Comparative evaluation on uniform corrosion resistance behaviour of ferritic stainless steels: experimental studies of electrochemical tests

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Ferritic stainless steels were exposed to electrochemical polarization tests in 1N sulfuric acid solution. Some critical parameter to uniform corrosion, as critical intensity (I_{cr}), passive intensity (I_p) and corrosion rate (V_{corr}), were determined from the polarization tests. To understand uniform corrosion behavior of this family of stainless steel, a new equation has been determined taking the most relevant elements (Ni, Cr, Mo and N) into account. An excellent correlation between predicted and experimental results was obtained. The development of the new equation is really useful to simulate the relation between the uniform corrosion and the chemical composition in a defined Ferritic Stainless Steel.

Keywords: Ferritic stainless steel, Uniform corrosion, Electrochemical tests, Nickel effect, Uniform resistance equivalent

INTRODUCTION

Nowadays, Ferritic Stainless Steels are at their height. They can be considered the most inexpensive and stable stainless steel in the market due to the absence of nickel in their chemical composition. It is true that Austenitic Stainless Steels are frankly developed because of their excellent mechanical properties and corrosion resistance. However, these grades are susceptible to high price variations, because of the nickel cost, which is one of their principal alloying elements. This fact makes Ferritic Stainless Steel an excellent option so as to substitute Austenitic in a large number of applications.

This report belongs to an extensive study of Ferritic Stainless Steels with the aim of giving a behavior ranking in each real working condition. With the final acquired knowledge, it can be possible to predict the comparative behavior of different Ferritic Stainless Steels in generalized corrosion. In particular, this report is based on the study of one environment that makes stainless steels suffer from uniform corrosion.

Uniform corrosion is the uniform thinning of a metal and does not penetrate very deep inside. Its mechanism in aqueous solution has been amply demonstrated. Anodic reaction takes place at anodic areas, dissolving the metal. The electrons flow from the anode to cathode in the metallic circuit.

Taking the duality metal-environment into account, in general it can be said that stainless steels correctly applied have an optimum resistance to this type of corrosion. However, this fact is not checked enough in Ferritic stainless steel as regards the effects of this environment in the comparative behavior of these grades.

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Paper presented at the 7th European Stainless Steel Conference - Como, 21-23 September 2011, organized by AIM

Electrochemical test is fast enough to characterize the uniform corrosion behavior of Ferritic stainless steels in a comparative way. The prediction of uniform corrosion behavior by means of electrochemical tests, based on the chemical composition, is the basic stage in order to acquire an effective control of corrosion, besides to be able to select the adequate Ferritic stainless steel for a defined application.

The objective of this paper is to determine a new equation based on the chemical composition, in order to be able to predict, in a simple way, uniform corrosion behavior of Ferritic stainless steels. With this purpose, some critical parameter to uniform corrosion, as critical intensity (I_{cr}), passive intensity (I_p) and corrosion rate (V_{corr}), were determined by polarization tests in sulfuric acid.

EXPERIMENTAL PROCEDURES

Cold rolled, annealed and pickled ferritic stainless steels have been selected with different chemical composition. A conventional austenitic stainless steel, type EN 1.4301, was used as reference.

Table 1 shows the chemical composition of the eight selected materials.

Specimens of 40x40mm^2 dimensions were polished up to a fine-grained surface finish (Grain #600).

As electrolyte a 1N sulfuric acid solution at 30ºC temperature was used[1-3].

