However, one has to make the distinction between local ductility and global brittleness. According to the HELP mechanism, H enhances local plasticity to the extent that local fracture strains are exceeded causing microfractures. These cracks initiate more cracking as the hydrogen diffuses ahead of the crack tip. Thus while the local processes are ductile, the global effect is a loss in ductility. The HELP mechanism has been able to explain a number of observations related to HE and is the most popular theory today for explaining the low fugacity Hydrogen embrittlement phenomenon.

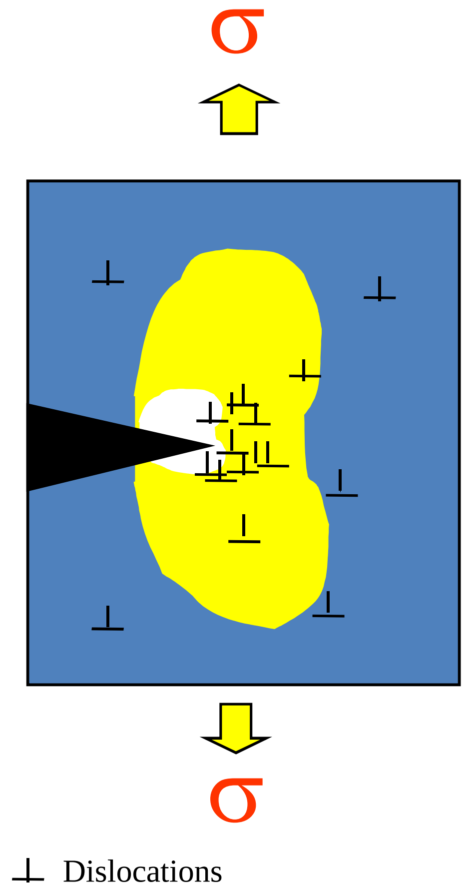


Fig. 34. Schematic of HELP mechanism

C. 3. Mechanisms of Hydrogen degradation

Why does H have so much damage potential?

H is quite an unique element. It is the lightest element, has a small atomic size and high diffusivity. Hydrogen in the positively ionized state is essentially a proton and thus can "tunnel" through activation barriers. Thus H entry into materials is very difficult to prevent. As is evident from the earlier discussion, H can cause any or all of the following : a change in the interatomic bonding ("*decohesion theory*"), a change in the surface energy ("surface energy reduction theory"), or an increase in local dislocation activity ("*HELP mechanism*"). Added to that is the frequent occurrence and easy availability of H. Most aqueous electrochemical reactions produce hydrogen. A number of important industrial components including those dealing with oil exploration and transport, are exposed to hydrogen. Similarly a number of fabrication and post–processing techniques introduce H. Hydrogen also responds to stress gradients and tends to segregate in regions of high tensile stresses. All these cause H to have a great damage potential.

What then are the factors controlling degradation by H?

The factors controlling H activity and therefore material degradation by H can be categorized into three groups:

i. Factors affecting H availability & severity
ii. Factors affecting H transport
iii. Factors related to stress conditions

Factors affecting H availability & severity

These are the environmental and surface chemistry factors. The amount of H that is available is largely decided by the H in the environment, type of cathode/anode, and the cathode/anode ratios. The amount of H that is adsorbed depends on the surface kinetics which is material specific as well as the presence of inhibitors and poisons.

Factors affecting H transport

The transport of hydrogen through the material and its residence at favored sites called traps have important bearing on the crack growth. H diffusion is affected by stress gradient, that is, it tends to accumulate at regions of high tensile stresses. There is a school of thought which

C. 3. Mechanisms of Hydrogen degradation

believes that H transport is aided by dislocation motion, and therefore the strain rate as well as the magnitude of plastic strain are important in H transport. It has been observed that HE occurs only below a particular strain rate (~10^{-6} s^{-1}).

Factors related to stress conditions

The stress conditions are defined by: a) the mode of loading, b) stress intensity and c) stress triaxiality. The cracking rate is dependent on stress intensity, while the mode of cracking is modulated by the stress triaxiality as well as the mode of loading. The H transport, as discussed earlier is affected by the hydrostatic stress magnitude as well as the sign of the stress (tensile or compressive). It may be mentioned that under constant or monotonically increasing load situations, the hydrostatic stress maximum normally occurs a finite distance from the crack tip. Thus in HE the cracking may occur slightly ahead of the existing crack and then joining of the two causes crack growth.

It may be mentioned here that susceptibility to HE is normally directly proportional to the material strength.

Prevention of hydrogen embrittlement

As the hydrogen degradations mentioned here are all special types of stress corrosion cracking, the general philosophies of prevention for SCC apply here too

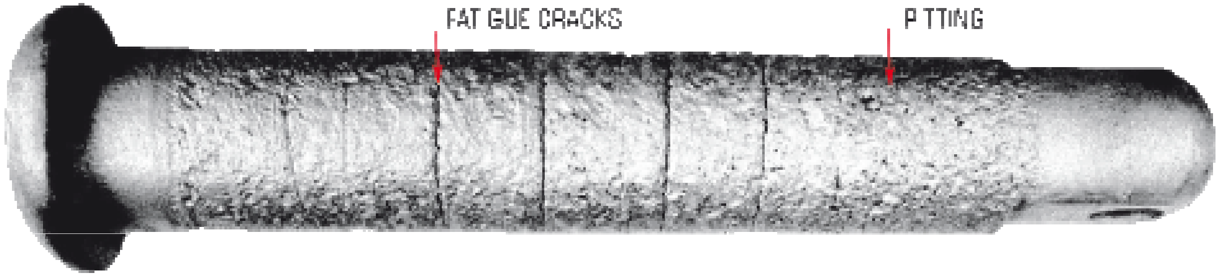
1. Material control – the mechanical property, microstructure and alloy composition which also affect the crystal structure are important factors. The softer and cleaner materials are less susceptible and so are FCC matrices (compared to BCC).
2. Stress control – while operational stresses can not be controlled per se, unwanted residual stresses like those which occur during welding and fabrication can be annealed out. Also introduction of surface compressive stresses retard hydrogen entry.
3. Environmental control – the presence of cathodic protection, hydrogen recombination poisons, acidic or sour environments promote hydrogen entry. Inhibitors can reduce hydrogen entry.

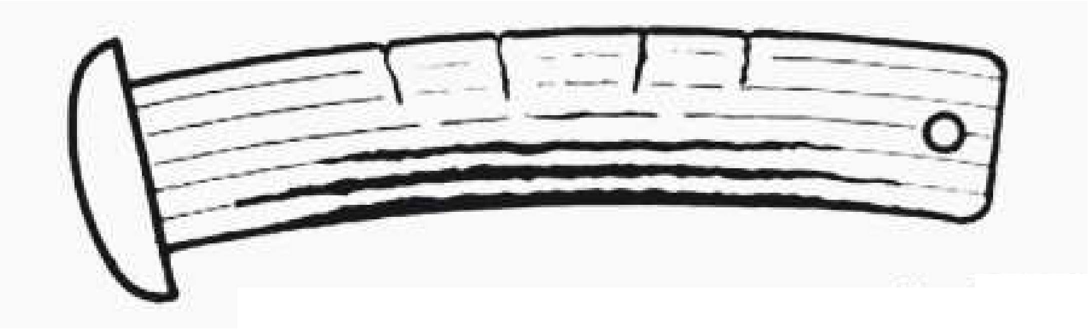
C. 3. Mechanisms of Hydrogen degradation

What makes ferritic steels so prone to H degradation?

