PITTING CORROSION OF STAINLESS STEELS: THE IMPORTANCE OF BEING A METALLURGIST

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ABSTRACT

Pitting corrosion of passivable alloys has already formed the subject of a lot of works. The behaviour of industrial materials is known to mainly depend on some metallurgical features, among which the nature and distribution of the non metallic inclusions present in the steel. It is intended in this paper to illustrate this point in the case of stainless steels, recalling that both passive films and metallurgical properties have to be taken into account when analysing this corrosion risk.

INTRODUCTION

Pitting Corrosion mechanisms have already been discussed extensively in the corrosion literature (see e.g. ref. 1), and it is not intended in this talk to go further into their fundamental understanding, but rather to shed light on some points of practical importance. The examples will be restricted to stainless steels, in weakly acid chloride containing aqueous media whose pH is larger than the depassivation pH, so that the passive film remains stable excepting in the pit itself.

The role of the chloride ions in pitting initiation can be related to a local passive film destabilisation, together with a counteracting effect vis a vis the passive film healing. However, it should be noticed that the passive film breakdown and healing phenomena act on the microscopic scale (some nanometers), whereas the pits which are observed in the practical situations are at a macroscopic scale (some 10 micrometers). Between the microscopic and the macroscopic size scales, many phenomena can occur, such as pit growth, modifications of the local solution composition, dissolution of the non metallic inclusions present in the steel, which act generally at the scale of some µm. In the same way, electrochemical assessment of the pitting corrosion resistance generally involves the measurement of anodic currents of the order of some µA (or some 10 µA). Measuring 1 µA during 1 sec corresponds to a pit size of the order of some µm. This size scale will be referred to as the "mesoscopic scale". It should be pointed out that the pit repassivation can occur as well in these mesoscopic stages as in the microscopic one, so that the passive film breakdown theories are often unable to predict the actual behaviour of the alloy.

Fig.1 presents a semi-developped pit observed at the scale of 10µm on a 17%Cr stainless steel immersed in a NaCl containing solution. The pit consists in an undermining hollow, covered by a thin metallic cap, leading to the formation of an occluded zone. Some secondary pits are visible all around the main hole. The possible collapse of the metallic cap can suppress the occlusion and provoke the pit repassivation.
Fig. 1. Scanning electron microscopy X1000. Typical view of a semi developed pit at the end of the mesoscopic stage: A thin metallic film is still present and covers a part of the pit. Secondary pits are visible all around the main hole. The pit may either go on or repassivate if the thin "top" film breaks down.

The pitting resistance of industrial steels strongly depends on their metallurgical properties as well. It is obvious to say that the steel composition plays a major role, but the phenomena can be rather complex, depending on the pitting stage under consideration. The steel microstructure is a relevant factor as well, although scarcely taken into account by the current models. The unavoidable presence of some non metallic inclusions in industrial steels, and the properties of these inclusions (which may act as pitting sites) is often more determining for the pitting resistance than the addition of expensive alloying elements. Last, the metallurgical processing of the product (bars, wires, plates or sheets) can play a major role in some circumstances.

For stainless steels, the Chromium content is obviously one of the major parameters which controls the passive film properties and then the pitting resistance, at least for some given conditions of passive film formation. Other oxidisable elements, such as Silicon, which is present at the level of some tenth weight % in industrial AISI 430 or 304 type steels, can also enter the passive film and improve the pitting resistance.

The sulphur content is also determining for the pitting resistance, due to the formation of sulphides which may act as pitting sites (see after). The free machining steels, such as AISI 303 type austenitic steels contain 0.2% to 0.3% Sulphur, which forms some numerous and large size Manganese sulphides. These inclusions are known to dramatically improve the steel machinability, but also to decrease the pitting resistance. AISI 430 or 304 contain less than .03%S, which leads to less numerous and smaller sulphides. Among them, the grades used for long products (bars and wires) often contain typically .02%S in order to insure a sufficient machinability. At the opposite, the grades used for flat products (sheets and plates) generally contain less than 30 ppm S, which lead to an improved pitting resistance. The precise role of Mn sulphides in pits initiation has been extensively studied in the past (see e.g. ref.3,4,5) and will be detailed later. It is known that sulphide dissolution provides some harmful sulphur species, but that alloying elements such as Cu, Ni and also Mo may combine in the aqueous solution with these sulphur species, and then decrease their noxious effect.
The reasons of the beneficial effect of some alloying elements which do not enter the passive film in a large extent (Ni in 304 or 316 steels, Mo in 434 or 316 steels) is not so clear for industrial steels, despite the numerous hypotheses which have been proposed on the basis of academic works. They might (i) lower the ionic current throughout the metal/passive film interface, (ii) favour the pit repassivation by changing the solution composition in an initiated pit (for instance, by preventing a too large pH decrease inside the pit) or (iii) counteract the harmful effect of sulphur species as indicated above. The third mechanism fairly accounts for the Mo effects in 434 and 316 type stainless steels: accepting the idea that adsorbed sulphur plays a major role in pit initiation on such materials, Mo could act by favouring the desorption of sulphur, possibly in a combined state with Mo.

