Long-lasting outdoor atmospheric corrosion tests

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Abstract

Since its introduction in 1933, the concept of patinas as a corrosion-controlling mechanism has been playing an important role in many structural applications. The analysis of the initial stages of the corrosive attack showed that this phenomenon, which was considered uniform at first, is actually a moderate one, non-metallic inclusions in structural steels being the preferred points of attack. Long-lasting tests were carried out in Argentina, at the urban site of Villa Martelli's outdoor test station. Specimens were obtained from a hot-rolled structural steel sample of 3.5 mm thickness, 45 mm wide and 300 mm long. The outdoor tests were carried out over 35 years. The results obtained by optical microscopy, electron scanning, and electron probe microanalysis showed that the addition of micro-alloying elements modifies steel behaviour. This modification means an increase in steel resistance to atmospheric corrosion.

Keywords: atmospheric corrosion, weathering steel, micro-alloying elements, patina, outdoor tests.

1 Introduction

The term “weathering steels” describes a class of low-alloy structural steels that develop an adherent protective rust layer, called patina, during exposure to the atmosphere. As a result of this, weathering steels, unlike ordinary plain carbon steels, do not require painting, which brings important advantages, namely avoiding associated costs of initial painting, periodic repainting, containment and disposal of blasting debris during repainting.

Since the beginning of the study of atmospheric corrosion, the latter was basically considered as an electrochemical phenomenon. The analysis of the initial stages of the corrosive attack showed that this phenomenon which was considered

uniform at first is actually of a moderate extent, the non-metallic inclusions in steels being the preferred points of attack. Evans electrochemical model for the atmospheric corrosion shows the reactions that explain the behaviour of corrosion product films as well as the influence of micro-alloying elements on the size of colloidal aggregate particles that form patinas. There have been many propositions to explain the protection mechanism. However, there seems to be no generally accepted theory up to now [1]. Initially there were two tendencies in research: the first one was to attribute the protective nature to the chemical characteristics of the species present, and the second one was to attribute the said protective nature to the morphology of the protective films. Many techniques were used for the characterization of patina corrosion products, which were formed because of exposure to a natural environment. Non-metallic inclusions of MnS with or without Fe have a principal role at the beginning of the corrosion process. Klund [2] found that around the MnS inclusions there is an area, attributed to the steel cooling rate from its tapping temperature, along the inclusion contour. This is called MnS micro inclusions infected area and is very reactive. While the MnS inclusion works as a cathodic area, the said infected area works as an anodic one. The progress of this process leaves the non-metallic inclusion not providing support to the steel matrix, since the infected area is removed. Therefore, a hole or pit filled with corrosion products is originated and acts as an anodic area. Sometimes it is the inclusion itself the one that dissolves. This occurs when the inclusion has other chemical elements, like the lanthanum, which are easily attacked.

Previous results verified by optical microscopy, electron scanning, and electron probe microanalysis showed that the addition of rare earths modifies steel behaviour towards atmospheric corrosion because of the different chemical composition of the non-metallic inclusions developed in the process.

Szumner and Janik-Czachor [3] point out that the presence of non-metallic inclusions, which were morphological modified by rare earths, is detrimental to corrosion resistance, and that the CeS attack nucleating effect is bigger than the MnS one, usually found in steels.

2 Evans electrochemical model

Outdoor tests carried out during long periods of exposure have revealed that weathering steels (WS) with small additions of Cu, Cr, and P have much better atmospheric corrosion resistance than those steels without micro-alloying elements. Laboratory research by Pourbaix [4] and Pourbaix and de Miranda [5] has clearly shown that the said difference only occurs when steel samples are subject to repeated cycles of drying out and humidification. These tests like the ones carried out in a natural environment with a relative humidity always near saturation [6] have shown that there is no advantage in substituting ordinary steels for WS under the said environmental conditions. Many authors [7, 8] have pointed out the key influence of Cu as the most significant micro-alloying element to enhance atmospheric corrosion resistance, and they relate Cu to the formation of an inner denser and tightly adherent layer, which coats steel without cracks or

defects. According to this, the tests carried out by Electron Probe Microanalysis (EPMA) [9] show that Cu concentrates mainly in those cavities resulting from the initial attack to non-metallic inclusions, and in the space among them, which is in contact with steel. Infrared (IR) spectroscopy tests show that the main components of protective patinas are first the δ ferric oxyhydroxides (δ -FeOOH), called lepidocrocite, and then the α and β oxyhydroxides and magnetite (Fe_3O_4) in smaller amounts.

