

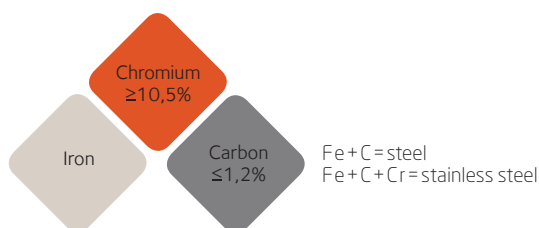
Stainless Steel and Corrosion

What is corrosion?

Metals, with the exception of the precious metals such as gold and platinum, that are found in their natural state are always extracted from ores; metals have therefore a tendency to revert to their stable state, which corresponds to their original state, that is to say their oxide form. Metal corrosion is essentially an electro-chemical reaction at the interface between metal and surrounding environment.

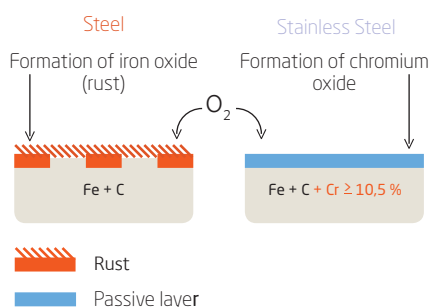
Stainless Steel and the passive layer

Steel is an alloy of iron and carbon. Contrary to carbon steel, the presence of a minimum of **10.5 %** chromium in the stainless steel gives it the property of corrosion resistance.



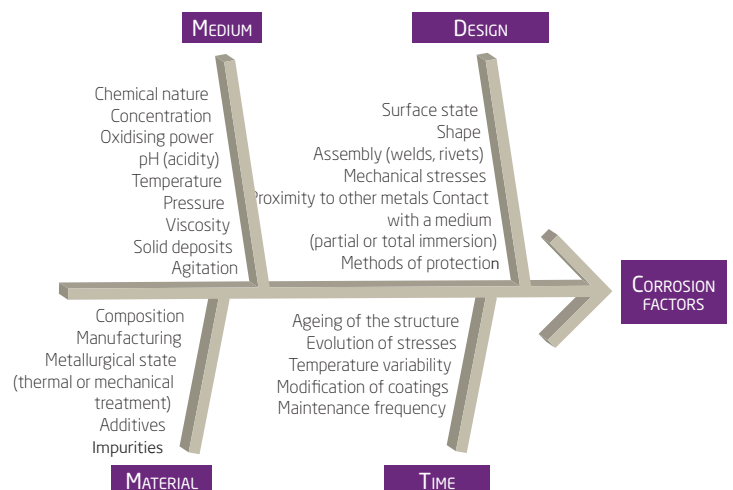
Indeed, on contact with oxygen, a chromium oxide layer is formed on the surface of the material. This passive layer protects it and has the particular ability to self repair.

Reaction of steel and stainless steel in contact with moisture in the air or water.

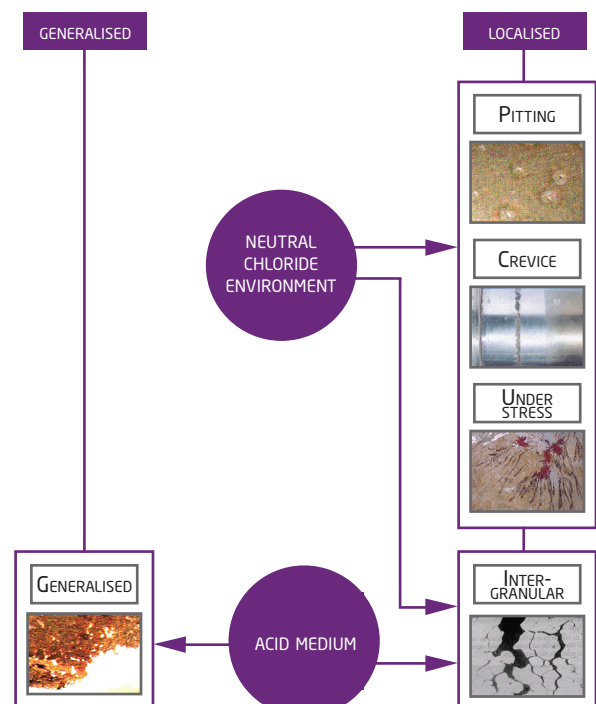


However if this protective layer is damaged, the start of corrosion can appear

What are the major factors of corrosion?



