ESSC & DUPLEX 2019

10th European Stainless Steel Conference - Science and Market,
6th European Duplex Stainless Steel Conference & Exhibition

30 September - 02 October 2019
Schönbrunn, Vienna

Copyright: Schloß Schönbrunn Kultur- und Betriebsges.m.b.H.
Fotograf: Alexander Eugen Koller

ASMET
THE AUSTRIAN SOCIETY FOR
METALLURGY AND MATERIALS

TU Graz

CALUSCIO DOS SANTOS, Daniella; MONFRINATTI MACARRÃO, Isabelle; MAGNABOSCO, Rodrigo[1]

RELATION BETWEEN PITTING POTENTIAL AND PREN VALUES FOR FERRITE AND AUSTENITE IN DUPLEX STAINLESS STEELS

Abstract

This work aims to investigate the relation between PREN of ferrite and austenite and the pitting potential of UNS S31803 DSS. Samples were solution-threated between 1040 and 1150 °C generating different phase fractions and, consequently, different alloy element contents. ThermoCalc® thermodynamic simulations were performed to predict the chemical composition of each phase allowing the PREN calculations. Besides, potentiodynamic polarization tests were conducted in 0.6M NaCl solution at 70°C to correlate pitting potential (Epit) and PREN. Thermodynamic simulation reveals that PREN for ferrite is higher than austenite between 975 and 1300 °C. Nevertheless, the electrochemical results show a slight reduction of pitting potential with increasing ferrite content, probably related to the reduction of Cr and Mo contents in this phase. Pits were found preferably in ferrite and in ferrite/austenite interfaces. This behavior suggests that even with only a slight reduction of pitting potential and, consequently, a discrete corrosion resistance reduction, ferrite is more susceptible to pitting. No pits were found in austenite, suggesting that higher N contents are fundamental to maintain the corrosion resistance of this phase.

Keywords: Duplex. Pitting. Polarization. PREN.

1. Introduction

Duplex Stainless Steels (DSS) are composed by ferrite (α) and austenite (γ) in approximately equal amounts and have been used in applications where is required both high mechanical and corrosion resistances [1-3]. The higher N contents enhances both properties and also, its weldability [3], allowing its application in chemical, oil and gas, pulp and paper, food and energy industries. Thus, the microstructure and the alloy element additions as Cr, Mo and N [2] contribute to the DSS properties.

The Pitting Resistance Equivalent Number (PREN) [4-5] is widely used to categorize duplex steels as super duplex (above 40), standard duplex (between 30 and 40) and lean duplex (below 30), and is also used to rank this material on corrosion resistance using chemical composition (%wt) as presented in equation (1)

$$PREN = \%Cr + 3.3 \, (\%Mo + 0.5\% \, W) + 16 \, \%N \tag{1}$$

Nevertheless, the PREN do not consider microstructural effects as grain size, intermetallic and/or secondary phases, other non-homogeneities like inclusions, and the alloy element partition in duplex microstructure that may influence the electrochemical behaviour of this materials [4-5]. In DSS, ferrite contains the highest contents of Cr, Si and Mo. In contrast, Ni, Mn, Cu, C and N are preferably partitioned to austenite [1-2,6].

Garfias-Mesias [7] suggest that the use of PREN to predict pitting corrosion resistance in DSS assumes that the steel production used the correct heat treatment to adjust the recommended ferrite and austenite volume fractions, the absence of intermetallic phases or precipitates, and the partition of alloy elements of the material. Furthermore, the quality control must ensure that P, S and C contents, and the nucleation sites for pitting formation, are maintained in low levels.

Not only the presence of alloy elements but also its partition between ferrite and austenite may influence the corrosion resistance of DSS. Magnabosco [8] found pitting corrosion in both ferrite and austenite phases. Nevertheless, austenite presents the high N contents suggesting high corrosion resistance of this phase. The evidences found in literature indicates that PREN may not be evaluated for the global chemical composition of DSS, but for each phase separately and then, the PREN to be considered for the material is the lower value found.