- ❑ A number of characteristics of ferritic steels make them especially susceptible to hydrogen degradations. These are:
- ❑ *Presence of carbon /carbides in ferritic steels* - carbides are H traps for HIC and they are also used in methane production in HA
- ❑ *High strength alloys* – steels are normally high strength materials which make them prone to HE
- ❑ *BCC structure* - a relatively open crystal structure means that H can diffuse easily through these materials
- ❑ *Joined extensively by welding* – welding may cause increase in H absorption, as well as introduction of residual stresses
- ❑ *Presence of high hardness phases* - presence of martensite, certain inclusions make the material prone to HE
- ❑ *Transition element* - Spatial electronic arrangement (orbitals) facilitate H aided decohesion

D. Corrosion Fatigue





http://www.johnkingchains.com/technical-data/

D. Corrosion Fatigue

Basics and Terminology in Fatigue

Fatigue is the loss in mechanical properties brought about by repeated loadings. Fracture initiates at the surface and then proceeds generally in a stop - start morphology as is evident from the crack arrest markings shown in Fig.35.

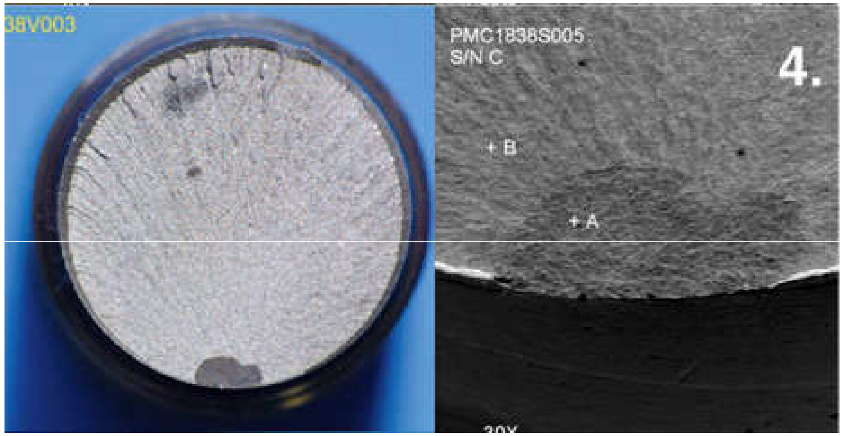


Fig. 35. Crack initiation and propagation in fatigue [http://arp-bolts.com/pages/technical_failures.shtml]

In a real component the stress variation is non-uniform as shown in Fig. 36. But in experiments and in rare practical applications the stress can cycle between fixed stresses as shown in Fig. 37. The fatigue damage in every cycle is incremental and cumulative leading to

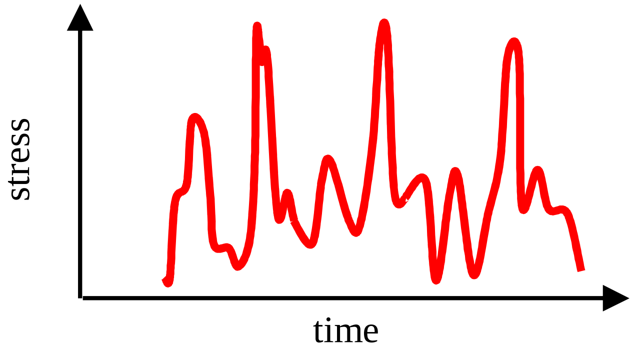


Fig. 36. Stress cycles in practical situations in fatigue

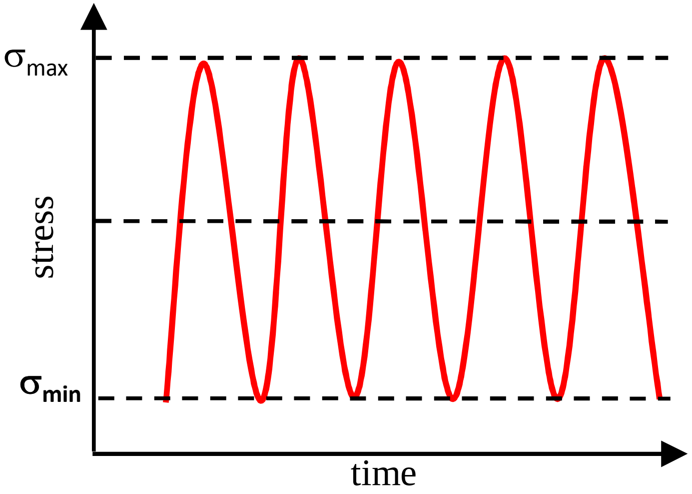


Fig. 37. Stress cycles in experimental fatigue

D. Corrosion Fatigue

the final failure. The stress cycles between a minimum (σ_{min}) and a maximum (σ_{max}) value. The ratio of these two is an important parameter called the stress ratio or load ratio (***R***), i.e.

$$R = \frac{\sigma_{min}}{\sigma_{max}} \qquad \text{.......D1}$$

R can have negative values when the minimum stress is compressive or zero values, although the latter is rare. For smooth specimens one can determine the fatigue life, which varies with the applied stress range $\Delta\sigma = (\sigma_{max} - \sigma_{min})$ as shown in Fig. 38. This is expressed as the ***Basquin's law***:

$$N_f^{\alpha}\,\Delta\sigma = C_1 \qquad \text{.......D2}$$

Where N_f is the number of cycles to failure

Fatigue and endurance limits

The curve shown in Fig. 38 is also known as the *S-N* curve (S for stress range and N for no. of cycles to failure). It is observed that for strain-hardening materials (e.g. ferritic steels), there is a minimum value of $\Delta\sigma$ below which there is no fatigue. This is called the Fatigue Limit. Non-strain-hardening materials do not demonstrate a fatigue limit, therefore an artificial life limit is set at 10^8 cycles. The corresponding value of stress range is called the Endurance Limit.

