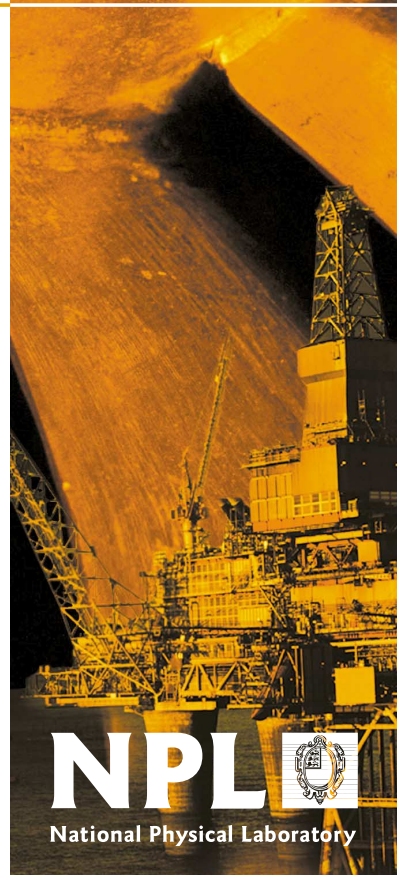


Guides to Good Practice
in Corrosion Control

Stress Corrosion Cracking



NPL 
National Physical Laboratory

Stress Corrosion Cracking

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1.0 Introduction

Stress corrosion cracking is cracking due to a process involving conjoint corrosion and straining of a metal due to residual or applied stresses.¹

Despite the introduction of polymers and composites in recent years, metals remain important in structures because of their strength, stiffness, toughness and tolerance of high temperatures.

Unfortunately, metals are subject to corrosion. (The noble metals, such as gold and platinum are an exception to this, but they are rather too rare for common use). Corrosion can take many forms; the form that concerns us here is the interaction of corrosion and mechanical stress to produce a failure by cracking. This type of failure is known as stress corrosion cracking, often abbreviated to SCC.² As will be explained below, SCC may occur by a number of mechanisms; when cracking is clearly a result of hydrogen embrittlement, this term may be used in place of SCC. However, this distinction is rather arbitrary; we are often unsure of the mechanisms of SCC, and many failures that are actually due to the effects of hydrogen would conventionally be ascribed to SCC. Similarly other specific stress corrosion cracking processes have acquired their own names; 'season cracking' for the cracking of brass in environments containing ammonia, 'caustic cracking' for the cracking of steel in strong alkalis etc.



Figure 1. Aftermath of boiler explosion, probably caused by caustic cracking. Picture courtesy of IMechE.

SCC is an insidious form of corrosion; it produces a marked loss of mechanical strength with little metal loss; the damage is not obvious to casual inspection and the stress corrosion cracks can trigger mechanical fast fracture and catastrophic failure of components and structures. Several major disasters

have involved stress corrosion cracking, including the rupture of high-pressure gas transmission pipes, the explosion of boilers, and the destruction of power stations and oil refineries.

Fortunately, the occurrence of SCC depends on the simultaneous achievement of three requirements:

- a susceptible material,
- an environment that causes SCC for that material, and
- sufficient tensile stress to induce SCC.

Consequently, SCC is relatively rare, though failures can be very costly and destructive when they do occur.

2.0 What causes stress corrosion cracking?

2.1 Introduction

Three basic mechanisms of stress corrosion cracking have been identified as described below.

2.2 Active path dissolution

This process involves accelerated corrosion along a path of higher than normal corrosion susceptibility, with the bulk of the material typically being passive. The most common active path is the grain boundary, where segregation of impurity elements can make it marginally more difficult for passivation to occur. For example, when an austenitic stainless steel has been sensitised by precipitation of chromium carbide along the grain boundary, the local chromium concentration at the grain boundary will be reduced, and this region will be slightly less easily passivated. Consequently, a form of crevice corrosion can occur, whereby the grain boundary corrodes, with the specimen surface and the crack walls remaining passive. This process can occur in the absence of stress, giving rise to intergranular corrosion that is uniformly distributed over the specimen. The effect of the applied stress is probably mainly to open up the cracks, thereby allowing easier diffusion of corrosion products away from the crack tip and allowing the crack tip to corrode faster. Active path corrosion processes are inherently 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, and crack growth rates are often much lower, down to around 10^{-8} mm/s (about 1 mm in 3 years) or less.

¹ This definition is based on that due to ISO. It may be slightly misleading, in that the word 'straining' may be taken to imply plastic strain, whereas stress corrosion cracking may occur as a result of elastic strain alone, at least at the macroscopic level.

² Other forms of interaction between mechanical stress and a corrosive environment may also occur, including corrosion fatigue under the influence of fluctuating stress and corrosion, liquid metal embrittlement and a range of fretting and wear process. These are not considered here: see Shreir et al. (1994) for further coverage of these. The terms "environmentally-assisted fracture" or "environmentally-assisted cracking" are used to cover all of these processes, including SCC.

