Evaluation of 475 °C embrittlement in UNS S32750 super duplex stainless steel using four-point electric conductivity measurements

Gildardo Gutiérrez-Vargas a, Alberto Ruiz a,*, Víctor H. López-Morelos a, Jin-Yeon Kim b, Jorge González-Sánchez c, Ariosto Medina-Flores a

a Instituto de Investigación en Metalurgia y Materiales, Universidad Michoacana de San Nicolás de Hidalgo, Edificio U, Av. Francisco J. Múgica S/N, C.P. 58030, Morelia, Michoacán, Mexico
b GWW School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA, 30332, USA
c Center for Corrosion Research, Autonomous University of Campeche, Av. Agustín Melgar s/n, Col. Buenavista, C.P. 24039, Campeche, Mexico

1. Introduction

Due to their excellent mechanical properties, good machinability, and high corrosion resistance, duplex stainless steels (DSSs) are widely used in oil, chemical, nuclear, and other power generation industries [1]. In the industry, the standard grade 2205 DSS (UNS S32205/S31803) is commonly used which typically has 22Cr, 5Ni, 3Mo, and 0.18 N wt. % as the main alloying constituents; the alloy has a higher ultimate tensile strength (UST) compared to the 304 austenitic stainless steel. The 2507 SDSS (UNS S32750) is a newer grade that exhibits a higher alloying content 27Cr, 7Ni, and 3.8Mo which conveys a higher pitting and stress corrosion resistance as well as higher tensile properties in comparison to the 2205 DSS [1]. Their superior properties are due to their two-phase ferrite/austenite duplex microstructure provides synergistically both the mechanical and electrochemical properties of the ferrite and those of austenite. However, the properties of DSSs deteriorate when exposed to a temperature range between 280 °C and 550 °C [1–5]. In the literature, it is generally accepted that 475 °C embrittlement the deterioration of mechanical and physical properties can be caused depending on the temperature and chemical composition by either spinodal decomposition and/or nucleation and growth of δ’ (Cr-rich) phase [6,7]. It has been reported that the embrittlement rate is highest at 475 °C, therefore it is called 475 °C embrittlement [8,9] and the phenomenon has been deeply investigated in numerous studies [2,8,10,11]. Work by Grobner [3] reported that nucleation and growth occur for Cr contents lower than 17%, spinodal decomposition will occur otherwise. In the case of SAF2507 super DSS, a work by Hattestrand et al. [12] reported that depending on the temperature and aging time δ’ may form in the

* Corresponding author.
E-mail address: alberto.ruiz@umich.mx (A. Ruiz).

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ferrite phase either through nucleation-and-growth or spinodal decomposition and whether the material is plastically deformed.

Numerous reports on the effects of temperature and aging time on the mechanical properties indicate loss of impact energy and increase in hardness of different duplex alloys [13–16], changes in tensile properties and ductility properties [17–19], besides the loss of corrosion resistance has been reported at long holding times [4,5]. Interestingly, in the case of short aging times, an increase in the pitting corrosion resistance has been reported to occur at 8 h in the case of 2507 SDSS [20].

It has been reported that other reactions in the ferrite such as the precipitation of the intermetallic G-phase can affect the electrochemical response and also partially contribute to the embrittlement. This phase is a ternary intermetallic compound and reports show that in a DSS it precipitates at grain boundaries and dislocations in both ferrite and austenite phases when aged at low temperatures [18,21–23]. For instance, Li et al. [22] reported that G-phase homogeneously precipitates in ferrite of DSS after long-term thermal aging in 300–450 °C. Precipitates of this phase were observed in the material aged at 450 °C for 3000 h [22] and it has been reported that this precipitation might affect the electrochemical behavior of DSS [24]. Also, G-phase precipitation (or Ni Mn Si clustering) affects the hardness of ferrite during aging [25]. The embrittlement is an important practical issue for applications of DSSs in the temperature range (280–500 °C).

