STRESS CORROSION CRACKING (SCC)

With the ravages of corrosion around, we sometimes wonder how components manage to stay in one piece. Many don't of course, leading to some notable disasters like the one at Flixborough described below. But one corrosion mechanism, stress corrosion cracking (SCC) is particularly problematic, as it can be unpredictable, resulting in sudden crack growth in minutes after many years of service. Luckily, it can be guarded against, once we've explained how the mechanism works.

SCC or 'environment-sensitive cracking' requires a particular set of conditions, the three most important of which are the presence of a stress, a corroding medium and a susceptible material. Most alloys are prone to SCC but the necessary conditions don't occur that often. This can be dangerous because when they do, failure could be unexpected. Many technical papers tend to overcomplicate SCC by sub-dividing it, but this is rather academic and can actually be confusing. Here we discuss the key factors that are involved.

SCC in hardened and tempered steel, here cracks are intergranular due to nitrates.

Virtually all metals and alloys are susceptible to SCC under certain conditions that include stress, environment, electrode potential, temperature, contamination, physical damage, or changes in its microstructure. Stress may be applied (pressure, thermal, centrifugal, load etc.) or residual (welding, poor fit, cold work etc). It can be affected by local stress concentrations too (pitting, geometry, microstructure, corrosion product wedging) and by corrosion concentration (evaporation, differential aeration, build up under scabs and in cracks etc).

However, most components operate outside the SCC boundary either by good fortune or because of some limited understanding of the problem. And some have a wider 'limit of intolerance' than others.

One reason SCC is unpredictable is that it requires a crack initiation stage, but at the start, the growth rate can be as low as 30 microns a year. This means the embryo crack will almost certainly go unnoticed as it will be filled with corrosion product. And it is not unknown for components to resist many thousands of hours of the corrosive environment with apparently little attack until the embryo cracks develop. Then, growth can be rapid.

It is generally agreed that each alloy is only susceptible to particular corroding species, though this is not strictly true, as unusual combinations do occasionally occur. In 1969 a turbine disc at Hinckley Point A Station failed by SCC in pure steam; a combination previously unreported. Subsequent rig tests showed that cracks can initiate and grow in normal deoxygenated power station steam, with no contamination at all, which is rather worrying. But in the main, there are certain alloys and chemicals that should be avoided, providing a means to control the risks of SCC occurring.

One such combination, that of ferritic steel exposed to nitrates, provides us with a good example of how disastrous SCC can be. In 1974 Britain was in the midst of the miner's strike and the three day week so the Flixborough plant saved energy by turning off the stirrers in its six cyclohexane vessels made from 12mm thick ferritic steel with a 3mm thick stainless cladding. The vessels made something called caprolactam, the raw material for nylon. Amongst other things, surplus caprolactam was also used to render animal offal.

The valve between vessels 5 and 6 was in poor condition, requiring it to be sprayed with water from the local river to keep it cool. But ferritic steel + heat + nitrate is one of those potentially nasty SCC conditions mentioned above (an example of cracking due to this mechanism is shown to the left). Due to the combination of river water and heat, nitrates in the water from fertiliser run-off from agriculture concentrated up and caused stress corrosion cracking of vessel 5. Fortunately, the early sign was leakage through the cracks, which was noticed, and vessel 5 was taken out of service. To continue manufacturing, vessel 4 was connected to vessel 6 with a temporary pipe but in haste, this was poorly positioned and supported.

Stress corrosion cracking at Flixborough resulted in Mad Cow Disease

A couple of months later, a small fire nearby was thought to have allowed zinc from a galvanised walkway to melt and drip onto a hot stainless pipe, embrittling it and causing it to fail catastrophically. (You'll be able to read about liquid metal embrittlement in a later Bulletin). The resulting small explosion destroyed the poorly positioned bypass pipe, resulting in spillage of a large quantity of cyclohexane. This would have been bad enough, but recent evidence suggests that water which had accumulated in the vessels because of the lack of stirring, flashed off to steam as soon as pressure was released, rapidly expelling 40 tonnes of cyclohexane into the immediate area and culminating in a massive explosion equivalent to 15 tonnes of TNT that killed 28 people and destroyed the plant and 1800 buildings in the vicinity.