2.3 Hydrogen embrittlement

Hydrogen dissolves in all metals to a moderate extent. It is a very small atom, and fits in between the metal atoms in the crystals of the metal.³ Consequently it can diffuse much more rapidly than larger atoms. For example, the diffusion coefficient for hydrogen in ferritic steel at room temperature is similar to the diffusion coefficient for salt in water. Hydrogen tends to be attracted to regions of high triaxial tensile stress where the metal structure is dilated. Thus, it is drawn to the regions ahead of cracks or notches that are under stress. The dissolved hydrogen then assists in the fracture of the metal, possibly by making cleavage easier or possibly by assisting in the development of intense local plastic deformation. These effects lead to embrittlement of the metal; cracking may be either inter- or transgranular. Crack growth rates are typically relatively rapid, up to 1 mm/s in the most extreme cases.

The bcc (body-centred cubic) crystal structure of ferritic iron has relatively small holes between the metal atoms, but the channels between these holes are relatively wide. Consequently, hydrogen has a relatively low solubility in ferritic iron, but a relatively high diffusion coefficient. In contrast the holes in the fcc (face-centred cubic) austenite lattice are larger, but the channels between them are smaller, so materials such as austenitic stainless steel have a higher hydrogen solubility and a lower diffusion coefficient. Consequently, it usually takes very much longer (years rather than days) for austenitic materials to become embrittled by hydrogen diffusing in from the surface than it does for ferritic materials, and austenitic alloys are often regarded as immune from the effects of hydrogen.

2.4 Film-Induced cleavage

If a normally ductile material is coated with a brittle film, then a crack initiated in that film can propagate into the ductile material for a small distance (around 1µm) before being arrested by ductile blunting. If the brittle film has been formed by a corrosion process then it can reform on the blunted crack tip and the process can be repeated. The brittle films that are best-established as causing film-induced cleavage are de-alloyed layers (e.g. in brass). The film-induced cleavage process would normally be expected to give a transgranular fracture.

³ Technically it is described as an interstitial solute.

3.0 When will SCC occur?

SCC is not an inevitable process, and for most metals in most environments it will not occur. We can therefore identify specific combinations of metal and environment that are subject to the problem. Unfortunately, of course, as time goes by we identify more and more such combinations, especially as engineers strive to use materials more efficiently by increasing working stresses and using less expensive materials. Table 1 lists some combinations of metal and environment that we most commonly associate with SCC.

Table 1. Common SCC systems⁴

Material	Environment	Concentration	Temp	Mode
Carbon steel	Hydroxides	high	high	I
	Nitrates	moderate	moderate	I
	Carbonate/bicarbonate	low	moderate	I
	Liquid ammonia	-	low	T
	CO/CO ₂ /H ₂ O	-	low	T
	Aerated water	-	very high	T
Low Alloy Steel (e.g. Cr-Mo, Cr-Mo-V)	Water	-	moderate	T
Strong Steels M	Water (σ _y >1200 MPa)	-	-	low
	Chloride (σ _y >800 MPa)	-	-	low
M	Sulphide (σ _y >600 MPa)	-	-	low
Austenitic Stainless Steel (including sensitised)	Chloride	high	high	T
	Hydroxide	high	high	very
high Sensitised Austenitic	M Aerated water	-	very high	I
Stainless Steel	Thiosulphate or polythionate	low	low	I
Duplex Stainless Steels high	Chloride	high	high	very
	T	-	-	-
Martensitic Stainless T	Chloride + H ₂ S	high	high	moderate
	Chloride (usually + H ₂ S)	high	high	moderate
Steels	Water vapour	-	low	T
High Strength Aluminium Alloys	Chlorides	low	low	I
Titanium Alloys	Chlorides	high	low	T
	Methanol	-	low	T
Copper Alloys I (excluding Cu-Ni)	N ₂ O ₄ high	-	low	T
	Ammoniacal solutions and other nitrogenous	-	low	low

⁴ Table based on original classification due to R C Newman.

Stress Corrosion Cracking

Notes to Table

1. This Table presents the systems for which SCC problems are well established and of practical importance. The absence of a metal-environment combination from this Table does not mean that SCC has not been observed.
2. There are rarely well-defined temperature or concentration limits for SCC, and the ratings given here are indicative only. As an approximate guide the terms used equate to the following ranges of values:

	Concentration	Temperature
Low	Up to 10^{-2} M	Ambient
Moderate	Up to 1 M	Below 100 °C
High	Around 1 M	Around boiling
Very high	Near saturation	Above boiling

Note that significantly increased local concentrations may be obtained under the influence of local boiling or evaporation, or by accumulation in pits and crevices, and cracking is often obtained for nominal concentrations that are much lower than is indicated here.

3. The fracture mode is classified as intergranular (I) where cracks go along the grain boundaries, trans granular (T) where cracks go across the grains, or mixed (M) where there is a combination of the two modes, or where the mode can vary depending on the conditions. There are often circumstances that can cause the fracture mode to change (e.g. chloride SCC of sensitised austenitic stainless steel may give intergranular cracking).
4. Very high temperature (> 200 °C) water environments are very aggressive, and will cause SCC of a wide range of materials. Expert advice is essential for materials selection for such conditions.

The requirements for SCC are somewhat different for hydrogen embrittlement than for the other two mechanisms, with the only requirement being the availability of a source of hydrogen, coupled with a material that is susceptible to hydrogen. The other SCC mechanisms are rather more specific, and normally occur when the metal has a low rate of general corrosion as a result of a protective surface film, such as the protective passive oxide film that forms on stainless steel.

4.0 Particular problem systems

4.1 Introduction

Table 1 gives an indication of the range of metal-environment combination that have given problems, but it is useful to examine the most common problems in more detail.