This work aims to investigate the relationship between PREN of ferrite and austenite, in UNS S31803 samples with different volume fractions, and the pitting potential registered to each sample condition. The chemical composition of ferrite and austenite with different volume fraction was determined by thermodynamic calculations.

2. Methodology

The studied material, an Outokumpu UNS S31803 DSS, has the chemical composition given in Table 1. The specimens were obtained from a 3 mm sheet with dimensions of approximately 30 mm width and 60 mm length with different solution heat treatments conditions.

Table 1. Chemical composition of UNS S31803 DSS (wt%)

Cr	Ni	Mo	Mn	N	C	Si	Cu	Co	P	S	Nb	Fe
22.48	5.74	3.20	1.42	0.162	0.018	0.35	0.15	0.07	0.019	0.001	0.006	Bal.

Heat-treated specimens were abraded to a 220-grit finish before mounting in thermosetting plastic, leaving an exposed surface area of approximately 0.5 cm^2, parallel to the rolling direction. The mounted samples were metallographic polished with final polishing provided by 1-µm diamond abrasive. The samples were etched with modified Beraha reagent (composed of 20 mL HCl, 80 mL distilled water and 1 g $K_2S_2O_5$; to this stock solution, 2 g of $NH_4F.HF$ were added just before the etching) just before the metallographic characterization through optical microscopy.

Thermodynamic simulation using ThermoCalc$^®$ version 2018b software was performed using TCFE8 thermodynamic database. The PREN calculation was obtained from the simulated Cr, Mo, and N equilibrium contents and its relation to the pitting potential was determined through electrochemical testes.

Potentiodynamic polarization tests were conducted in 0.6M (3.5%wt) sodium chloride solution (pH=6.5) exposed to laboratory air, in a jacket cell at 75°C at a scan rate of 1 mV/s, beginning 200mV below the open circuit potential (OCP) measured after 5 min of immersion. The test cell had a platinum wire as counter electrode and Ag|AgCl (silver|silver chloride) as a reference electrode. Immediately after the polarization, sample surfaces were washed with distilled water and then with ethyl alcohol (C_2H_5OH), dried with hot blown air, and then analysed through OM.

3. Results and Discussion

The thermodynamic simulation using ThermoCalc® software with TCFE8 database is presented in Fig. 1, and shows that above 975°C only ferrite and austenite coexists in equilibrium. Both sigma and chromium nitride only appear below this temperature.
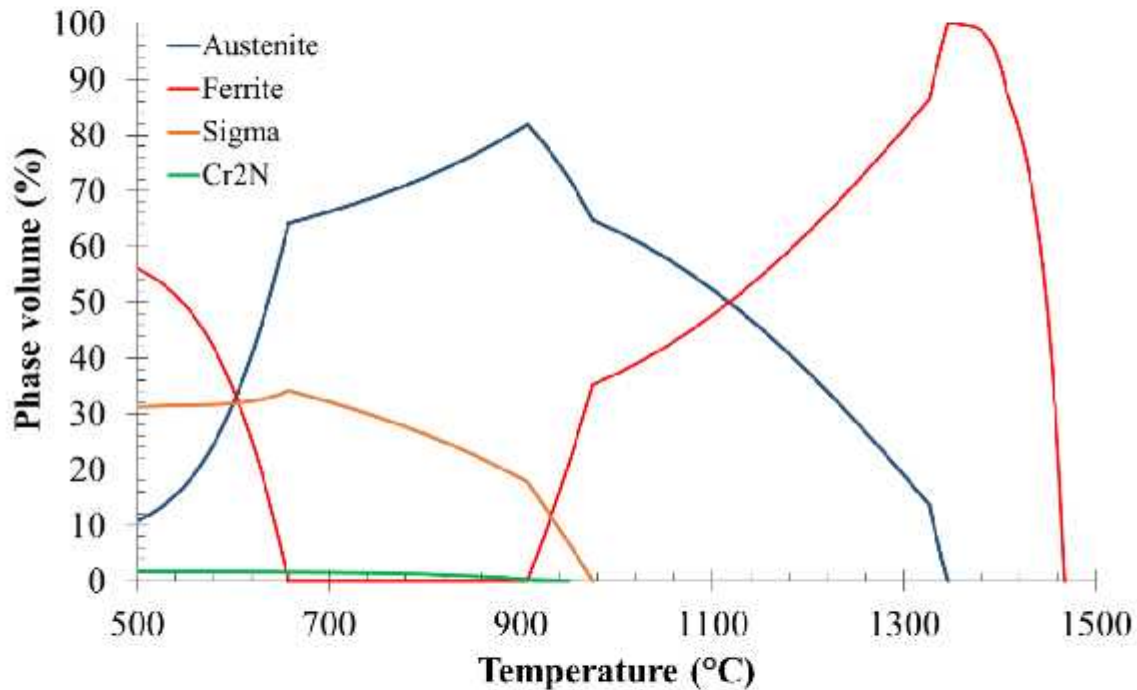