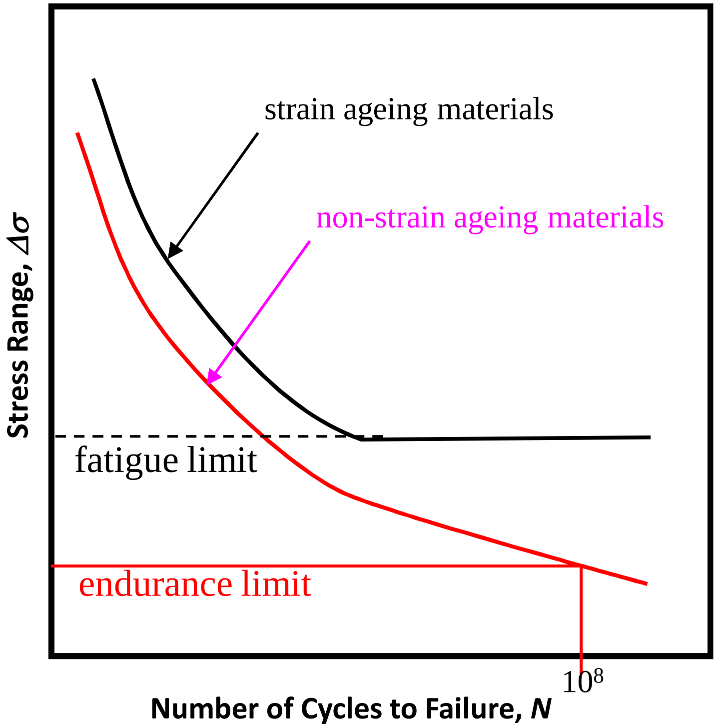


Fig. 38. S-N curves providing fatigue life

D. Corrosion Fatigue

Revisiting Stress Intensity Factor

K is the most definitive parameter in fracture mechanics. In corrosion fatigue, instead of absolute stress or ***K*** values, we are interested in the stress range $\Delta\sigma$, or the ***K*** range, ΔK ($= K_{max} - K_{min}$) where K_{max} corresponds to the K value for maximum stress, and so on. The alternate definition of ΔK is

$$\Delta K = Y\Delta\sigma\sqrt{(\pi a)} \qquad \text{.......D3}$$

The importance of ΔK lies in that most empirical or phenomenological laws of crack growth during fatigue has this as a defining parameter. The most well known law for Fatigue is the ***Paris Law*** which relates crack growth rate per cycle (da/dN) to ΔK

$$da/dN = C_1(\Delta K)^m \qquad \text{.......D4}$$

Where C_1 and m are material and environment dependent constants. Please note that in fatigue, crack growth is expressed as “per cycle”.

The crack growth rates when plotted against ΔK show a three stage behaviour as shown in Fig. 39. The Paris Law is valid in regime B. A threshold value for ΔK is observed, below which no crack growth occurs.

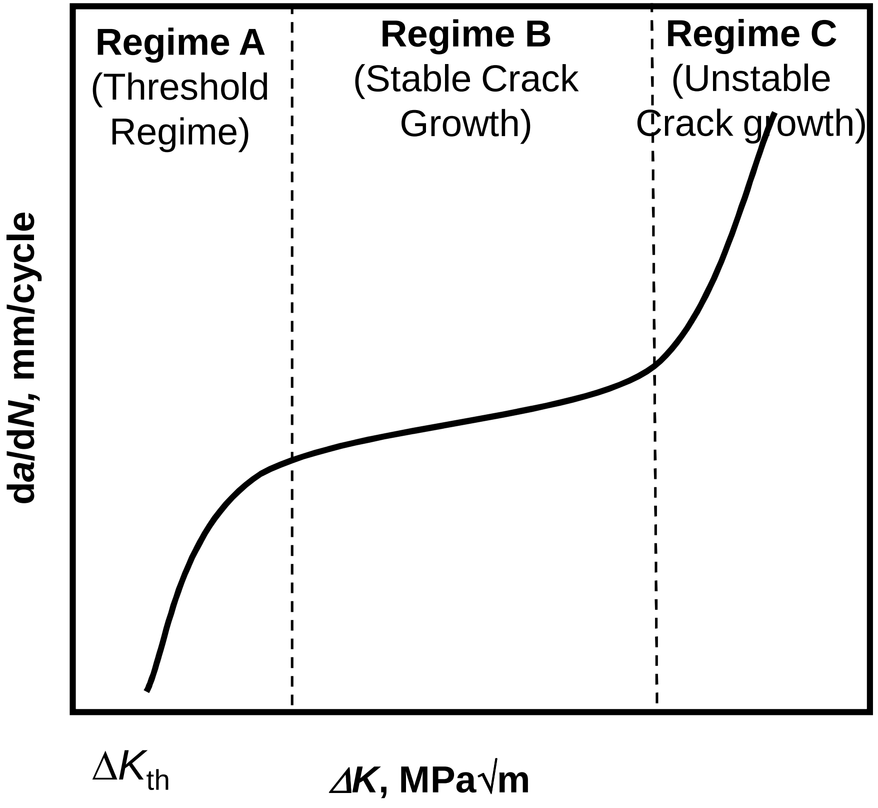


Fig. 39. Different stages of fatigue

D. Corrosion Fatigue

Definition

Corrosion Fatigue is the failure of materials under the combined action of cyclic stresses and a corrosive environment.

Manifestations

Corrosion fatigue causes the following deviations from normal fatigue, which are also illustrated in Figs. 40 and 41

1. The threshold value for crack growth (ΔK_{th}) is reduced (Fig. 40)
2. The Fatigue limit disappears even for strain-hardening materials (Fig. 41)
3. The crack growth rates are significantly higher in all the three regimes

To understand how these deteriorations are brought out , we have to look at the mechanisms believed to cause fatigue initiation and growth and how they are altered in the presence of a corroding medium. Like SCC, corrosion fatigue can occur in the anodic or the cathodic regimes of potential. In the latter case, hydrogen would be produced and the enhancement of fatigue is due to hydrogen embrittlement mechanisms.