The incident led to a world shortage of caprolactam, so, unable to render animal waste, Britain fed offal back to cattle via an alternative rendering process, resulting in Mad Cow Disease which cost British taxpayers £4 billion. Ironically, the whole episode was initiated by nitrates from agricultural fertilisers that had contaminated the river.

THE SSC MECHANISM - INITIATION

SCC occurs when metals are exposed to 'fluids' (aqueous, steam, vapour and molten salts). Usually, but not always, temperatures above 50 degrees Celsius are involved too. The all important initiation stage requires time-dependent changes in either the attacking solution or the metal, through chemical or electro-chemical action to locally concentrate the attack at the atomic level. Sometimes, local concentration increases through physical means such as evaporation or localised conductivity changes

through the setting up of an electrical cell where different metals or different oxygen levels exist. This cell can also be set up by any discontinuity in the metal surface. It is this variability in initiation conditions that makes SCC rather difficult to predict.

Machining marks and scores (especially poor machining surfaces), generate residual stresses at the surface as well as providing pits and crevices for cells to develop. Lapped and smeared metal seems particularly susceptible to SCC, therefore machining should be done with appropriate sharp tools and adequate feed speeds. When keyways are cut by milling, avoid smearing or lapping the metal on the sides or corners. Such damage at a machined keyway was thought to be the contributing factor in the 1969 Hinckley failure.

Transgranular cracking in an austenitic stainless steel.

Controlled experiments have shown that rough surfaces fail by SCC faster than smoother surfaces. This is probably because machining that disturbs the metal more deeply will leave behind higher residual stresses, as it is not uncommon for machining to influence metal several millimetres below the surface. Often, SCC could be avoided by generating only machining marks that run in a different direction, so avoid any tendency to leave pipes and bars with coarse, circumferential score marks from rough machining or grinding.

Non-metallic inclusions are another source of SCC targets. Some types of inclusions are more harmful than others depending on the alloy, due to three significant effects.

- Firstly, in stagnant conditions the inclusion will affect the local chemistry,
- secondly dissolution of inclusions will leave a pitted surface,
- thirdly sulphides when attacked chemically will generate hydrogen sulphide locally that removes passive oxide films and forms hydrogen in the surrounding metal.

All wrought metals have a 'grain direction' that originated from the rolling of the bulk billet or continuous cast strand. The orientation of the rolling direction can be important, because it has been found that SCC occurs more frequently from surfaces perpendicular to the rolling direction than along the rolling direction. Since most steels contain some degree of manganese sulphide inclusions that have been elongated into rod shapes by steel manufacture, inclusions exposed on a cross section penetrate much deeper than those exposed in their aligned direction. It is thought that manganese sulphide rods that penetrate into the metal provide a much greater reservoir of hydrogen sulphide and hydrogen. Therefore, if there is an option, expose only the plate or bar surface and not the cross section. Also, sulphides that break the surface are more prone to SCC in stagnant conditions due to bacterial attack.

It has also been noted that oxides form preferentially at these sites when temperatures are high enough for oxidation to occur. Iron oxide has a volume that is about twice that of the metal it formed from. As a finger of oxide grows preferentially down the rod-like inclusion, it results in a process called oxide wedging in which the expanded oxide volume stresses the surrounding metal, leaving it more prone to SCC. Oxide is also very brittle, so a change in stress can fracture this oxide wedge, resulting in a crevice that exacerbates the situation.

This is another reason to avoid end-grain exposure but it also suggests that low sulphur steels are better than high sulphur steels. A similar situation develops in pipeline steels for sour gas service, though for slightly different reasons. Sulphide stress corrosion cracking is caused by hydrogen diffusion from corrosive attack, and here steels are almost always specified as 0.003% sulphur max.

