

Study of the Distribution of Cr, Mo, Ni and N in δ Ferrite and Austenite in Duplex Stainless Steels

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Abstract

The PREN value of the alloy may lead to a misleading prediction of pitting corrosion resistance because in the event of an imbalance of δ ferrite and austenite volume fraction, the chemical composition of the phases may be very different from that of the alloy. In this case, the PREN of one of the phases may be below the PREN of the alloy. Three laminated duplex stainless steels with different PRENs were characterized: UNS S32304 (Lean Duplex), UNS S31803 (Duplex) and UNS S32750 (Super Duplex). Several complementary techniques of microstructural analysis were used, such as optical emission spectrometry, optical microscopy and scanning electron microscopy with coupled EDS. Quantitative metallographic analyzes were carried out to determine the volume fraction of δ ferrite and austenite, and semi-quantitative chemical analyzes of the present phases, using a coupled EDS-SEM. For all the alloys studied, it was observed that the δ ferrite presents higher Cr and Mo contents than the austenite phase, which had N contents higher than the δ ferrite. The PREN of δ ferrite is higher than that observed for austenite for both UNS S32304 (Lean Duplex) and UNS S31803 (Duplex). In UNS S32750 (Super Duplex), the PREN of the austenite is higher than that observed for δ ferrite due to the higher content of N of this alloy.

Keywords: Duplex Stainless Steels; PREN; Volume Fraction.

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INTRODUCTION

The duplex stainless steels solidify according to ferritic-austenitic solidification ($L \rightarrow L + \delta \rightarrow L + \delta + \gamma \rightarrow \delta + \gamma$). δ ferrite solidifies as the primary phase in dendritic or cellular fashion. As temperature decreases, austenite is formed by a peritectic ($L + \delta \rightarrow \gamma$) or eutectic ($L \rightarrow \delta + \gamma$) reaction. In the case of a peritectic reaction, the initially formed austenite completely surrounds the ferrite and subsequently grows into ferrite and liquid. Depending on the rate of diffusion through the austenite, the reaction may or may not be complete, and at the end of the solidification ferrite may be involved in austenite. Between the two reactions - peritectic and eutectic - the transition takes place where, during the initial formation of austenite by peritectic reaction, ferritizing elements secrete to the liquid, provoking their enrichment in these elements and consequently the simultaneous

formation of ferrite and austenite by means of a eutectic reaction [1].

Duplex stainless steels (DSS) are steels that present biphasic microstructure containing ferrite and austenite in volumetric fractions approximately equal to 50%.

Due to their biphasic microstructure, these steels present a favorable combination of the properties of ferritic and austenitic stainless steels. They present high mechanical strength, good toughness and ductility and good corrosion resistance in various media. This favorable combination of properties makes this class of stainless steels widely used in the petrochemical, pulp and paper and, more recently, hydro generation industries [1-9].

The duplex steels are based on the Fe-Cr-Ni ternary phase diagram shown in figure 1.