Fig.1. Equilibrium phase volume percent of UNS S31806 DSS between 500 and 1500°C.

Cr, Mo and N contents estimated by ThermoCalc® software are shown in Fig. 2 (a-c), and are the base for PREN calculations showed in Fig. 2 (d). As expected, ferrite is richer in Cr and Mo and austenite in N. Nevertheless, analysing Fig 2 (d), PREN of ferrite (PREN α) is higher than PREN of austenite (PREN γ) in all temperature range between 500 and 1500°C, with an exception of the temperature of 1320°C where the PREN of ferrite and austenite are equal. Thus, considering only the chemical composition of the material, ferrite could be more corrosion resistant than austenite.

Figure 3 explore the metallographic analysis of the samples with different ferrite volume percent. The quantitative stereology of those samples for ferrite volume fraction determination allowed the prediction of the equilibrium temperature through ThermoCalc® software and the precise values of PREN of ferrite and austenite, as shown in Table 2.

Table 2. UNS S31803 duplex stainless-steel sample characterization parameters.

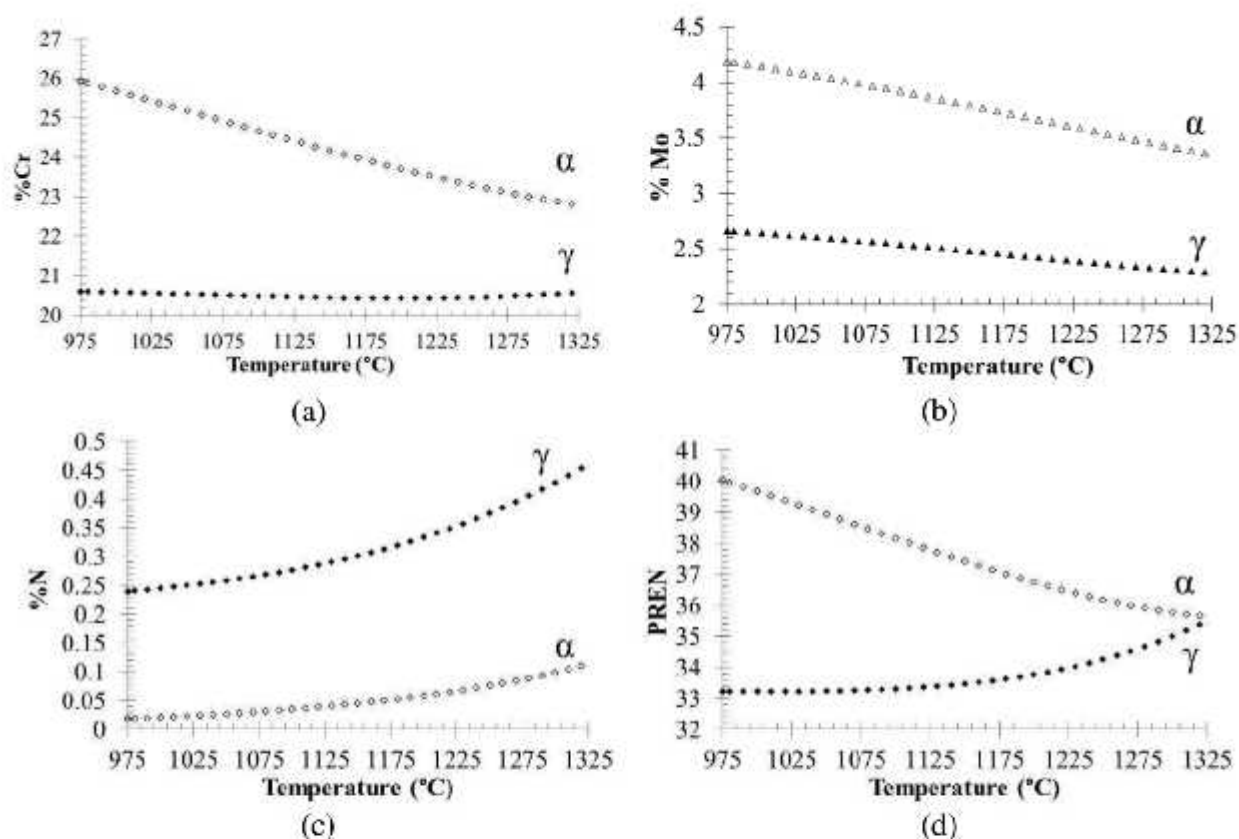| Sample	% ferrite	ThermoCalc® predicted equilibrium temperature (°C)	PREN(α)	PREN(γ)
(a)	44.9 ± 2.8	1070	39.1	33.1
(b)	49.0 ± 3.8	1110	38.3	33.2
(c)	82.7 ± 1.9	1310	37.9	33.4
(d)	96.6 ± 1.4	1340	37.4	33.4

