Design of Experiment Based Prediction of Passivity Breakdown Potential for 304L Stainless Steel

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ABSTRACT

Stainless steels usually have a good corrosion resistance due to the protective passive film that forms on their surface, however these are prone to localized corrosion (pitting and crevice) which causes the breakdown of the passive film. To evaluate corrosion behavior of stainless steels in chloride containing environment Pedeferri diagram is proposed, aiming to define corrosion and passivity potential ranges as a function of the potential and the chloride content.

The aim of this paper is the study of the effects of three parameters (chloride content, pH and temperature) on pitting corrosion of AISI 304L stainless steel by using design of experiment approach.

The results revealed strong influence of pH, temperature and chloride concentration on the breakdown potential E_{pit}. The data achieved through potentiodynamic polarization tests were used for modelling a quadratic regression equation capable of evaluating E_{pit} as a function of the evaluated parameters, and for the setting - up of Pedeferri diagram.

Keywords: Stainless steel, pitting corrosion, crevice corrosion, potentiodynamic polarization test, design of experiment.

1 INTRODUCTION

Stainless steels can be used for a wide variety of industrial applications thanks to their resistance to general corrosion, mechanical properties, good workability and weldability. However, these steels are susceptible to some forms of localized corrosion attacks, such as pitting and crevice corrosion, in presence of oxygen and chlorides over a critical threshold [1,2].

The susceptibility of stainless steels to pitting and crevice corrosion depends on many factors, such as the steel chemical composition, its surface finishing, or the environmental conditions; the most significant of these are the chloride concentration, the temperature and the pH [3].

The corrosion behavior of stainless steels in a chloride containing environment can be evaluated by using Pedeferri diagrams, which report potential versus chloride content, allowing to identify potential ranges in which the material is corroding, passive or immune. According to Pourbaix, passivity can be perfect or imperfect: perfect passivity defines an area where the corrosion process can neither initiate nor propagate, while imperfect passivity is the region in which corrosion process cannot initiate but it can propagate if it already started [4].

Nowadays Pedeferri diagrams are included in ISO 12696 standard and they are currently used for the prediction of pitting passivity zones of carbon steel rebars, providing a useful tool for cathodic protection [5].

To determine the effects of chloride content, pH and temperature on pitting potential together with their interactions, nontraditional approaches based on design of experiment (DOE) methods are a viable alternative. Here we present a statistical approach based on the circumscribed central composition design (CCC), one of the most important DOE modes belonging to the response surface methodology family, in order to develop an empirical quadratic regression equation capable of predicting the pitting potential (the response), in different environments in terms of chloride content, pH and temperature (the considered factors) [6-9].

This mathematical model was exploited for the building up of Pedeferri diagrams for some fixed conditions, in order to evaluate the effects of the environmental parameters on the Pedeferri diagram of AISI 304L stainless steel.

2 EXPERIMENTAL

2.1 Laboratory Tests

Experimental tests were performed on AISI type 304L stainless steel. Cylindrical samples of 14 mm diameter were polished using SiC sandpaper sheets up to P1200 grits and then cleaned with acetone. The specimens were so stored in the open air for 24 hours and then they were immersed in different solutions in terms of pH and chloride content in order to measure the time required for getting a stable open circuit potential (OCP) value and so for the growth of a stable passive layer, i.e. the preconditioning time.

After the preconditioning tests, cyclic potentiodynamic polarization tests were performed in accordance with ASTM

G61 standard [10] by means of a Metrohm Autolab® M204 potentiostat, referring to SSC reference electrodes. All the performed tests were started from a value of - 0.1 V vs. OCP, and the potential was scanned (600 $mV\cdot hour^{-1}$) until the current density reached a value of 10 $A\cdot m^{-2}$; at this point, the potential scan was reversed, and the test stopped when the potential reached the initial potential value [11].

The different solutions in terms of chloride content were obtained from analytical-grade NaCl and distilled water. The pH was measured by a pH meter Delta OHM® HD 8705; acidic solutions were obtained adding HCl, whereas basic ones by the addition of NaOH.