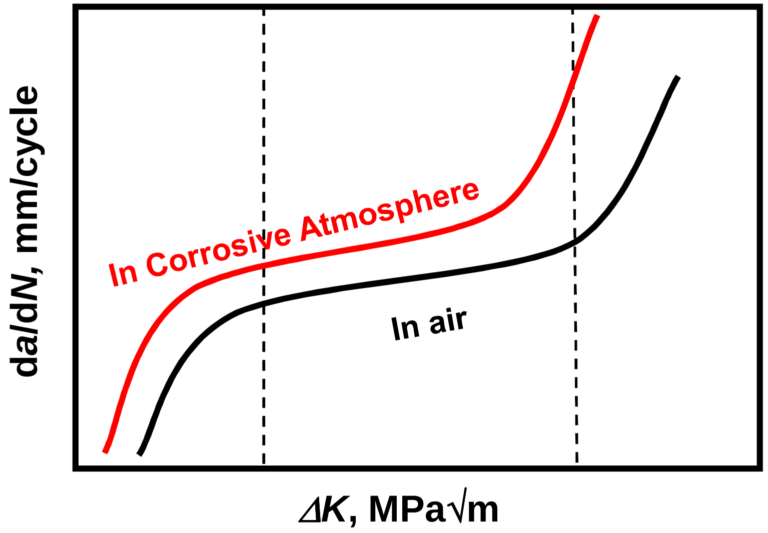


Fig. 40. Change in threshold and crack growth rates in corrosion fatigue

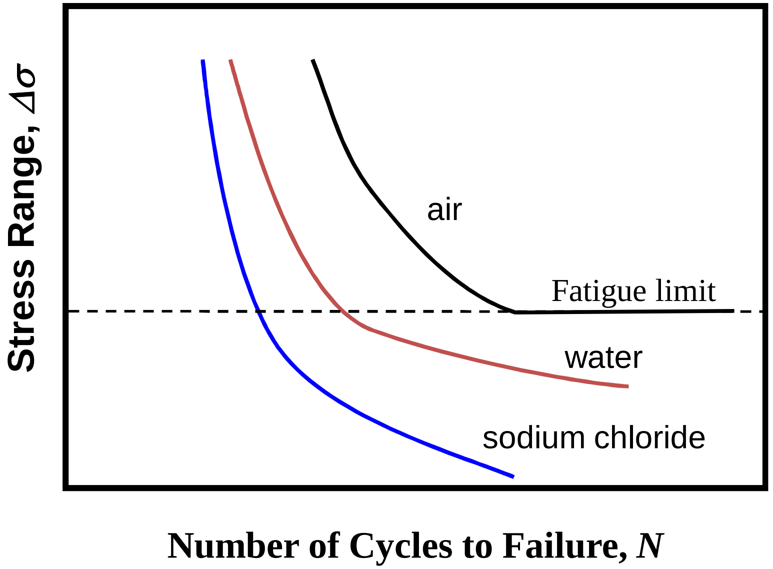
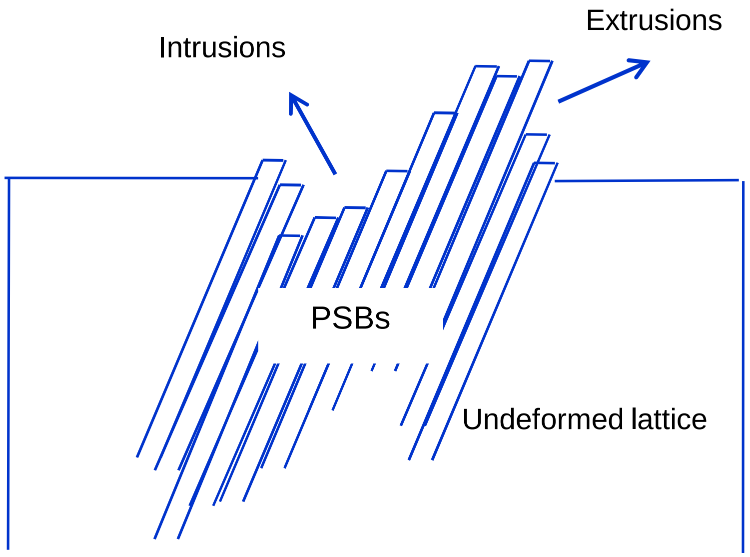


Fig. 41. Disappearance of fatigue limit in corrosion fatigue

D. Corrosion Fatigue

Mechanism of normal fatigue

For normal fatigue, co-ordinated dislocation motion, which is collectively known as slip bands, occurs at the surface resulting in the creation of intrusions and extrusions as shown in Fig. 42. This is the precursor to fatigue cracks. The initial crack propagation occurs along slip bands. In the regime II, the normal crack growth processes of crack extension, crack tip blunting and crack resharpening take place.



42. Fatigue crack initiation

How Corrosion interferes with normal fatigue

In the above sequence of events there are a number of steps in which corrosion in addition to fatigue would affect crack growth. With regards to crack initiation by “intrusions-extrusions” in the unloading part of a fatigue cycle, some of the slip bands are expected to fall back to their original positions reducing the size and extent of crack precursors. If anodic dissolution occurs simultaneously and as this would occur preferentially on the “intrusions-extrusions” the relapse of slip bands is prevented leading to a persistent crack precursor. Additionally, pitting or grain boundary attack can itself create crack precursors. This would explain the lower ΔK_{th} observed in corrosion fatigue. Another effect of corrosion would be in the stage II regime, where it would prevent crack tip blunting by dissolution at the crack tip. The crack tip blunting is tantamount to a reduction in the driving force for fatigue. Thus crack tip dissolution, by ensuring a sharp crack also

D. Corrosion Fatigue

increases the driving force for crack growth. This explains the faster regime II crack growth rates in corrosion fatigue.

How does cathodic processes, which cause no material dissolution, affect fatigue? In cathodic processes, hydrogen is produced. H has a propensity for enhancing activities in preferred slip planes as well as slip planarity, both of which enhance sharp crack. This means that crack initiation as well as crack growth are enhanced by hydrogen. Moreover, the natural embrittling effect of hydrogen on the metal matrix, also enhances fast fracture.

Preventive measures

Many of the measures are the same as that for increasing fatigue resistance and these include

❑Proper design to reduce stress concentration, avoid stress concentrators, reduce residual tensile stresses

❑ Proper metallurgy to reduce inclusions, select optimum grain size

.

❑Induce surface compressive stresses by

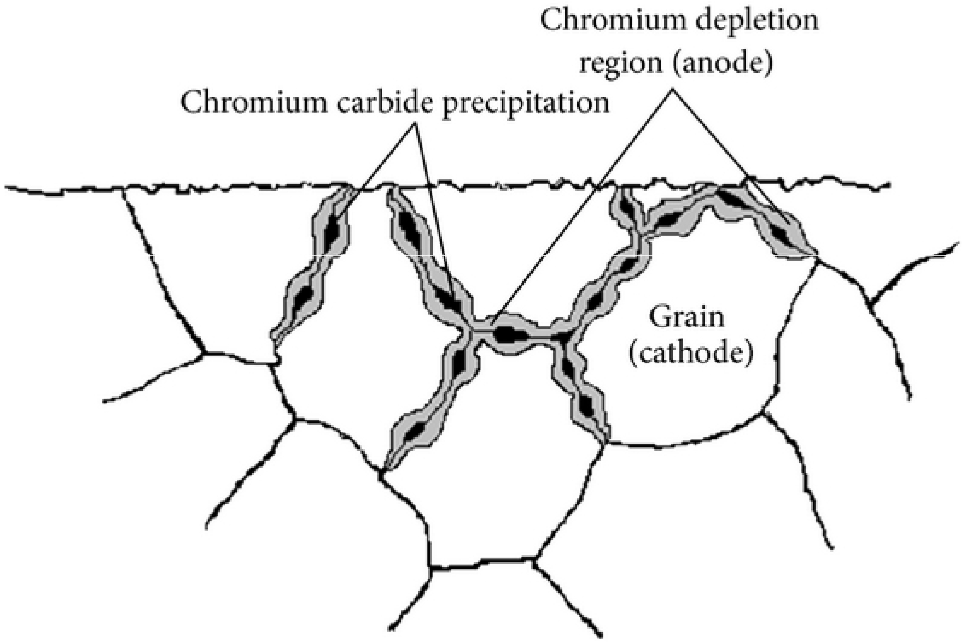
surface rolling
shot peening
case hardening
polishing