THE METALLURGICAL PROCESSING

The metallurgical processing of the steel (hot and cold rolling, heat treatments, welding, surface treatments...) may dramatically modify the pitting resistance of a steel grade as well. The effect of heat treatments on the phase equilibria, recrystallisation, minor elements segregation will not be discussed here, but some known or less known evidences must be recalled. First, the steel generally contains some non metallic phases such as precipitates (Cr carbides in ferritic steels for instance) or inclusions (oxides, sulphides, etc.). The difference between precipitates and inclusions is that the former are produced in the metal solid state and the latter during (or at the end of) the melting process, in the metal liquid state. Then, the inclusions do not generally produce any segregation at their interface with the metallic matrix, which is not the case of the precipitates (the chromium carbides for instance). However, non metallic inclusions can be unstable in the corrosive medium: that is the case for sulphides and even for oxides in some cases. Furthermore, since their ductility is generally not the same that the metallic matrix one, hot and cold rolling may produce some micro-decohesions at the metal-inclusion interface, which behave as micro-crevices and may be some preferential pitting sites, depending mainly on the cold rolling ratio. Anyway, it is now well established that, in industrial steels, inclusions may act as pitting sites. From another hand, chromium carbides may provoke some chromium depletion in the metal around the precipitate, either after a welding treatment or even after the metal cooling at the end of a hot transformation process. Even when these local negative segregation are too weak to produce intergranular corrosion, they may lead to a decrease in the pitting resistance. For this reason, the final annealing must be carefully controlled, mainly for ferritic steels (due to the low carbon solubility in b.c.c. structures).

Another point is the surface condition of the industrial product in the as delivered state. There are two main types surface finishing corresponding to different passive films. The most usual is the 2B finish state, where the metal is pickled, generally in a combination of acids, after the final annealing treatment. Bright annealing (BA) is another standard finish state, when the final annealing is performed in a hydrogen containing atmosphere, and no pickling in acids is needed before delivery. BA finishes are known to offer better resistance to localized corrosion than 2B ones (see fig. 2).

Other surface conditions should also be considered in some cases, due to final conditioning of steel parts. Typical finish is mechanical or chemical polishing, which drastically change the passive film properties. In case of mechanical polishing, the final film is formed from rinsing water or subsequent natural ageing. In case of chemical (or electrochemical) polishing, the chemical changes in surface composition (at the scale of nanometers) is not the one phenomenon to be taken into account. Modification in surface metallurgy (at the
scale of micrometers), such as dissolution of soluble inclusions for instance, should also been considered. Last, passivation treatments are often performed, for instance by immersing the steel in nitric or phosphoric acids. These treatments aim to maintain the surface in a high potential range favourable for passive film growth. For being efficient they should be carried on a long enough time and/or high enough temperature; short treatments, particularly at ambient temperature are not passivating but rather decontaminating, regarding for instance the ferrous pollution. They also dissolve soluble inclusions (such as manganese sulphides) which are located close to the steel surface, which improve the corrosion resistance but with no reference to any direct improvement of passive film properties.

![Graph of steel surface condition](image)

Fig.2: Effect of the surface condition: Number of metastable pits observed in the course of time during immersion in NaCl (1M) neutral solution of an AISI 304 cold rolled sheet in different delivery states. The as rolled state exhibits the larger number of transients and the BA state, the smaller. The pitting resistance is assumed to range in the same way: As rolled<2B<BA

Last, In service long term ageing (ageing in water containing atmospheres, or immersion in a non corrosive aqueous electrolytes) is also known to reinforce passivity (particularly after mechanical polishing which produces poorly protective passive layers in the initial stage). The kinetics of reinforcement (passive film growth and transformation hydroxide into oxide) is of the order of some days, weeks or months. Aged surface are known to offer better corrosion resistance than freshly produced ones. In service cleaning can also improve (or make poorer following the cleaning process) the passivation of the surface. Last, secondary processing plays also a major role in surface passivation: for example undesirable heating (due for instance to poor protection close to weldments, or to severe mechanical polishing) can locally form iron oxides instead of protective chromium oxides, which should be removed by appropriate pickling treatment.

