EVALUATION OF FERRITE QUANTIFICATION METHODS APPLIED TO DUPLEX STAINLESS STEELS*

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Abstract

Three techniques for ferrite quantification were applied in a duplex stainless steel UNS S31803 solution treated at three different temperatures, 1000, 1100 and 1200°C, in order to verify their compliance with the results from ThermoCalc® prediction. It is verified that only austenite and ferrite phases are present in the samples and that an increasing in solution treatment temperature led to the increase of the volume fraction of ferrite. It is also observed that quantitative stereology technique shows absolute values closer to ThermoCalc® predictions. On the other hand, measurements by ferritoscope and XRD show significant deviations, probably due to texturing effect imposed by the rolling process.

Keywords: Duplex Stainless Steels; ferrite quantification; ferritscope; quantitative metallography; X-ray diffraction.

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1 INTRODUCTION

Steels which have in their chemical composition contents of free chromium in the matrix higher than 11% are called stainless steels, due to their ability to form an adherent surface film - passive film - which protects the steel from the action of corrosive agents, providing corrosion resistance [1].

Duplex stainless steel (DSS) is characterized ideally by equal amounts of ferrite and austenite in the microstructure, which provides increased mechanical resistance, due to the fine grain size, typical of these steels. It has higher corrosion resistance when compared to ferritic stainless steels, promoted by high content of chromium, nitrogen and molybdenum in their chemical composition, and due to the presence of austenite in its duplex structure presents good ductility and toughness, similar to austenitic stainless steels [2].

The excellent mechanical behavior and the high corrosion resistance are related to approximately 50% volume fraction of ferrite [3], and so the control of the ferrite content of the DSS is an important tool to ensure the desired properties.

Due to those excellent properties, its utilization has increased considerably in various industrial applications, such as pressure vessels, heat exchangers, pipelines, evaporators, storage towers and pipelines in oil and gas industries for transportation of dry and / or wet carbon dioxide [3].

The increase of the demand for DSS in industrial applications made mandatory the control of the manufacturing processes and the necessity to know accurately the quantities of the phases before its final use. Unfortunately, values found in phase quantification can be influenced by the existing measurement techniques. Previous work [4,5] showed quantification of the ferrite volume fraction of duplex stainless steels using two different techniques: quantitative metallography after Beraha metallographic etching and magnetic measurements with the aid of a ferritoscope. The results showed considerable discrepancies between the values obtained by these techniques, and none of them are similar to the values calculated using ThermoCalc® software [4].

Other possibility to evaluate the volume fraction of the phases is by analyzing the peak intensity of the present phases in the X-ray diffraction (XRD). For a randomly oriented duplex stainless steel sample, quantitative measurements of the relative ferrite and austenite can be made from X-Ray diffraction patterns because the total integrated intensity of all diffraction peaks for each phase is proportional to the volume fraction of that phase. If the crystalline phase or grains of each phase are randomly oriented, the integrated intensity from any single diffraction peak (*hkl*) crystalline plane is also proportional to the volume fraction of that phase [6]. Relying on this principle, it is possible to determine the volume fraction of the phases calculating the peak areas of ferrite and austenite from the results of XRD test. Thus, the value of the volume fraction of ferrite (%α) will be the sum of ferrite peak areas divided by the total sum of all peaks (ferrite + austenite) as shown in equation 1. The area of each peak for the ferrite and austenite phases (S_α e S_γ) can be calculated by multiplying the peak intensity value by the Full Width at Half Maximum (FWHM) of each individual peak [7].

$$\%\alpha = \left[\frac{\sum S_\alpha}{\sum \left(S_\alpha + S_\gamma \right)} \right] \cdot 100$$

(1)

The other way to determine phase content from XRD tests is described in Moser et al., 2014 [8]. The quantitative estimation is based on the use of internal ratios. Assuming that the grains are randomly oriented, the integrated intensity of a given phase "*i*" is proportional to the volume fraction of that phase, "*Vi*", as shown in equation 2:

$$V_i = \frac{\frac{1}{n}\sum_1^n \frac{I_i^j}{R_i^j}}{\frac{1}{n}\sum_1^n \frac{I_\gamma^j}{R_\gamma^j} + \frac{1}{n}\sum_1^n \frac{I_\alpha^j}{R_\alpha^j}} \qquad (2)$$