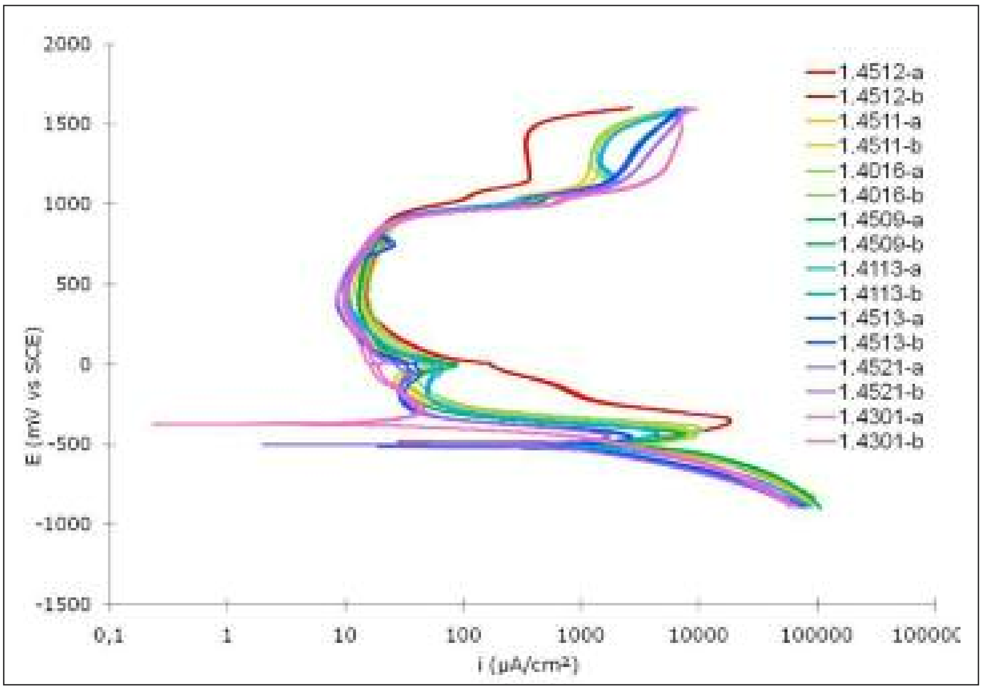
The tests were carried out in a potentiostate/galvanostate EG&G Parc model 273 by means of the software “model 352/252 SoftCorr II”. A flat corrosion cell was used to make the tests.

The acid solution was deareated with nitrogen for about 30 minutes before the start of each test.

Besides, throughout the test time, the solution was stirred and deareated with nitrogen. As reference a saturated calomel electrode (SCE) was used. The test was initiated at –0,9V vs. SCE and finished at 1,6V vs. SCE (Scan rate = 1,6mV/sec) [2-7].

At least two valid polarization curves were carried out for each material to ensure results reproducibility.

FIG. 1
Polarization curves of studied materials.
Curve di polarizzazione del materiale studiato.



	Weight %							
	C	Ni	Cr	Mo	Ti	Nb	Cu	N
EN 1.4016	0.056	0.23	16.26	0.02	0.004	-	0.05	0.0371
EN 1.4113	0.063	0.19	16.28	0.94	0.005	-	0.09	0.0289
EN 1.4512	0.011	0.20	10.93	0.02	0.212	-	0.04	0.0127
EN 1.4511	0.024	0.16	16.24	0.01	0.005	0.52	0.04	0.0127
EN 1.4513	0.027	0.40	17.33	1.15	0.500	-	0.05	0.0138
EN 1.4509	0.017	0.23	17.88	0.02	0.185	0.46	0.06	0.0214
EN 1.4521	0.029	0.21	17.66	2.11	0.078	0.42	0.07	0.0213
EN 1.4301	0.049	8.13	18.18	0.22	0.005	-	0.22	0.0585

TAB. 1 ***Chemical composition.***
Composizione chimica.

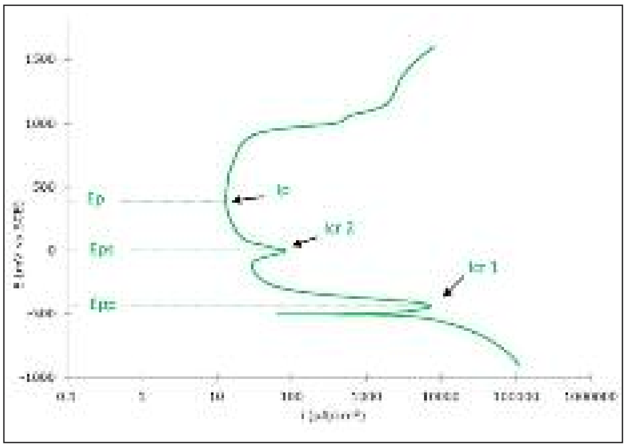


FIG. 2 ***Potentiodynamic polarization curve.***
Curva di polarizzazione potenziodinamica.