The temperature was controlled by a vertex thermoregulator linked to a hot plate stirrer Velp Scientifica® AREX, with a precision of ± 2 °C, whereas tests at 10 °C were carried out by means of a refrigerated-heating circulator Julabo® F33-ME.

2.2 Experimental Design

Three factors (chloride content, temperature and pH) were considered during the experimental part.

Among the different DOE approaches, circumscribed central composite design (CCC) was selected for this work, since it allows both to manage different factors at the same time and to provide a quadratic regression equation [12] which correlates the three factors, together with their interaction, with the pitting potential; Minitab® is the software by which the planning of the CCC design and the analysis of the response were achieved.

For each factor, a maximum and a minimum value define the operative range; these were chosen considering the normal operating conditions in which this austenitic stainless steel is used, bypassing the circumstances in which it behaves as an active material. The working range of these three factors and their levels are shown in Table 1; the minimum and maximum values coincide respectively with the -1 and 1 level.

Starting from these levels, Minitab® provided all the experimental conditions needed to obtain a multiple regression equation able to correlate the pitting potential with chloride content, temperature and pH (Table 2).

	Units	Levels				
		-1.633	-1	0	1	1.633
Chloride content (in log_{10} scale)	ppm	1.367	2	3	4	4.633
Temperature	°C	10.5	20	35	50	59.5
pH	-	2.7	4	6	8	9.3

Table 1: Five-level coded values for each studied factor.

Number of test	Chlorides (ppm)	Temperature (°C)	pH
2	1000	35	2.7
2	100	20	4
2	100	50	4
2	10000	20	4
2	10000	50	4
2	23	35	6
2	1000	10.5	6
12	1000	35	6
2	1000	59.5	6
2	43000	35	6
2	100	20	8
2	100	50	8
2	10000	20	8
2	10000	50	8
2	1000	35	9.3

Table 2: Conditions for the 40 cyclic potentiodynamic polarization tests.

40 runs are required for the regression analysis; this value depends on the total number of run required for a CCC design, i.e. 20, multiplied by the repeatability, i.e. 2. The responses from these tests, that are the pitting potential values, were used for the setting-up of the regression model by means of the analysis of variance. A second-order model was chosen in order to consider the relationships between the evaluated environmental parameters.

3 RESULTS

Firstly, the preconditioning time, i.e. the time required for the growth of a stable oxide layer, was investigated by measuring the OCP over 24 hours. The development of a solution-formed passive layer, in fact, must be done in order to remove any trace of the air-formed oxide layer. Even if ASTM G61 standard [10] recommends a preconditioning time of 1 hour for a specimen of AISI type 304 in 3.56% (in weight) NaCl solution, it is not possible to fix a priori 1 hour of preconditioning due to the chosen operative conditions that differs from the ASTM standard ones.

Different conditions in terms of pH (from 2.7 to 9.6) and chloride content were analyzed. Firstly, it was noticed that in solutions having pH values higher than 3, all the corrosion potential values are in a range –0.1 to 0.05 V vs. SSC. However, it was noticed that is solutions having the same pH value the corrosion potential decreases as the amount of chlorides increases, showing that the material results more prone to pitting attack during the preconditioning time tests.

Based on the obtained results, the preconditioning time was set at 4 hours both for neutral or basic solutions (pH higher than 6) with a chloride amount higher than 10000 ppm and for acidic solutions (pH between 3 and 6) with a low chloride amount (lower than 100 ppm).

In case of acidic solution with a chloride content higher than 10000 ppm or strong acidic solutions (pH lower than 3) the chosen preconditioning time is 1 hour, otherwise for all the other conditions it was set at 24 hours.

Subsequently, all the cyclic potentiodynamic polarization tests were performed in accordance with the CCC design provided by Minitab®. From the cyclic potentiodynamic polarization curves, it is possible to identify E_{pit} with the potential value at which the current density sharply increases (Figure 1).