Lower sulphur is usually better, except that inclusions act as hydrogen sinks, and very low sulphur steels require care in welding to avoid hydrogen cracking, as the gas has literally nowhere to hide.

SCC will also initiate from silicate inclusions, but of particular concern is the presence of silicate particles and slag stringers breaking the surface of welds. These act as insidious SCC sites especially when hidden in pipe butt weld roots and the like, sometimes resulting in failure of pipes after hydraulic testing, poor storage or badly designed, incompletely drainable systems.

It is not widely appreciated that SCC occurs more readily in metals that are subjected to a very low frequency stress cycle, such as might occur from on/off cycles in a heating system.

THE SCC MECHANISM - PROPAGATION

Many mechanisms such as fatigue can be identified by the way the crack grows, but in SCC the crack growth can be either intergranular (between grains) or transgranular (across grains). Some fractures even have transitions from one to the other due to differences in residual stress levels or microstructure. This definitely makes diagnosis of the problem a job for an expert.

INTERGRANULAR ATTACK

Intergranular fracture can be identified by smooth facets on the grain boundary surface when examined by electron microscopy. Brittle fracture and cleavage on the other hand tends to generate river marks. Often, a layer of corrosion product can be seen on the fracture surface, or the exposed surface may even be darkened and indistinct. Usually, there is a well defined area of the final fracture that occurred by overload due to the weakening effects of the SCC. Fortunately, our electron microscope incorporates a very sophisticated EDAX analyser capable of finding and quantifying all elements from Boron upwards in the periodic table. It makes the identification of the mechanism so much easier, though you do still have to know what to look for.

Intergranular cracking is common in carbon steels exposed to caustic, nitrate, acetate and carbonates; in low alloy steels with water and steam; in sensitised stainless steel and oxygenated water; in alpha-brass exposed to ammonia; in aluminium alloys and steam or water vapour; in beta-titanium alloys exposed to methanol and water, and in tempered martensitic stainless steels and chlorides.


With intergranular attack, the grain boundary is the preferred route for the crack to grow because in these alloys the grain boundaries and the grains themselves have different compositions. The reasons for this are worth explaining.

An alloy is a mix of one or more metals, and as an alloy solidifies the growing crystals of solid metal in the melt attract a greater proportion of the main elements while the lesser elements are pushed aside into the liquid. As the liquid cools and the crystals grow, they develop a shell of solidifying metal with an increasingly greater proportion of less pure metal, until the last portions to solidify have a much greater level of the alloying elements compared with the metal at the centre of the grains. These last portions to solidify are the grain boundaries. They have a different composition to the grains and some SCC systems prefer them.

Some alloys have a wide freezing range, and develop this effect to a greater extent. Their wide freezing range makes them difficult to cast without shrinkage defects. Etching a cross section of these

alloys shows the alloy distribution in a pattern known as 'coring'.

Other alloys have a narrow freezing range, and develop less coring. One such alloy, aluminium containing 12% silicon, has a much narrower freezing range, so it can be cast with thinner cross section without the risk of shrinkage. This property enabled it to form the basis of very successful Cosworth racing engines in the 1980's partly because sound engine blocks could be cast in thinner sections, allowing for greater efficiency and better power to weight ratio. It probably follows that alloys with a narrow freezing range are less likely to be susceptible to intergranular SCC mechanisms.
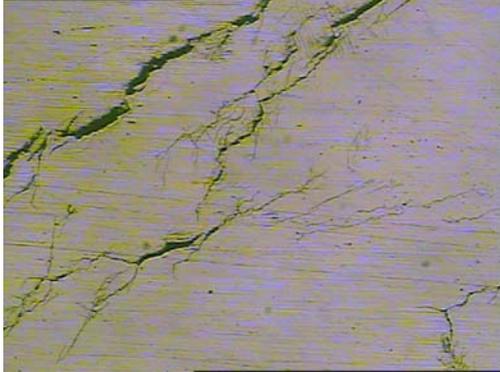
The Al-12%Si develops two distinct phases. Other alloys that produce distinct phases, like Al-Mg alloys that can develop continuous precipitates of Mg_5Al_8 generate anodic cells with respect to the matrix. This induces intergranular SCC in chloride solutions.

