Evaluation of selective corrosion in UNS S31803 duplex stainless steel with electrochemical impedance spectroscopy

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Abstract

The precipitation of certain phases, in particular of sigma phase, in duplex stainless steels makes them susceptible to selective corrosion. In the present work, the effect of heat treatments upon selective corrosion of UNS S31803 duplex stainless steel was investigated in 2 M H_2SO_4 + 0.5 M NaCl + 0.01 M KSCN solution at 30 °C using electrochemical impedance spectroscopy (EIS). For this purpose, samples were solution annealed at 1050 °C for 30 min and, subsequently, heat-treated at 750 °C or 850 °C for times varying from 1 h to 30 h in order to precipitate the sigma phase and other phases. After these heat-treatments the specimens were immersed in the test solution and submitted to EIS tests. These tests, performed at the open circuit potential after 84 h of immersion in the test solution, showed higher impedances for samples tested at 850 °C than at 750 °C, implying lower selective corrosion rates for the former samples. Moreover, for samples tested for longer times at 850 °C, there are evidences of an increase of the high frequency phase angle, which seems to be associated with the recovery of Cr and Mo content in the depleted zone near the precipitated sigma phase. These results are in good agreement with those obtained in tests performed with the electrochemical potentiodynamic reactivation double loop method.
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1. Introduction

Due to their microstructure, composed of approximately equal volumetric fractions of ferrite (α) and austenite (γ), duplex stainless steels display adequate mechanical properties and resistance to corrosion in an ample range of applications, thus justifying their increasing use in several fields such as chemical processing, electrical energy generation and others. Notwithstanding these advantages, in some applications involving welding and high temperature, these steels are susceptible to the precipitation of additional phases that affect both the corrosion and the mechanical properties.

Depending on temperature, different phases can precipitate, such as sigma (σ), chi (χ), nitrides (Cr_2N) and carbides ($M_{23}C_6$ and M_7C_3) [1–3]. In a duplex stainless steel such as UNS S31803, heat-treated at 850 °C for 5 h, the main components of sigma phase are Fe, Cr and Mo in approximate wt% amounts of 57, 31 and 7, respectively. The remaining 5 wt% is Ni, Mn and Si [4]. The chi phase, which is formed in lesser amounts, has also the same main components in approximate amounts of 56 wt% Fe, 17 wt% Cr and 27 wt% Mo [5]. During their precipitation these phases remove from their vicinity elements responsible for the corrosion resistance of the steel. In this way, regions depleted in these elements are formed, making the material susceptible to selective corrosion in a manner similar to sensitization of austenitic stainless steels, which renders them susceptible to intergranular corrosion. The latter is a peculiar type of selective corrosion, in which the chromium depleted regions form along the grain boundaries. In duplex stainless steels the regions susceptible to selective corrosion are chromium and molybdenum depleted and they

usually form along the interfaces between the precipitated sigma phase and the austenite grains. There is no corrosion observed along the austenite grain boundaries [6].

The harmful effect of the sigma phase on the corrosion resistance of duplex stainless steels was reported in several works [7–19]. This effect has been evaluated through different tests, such as general corrosion tests [9], pitting potential tests [9,11,12,14,16], crevice corrosion tests [14], intergranular corrosion tests [12,15–17] and stress corrosion tests [12]. Moreover, this effect has been of great concern in welding of duplex stainless steels, because during this process the sigma phase is formed in the heat affected zones (HAZ) [10,18,19]. Leaks in pipelines fabricated with this type of steel were reported to occur in these zones [18].

According to Truman and Pirt [8] this effect is a consequence of chromium and molybdenum content decrease in the matrix phases, because the sigma phase is considerably richer in these elements than either the ferrite or austenite. Adhe et al. [16] proposed that this decrease is confined to regions adjacent to sigma phase. Wilms et al. [14], on the other hand, observed that the localized corrosion starts next to the sigma phase in the newly formed secondary austenite. Using mass balance Kobayashi and Wolynec [4] determined theoretically the composition of this new austenitic phase showing that it is poor in Cr and is Mo free, which explains its severe selective corrosion.

