A study of carbon steels in basic pitting environments

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Abstract

Purpose – Aims to study the behaviour of four polycrystalline carbon steels in basic pitting solutions.
Design/methodology/approach – Electrochemical investigations were carried out on four steels: Fe.06C, Fe.18C, Fe.22C and Fe.43C. The analysis was made using an X-ray fluorescence apparatus. The performance indicator was the pitting potential, which was obtained through potentiodynamic sweeping. Emphasis was placed on the influence of the pH, chlorine concentration, phase proportions in the steel and the initial electrode surface state.
Findings – The results showed that in a solution with a low chlorine concentration, the performance of the steels according to pitting corrosion resistance decreased with the increase in carbon content. By raising the chlorine concentration, the order of performance was inverted gradually, while at a high chlorine concentration, the behaviour of the steels tended to be similar. The interpretation of the results is based on the consideration of cathodic reactions on the level of the cementite phase and the difference in the local chemical properties of the solution. In neutral solutions, pitting potentials were shifted cathodically, but the main observations developed for basic solutions remained valid.
Originality/value – Provides further research on pitting corrosion.

Keywords Steels, Pitting corrosion

Paper type Research paper

Introduction

In general, it is considered that pitting corrosion is the most disastrous form of corrosion as its occurrence can be extremely difficult to predict. Predictors are less accurate as the complexity of the corrosive environment increases. The pitting process occurs as the result of a series of steps. In some cases, the most important such step is the initiation stage, which is still the subject of a great number of studies and various assumptions (Szklarska-Smialowska, 1986; Strehblow, 1995; Natishan et al., 1995; Frankel, 1997, 1998; Maurice et al., 2001). The initiation of pits can be considered as an event that results from conjunction of various phenomena. These phenomena are related to several factors that are mainly properties of the solution and those of the metal, which exert themselves through a broad range scale.

The most reported key factor of pitting initiation is the inclusion concentration (Webb et al., 2001a, b; Suter and Alkire, 2001; Suter et al., 2001; Williams and Zhu, 2000). By using a micro electrochemical cell, Alkire (Webb et al., 2001a, b) found that the geometric orientation of the MnS inclusions was significant for the initiation of pitting corrosion. The onset of pitting at areas without inclusions was shifted to very high potentials (Suter and Alkire, 2001). In addition, the presence of mechanical stresses reduces pitting potential appreciably in the presence of MnS inclusions (Suter et al.,

2001). It has been found that the weak regions are the inclusion/metal interfaces and occurrences when the inclusions are deep, as they generate locally a strong acid medium and a high chlorine concentration. Experimental observations on artificial inclusions allowed Williams and Zhu (2000) to explain pit initiation and the high dissolution rate of sulphide inclusions through the chemical changes induced in the sulphide as the steel cools from its melting temperature to the solidification temperature of the sulphide.

In addition to the inclusions, the phase structure of the material seems to play an important part in the pitting initiation. By means of *in-situ* high-resolution microscopic investigations on duplex stainless steels, Garfias and Siconolfi (2000) reported that pits and corrosion products develop in the austenite grains and in particles contained within the ferrite matrix. The lateral distribution of elements in passive films formed on duplex stainless steels was found to be dependent upon the underlying phase structure. On the other hand, as each grain presents a specific crystallographic orientation, we can imagine that pitting conditions differ from one grain to another. Kruger (1959) was the first to report this phenomenon. Subsequently, several studies have been published on the influence of the crystallographic orientation on the initiation and propagation of pits (MacDougall and Cohen, 1978; Yasuda et al., 1990; Treacy and Breslin, 1998; Yu et al., 2000; Sato et al., 1996; Lillard, 2001a). Kruger found that pitting density is maximal on {110} planes. In addition, MacDougall and Cohen's (1978) work on nickel allowed them to link the susceptibility to pit initiation with the mismatch in orientation between the crystallographic planes of the oxide film and those of the metal. Similar observations were carried out on other materials such as aluminium (Yasuda et al., 1990; Treacy and Breslin, 1998; Yu et al., 2000), stainless steels (Sato et al., 1996) and berylium (Lillard, 2001a, b).

Another key factor in pit initiation is the presence of hydrogen in the passive film. Usually, experimental

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procedures are conducted with a prior cathodic polarization in order to reduce any natural oxides that may be present on the surface of the working electrode. However, this operation generates atomic hydrogen at the metal/solution interface and it is possible for some of the hydrogen so formed to diffuse into the metal. The decrease in the stability of the passive film by the presence of hydrogen has been reported for some time (Hasegawa and Osawa, 1980). Recently, however, Yang and Luo (2001) have studied more deeply these effects in stainless steel type 310. The pitting potential was found to be less anodic if the passive film was previously charged by hydrogen. The passive film exhibited n-type semi-conductivity and its disorder increased with the amount of hydrogen absorbed.

