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Corrosion resistance evaluation of the UNS S31803 duplex stainless steels aged at low temperatures (350 to 550°C) using DLEPR tests

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This work describes the investigation of the corrosion evaluation of UNS S31803 duplex stainless steels aged at low temperatures using double loop electrochemical potentiokinetic reactivation tests (DLEPR). A wrought duplex stainless steel (DSS) UNS S31803 was aged at four temperatures in the 350—550°C range for times up to 1000 h. The hardening and embrittlement effects due to aging were also determined. An important decrease in corrosion resistance was observed in the samples aged at 475 and 550°C, but the samples aged at 350 and 400°C were not affected. Healing was observed in the samples aged for long times (1000 h at 475°C and 500 h at 550°C).

1. Introduction

The duplex stainless steels (DSS) are high strength and corrosion resistant materials for special purposes in the chemical, petrochemical and nuclear industries. The aging of these steels in the range of temperature between 350 to 550°C causes the spinodal decomposition of the ferrite phase into chromium-depleted (α'') and chromium-rich (α') regions [1–3]. This precipitation reaction promotes the hardening and embrittlement of the ferritic phase present in the DSS.

It is also found that aging at 475°C decreases the corrosion resistance of the ferrite phase, as it creates submicro chromium depleted regions [4, 5]. According to Tsuchuya *et al*. [5], if the chromium content becomes locally lower than 14 at.% small pits may be observed in the ferrite phase, after etching with a 10%HNO_3 + 0.05%HF solution.

The DLEPR (double loop electrochemical potentiokinetic reactivation) is a well established electrochemical test initially developed to austenitic stainless steels [6]. In a previous work [7], DLEPR test was used to evaluate the degree of sensitization and embrittlement in an austenitic stainless steel AISI 304. Recently, the DLEPR test was also applied to the DSS aged at high [8] and low [9] temperatures. Park and Kwon [9] used this test to measure and compare the degree of depletion of Cr near α' precipitates in two 25Cr-7Ni superduplex steels aged at 475°C for 1, 10, 100 and 300 h.

TABLE I Chemical composition of the UNS S31803 steel

Chemical analysis (%wt.)				
Cr	Ni	Mo	C	N
22.3	5.44	2.44	0.02	0.160

The majority of the research works on the low temperature aging of DSS study the effects produced at 475°C, where the precipitation kinetics is higher. The aim of this work is to investigate the corrosion resistance degradation of the UNS S31803 DSS steel aged at 350, 400, 475 and 550°C using the DLEPR. The mechanical properties changes were also evaluated in the aged samples.

2. Experimental

A 3.5 mm thick plate of UNS S31803 DSS (composition shown in Table I) was cut and machined into samples for DLEPR test (10 × 15 mm) and Charpy test (reduced size sample [10]). Then, the samples were aged at 350, 400, 475 and 550°C for 24, 100, 300, 500 and 1000 h.

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The DLEPR tests were conducted in a conventional three-electrode cell using a Pt foil as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference one. The working electrode was constructed using the DSS samples embedded in epoxy resin. The tests were initiated after nearly steady-state open circuit potential (E_{oc}) had developed (about 30 min) followed by the potential sweep in the anodic direction at 1 mV s^{-1} until the potential of 0.3 V (vs. SCE) was reached, then the scan was reversed in the cathodic direction until the $E_{oc.}$ Prior each experiment, the working electrodes were polished with grid 400 emery paper, degreased with alcohol and cleaned in water. The electrolyte was 0.05 M H_2SO_4 + 0.01 M KSCN solution. The loss of corrosion resistance due to the chromium-depleted regions was evaluated from the ratio I_r/I_a, where I_a is the peak current of the anodic scan and I_r is the peak current in the reversed scan.

The Charpy impact tests were carried out at room temperature in a Universal machine with a maximum capacity of 300 J and estimated error of about ±0.5 J. The Vickers hardness tests were performed to evaluate the degree of aging in each condition.

3. Results and discussion

Fig. 1 shows the hardness *versus* aging time curves for the four aging temperatures. As expected, the aging at 475°C promotes the higher and faster hardening effect. At this temperature, overaging is observed after 500 h. A considerable hardening is also produced in the samples aged at 400°C, without overaging till 1000 h. The aging at 350°C causes a small hardening effect (264 to 284 HV after 300 h). The aging at 550°C slightly increases the hardness in the first 24 h. It is a matter of discussion if this sharp hardening and the other effects observed at 550°C in this work are due to the spinodal decomposition of the ferrite phase or not. Solomon and Koch [1] showed that α' can precipitate at 600°C in a DSS. On the other hand, two other chromium-rich phases (R and π) are reported at this temperature [11].