Where "*n*" is the number of peaks examined for each phase (being *i* the phases *γ* or *α*). *R* is the material scattering factor and is described by equation 3:

$$R_{hkl} = \left(\frac{1}{V^2}\right)\left[|F|p\left(\frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta}\right)\right]e^{-2M} \qquad (3)$$

where "V" is the volume fraction of the unit cell, "*F*" is the structure factor, "*hkl*" are the Miller indexes of the reflection plane, "*p*" is the multiplying factor, and "e^{-2M}" is Debye-Waller Factor (DWF). Table 1 shows these values for austenite and ferrite phases. The volume fraction of the unit cell "*V*" is obtained through the lattice parameter "*a*" of ferrite and austenite, which can be calculated according to equation 4:

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \qquad (4)$$

where "*d*" is the interplanar distance for a given plane. The volume fraction of the unit cell "*V*" of ferrite and austenite can be calculated as "a^3".

Table 1 – Values to determine phase volume fraction according to Moser et al., 2014 [8].

Austenite (FCC)				Ferrite (BCC)			
hkl	*F*	*p*	*DWF*	*hkl*	*F*	*p*	*DWF*
(111)	18,16	8	0,963	(110)	18,16	12	0,961
(200)	16,55	6	0,951	(200)	15,04	6	0,925
(220)	13,66	12	0,904	(211)	12,43	24	0,889
(311)	11,36	24	0,871	(220)	11,36	12	0,86

The main objective of this work is to perform a comparison between different methodologies of ferrite phase quantification: quantitative stereology by optical microscopy, magnetic measurement by ferritoscope and finally, comparative analysis of the peak intensities of the phases by X-ray diffraction and all of them compared to ThermoCalc® fitting.

2 PROCEDURES

It was investigated a hot rolled duplex stainless steel plate with 300 mm long x 200mm wide x 3 mm thick (UNS S31803) with the chemical composition shown in Table 2.

Table 2 – Chemical composition (mass percentage) of DSS.

Cr	Ni	Mo	Mn	N	C	Si	P	S	Fe
22,07	5,68	3,20	1,38	0,17	0,017	0,34	0,02	0,001	balance

Samples from the original plate were solution treated under nitrogen atmosphere at 3 temperatures, 1000, 1100 or 1200°C for 30 minutes and then cooled in water. For each temperature, the solution treated strips samples were cut into specimens of 10 mm x 10 mm, subsequently embedded in thermosetting resin. The samples were analyzed considering the plan surface of the plate viewing from the rolling direction. Further, the specimen were ground to 500-mesh emery paper and then polished down to 1 µm size diamond paste lubricated with ethanol in a semi-automatic polishing equipment.

After polishing, the specimens were revealed (etched) in a modified Beraha etchant, whose composition is 20 ml of hydrochloric acid + 80 ml of distilled and deionized water, and to this stock solution is added 1 gram of potassium metabisulphite + 2 grams of ammonium bifluoride. The etching time was approximately 30 seconds then the samples were immersed in water. The observed surface was dried by ethanol evaporation, aided by a cold air jet, enabling the micrograph recording of the samples.

For measuring the volume fraction of ferrite, it was used four different techniques:

Magnetic measurement by ferritoscope: after polishing of the specimens, ten measurements of the volume fraction of ferrite of each sample were performed with a FISCHER MP30 ferritoscope; the equipment was calibrated with appropriate standards, with detection limit of 0.1% ferrite.

Optical microscopy: after polishing and etching, measurements of phase contents were made through QMetals software, part of the image analysis Leica Q500 / W, connected to a LEICA DMLM microscope. Ten fields per sample were analyzed at 500X magnification.

X-ray diffraction: To confirm the existence of ferrite and austenite, X-ray diffraction patterns were obtained using a Shimadzu XRD-7000 diffractometer under Cu-Kα radiation and a Ni monochromator; diffraction scan were performed at 35° <2θ <120° at a rate of 1° / min sampling every 0.04°; Cu source was excited at acceleration voltage of 30 kV and current of 30 mA. Ferrite and austenite volume fractions could be calculated by two different methods:

- **Method 1:** volume fraction of phases was obtained by analysis of peak intensity of the existing phases, using equation 1.
- **Method 2:** the volume fraction of the phases were determined by the method described by Moser et al [8], using equation 2.