In figure 1, the potentiodynamic curves obtained in the sulfuric acid solution are shown.
The repeatability of the curves is very good. Austenitic stainless steel (EN 1.4301) shows a different behavior to the ferritic stainless steels. In this group, EN-1.4512 presents a very high critical intensity and the lower value of passive area.

RESULTS DISCUSSION

Uniform corrosion can be steady or irregular depending on how the face attack stand for, but, in any case, it becomes in a progressive aggression form and in a constant rate during the time in every point of the stainless steel surface exposed to the aggressive environment. If the media is aggressive enough, the protective film of the surface can be destroyed. This fact leads to the uniform attack (unstable passivity), causing a thickness loss, so a decrease of the mechanical resistance.
In these polarization curves, after reduction area the current increases and a maximum in the intensity occurs, named critic "Icr1", which corresponds to the primary passive potential "Epp".
This current value (Icr1) is one of the most interesting parameter to evaluate generalize corrosion (figure 2).
After Icr1, the passive region appears. The current density falls significantly in this zone until the passive intensity "Ip" which corresponds to the passive potential "Ep" (figure 2).[1-3, 8].
In the ferritics stainless steels appear a second important current increase (Icr2), between Icr1 and Ip (figure 2). This point correspond to the secondary passive potential "Eps"
In general, stainless steel is the more resistant in a defined corrosive media, the lower the value of Critical Intensity and Passive Intensity and the larger the range of potentials in the passive zone.
To evaluate the resistance to uniform corrosion of ferritic stainless steels, the chemical composition must be taking in account. In particular, this study must be focused on the alloying elements that can be considered most influential in uniform corrosion of sulfuric acid.
Some authors suggest that the rise of nickel, molybdenum and copper contents increases the corrosion resistance in sulfuric acid media. In some cases, they refer to the nitrogen as influential element too. Besides, chromium is the basis element of stainless steel and it protects from uniform attack [14-19].

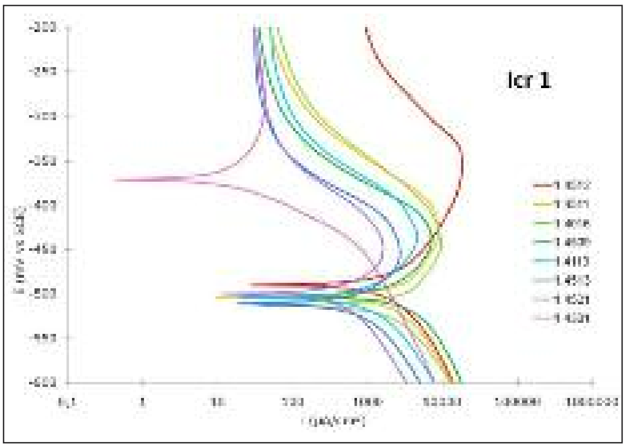


FIG. 3 ***Icr1 area.*** *Area Icr1.*

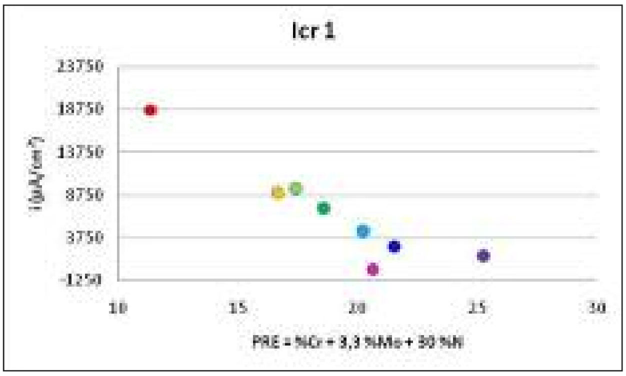


FIG. 4 ***Icr1 vs PRE.*** *Icr1 vs PRE.*

To estimate and quantify the influence of aforementioned elements in uniform corrosion resistance of Ferritic stainless steel, nickel, chromium, molybdenum and nitrogen have been considered as the most relevant alloying elements. In this case, the effect of copper have not been considered due to the no variation in this element.
The relation between chromium, molybdenum and nitrogen with corrosion resistance of stainless steel is defined by the "Pitting Resistance Equivalent" (PRE), a well-known parameter used in the study of pitting corrosion [7, 9-14]. In this study the relations between Icr1 vs PRE, Icr2 vs PRE and Ip vs PRE have been studied. On the other hand, the influence on nickel has been included and a new value "URE" has been studied.