**THE SULPHIDE INCLUSIONS**

The sulphide inclusions play a major role in pitting initiation on iron alloys, and among them stainless steels. It is then worthy to draw attention to some of their physicochemical and metallurgical properties.

For AISI standards 430,434,304,316, and more generally for all Ti free stainless steels, Sulphur is combined with Mn to form manganese sulphides MnS, which act as pitting sites in current corrosive media (see after). Following the sulphur content of the steel and the metallurgical processing, MnS are found either isolated or stuck to other inclusions (generally oxides), or even combined in complex inclusions. Chromium may also substitute to Mn to form some (Mn,Cr)S sulphides, the Cr content of which depends on the Mn content of the steel (currently 0.4% for ferritic steels and 1% or more for austenitic ones) as shown on fig. 3. The higher the
chromium content in the sulphide, the higher the pitting resistance of the steel, resulting in a better pitting resistance for low Mn containing steels\textsuperscript{10}, at least when other metallurgical parameters are not modified by the Mn content lowering. In Ti bearing steels (Ti > some 0.1% weight or more), the MnS formation is prevented, since Ti sulphides (Ti\textsubscript{x}S) are formed at higher temperature during the melting process. Ti sulphides are considered as less harmful than MnS for pitting corrosion, but are also able to act as pitting sites in some conditions\textsuperscript{11,10,12}.

Three basic characteristics of manganese sulphides are worthy to notice\textsuperscript{7} as far as they can influence the pitting initiation process: (i) They are electronic conductors, but less than the surrounding metal, leading to pit initiation at the inclusion/matrix interface. Their conductivity should depend on their exact chemical composition. (ii) They are polarised together with the surrounding metal, but should be unstable in the potential range where the metal is passive, and then readily dissolve, providing some local chemical and electrochemical conditions which differ from the ones which prevail on other parts of the surface. (iii) Their size morphology, together with their composition, play an important role on their ability to promote pitting\textsuperscript{13}. Rapid solidification, or laser surface melting\textsuperscript{14} provide the removal or at least the redistribution of the Mn sulphides, resulting in a strong pitting resistance improvement.

It should also be noticed that all the sulphides present at the steel surface do not promote pits initiation, what some authors explained by the differences existing in their composition and the morphology of the metal/sulphide interface. However the question is not so clear, since the number of MnS acting as pitting sites is much smaller than the total number of Mn sulphides at the steel surface. In our opinion, the competition between sulphide dissolution and local modifications in the passive film properties could result in a low probability stochastic initiation process, which might account for the small number of sulphides which are found to initiate pitting. Some authors underlined the importance of the pitting test procedure for the relation between the MnS dissolution kinetics and the pitting sensitivity\textsuperscript{13}, which evidences once more the absence of any "intrinsic" pitting potential.

![Graph showing composition of sulfide inclusions in type 416 (13%Cr0.3%S) steel as a function of the steel Mn content.](image)

Fig.3 (from ref. 6) Composition of sulfide inclusions in type 416 (13%Cr0.3%S) steel as a function of the steel Mn content.
Last, the recognition that manganese sulphides are probably the least resistant pit initiation sites in standard industrial stainless steels motivated a severe control of the steel microstructure, either by lowering the Mn content (which has unfortunately also some undesirable secondary effects) or, better, by adding some small amounts of Ti as alloying elements, preventing the formation of Mn sulphides. However, this way of improving the pitting resistance is itself limited, since in the absence of MnS, pits can initiate on other inclusions, namely Ti sulphides, oxides, silicates, or possibly on the passive surface itself, as the electrode potential or the chloride concentration increase.

The first idea to be proposed for accounting the effect of soluble sulphides on pitting initiation was that MnS dissolution provokes locally the formation of a virgin metal surface. This micro-area is exposed to an acidified and sulphur species enriched environment produced by the sulphide dissolution. When the solution near from the microarea has reached a certain composition, the contacting metal can no longer repassivate and the metal starts to dissolve. Following other workers, the complete MnS dissolution is not needed, as the pits preferentially initiate at the metallic matrix/MnS interface. This model keeps opened the questions of (i) the MnS dissolution mechanisms, (ii) the nature and the effect of the dissolved sulphur species which form during this dissolution and (iii) the role played by the passive film, either close to or possibly on the inclusion. From this last viewpoint, the surface condition of the steel is of major importance. The effect of MnS is probably not the same on freshly mechanically polished surfaces or after various surface treatments, including pickling, bright annealing or electrochemical treatments.