Fig. 2. Cr (a), Mo (b) and N (c) contents and PREN calculus (d) in ferrite and austenite as a function of solution-treatment temperature.

Analysing the Table 2 it is evident the PREN-α reduction with increasing ferrite volume fraction as PREN-γ remains almost constant. The partition of alloy elements on both phases suggests that as ferrite volume fraction increases, the ferrite corrosion resistance decreases as Cr and Mo contents also decreases.

Electrochemical tests through polarization curves were conducted in all the samples, and typical results are presented in Fig. 4. The pitting potential, from which a pit nucleates and growth in stable conditions, decreases as ferrite volume fraction increases, probably caused by Cr and Mo reduction in this phase leading to PREN-α reduction. This observation suggests that ferrite plays an important role in pitting corrosion resistance of the material.
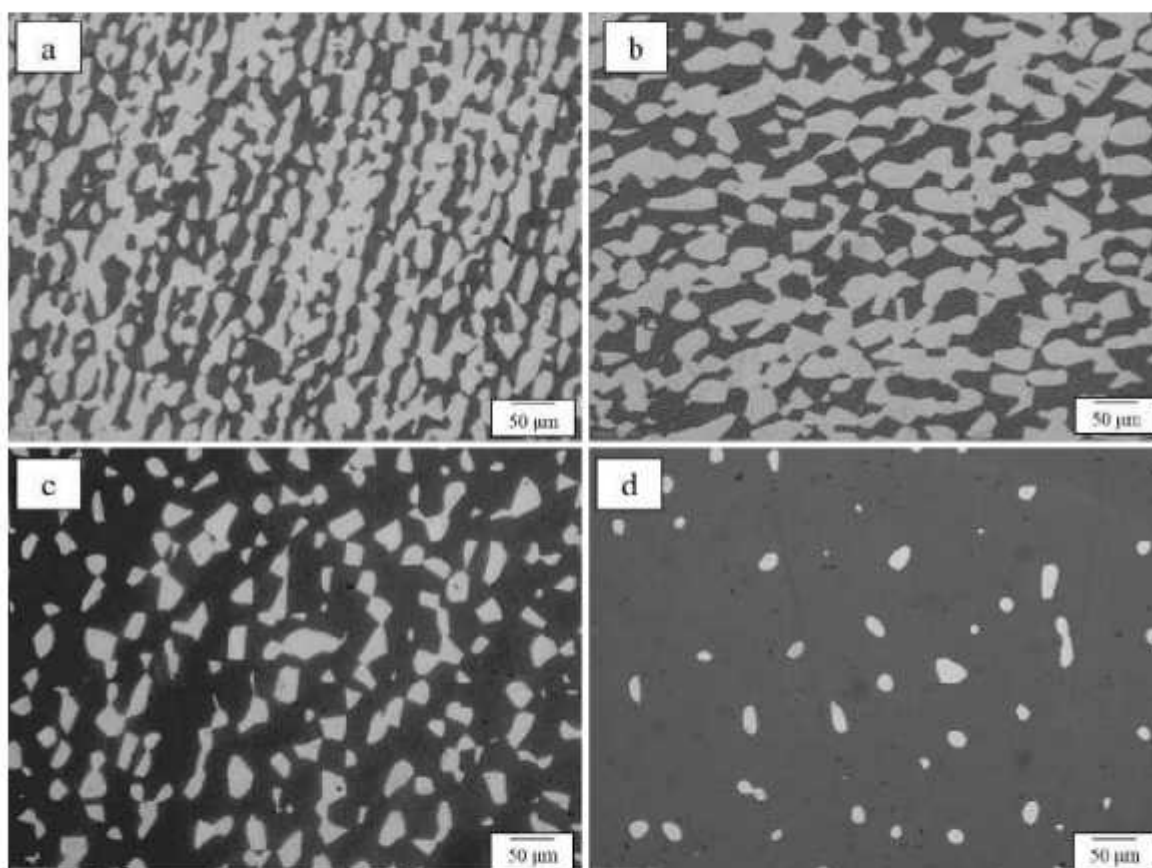
Fig. 3. UNS S31803 duplex stainless steel with different ferrite (black) volume fraction: (a) 44.9±2.8%; (b) 49.0±3.8%; (c) 82.7±1.9%; (d) 96.6±1,4%. Modified Beraha etching.
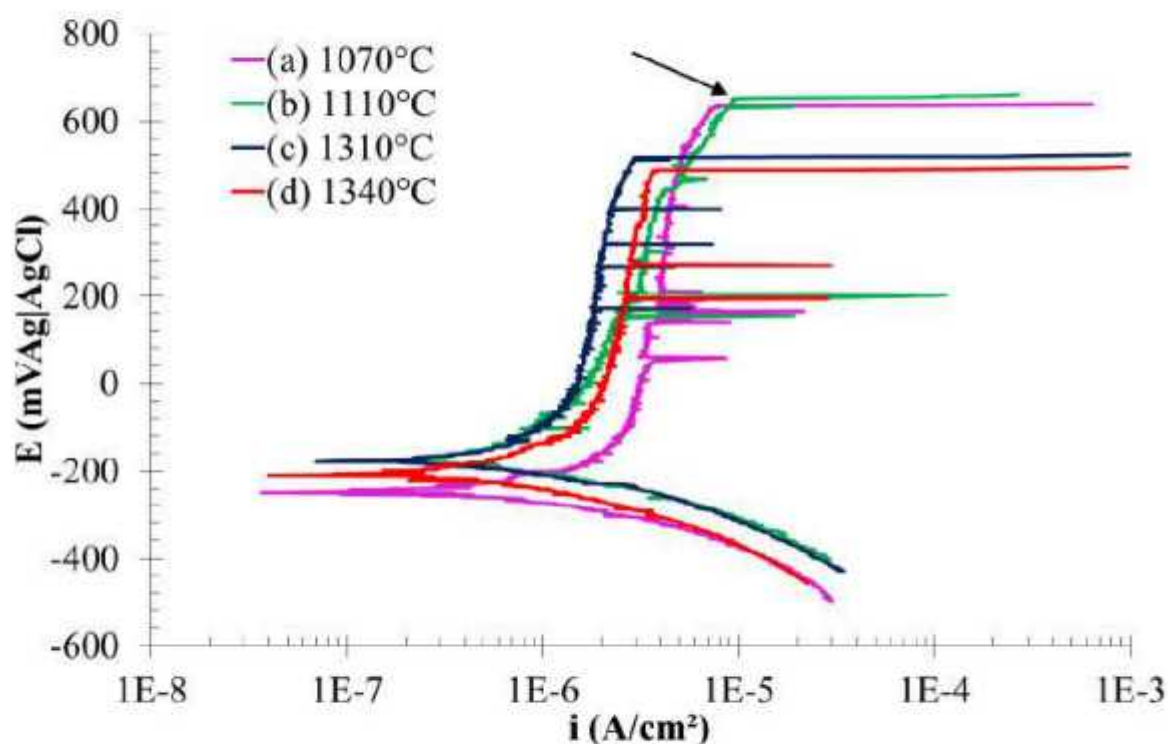