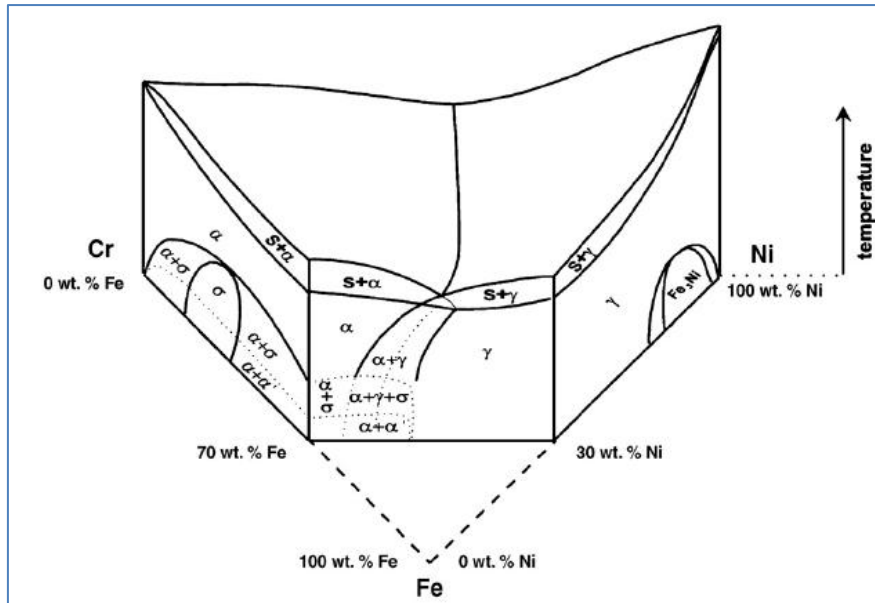


Fig-1: Fe-Cr-Ni ternary phase diagram highlighting the pseudo-binary Cr-Ni diagram for 70% Fe [3]

One way of empirically quantifying pitting corrosion resistance is through the PREN (*Pitting Resistance Equivalent Number*), $PREN_N$ (equation 1)

$$PREN_N = \%Cr + 3,3 x(\%Mo) + 16x(\%N) \quad \text{(Equation 1) [3]}$$

$$PREN_W = \%Cr + 3,3 x(\%Mo) + 0,5 \%W + 16x(\%N) \quad \text{(Equation 2) [3]}$$

The main alloying elements, besides iron, present in the chemical compositions of duplex stainless steels are:

Chromium (Cr): is the element responsible for the formation of the protective layer, its concentration by weight in the duplex is at least 22%. Cr stabilizes the body centered cubic structure (ferrite). The concentration of this alloying element must be controlled, due to the fact that at high concentrations it promotes the formation of intermetallic compounds. The higher the Cr content, the higher the content of Ni (austenite former) in order to ensure a balance between the austenite and ferrite phases [1-9].

Molybdenum (Mo): increases the passivity and chemical resistance of stainless steels. Its action is especially important in increasing resistance to corrosion by pits. It acts together with Cr to form the ferrite phase. At high concentrations, like Cr, it contributes to the generation of harmful intermetallic compounds [1-9].

Nickel (Ni): it is a strong austenitizing element, giving greater ductility, mechanical resistance and weldability, besides delaying the formation of intermetallic phases, making the steel nonmagnetic. Associated with Cr, favors the increase of corrosion resistance. Ni excess may lead to imbalance between ferrite and austenite phases. The percentage of austenite may well exceed 50%. The consequence of this is that the remaining ferrite will have an excessive

concentration of Cr and Mo, so there is a risk that the ferrite will easily decompose to form intermetallic phases when exposed to a temperature between 650 and 900 °C [1-9].

and $PREN_W$ (equation 2), when dealing with materials having Tungsten (W) in their composition [3].

Nitrogen (N): it is a strong austenite former. Nitrogen guarantees high mechanical resistance. This element delays the precipitation of chromium carbides at temperatures between 650 and 900 °C, due to the preferential formation of nitrides, thus avoiding a marked impoverishment of chromium in intergranular regions under these conditions. It is also used to reduce the production cost of the stainless steels since adding this element can significantly reduce the addition of Ni. It can also be added during the welding process through the shielding gas [1-9].

Manganese (Mn): its main function is to eliminate the effect of impurities in steels, such as oxygen and sulfur. Small amounts of this element, associated with the presence of nickel, improve substantially the mechanical resistance, however, decreases the ductility [1].

Tungsten (W): the addition of W in contents of up to 2% improves the resistance to corrosion by pits mainly in hydrochloric environments due to the stabilization of the protective layer of oxides. W favors the formation of intermetallic phases between 700 and 1000 °C as well as the formation of secondary austenite in the weld pool in the case of welded joints [1-9].

Figure 2 shows a typical TTT curve of a super duplex stainless steel highlighting the effect of the

major alloying elements on the precipitation of deleterious phases.