The change in the elastic constants of the duplex stainless steel aged at 475 °C affects the hardness of ferrite during aging [25]. The transfer resistance $R_{t}(=-V_{1}/I_{1})$ is obtained by injecting alternating current $I_{1}$ at electrodes $A_{1}$–$A_{2}$ and measuring the resulting in-phase voltage drop $V_{1}$ between electrodes $C_{1}$–$C_{2}$. The

### 2. Material and experiments

#### 2.1. Specimen preparation and mechanical tests

A 12.7 mm thick UNS S32750 super duplex stainless steel (SDSS) plate with the chemical composition given in Table 1 and a pitting resistance equivalent number (PREN) of 42 was used in this study. Six specimens in rectangular shape were obtained from the same plate; each has dimensions $160 \times 60 \times 12.7$ mm$^3$. One sample was kept in the as-received condition and the remaining samples were thermally treated to induce the embrittlement by keeping them in an oven at 475 °C for periods 1, 10, 50, 100, and 300 h, followed by water quenching. Vickers microhardness of the ferrite phase was measured using a computer-controlled microhardness tester that is equipped with a manually controlled x-y stage unit and digital micrometer heads with 1 µm spatial resolution and a load of 10 g were used. The measurements were performed in the area of the thickness oriented in the rolling direction. Charpy impact test is conducted at –20 °C on standard specimens with dimensions of $55 \times 10 \times 10$ mm$^3$ and a notch depth 2 mm (a 0.25 mm root radius and a 45° angular aperture).

#### 2.2. ACPD measurement

Fig. 1(a) shows the square-electrode ACPD probe used in this research. As described in Ref. [35], the probe has four spring-loaded heavy-duty needle-shaped pins with 4 mm separation (a) which are molded in a Plexiglas fixture. The four pins are placed in contact with the specimen and hold in position while the measurement is done. A pair of electrodes on the left injects alternating electric current into the specimen and the other pair of electrodes detects the resulting voltage difference and thus measures the electric resistance in the x-direction as shown in Fig. 1(b). The injected alternating current is limited in the penetration depth (δ) beneath the surface, and the depth can be controlled by the inspection frequency as follows:

$$\delta = \frac{1}{\sqrt{\pi \mu \sigma f}}$$

where $\mu$ is the magnetic permeability, $\sigma$ is the electric conductivity of the material, and $f$ is the frequency of the injected alternating current. This research uses a low frequency (3 Hz) which is low enough to neglect the influence of magnetic property variations induced by the ferromagnetic properties of DSSs. The setup is capable of accurately measuring the potential drop at a very low frequency; this low-frequency measurement is essentially a quasi-static operation to avoid the effects of magnetic permeability, typical of a wide range of materials including the paramagnetic austenitic 304 stainless steel and ferromagnetic low-alloy chromium/molybdenum steels [35].

The transfer resistance $R_{t}(=-V_{1}/I_{1})$ is obtained by injecting alternating current $I_{1}$ at electrodes $A_{1}$–$A_{2}$ and measuring the resulting in-phase voltage drop $V_{1}$ between electrodes $C_{1}$–$C_{2}$. The

#### Table 1

Chemical composition of the 2507 super duplex stainless steel (wt.%).

<table>
<thead>
<tr>
<th>C</th>
<th>Cr</th>
<th>Mn</th>
<th>S</th>
<th>Ni</th>
<th>Mo</th>
<th>N</th>
<th>Al</th>
<th>Si</th>
<th>Cu</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.017</td>
<td>25.37</td>
<td>0.82</td>
<td>0.001</td>
<td>7.09</td>
<td>3.87</td>
<td>0.28</td>
<td>0.18</td>
<td>0.32</td>
<td>0.24</td>
<td>0.12</td>
</tr>
</tbody>
</table>
spring-loaded electrodes would ensure a constant electrode separation \((a)\) for repeated measurements. The amplitude of the injected alternating current is 10 mA. Therefore, the probe is insensitive to geometrical effects and can be used selectively to detect material changes only. The measured resistance \((R_1)\) is related to the electric conductivity and electrode separation by:

\[
R_1 = \frac{1}{\sigma \pi a^2} \left( 1 - \frac{1}{\sqrt{2}} \right)
\]