The reduction of the particle size resulting from an enrichment of Cu occurs with a reduction of the pore size and a greater tortuosity in the aggregate. According to Evans model, the reduction conditions exist over a large part of the film if the pores are filled with water (from rain or mist). However, the oxidation conditions prevail during the drying out periods. The balance between these two conditions moves to the steel during the drying out periods and to the atmosphere during the humidification periods.

The excellent atmospheric corrosion properties of WS cannot entirely be explained by the presence of alloying elements. Although it seems that the phosphorus in steel improves the atmospheric corrosion resistance, it also seems that sulphur or sulphur oxides in air have an effect on protective patina formation on the steel.

Electrochemical curves show that at the potential at which the maximum anodic current is produced, the oxidised element is now the Fe^{+2} intermediary on the surface of FeOOH globules instead of the magnetite [10]. Moreover, the patina inner layer would be protected due to an increase of its compactness, according to test results by Moroishi and Satake [9], Inouye *et al.* [11] and Rosales [12]. Where there are neither micro-alloying elements or long humidification periods, the δ -FeOOH would have been transformed into Fe_3O_4 , because there is no controlling effect on the Fe_3O_4 production, which does not have a protective attribute, as reported by Kihira *et al.* [13].

3 PA steel formulation

According to what has been mentioned in previous work [14], the conclusion is that a formulation containing the necessary micro-alloying elements (Cu, Cr, and Si) to produce the film of corrosion products on steel and non-metallic inclusions – modified by rare earths additions (particularly Ce) – is considered to meet both criteria: weatherability and better mechanical properties.

Following these criteria, a weathering steel experimental tapping was planned with the addition of rare earths as modifiers of non-metallic inclusions from their morphological as well as from their chemical reactivity point of view.

A minimum C content was planned to provide the mechanical strength and ferritic attribute of structural steels. The percentage of the main micro-alloying elements, Cu and Cr, were fixed on a practical basis. The available ferroalloys for steel production were considered as well as their use under the fusion conditions to be adopted. The recommendations given by specialised literature were adopted for the rare earths percentage and addition process to the ladle [15].

The percentage of Ni added – almost similar to the Cu’s percentage – is the suggested one to neutralise the detrimental effect of the latter in a hot-rolled process, widely known as hot shortness. The vanadium – together with the aluminium – is a ferritic grain-refining agent. Due to its availability and ease of handling, the rare earths silicide was adopted (Fe: 35%, Si: 31% and rare earths: 34%; the latter with a composition of Ce: 50%, La: 25%, Nd: 10% and Pr: 5%) in a percentage of 1.0 g/kg of melting steel as a means of containing these rare earths.

The chemical composition of steel – analysed in the hot-rolled product – in comparison with the one of the currently produced Cor-ten A and the QST-52 non-alloyed steel is shown in Table 1.

Table 1: Chemical composition of hot-rolled PA steel, as well as Cor Ten A steel and QST-52 non-alloyed steels used as a reference samples.

Steel	C	Si	Mn	P	S	Cu	Cr	Ni	Al	Sn	As	V
PA	0.15	0.41	1.01	0.086	0.105	0.46	1.0	0.38	0.02	0.01	0.013	0.006
Cor-ten	0.10	0.36	0.34	0.093	0.018	0.31	0.60	0.12	1	-----	0.005	0.008
A	0.16	0.36	1.36	0.013	0.035	0.05	0.07	0.06	-----	-----	-----	-----
QST-52									-----			

An induction furnace was used and 4 ingots of 60 kg net were tapped (without dead heads). The final temperature of the process after a careful bath deoxidisation by Mn, Al and Si addition was 1673°C in the furnace and 1620°C in the ladle. The temperature of this process was between 1590 and 1600°C.

After the tapping, the ingots were heated again at a rolling initial temperature of 1150°C. The final rolling temperature was between 950–1000°C. The final thickness was 3.5 mm and the hardness was $H_B = 283$. Upon completion of the rolling, the steel underwent a thermal treatment process to set the mechanical properties at the usually recommended ones under the Cor-ten A steel specifications (ASTM A-588 and A-242):

- Austenitised treatment: $T = 870/880^\circ\text{C}$ for 10 minutes.
- Water cooling at room temperature.
- Tempering at 750°C for 1 hour.
- Cooling inside furnace down to 400°C , then in the air.
- Final hardness of $H_B = 160$, corresponding to a resistance to rupture of $53 \text{ kg}\cdot\text{mm}^{-2}$ (52 MPa).