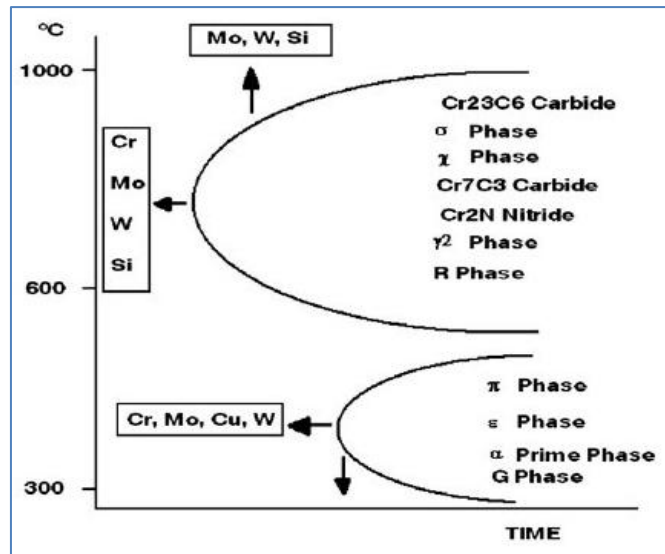


Fig-2: Typical TTT curve of a super duplex steel highlighting the effect of some alloying elements on the precipitation of deleterious phases [3]

The calculation of the PREN of the alloy will be important to predict the pitting corrosion resistance. In the case of duplex steels, the PREN value of the alloy may lead to an erroneous prediction of pitting corrosion resistance because, in the event of an imbalance of δ ferrite and austenite volumetric fractions, the chemical composition of δ ferrite and austenite be very different from that of the league. In this case, the PREN of one of the phases, δ ferrite or austenite, may be below the PREN of the alloy. The absence of deleterious phases is also of fundamental importance. It makes sense, then, to measure the chemical compositions of the ferrite and austenite phases and then calculate their PRENs and compare them with the PREN of the alloy. The true PREN will be the lowest PREN found.

EXPERIMENTAL

Three sheets of duplex stainless steels with a thickness of 16.00 mm were used. The duplex stainless steels used are UNS S32304 (Lean Duplex), UNS S31803 (Duplex) and UNS S32750 (Super Duplex). Chemical analyzes were carried out in all samples by means of an optical emission spectrometer, according to ASTM E 1086-08 [10].

The specimens were removed from the plates using a cut-off. Afterwards, the samples were embedded in hot-cure resin (bakelite). The conventional manual polishing was applied using water slicks (100, 240, 320, 400, 600 and 1000 mesh) in order to standardize the surface finish of the samples. Afterwards, a cloth polishing with 9, 3 and 1 μ m diamond abrasive paste was carried out in this sequence. The samples were electrolytically attacked in 20% NaOH solution, 6V, for 90 seconds. This allowed the microstructural characterization of the samples through optical microscopy, as well as a better observation of the present phases in Scanning Electron Microscopy (SEM). The quantitative metallographic analyzes for the determination of volumetric fractions of δ ferrite and austenite were performed according to ASTM E 562 ed. 08 [11], using a 4 X 5 grid (20 points) with a magnification of 400 X in 30 different regions per test piece. Semi-quantitative chemical analyzes of the present phases were performed using a Scanning Electron Microscopy coupled with Energy Dispersive Spectrometry (SEM/EDS).

RESULTS AND DISCUSSION

Table 1 presents the chemical compositions as well as the PRENs of the studied stainless steels.

Table-1: Chemical compositions of the studied stainless steels (% by weight)

	%C	%Si	%Mn	%P	%S	%Cr	%Ni	%Mo	%Cu	%N	PREN
UNS S32304 (Lean Duplex)	0.018	0.38	1.41	0.025	0.002	23.39	4.84	0.19	0.32	0.12	25.94
UNS S31803 (Duplex)	0.015	0.43	1.51	0.023	0.001	22.61	5.80	3.13	0.12	0.17	35.66
UNS S32750 (Super Duplex)	0.013	0.43	0.64	0.024	0.000	24.91	6.97	3.76	0.08	0.28	41.80

Figure 3 shows the micrographs of the duplex stainless steels studied. The typical microstructures of

laminated duplex stainless steels are observed. Where the dark phase is δ ferrite and the clear phase austenite.