There are some experimental evidences that Cl$^-$ ions cluster either on the non metallic inclusions or at their boundaries with the metallic matrix. When the MnS is directly exposed to the electrolyte, Cl$^-$ can preferentially adsorbs on the inclusion due to its higher electronic conductivity, giving stronger electrostatic image forces that on the surrounding oxide film. In our opinion, Cl$^-$ adsorption is followed by the potential assisted formation of the adsorbed complex MnCl$^+$ which then dissolves in the aqueous solution according to $(\text{MnCl})^{\text{ads}} + \text{Cl}^- \rightarrow \text{Mn}^{3+} + 2\text{Cl}^-$. Since there is some evidences that pitting initiation on MnS containing steels is strongly dependent on the solution pH (see below), it is suggested that Cl$^-$ and OH$^-$ adsorption compete on Mn sulphides surfaces, resulting in a pH dependent dissolution kinetics.

The MnS dissolution provokes the formation of a Mn$^{3+}$ and Cl$^-$ enriched local electrolyte (the Cl$^-$ ions being attracted by the local excess in positive charges in the solution). As long as the concentration remains below a critical level, the pits walls can repassivate, but beyond this critical level a MnCl$_2$ salt layer is formed which may prevent the repassivation. The question of what happens at the metal/salt layer interface was discussed and it was suggested that a FeCr oxichloride could form, whose properties, and also possible remnance once the salt layer has dissolved, could play a determining role in repassivation mechanisms. Following another idea MnS would be covered with a defective passive film on which the chloride ions first adsorb then penetrate, leading to the formation of a non protective salt chloride layer. The hydrolysis of this salt layer would then increase the local acidity, resulting in the dissolution of the defective passive film. Anyway, whatever the proposed mechanisms, chloride adsorption seems to be the first stage of the sulphide dissolution.

Several models have been proposed for the dissolution of sulphur from MnS inclusions. The first idea is that, in acidified media, MnS dissolves according to:

\[
\text{MnS} + 2\text{H}^+ \rightarrow \text{H}_2\text{S} + \text{Mn}^{3+},
\]
or

\[
\text{MnS} + 2\text{H}^+ + 2\text{OH}^- \rightarrow \text{H}_2\text{S} + \text{Mn}^{3+} + 2\text{H}_2\text{O}.
\]
MnS + 2H^+ → S + Mn^{++} + H_2

These reactions can be split into the anodic reaction\textsuperscript{4,15}
MnS → S + Mn^{++} + 2e^−, whose the potential is V(Volts) = -0.12 + 0.03 log [Mn^{++}], and the cathodic ones:
H^+ + e^− ↔ \frac{1}{2} H_2

or\textsuperscript{4}
2H^+ + 2e^− + S ↔ H_2S with V = 0.14 - 0.06pH - 0.03 log [H_2S],

and possibly\textsuperscript{21}
H_2S ↔ H^+ + HS^−, then H^+ + 2e^− + S ↔ HS^−

Direct action of water to form sulphates, sulphites or thiosulphates should also be considered\textsuperscript{4,6,20,22}
MnS + 4H_2O ↔ Mn^{++} + SO_4^{−−} + 8H^+ + 8e^−, with V = 0.23 - 0.06pH - 0.074 log[Mn^{++}] [SO_4^{−−}],
MnS + 3H_2O ↔ Mn^{++} + HSO_3^{−} + 5H^+ + 6e^−, then HSO_3^{−} + 5H^+ + 4e^− → S + 3H_2O,

2MnS + 3H_2O ↔ 2Mn^{++} + S_2O_3^{−−} + 6H^+ + 8e^−, then:
S_2O_3^{−−} + 3H_2O → S_{ads} + SO_4^{−−} + 2H^+ + 2e^−

All these reactions are potential and/or pH dependent, so that they can occur or not, following the actual conditions in, or close to, the pit embryo. It makes rather complex the interpretation of the pitting potential pH dependence when sulphides act as pitting sites (see below). Furthermore, they do not explicitly take into account the effect of chloride ions for the dissolution of Mn^{++} (see above): they should then be slightly modified for this purpose, introducing the solution chloride content as the third critical parameter for the MnS dissolution kinetics.

