Short Communication

Corrosion, Microstructure and Mechanical Performance of Ultra Low C/Cr Stabilized Steel

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An experimental controlled rolled ultra-low carbon steel sheet with 0.035 wt.% Cr addition (ULC-Cr/stabilized steel) was evaluated in different concentration NaCl solution (neutral pH) to assess their corrosion performance. The mechanical properties were obtained by conventional monotonic axial test. Techniques were used to evaluate the corrosion behaviour such as electrochemical impedance spectroscopy (EIS), and Potentiodynamic polarization (PP). Characterization of microstructure was carried out in the steel by means of TEM and optical microscopy. The results show that ULC-Cr/stabilized steel in the as-annealed condition has the higher corrosion resistance along better microstructural and mechanical properties. The corrosion and mechanical properties observed are attributed to the presence of a high density of precipitates, and phases which induces chemical stability. In the same way, the rolling and annealed process induces a structural stability of the no passive-permeable film preventing the growth of corrosive pittings as the diffusion of metal ions, which reduces the corrosion rate.

Keywords: Ultra low carbon steel; Cr stabilized; Corrosion resistance; Electrochemical techniques, Mechanical properties.

1. INTRODUCTION

The Interstitial free (IF) and/or ultra-low carbon (ULC) steels were developed on the last decades as an alternative to improve the formability in flat products for extra deep drawing. The
carbon and the nitrogen in the IF steel normally are in the condition of carbonates and nitrates of Ti, Nb and Al, depending on the steel kind. The precipitate morphology and the hot-rolling product microstructure are controlled by the hot processing condition, as: reheating temperature, finishing, reduction, pass numbers, rolling speed and rate of cooling. These steels present an excellent formability together with non-aging properties, which it has given opportunity to the automotive industry to produce high formability parts more easily and with high resistance [1]. As characteristic the IF and ULC steels have excellent mechanical properties such as ductility, high \( r_m \)-values (Lankford mean value), high \( n \)-value, (strain hardening exponent) and high tensile strength.

Recent researches related to IF and ULC steels, mainly focused in microstructural characterization and mechanical properties in terms of fatigue, 0.2% yield strength, ultimate tensile strength, percentage elongation, the average Lankford value and creep properties [2-7]. Moreover, corrosion behavior of these steels has not been studied extensively.

This research presents the results of the corrosion behavior, microstructure and mechanic properties, development of the ULC/Cr stabilized steel, after 7 passes lamination, with different rolling temperatures and 0.035 % Cr addition. The ULC/Cr stabilizer steels in the as-annealed condition exhibit an excellent deep-draw ability, which is used mainly in automotive applications and household appliances. However only exist to limited knowledge of the corrosion behavior of defined particular microstructures and none of the corrosion properties of this material in a present form (thermomechanical condition and Cr content).

2. EXPERIMENTAL

The composition of the experimental Cr stabilized ULC steel is as follow: 0.015 wt.% C, 0.11 wt.% Mn, 0.050 wt.% Al, 0.040 wt.% Cr, 0.030 wt.% Si, 0.008 wt.% P, and 0.004 wt.% N\(_2\), S, Ni respectively. It was produced using 100% sponge iron into an electric arc furnace, vacuum degassed and continuously casted in order to obtain ingots of about 200 mm in thickness. The resulting slabs were reheat at 1100 °C before lamination to a rolling start temperature of 1200 °C, finishing the hot rolling operation at 874 °C to 3.42 mm in thickness, continuously plates were cold rolled at room temperature to 0.56 mm, which resulted in 83.6 % in total reduction, complete lamination was conducted up to 7 passes. Finally specimens were annealed for 5 min at 750 °C. Mechanical properties were obtained by tensile tests realized according to ASTM E-8M standard, using a servohydraulic Instron test machine on fully annealed specimens, with a deformation rate equals to 1s\(^{-1}\). The anisotropy coefficients were obtained using two extensometers, localized on the transverse and longitudinal directions. The transverse extensometer was responsible for the determination of the deformation on the width direction and the longitudinal, with 25 mm of useful length, was used for the determination of the deformation on the length direction of the test specimen. After this deformation, the final length and width were measured. The \( r_m \) and \( n \) values were determinate according to ASTM E 517 and ASTM E 646 standard test methods respectively.

Transmission electron microscopy (TEM) investigations were performed with a LEO 1450 VP electron microscope operated at 200 kV. Specimens for TEM were mechanically cut from the
uniformly deformed middle sections of ULC-Cr/stabilized steel processed specimens normal to the rolling direction. Thin foils were prepared by electro polishing in 6% HClO₄ solution in methanol at room temperature.

Corrosion measurements were carried out at room temperature using a conventional three-electrode ACM Gill-AC potentiostat with a Ag/AgCl electrode as a reference electrode.