Additionally, the following electrochemical measures would reduce corrosion fatigue

❑ Use of inhibitors and platings

❑ Avoid dissimilar metal contact

E. Sensitization and Intergranural Attack



http://www.hindawi.com/journals/ijelc/2013/970835/fig10/

E. Sensitization and Intergranular Attack

The corrosion resistance of Stainless Steels

The corrosion resistance of stainless steels is legendary and covers every day utensils to post-modern architecture (Fig. 43). The most important alloying element in it is Cr. This produces an oxide (chromium oxide) which is thin, impervious and protects the underlying substrate from any additional attack. This layer also has temperature resistant properties. It is invisible to the naked eye being only 130 A^0 thick. Cr and O have nearly similar atomic sizes, which is the reason for a compact layer. This layer is the reason why stainless steels demonstrate passivity in a host of corrosive environments. The other important element is Ni, which is essential to make the material austenitic which improves ductility and deformation behavior.

It is generally assumed that a Cr content of *10.5 wt%* is needed to produce enough oxide film on the surface to cover the entire surface. Thus it is essential to maintain at least 11-12 % Cr in the entire surface and sub-surface to ensure total protection. An oxidizing environment is necessary to produce the oxide film. Normally, exposure to air itself is sufficient to produce the protective layer. However, in strongly reducing environments the passive layer may not form or may be destroyed. Similarly if the chromium content is locally depleted to less than 12%, localized corrosion can take place.

Fig. 43. The stainless steel Arch of St. Louis

www.destination360.com

Pitting Resistance Equivalent Number [PREN]

The measure of passive film stability in stainless steels is how resistant it is to pitting corrosion. This resistance depends on the chemical composition of the steel. The indicative parameter for pitting resistance is called PREN and is expressed as

$$PREN = \%Cr + 3.3(\%Mo) + 16(\%N) \text{ ...... [E1]}$$

E.1. Sensitization

Definition

Sensitization has a literal meaning. It refers to the process which causes stainless steel to become sensitive to corrosion. The phenomenological definition is the formation of chromium carbides preferentially at grain boundaries leading to a depletion of Cr just adjacent to these carbides. Since a minimum amount of Cr is needed to afford total protection to the steel, this makes the grain boundary region susceptible to corrosion. The corrosion is accelerated by the small anode (grain boundary) to cathode (passive matrix) ratio (Fig. 44). Subsequent exposure to a corroding media causes attack of the grain boundary which is called *Intergranular corrosion (IGC) or Intergranular Attack (IA)*. If, additionally a suitable stress is present, the material fails by intergranular fracture.

The carbides that precipitate are normally mixed carbides of Cr and Fe, with a stoichiometric formula $M_{23}C_6$, but for most practical purposes they are assumed to be $Cr_{23}C_6$. The carbides are detectable only through a TEM or similar high resolution techniques. The extent of chromium depletion is limited to a few hundreds of nanometers. However, a sensitized stainless steel after exposure to corrosive media shows prominent and preferential grain boundary attack which is easily seen under an optical microscope (Fig. 45).

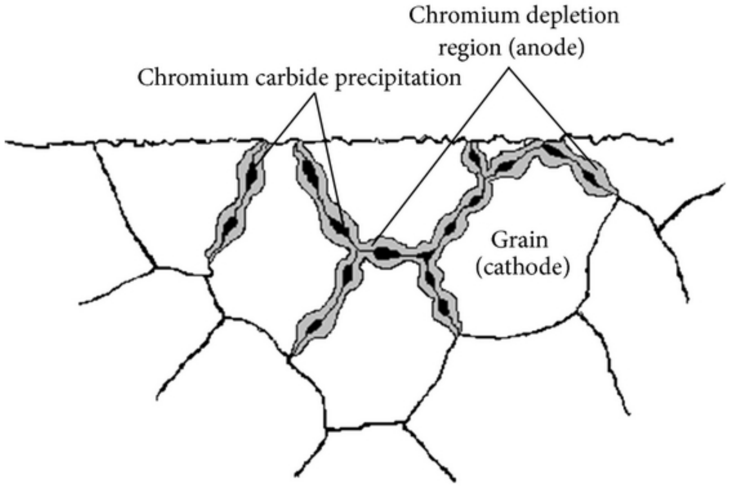


Fig. 44. Schematic of grain boundary carbide formation and resultant Cr depletion
http://www.hindawi.com/journals/ijelc/2013/970835/fig10/

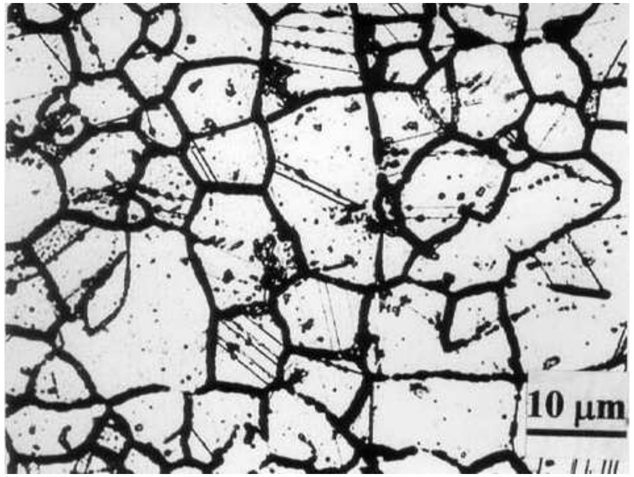


Fig. 45. Optical microscopy of corrosive attack of sensitized stainless steel
http://commons.wikimedia.org/wiki/File:Sensitized_structure_of_304_stainless_steel.jpg

E.1. Sensitization

Chromium carbide precipitation

The reaction of Cr and C present in the steel is

$$23Cr + 6C = Cr_{23}C_6 \;\ldots\ldots\ldots\; [E2]$$

The equilibrium constant [K_{eq}] for the above can be written as

$$K_{eq} = \frac{a[Cr_{23}C_6]}{a_{Cr}^{23} \cdot a_C^{6}} = \frac{1}{[\gamma_{Cr} \cdot [Cr]]^{23} \cdot a_C^{6}} \quad \ldots.[E3]$$

Where “a” is the activity, “γ” is the activity coefficient and [Cr] is the wt% Cr. In these developments it is assumed that the carbide has unit activity and the carbon concentration remains constant throughout the matrix. The above equilibrium refers to the concentrations at the carbide matrix interface and therefore the concentration of Cr at the interface in equilibrium with a carbide can be obtained from *[E3]*. It is also evident from the equation that the higher the carbon content in the steel the lower would be the interfacial Cr content.