What are the 5 principal types of corrosion linked with the surrounding environment ?

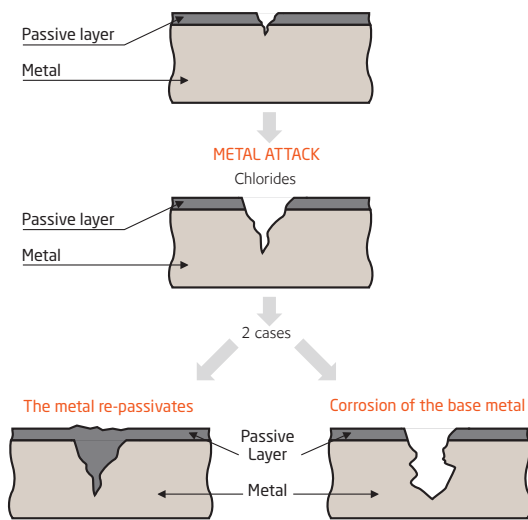


Generalised corrosion is noticed when stainless steel is in contact with an acid medium and localised corrosion is seen in the majority of cases when stainless steel is placed in a neutral chloride environment

Pitting Corrosion

To understand the phenomenon

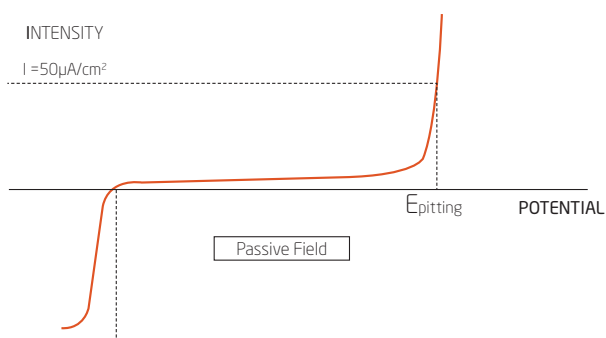
Pitting corrosion is a local break in the passive layer of the stainless steel provoked by an electrolyte rich in chloride and or sulphides. At the site of the pitting, where the metal is unprotected, corrosion will develop if the pit does not re-passivate, in other words if the speed of metal dissolution enables to maintain a sufficiently aggressive environment to prevent its re-passivation.



This dissolution gives rise to metal ions and electrons and thus the passage of current (of dissolution) which gives rise to an electrical potential difference between the anodic zone (pitting) and the cathodic zone (the rest of the metal).

To simulate this type of corrosion under laboratory circumstances, a sample is immersed in a corrosive electrolyte to which an increasing potential is applied until the passive layer is broken.

During this dynamic potential (intensity/potential) scan the sudden increase in intensity corresponds to the pitting potential $E_{pitting}$



The pitting potential corresponds to the potential necessary to initiate stable pits.