4.2 Brass in ammonia-containing environments

This was first experienced (or at least identified) when the brass cartridge cases used by the British Army in India were found to suffer from cracking (the ammonia comes from the decay of organic material). Two explanations have been given for the name applied to it of 'season cracking'; firstly that it occurred during the rainy season, and secondly that the cracks resembled the cracks in seasoned wood. It remains a problem, although the scale is probably reduced because of the substitution of plastics for many applications previously dominated by brass. The cracking is intergranular.

4.3 Chloride cracking of stainless steel

Austenitic stainless steels suffer from stress corrosion cracking in hot solutions containing chloride. A high chloride concentration is required, although relatively small amounts of chloride are sufficient at heated surfaces, where chloride concentration can occur, or where chloride is concentrated by pitting or crevice corrosion, and problems can be experienced in tap water.

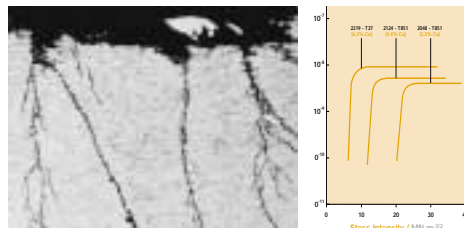


Figure 2. Intergranular cracking and transgranular cracking (micrographs and SEM Images)

The temperature usually needs to be above 70 °C, although SCC can occur at lower temperatures in some situations, notably more acid solutions. The cracking continues at low stresses and commonly occurs as a result of residual stresses from welding or fabrication. The cracking is normally transgranular, although it may switch to an intergranular path as a result of sensitisation of the steel.

4.4 Steels in 'passivating' environments

Carbon and low alloy steels can suffer from SCC in a wide range of environments that tend to form a protective passivating film of oxide or other species. Cracking will not normally occur when there is a significant corrosion rate (note that this is not the case for hydrogen embrittlement - see below). A wide range of environments have been found to cause SCC, including strong caustic solutions, phosphates, nitrates, carbonates, and hot water. The problems are important for both economic and safety reasons. Caustic cracking of steam-generating boilers was a serious problem in the late 19th century (the necessary strong caustic solution was produced by evaporation of the very dilute solution inside the boiler as it escaped through leaks in the riveted seams) and boiler explosions led to significant loss of life. More recently gas transmission pipelines have cracked in carbonate solutions produced under protective coatings as a result of cathodic protection systems. In this case the crack runs along the length of the pipe, and may propagate for very long distances by fast fracture. If the gas cloud that is released ignites, the resultant fireball is devastating.

4.5 Hydrogen embrittlement of high strength steels

All steels are affected by hydrogen, as is evidenced by the influence of hydrogen on corrosion fatigue crack growth, and the occurrence of hydrogen-induced cracking⁵ under the influence of very high hydrogen concentrations. However, hydrogen embrittlement under static load is only experienced in steels of relatively high strength. There is no hard-and-fast limit for the strength level above which problems will be experienced, as this will be a function of the amount of hydrogen in the steel, the applied stress, the severity of the stress concentration and the composition and microstructure of the steel. As a rough guide hydrogen embrittlement is unlikely for modern steels with yield strengths below 600 MPa, and is likely to become a major problem above 1000 MPa. The hydrogen may be introduced into the steel by a number

of routes, including welding, pickling, electroplating, exposure to hydrogen-containing gases and corrosion in service. The effects of hydrogen introduced into components prior to service may be reduced by baking for a few hours at around 200 °C. this allows some of the hydrogen to diffuse out of the steel while another fraction becomes bound to relatively harmless sites in the microstructure.

4.6 High strength aluminium alloys

Aluminium alloys are also susceptible to hydrogen embrittlement, although the fcc microstructure means that the transport of hydrogen is slower than in high strength steels, and hence the crack growth rate may be lower. The cracking is normally intergranular. As with steels the susceptibility becomes more severe as the strength of the alloy is increased. However, there is also a strong effect of heat treatment and microstructure, and quite high strengths can be obtained with good SCC resistance (as is demonstrated by the use of these alloys in aircraft construction). Any environments that can provide hydrogen can lead to SCC of susceptible alloys, ranging from humid air to salt solution.

5.0 Environments causing SCC

As noted above, hydrogen embrittlement processes are usually not very strongly influenced by the environment, and all that is required is conditions that allow hydrogen to be formed by the cathodic corrosion reaction and to enter the steel.

The two other SCC mechanisms are much more particular, and quite specific environments may be necessary for cracking to occur. This is because cracking depends on the possibility of specific corrosion reactions at the crack tip, with other reactions occurring on the crack walls and the specimen surface. With only minor changes in the environment one or other of these requirements may not be met, and cracking will not occur.

While the requirement for a specific environment is beneficial in that it means that SCC is relatively infrequent, it also makes life difficult for the materials specialist, as it makes the occurrence of fracture rather unpredictable, with subtle differences in service conditions leading to a marked difference in behaviour.

⁵ Hydrogen-induced cracking (HIC) results from the precipitation of hydrogen gas on planes of weakness in the steel, notably rolled-out sulphide inclusions. It leads to internal cracks lying parallel to the rolling direction, which appear as blisters when close to the surface of the plate. HIC is primarily a problem in the production of sour oil (oil containing H₂S), as the H₂S enhances the entry of hydrogen into the steel.