3 RESULTS AND DISCUSSION

The Figures 1, 2 and 3 show the micrographs of specimens solution treated at 1000, 1100 and 1200 °C, respectively after modified Beraha etching. It is verified the

presence of only two phases: ferrite and austenite, as confirmed by others researchers [9,10] and X-ray diffraction of this work. The austenite can be identified as the light gray phase and the ferrite phase as dark gray color.

Micrographs showed that ferrite and austenite grains distribution present a preferred orientation in the longitudinal rolling direction as indicated by double arrows. Those preferred grain orientation decrease as the solution treatment temperatures increase, and the random structure needed for stereology and XRD determination of ferrite phase previously discussed is impaired. As expected, the increase in solution treatment temperature leads to larger grain sizes.
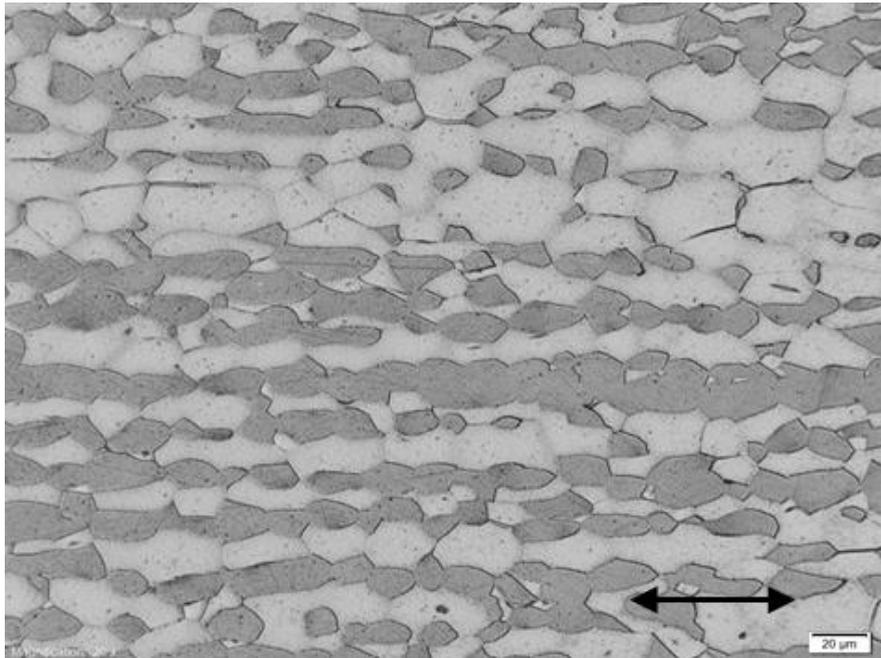

Figure 1 - Micrograph of the heat-treated material at 1000°C. Ferrite (dark) and austenite (light) phases after modified Beraha etching, (the double arrow indicates the rolling directions).
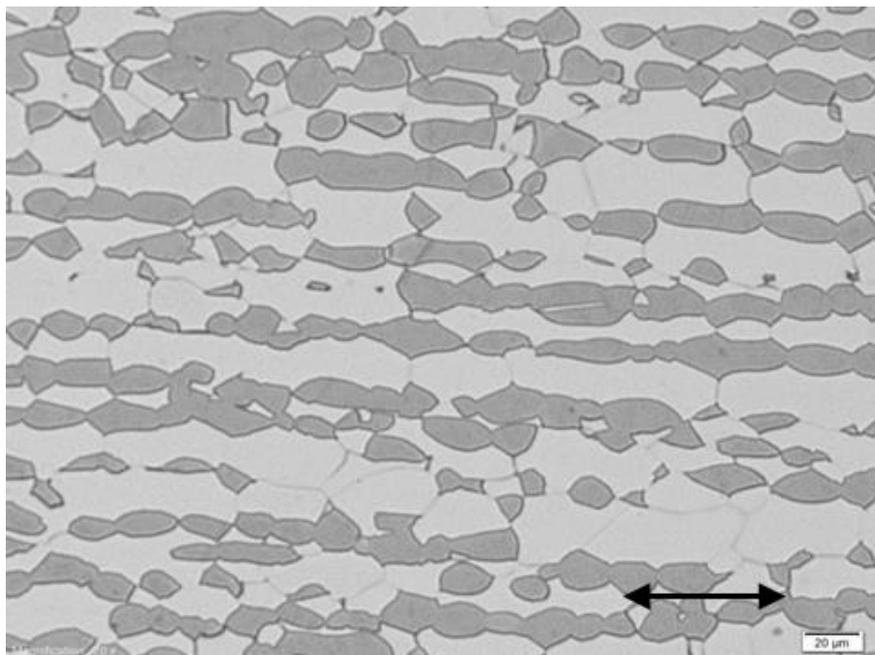