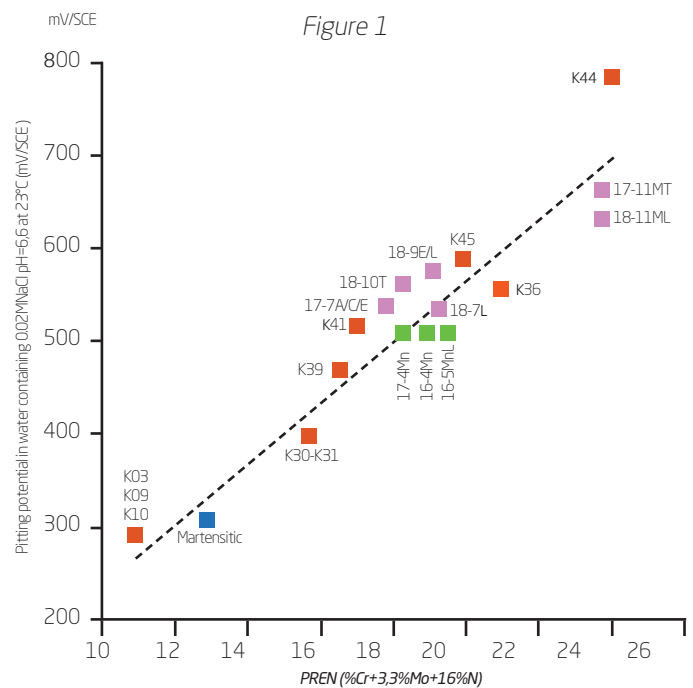
> If the potential of the stainless steel in the given medium is inferior to the pitting potential => pitting does not start

In the document which follows we describe the 5 principal types of corrosion and we rank the majority of Stainless Europe grades from standard laboratory tests. However, the phenomena of corrosion in real life are always specific, the data described does not exclude extra trials to choose the optimal material.

> If the potential of the stainless steel in the given medium is superior to the pitting potential => the stainless steel corrodes. Note: the higher the pitting potential, better shall be the corrosion resistance of the grade. Outside the pits, the passive layer is always present to protect the stainless steel.

Figure 1 shows pitting potentials obtained for different stainless steels in water containing 0.02M NaCl (710mg/l Cl) at 23°C.

It shows the influence on the resistance to pitting corrosion with the content of chromium and molybdenum for the ferritics, and chromium, molybdenum and nitrogen content for the austenitics.



Commercial Designations	Standards	
	ASTM	EN
	Designation: Type	
Martensitic	420	1.4021
K09+	409	1.4512
K03		1.4003
K10	410S	1.4000
K30-K31	430	1.4016 - 1.4017
K39	439	1.4510
K41	441	1.4509
K36	436	1.4526
K45	445	1.4621
K44	444	1.4521
16-4Mn	201.2	1.4372
16-5Mn	201LN	1.4371
17-4Mn	201.1	1.4618
17-7A/C/E	301	1.4310
18-7L	301LN	1.4318
18-9L	304L	1.4307
18-11 ML	316 - 316 L	1.4401 - 1.4404
17-11MT	316Ti	1.4571

As figures 2 and 3 show, this pitting potential can only be used to rank the grades in a given medium. It diminishes notably when the temperature (figure 2) or the concentration of chlorides in the medium increases. (figure 3)