In many situations HIC is relatively non-damaging, as the cracks lie parallel to the plane of the plate, so there is little stress at right angles to the cracks. However, if the cracking is sufficiently severe and the applied stresses high, the cracks may join up to produce a fracture, known as 'Stress-Oriented Hydrogen-Induced Cracking' or SOHIC.

6.0 The effect of electrode potential

The electrochemical potential of the alloy can have a marked influence on the tendency for SCC to occur. For hydrogen embrittlement of high strength steel a more negative potential will tend to increase the rate of hydrogen evolution, and thereby the susceptibility to hydrogen embrittlement. It is less obvious how it happens⁶, but more positive potentials than the typical free corrosion potential may also increase the entry of hydrogen. Figure 3 shows the amount of hydrogen permeating through a steel membrane as a function of the applied potential. The SCC of high strength aluminium alloys is also thought to be due to hydrogen embrittlement, but in this case the dominant effect is the protective nature of the aluminium oxide passive film. As soon as water comes into contact with metallic aluminium, it will react readily to produce hydrogen (since aluminium is a very reactive metal).

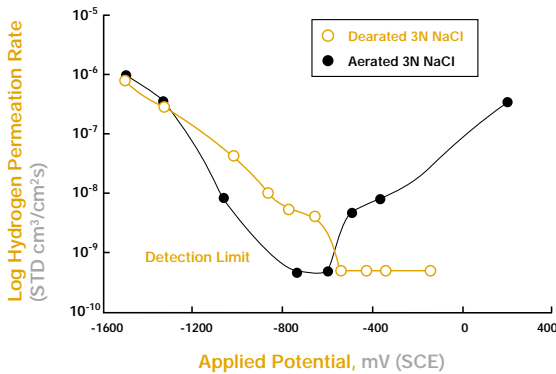


Figure 3. The effect of potential on hydrogen entering steel.

SCC processes that do not involve hydrogen typically occur over a limited range of electrode potential. It is often found that cracking occurs in the transitional potential regions between active and passive or between passive and pitting (Figure 4). In these regions the surface of the component will be in the passive region, while the crack tip will be in the active or pitting state.

In service the electrode potential is not usually controlled directly, with applied cathodic protection being the main example. Rather the potential is determined indirectly by the composition of the environment, particularly the presence of oxygen and other cathodic reactants. Thus modification of the oxygen content can often have a profound influence on SCC susceptibility.

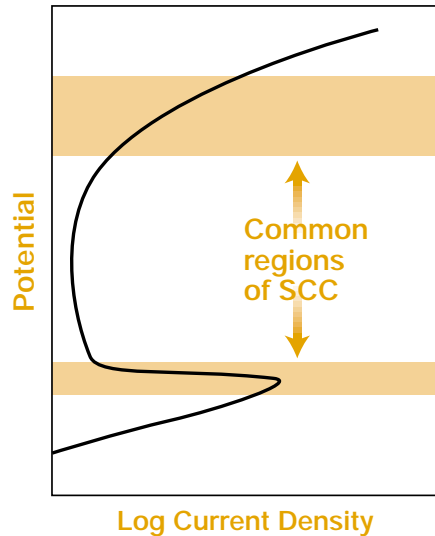


Figure 4. The effect of potential on SCC susceptibility

7.0 Alloy dependence

The exact alloy composition, microstructure and heat-treatment can have a marked effect on SCC performance.

There are few general rules governing the influence of material strength on SCC susceptibility. For hydrogen embrittlement processes a higher strength normally increases the susceptibility; additionally, higher strength materials generally have a low K_{IC} , and therefore fail by fast fracture with a smaller SCC crack. Processes that rely on plastic strain at the crack tip will be easier for lower strength materials. Hence, many SCC systems, such as caustic cracking of carbon steels, will become more susceptible as the strength decreases.

Quite small changes to the composition of an alloy can have a marked influence on the SCC behaviour. For example Figure 5 shows the effect of Cu content on the crack growth rate of a series of Al-Cu-Mg alloys. Some care needs to be exercised in interpreting this graph. The change in copper concentration of the alloy will have a marked effect on the corrosion behaviour of the alloy (since the copper-containing precipitates are active cathodic sites), but it will also modify the mechanical properties of the alloy and its response to heat treatment. Consequently, it would probably be possible to change the relative orders of the curves by using different heat treatments.

⁶ For an explanation of how the hydrogen is produced, see Chapter 8 in "Corrosion", by Shreir, Jarman and Burstein. Many early workers assumed that cracking under the influence of more positive potentials could not be due to hydrogen, and must, therefore, be evidence for a dissolution mechanism of SCC. We now know that this is not correct, and such arguments should be re-assessed.

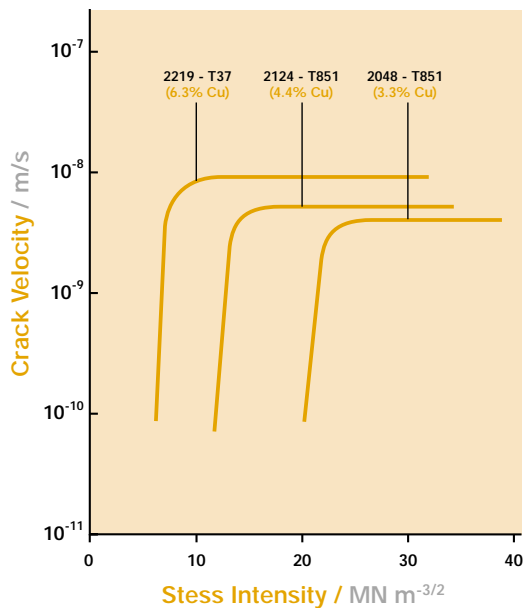


Figure 5. Effect of Cu-content on crack growth rate.