More recently the susceptibility to selective corrosion of duplex stainless steels has been evaluated with the double loop electrochemical potentiokinetic reactivation (DL-EPR) technique [17,20–23]. In this technique, first developed for austenitic stainless steels, the testing solution consists of $0.5\,M\,H_2SO_4 + 0.01\,M\,KSCN$ at $30\,°C$. The role of KSCN is to help to break the passive film during the reactivation cycle of the test. For duplex stainless steels, this solution showed itself inadequate. Attempts were made to run the test at $70\,°C$ [20] or to increase the KSCN content to $0.5\,M$ [22]. Lopez et al. [17] proposed to add NaCl to the solution and to increase the amount of sulfuric acid. In this way, they increased the ability of the solution to break the passive film during the reactivation cycle of the test, since it is well known that the chlorides are highly efficient in doing this. Chaves and Wolynec [23] conducted comparative DL-EPR tests in solutions proposed by Garz et al. [20], Lopez et al. [17] and a third solution similar to the latter, in which the KSCN was replaced by $0.01\,M$ thiocetamide (C_2H_5NS). They found that the testing solution proposed by Lopez et al. [17] is the most efficient for detecting this susceptibility. Using their solution, which consists of $2\,M\,H_2SO_4 + 0.5\,M\,NaCl + 0.01\,M\,KSCN$ at $30\,°C$, they [24] investigated the selective corrosion kinetics of UNS S31803 duplex stainless steel.

To obtain further knowledge about this selective corrosion, it was decided to perform also electrochemical impedance spectroscopy (EIS) tests in the above solution and to check the possibility of these EIS tests being used to assess the susceptibility of duplex stainless steels to selective corrosion. The present work reports the results obtained by this

Table 1
Chemical composition of the duplex stainless steel used in present investigation (in wt%)

C	0.026
Si	0.19
Mn	1.65
P	0.028
S	0.004
Cr	22.17
Ni	5.82
Mo	3.13
V	0.05
W	0.05
Co	0.15
Cu	0.18
Nb	0.015
Ti	0.006
Al	0.0025
N	0.183

technique and compares them with those obtained with the DL-EPR tests.

2. Experimental

The material used in the present investigation was an UNS S31803 duplex stainless steel[1] also known as DIN N 1.4462 or AV2205. Four different laboratories determined its chemical composition and the average values are given in Table 1.

The available material was a $10.5\,cm \times 20\,cm$ rectangular piece of rolled plate about $1.9\,cm$ thick. Square samples, measuring about $1\,cm \times 1\,cm$, were removed from this plate and submitted to solution-anneal at $1050\,°C$ for $30\,min$ in inert argon atmosphere, followed by cooling in water. After this they were submitted to heat-treatments at $750\,°C$ and $850\,°C$ for times varying from $1\,h$ to $30\,h$, with the purpose of precipitating the sigma and other phases.