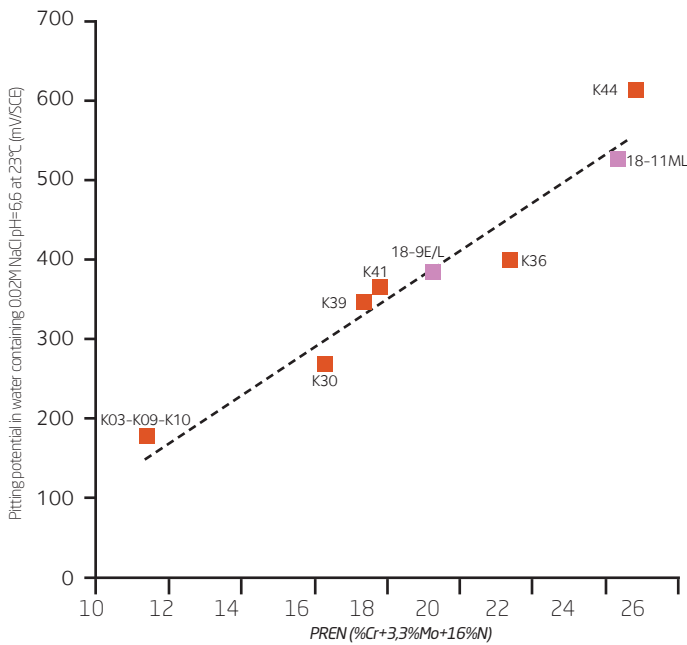


Figure 2

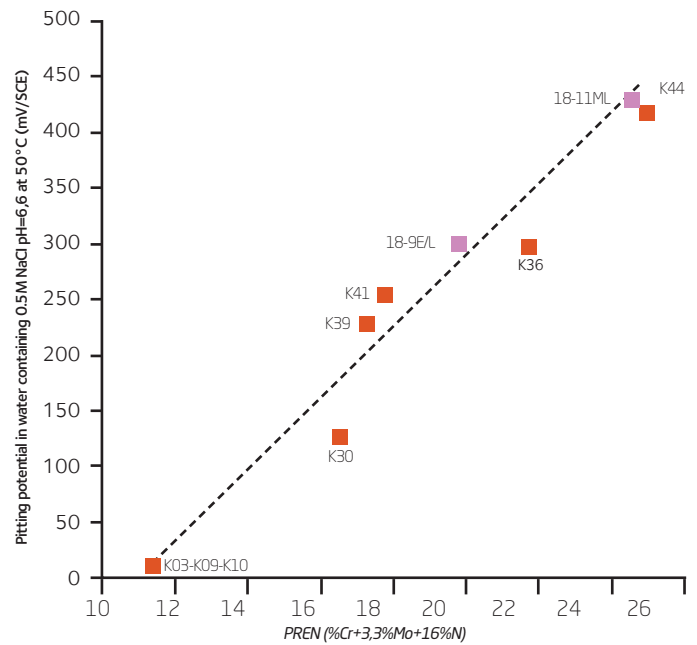


Figure 3

In order to map the duplex range, tests in the most severe medium, 0.5M NaCl (17.75g/l Cl⁻) at 50°C, were carried out. The results obtained are shown below.

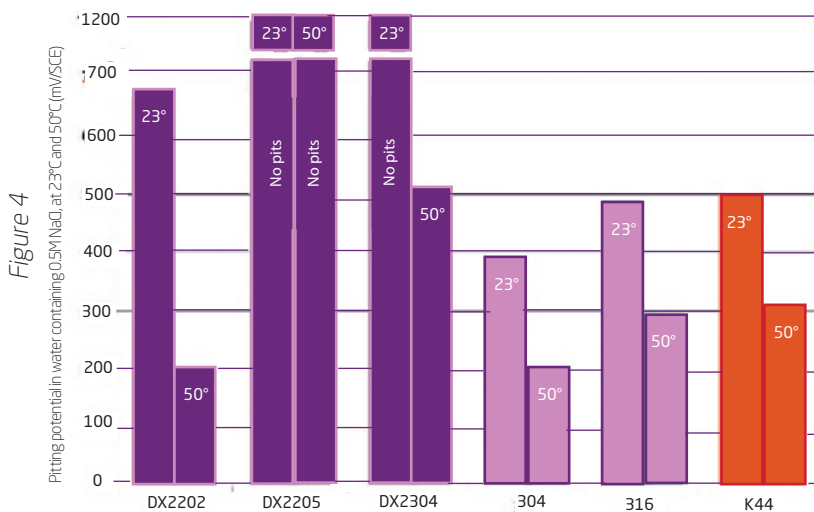


Figure 4

Commercial Grades	Standards		
	ASTM		EN
	Type	UNS	
DX2202	2202	UNS 32202	1.4062
DX2304	2304	UNS 32304	1.4362
DX2205	2205	UNS 32205	1.4462

Usually we use the PREN (Pitting Resistance Equivalent Number) of the grades to rank their general pitting behaviour. The PREN, %Cr+3.3%Mo+16%N, demonstrates the major influence of these alloy elements.

Our recommendation

To avoid pitting corrosion:

- > We would look to see if it is possible to lower the corrosiveness by lowering the temperature of the medium, limiting contact time, avoiding stagnant areas and reducing the concentration of halogens and the presence of oxidants.
- > We would choose a grade high in chromium or containing molybdenum.