In an aqueous environment with strong chlorine concentration, pitting corrosion of stainless steels is limited because of the presence of the chromium, which exerts a preventive role (Boucherit, 1992 a, b), and notably of the molybdenum content which has complementary pitting resistance properties (Boucherit and Hugot-Le Goff, 1992; Boucherit et al., 1991; Ilevbare and Burstein, 2001; Bastidas et al., 2002; Kaneko and Isaacs, 2002). In low chlorine concentration environments, the use of carbon steel is economically more advantageous. The important constituent of carbon steel is the carbon proportion, which has a substantial influence on microstructure. Thus, the difference in the composition of carbon steels should result in different behaviours in some pitting environments and these should be more or less significant according to the pH and the concentration of the pitting element. In the present study, the behaviours of four carbon steels containing different carbon proportions: 0.06C, 0.18C, 0.22C and 0.43 per cent C, were investigated.

Methodology

The electrochemical investigations were carried out on the four steels, noted in the text by: Fe.06C, Fe.18C, Fe.22C, and Fe.43C. Their chemical compositions, in per cent weight, are reported in Table I. The analysis has been made using an X-ray fluorescence apparatus.

Before the electrochemical tests, the surface of the working electrode was polished with 600 emery paper. In order to guarantee a constant exposed surface and to protect the material from lateral attack, the outline of the surface was coated with varnish, which is an electrical insulator and is chemically inert. The total exposed surface in all cases was 0.1 cm^2. A saturated calomel electrode SCE was used as the reference electrode, and a 2×5 cm platinum sheet was employed as the counter electrode. After the polishing and rinsing with deionised water, the working electrode was introduced into the solution and was polarized at -0.8 V/ SCE. The voltametric sweep was initiated immediately in order to minimize hydrogen evolution and limit its introduction into the working electrode.

All of the potentiodynamic experiments were made at a low scan rate: 1 mV/s, using an EG&G PAR 273A potentiostat with a current limit of 100 µA and M352 SoftCorr III software.

Results

The main measurements were taken in basic solutions containing 0.01 mole/litre of NaOH and a chlorine concentration varying from 0.01 to 0.4 mole/litre. The measured pH was 11.6 and it has been verified that it is very little influenced by the chlorine concentration. The choice of the pH and the chlorine concentrations was adopted in order to produce pits in the passivity region, between the active dissolution around -0.5 V/SCE, and the oxygen evolution which starts at 1 V/SCE.

Figure 1 was drawn to show both the influence on pitting potential of: chlorine concentration and of steel composition, and to estimate the reproducibility of the results. The horizontal axis corresponds to the chlorine concentration of the solution. For the sake of clarity, values for a same chlorine concentration corresponding to each steel were shifted slightly horizontally.

For the same steel and the same chlorine concentration, as measurements were repeated several times we reported the average of the pitting potentials: $\bar{x}$ accompanied by a vertical segment representing the standard variation of the mean SVM computed according to the formula:

$$\mathrm{SVM} = \frac{1}{\sqrt{n}} \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (x_i - \bar{x})^2}$$

In the most dilute solution, which contained 0.01 mole/l of chlorine, pits did not appear frequently below 1 V/SCE. The oxygen evolution, which started near this potential, prevented further observations at higher potentials. However, by doubling the chlorine concentration, all of the steels became vulnerable before commencing oxygen evolution. The non-reproducibility of the results in low chlorine concentrations was substantial, as is indicated by the height of the vertical segments. However, pitting potential values became more consistent as the chlorine concentration was increased.

Observation of the mean pitting potential values shows that the ranking order of performance of the steels depended upon the chlorine concentration. In diluted solutions, Fe.43C steel appeared to be the more vulnerable, whereas in more concentrated solutions, for example, the 0.2 mole/l solution, the higher carbon steels were more resistant. The change in the ranking order occurred in a continuous manner. Thus, with 0.03 mole/l of chlorine, Fe.18C steel was followed by Fe.22C, which was slightly more resistant. Nevertheless, in the highest chlorine concentration solution, all of steels exhibited similar pitting potentials.