The effects of alloying additions are not necessarily consistent from one environment to another. Thus, a higher molybdenum content improves the resistance of a low alloy steel to carbonate-bicarbonate cracking, but makes it more susceptible to caustic cracking.

Changes in the thermomechanical treatment of the alloy can change the sensitivity to SCC, the mode of fracture and even the fracture mechanism. To take a specific example, austenitic stainless steels suffer from SCC in chloride solutions. In a correctly heat-treated steel the SCC cracks are transgranular. The mechanism is not fully established; film-induced cleavage (by way of a de-alloyed layer) is probably the most likely, although all mechanisms remain plausible.

If the same alloy is sensitised by a suitable heat treatment, this depletes the grain boundary regions of chromium as a result of chromium carbide precipitation, and the SCC crack path switches to intergranular. The cracking mechanism in this case may change to active path dissolution, although the other mechanisms remain possible.

If the same alloy is rolled, a certain amount of strain-induced martensite will be formed, and this, combined with the higher strength of the work-hardened material, leads to a susceptibility to hydrogen embrittlement.

8.0 The effect of stress

Of necessity stress corrosion cracking requires stress, and it is often found that there is a threshold stress below which cracking does not occur (at worst the crack growth rate will become so low that failure will not occur in realistic times). For example Figure 6 shows the time to failure of maraging steel in salt solution. Some care needs to be exercised in the use of such a threshold stress.

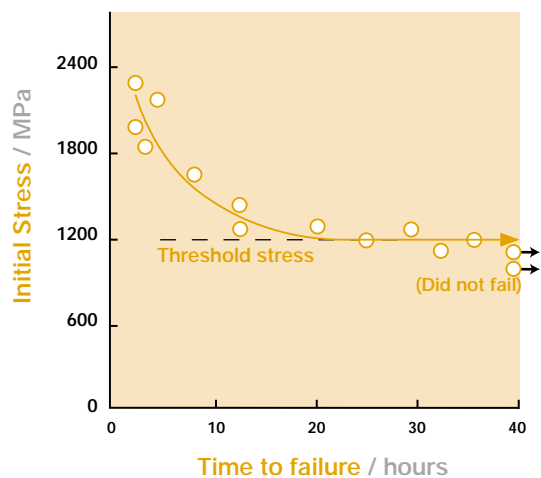


Figure 6. The effect of initial stress on time to failure of maraging steel in 3.5% NaCl solution.

Real components will typically contain defects and design details, such as notches, sharp changes in section, welds, corrosion pits etc, that will produce a stress concentration, hence allowing the threshold stress to be exceeded locally even though the nominal stress may be well below the threshold. Furthermore, residual stresses produced by welding or deformation will frequently be close to the yield stress.

The methods of fracture mechanics⁷ provide a means of allowing for defects in the structure. Rather than determining the time to failure for a specimen exposed to a given stress, the rate of growth of a pre-existing crack is measured as a function of the stress intensity factor at the tip of the crack.

⁷ See "Engineering Materials", by Ashby and Jones for an excellent introduction to fracture mechanics.

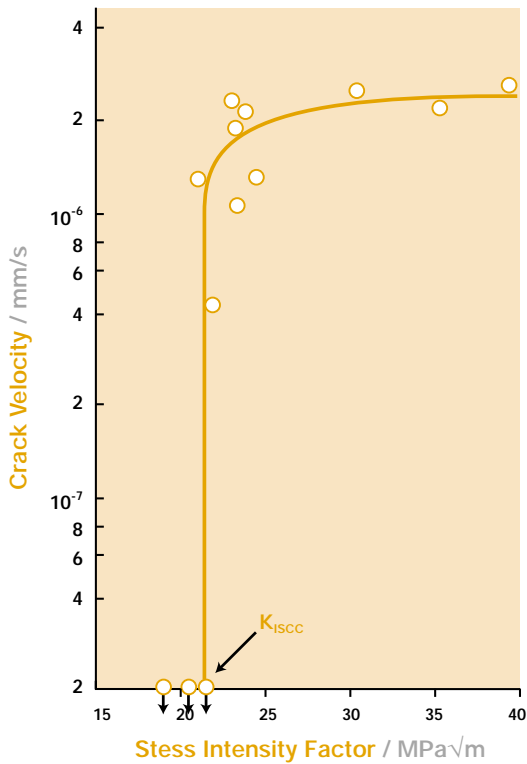


Figure 7. Relation between crack growth rate and stress intensity factor.

This typically results in a graph of the form shown in Figure 7. This exhibits a threshold stress intensity factor below which stress corrosion cracks will not propagate. This threshold is commonly given the symbol K_{ISCC} , which signifies the threshold stress intensity factor for stress corrosion crack growth in mode I plane strain loading.