Critical Intensity 1.
In figure 3 the Icr1 area is observed.
The correlation between Icr1 vs PRE and Icr1 vs URE is represented in figure 4 and 5.
Although the ferritic stainless steel generalize corrosion behavior show a good correlation with "PRE" (%Chromium + 3,3%Molibdenum + 30%Nitrogen), in order to relate with austenitic stainless steels, the effect of Nickel have been taking into account. A new value have been established "URE" (%Crhomium + 3,3%Molibdenum + 30%Nitrogen + %Nickel) .There is a good correlation between Critical Intensity 1 versus Chromium, Molibdenum, Nitrogen and Nickel content.

Critical Intensity 2.
In figure 6 the Icr2 area is observed.
The correlation between Icr2 vs PRE and Icr2 vs URE is represented in figure 7 and 8.

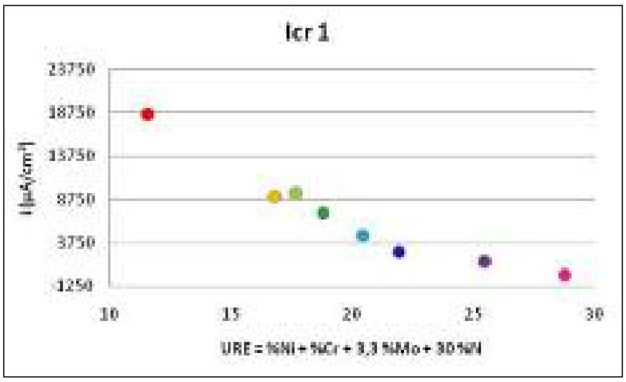


FIG. 5 ***Icr1 vs URE.*** *Icr1 vs URE.*

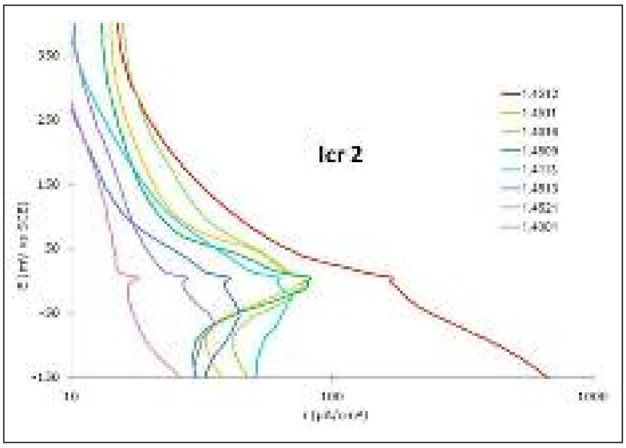


FIG. 6 ***Icr2 area.*** *Area Icr2.*

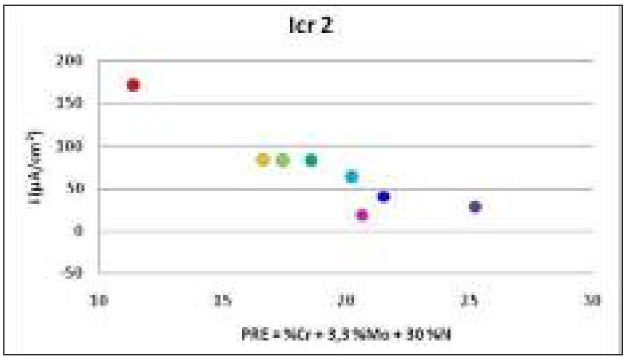


FIG. 7 ***Icr2 vs PRE.*** *Icr1 vs PRE.*

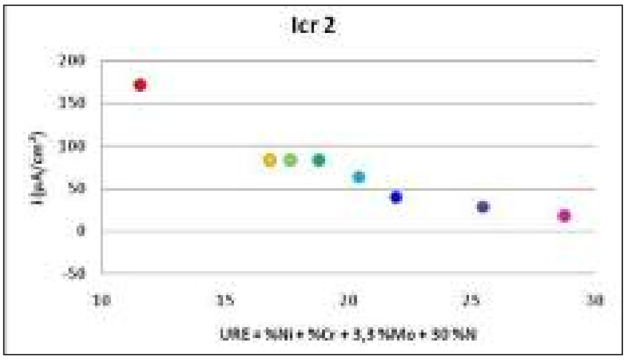


FIG. 8 ***Icr2 vs URE.*** *Icr1 vs URE.*

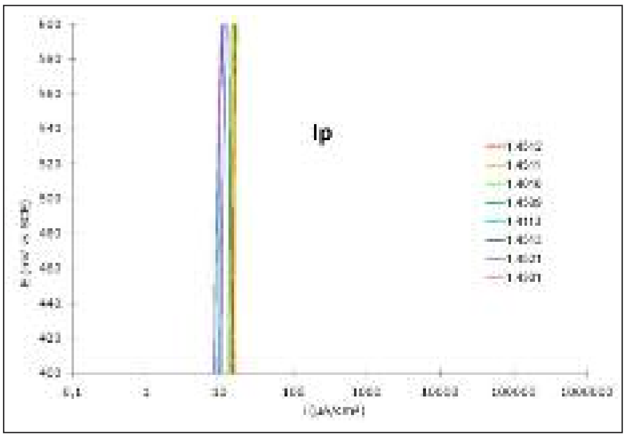


FIG. 9 *Ip area.* *Area Ip.*

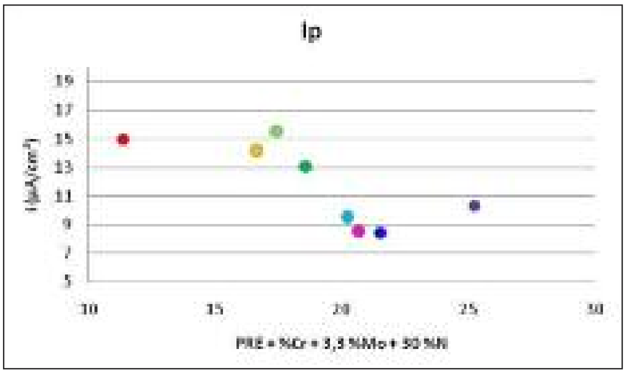


FIG. 10 *Ip vs PRE.* *Ip vs PRE.*

As in the case of Critical intensity 1, there is a good correlation between Critical intensity 2 and the Uniform Resistance Equivalent "URE".
Ferritic stainless steels generalize corrosion behavior will depend on Cromium, Molibdenum, Nitrogen and Nickel contain.

Passivation Intensity.
In figure 9 the Ip area is observed.
The correlation between Ip vs PRE and Ip vs URE is represented in figure 10 and 11
Although a light tendency is observed with the increase of Uniform Resistance Equivalent, the current intensity for the passive area is very similar for all the stainless steels. The values go from 8 to 15 µA/cm2.

Corrosion Velocity.
The corrosion velocity obtained from Icorr is represented in figure 12 and 13.
In that case it is not possible to obtain a good correlation for Vcorr. The value obtained for ferritic stainless steels EN-1.4016 and EN-1.4509 is too high for the expected value.
Stainless steels are passive materials and after critical intensity, the current fall significantly. For this reason, to obtain a good corrosion intensity value is difficult. The anodic curve does not show an exponential behavior like no-passive metals. Also the potential where the steady state in sulfuric acid media is reached "Ecorr", the current that circulate between the anode and the cathode at this corrosion potential, is difficult to measure accurately.