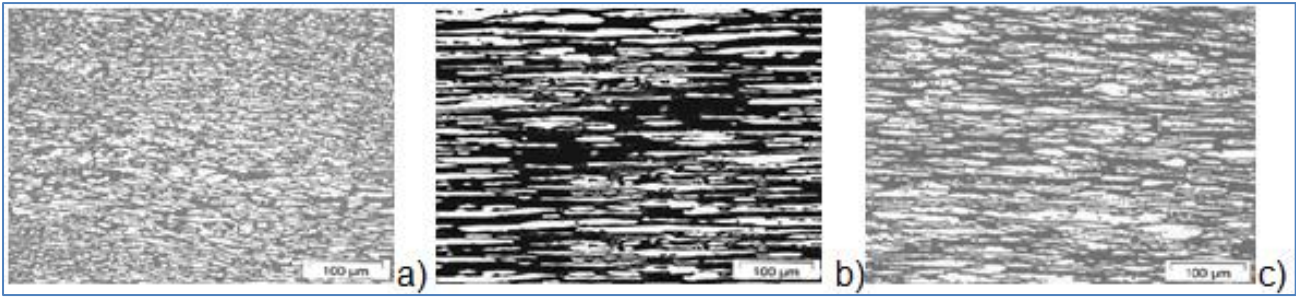


Fig-3: Micrographs of stainless steels: a) Lean Duplex UNS S 32304. b) UNS S31803 (Duplex) and c) UNS S32750 (Super Duplex)

Table 2 presents the volumetric fractions of δ ferrite and austenite obtained by measurements in 30 different regions per test specimen.

Table-2: Volumetric fractions of δ ferrite and austenite

	% δ	95% CI	% RA
UNS S32304 (Lean Duplex)	50.17	4.32	8.61
UNS S31803 (Duplex)	52.48	3.26	6.21
UNS S32750 (Super Duplex)	51.97	3.98	7.66

Analyzing the data in Table 2, it can be seen that the mean volumetric fractions of δ ferrite and austenite are close to 50% each. In this way it is reasonable to predict that there is an ideal solute partition between the two phases and the δ ferrite should have higher levels of the ferritic alloying elements chromium and molybdenum. Similarly, the austenite should present higher levels of the austenitizing elements nickel and nitrogen. In this ideal

condition of volumetric fractions of δ ferrite and austenite close to 50% each, it is reasonable to expect PRENs, of both phases, close to the PREN of the alloy. Figures 4, 5 and 6 presents the metallographic analyzes and the respective characterizations of Lean Duplex, Duplex and Super Duplex stainless steels, as well as the respective semi-quantitative chemical analyzes of ferrite and austenite through SEM with coupled EDS.

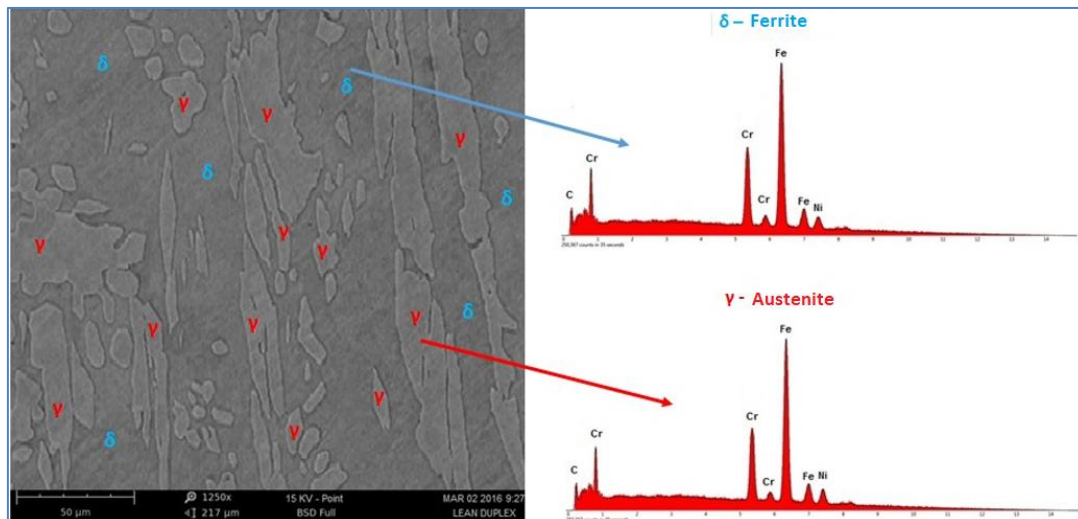


Fig-4: Metallographic analyzes and respective characterization of UNS S32304 (Lean Duplex stainless steel), as well as, the respective EDS of the phases δ ferrite and austenite

It is observed in Figure 4), the absence of well-defined peaks of molybdenum in the EDS of the δ ferrite and austenite phases of Lean Duplex stainless steel. Such observation is consistent with the values set forth in Table 1, where the average content of molybdenum alloy element is only 0.19% by weight.