Pitting potential values were used for the elaboration of Pedeferri diagrams for further analyses of the effects of chloride ions content of the solution on the pitting and for evaluate whenever the stainless steel is safe or unsafe in specific environmental conditions (pH, temperature and chloride content). In particular, it was noticed that the relationship between the chloride content (in logarithmic scale) and the pitting potential is confirmed (Figure 2), so that E_{pit} decreases as the chloride ions concentration rises [3,13,14].

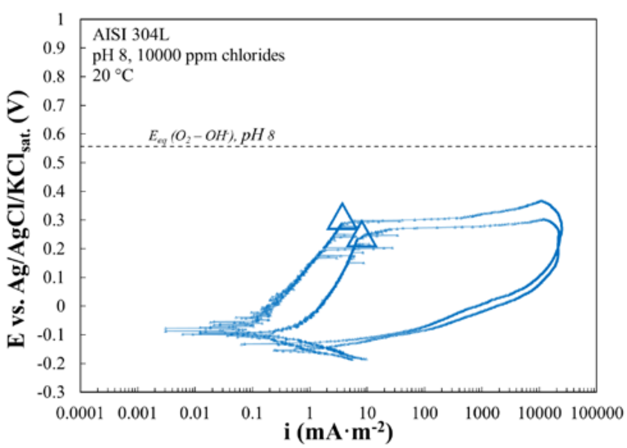

Figure 1: Cyclic potentiodynamic polarization curves in pH 8 solutions at 20 °C containing 10000 ppm of chlorides.

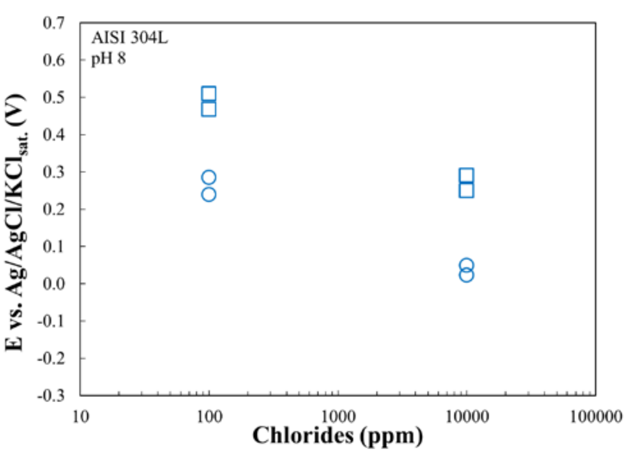

Figure 2: Pedeferri diagrams in pH 8 solutions at 20 °C (empty square) and at 50 °C (empty dot).

Different analyses of the experimental points were carried out in order to study the pH and temperature effects.

It was seen that, as the temperature increases, the pitting potential is decreased (Figure 2), whereas it increases as pH increases (Figure 3). In particular, the effect of temperature seems the most influent above the pitting behavior in pH 4 solutions, so that an increase in temperature induce a lowering of the pitting potential more evident than the one obtained with an increase of the chloride content.

After the analysis and the individuation of the pitting potential values, these ones were analyzed through Minitab® in order to implement the regression equation. Since it is a full quadratic second-order model, the software analyzed the effects of the single factors (pH, T and chlorides), the interaction among them (chlorides-T, pH-T and pH-chlorides) and also the squares of the factors (pH-pH, T-T and chlorides-chlorides). A default confidence level of 95% was chosen, to which corresponds an uncertainty degree of 5%.

Firstly, the analysis of variance was carried out, allowing to compare two or more groups (chloride, temperature, pH, pH - pH etc.) by comparing the variance within the groups and the variance between the groups.

The results are shown in Table 3. The column "Adj MS" reports all the mean sum of squares, whose square root is the standard deviation, whereas the column "F-Value" reports all the ratios between mean sum of square ("Adj MS") of each group and the error mean sum of squares (first column, last row). For each "F-Value", the software analyzed the Fisher distribution and provide a "P-Value", which is the probability to find a value above the correlated "F-Value". Being the confidence level of 95%, all the terms with a "P-Value" higher than 0.05 must be discarged since they are not statistically relevant. It is possible to see that the terms "Chloride·Temperature" and "Temperature·pH", which represent respectively the interaction effects between chloride content-temperature and temperature-pH, have a "P-Value" higher than 0.05, so they will be not included in the quadratic regression equation.