Although low and medium carbon steels have a microstructure of ferrite and pearlite when normalised, or bainite or martensite when hardened, what we cannot see are the previous austenite grain boundaries that existed when the metal was solidifying, unless we use a special etch to reveal them. These steels can suffer from SCC along prior-austenite grain boundaries after they have been temper-embrittled by heating in the range 350—550 degrees Celsius. This also includes cooling slowly through this temperature range, requiring a faster cooling rate or intermediate quench into a salt bath to prevent the problem. Various damaging media have been reported including water, steam, caustic, and sugar solutions. Embrittlement involves the formation of grain boundary carbides while strengthening the grains with fine carbide precipitates, both of which drive an intergranular mechanism due to electrochemical cells and internal stresses.

Several academic theories of sensitisation abound, centred on cathodic hydrogen formation at precipitates or localised slip of planes of atoms generating dislocations, but the message should probably be to avoid temper embrittlement at all costs. Unfortunately, many fabricators such as chain manufacturers are forced to heat treat components close to these temper embrittlement parameters due to specific requirements for strength and durability. The presence of SCC in these materials has sometimes been confused with quench cracking, though the two are actually readily separated by electron microscopy and EDAX.

A similar phenomenon occurs in austenitic stainless steels and nickel-based alloys, where intergranular failures are associated with formation of carbides at grain boundaries in a process known as sensitisation. These form in a temperature range between 520 and 800 degrees Celsius, and the effect can develop quickly enough for it to occur while cooling from hot forming or welding.

Formation of massive carbides at grain boundaries are associated with intergranular corrosive attack, but to a lesser degree boundary carbides can initiate SCC instead, especially when the carbides are not sufficiently continuous along boundaries to produce full intergranular attack. The mechanism however is principally the same. The effects of a grain boundary are felt over several hundred Angstroms, offering a more suitable home for carbon atoms which in turn attract chromium atoms for a stable carbo-nitride with the formula $(Cr,Fe)_{23}(CN)_6$. Similar effects can occur in aluminium due to the presence of small amounts of iron.

An interesting phenomenon occurs with mild steel and nitrates. When thermally cycled the normally protective magnetite oxide coating on the steel can rupture, and before it has time to heal,

SCC develops from nitrate attack wherever the rupture positions coincide with grain boundaries. Adding chlorides, which promote general corrosion, or nitrites which provide fast passivation of the ruptured surface will inhibit SCC.

TRANSGRANULAR ATTACK

Transgranular cracks are commonly observed in failure investigations, especially in stainless steel exposed to acidic chlorides, in low strength ferritic steels exposed to acids, in alpha brass exposed to ammonia solutions, in aluminium alloys exposed to chlorides, and in magnesium alloys exposed to dilute fluorides.

Transgranular fractures appear to have cleavage-like facets, with fan-like river markings. There is usually a 'tunnelling' effect from side branches that can only be seen on cross sections, though electron microscopy does reveal fissures between grains that have characteristic tunnelling inconsistent with overloading. There is often a tendency to target grain boundaries close to inclusions, with dissolution of the local area through corrosion. Sometimes a coating of corrosion product can be analysed to identify the chemicals responsible.

In india, brass bullets cracked by SCC in summer heat due to ammonia from horse dung, coining the phrase 'season cracking'

The theory of tunnelling comes from the mechanism of attack which is thought to develop primarily along planes of atoms. Metal grains consist of ordered arrays of atoms arranged rather like trays of eggs, one stacked on top of the other. These planes can be seen in austenitic stainless and brass that have been annealed, when the assembly of stacked atoms generate a 'stacking fault' known as a twin boundary. We see them as a series of parallel lines, running across the grain (see picture opposite).