4 Open air exposure test

Long-lasting tests were carried out at the urban site of Villa Martelli’s outdoor test station [16]. Specimens were obtained from 45 mm wide and 300 mm long hot-rolled material of 3.5 mm thickness and from the same cold-rolled of 2 mm thickness. Holes of 22 mm diameter were made to set the samples in the same frame insulators, which were used in the previous tests (Fig. 1) [17]. The superficial preparation was the sanding up to Sa3 grade of SIS 05 59 00 standard (1967) and weighing the samples. Three samples exposed over 3, 6, 9, 12, 18, 24,

30, 36, 42, 48, and 60 months were removed each time, and after measuring their electrochemical potential in situ [18], they were weighed (for weight increase).

Besides there were samples exposed over 35 years and the results were obtained by optical microscopy, electron scanning and electron probe microanalysis, following the same techniques which were applied to the those samples exposed over 60 months.

Then, acid pickling was carried out at 80°C in a HCl solution (50%) with urotropine (0.1%) as inhibitor of steel attack. The samples were weighed at intervals of 10 minutes each until achieving almost linear weight variations between 30 and 50 minutes, according to DP/8407 ISO standard. The ΔW (g) value was determined by the intersection of the line obtained by linear regression by minimum squares with the vertical axis (Fig. 2) [19].

Figure 1: PA steel outdoor test at Villa Martelli's urban site.

Figure 2: Weight loss based on pickling time and pertinent linear regression.

Three hot-rolled PA steel specimens were exposed for 5 years in Villa Martelli's station. The results were graphically represented by the equation

$$\Delta W = kt^n \tag{1}$$

The constants k and n were determined from experimental data by regression analysis; the results are shown in Table 2.

Table 2: Constants of the linear regression.

Steel	Thickness		Values
PA hot-rolled	3 mm	k	1.2177
		n	0.1652
PA cold-rolled	2 mm	k	1.9232
		n	0.3641

As shown in Fig. 3, the values of exponent n for hot-rolled PA steel are lower than those for Cor-ten A steel and the QST 52 non-weathering steel, which were determined in previous tests [17].

Figure 3: Time-based weight loss of hot-rolled PA steel, extrapolated at 10 years.

Figs. 4–7 show the weight loss ΔW (g) in relation to the weight of the corrosion products that form the patina as well as the line of experimental data obtained by linear regression at Villa Martelli's urban site. In those same figures, two additional lines can be seen passing through the coordinate origin; these correspond to two extreme cases of patina chemical composition. If all the Fe dissolved in the corrosive process had combined and formed FeOOH , the representative points would have been located on the line with the lowest slope; if it had been fully combined forming magnetite, they would have been located on the line with the highest slope relative to the horizontal axis.

Figure 4: Hot-rolled PA steel in urban site: a) Regression; b) Fe_3O_4 ; c) FeOOH ; d) $0.925 \text{ FeOOH} + 0.075 \text{ Fe}_3\text{O}_4$.

Figure 5: Cold-rolled PA steel in urban site: a) Regression; b) Fe_3O_4 ; c) FeOOH .

Since a mixture of the two compounds forms the patinas, the representative points should be located in the area between these two boundaries.

The abscissa difference between the line resulting from linear regression of experimental data and the lines pertaining to Fe_3O_4 and FeOOH provides the extreme values of corrosion products weight loss by rain wash. If the experimental result for hot-rolled PA steel is compared with those for Cor-ten A steel and QST-52 steel (Figs. 6 and 7) [17], it will be noticed that the corrosion products that are let loose from PA steel are decreased relative to those from Cor-ten A steel and non-weathering steel, when they are all exposed to open air.

The metal weight swept away by dew or rain-wash may be estimated as follows:

The difference between the abscissa W_P of the line obtained by regression from experimental data for ΔW (g) and the one corresponding to the FeOOH (W_c) – as the most unfavourable case – represents the weight loss by wash ΔW_L :

$$\Delta W_L = W_c - W_P$$

Considering the abscissas as functions of the common ordinate ΔW (g), the weight loss of the specimens is given by

$$\Delta W_L = (b_c - b_p) \Delta W \quad (2)$$

where b_c and b_p are, respectively, the gradients of the FeOOH line and the line obtained by regression from experimental data relative to the ΔW vertical axis.