Once the stress intensity factor exceeds K_{ISCC} , the crack growth rate increases rapidly, but then reaches a limiting rate, known as the plateau crack growth rate or velocity. As the stress intensity factor is increased further the crack growth rate eventually starts to increase again as the stress intensity factor approaches the critical stress intensity factor for fast fracture, K_{IC} . In this regime part of the crack growth occurs by purely mechanical processes, with the environment serving only to propagate the crack through the toughest regions of the microstructure.

In principle K_{ISCC} provides a good basis for the management of stress corrosion cracking. By ensuring that the combination of stress and maximum defect size give a stress intensity

factor below K_{ISCC} , crack growth, and hence stress corrosion failure, can be avoided. However, it should be appreciated that K_{ISCC} is not an invariant material property, and will be affected by all of the material and environmental factors that influence other aspects of SCC. Consequently it is important to be sure that an appropriate value of K_{ISCC} is used.

9.0 Stress corrosion cracking tests

In essence, tests for stress corrosion cracking simply require the exposure of the stressed sample of the material or component in question to the environment of interest. However, there are various classes of test with differing objectives:

- Standard tests (see BS, ASTM, ISO and other standards for examples) are generally designed to test a material for its susceptibility to SCC in an environment that is known to give problems, or to test components to determine whether they have the necessary combination of material properties and residual stress to suffer from cracking. For example, boiling 42% $MgCl_2$ solution is widely used as a test for the susceptibility of austenitic stainless steels to chloride stress corrosion cracking, and this test may be used to rank alloys or to check components for the presence of residual stresses.
- Constant stress or constant displacement tests essentially describe a specimen and a loading method that stresses the specimen while exposed to the solution. The susceptibility to SCC is then assessed by the time taken for failure of the specimen, or the development of cracks in the surface of the specimen. A common constant displacement test use a U-shaped specimen, produced by bending a flat plate, and then stressed by drawing the arms of the U together with a loading bolt (known as a U-bend test).
- Fracture mechanics tests use a specimen with a pre-existing crack (often produced by fatigue cycling). The tests may be evaluated simply by recording the time to failure, but it is more common to measure the change in length of the crack with time, and thereby derive a graph of crack growth rate as a function of stress intensity factor. With a suitable loading arrangement and specimen geometry it is possible to arrange for the stress intensity factor to fall as the crack grows, and this provides a useful method of estimating K_{ISCC} . The stress corrosion crack is initiated at a relatively high stress intensity factor, but as the crack grows the stress intensity factor falls, until the crack arrests at K_{ISCC} .

- The slow strain rate test, or, more accurately, the constant extension rate test, applies a slow rate of extension to a specimen. This ensures that there is a continuing plastic strain at the surface of the specimen, and encourages the initiation and growth of stress corrosion cracks. The result of the test is evaluated in terms of the time taken for failure to occur, the extension at failure or the appearance of the fracture surface. This test has several advantages, including the limit to the time taken for the test (mechanical failure will inevitably occur even if no SCC occurs), and the relatively severe nature of the test, which means that it usually gives conservative results (i.e. failure is unlikely to occur in service if it does not occur in the test). The slow strain test is normally applied to smooth tensile specimens, although pre-cracked samples may also be used.

10.0 Control of stress corrosion cracking

10.1 Introduction

In order for SCC to occur, we require a susceptible material, an environment that will cause cracking of that material and a high enough stress or stress intensity factor. There are, consequently, a number of approaches that we can use to prevent SCC, or at least to give an acceptable lifetime. In the first edition of this booklet this section was entitled "Prevention of Stress Corrosion Cracking". We prefer the word "control" because there are often situations where we must live with a stress corrosion cracking problem and can only aim to have sufficient control over the process to avoid catastrophic failure.

In an ideal world a stress corrosion cracking control strategy will start operating at the design stage, and will focus on the selection of material, the limitation of stress and the control of the environment. The skill of the engineer then lies in selecting the strategy that delivers the required performance at minimum cost. In this context we should appreciate that a part of the performance requirement relates to the acceptability of failure. For the primary containment pressure vessel in a nuclear reactor we obviously require a very low risk of failure. For the pressed brass decorative trim on a light switch, the occasional stress corrosion crack is not going to be a serious problem, although frequent failures would have an undesirable impact on product returns and the corporate image.

10.2 Selection and control of material

The first line of defence in controlling stress corrosion cracking is to be aware of the possibility at the design and construction stages. By choosing a material that is not susceptible to SCC in the service environment, and by processing and fabricating it correctly, subsequent SCC problems can be avoided. Unfortunately, it is not always quite that simple. Some environments, such as high temperature water, are very aggressive, and will cause SCC of most materials. Mechanical requirements, such as a high yield strength, can be very difficult to reconcile with SCC resistance (especially where hydrogen embrittlement is involved). Finally, of course, Murphy's Law dictates that the materials that are resistant to SCC will almost inevitably be the most expensive (and that they will be found to be susceptible to SCC in your environment as soon as you have used them!).

10.3 Control of stress

As one of the requirements for stress corrosion cracking is the presence of stress in the components, one method of control is to eliminate that stress, or at least reduce it below the threshold stress for SCC. This is not usually feasible for working stresses (the stress that the component is intended to support), but it may be possible where the stress causing cracking is a residual stress introduced during welding or forming.