Table I Chemical composition of the studied steels

Steels	C	Mn	Si	P	S	Cu	Al	Ti	Ni	Cr	Mo	Sn
Fe.06C	0.06	0.35	0.15	0.023	0.021	0.049	0.004	0.002	0.015	0.020	0.007	0.007
Fe.18C	0.18	0.52	0.22	0.009	0.008	0.11	0.007	0.003	0.039	0.063	0.015	0.003
Fe.22C	0.22	0.44	0.06	0.036	0.016	0.062	0.004	0.002	0.012	0.012	0.004	–
Fe.43C	0.43	0.71	0.26	0.014	0.022	0.096	0.040	0.004	0.029	0.064	0.013	0.013

Figure 1 Pitting potential and its regularity versus the chlorine concentration for the four studied steels
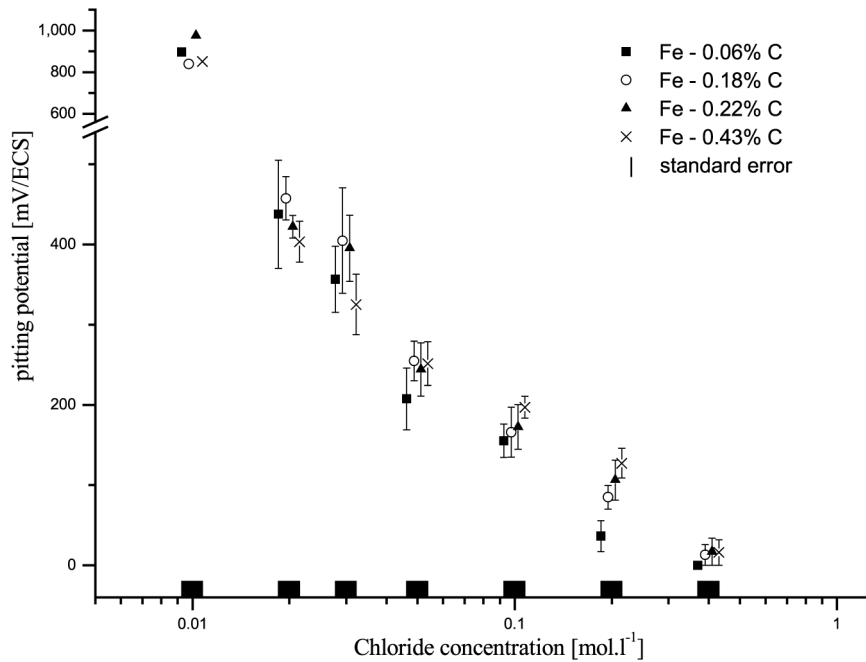
In neutral solutions, the passive film was less established. The pitting potential consequently should move towards less anodic potentials. In addition, very high chlorine concentrations would cause pits to occur in the active dissolution region and impede the identification of a defined pitting potential. In Figure 2, we collected the mean of the pitting potentials of the four steels, by maintaining the chlorine concentration at 0.03 mole/l and reducing the pH of the solution until the pitting current was intermingled with the current of the active dissolution process. The pH limit was 8.5.

With any pH value, the ranking order of the steels remained the same. In particular, the Fe.22C steel always presented the highest pitting potential. An investigation of the influence of the solution pH on the performance order of steels was carried out with various chlorine concentrations. It was observed that this order was related only to the chlorine concentration of the solution, and not to its pH.

Figure 3 shows microscopic examinations on surfaces of steels after they were pitted. The magnification was $200 \times$. Before the observations, the working electrodes were subjected to a polarisation sweep up to 1 V/SCE in the most concentrated solution. Subsequently, the potential of each sample was maintained for a duration of 1 min before proceeding with the microscopic observations, which were conducted according to the AFNOR procedure (Barralis and