Figure 6: Hot-rolled Cor Ten A steel in urban site: a) Regression; b) Fe₃O₄; c) FeOOH.

Figure 7: Hot-rolled QST – 52 steel in urban site: a) Regression; b) Fe₃O₄; c) FeOOH.

According to eqn (1)

$$\Delta w(\text{g} \cdot \text{dm}^{-2}) = \frac{\Delta W(\text{g})}{A(\text{dm}^2)} = k't^n$$

where A (dm^2) represents the specimen area exposed to the open air; k and n are the regression coefficients depending on the outdoor exposure site and the material. Substituting from the above equation into eqn (2)

$$\Delta W_L = (b_c - b_p)Ak't^n = Kt^n \quad (3)$$

The values of the parameters in eqn (3) for the calculation of ΔW_L are shown in Table 3 and results are shown in Fig. 8.

Table 3: Values for parameters in the relations of eqns (3) and (4).

Steel	k'	n	A (dm^2)	b_c	b_p	K	nK
Urban site							
PA H.R.	1.2173	0.1652	2.87	1.5910	1.2834	1.0746	0.1775
PA C.R.	1.9232	0.3641	3.01	1.5910	0.9522	3.6979	1.3664
Cor-ten A H.R.	1.2734	0.1901	3.00	1.5910	0.8598	0.8598	0.5310

H.R.: Hot-rolled; C.R.: Cold-rolled.

Figure 8: Comparison between the total weight loss and the corresponding one due to dew and/or rain-wash at Villa Martelli's urban site. a) ΔW Cor-ten A; b) ΔW PA H.R.; c) ΔW_L Cor-ten A; d) ΔW_L PA H.R..

The rate of change of the weight loss by wash ΔW_L with respect to time is expressed by the function derivative:

$$\frac{d}{dt} \Delta W_L = nKt^{n-1} \quad (4)$$

with the value of nK given in Table 3 while the rate of change of ΔW_L can be seen in Fig. 8.

5 Corrosion potential in-situ measurements

The purpose of this technique is to use a non-destructive methodology to evaluate the characteristics of the corrosion products, which are formed on steels in the open air.

An agar KCl bridge-electrode holder is used to set the calomel-saturated reference electrode, and also the potential recording equipment, i.e. a millivoltmeter or high impedance recorder. As the heading suggests, the technique can be used to record the potential evolution of the specimens exposed to the open air, without removing them from the site.

In order to establish electric continuity on its corners, the sample is polished as little as possible on both sides, and contact is made through a small clamp, wire and plug to the recording equipment. The other equipment input is connected to the calomel-saturated reference electrode, which has been already set in the agar KCl bridge-electrode holder. The electrode holder open bottom is the specimen area, whose corrosion potential or open circuit (E_c) is to be measured. This is done in three different spots of the specimen starting in 10 minutes upon the closure of the circuit. Readings every 30, 60 and 90 s are recorded keeping the electrode holder in contact with every area of the specimen to measure. The potential is the result of the readings average at a same interval in the three chosen areas of the sample.

In the case of the Cor-ten A weathering steel exposed at Villa Martelli's outdoor test station for 15 years, the value obtained was +217 mV_{scc}, the same value as the one given by Pourbaix [18] for well weathered steels in industrial sites. According to the same technique, the average value of 3 samples at 35 years was +150 mV_{scc}.

6 Conclusions

Based on the long time experimental results, lasting 35 years, the conclusions are that a formulation containing the necessary micro-alloying elements (Cu, Cr, and Si) produces a protective corrosion film on the steel.

Experimental samples of PA steel were tested outdoors in an urban exposure site which produced a very effective passive patina. This aim was achieved through an increase of the density, great chemical reactivity and very small size of non-metallic inclusions with spherical morphology.

Steel with non-metallic inclusions modified by rare earth additions, particularly Ce, was considered to combine weatherability and better mechanical properties.

The outdoor tests were carried out over 35 years. The results were obtained by optical microscopy, electron scanning and electron probe microanalysis showing that the addition of micro-alloying elements modifies steel behaviour. This modification results in increased steel resistance to atmospheric corrosion.

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