It should be noticed that some recent photo-electrochemical investigations\textsuperscript{22} suggest that the two last reactions, involving the formation then dismutation of S_2O_3^{−−} and resulting in the formation of adsorbed sulphur, are operating in some cases. Photo-electrochemical microscopy shows the deposition around the inclusions of a ring of material deduced to be sulphur, which is consistent with the results of several other works\textsuperscript{4,15}.

**AN EXAMPLE OF THE EFFECT OF NON METALLIC INCLUSIONS**

**Steel under study**

In the following, the steels under consideration are mainly some annealed AISI 430 type FeCr ferritic alloys containing also either Nb (steels A and A') or Ti (steels B and B') additions. Additionally some solution treated 304 and 321 AISI type steels were considered (resp. C and D), in order to separate the matrix an the inclusion effects. These two steels are austenitic and Ni bearing but the latter contains Ti and is then MnS free, whereas the former contains MnS inclusions.

Excepting for steel A, some Al additions are used as deoxidising agent during the melting process, which leads to Al~ 0.030% and induces the presence of some Al_2O_3 inclusions. Let us note the low sulphur content, which is easily attained with the modern steelmaking techniques, and the presence of some stabilising elements (Ti or Nb) which trap the carbon and avoid the formation of chromium carbides. For both steels A and A', Sulphur is trapped under the form of Manganese sulphide.

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<th>Cr</th>
<th>Ni</th>
<th>Si</th>
<th>Mn</th>
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<th>(S)</th>
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<td>A</td>
<td>16.4</td>
<td>.4</td>
<td>.45</td>
<td>.5</td>
<td>40</td>
<td>240</td>
<td>n.d.</td>
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The difference between steels B and B' is their Cr content; both contain Ti, which also traps Nitrogen under the form of Titanium nitrides and Sulphur under the form of Ti sulphides; this trapping occurs during the steelmaking process before the steel solidification. Concerning Steel A', some MnS are found around Aluminium oxides (fig. 4). Since these oxides have a poorer ductility than the metallic matrix, the cold rolling process provokes some microdecohesions around the inclusion, where some manganese sulphides are often located, leading to the possible formation of very noxious microcrevices. This phenomenon is not observed on Al free steels, where oxides are mainly malleable silicates. However, the art of the steelmaker consists in avoiding the formation of Cr oxides, which could produce a similar but worst effect than Al oxides. In every case, some MnS are also found closely stuck to Nb carbonitrides (fig 5a). Since these carbonitrides precipitate at ~ 1200°C, this shows that (for the considered sulphur content), the high temperature sulphur solubility is sufficient for the MnS precipitation to occur in the solid steel (lower than 1200°C) while for higher sulphur contents MnS are generally considered to precipitate at the end of the steel solidification. Note that very few isolated MnS precipitates are found, probably because Nb(C,N) acts as precipitation sites. This situation contrasts with the behaviour of steel C (304) for which (i) no carbides may nucleate the MnS. Fig 4b and 5b show the location of Ti sulphides on steel B, i.e. around the Titanium nitrides, embedded in a Ti carbide belt. Detailed examination suggests that at high temperature an homogeneous Ti carbossulphide belt precipitates around the Ti nitrides (which formed in the liquid steel). Then, lowering the temperature, Titanium sulphides and carbides separate at some points as shown on fig. 4b, producing the Ti carbide TiC and a Ti

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<td>.4</td>
<td>.45</td>
<td>.7</td>
<td>50 340 340</td>
</tr>
<tr>
<td>B</td>
<td>16.8</td>
<td>.4</td>
<td>.45</td>
<td>.4</td>
<td>30 260 140</td>
</tr>
<tr>
<td>B'</td>
<td>17.4</td>
<td>.4</td>
<td>.45</td>
<td>.4</td>
<td>30 250 110</td>
</tr>
<tr>
<td>C</td>
<td>17.6</td>
<td>8.2</td>
<td>.4</td>
<td>1.4</td>
<td>20 530 470</td>
</tr>
<tr>
<td>D</td>
<td>17.8</td>
<td>9.3</td>
<td>.4</td>
<td>1.3</td>
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| Steels composition in weight% or in ppm (brackets) |
sulphide, identified in some cases (using electron diffraction) as the hexagonal phase Ti$_2$S. As an other result, note that Al oxides have been identified in the core of the Ti nitrides (which is not shown on the presented figures), playing the role of nuclei for the TiN precipitation.