Crevice Corrosion

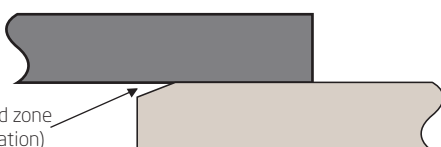
To understand the phenomenon

A/Initiation of corrosion

In an electrolyte high in chloride, a confined (occluded) zone linked for example to bad design, favours the accumulation of chloride ions. The progressive acidification of the medium in this zone facilitates the de-stabilisation of the passive layer. When the pH in this zone reaches a critical value called « depassivation pH », corrosion starts. The depassivation pH or pH_d is used to characterize the resistance to crevice corrosion initiation.

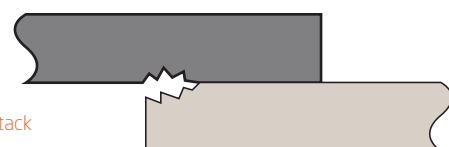
WHY?

Confined zone (acidification)



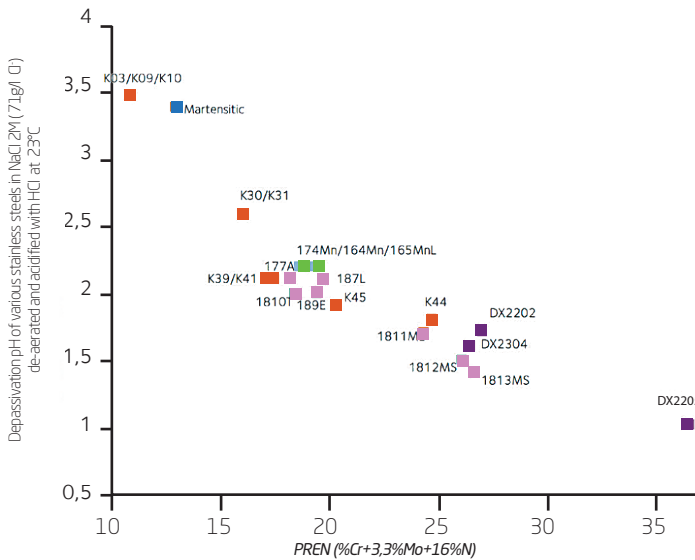
HOW?

Break in the passive layer and metal attack



Some pHd values for our stainless steels are given in figure 5. The lower the value pHd the better the resistance to crevice corrosion.

Figure 5: Depassivation pH of various stainless steels in NaCl 2M (71g/l Cl⁻) de-aerated and acidified with HCl at 23°C



B/ Propagation of corrosion

Once corrosion is initiated, its propagation occurs by active dissolution of the material in the crevice. In the laboratory, we simulate this type of corrosion by recording the potentiodynamic scans in chloride mediums of increasing acidity.

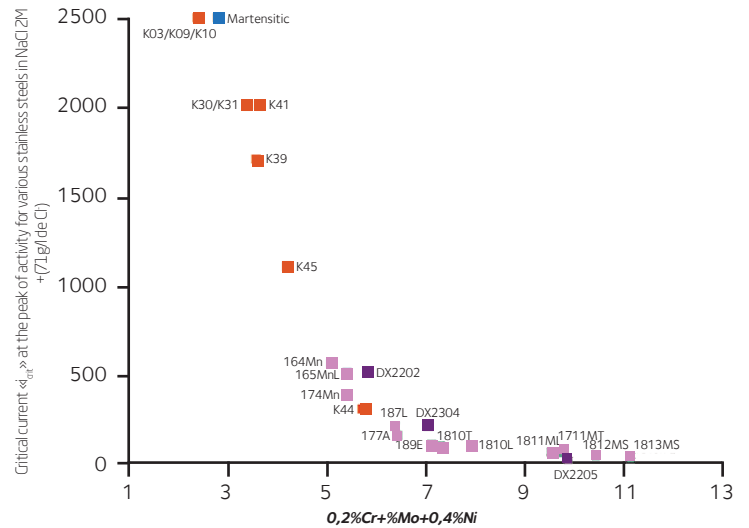
If on a recording we detect a current peak (activity), crevice corrosion is starting, in the opposite case repassivation takes place.