Fig. 4. Potentiodynamic polarization curves of UNS S31803 duplex stainless steel in 0.6M NaCl solution at 75°C in samples with different ferrite fractions.

The analysis of both pitting potentials (E_{pit}) and the PREN for ferrite and austenite with increasing ferrite percent is necessary and presented in Figure 5. A light decrease in the medium pitting potential values with increasing ferrite percent (and reduction of PREN α) is observed. The increase in ferrite percent leads to the decrease in Cr and Mo contents more sharply in ferrite if compared to austenite as previously seen in Figure 2 (a) and (b). This behaviour may be related to the slight decrease of pitting potential and in PREN α observed in Figure 5. Instead, the PREN γ is almost constant even in different ferrite volume contents.
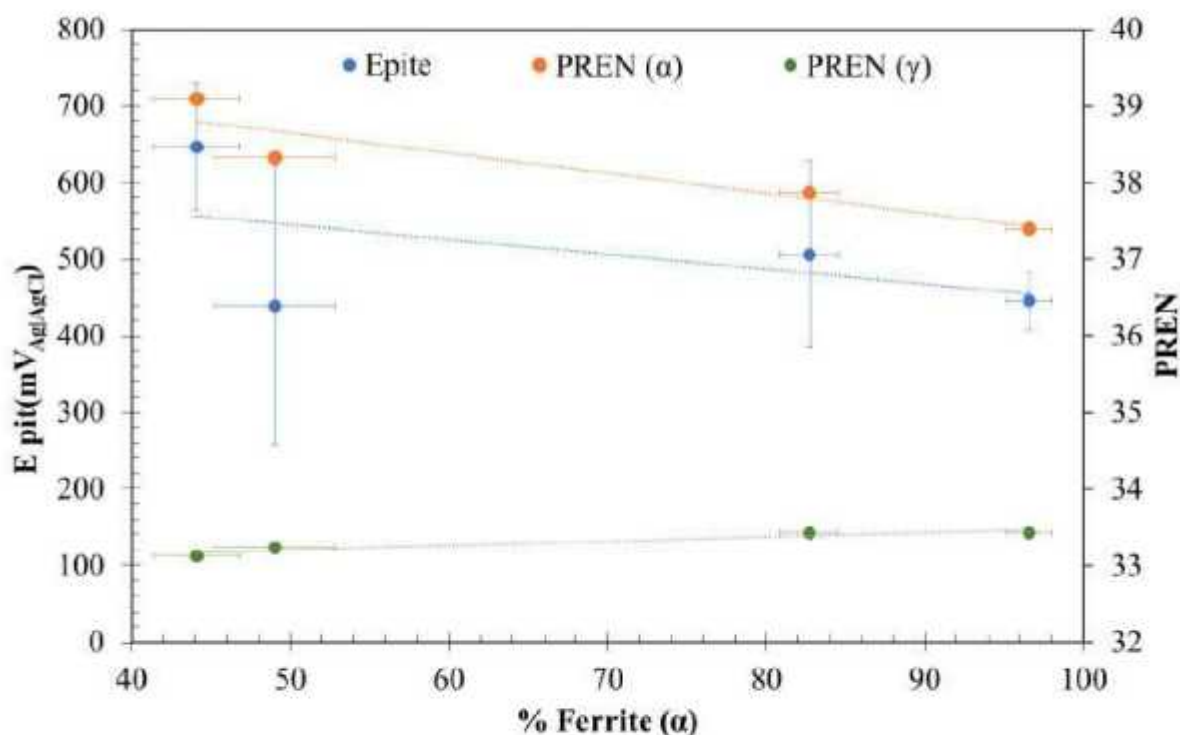

Fig. 5. Pitting potential (E_{pit}) and PREN as a function of ferrite percent.