Chromium depletion due to sensitization

The equilibrium equation does not provide any idea of the spatial Cr depletion near the grain boundary. To obtain that we have to resort to the kinetics of carbide precipitation. This requires the diffusion of Cr and C atoms to the grain boundaries. The diffusion of C is orders of magnitude higher than that of Cr. Thus Cr diffusion is the rate controlling factor in formation of carbides. The grain boundary happens to provide an easy path for diffusion of any atoms on account of its disordered structure. Thus, while volume diffusion is relatively slow, the grain boundary diffusion allows carbide formation. This is the main reason why in sensitization almost all the precipitation happens at the grain boundary. Another reason for the grain boundary preference is that it provides a heteregeneous nucleation site.

Since the process is diffusion controlled, the Cr depletion near the grain boundary increases as the carbide grows. This is shown in Fig. 46. The carbide is shown to grow in one direction for convenience. Please note that the interfacial Cr content is unchanged and decided by the equilibrium value of eqn. *E3.* But the extent of Cr depleted zone increases. The extent of this depletion is generally much less than the grain size of the material. Consequently the corrosion resistance is localized to the grain boundary only.

E.1. Sensitization

Kinetcis of sensitization

The driving force for sensitization is the supersaturation of Cr and C with regards to carbide formation. This increases with a decrease in temperature. However, the diffusivity of Cr is an exponential function of temperature. Thus an intermediate temperature range (450 – 750 ^{0}C) exists where sensitization happens. Occurrence of sensitization is represented by Time-Temperature- Sensitization (TTS) curves as shown in Fig. 47. It is evident that with increasing C content the time for sensitization decreases at any given temperature.

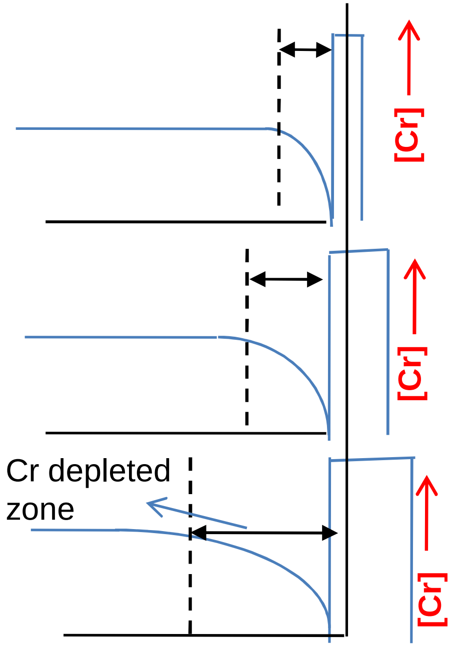


Fig. 46. Cr depletion near carbide

Desensitization

What the TTS curves show is that on prolonged heating in the sensitizing temperatures as shown by the heat treatment schedule A-B-C in Fig. 47, the material can become unsensitized. This is called desensitization. After sensitization, the existence of a Cr depleted zone accelerates volume diffusion and the Cr tries to diffuse into this depleted zone. The Cr diffusion through the matrix is sluggish, thus while sensitization can take place in minutes, desensitization takes hundreds of hours. So, while sensitization is controlled by the rate of grain boundary diffusion of Cr, desensitization is controlled by the rate of volume diffusion of Cr.

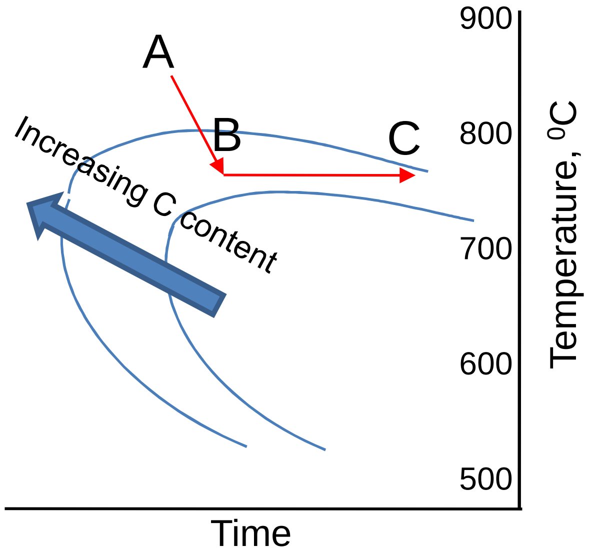


Fig. 47. Time – Temperature – Sensitization (TTS) curves for different C contents

E.1. Sensitization

Testing for sensitization

The basis for testing is the preferential corrosion of grain boundaries while the grains remain unattacked.

1. Strauss test: This was the first test developed for IGC detection. Samples are exposed to a boiling solution of 16% H_2SO_4 + 6% $CuSO_4$ for 72 hours. The sample is bent and examined. Cu^{2+} ions act as oxidizers and preferentially attack the Cr-depleted zone. The bent sample is examined at 20X and IGC can be observed. This method is used on highly sensitized materials because the rate of attack is low.

2. Streicher test: In this the sample is exposed to boiling 50% H_2SO_4 + 2.5% $Fe_2(SO_4)_3$. This test is faster than the Strauss test because of the increased acid concentration and stronger oxidizing action of Fe^{3+}, compared to Cu^{2+}. Weight loss is used to measure the attack rather than macroscopic evaluation. In this regard, it is more quantitative than the Strauss test.

3. Oxalic acid etch test: This is a much faster test. The sample is exposed to 10% oxalic acid and an anodic current of 1A/cm^2 is applied for 90 secs at room temperature to a polished sample. If after microscopic examination, the material appears sensitized, it is subjected to further examination by any of the earlier tests. The microstructures show up either with steps (unsensitized) or ditches at the grain boundary (sensitized).

4. Electrochemical Potentiokinetic reactivation test: The specimen is polarized in 0.5 M H_2SO_4 + 0.01 M KSCN solution starting at its corrosion potential up to a potential of 200 mV with respect to a Saturated Calomel Electrode and held for 2 min. The potential is then decreased to its open-circuit value at a constant rate of 1.67 mV/s (Fig. 48). This reactivation leads to the breakdown of the passive film on the sensitized specimens. As a result, a loop is generated in the potential-current curve. The area under this loop is a meausre of the degree of sensitization.