Activity peak measurement for a pH lower to the depassivation pH can then be considered to quantitatively compare the speed of crevice corrosion propagation for different grades.

This value is sensitive to the alloy elements which improve the passivity and limit active dissolution, principally molybdenum, nickel and chromium (see figure 6).

The speed of propagation is also a function of local aggressiveness and temperature of the medium.

Figure 6: Critical current i_{crit} at the peak of activity for various stainless steels in NaCl 2M (71g/l de Cl⁻) deaerated and acidified with HCl at 23°C.



Our recommendation

Our first recommendation to avoid crevice corrosion is to optimise the design of the piece to avoid all artificial crevices. An artificial crevice can be created by a badly made joint, a rough or bad weld, deposits, gaps between two plates etc.,

If the confined zone is unavoidable, it is preferable to enlarge this zone and not to make it smaller.

If the design of the pièce is not modifiable or if the fabrication process makes difficult to avoid confined zones, the risk of crevice corrosion is very high. We recommend, in this case, choosing an appropriate grade, in particular a stainless steel austenitic or duplex when the product will be in contact with corrosive media or part of the process equipment.

If ferritics with 20% chromium limit the risk of crevice corrosion initiation, they do not, with the exception of K44 containing 2% molybdenum, curb its propagation unlike austenitic or duplex more highly nickel and / or molybdenum alloyed.

Intergranular Corrosion

To understand the phenomenon

At temperatures greater than 1035°C, the carbon is in solid solution in the matrix of the austenitic stainless steels. However, when these materials are cooled slowly from these temperatures or even heated between 425 and 815 °C, chromium carbides precipitate at the grain boundaries. These carbides have a higher chromium content in comparison to the matrix.

Consequently, the zone directly adjacent to the grain boundaries is greatly impoverished.

The sensitisation state takes place in a lot of environments by privileged initiation and the rapid propagation of corrosion on the de-chromed sites.

For unstabilized ferritic stainless steels, the sensitisation temperature is greater than 900°C.

Our recommendation

In practice, this case of corrosion can be encountered in the welded zones. The solution for the austenitic consists of using a low carbon grade called « L » (Low C% < 0.03%) or a stabilized grade, and the titanium or niobium stabilized ferritic grades.

The volume of the piece permitting a thermal treatment of the quenching type (rapid cooling) at 1050/1100°C or a tempering of the welded piece can be done.

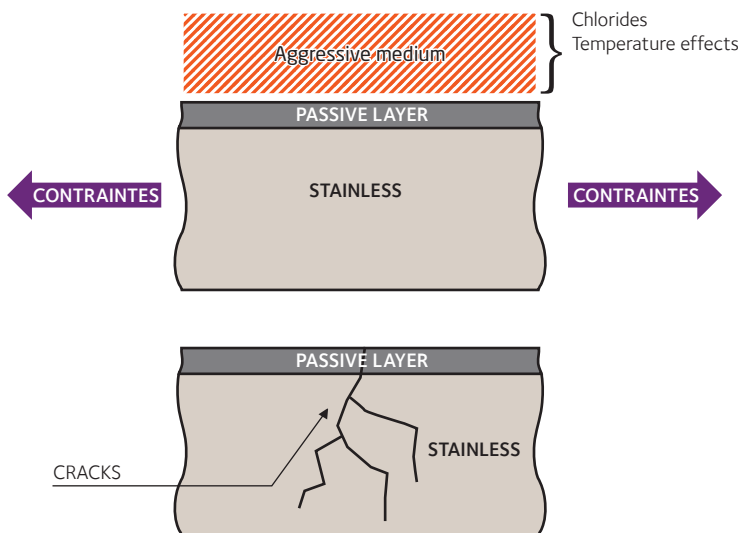
Stress Corrosion

To understand the phenomenon

We mean by « stress corrosion » the formation of cracks which start after a period of long incubation and which afterwards can propagate very rapidly and provoke downtime of the equipment by cracking.