Source	**Adj MS**	**F-Value**	**P-Value**
Chloride	0.1544	203.61	0.000
Temperature	0.3675	484.62	0.000
pH	0.0746	98.36	0.000
Chloride*Chloride	0.0047	6.14	0.020
Temperature*Temperature	0.0546	71.98	0.000
pH*pH	0.0291	38.41	0.000
Chloride*Temperature	0.0029	3.85	0.060
Chloride*pH	0.0212	27.92	0.000
Temperature*pH	0.0003	0.40	0.530
Error	0.0008	/	/

Table 3: Analysis of variance of the elaborated CCC.

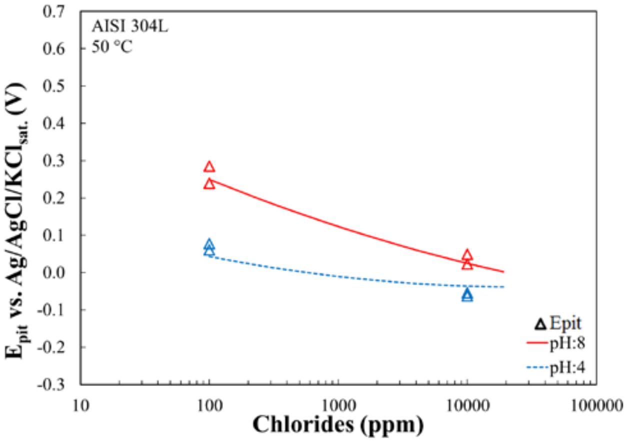

Figure 3: Comparison between experimental data and regression model by means of Pedeferri diagrams at 50 °C.

After the analysis of the variance, the software provides the regression equation together with its R^2 value which is equal to 0.9739:

$$E_{pit}\text{ (V vs. SSC)} = 0.082 - 0.076A - 0.117B + 0.067C + 0.014A^2 + 0.047B^2 + 0.045C^2 - 0.036AC \quad (1)$$

where $A=(Log[Cl–]–3)$, $B=[(T–35)/15]$ and $C=[(pH–6)/2]$.

In order to evaluate the reliability of the model (1), comparisons between the fitted pitting potential and the experimental E_{pit} value were carried out. In all the evaluated conditions a decrease in pitting potential as the chloride ions amount increases was confirmed [13,14].

It was also noted that the effect of the pH is quite significant, particularly in acidic solution scenario where the effects of chloride content seems less severe with respect to the basic solution scenario. Particularly, as the pH of the solution increases the slope of the regression equation rises due to an increase in the potential gap between the E_{pit} values of 100 ppm chloride-containing solutions chlorides and the ones containing 10000 ppm of chlorides (Figure 3).

Regarding the effect of temperature, the regression model confirms that, as the temperature increases, the pitting potential decreases. It was also observed that the slope of the regression equation does not change even if the temperature is modified, highlighting that the temperature effects are different from the pH ones.

However, it was observed that the model shows some inconsistencies for low pH solutions containing 10000 ppm of chlorides at 20 °C, showing a slight increase of pitting potential as the pH decreases below 5. The model shows also an increase in pitting potential between 50 and 60 °C, a trend in contradiction with the literature data [14], since the pitting potential decreases (or reaches a plateau) as the temperature increases.

4 CONCLUSIONS

In this paper it was confirmed that there is a strong influence of chloride content, pH and temperature on pitting potential. In particular, E_{pit} decreases as the chloride content, the acidity and the temperature increase.

Furthermore, the so – obtained regression equation seems to be promising due to its capability of predict the pitting potential value starting from the knowledge of the chloride content, the pH and the temperature of the solution, allowing to say that the used statistical approach can be considered valid. However, it must be considered that this equation based on the quadratic model is a preliminary version, due to anomalies in some of the harshest evaluated conditions.

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