Figure 2 - Micrograph of the heat-treated material at 1100°C. Ferrite (dark) and austenite (light) phases after modified Beraha etching (the double arrow indicates the rolling directions).
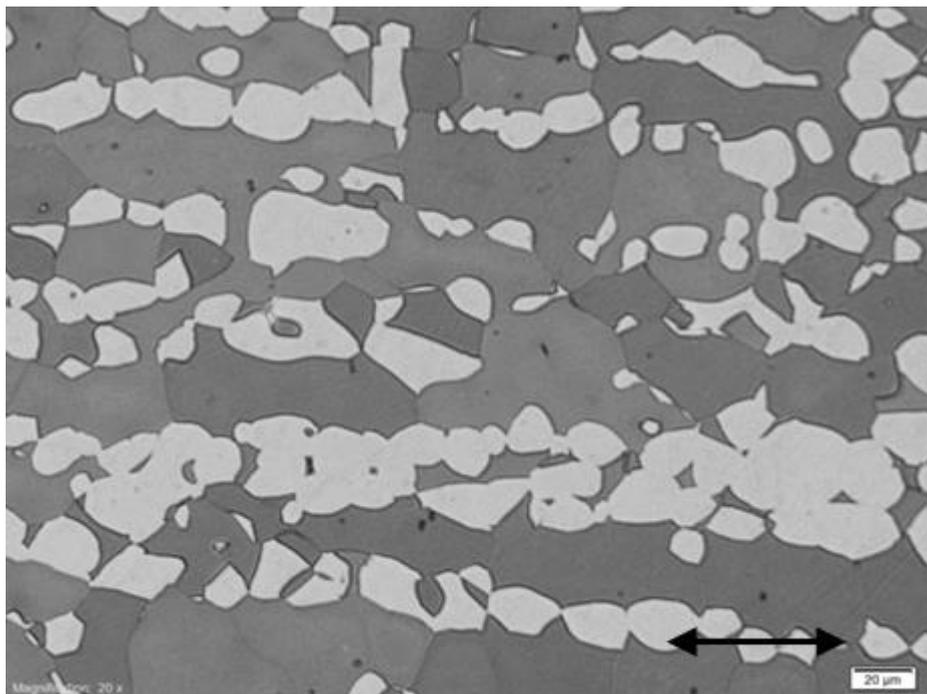
Figure 3 - Micrograph of the heat-treated material at 1200°C. Ferrite (dark) and austenite (light) phases after modified Beraha etching (the double arrow indicates the rolling directions).

As shown in Figure 4, the X-ray diffraction for solution treated samples at 1000, 1100 or 1200 °C indicate that the phases present are ferrite and austenite proving what has already been exposed by microstructures analysis, Figures 1 to 3. From XRD results, ferrite and austenite unit cell parameters (*a*) were determined as 2,880 Å for ferrite and 3,601 Å for austenite, resulting in volumes of unit cell (*V*) of 23,879 Å^3 and 46,711 Å^3 respectively.
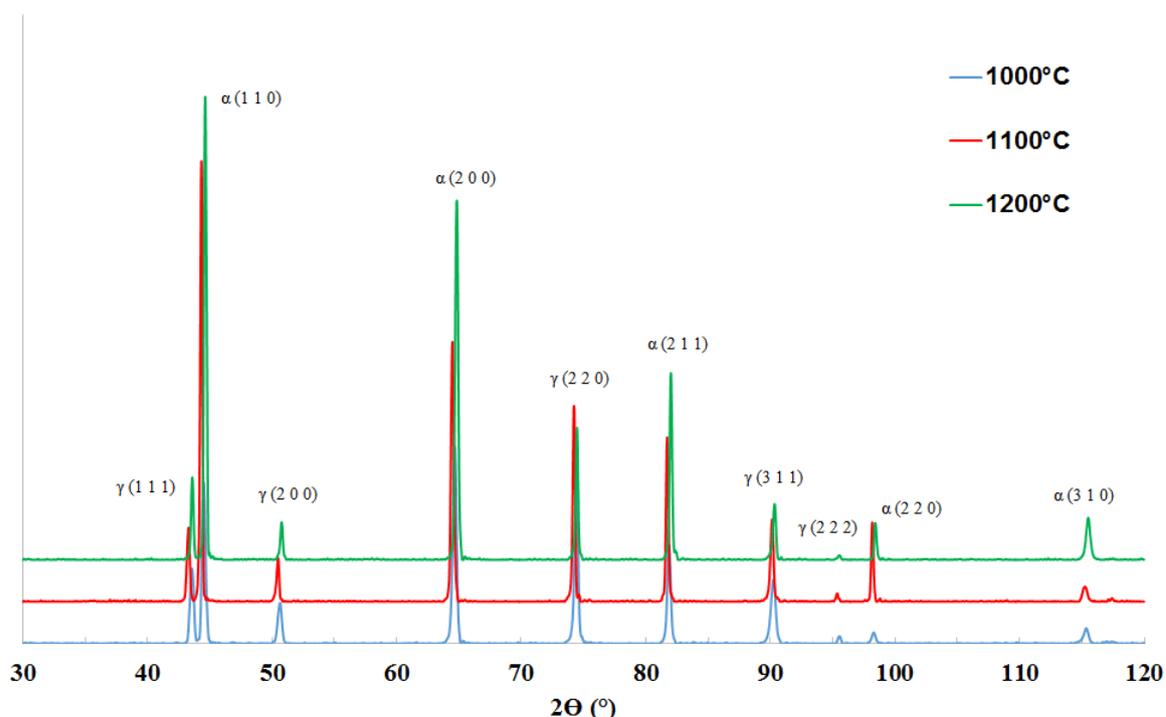

