Atlas Tech Note No. 2
Pitting & Crevice Corrosion of Stainless Steels

Stainless Steels are a family of alloys exhibiting good resistance to attack by many of the environments encountered in industry and in domestic, commercial and marine exposure. Their resistance is not perfect, however, and the large number of grades of stainless steel now available is largely because of this challenge of finding cost-effective resistance to these various environments.

The resistance of stainless steels to some environments can be described by corrosion resistance tables, as the corrosion which does occur is a fairly uniform metal thinning over time. This is termed “General Corrosion” and most commonly occurs in strongly acidic conditions. “Localised Corrosion” by contrast results in attack at certain specific sites while other parts of the metal may remain totally unaffected.

This Atlas Tech Note describes two closely related forms of localised corrosion of stainless steels, **Pitting Corrosion** and **Crevice Corrosion**.

Studies of corrosion failures of stainless steel have indicated that pitting and crevice corrosion are major problems, and together account for perhaps 25% of all corrosion failures.

What is Pitting Corrosion?
Under certain specific conditions, particularly involving chlorides (such as sodium chloride in sea water) and exacerbated by elevated temperatures, small pits can form in the surface of the steel.

Dependent upon both the environment and the steel itself these small pits may continue to grow, and if they do can lead to perforation, while the majority of the steel surface may still be totally unaffected.

A common corrosion form encountered particularly on stainless steel in coastal areas is “tea staining”. This appears to be a form of pitting corrosion although it rarely proceeds beyond initiation of multiple minute pits, so the result is largely superficial but unsightly staining of the surface.

What is Crevice Corrosion?
Crevice Corrosion can be thought of as a special case of pitting corrosion, but one where the initial "pit" is provided by an external feature; examples of these features are sharp re-entrant corners, overlapping metal surfaces, non-metallic gaskets or incomplete weld penetration.

To function as a corrosion site a crevice has to be of sufficient width to permit entry of the corrodent, but sufficiently narrow to ensure that the corrodent remains stagnant. Accordingly, crevice corrosion usually occurs in gaps a few micrometres wide, and is not found in grooves or slots in which circulation of the corrodent is possible.

Environmental Factors
The severity of the environment is very largely dependent upon two factors - the chloride (Cl-) content and the temperature – and the resistance of a particular steel to pitting and crevice corrosion is usually described in terms of what % Cl- (or ppm Cl-) and °C it can resist. It should be noted that the most common grade of stainless steel, 304, may be considered susceptible to pitting corrosion in seawater (2% or 20,000 ppm = 20,000mg/L chloride) above about 10°C, and even in low chloride content water may be susceptible at only slightly elevated temperatures. A safe chloride level for warm ambient temperatures is generally about 200mg/L, reducing to about

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150mg/L at 60°C. Grade 316 is more resistant and is commonly used near ambient sea water, but its resistance is marginal, so it can be attacked in crevices or if the temperature increases even slightly. The safe chloride level for 316 is about 1000mg/L at ambient, reducing to around 300mg/L at 60°C.

The velocity of the liquid is also significant; a stagnant solution is more likely to result in pitting and crevice attack, particularly if there are particles to settle out of the liquid. Liquids that pool and can then evaporate over time result in the chlorides becoming more concentrated in the liquid residue, and hence more highly corrosive. This is a particular problem in intermittently used piping or tanks and has caused serious pitting problems when hydrostatic test water containing quite low chlorides has been left to pool in piping and tanks.

Note that there may also be a problem from stress corrosion cracking if austenitic stainless steels are used in chloride containing water at temperatures over about 60°C.

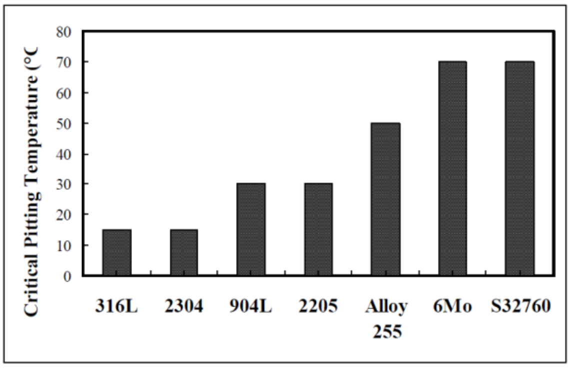
Which Steels are Susceptible?

All stainless steels can be considered susceptible, but their resistances vary widely. Their resistance to attack is largely a measure of their content of chromium, molybdenum and nitrogen. Another factor of importance is the presence of certain metallurgical phases (in particular the grades 303, 416 and 430F containing many and large inclusions of manganese sulphide have very low resistances). A clean and smooth surface finish improves the resistance to attack. Contamination by mild steel or other "free iron" greatly accelerates attack initiation.