Analyzing all the EDS shown in figure 4, 5 and 6, the δ ferrite phase presents higher Cr and Mo contents than the austenite phase. On the other hand, the austenite presents Ni contents higher than the δ ferrite.

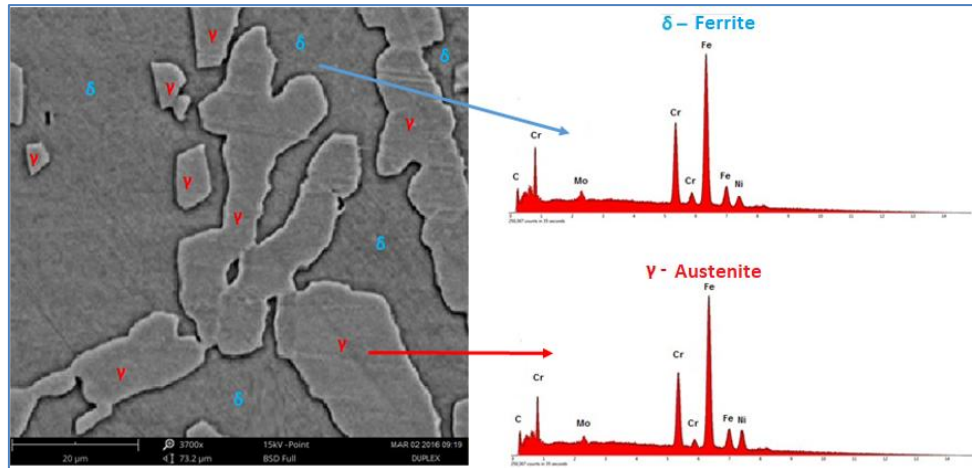


Fig-5: Metallographic analyzes and respective characterization of UNS S31803 (Duplex stainless steel), as well as, the respective EDS of the phases δ ferrite and austenite

The technique did not allow measuring the N content of the phases. In the Fe-N phase diagram, the nitrogen solubility limit on the ferrite is 0.10% by weight at 592 °C, and that the nitrogen solubility limit

on austenite is 2.8% by weight at 650 °C. Duplex stainless steels are multinary alloys and therefore the use of a Fe-N binary diagram may seem very simplistic.

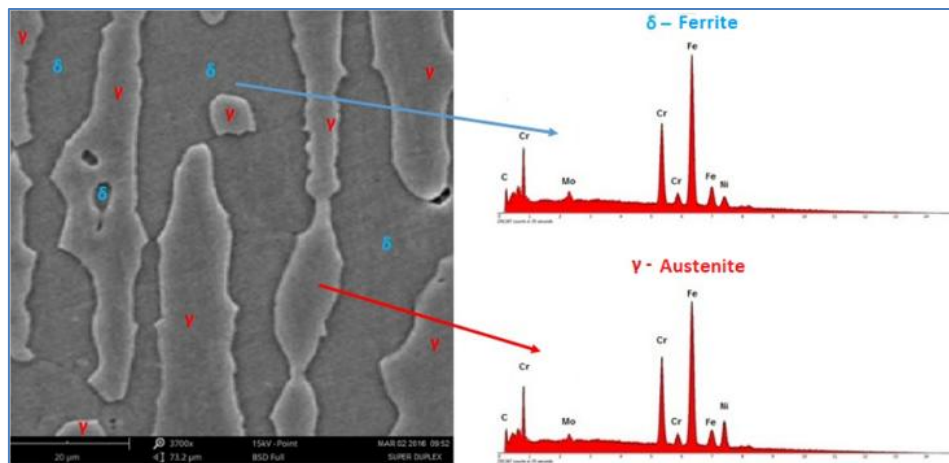


Fig-6: Metallographic analyzes and respective characterization of UNS S32750 (Super Duplex stainless steel), as well as, the respective EDS of the phases δ ferrite and austenite

However, due to the difficulty of measuring the nitrogen content in the phases, the Fe-N diagram shown in figure 7 was taken as a reference. In this way, it was considered reasonable to consider that the maximum content of nitrogen in the δ ferrite is exactly

the limit of solubility of this element in the ferrite, that is, 0.10%.