Figure 4 – X-Ray diffraction for solubilized samples at 1000, 1100 and 1200°C.

Figure 5 compares the values of ferrite volume fraction obtained by the four methods (quantitative stereology, ferritoscope and XRD by methods 1 or 2) to that calculated by ThermoCalc® database TCFe7, considering as chemical composition of 22.07% Cr; 5.68% Ni; 3.20% Mo; 1.38% Mn; 0.34% Si; 0.17% N; 0.017% C; 0.02%P; 0.001%S; Fe – balance.
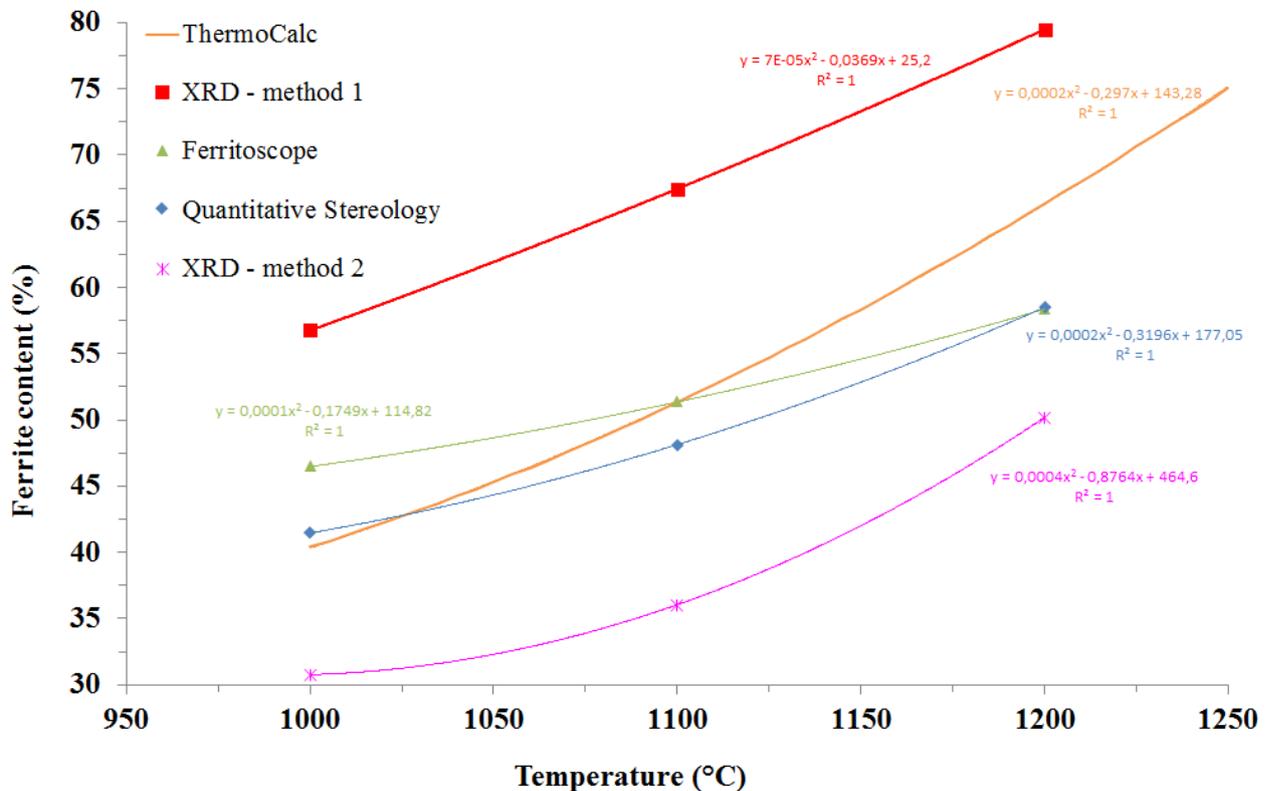