EIS experiments were carried out in $2\,M\,H_2SO_4 + 0.5\,M\,NaCl + 0.01\,M\,KSCN$ solution at $30\,°C$. They were performed with a classical three-electrode system using Ag/AgCl and platinum as reference and counter electrodes, respectively. Prior to the experiments the working electrodes were embedded in thermosetting plastic, leaving an exposed area to the solution of $1\,cm^2$, and grounded with 400 and 600 grit emery paper. The tests were performed at the open circuit potential (OCP) with a perturbation amplitude of $20\,mV$ at an acquisition rate of 10 points per decade. The experimental setup was controlled using a Perkin Elmer Instruments model 1025 frequency detector with a model 283 potentiostat. In order to guarantee stationary and linear conditions, the OCP was left to stabilize during $84\,h$ prior to the beginning of impedance tests. Under these circumstances a potential plateau was attained and no potential drift was observed after the EIS experiments were finished.
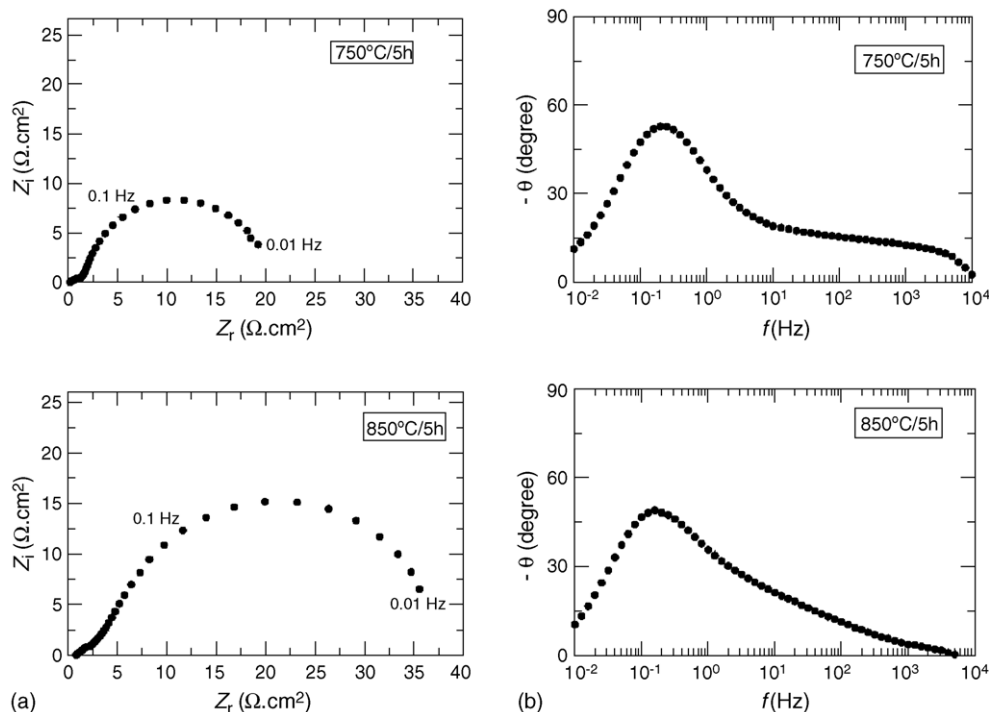
Fig. 1. Nyquist (a) and Bode phase angle (b) plots obtained in 2 M H_2SO_4 + 0.5 M NaCl + 0.01 M KSCN test solution for samples heat treated at 750 °C and 850 °C for 5 h.

3. Results

Nyquist and Bode phase angle plots obtained in the 2 M H_2SO_4 + 0.5 M NaCl + 0.01 M KSCN test solution for samples heat treated at 750 °C and 850 °C for 5 h are shown in Fig. 1.

The Nyquist plots (Fig. 1(a)), appear to be composed of a well defined capacitive loop, with small low frequency impedance limit, which is typical of materials undergoing general corrosion, and a very small and depressed high frequency capacitive loop, indicating that a very fast charge transfer process is taking place at the interface. Moreover, the Bode phase angle plots (Fig. 1(b)), are characterized by a well defined phase angle maximum (θ_{max}), with its peak at

approximately 0.2 Hz, and a broad time constant with very low phase angle in the high frequency region. However, for samples heat treated at 850 °C for longer times (20 h and 30 h), there is an increase in the impedance value (Fig. 2(a)), and the phase angle located in the 10 Hz to 10,000 Hz range presents a slight upward curvature (Fig. 2(b)), suggesting that the high frequency process is being hindered. This upward curvature can be better visualized in Fig. 3, in which the phase angle curve of sample heat treated for longer time (30 h) is compared with curves obtained for sample solution-annealed at 1050 °C for 30 min and for sample heat-treated at 850 °C for 5 h.

Using the Nyquist plots it was possible to make an approximate estimate of the polarization resistance (R_p) for all testing
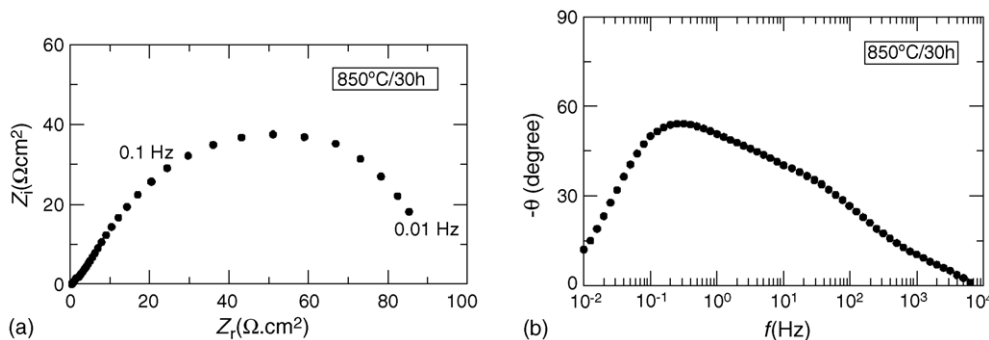