![Fig. 5](image_url)

**Fig. 5.** Non metallic inclusions (before pitting). STEM (x18000) on thin foils. (a) : Steel A’. MnS nucleated on a Nb carbonitride. Intermetallic (Fe, Nb) phases are also observed.. (b) : Steel B. Ti nitride surrounded by a Ti carbide, in which some Ti sulfides are embedded.

**Precipitation (ii)** sulphides can precipitate in austenite at the delta→gamma transformation temperature.

**Pitting potentials**

The pitting potentials were measured for all these steels using the potentiokinetic method (see above) in some NaCl aqueous media, the pH of which was varied from 3 to 6.6. The results for steels A’ and B in NaCl (0.02M) are shown on figure 6a. No pH dependence is observed for steel B. At the opposite, for steel A’, a sharp pitting potential decrease is evidenced when the pH is lowered under a critical value pH$_c$ ranging between 4.5 an 5. Since the main difference between the 2 steels is the presence or absence of MnS, and that Ti sulphides are known to have a better stability in aqueous electrolytes than MnS, one can assume that this decrease is due to the pH assisted MnS dissolution. Note that the same phenomenon is observed (fig. 6b) when comparing the two steels C and D, which are respectively MnS containing and MnS free, showing that the observed effect is related to the nature of sulphides present in the steel and not to other metallurgical factors. Fig 6b also shows the results obtained for steels A an B’, which confirm the here above findings. The slight difference between steels B and B’ may be attributed to the difference in Cr concentration. The strong difference between steels A and A’ may be due both to the difference in Cr concentration and sulphur contents, but also to the Al oxides present in steel A’ and around which MnS are found. The effect of the solution chloride content was also investigated between 0.02M and 0.5M. Fig. 6c shows that for high enough chloride concentrations, a pitting potential pH dependence is found even for Ti containing steels, suggesting that Ti sulphides are not so stable in such electrolytes. The discontinuity of the pitting potential vs pH variations should then be related to the dissolution of sulphur species, which occurs easily for MnS containing steels (whatever the steel matrix composition) but only for high enough chloride contents for Ti bearing steels. Let us note that the critical pH which is found (4.5<PH<5) is the same for Ti free and Ti bearing steels and is close to the one which was deduced from the potential/pH equilibrium diagrams in some chloride containing aqueous solutions. This could support the idea that the critical pH can be deduced...
from the sulphur species/pH equilibria, irrespectively of the nature of the dissolved cation (Manganese or Titanium), once the conditions are reached for the sulphide to dissolve.

Fig. 6. Effect of the solution pH on the pitting potentials (measured vs SCE using the potentiokinetic technique at 100 mV/min after 15 min at rest potential on mechanically polished (P1200) then 24h air aged specimens.

(a) steels A' and B in NaCl (0.02M).
(b) steels A, B' (FeCr steels) and C, D (FeCrNi steels) in NaCl (0.02M).
(c) Effect of the solution chloride content dependence for a Ti containing steel. For low chloride contents (0.02 and 0.1M), there is no pH effects. For 0.5M, lowering the pH decreases the pitting resistance.
Pitting sites

Fig. 7 shows the typically observed pits initiation sites. For steel A', whatever the pH or the chloride content, pits initiate either around Al oxides (fig. 7a), where some MnS are located, or on MnS inclusions (fig. 7b) around Nb(C,N) or (seldom) isolated. This confirms the preceding hypothesis. For Steel B in NaCl(0.5M) solution, pitting generally occurs at the TiN boundary (fig. 7c), where Ti sulphides are present. This shows clearly that for such chloride concentrations, Ti sulphides act as pitting sites and become unstable when the potential increases. For lower chloride concentration (NaCl 0.02M), the situation is not so clear and pits could initiate directly on the metallic matrix, with no direct relation to non metallic inclusions, or in some cases on titanium nitrides. In the two situations however, Ti sulphides do not seem to act as pitting sites, which is consistent with the absence of any pitting potential pH dependence.