### 2.3. Electrochemical determination of the corrosion resistance

The resistance to localized corrosion of the specimens subjected to aging (475 °C embrittlement) for different holding times was evaluated using two electrochemical methods: the critical pitting temperature (CPT) and the double-loop electrochemical potentiokinetic reactivation (DL-EPR) tests. Before each electrochemical test, the specimen surface was ground mechanically using successive grade emery paper up to 1000 grit, washed with distilled water, and degreased with acetone. In the DL-EPR experiment, the specimen was embedded in epoxy resin with an exposure area of 1 cm² on one side and a Cu wire was attached on the other side which is connected to the potentiostat. The DL-EPR test was conducted using a conventional three-electrode electrochemical cell with a saturated calomel electrode (SCE) as the reference electrode, a graphite bar, and the specimen, each as a reference, auxiliary electrode, and working electrode respectively. Note that all potentials recorded are referred to as SCE. The working electrode was allowed to stabilize at open circuit potential for 10 min at 15 °C. Then, an anodic potential of 750 mV to the SCE was applied and a heating ramp of 0.8 °C/min was applied to the electrochemical cell that was immersed in water. The real temperature of the NaCl solution in contact with the working electrode was measured continuously every 0.5 s. The CPT value was determined as the temperature where the current density exceeded 100 μA/cm² [41,42].

### 3. Results and discussion

#### 3.1. Effect of embrittlement on electric conductivity

The electric conductivity variations are shown in Fig. 2 as a function of aging time. The electric conductivity increases by a small amount (1.16 ± 0.31%) for aging times up to 10 h and remains unchanged for times up to 50 h. For longer aging times (100 h and 300 h), the electric conductivity increases rapidly to a total change of approximately 4.3% at 300 h. The gradual changes in electric conductivity can be related to the presence of multiple microstructural changes that occur in parallel as the 8/1 phase and G-phase precipitates, it seems that in the current study, the gradual changes in electric conductivity can be mainly related to the gradual increment of Cr-rich concentration 8/1-regions within ferrite phase as aging time progresses. Our results in electric conductivity are similar to the behavior of thermoelectric power (TEP) done by...
Kawaguchi and Yamanaka [43] in their research they concluded that the change in the structure of the X-ray photoelectron spectroscopy (XPS) spectrum for the Fe–Cr–Ni alloys due to Cr concentration exhibited the same trend of their TEP measurements in the aged Fe–Cr–Ni alloys investigated.

3.2. Determination of the corrosion resistance

Fig. 3 shows the DL-EPR curves obtained for the specimens with different aging times. The results concerning the susceptibility to localized corrosion obtained in this study are very similar to those previously reported for DSSs by many researchers [9,44,45]. For example, with results from Chandra et al. [9] where the peak current density during the anodic scan in DL-EPR test increased with increasing aging time.

The resulting ratio \( I_r/I_a \) shows how it changes sensitively concerning the material state. Fig. 4 shows this ratio which initially remains almost unchanged up to 50 h aging time and after 50 the ratio rapidly increases at 100 h and tends to saturate at 300 h. This behavior is in agreement with that of the electric conductivity.

Fig. 5 shows the result of the CPT test. The CPT decreases drastically with aging time these results are in agreement with those found in the literature [41,46,47]. This decreasing trend is qualitatively similar to that of Charpy impact energy which is shown below and is opposite to the trends of the electric conductivity (Fig. 3), the ratio \( I_r/I_a \) (Fig. 4), and the hardness of ferrite phase also as shown below.

3.3. Effect of aging on mechanical properties

Fig. 6(a) shows the Vickers hardness values measured in multiple grains of austenite and ferrite phase. There is a 14% (~350 HV) increment in Vickers microhardness in the austenite at 10 h and after this time austenite microhardness remains unchanged for the rest of the aging treatments. Horvath et al. [48] attributed the increase in the hardness of austenite to the presence of nitrogen that can be either a solid solution or/and as precipitates. Conversely, at 10 h, ferrite also increases and shows a higher change (21%) with the difference that ferrite microhardness continuous to increase as aging time progresses to show an overall change of 88% (582 HV) in microhardness at 300 h. This indicates that the 475 °C aging treatment initially affects both phases, but, after 10 h the saturation in the microhardness of austenite suggests that the 475 °C embrittlement is dominated by the changes occurring in the ferrite phase. This effect on the ferrite is also in agreement with the result of Weng et al. for 2205 DSS [11] and results reported by Tucker et al. [49] for 2003 and 2205 duplex stainless steels. The characteristic change of the microhardness of the ferrite phase allows for the conclusion that the microstructural changes associated with the decomposition of this phase begin even at short aging times.