The electrochemical test were obtained in neutral solutions of 3.5% NaCl (pH 9.2), 22% NaCl (pH 10.6). All solutions were prepared with distilled water and analytical grade reagents. Prior to the potentiodynamic tests, the specimens were kept in the test solution for 10 min at open circuit potential (OCP). Potentiodynamic curves were obtained by potential sweeps of 1mVs⁻¹, in EIS measurements an alternating current (AC) signal, with an amplitude of 10 mV, was applied at the open-circuit potential (OCP) in the frequency range of 1 MHz to 10 KHz. The LPR analysis was conducted following the recommendations of the ASTM G 59-91 Standard, polarizing between -100 and +100 mV.

3. RESULTS

3.1. Microstructure and mechanical properties

Figure 1 shows the microstructure observed from the Cr stabilized steel samples obtained after annealed treatment at 750 ºC. A fully recrystallized microstructure was obtained with polygonal ferritic grains with the mean grain size of 15 µm and a fine dispersion of precipitates.

![Figure 1](image1.png)

**Figure 1.** Microstructure observed in ULC-Cr/stabilized steel annealed at 750 ºC.

Figures 2a and 2b show the TEM image and microanalysis respectively, and they reveal that precipitates composition correspond mainly to Fe₃C and Cr₃C₂ type carbides, with an average size of 1 µm - 1.5 µm. On the other hand it observed a major precipitated density on annealed steel that in rolling condition, this expects a solution carbon decrease to form chromium carbides.
The table 1 presents the values of mechanical properties for the ULC-Cr/stabilized steel such as, yield point 0.2% ($Y_s$), ultimate tensile strength (UTS), % elongation, $r_m$ and $n$. Figure 3 shows the stress-strain behavior of Cr stabilized steel annealed at 750 ºC. The microstructural and mechanical results showed that Cr stabilized steel presents similar mechanical properties with regard to formability of Ti and/or Nb stabilized IF steels [4,5,8-12] what means, high elongation value from 35% to 50% and $r_m$ higher than 2.

![Micrograph](image)

**Figure 2.** (a) TEM micrograph showing the precipitate morphology and (b) TEM precipitate microanalysis

<table>
<thead>
<tr>
<th>Annealed temperature (°C)</th>
<th>$Y_s$ 0.2% (MPa)</th>
<th>UTS (MPa)</th>
<th>Elongation (%)</th>
<th>$r_m$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>750</td>
<td>347±15.1</td>
<td>376±7.3</td>
<td>51.7±1.8</td>
<td>2.08±0.09</td>
<td>0.31±0.04</td>
</tr>
</tbody>
</table>
Figure 3. Stress-strain curve for the experimental ULC-Cr/stabilized steel annealed at 750 °C.

3.2. Electrochemical properties

$E_{corr}$ (corrosion potential), $I_{corr}$ (corrosion current density) and $b_{a,bc}$ (cathodic Tafel slope) were evaluated as indicator of corrosion behavior from the potentiodynamic curves using the Tafel extrapolation.

Fig. 4 shows potentiodynamic polarization curves in NaCl solutions for the Cr stabilized steel specimen. With increasing concentration of NaCl, the $I_{corr}$ values increases while $E_{corr}$ decreases. The $I_{corr}$, $E_{corr}$, $b_{a,bc}$ and EIS results in both solutions are presented in Table 2.

Figure 4. Potentiodynamic polarization curves in 3.5% and 22% NaCl solution for the ULC-Cr/stabilized steel.
As seen on fig. 4 any of polarization curves exhibit passivation behavior, only can appreciate a continuous dissolution process. In Nyquist plot of EIS test (Fig 5.) shows that in both NaCl solutions the principally corrosion mechanism for the ULC-Cr/stabilized steel is charger transfer, denoted by the tendency to form semicircles on $Z'$ and $Z''$ axis.

On the other hand the impedance modulus values ($|Z|$) (Table 2) is consistent with $I_{\text{corr}}$ measurements and NaCl solution content. The corrosion rate increases due to the increase in Cl$^-$ ion, and $|Z|$ decrease generating a more conductive solution.

**Table 2.** Corrosion parameters for the experimental low C-Cr/stabilized steel in NaCl solutions by PP and EIS.

| Solution | $E_{\text{corr}}$ | $I_{\text{corr}}$ | $|Z|$ | Corr rate | $ba$ | bc |
|----------|------------------|------------------|------|-----------|-----|----|
|          | (mV$_{\text{SCE}}$) | (A-cm$^2$) | (Ohm-cm$^2$) | (mm-year) | (mV/decade) | (mV/decade) |
| 3.5%NaCl | -287.54          | 2.06E-06        | 9020 | 0.0000191 | 146 | -240 |
| 22%NaCl  | -403.41          | 2.92E-06        | 4153 | 0.0000259 | 158 | -265 |

