Corrosion of Stainless Steel

Types of Corrosion, Alloying Elements and Environmental Conditions

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With regard to corrosion, stainless steel is a very smart group of metals. The excellent corrosion resistance combined with a (still!) affordable price has made stainless steel the most frequently used group of metals within critical sectors such as the food and pharmaceutical industries as well as the chemical industry.

The excellent corrosion resistance of stainless steel is caused by a very thin layer of oxides in particular chromium and iron oxides, and despite a thickness of only a few nanometres, this oxide layer is so strong that it effectively isolates the steel from the environment. Should the oxide layer suffer from a breakdown, it is quickly regenerated, and the corrosion protection is re-established.

Unfortunately, this ideal scenario does not always take place; the oxide layer may be damaged without repassivating, and the sad result may be serious corrosion. Once the corrosion has started, rapid penetration may occur causing the stainless steel to be a very short-lived construction material. The difference in between the two extremes is sometimes very small: If repassivation takes place, corrosion is prevented and, theoretically, the steel may last forever. If not, severe corrosion may take place, and the life-span of the equipment may be very, very short. The types of corrosion occurring on stainless steel are as follows:

General Corrosion

Also named acid corrosion (abtragenden Korrosion, generel korrosion), general corrosion is a type of corrosion frequently occurring in very strong acids; however, corrosion may occur in strong alkalines as well. Unlike any other type of corrosion, general corrosion is recognized by the fact that the whole surface suffers from corrosion. The corrosion is almost uniform and expressed as a number of grams per square meter, the loss of material may be very high whereas penetration is rather slow.

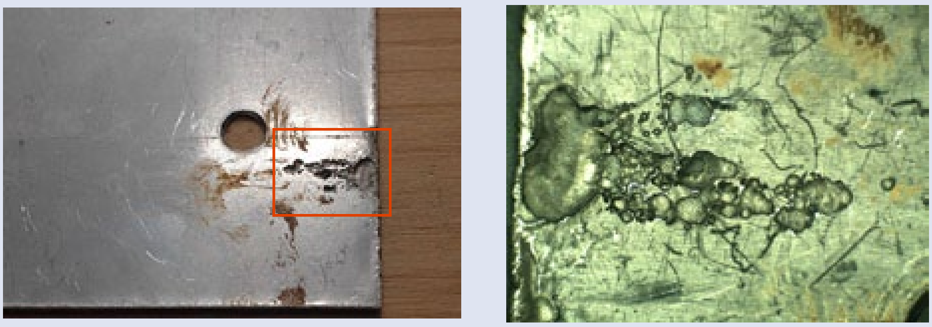
4301 stainless steel bolt suffering from severe general corrosion after having spent a number of months in a nitric acid-hydrofluoric acid pickle bath. Please note that the loss of metal is quite uniform and quite large, while no penetration has occurred yet.

As mentioned above, general corrosion takes place at extreme pH values, i.e. in very strong acids or, less common, in strong alkalines. Typical media are sulphuric acid, phosphoric acid and so on, and apart from the type of media and the strength, corrosion velocity is highly dependant upon the temperature and the presence of impurities, in particular chloride. As a rule, the corrosion increases with increasing temperature and increasing chloride concentration.

The most useful elements in the steel are nickel and molybdenum. In general, low-alloyed ferritic and, in particular, martensitic steels should not be used in strong acids and alkalines.

Pitting and Crevice Corrosion

Pitting corrosion (Lochfraß-Korrosion, punktfrätning, grubetæring) is a type of corrosion caused by a local break-down of the protective oxide layer. Unlike the ideal situation, repassivation does not occur, and severe corrosion will take place. Pitting corrosion is the perfect example of the edge-like nature of stainless steel. Either repassivation occurs and the steel lasts forever, or corrosion takes place, and penetration may occur rapidly.