CONCLUSIONS
Ferritic stainless steels were exposed to electrochemical test in

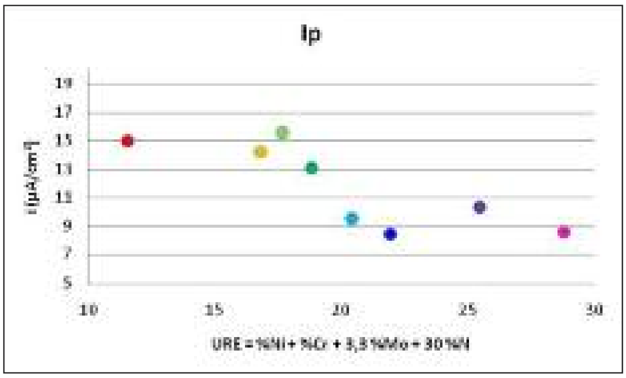


FIG. 11 *Ip vs URE.* *Ip vs PRE.*

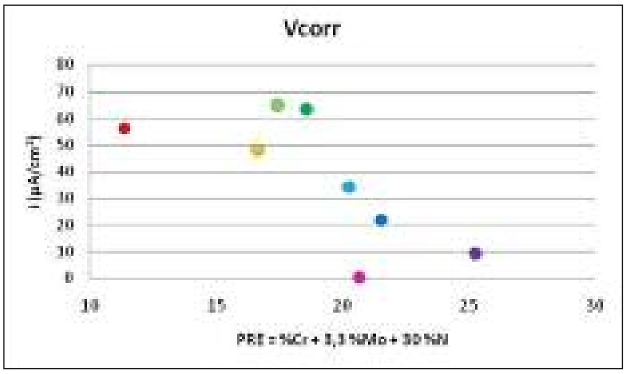


FIG. 12 *Vcorr vs PRE.* *Vcorr vs PRE.*

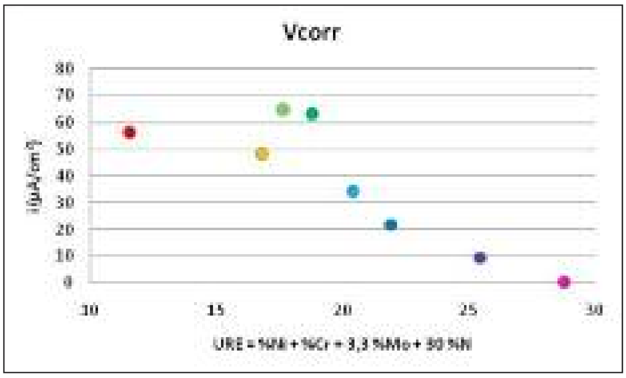


FIG. 13 *Vcorr vs URE.* *Vcorr vs PRE.*

1N sulfuric acid solution so as to evaluate the uniform corrosion resistance.
A new equation was developed with the intention of predicting the behavior of Ferritic stainless steels as regards uniform corrosion resistance, taking only some alloying elements of their chemical composition into account. This equation, named "Uniform Resistance Equivalent" (URE), consider nickel, chromium, molybdenum and nitrogen as the most important elements in order to characterize the uniform corrosion behavior of Ferritic Stainless Steels.

$$URE= \%Ni + PRE = \%Ni + \% Cr + 3.3\% Mo + 30\%N \quad (1)$$

In general, Ferritics stainless steels in contact with sulfuric acid solution exhibit a correlation with the URE value, increasing their uniform corrosion resistance when this parameter increases too. In this case, it has not been able to study the influence of copper element, because there are not significant variations in its composition.

The data treatment has confirmed that the most important value to evaluate generalize corrosion by means of electrochemical tests, is the critical intensity (Icr1 and Icr2).
On the whole, it is demonstrated that the URE is an interesting parameter to determinate the behavior of Ferritic stainless steels in this environment, showing the improvement of uniform corrosion resistance with the increase of URE value. In short, it is a really interesting option to have a quick idea of the behavior of Ferritics in a sulfuric acid environment.

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Abstract

Valutazione comparativa del comportamento uniforme di resistenza alla corrosione generalizzata degli acciai inossidabili ferritici: studi sperimentali di prove elettrochimiche

Parole chiave: acciaio inossidabile – corrosione – prove

Gli acciai inossidabili ferritici sono stati esposti a prove di polarizzazione elettrochimica in soluzione di acido solforico 1N. Mediante le prove di polarizzazione sono stati determinati alcuni parametri critici della corrosione generalizzata, come intensità critica (Icr), intensità di passività (Ip) e velocità di corrosione (Vcorr). Per comprendere il comportamento a corrosione generalizzata di questa famiglia di acciaio inossidabile, è stato determinata una nuova equazione prendendo in considerazione gli elementi più rilevanti (Ni, Cr, Mo e N). E' stata ottenuta una eccellente correlazione tra i risultati previsti e quelli sperimentali. Lo sviluppo della nuova equazione è molto utile per simulare la relazione tra corrosione generalizzata e composizione chimica in uno specifico acciaio inossidabile ferritico.