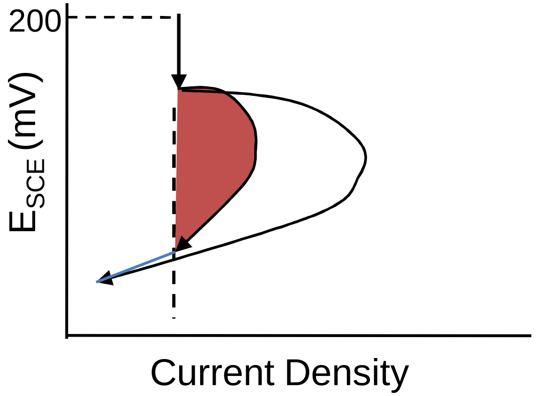


Fig. 48. EPR curve . The loop area is a measure of degree of sensitization

E.2. Intergranular Attack (IGA)

While intergranular attack is most common in sensitized stainless steels, it happens quite frequently in a number of other alloys. For example in heat treated Aluminum alloys, a precipitation free zone may form near the grain boundaries. The essential requirement is that the grain boundaries should be inherently weaker or made weaker compared to the grains by processing or heat treatments. The mechanical strength may or may not be affected by this process, but the electrochemical resistance definitely is. The difference in the chemical composition of the near-grain boundary regions and the grain manifests in two ways. Either the formation of a passive protective layer is hindered or a galvanic coupling is set up, both cause accelerated corrosion of the weaker grain boundaries.

When such materials are subjected to a stress in the presence of a corrosive medium, the cracks initiate at and propagate through the weaker grain boundaries. This propagation is by active path dissolution. As the cracks move through the grain boundaries, the corrosion at crack tip is enhanced due to the weaker grain boundaries.

While the grain boundaries may not form a perfectly orthogonal surface to the stress, the crack moves through those grains which have the maximum resolved stress condition and thus the crack path is roughly perpendicular to the stress direction (Fig. 49). Thus K_I dominated cracking is applicable and a K_{ISCC} can be obtained for fracture. However, while K_{IC} is material specific, K_{ISCC} is material-environment specific

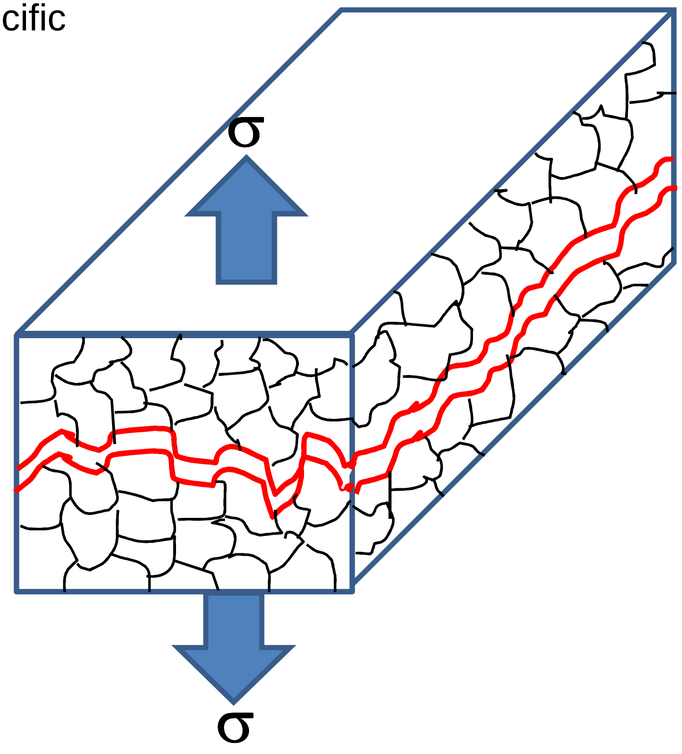


Fig. 49. Crack propagation through sensitized material along grain boundaries

E.2. Intergranular Attack (IGA)

Weld decay

Welding of stainless steels results in a variation of microstructures going away from the weld centreline (Fig. 50). This is a result of the different thermal profiles for different zones at and near the weld (Fig. 51).

It is at once evident that while the fusion zone and the partially melted zones do not intrude into the sensitization conditions, the heat affected zone (HAZ) can spend a significant amount of time in the sensitization temperatures. This causes only the HAZ to be sensitized and subsequent exposure to corrosive environment shows the HAZ to be preferentially attacked at the grain boundaries. This phenomenon is called Weld Decay.

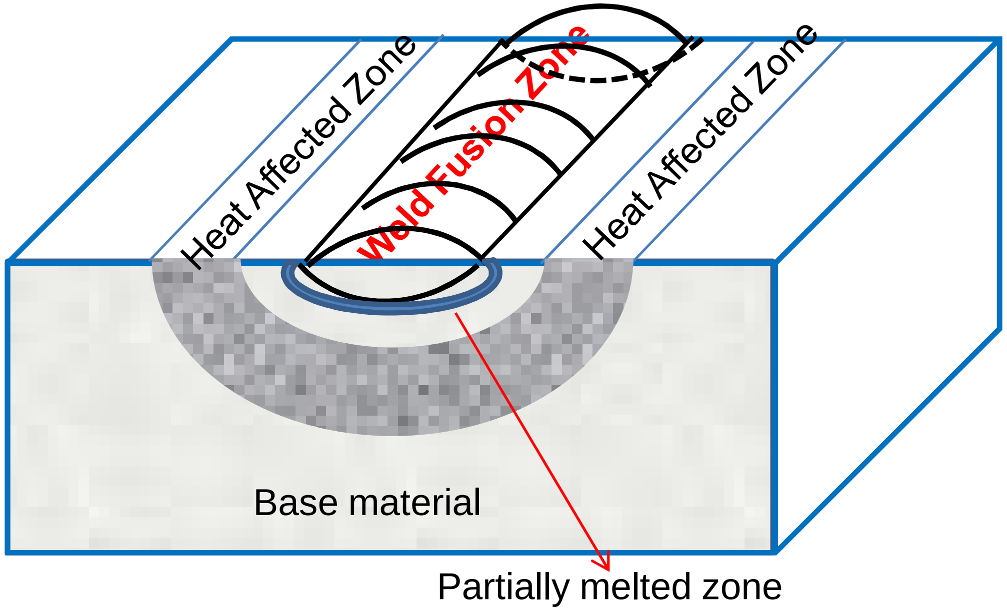


Fig. 50. Various zones near the weld

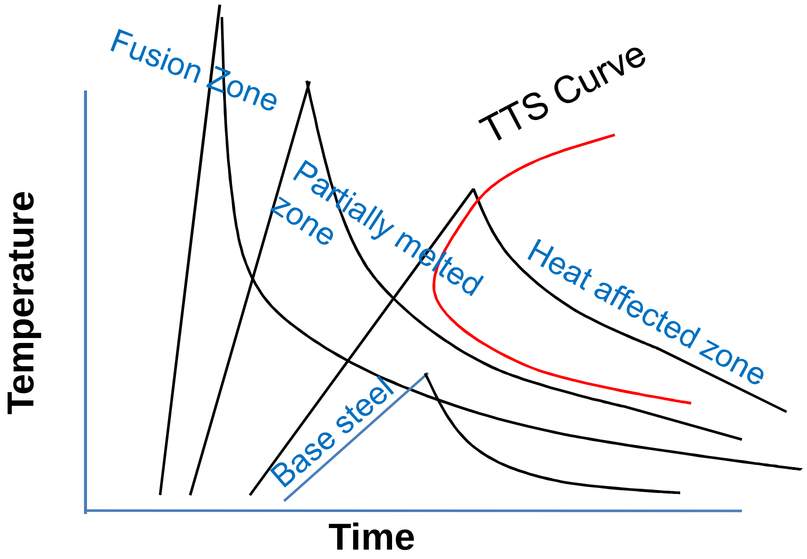


Fig. 51. Thermal history of the various zones

E.2. Intergranular Attack (IGA)

Knifeline Attack (KLA)

In certain stainless steels, like SS 347, carbide stabilizing elements like Ti and Nb are intentionally added to lock up the C so that it is not available for sensitization. This process is called *stabilization*. Stabilized stainless steels may be exposed to high temperatures during welding. The Ti/Nb carbides may dissolve if the temperatures are high enough. This zone very near to the weld zone may not be able to reprecipitate the stabilizing carbides on quenching and may thus be susceptible to sensitization when exposed to the suitable temperatures. In the sensitization temperatures (450 – 750 ^{0}C), Cr-carbides precipitate faster than the Ti/Nb carbides.