Stainless steel (4301) specimen after a few days of exposure in a saltwater (NaCl) solution doped with hydrogen peroxide (H2O2). While 99 % of the steel remains unharmed, some of the pits (the arrows) have caused penetration. The microscopic photo to the right shows a magnification of the framed section.

Crevice corrosion (CC, Spaltkorrosion, spaltekorrosion) reminds a lot about pitting corrosion; how-ever, CC takes place in crevices, pores and narrow geometries where there is a poor exchange of media – or none at all. Such places, all transport is controlled entirely by diffusion, and compared to the ”free surfaces”, the risk of corrosion in crevices is always higher than the risk of pitting corrosion.

An old “rule of the thumb states” says that the risk of CC is substantial at a temperature 20-25 ºC below that of pitting corrosion (i.e. the critical pitting temperature, CPT). If the steel is close to its corrosion limit, the equipment should be designed so that no crevices are present. If this is not possible, a more corrosion resistant steel must be chosen.

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The risk of pitting corrosion as well as crevice corrosion increases with

- Increasing chloride content,
- Increasing temperature,
- The presence of oxidants and
- Low pH (acid conditions)

With regard to the alloying elements, an increased content of Cr, Mo and N all benefit the corrosion resistance, while the effect of Ni is comparatively small. Non-metallic impurities, such as S and P, tend to lower the corrosion resistance severely.

Based upon hundreds of practical experiments, the resistance of a stainless steel against pitting corrosion can be expressed as a Pitting Resistance Equivalent (PREN):

PREN = % Cr + 3.3 x % Mo + 16 x % N

By experience, two steel types with the same PREN will perform approximately equally well against pitting corrosion. Please note that, in theory, it doesn't matter if we increase the PREN by adding 1 % Mo or 3.3 % Cr. The important thing is the PREN increase.

Normally, conditions are worst when the steel is immersed completely into the water, whereas the problems above the water line usually limit themselves to superficial pitting corrosion. From a cosmetic point of view, such attacks may be very annoying, in particular in the case of very expensive equipment (such as a Danish opera house!). However, it rarely leads to equipment failure.

Stress Corrosion Cracking

Stress corrosion cracking (SCC, Spannungsrißkorrosion, spændingskorrosion) is a type of corrosion giving rise to cracks. SCC is the most severe type of corrosion, and penetration may occur as a matter of days rather than months or years, even in thick steel plates. The name itself indicates that the corrosion takes place in regions of the steel, where tensile stress is present. Such tensile stress is common and may occur as a result of any kind of mechanical process including welding and grinding.

The risk of SCC increases with

- Increasing chloride content,
- Increasing temperature,
- Low pH (acid conditions), and
- Evaporation

In particular the temperature is important, and SCC is more dependent upon the temperature than any other type of corrosion.

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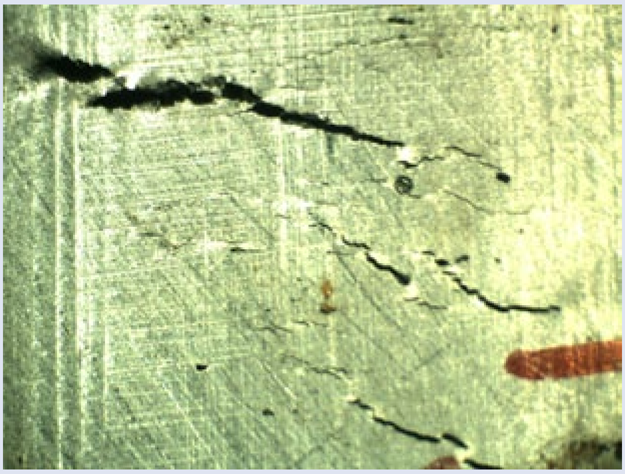 

Left: SCC cracks in a milk tank (4301). The longest crack is about 15 mm long, and the corrosion has been caused by high-temperature disinfection.