Residual stresses can be relieved by stress-relief annealing, and this is widely used for carbon steels. These have the advantage of a relatively high threshold stress for most environments, consequently it is relatively easy to reduce the residual stresses to a low enough level. In contrast austenitic stainless steels have a very low threshold stress for chloride SCC. This, combined with the high annealing temperatures that are necessary to avoid other problems, such as sensitisation and sigma phase embrittlement, means that stress relief is rarely successful as a method of controlling SCC for this system.

For large structures, for which full stress-relief annealing is difficult or impossible, partial stress relief around welds and other critical areas may be of value. However, this must be done in a controlled way to avoid creating new regions of high residual stress, and expert advice is advisable if this approach is adopted.

Stresses can also be relieved mechanically. For example, hydrostatic testing beyond yield will tend to 'even-out' the stresses and thereby reduce the peak residual stress. Similarly shot-peening or grit-blasting tend to introduce a surface compressive stress, and are beneficial for the control of SCC. The uniformity with which these processes are applied is important. If, for example, only the weld region is shot-peened, damaging tensile stresses may be created at the border of the peened area.

10.4 Control of environment

The most direct way of controlling SCC through control of the environment is to remove or replace the component of the environment that is responsible for the problem. Unfortunately, it is relatively rare for this approach to be applicable. If the active species is present in an environment over which we have some control, then it may be feasible to remove the active species, although even then it may be difficult. For example, chloride stress corrosion cracking of austenitic stainless steels has been experienced in hot-water jackets around chocolate pipes (that is to say, pipes carrying molten chocolate) in the food industry. In this situation we can't easily change the material or the temperature, and it is virtually impossible to eliminate the residual stresses associated with welding and forming of the stainless steel. However, we can remove the chloride from the water by an ion exchange process, and, with proper control and monitoring, this approach could be successful. Of course if we were dealing with hot tomato ketchup, which has a low pH and may contain enough chloride to cause SCC, we have a far more difficult problem!

In the latter situation, where the species responsible for cracking are a required component of the environment, the environmental control options consist of adding inhibitors, modifying the electrode potential of the metal, or isolating the metal from the environment with coatings.

To take another example of chloride SCC of austenitic stainless steels, tube and shell heat exchangers are frequently constructed using stainless steel tubes (since these must be thin-walled and corrosion cannot be tolerated) with carbon steel tube plates and shell (since these can be made much thicker to provide a corrosion allowance). Chloride SCC is rarely experienced with this construction. However, it is quite common for an enthusiastic engineer to decide that the replacement heat exchanger should use an "all-stainless" construction to avoid the unsightly corrosion of the carbon steel. The result is frequently a rapid failure of the

heat exchanger by SCC or pitting corrosion. This is because the carbon steel adopts a relatively low electrode potential that is well below that required to cause SCC or pitting of austenitic stainless steel, which is thereby protected. When the all-stainless construction is adopted, this unintentional electrochemical protection is lost and failure occurs.

Corrosion inhibitors are chemicals that reduce the rate of a corrosive process. They are generally rather specific to a particular alloy system, and they typically also have specific requirements in terms of the composition of the environment. Inhibitors may be effective at controlling SCC, although the requirements are rather different from those for the inhibition of general corrosion. Indeed chemicals that inhibit general corrosion may create the necessary conditions for stress corrosion cracking (e.g. hydroxides, carbonates and nitrates for carbon steel). Even when inhibitors are effective against SCC, higher concentrations may be required than for the inhibition of general corrosion.

Metallic coatings isolate the metal from the environment, and can, thereby, prevent SCC. However, the possibility of the coating being penetrated by imperfect application or by mechanical damage in service must be taken into account. For this reason zinc is a popular coating for carbon steel. The normal corrosion potential for zinc is relatively low, and if any of the underlying steel is exposed, this will be cathodically protected. However, the low electrode potential will also encourage hydrogen evolution, and this may lead to hydrogen embrittlement. Hydrogen embrittlement may also occur as a result of the hydrogen evolution during the initial electroplating operation, as noted above. Consequently, zinc plating must be used with care on strong steels. Cadmium adopts a rather more positive potential, and produces a much lower risk of hydrogen embrittlement, while still protecting the underlying steel. Unfortunately the toxicity of cadmium compounds means that it is essentially banned as a coating material.

Paints and other polymeric coatings protect the underlying metal largely by virtue of their high electrical resistance, which restricts the passage of current from the anode to the cathode (both oxygen and water diffuse relatively easily through most polymers, so paints don't, as is often thought, work by isolating the metal from the environment). Paints may be effective at restricting SCC, particularly where they incorporate inhibitors that can inhibit any solution that does find its way to the metal. However, as with metallic coatings, it is important to think about what will happen if the coating is removed by mechanical damage.

11.0 Living with SCC

It is often necessary to operate in conditions in which SCC is possible. This may result from a deliberate decision to use a system that may be subject to SCC, but more commonly it arises because of unanticipated susceptibility. An important example of such a problem arose after the failure of a steam-turbine disc at the Hinkley Point Power Station in 1969.