This region is adjacent to the weld and very thin (Fig. 52). On subsequent exposure to a corrosive medium or to a stress corrosion environment, the material fails by a sharp crack along the sensitized region and this is called Knifeline attack (KLA).

KLA is accelerated by the presence of residual stresses in the weld – base interface. The KLA and weld decay differ in two respects:

a. Weld decay occurs in non-stabilized steels, while KLA occurs in stabilized steels
b. Weld decay occurs in the heat affected zone while KLA occurs in the weld-base interface

The KLA can be remedied by solution annealing at temperatures greater than 1065^{0}C where the chromium carbides dissolve fully, and then holding either at that temperature or above 850^{0}C to allow TiC or NbC to form.

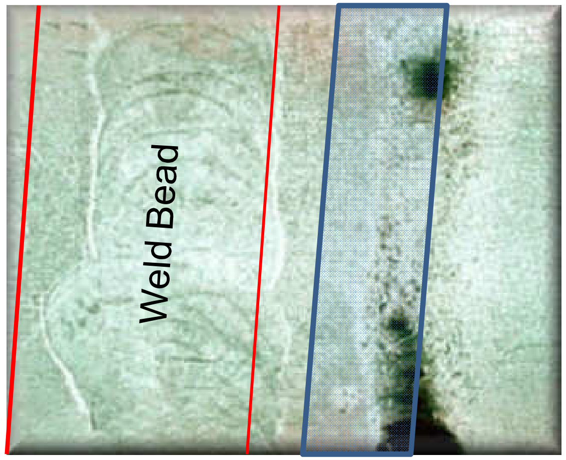


Fig. 52 Knifeline attack in the partially melted zone

http://www.corrosionclinic.com/types_of_corrosion/weld_decay_weldment_corrosion.htm

E. Sensitization and Intergranular Attack

Factors affecting sensitization

The factors which affect sensitization are those which affect either the availability of C or the nucleaction or growth mechanisms of Cr-carbides and are as follows:

1. C content of the alloys
2. Other alloying elements: Alloying elements affect the solubility of carbon in austenite. Mo and Ni accelerate the precipitation by reducing the solubility of carbon. Cr and N increase the solubility of carbon and thus retard precipitation. Although the presence of N may lead to Cr_2N precipitation and Cr depletion, N has a much higher solubility than C in austenite and this is rarely an issue in austenitic grades
3. Cold work will enhance precipitation by providing defects in the material which enhance Cr diffusion
4. Sensitization is enhanced by larger austenitic grain sizes. This is due to the much higher availability of C per grain boundary.
5. The grain boundary character, i.e., the surface energy of the grain boundary determines the ease of nucleation. The coincident site lattice (CSL) is used to describe the grain boundary order – the lower the no., the more ordered the boundary
6. Presence of stabilizing elements like Ti and Nb.
7. Thermal history especially excursions into the sensitizing temperatures during processing or welding

Prevention and remedies

Sensitization and consequent intergranular attack may be prevented or remedied through the following:

1. Reducing C content: modern steelmaking allows very low C grades like the 316L. Lower C reduces the probability of carbide precipitation
2. Avoiding sensitization temperatures
3. Avoid high input welding and follow post-weld treatments
4. Using stabilizing elements like Ti or Nb: these form stable carbides and thereby reduce the available C for $Cr_{23}C_6$ formation. However, kinifeline attack in stabilized steels is a major concern
5. Post –weld treatments which redissolve any Cr-carbides formed
6. Grain boundary engineering: This entails special mechanical processing resulting in grain boundaries with less preference for carbide precipitation
7. Alloying additions: N seems to be a good addition in view of its effect on increasing C solubility

In a nutshell . . . .

Stress in industrial components can not be avoided. The geometry of the component or flaws present may cause stress intensification locally. The best way to treat flawed components is through fracture mechanics concepts. The stress intensity factor, K_I, is the most important parameter and limiting critical values of it define material fracture. If conducive environments are present, the conjoint action of stress and corrosion can cause the material/component to crack. This is stress corrosion cracking (SCC). The mechanism of SCC is either active path dissolution or film induced cleavage.

If the corrosion process involves liberation of hydrogen in sufficient amounts, hydrogen embrittlement may be the cause of component failure. In certain situations, when the environmental hydrogen fugacity is very high, internal blistering and subsequent cracking can occur without the presence of any external applied stress. This is illustrated in hydrogen induced cracking in sour service, at ambient temperatures, or hydrogen attack, at elevated temperatures .

Corrosion fatigue is a special case of SCC where the stresses experienced by the component are cyclic in nature. Corrosion fatigue is more severe than mechanical fatigue.

Sensitization refers to the process causing the grain boundaries to become susceptible to corrosion. In stainless steels this occurs due to the grain boundary precipitation of chromium carbides. This occurs in certain specified temperature ranges and demonstrates a “C” shaped time-temperature curve. Welding may cause stainless steels to become sensitized.

The remedial measures/ corrective steps to combat these different corrosion types have been provided. Susceptibility to most of these forms of corrosion can be evaluated using standard tests and practices.

Appendix

Some Indian Organizations/ Institutions involved in Research on Stress Assisted Corrosion

Organization	Link
BARC, Trombay	www.barc.ernet.in
BHEL, Hyderabad	www.bhelhyderabad.com
CECRI (CSIR), Karaikudi	www.cecri.res.in
EIL,R&D, New Delhi	www.engineersindia.com/Research_and_Development/research_and_development.html
GE Global Research, Bengaluru	www.ge.com/research/
IGCAR, Kalpakkam	www.igcar.ernet.in
IIT Bombay, Mumbai	www.iitb.ac.in
IIT Kharagpur, Kharagpur	www.iitk.ac.in
Indian Oil, R&D, Faridabad	www.iocl.com/Aboutus/Research_Development.aspx
NAL (CSIR), Bengaluru	http://nal-ir.nal.res.in
NML (CSIR), Jamshedpur	www.nmlindia.org
SERC (CSIR), Chennai	www.sercm.org