Right: Micro section of SCC cracks through a distillation unit. Sheet and pipe section are both made of 4301, the temperature has been 60-70 ºC, and the conditions have severely worsened because of the “pocket” in the center, thus being able to trap chloride containing water. After a while, some of the water has evaporated, and the chloride concentration will increase.

SCC is a type of corrosion which almost selectively attacks the lowest grades of austenitic steels, such as the 4301 group, and normally, 4301 will be in danger at temperatures above 60-70 ºC. In practice, though, 4301 may suffer from SCC at even lower temperatures, even at room temperature. Due to its content of Mo and Ni, the 4401 group is somewhat more resistant, and the temperature limit is usually around 100-110 ºC. However, even this limit cannot be regarded as being ”safe”. SCC in 4401 steel at 30-40 ºC has been observed.

Ferritic and duplex steels are significantly less sensitive to SCC than the austenitic steels. Consequently, if SCC is the critical type of corrosion, it is no bad idea to replace the pipes and sheets of 4301 or 4404 by 4509 or 4521, respectively.

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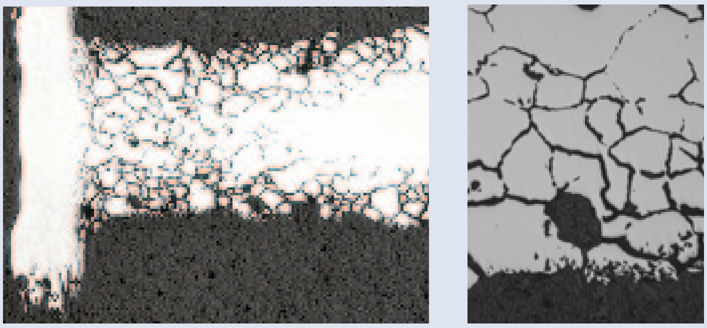
Intergranular Corrosion

Intergranular corrosion (IG, interkristalline Korrosion, interkrystallinsk korrosion) is a type of corrosion which is caused by the formation of chromium carbides in the grain boundaries of the steel. Heating the steel to a temperature in the range of 500-850 ºC, carbon is binding the useful chromium causing a weakening of the zones adjacent to the grain boundaries. In popular, this corresponds to dissolving the cement in between the bricks of a house.



Micro section showing a nice example of intergranular corrosion in a bolt made of 4307.The cause of the sensitization is not the C from the steel itself, but rather the use of oil. A subsequent heating process has released the carbon, which in turn has diffused into the steel. Thereafter, the Cr has been bound as carbides, and a subsequent pickling process caused the sensitiza-tion to turn into IG.

The risk of IG increases rapidly with the carbon content of the steel, and this risk is the main reason why one should always chose low-carbon steel (i.e. 1.4306, 4307, 4404 or 4435) or titanium stabilized types (4541, 4571), as compared to normal types (4301, 4401). The thicker the steel (= increased heating time), the more important it is to use low-carbon steel. Due to the increased effort of the steel works in order to remove the carbon, IG is a rare bird these days.

Time

For all types of corrosion, time is a very important factor, and generally, long-time exposure to a corrosive media is always worse than a short-term dip. Frequently, one can get away with exposing the steel to a much too corrosive environment provided that the contact time is very short, a fact which is utilized in i.e. the dairy business where disinfectants are frequently too corrosive to the common 4301 steel. As long as the cleaning is done in a matter of minutes, it works. On the other hand, remaining pools of disinfectant may cause severe corrosion.

This effect is even more obvious when considering the conditions above water. There, the environment is governed by splashes of water and salts, and provided that the construction is made in such a way that the water is drained off quickly, the stainless steel may last forever. If salt-containing pools or drops are allowed, the risk of corrosion may include cosmetically superficial pitting corrosion to SCC at elevated temperature.

All corrosion data above are based on long-term exposure. If the exposure time can be kept short, the steel may last much better than predicted by the books.