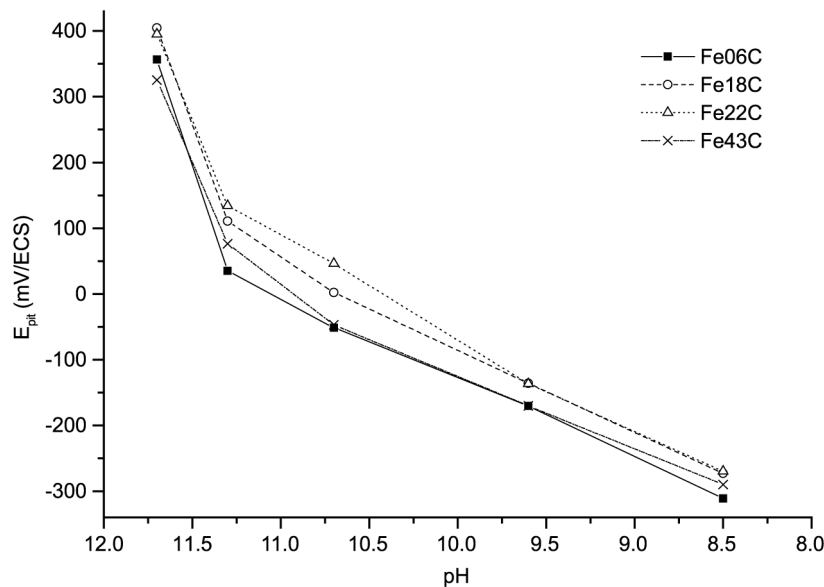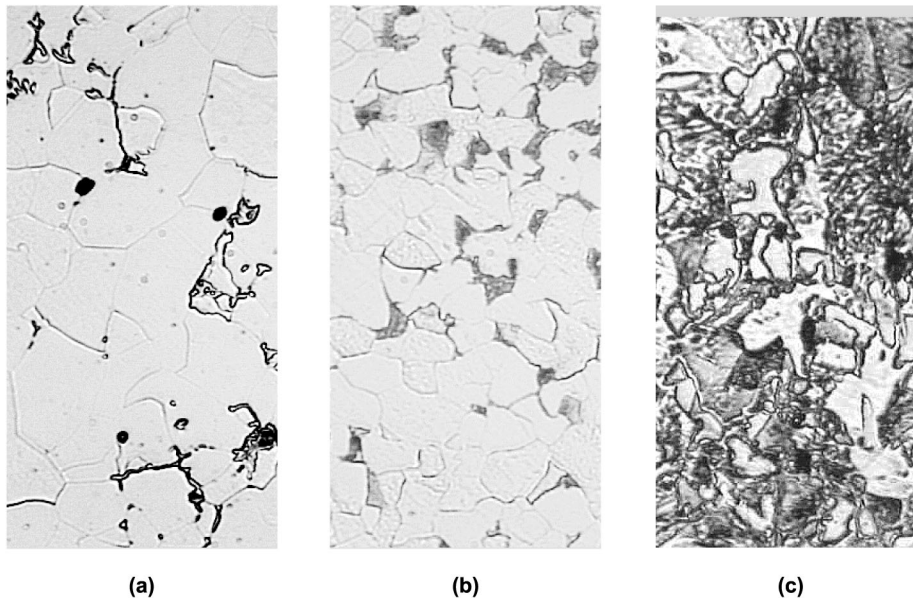**Figure 2** Pitting potential versus pH, $[Cl^-] = 3.\ 10^{-2}$ mole/l

Figure 3 Micrographic observations: (a) Fe.06C; (b) Fe.18C and (c) Fe.43C

(a)   (b)   (c)

Maeder, 1990). Steels have a two-phase structure: They are composed of the ferrite, which appears in white in the micrography, and of the pearlite, which is darker. Pearlite is a mixture of ferrite and cementite (Pollack, 1988).

Fe.06C steel is composed of mainly of ferrite in which carbon is partly trapped (Le livre de l'acier *et al.*, 1994). Carbon is also present in the composition of the iron carbide at the grain boundaries. In the Fe.18C steel, the two phases are present with comparable proportions, whereas for the Fe.43C the pearlite phase predominates. Small quantities of inclusions were evident in all of the steels. The reason is probably related to the low amount of sulphur they contained. In addition, the size of the ferrite grains in the first two steels was similar.

Interest in the microscopic observations of pits lies in their distribution and dimension. In the Fe.06C steel, pits were localised in the region of the grain boundaries, as has been reported by Yamashita *et al.* (1999), whereas in the Fe.18C and the Fe.43C, they were confined within the pearlite. However, by increasing the resolution it could be observed that attack often occurred close to the pearlite/ferrite interface and hardly at all in the centre of the pearlitic grains.

Discussion

The studied steels present different phases ratios and, under the chosen experimental conditions, pits were never observed in the ferrite phase. Pits always evolve in the pearlitic zones, which consist of cementite and ferrite mixtures. Taking into account the heterogeneity of the pearlite and the fact that cementite is more noble than ferrite (Le livre de l'acier *et al.*, 1994), it is conceivable that regions of local polarisations may occur where the dissolution of iron from a ferritic area is supported by complementary cathodic reactions at the closest cementite zone. The resulting local acidification and chloride enrichment then expose the pearlite to an environment that is much more aggressive than is that on the ferrite grains. The micrographic observations allowed pits only to be identified in advanced stages of development. It is possible that in the surface of the ferritic grains, the passive film breaks down as early as on the ferrite contained in the pearlite. However, since the chemical environment is not sufficiently aggressive, metastable pits in ferritic grains repassivate better than do those in the pearlitic regions. At this point, if we imagine the establishment of local polarisations on the surface of the working electrode, we must accept the idea that a proportion of the anodic current density cannot be measured by standard electrochemical equipment.