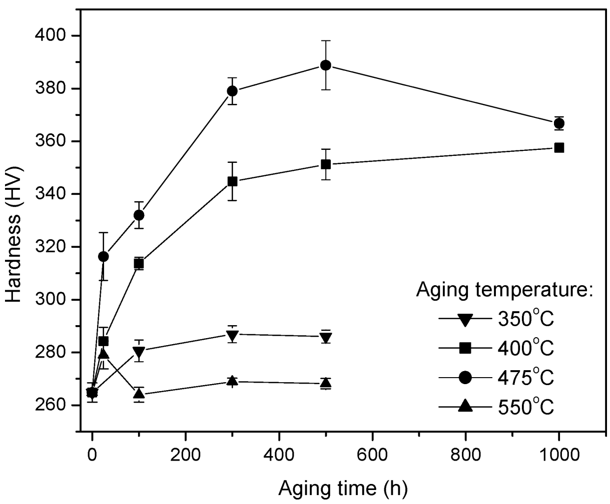


Figure 1 Aging curves.

The result of DLEPR tests is the ratio between the reactivation current (I_r) and the activation current (I_a). The unaged sample presented $I_r/I_a = 0$, which means that it is not susceptible to corrosion due to chromium depleted regions. Figs 2, 3, and 4 show the EPR curves of the samples aged at 475°C for 500 h, 400°C for 1000 h and 350 for 100 h, respectively. Fig. 5 show the I_r/I_a *versus* aging time behavior for the four aging temperatures. The samples aged at 350°C and 400°C do not present any substantial loss of corrosion

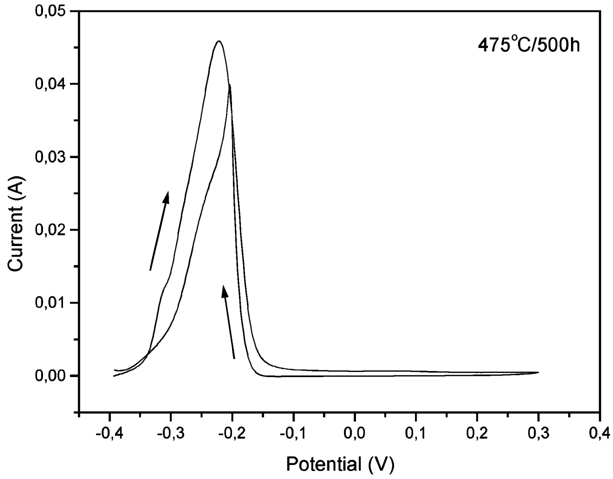


Figure 2 DLEPR curve of the sample aged at 475°C for 500 h.

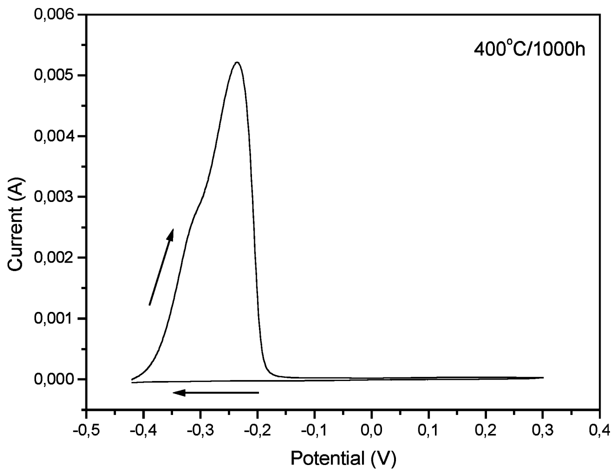


Figure 3 DLEPR curve of the sample aged at 400°C for 1000 h.

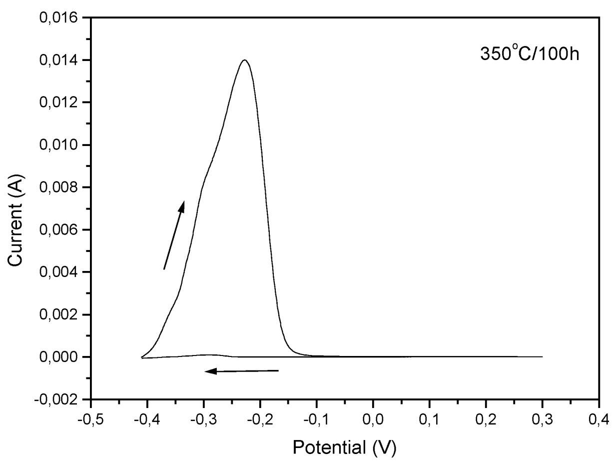


Figure 4 DLEPR curve of the sample aged at 350°C for 100 h.