This particularly dangerous phenomenon is the result of the combined effects of 3 parameters:

- temperature, since stress corrosion rarely develops under 50°C
- the applied or residual stresses
- the corrosiveness of the medium : presence of Cl^- , H_2S or caustic media NaOH



The metallurgical structure of stainless steels influences their behaviour in this type of configuration.

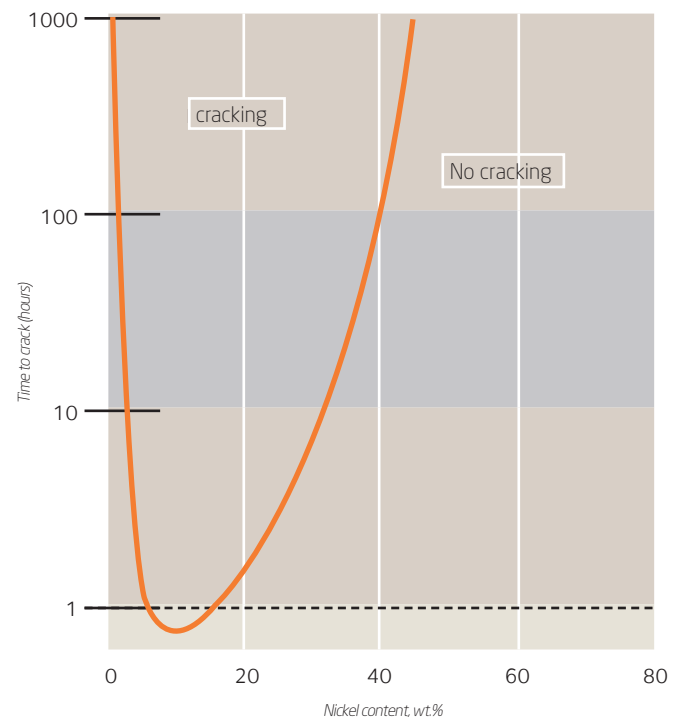
> Although stress corrosion of ferritics can be provoked by particularly aggressive tests in the laboratory, their body cubic centred structure rarely renders them subject to this type of phenomena in practice.

> The face cubic centred structure of austenitic stainless steels can present a risk.

In effect, it favours a mode of planar deformation which can generate very strong stress concentrations locally. As shows the graph below, this is particularly true for classic austenitic stainless steels with 8% nickel; an increase in nickel above 10% is beneficial.

> In austenitic stainless steels, the austenitic stainless steels with manganese perform worse.

> The austeno-ferritic structure of the duplex gives them an intermediate behaviour, very close to the ferritics in the chloride medium and even better in the H_2S medium.



Effect of nickel content on the resistance to stress corrosion of Stainless steel containing from 18-20% chromium in magnesium chloride at 154°C [From a study by Copson [ref]. Physical Metallurgy of Stress Corrosion Cracking, Interscience, New York, 247 (1959).]

Our recommendation

To avoid this type of corrosion:

- > Suppress the stresses or have a better redistribution, by optimising the design or by a stress relieving treatment after forming and welding of the pieces concerned.
- > lower the temperature if possible.
- > If not practicable, choose the grade most adapted, favouring as a solution a ferritic or duplex but bearing in mind the other corrosion problems encountered.