Other evidences of this behaviour may be observed in the optical microscopy of the samples after polarization tests (Fig. 6). Pitting formation occurs preferably in ferrite and in ferrite/austenite interfaces. In the samples with a less ferrite volume fraction, pits were found preferably in ferrite/austenite interfaces as presented in Fig. 6 (a), but also some pits were present inside ferrite phase. As with low solution treatment temperatures leads to a higher number of interfaces, as shown in Fig. 3 (a), and knowing that pitting occurs preferably in non-homogeneities like grain boundaries, inclusions and interfaces, the occurrence of pitting in ferrite/austenite interfaces is justified.

However, in the samples where the ferrite volume percent is high (Fig. 3 c-d), pits are found in ferrite phase or in non-homogeneities like inclusions (Fig. 6 c-d). No pitting was found in austenite islands, showing that even PREN-α being higher PREN-γ, apparently ferrite is less pitting resistant than austenite in the tested conditions. Probably the explanation for this behaviour is not in Cr and Mo contents on both phases, but the presence of N in austenite. This result corroborates other authors conclusions [2,8] which stated that austenite phase is more corrosion resistant than ferrite in duplex steels. As reported in those publications, ammonia formation as the product of the reaction of N with H dissolved in the solution would raise locally the pH leading to the passivation of the materials surface, reducing the tendency to pitting occurrence [2,9].
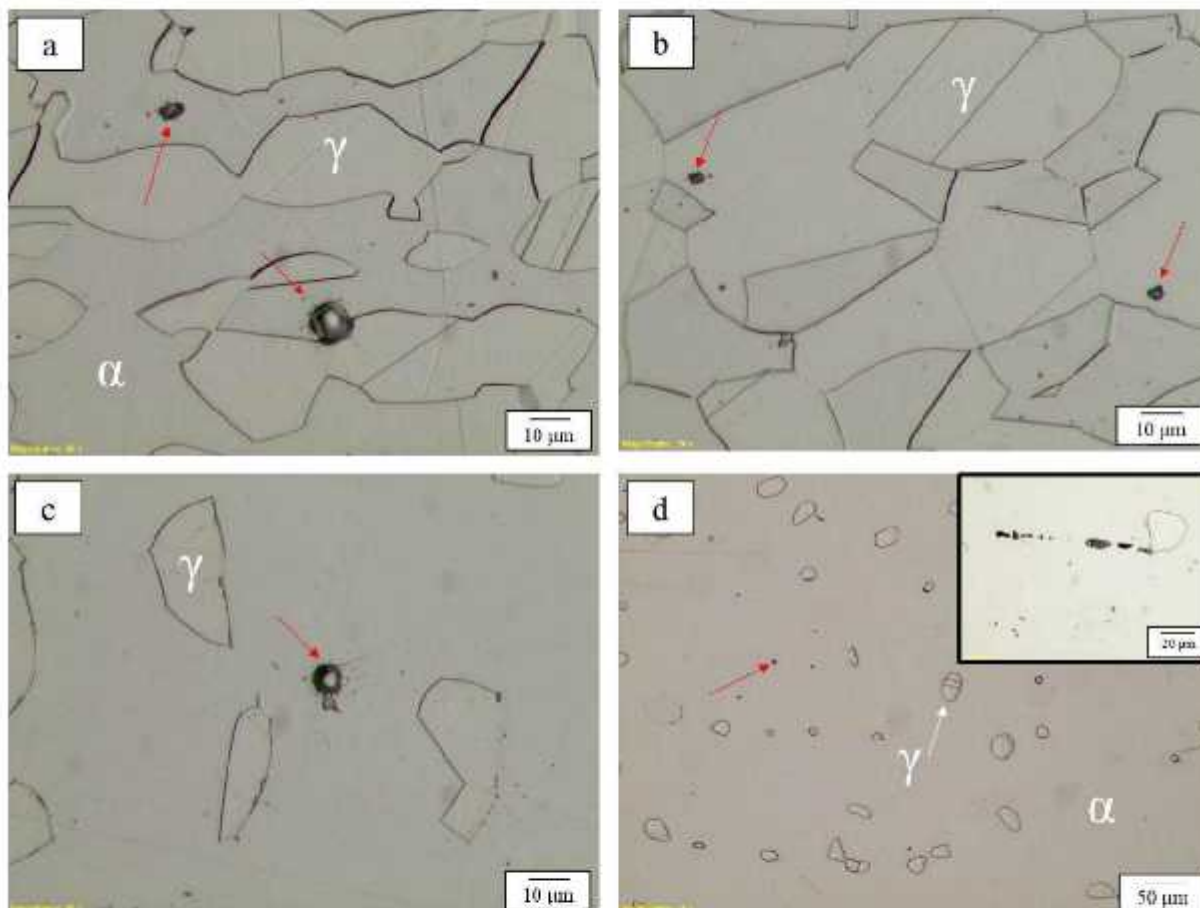
Fig. 6. Optical micrography of UNS S31803 after potentiodynamic tests in 0.6M NaCl solution at 75°C etched with oxalic acid. Pits are indicated by red arrows.