Measurement of Resistance to Attack

Laboratory tests have been developed to measure the resistance of metals to both pitting and crevice corrosion.

This testing has two main aims – firstly to enable ranking of each alloy in order of resistance, and secondly as a quality control measure, to ensure that particular batches of steel have been produced not just with correct composition, but also have been properly rolled and heat treated.



A commonly used test is that in ASTM G48, which measures resistance to a solution of 6%ferric chloride, at a temperature appropriate for the alloy, shown in the graph above. If an artificial crevice is added to the sample the test measures crevice corrosion resistance rather than pitting resistance. The temperature which is just high enough to cause failure of this test is termed the Critical Pitting Temperature (CPT) or the Critical Crevice Temperature (CCT).

Alternative laboratory tests can be carried out using electrochemical cells with a variety of test solutions. The results obtained in laboratory tests are approximate only, as factors such as surface finish, water velocity, water contaminants and metallurgical condition of the steel are all important.

Pitting Resistance Equivalent Number (PRE)

From experience it has been found that an estimate of resistance to pitting can be made by calculation from the steel's composition as the Pitting Resistance Equivalent Number (PRE or PREN):

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

Various multipliers (up to 30) for Nitrogen have been used in this equation; with the higher values often used for the austenitic stainless steel grades; in any case the effect of nitrogen is very important. Hence the emergence of the more highly resistant 2205 grade S32205 with a minimum nitrogen content of 0.14%, plus, higher minimum contents of chromium and molybdenum compared to the original S31803 variant. This also explains the trend in extremely high pitting resistant alloys for even higher nitrogen levels. The super duplex grade 2507 (UNS S32750) typically contains 0.26% nitrogen, while the super austenitic grade 4565S (UNS S34565) typically contains 0.45% nitrogen.

Typical PRE for Common Grades

Grade	%Cr	%Mo	%N	PRE
3CR12	11			11
430	17	0		17
304	18			18
2304	23	0.3		24
444	18	1.8		24
316	17	2.2		24
904L	20	4.2		34
2205	22	3	0.15	34
2507	25	4	0.26	42
6Mo	20	6.1	0.20	43

NACE specificationMR0175 recognises the positive effect on pitting corrosion resistance of the element tungsten, and adds a factor at half the rate of molybdenum. The PRE formula is therefore:

PRE = %Cr + 3.3 x (%Mo + 0.5 x %W) + 16 x %N

It must be kept in mind that the PRE calculation is only a convenient way to compare grades; it is an approximation and should not be used to differentiate between grades that have close PRE values.

Effect of Welding

The welding process results in metallurgical changes in both fusion zone and heat affected zone. In most alloy systems some degradation in pitting and crevice corrosion resistance occurs in welding, but these effects can be minimised if proper materials and practices are used. Proper materials are often over-alloyed consumables and proper practices include appropriate heat inputs. It is important that correct information be sought from suppliers.

Measures to Reduce Pitting and Crevice Corrosion

1. Control the environment to low chloride content and low temperature if possible. Fully understand the environment.
2. Use alloys sufficiently high in chromium, molybdenum and/or nitrogen to ensure resistance.
3. Prepare surfaces to best possible finish. Mirror-finish resists pitting best.
4. Remove all contaminants, especially free-iron, by passivation or by pickling (refer Atlas Tech Note No. 5).
5. Design and fabricate to avoid crevices.
6. Design, fabricate, commission and operate to avoid trapped and pooled liquids.
7. Weld with correct consumables and practices and inspect to check for inadvertent crevices.
8. Pickle to remove all weld scale (refer Atlas Tech Note No. 5).

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References & Further Information

1. Atlas Steels website has information covering many of the grades and products mentioned in this Tech Note.
2. ASSDA Technical Bulletin, "Preventing coastal corrosion (tea staining)".
3. Gümpel, P. and Ladwein, T., "High Strength Austenitic Stainless Steels for Use in Marine Environments". Eighth International Conference on Offshore Mechanics and Arctic Engineering. The Hague, March 1989.
4. Sedriks, A.J., "Corrosion of Stainless Steels", John Wiley & Sons, New York, 1996.
5. Turnbull, B.W., "A Guide to the Corrosion Resistance of Stainless Steel and Nickel Based Alloys", Australian Defence Industries, 1991.
6. Watts, M.R., "Material Development to Meet Today's Demands", Inspection, Repair and Maintenance Conference, Aberdeen, November 1988.
7. NACE MR0175 / ISO 15156-3 "Materials for use in H2S-containing environments in oil and gas production – Part 3 – Cracking-resistant corrosion resistant alloys and other alloys".