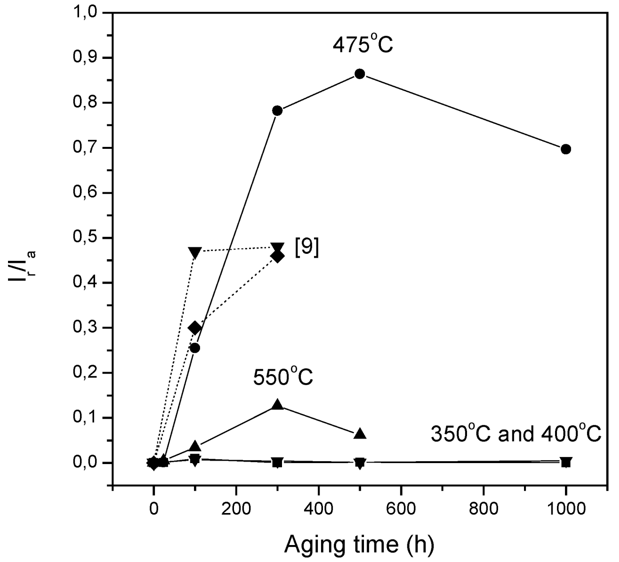


Figure 5 I_r/I_a *versus* aging time curves.

resistance even after 1000 h. At the aging temperature of 475°C, the material undergoes the most rapid and intense decrease in corrosion resistance. The behavior of the I_r/I_a and the hardness against aging time are very similar at this temperature. Both of them decrease after aging for 500 h. The decrease in hardness is usually associated to the coarsening and/or loss of coherency of precipitates. On the other hand, the decrease in I_r/I_a is due to a healing or desensitization process [12], which is caused by the chromium diffusion reducing or eliminating the gradient of concentration of this element. Just for comparison, in the work of Park and Kwon [9] the 25Cr-7Ni-3Mo and 25Cr-7Ni-3W-1.5Mo steels did not showed healing in the agings at 475°C up to 300 h.

The samples aged at 550°C also show an increase in I_r/I_a ratio with the aging time, but the behavior is quite different from the aging curve were a small peak of hardness (279 HV) is observed in the first 24 h (Fig. 1). The peak value of I_r/I_a is more important and is attained at 300 h of aging. Healing is also observed after this time. The DLEPR curve of the sample aged at 550°C for 300 h (Fig. 6) show a particular behavior with two activation and two reactivation peaks (see arrows),

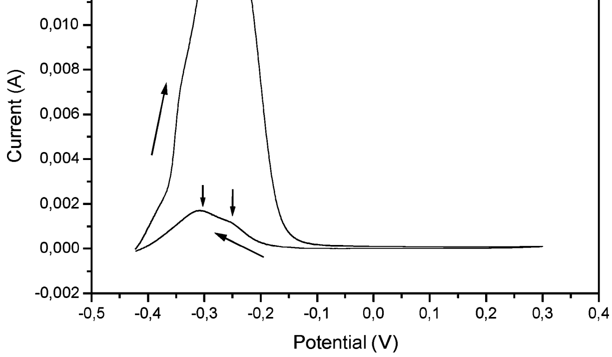


Figure 6 DLEPR curve of the sample aged at 550°C for 300 h.

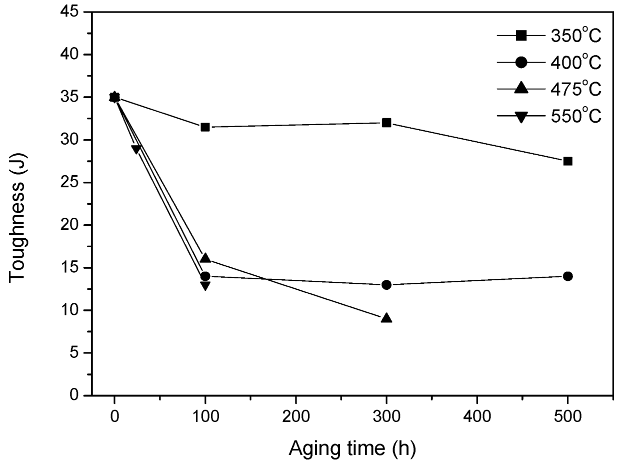


Figure 7 Impact energy *versus* aging time curves.

which suggests that two chromium-rich phases may be present at this condition.

Fig. 7 shows the toughness *versus* aging time curves. Aging at 350°C causes only a little embrittlement effect. At this temperature the impact energy decreased from 35 to 27.7 J after 1000 h. The aging at 400, 475 and 550°C cause a considerable loss of toughness and the change in the fracture mode from ductile to brittle.