Fig. 2. Nyquist (a) and Bode phase angle (b) plots obtained in 2 M H_2SO_4 + 0.5 M NaCl + 0.01 M KSCN test solution for sample heat-treated at 850 °C for 30 h.
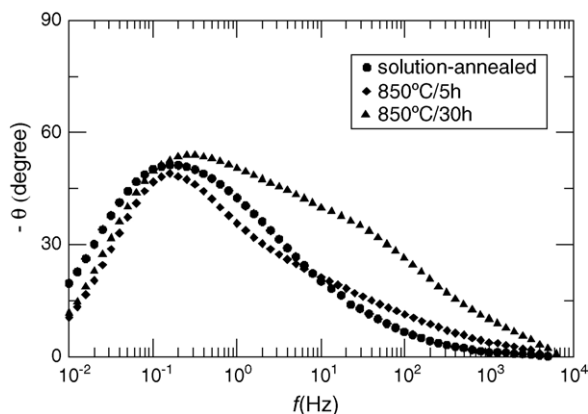
Fig. 3. Comparison of Bode phase angle plot shown in Fig. 2 with those obtained for sample solution-annealed at 1050 °C for 30 min and for sample heat-treated at 850 °C for 5 h.
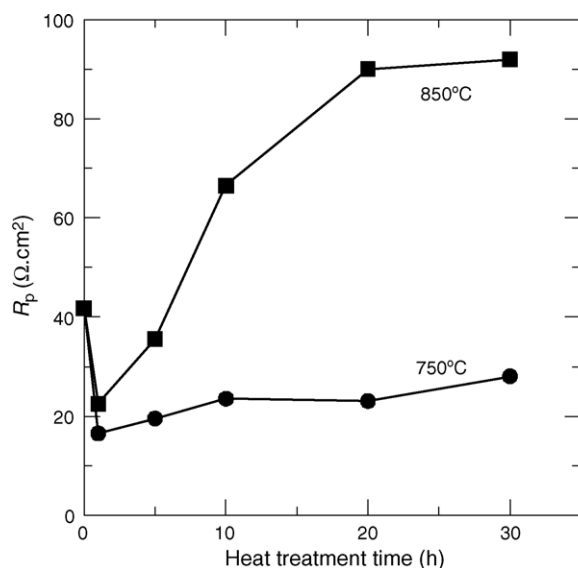

Fig. 4. Variation of polarization resistance (R_p) in 2 M H_2SO_4 + 0.5 M NaCl + 0.01 M KSCN test solution, estimated from Nyquist plots, with heat treatment time.

times by extrapolating the capacitive loop to the real axis. Their values are plotted in Fig. 4. It can be noticed that, for samples heat treated for 1 h, the R_p decreases almost by half when compared to the value presented by the solution-annealed sample (0 h). For larger heat-treatment times, the R_p increases. This increase is very small for samples heat-treated at 750 °C, but for those heat-treated at 850 °C this increase is large. For samples heat-treated for more than 5 h, the R_p value surpasses that of the solution annealed sample, reaching values two times larger for samples heat-treated for 20 h and 30 h.

4. Discussion

The response obtained with the EIS technique is consistent with the highly corrosive characteristics of the testing solu-
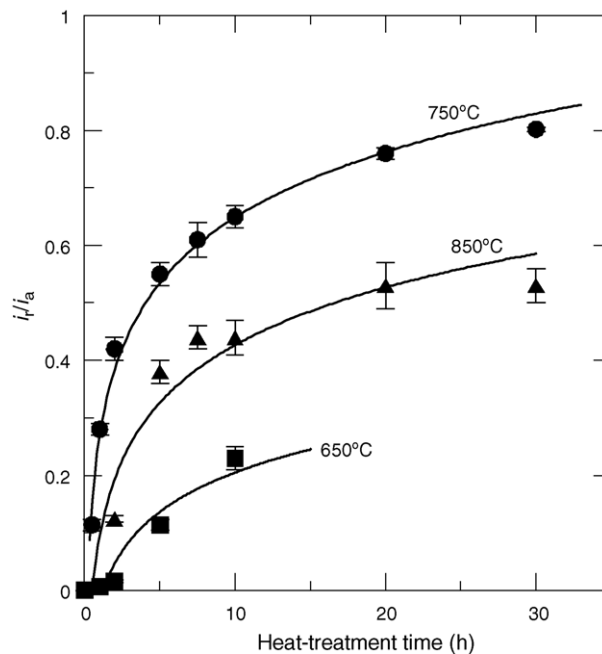