In this way, for the average calculation of the PRENs of the phases, the nitrogen content in the ferrite was evaluated as 0.09% by weight for all the stainless steels studied.

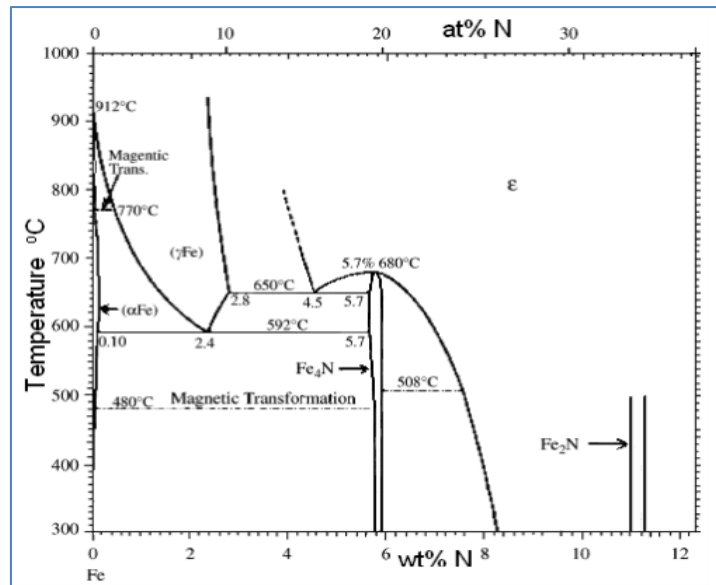


Fig-7: Fe-N phase diagram [12]

From the chemical analyzes of the alloys presented in Table 1, and the semi-quantitative chemical analyzes of the δ ferrite and austenite phases obtained by scanning electron microscopy with EDS coupled, the PRENs were calculated using the formula presented in equation 1. Table 3 presents the average chemical compositions of the alloys, δ ferrite and austenite phases.

Table 3 presents the PRENs results calculated for the three stainless steels studied and for the ferrite and austenite phases, respectively.

The percentage errors in the measurement of the chemical composition of the δ ferrite and austenite phases by EDS is 2%. The N contents in the phases were calculated from the average N content of the alloys considering that the % N in the ferrite is 0.09% by weight.

Table-3: Chemical compositions of alloys, δ ferrite and austenite phases, PREN calculations and volumetric fractions

	Cr	Mo	N	PREN	Volumetric Fractions (%)
Lean Duplex	23.39	0.19	0.12	25.94	
Ferrite	24.23	0.20	0.09	26.33	50.17
Austenite	21.87	0.18	0.15	24.86	49.83
Duplex	22.61	3.13	0.17	35.66	
Ferrite	23.92	3.11	0.09	35.62	52.48
Austenite	20.44	3.08	0.25	34.61	47.52
Super Duplex	24.91	3.76	0.28	41.80	
Ferrite	25.84	3.88	0.09	40.08	51.97
Austenite	23.13	3.57	0.47	42.44	48.03

It is observed in Table 3 that the δ ferrite phase presented higher chromium and molybdenum contents than the austenite phase.

δ ferrite and austenite volumetric fractions, the chemical compositions of δ ferrite and austenite will be different from that of the alloy.

As expected, there are important differences between the chemical compositions of δ ferrite and austenite phases. These different chemical compositions result in different PRENs for δ ferrite and austenite phases, than those of the alloys compositions.

For all the duplex stainless steels studied, it was observed that the δ ferrite phase presents higher Cr and Mo contents than the austenite phase. On the other hand, the austenite presents Ni contents higher than the δ ferrite.

CONCLUSIONS

In the case of duplex steels, the PREN value of the alloy may lead to an incorrect prediction of pitting corrosion resistance due to, if there is an imbalance of the

For all duplex stainless steel studied, the PREN of one of the phases, δ ferrite or austenite, was below the PREN of the alloy.

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