The four studied steels were polycrystalline and the surface preparation before each experiment required a polishing procedure that led to a consumption of material. The thickness of material lost after each preparation was equivalent to approximately one-grain size. Thus, after each polishing, a new surface condition was generated that was characterised by a new granular landscape, and particularly by the appearance of different crystalline planes on the surface of each phase. This irregularity in the initial state of the surface inevitably leads to an irregularity in the pitting potential values, in spite of the fact that electrochemical conditions were maintained rigorously constant. However, when the chlorine concentration increased it was evident that the values of the pitting potentials were increasingly reproducible.

It is important to emphasise that the recorded potentials corresponded to an irreversible evolution of metastable pits which, in fact, appeared at lower potentials (Frankel *et al.*, 1987; Maurice *et al.*, 1999; Kojima and Sujikawa, 1998; Cheng and Luo, 2000). Around a metastable pit, the metal dissolution and the hydrolysis of its cations result in local acidification. This enrichment in proton causes, moreover, an electromigration of chloride toward the pit in order to maintain the electroneutrality of the medium (Natishan *et al.*, 1995). The rapidity of local chloride enrichment is important, as the total chlorine concentration of the solution is high (Leckie and Uhlig, 1966; Mankowski and Szklarska-Smialowska, 1975). It is possible, therefore, to consider that when the passive film breaks down in a solution with a high chlorine concentration, its environment

quickly becomes enriched in protons and chlorine ions. Consequently, the aggressiveness of the local environment essentially will impede the repassivation process of the metastable pits. Thus, in the high chloride concentration mid-section, we can conclude that the intrinsic properties of a carbon steel and its surface state do not exert a significant control over pitting potential values.

The number of local polarisations increases with the quantity of pearlite in the steel surface and, thus, of its carbon rate. In solutions with small quantities of chloride, the evolution of pits is slowed by the weak local enrichment of anions that are essential for electrical neutrality. Local dissolutions appear early in the passive range but are continuously repassivated. At higher potentials, the dissolution process increases and the repassivation capacity of pits decreases. The pitting potential is considered to be reached when only one pit develops fatally. The probability that the irreversible rupture of the film intervenes grows with the number of initiated pits and thus of local polarisations in the pearlitic zones. At this point, it becomes reasonable to accept that in low chlorine media the performance of steels decreases with the increase of the carbon content.

In solutions with high chlorine concentration, anion enrichment around the initiated pits is assured and the irreversible evolution of the pits appears at lower potentials. It remains the case, however, that this enrichment around a metastable pit is competitive with the presence of other metastable pits. This competition increases with the quantity of pearlite on the surface. From there, we can state that, in a high chlorine environment, the more carbon a steel contains, the more the irreversible evolution of metastable pits is delayed. If the increase of the chlorine concentration results in a reduction of the influence of the metastable pit, then it becomes clear that at very high concentrations, the difference in the performances of steels is reduced.

Localised corrosion is a complex process and the pitting potential is an indicator which depends on a large number of parameters: the global pH of the solution, its chlorine concentration, the carbon rate of the steel and the surface state of the working electrode are only some of the parameters which influence substantially the localised corrosion process. In addition, it is significant that the range of influence of each one of these factors is delimited by the conditions created by the other parameters. Thus, the carbon rate is a factor, which determines the performances of steel differently according to the chlorine concentration of the aqueous environment, whereas the material surface state has an influence mainly in the low chlorine concentrations. In addition, the global pH of the solution manifestly affects the value of the pitting potential. However, in the selected ranges of chlorine concentration and carbon rate, the pH did not influence substantially the performance ranking order of the steels.

Conclusion

The capacity of a steel to resist to pitting corrosion depends strongly on the chlorine concentration of the aqueous environment to which it is subjected. In seawater environments which contain more than 0.1 mole/l of Cl^-, steels with a high carbon rate are more resistant, whereas in a low chloride concentrated environment, the local corrosion resistance increases with the reduction in carbon content of the steel.

Typical carbon steels are polyphase materials which, due to the differences in local composition, present a non-uniform potential distribution at the level of the solid/liquid interface. Consequently, it is possible in this situation to cause local cathodic reactions that cannot be observed with conventional electrochemical instruments.

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