Fig. 6(b) shows the absorbed energy determined from the Charpy impact test at −40 °C as a function of aging time. It was found that even for a short aging time there is a notable reduction in the impact energy to 201 J for 1 h, and 22 J for 300 h. This result is consistent with that of Sahu et al. [13] who observed that the impact energy reached a “saturation value” of 8 J for the aging times of 100, 200, and 300 h in a DSS DIN W Nr. 1.4462 (2205) aged at 475 °C up to 300 h. It has been reported that the fracture surface changes from a ductile fracture showing dimpled surface appearance at low holding times to a brittle fracture with cleavage facets at high holding times [50–52].

3.4. Microstructural analysis

From optical images, it was established that the 2507 SDSS has a 50/50% phase ratio. Fig. 7 shows SEM images for specimens after the DL-EPR test. From as-received condition to 10 h aging treatment no indication of noticeable corrosion attacks in the ferritic and austenitic phases is observed (Fig. 7(a–c)). Sample aged for 50 h shows significant pitting corrosion in the ferrite phase but minimal effects in the austenitic phase (Fig. 7(d)). With increasing aging time, the attack in ferrite grains becomes more and more severe; some ferrite grains begin to dissolve (Fig. 7(e)) and the ferrite phase is dramatically consumed (Fig. 7(f)). This is attributed to the fact that Fe and Cr depleted zones formed in the ferrite phase by the
embrittlement are susceptible to preferential corrosion attack. On the contrary to this, the aging treatment does not have noticeable corrosion effects on the austenitic phase.

3.5. Correlations among different test results

The correlation among electric conductivity and measured parameters: microhardness, $I_r/I_a$, CPT and impact energy is shown in Fig. 8. For all cases and depending on the measured parameter, the correlation can be approximated with good agreement using polynomials in all cases; but ferrite’s microhardness and CPT showed the best coefficient of determination $R^2$.

Fig. 8(a–b) indicate that the embrittlement of the 2507 SDSS impacts the measurements at short times with rapid changes in microhardness and CPT within electric conductivity values below $1.2 \times 10^6$ S/m h while a considerable drop in CPT for the same range. Initially, the DOS does not show appreciable changes and after a conductivity value of $1.18 \times 10^6$ S/m it rapidly increases, in this case, the fitting was done for the last three. These results agree with the SEM evidence that only after 50 h the material is sensitive to corrosion.

The electric conductivity shows a reasonably good correlation with the microhardness ferrite phase and the drop observed at $1.2 \times 10^6$ S/m seems to be related to the fact that microhardness seems to saturate as holding time increases. This good correlation between measurements indicates that electric conductivity measurements using a square four-pin sensor could be used for continuous monitoring of embrittlement at a temperature of 475 °C.

4. Conclusion and perspective

This work investigated the use of the electric conductivity measurement using an ACPD probe with the square-electrode configuration for monitoring 475 °C embrittlement of 2507 duplex stainless steel. It is shown that the electric conductivity changes considerably and it is well correlated with the other measured parameters including the $I_r/I_a$ ratio, ferrite phase microhardness, CPT, and Charpy impact energy. Therefore, the electric conductivity based on the ACPD probe can be used for the detection and possibly for quantitative evaluation of the 475 °C embrittlement damage that is caused by thermally activated microstructural changes due to the formation Cr-rich and Fe-rich depleted regions and to the precipitation of G-phase as has been suggested by some researchers. Consequently, the present research demonstrates the feasibility of using the ACPD probe for in-situ monitoring of 475 °C embrittlement in 2507 SDSS. The intended temperature range of the present ACPD device is (280–350 °C) where the critical components may operate.

In this work, the NDE measurements have been performed at room temperature on samples that for convenience and to save time were aged at 475 °C. Future works include the validation of the ACPD probe in the above-mentioned temperature range for longer aging periods. Since the contact is through very fine tips and the
Fig. 7. SEM micrographs showing the surface characteristics of 2507 SDSS after DL-EPR tests (a) as-received condition and aged at 475 °C for (b) 1 h, (c) 10 h, (d) 50 h, (e) 100 h and (f) 300 h respectively.
contact time required for measurement is just a few seconds, no significant issues are expected. However, some temperature corrections may need to be introduced for accurate measurements over this temperature range. Then the next step of the research is to take this technique out to field structures and assess the reliability and adaptability of the technique.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.net.2021.03.018.

References