Fig. 5. Variation of i_r/i_a ratio with heat-treatment time for samples heat-treated at different temperatures. The 0 h refers to the as received sample. Results obtained through DL-EPR test in 2 M H_2SO_4 + 0.5 M NaCl + 0.01 M KSCN solution at 30 °C (Ref. [24]).

tion. In fact, the polarization resistance (R_p) values estimated from the capacitive loops are considerably low (between 15 Ω cm^2 and 100 Ω cm^2), and suggests a very fast mechanism. This implies a generalized corrosion process with a considerably large corrosion rate. However, in the present case, there were no evidences of generalized corrosion in the samples, so it appears that this type of behavior can be associated with selective corrosion caused by the sigma phase precipitation.

The fact that the R_p values of samples heat-treated at 750 °C are always smaller than those of samples heat-treated at 850 °C (see Fig. 4) are consistent with the results obtained by the double loop electrochemical potentiokinetic reactivation (DL-EPR) technique [24], as can be observed in Fig. 5. In this figure, the degree of susceptibility of the material to selective corrosion is indicated by the i_r/i_a ratio, where i_a is the peak current density in the anodic polarization scan from the corrosion potential to the fixed potential in the passive region and i_r is the peak current density obtained in the reverse scan from the fixed potential in the passive region to the final potential. It can be observed that samples heat-treated at 750 °C are more susceptible to selective corrosion caused by the sigma phase precipitation, characterized by a higher i_r/i_a ratio, which leads to the formation of regions depleted in Cr and Mo. At 850 °C, these regions are also formed, but due to the higher temperature the depletion is partially recovered by the diffusion of these elements from the unaffected areas, rendering these regions less depleted in these elements, and consequently more corrosion resistant.

The large R_p values displayed by samples heat treated at 850 °C for times larger than 5 h are unexpected. This implies that their corrosion rate is lower than that of solution-annealed sample, which is highly inconsistent with the results obtained by other techniques [23,24]. However, it must be pointed out that while in impedance tests the OCP was left to stabilize during 84 h, in the DL-EPR tests this time was only of 5 min. These results deserve a more detailed investigation. The presence of the second time constant on samples heat-treated at 850 °C for 20 h and 30 h must certainly be related to this observed increase in corrosion resistance. It appears that this time constant is probably associated with the presence of a more protective passive layer, which was formed due to the recovery of regions depleted in Cr and Mo. In order to verify this latter hypothesis, an estimate of the capacity of the high frequency capacitive loop was performed for the sample treated during 30 h, considering that its diameter is in the order of units of $\Omega\,cm^2$ and that the maximum frequency lies near 10^3 Hz. The estimated capacity was approximately $80\,\mu F\,cm^{-2}$, which is typical of a double layer capacity or either of an oxide layer, which can be eventually coupled, as suggested by Aoki et al. [25].

5. Conclusions

The EIS tests of UNS S31803 duplex stainless steel samples, carried out in $2\,M\,H_2SO_4 + 0.5\,M\,NaCl + 0.01\,M\,KSCN$ solution at 30 °C, were sensitive to the effects of heat-treatments carried out at 750 °C and 850 °C. All samples presented a single capacitive loop in the Nyquist plot and a maximum phase angle (θ_{max}) at approximately 0.2 Hz in the Bode phase angle plot. Moreover, samples heat-treated at 850 °C for 20 h and 30 h displayed the presence of a second maximum phase angle in the 10–200 Hz range. These tests, performed at the open circuit potential after 84 h of immersion in the test solution, showed higher impedances for samples heat-treated at 850 °C than at 750 °C, implying lower selective corrosion rates of the former samples, which are in good agreement with those obtained in tests performed with the electrochemical potentiokinetic reactivation double loop method. However, the polarization resistance values estimated from capacitive loops for samples heat-treated for more than 5 h at 850 °C imply corrosion rates lower than those of the solution-annealed sample, which is highly improbable. Further research is needed to clarify this inconsistency, which seems to be closely linked to the second time constant.

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