Transgranular SCC develops from a boundary, stacking fault or locally slipped stack of packed atoms that breaks the surface. The boundary interface is breached by the chemical ions, driven by the electrochemical cell that develops during passivation of the surface. This local attack causes a pit and is accompanied by sliding of the
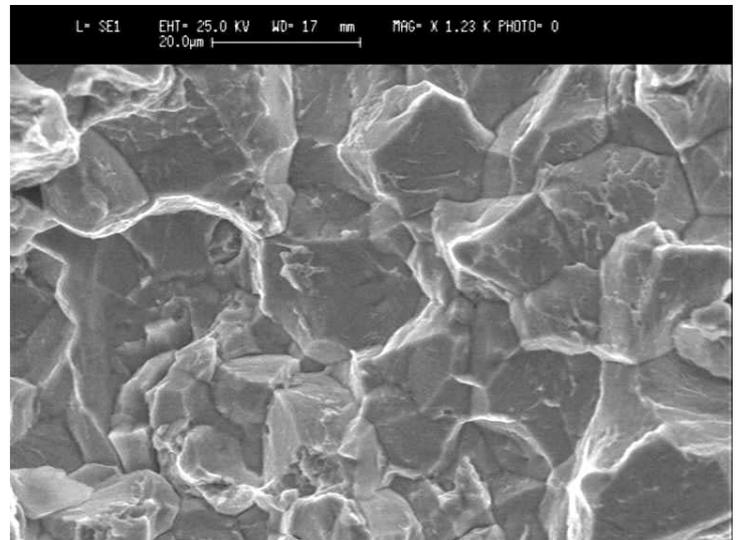
Intergranular SCC leaving grains showing crevices where they are being wedged apart

packed atoms over each other, producing a misfit known as a dislocation. The dislocation is penetrated by the corroding chemical, and the process is repeated. Although the effect usually develops slowly, sometimes cracking propagates at an alarmingly fast rate of minutes or hours, especially worrying when the component may have been operating quite successfully for years previously. On such occasions the term 'electrochemical knife' has been used to describe the cleaving open of planes of atoms in a transgranular path.

A common example of transgranular SCC attack comes from the nearby brewing town of Burton on Trent. Brewing beer requires stainless vessels, pipes and valves, as well as lots of heat and water. Although chloride-free foams and cladding materials are

specified, external cleaning using distilled water and proprietary cleaners still manages to leach out any traces of chloride in the lagging surrounding the vessels and pipes. This runs down and accumulates at the bottom of the lagging, where it evaporates, concentrates up, and attacks susceptible areas such as weld heat affected zones.

THE SCC MECHANISM - ANALYSIS

When a crack or fracture occurs, it is important not to wash away the contaminating substances, as the analysis of the exposed surfaces can give important clues about the cause of the problem. Our EDAX analyses the nitrogen in nitrates, the carbon in carbonates, and the chlorine in chlorides, but all these salts are water soluble, and you could easily flush them away by washing the surface. You can check out our Bulletin 1 for help in securing and sending samples to achieve the best results. It's also best to avoid handling the fracture as even fingermarks will yield a good level of chloride in the analysis. If you have to cut off the part that has

Transgranular SCC in brass

fractured, be sure to avoid overheating it excessively. The more information you can provide about the environment and the service conditions the better. Occasionally, such as the case of the lagging causing accumulation of chloride at the bottom of a tank, we might ask if there is more supporting material from site. But most assignments are quite straightforward.

So what do we look for? Well, visually SCC is quite distinct, and we'll look at geometry, pitting, surface corrosion, and take wipe tests for analysis from the surface. Cross sections can be etched in different ways to reveal individual features., for example a saturated aqueous solution of picric acid (known in the trade as ASAPA for short) is perfect to reveal prior austenite grain boundaries. We may carry out EDAX analysis of the material in a crack if we think it could help with the interpretation. And there are usually additional cracks and branches in those cracks that become too fine to resolve in a light microscope even at x1000. The separation of the cracks will provide clues about the original residual stress in the component too. This information together with the analysis of the base metal.