A practical consequence can be drawn from these results: Ti stabilised steels exhibit a better pitting resistance than Ti free ones, provided that the corrosive medium is not "severe", i.e. when the chloride content does not exceed a critical value, depending on the solution pH, which could cause the Ti sulphides destabilisation.
In the case of crevice corrosion, the situation is more complex. Inside the crevice, the pH decreases and the chloride concentration increases with time. It is an accepted idea that corrosion occurs when the pH becomes lower than a critical value, which is referred to as the depassivation pH. However, at least for the less resistant steels, pitting corrosion may occur in the crevice before this general depassivation. From the here above results, it results that MnS containing steels are much more sensitive to this "pitting induced" crevice corrosion than Ti bearing ones. For very severe crevices however, the chloride content can drastically increase with time and Ti stabilised steels are no longer different from Ti free ones.

The inhibitive effect of sulphate ions

Sulphate ions are known for inhibiting the pitting corrosion in chloride containing media. It has been found in the above study that this effect is more marked for steel A than for steel B, but that the difference between the two steels regarding the sulphate addition efficiency becomes smaller when the chloride concentration increases. More generally sulphates additions provide a deviation to the standard pitting behaviour (such as the statistical distribution of pitting potentials in a large series of experiments). The sulphate amount necessary for producing a noticeable deviation is much larger for steel A than for steel B. Further work is needed for interpreting these results, but the difference between the MnS containing and MnS free steels is now well established.

Prepitting events

Recording the anodic current i(t) during a polarisation below the conventional pitting potential (fig. 8a) shows some oscillations of this anodic current which, doing the same SEM observations as above, were seen to correspond to some initiated then repassivated pits. For MnS containing steels (A or A'), the prepitting events are very numerous and produce what one may call a "prepitting noise". At the opposite, for MnS free steels the anodic events are much less numerous and well separated, as shown on fig. 8b. It is therefore logical to relate the so called "prepitting noise" to the dissolution of Manganese sulphides. The current time signatures of the individual prepitting events (not visible on the figure) is found to be a current increase varying approximately as $t^2$, followed by a sharp current decrease (type I) for MnS containing steels, and (type II) a sharp increase followed by a slow current decay (as expected for a local passive film breakdown followed by the passive film healing) for MnS free steels.

(a) Typical prepitting noise (current intensity in µA) for MnS containing steels (after substracting the anodic current baseline).
Ageing effects

In the experiment above, it was evidenced that the current fluctuations density for MnS containing steels was a decreasing function of the polarisation time. The first idea is that the pitting sites having initiated an unstable pit become inactive after the pit repassivation, leading to a decrease of the available pitting sites and then of the further pits generation rate. However, it was also observed that ageing potentiostatically a MnS free steel decreases the further number of prepitting events as well. Since in this case the prepitting events are very rare, the here above explanation does not hold. It is believed that ageing rather increases the resistance of the passive film. In the same order of ideas, it was found that a pre-polarisation treatment increases the further pitting potential irrespectively of the type of sulphides present in the steel (fig. 9). This shows that not only the non metallic inclusions but also the passive film play a role in the pitting initiation. However, increasing the prepolarisation time showed that the effect of the ageing is more beneficial for MnS free steels than for MnS containing ones. It is believed that the dissolution of sulphur containing species counteracts in the latter case the beneficial effect of the passive film reinforcement.
CONCLUDING REMARKS: THE IMPORTANCE OF BEING A METALLURGIST

The onset of a stable pit finally results of a combination of both electrochemical and metallurgical factors and many problems come in mind when considering the relative or combined effects of these factors. First, the proper effect of the passive film is not clear when pitting initiate on non metallic inclusions. The current models on pits initiation generally refer to the passive film breakdown, while the investigated steels contain a lot of non metallic inclusions, which act as pitting sites. Secondly, the size effects are often disregarded, and microscopic models are frequently proposed to account for macroscopic effects.

As far as pit nucleation is concerned, three situations may occur. First, pit can nucleate directly on the passive film, far from any non metallic inclusion. This is the case generally considered in most theoretical models, but there is no evidence that it is the prevailing situation for industrial stainless steels and more work is needed for clarifying this point. Secondly, pitting can arise from the dissolution of unstable inclusions (such as MnS), leading to a small area of bare metal when the inclusion is entirely dissolved. The point to be clarified is then the proper role of the passive film properties in the pit nucleation process. Last, passive film and inclusions can interact together.