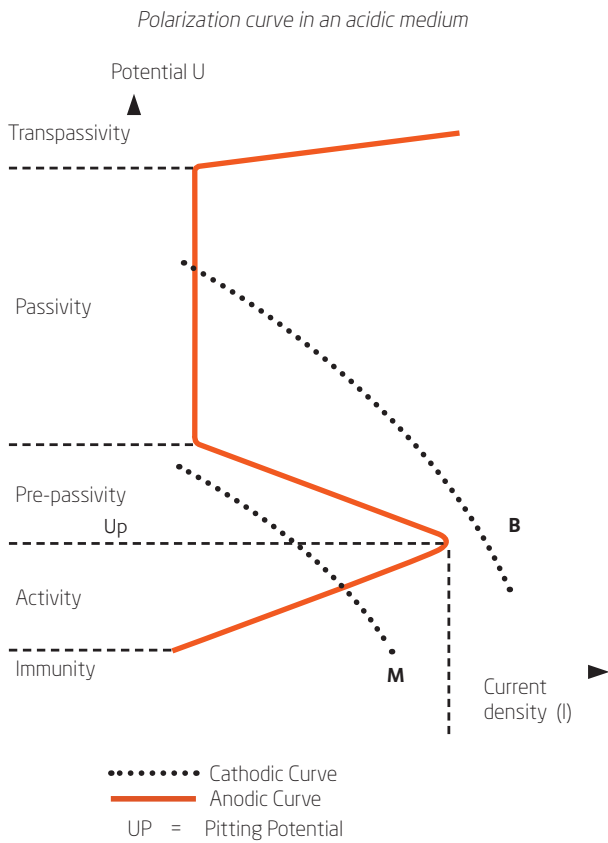
Uniform Corrosion

To understand the phenomenon

This is the dissolution of all the affected points on the surface of the material which are attacked by the corrosive medium. On the micrographic scale, this corresponds to a regular uniform loss of thickness or loss of weight (uniform or generalised corrosion as opposed to localised corrosion).

We see this corrosion in acid mediums. Indeed, below a critical pH value, the passive layer protecting the stainless steel is no longer stable and the material suffers a generalised active dissolution. The more acid the medium, the faster the corrosion and the loss of thickness of the stainless steel.

In the laboratory, we measure this speed of corrosion in an acid medium by graphing the polarisation curve (see below). An increasing potential scan is imposed on the metal and the corresponding intensity is recorded.



In a low oxidising medium, the cathodic curve (M) cuts the anodic curve below the pitting potential: metal remains intact.
 In a strong oxidising medium, the cathodic curve (B) cuts the anodic curve above the pitting potential: pits appear on the surface of metal.

The maximum current reading of the activity peak allows us to classify the resistance of different grades to this type of corrosion (see figure 7).

Generally, the higher the current, the faster and greater the dissolution, thus the less the grade will be resistant.

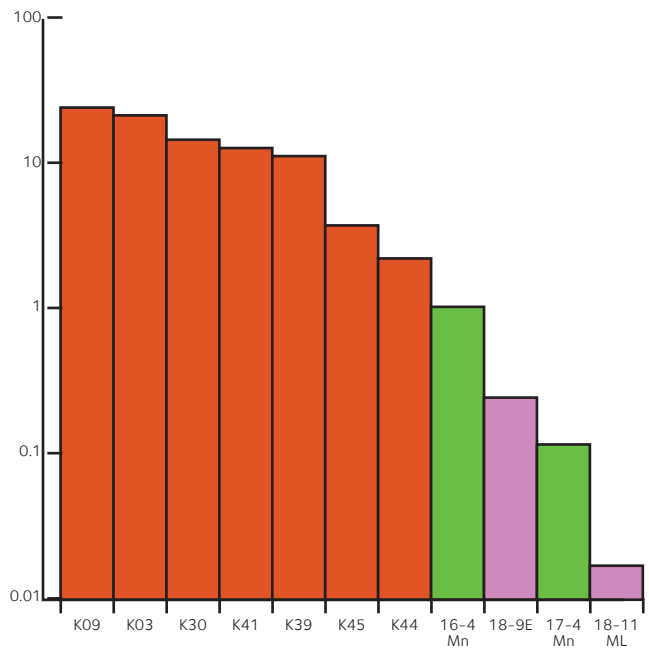


Figure 7: Critical current « i_{crit} » at the peak maximum in H_2SO_4 2M de-aerated at 23 °C



Our recommendation

To avoid this type of corrosion, choose the appropriate grade in regard to the acid medium used.

We note the favourable impact of chromium and molybdenum which reinforce the existing passive film but also the combined effect of noble alloys (nickel, molybdenum and copper) which slow down the dissolution of the material when the stability of its passive layer is broken.

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