Some SCC cracks are incredibly branched, while others are hardly branched at all, so visual appearances can be deceptive and require the experience and skills of a trained forensic metallurgist. Two members of our staff worked for many years at NEI International Combustion, and boilers, turbines and the ancillary plant associated with these brought a wealth of problems peculiar to certain industries, because most petrochemical and pharmaceutical sites have a boiler. There are probably very few people around with such an excellent grounding in failure mechanisms. One such customer manufactured nitric acid. Having now read about the problems of ferritic steel and nitrates, you can probably imagine the difficulty of segregating nitric acid in vast volumes from a power station next door fabricated principally from ferritic steel.

Even with the best practices the occasional contamination was inevitable, and it only takes a few parts per million of nitrate to cause SCC in boilers due to the high stress, pressure and volumes involved. And because of other considerations, adding nitrites or chlorides was not possible either.

The question of whether a crack should branch or not branch is an interesting one, and it's strongly related to the crack tip intensity factor known as $K1_{C\ SCC}$. There are three stages of crack development, and each one is dictated by the K1 value at that time. When $K1_{C\ SCC}$ values are low then SCC will not even begin. But once conditions favour SCC and the K1 value rises, cracking initiates. At high K1 values cracks tend to be transgranular, while at lower values the crack wants to become more intergranular. Because K1 is a function of the stress, cracks can change from one mode to another as they progress and stress at the crack tip alters. This also explains why low cycle stress applications can trigger the onset of SCC in materials if the other conditions (temperature, corrosive medium, susceptibility eg pitting) are already present. Those peak stresses increase K1, tipping the balance and initiating the SCC embryo.

In the second stage of SCC, K1 values remain high but within the body of the metal the rigidity is maintained by the bulk of metal either side of the crack. Planes of atoms are now 'unzipped' by the influence of the corroding medium. SCC can accelerate in this stage depending on the corroding medium and its concentration.

SOME OF THE RECOGNISED SCC SYSTEMS

Ferritic steel	OH, NO_3, CN, NH_4, H_2O, CO/CO_2, HCO_3, molybdates, propionates, phosphates, polythoinic acids, SO_4, H_2S, acetates
Austenitic steel	Cl, OH, H_2O, SO_4/Cl, H_2O/Pb contamination, SO_4, saturated steam, polythionic acids, Liquid sodium
High strength steel	H_2, H_2O, CN, HCl, HBr, H_2S, HCl gas, H_2+O_2, HN_3, SO_4, $NH_3/O_2/CO_2$
Copper base alloy	NH_4, citrate, tartrate, $FeCl_3$, H_2O,SO_2, Moist NO_x, moist NH_3 vapour
Aluminium alloy	Cl, Br, I, H_2O, organic solutions, moist H_2
Titanium base	Cl, HNO_3, fused salts, H_2O, methanol, Chlorinated hydrocarbons, Br, H_2
Nickel base	H_2O, OH, polythionic acids, HF acid vapour

In the third and last stage of SCC the cracks progress irrespective of the K1 value, and in this stage some metal structures favour the unzipping action of the corrosion mechanism. These metals tend to produce widely branching cracks, sometimes quite spectacular in their appearance. However, the absence of any branching should never rule out the possibility of SCC in a fractured component.

Possibly then, the lesson is to design around the material's K1 value. Keep peak stresses low, and know your alloy and its Achilles heel in terms of the susceptible fluids it doesn't like. Choose the cleanest metals you can, and avoid creating surface stresses in terms of machining marks, notches and exposed weld oxides where crevices can form. If you have a choice, expose the original surfaces, not cross sections. And try and design out fluid concentrators like non-draining pockets, gaps, leaching areas for lagging, and so on.

Hopefully, this information will help prevent problems in future, or might even alert you to an imminent disaster. Remember, we are here on call to respond to any questions or problems you may have. And we're well known for delivering advice that is simple to understand and easy to apply. Why not check out our other bulletins, or browse our extensive library of failures on www.scientifics.co.uk

REFERENCES
http://www.iom3.org/news/flixborough-disaster-uk-chemical-plant-explosion-and-bse-crisis
http://www.acetake.com/Documents/Al-Si-Alloys.pdf