Conclusions

Thermodynamic simulation reveals that, using Cr, Ni, Mo and N equilibrium contents, the PREN for ferrite is higher than austenite between 975 and 1300 °C. Nevertheless, the electrochemical results show a slight reduction of pitting potential with increasing ferrite content, probably related to the reduction of Cr and Mo contents in this phase. Pits were found preferably in ferrite and in ferrite/austenite interfaces. This behavior suggests that even with only a slight reduction of pitting potential and, consequently, a discrete corrosion resistance reduction, ferrite is more susceptible to pitting. No pits were found in austenite, suggesting that higher N contents are fundamental to maintain the corrosion resistance of this phase.

References

[1] H.S Solomon and T.M. Devine. Duplex Stainless Steels: A tale of two phases Proceedings, Conference Duplex Stainless Steels, ASM Metals Park, Ohio (1984), p.693.

[2] J.O.Nilsson. Super Duplex Stainless Steel, Materials Science and Technology (1992, Volume 8), p. 685.

[3] H.Vannevik, H. Effect of elemental partitioning on pitting resistance of high nitrogen duplex stainless steels, ISIJ international (1996, Volume 36), p 807.

[4] International Organization for Standardization. ISO15156-3, Petroleum and natural gas industries — Materials for use in H_2Scontaining environments in oil and gas production - Part 3: Cracking-resistant CRAs (corrosion resistant alloys) and other alloys, 2015.

[5] I. Alvarez-Armas, Duplex Stainless Steels: A Brief History and Some Recent Alloys, Recent Patents on Mechanical Engineering (2008), p.51

[6] J.A. Sedriks. Corrosion of stainless steels, John Wiley, New York (1996).

[7] L.F. Garfias-Mesias, Understanding why PREN alone cannot be used to select duplex stainless steels, Proceedings, Nace International Conference, Dallas (2005).

[8] R. Magnabosco, Alonso-Falleiros, N. Pit Morphology and its Relation to Microstructure of 850°C Aged Duplex Stainless Steel. Corrosion (2005. February 2005), p.130.

[9] G. Lothongkum, P. Wongpanya, S. Morito, T. Furuhara, T. Maki, Effect of nitrogen on corrosion behavior of 28Cr–7Ni duplex and microduplex stainless steels in air-saturated 3.5wt% NaCl solution, Corrosion Science (2006, Volume 48), p. 137.