A simple model can be proposed in this case of the MnS inclusions. It has been pointed out that MnS dissolution is pH and chloride assisted, producing some Mn$^{++}$ ions and some sulphur containing species, followed by a pH decrease and a local increase in chloride concentration. This increase in chloride concentration is provoked by the electromigration of chloride ions from the solution bulk to the pit embryo (due to a local excess in positive charges close to the dissolving sulphur) resulting in an increase in the [Mn$^{++}$][Cl$^{-}$] product, then the precipitation of a non protective salt layer. Another idea is that at the beginning of the MnS dissolution, the local excess in positive charges is not sufficient to increase significantly the local chloride concentration and that this process should be assisted by a passive film breakdown in the inclusion neighbourhood, which produces a large amount of metal cations, leading to a local Cl$^{-}$ enrichment due to electromigration. One suggests that beyond a critical electrode potential a large number of microscopic passive film breakdown events are randomly produced, generally followed by passive film healing, excepting close to the MnS sulphides where some dissolved sulphur species can prevent the repassivation. This phenomenon is a low probability event, explaining the small number of the inclusions acting as pitting sites. From this situation, the stable sulphide dissolution may arise, as proposed above. The question remains opened whether the sulphur species act only as inhibitors of the passive film healing or also increases the film breakdown probability at the atomistic scale. Anyway, such a model shows that the pitting rate is influenced by the passive film properties at the early stages of pit nucleation and accounts for the fact that pits initiate close to the inclusions. In a further step the inclusion may dissolve, producing a bare metal area (pit nucleus).

More generally, it should be pointed out that, whatever the pit nucleation mechanism, the survival probability of a pit nucleus (or even of a pit embryo) depends on the state of the surrounding passive film, since different passive films formed on the same alloy do not exhibit the same pitting resistance. The distribution of potentials and electric charges around the pit nucleus should likely provide a better assessment of the intensity of
the anodic reactions than the average potential difference \( V \), and are likely a function of both the pitting sites characteristics and the surrounding passive film properties.

Last, one should point out the importance of the solubility of sulfides in pitting resistance of stainless steels of different compositions: this resistance seems to increase in the same way that the sulfide stability: Ca, Mn, Cr, Ti, Ce. Finally, the role of the sulfides in pit initiation could be simply to provide sulfur species (more or less easily following the sulfur stability), which may re-deposit on the passive film around the sulfide, resulting in a poorer resistance to pit nucleation. This assumption is supported by thermodynamic data and also by some recent results obtained thanks to the scanning electrode vibrating technique, combined with AFM and XPS measurements. Following a model recently proposed, the sulfur species re-deposited around the sulfide can act as electron traps at the passive film electrolyte solution interface, which, for a potential larger than a critical value (the nucleation potential), may provoke the pinning of the Fermi level and then a dramatic increase of the film solution potential difference \( V_{fs} \), increasing consequently the concentration in cation vacancies in the passive film (cations dissolution due to adsorbed Cl ions is faster when \( V_{fs} \) is larger). Cation vacancies decreases the film cohesion and film breakdown can occur, due for instance to the electrostriction force.

Finally, we should drive attention on a model recently proposed, which we feel to neglect a lot of evidences, making its use for industrial purposes inappropriate, or even dangerous. This model basically assumes that the major effect of (Cr containing) Mn sulfides was simply the formation of a Cr depleted zone in the metal surrounding the sulfide, then less resistant to pitting, following a mechanism similar to corrosion in the neighbourhood of intergranular Chromium carbides. Even when this Cr depletion is actually observed by the authors, we feel that the general model drawn from this result fails on several important points: (i) the results were obtained on high sulfur grades, normally used for free machining and far from the most common steels, to which they cannot be extrapolated without further investigation. Moreover, no information is given on the steelmaking process (which does not seem standard at a first glance) followed by the specimens under investigation.

(ii) It is well known that the higher the Cr content in the sulfides, the larger the corrosion resistance of the steel. Decreasing as much as possible the Mn content is even a well-known means for increasing the pitting resistance, although the Cr depletion theory should predict exactly the opposite.

(iii) Ti stabilized steels (in which Mn sulfides are substituted by Ti ones) resist better to corrosion than standard steels, but may pit at higher potential or in more concentrated Chloride containing solutions. No Cr depletion around the pit can of course occur in this case.

(iv) Pitting occurs even on sulphide free alloys. It is a matter of fact that pitting was also observed on or close to the oxide inclusions. Some authors also found that pitting can occur on ultra pure steels, in more severe conditions however.

This illustrates the difficulty to deal with pitting mechanisms on industrial steels without carefully considering the metallurgical aspects of the question, a point which is not always taken into account with a sufficient attention, in our opinion.

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