Figure 5 – Polynomial trend curves of the values obtained by the four measuring techniques in comparison with the values of ThermoCalc®.

There is a difference between the values of volume fraction of ferrite obtained by XRD analysis and the values obtained by quantitative stereology and ferritoscope, and when compared to values calculated by ThermoCalc®. The values obtained by the analysis of the XRD method 1 are higher while the values obtained by method 2 are lower than simulations. Nevertheless, all techniques show the same trend of increasing ferrite volume fraction with increasing solubilization temperature, as provided in ThermoCalc®. The linear correlation coefficients (R^2) between the values obtained by ThermoCalc® and the experimental values were calculated in order to numerically display the relationship between them, as shown in Table 3.

The correlation coefficients (R^2) were calculated according equation (5); $\bar{x}$ and $\bar{y}$ are the average of the ThermoCalc matrix and the applied methodology matrix (stereology, ferritoscope and XRD matrix), respectively.

$$R^2 = \frac{\Sigma\left(x - \bar{x}\right)\cdot\left(y - \bar{y}\right)}{\sqrt{\Sigma\left(x - \bar{x}\right)^2 \cdot \Sigma\left(y - \bar{y}\right)^2}} \tag{5}$$

Table 3 – Correlation coefficient between experimental data and the calculated curve from ThermoCalc®.

Correlation coefficient (R^2)			
Ferritoscope	Stereology	XRD-1	XRD-2
0,9985	0,9994	0,9983	0,9864

It can be observed from Table 3 that the values obtained by quantitative stereology are more assertive when compared with the curve provided by ThermoCalc® than the values measured by the other two methods, XRD and ferritscope. This can be explained by the fact that the measurement by XRD and ferritoscope could be influenced by the texture of the material. Considering that the 3 mm thickness as received material was produced by hot rolling, the presence of a preferential texture in the direction of rolling is expected.

It is verified that solution treated samples at 1000 and 1100°C produced similar results comparing three techniques, stereology, ferritoscope and ThermoCalc®. However, at 1200 °C, the result obtained by ThermoCalc® simulation was greater than the obtained by stereology and ferritoscope, although both techniques showed equivalent results. This difference may be attribute to the fact that ThermoCalc simulation did not consider grain size and texture, which can affect the kinetics of phase formation.

XRD method 2 shows absolute values much lower than the values obtained by other methods, probably because the applied calculation methodology and adjustment factors, especially DWF factor, a temperature dependence factor, must be reviewed for this specific type of steel [11].

The four techniques gave different results, but all of them show a tendency to increase the volume fraction of ferrite as the solution treatment temperature increase; however, quantitative stereology seems to be the most assertive methodology to measure the volume fraction of the phases in duplex stainless steels.

4 CONCLUSION

1. Different techniques for determination of the volume fraction of ferrite were analyzed and simulation by ThermoCalc® was performed.
2. All techniques show the same characteristic, increased ferrite volume fraction with increasing solution treatment temperature.
3. Quantitative stereology and ferritoscope showed absolute values of ferrite that are closer to the predicted equilibrium values by ThermoCalc® then the other techniques.
4. The measurements made by XRD technique presented the largest deviations from the predictions, possibly influenced by texture imposed by hot rolling of the studied material.
5. Quantitative stereology seems to be the most assertive technique to measure volume fraction of the phases in duplex stainless steels.

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