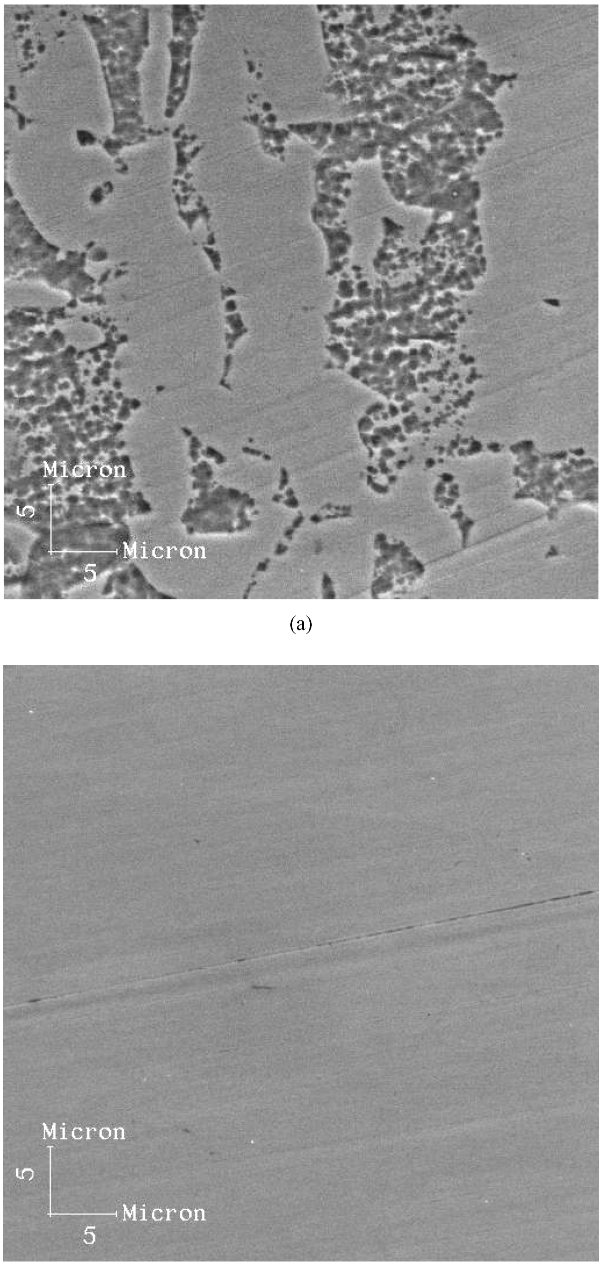
Fig. 8a show the SEM image of the sample aged at 475°C for 500 h ($I_r/I_a = 0{,}864$) etched with the 10%HNO_3 + 0.05%HF solution. As expected, the ferrite phase presented many microscopic pits, while the austenite phase was not etched. In agreement with the DLEPR results, the sample aged at 400°C for 1000 h was not etched (Fig. 8b). The sample aged at 550°C for 300 h (not shown) presented no corrosion pits, despite its relatively high I_r/I_a value (0.127). It is possible that at this condition the chromium depleted zones contain more than the limit value suggested by Tsuchuya *et al.* [5] (14%at.).

Table II summarizes the main effects of the thermal aging at the four temperatures studied. The agings at 400°C promote severe embrittlement but there is no considerable loss of corrosion resistance due to chromium depleted regions. The aging at 475°C cause the most severe embrittlement and loss of corrosion resistance. The aging at 550°C produces a very small hardening effect, but also cause embrittlement and creates chromium depleted regions as detected by the DLEPR tests. The aging at 350°C till 1000 h does not promotes severe embrittlement neither decreases the corrosion resistance. A small increase of hardness may be obtained at this temperature. We suggest future works on the effect of the aging at 350°C on erosion-corrosion and fatigue resistance properties.

TABLE II Effect of the aging at 350, 400, 475 and 550°C on the hardening, toughness and corrosion resistance of the UNS S31803 steel.

	350°C	400°C	475°C	550°C
Hardening	↑	↑	↑↑	→[a]
Impact toughness	→[b]	↓↓	↓↓	↓↓
Corrosion resistance	→	→	↓↓	↓

[a]Small increase in the first 24 h.
[b]Small decrease for long periods.



(a)

(b)

Figure 8 SEM images of the samples aged at 475°C for 500 h (a) and 400°C for 1000 h (b).

4. Conclusions

The DLEPR test was successfully used to evaluate the loss of corrosion resistance in the duplex stainless steel UNS S31803, aged in the temperature range between 350 and 550°C, due to the chromium depleted regions formed during aging. The samples aged at 475°C showed the most pronounced hardening, and increase in the I_r/I_a ratio. After 500 h at this temperature, the I_r/I_a decreases due to healing. An important decrease of toughness is also observed at this temperature. The samples aged at 550°C showed small hardening in the first 24 h, an important corrosion decay and embrittlement effects. At this temperature healing was also observed after 300 h. The samples aged at 350 and 400°C do not present considerable decrease in the corrosion resistance due to chromium depleted regions, but the aging at 400°C causes severe decrease of the impact toughness.

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