**Figure 5.** Nyquist plot for the ULC-Cr/stabilized steel in NaCl solutions.

**3. DISCUSSION**

The steel stabilized with Cr within a NaCl solution containing 22% of this salt exhibit upper corrosion rates compared with the same steel in 3.5% NaCl solution, as showed by their corrosion current measurement. Because water reduction is the only cathodic reaction that exist in the neutral solution with NaCl, the corrosion rate depend on Fe$^{2+}$ diffusion and the speed of H$_2$O can reaches steel surface. Thus any change in NaCl concentration will affect the reaction rate. While hydrogen development at higher rates in more acid regions in the solution increases the cathodic reaction.
The more hydrogen ions in the neutral solution makes the hydrogen electrode equilibrium potential nobler according to the following relation:

$$E_{H/H^+} = 0.0 - 0.059pH,$$

Even though $I_{o_{H/H2O}}$ continue constant, hence $E_{H/H^+} - E_{Fe/Fe^{2+}}$ turn to be larger and the subsequent corrosion current rises. This is the reason of the increment in the steel stabilized with Cr corrosion rate in NaCl solution while decreasing the pH in neutral solutions. Furthermore, the addition on Cl- ions improves the solution conductivity than in solely dilute NaCl solution.

On the other hand, the $E_{corr}$ measurements for the experimental low C/Cr stabilized steel (Table 2) showed that in both solutions, the steel exhibits higher equilibrium potentials and lower $I_{corr}$ as compared to typical IF steels in similar environments reported in corrosion studies [13,14]. The possible mechanisms for the corrosion behavior of the ULC-Cr/stabilized steel in the two different solutions are discussed on the basis of the electrochemical potentials of the steel, the thermodynamic stability of the individual alloying elements in the steel [15] (Pourbaix diagram) and the literature on the corrosion properties of related steels [16,17]. It is reported that chromium in steels forms stable chromium oxide due to high passivity coefficient and therefore increase their electrochemical corrosion resistances [18]. Hence, 0.035% Cr addition to steel is expected to promote the passivation ability. However according to our results the chromium addition to typical IF steels causes a shift in $E_{corr}$ towards to the less noble potential as compared to ultra-low C-Cr/stabilized steel and exhibit a continuous dissolution mechanism. This is suggested to be due to formation of a microgalvanic pair to the combined effect of Cr and C presents on formed precipitates which seems to promote the anodic ($Fe \rightarrow Fe^{2+} + 2e^-)$ reaction delay, this behavior tends to enhance the corrosion resistance of the ULC-Cr/stabilized steel. This assumption is in accordance with the study of S.Capelo et.al related to Cr galvanic cells potentials [19].

In alkaline solution, chromium precipitates to $Cr(OH)_{3}\cdot nH_2O$ which is only slightly soluble in pH $> 9$ to give dichromate ions $HCrO_2$ which does not passivate [15]. However Nyquist plot (Fig. 5.) shows in both NaCl solutions a charge transfer process, mainly attributed to the effect of a double layer theory [20] related to the presence of a thin film over steel surface. The steel sheet in both solutions present higher $Z''$ values as shown in their corresponding Nyquist diagrams on Figure 5. Thus demonstrating the existence of a large Capacitance (Cdl) at metal interphase with the solution that indicate the occurrence of a charge transfer big enough to be associated with the generation and permanence of a permeable and no passivating film. A valuable parameter is the Capacitance to measure the oxide layers semiconductor properties that are related to the alloys corrosion resistance [21]. In the study of all the test solutions their Nyquist plots started at $Z' =0$ indicating that solution resistance Rs is equal to zero. Thus the Na and Cl ions were available to move free in the electrolyte. Ions mobility were accordance with Polarization Curves (Fig 4) showing diffusion of generated oxide to the solution interacting with steel surface to develop the layer. As evidenced by their impedance modulus $|Z|$ (Table 2) are greater in 3.5% NaCl with respect to 22% NaCl solution. Furthermore, the anodic and cathodic Tafel slopes of polarization curves at 22% NaCl concentration are larger than 3.5%
NaCl concentration which indicates that in 3.5% NaCl solution, the anodic and cathodic processes are to some extent inhibited due to the formation of more protective no passive-permeable layer.

In summary the improvement of corrosion resistance of the experimental ULC-Cr/stabilized steel is strongly determined by the behavior of microstructure after annealed and Cr precipitates. This mean that 0.035 wt.% Cr addition promotes a diffusion corrosion mechanism that is much better in corrosion properties point of view in comparison with pitting corrosion catastrophic failure in automotive industry applications, almost has been corroborate that formability and mechanics properties are in accordance with requirements to forming equipment.

4. CONCLUSIONS

The microstructure, mechanical and corrosion characteristics of the ULC-Cr/stabilized steel after rolling and annealed at 750 ºC, were examined using the transmission electron microscopy, mechanical test, potentiodynamic polarization and electrochemical impedance spectroscopy measurements. The following conclusions can be drawn from this research:

1.- The processing conditions generate mechanical properties in the ULC-Cr/stabilized that can be considered as an excellent formable steel sheet comparable to IF steels stabilized with Ti and/or Nb.

2.- The results obtained, indicate that 0.035 wt.% Cr additions produce a higher corrosion resistance for the ULC-Cr/stabilized steel than typical IF steels with 0.010 wt.% Cr.

3.- The resistance of the material against the formation and growth of corrosion pits in NaCl solutions is characterized by the formation of a no passive-permeable layer.

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References

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