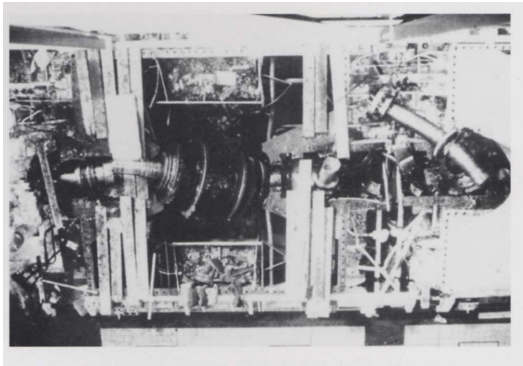


Figure 8. Overview of Hinkley site

This failure was initiated by stress corrosion cracks growing in condensed water in a keyway in the bore of the disc. The steel concerned had a relatively low fracture toughness as a result of temper embrittlement, and the disc failed by fast fracture when the crack had reached a length of about 2 mm. The failure itself was serious; when a massive chunk of steel rotating at 3000 rpm breaks into several parts the flying debris causes a lot of damage to the turbine and the turbine hall. What was potentially more serious however, was the fact that turbines of this design formed a major part of UK electricity generating capacity. The CEBG therefore could not afford to shut down all of these turbines, and had to live with a potentially catastrophic SCC problem. That they did so without further failure is a testament to the skill of the engineers and scientists involved. The method that they adopted would today be called risk-based inspection. The risk of failure of the individual turbines was assessed on the basis of the test results for the individual disc forgings. The turbines were then inspected in order of decreasing estimated risk (simply inspecting for cracks is a major exercise, as the keyway can only be inspected by disassembling the entire turbine).

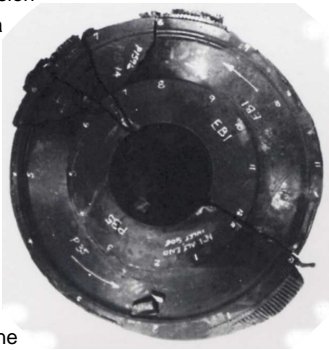


Figure 9. Hinkley Point Failed Disc

The technique of risk-based inspection is a valuable tool for the management of inspection schemes. In essence each component is categorised in terms of its probability of failure and in terms of the consequence of that failure. Then the priorities for inspection are reasonably clear; the first priority must be to inspect the components with a high probability of failure and a high consequence of failure (in practice there should be no components in this category - if there are the plant should probably be shut down immediately!) The inspection priorities then move down through the grid of probability and consequence until the components with a low probability of failure and a low consequence of failure are reached. Arguably it is not worth inspecting these, and they can simply be replaced as and when they fail. While the basic principle of risk-based inspection is very simple, it has proved to be a powerful tool. For example, it has been claimed that a reduction in failures of 90% has been achieved at the same time as a reduction in inspection costs of 50%.

In determining both the probability of failure and the consequence of failure by cracking processes the techniques of fracture mechanics may be very valuable. Ashby and Jones have given a very clear introduction to these techniques, and we shall only attempt to summarise the theory here. Fracture mechanics is concerned

with the mechanical conditions at the tip of a crack, and the properties of the material that determine whether or not that crack will propagate. Providing the region of plasticity at the tip of the crack is small compared to the crack length and the thickness of the specimen, we find that the stress state at the crack tip is defined by the stress intensity factor, K , given by:

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

where σ = applied stress

a = crack length

Y = geometrical correction factor ($\neq 1$)

The thickness of the specimen in the direction of the crack front is also important; the crack growing through aluminium foil as we tear it from the roll experiences very different conditions from a crack in a very thick aluminium plate. The mechanics for very thin samples depends strongly on the thickness, and cannot be analysed in a general way (the stress condition here is known as plane stress, as there cannot be any stresses developed out of the plane of the sheet).

Stress Corrosion Cracking

Whether or not a crack will propagate (in the absence of SCC effects) is determined by whether or not the applied stress intensity factor is greater than a critical value, known as the fracture toughness K_{IC} . Similarly it is generally found that SCC will only occur if K is greater than K_{ISCC} .

This provides us with a method of determining the likelihood of SCC failure of a given component, and indicates the requirements for crack detection during inspection. If we know the stress, s , to which the component is subjected, we can see that the crack length required to achieve a stress intensity factor of K_{ISCC} is given by:

$$a_{crit} = \frac{1}{\pi} \left[\frac{K_{ISCC}}{\sigma Y} \right]^2$$

If our crack detection system can guarantee to find any crack of length a_{crit} or above, we can be reasonably confident that SCC failure is not likely to occur until such time as

larger defects have grown (typically by pitting corrosion or corrosion fatigue).

If we are unable to detect cracks of size a_{crit} reliably, we must assume that such cracks exist, and base our inspection strategy on the time taken for the largest crack that we may fail to detect to grow to the size required to achieve K_{IC} . If the plateau crack growth rate is reasonably low this may give us an acceptable time between inspections, but for many systems the crack growth rate is too rapid and failure will occur in an unacceptably short time.

Corrosion pits are common sites for the initiation of stress corrosion cracks (the cracks in the Hinckley Point disc initiated at a corrosion pit). To a first approximation a pit can be treated as a crack with the same cross-section, and a fracture mechanics approach used to determine the size of pit necessary to exceed K_{ISCC} and hence cause cracking.

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The National Corrosion Service (NCS) is operated by NPL on behalf of the DTI to provide a gateway to corrosion expertise for UK users. By acting as a focal point for corrosion enquiries, the NCS can make the UK's entire base of experts available to solve problems or can, using in-house expertise or teams, carry out consultancy. The NCS also helps raise awareness of corrosion problems and methods of control.

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