FERRITE CONTENT DETERMINATION. METHOD VALIDATION FOR USE IN DUPLEX STAINLESS STEELS: TRADITIONAL VERSUS DIGITAL APPROACHES

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Abstract

The use of duplexes has expanded widely across an extensive number of industries e.g. oil, gas, petrochemical, pulp and recycling, as a structural and engineering material. These steels are mainly used in aqueous environments containing chlorides and as replacements for austenitic stainless steels that have suffered pitting or stress corrosion in service.

The properties of these duplex steels depend on the volume fraction (VF) between austenite and ferrite, which is provided by high temperature heat treatment. Duplex stainless steels are intended to present a microstructure composed of similar VF of austenite and ferrite; this is the phase composition leading to the best compromise of mechanical and corrosion properties. The characterization of this volume content is done by readily available metallographic means, as described in the standard ASTM E562 for the measurement of ferrite content by point counting over a significant number of micrographs. This is, however, an outdated and time-consuming approach.

The aim of this work is to validate the VF determination method that is more suitable for industrial use, knowledge creation and transfer. Two duplex stainless steels were analysed by two different metallographic approaches (ASTM E562, ASTM E1245), by varying magnification and the number of fields used. Ferrite content and its variability within techniques due to the analytical variables are discussed. Finally, comparison is made between the final values for the ferrite content determined by each metallographic approach. The results highlight the recommendation for the use of the digital automatic image analysis, over the common traditional manual counting point approach. Since the digital approach allows a more efficient and comprehensive process in terms of practical results, simplicity, time and output representativeness of the total volume of the material. Digital automatic image analysis approach can be nowadays more efficiently and accurately used to perform the same analysis.

Keywords: *duplex stainless steel, ferrite content, method validation, digital automatic image analysis, knowledge transfer*

1. INTRODUCTION

Stainless steels can be divided into five major classes of materials, namely ferritic, austenitic, martensitic, precipitation hardenable and duplex. The first three have a matrix that is respectively ferritic, austenitic or martensitic, due the manipulation of their chemical composition and in particular the chromium equivalent and nickel equivalent content (Vander Voot, 1988). As the chromium is a stabilizer of the ferrite and nickel a stabilizer of austenite, it is understandable that through the adjustment of the chemical composition the steel, a certain microstructure composed of mixture between these two phases occurs.

The fourth class of stainless steel mentioned above, precipitation hardenable, corresponds to materials with a microstructural composition semi-austenitic or martensitic, that increase their mechanical strength in the heat treatment precipitation of intermetallic compounds. Finally, the duplex stainless steels (with 18 to 25% Cr and 4 to 7% Ni) are materials with a mixed microstructure of ferrite and austenite. (Davis, 2010)

Duplex stainless steels (d2s) are a family of materials with the virtues of the austenitic and the ferritic stainless steels (Krauss, 1989); they exhibit a high 0.2% proof stress and a good local corrosion resistance in chloride environments typical of the ferritic stainless steels and they maintain a high toughness and high general corrosion resistance characteristic of the austenitic stainless steels while maintaining a high toughness and high general corrosion resistance characteristic of the austenitic stainless steels (Holmes, et al., 2019).

These materials are used as a wrought semi-product to be transformed by cutting and forming technologies to produce finished structural components or casted by foundries to produce corrosion resistance cast parts.

The chromium and molybdenum used in stainless steels are ferrite stabilizers in order to compensate their action to obtain the duplex microstructure, one must add some austenite stabilizer elements such as nickel, copper and nitrogen carbon is not employed to avoid the carbide formation responsible for the sensitization of the stainless steels. (Santos, et al., 2006)

The general characteristics of d2s result from their chemical composition and processing ability. Their microstructure is composed of roughly composed of equal fractions of ferrite and austenite, having in mind the optimization of their practical application as a corrosion and strength resistant material.

Solidification of d2s lead to an essentially ferritic dominant structure needing of an addition high temperature heat treatment, in order to promote the elimination of detrimental sigma phase and nucleation of austenite within the ferrite grains. Depending on the temperature on bi-phasic domain, equal volume fractions of ferrite are obtained after rapid cooling from high temperature isothermal stage (Davis, 2010).

Product characteristics are confirmed by performing mechanical and metallographic tests. The microstructure is the link between the manufacturing parameters and the material properties. When the microstructure is analysed (phases, grain size, purity) two directions, to the past and to the future, can be achieved. The microstructure tells us how the steel has been created and changed, leading to the final material condition and the mechanical properties can be predictable (Leica Microsystems, 2020).

Quantitative metallography is usually performed over the material, after final processing, to confirm the material microstructure and thus to associated material properties.

Several methods may be used for determining the ferrite content in d2s, being manual point counting - ASTM E562 (ASTM, 2020) widely used since it is always available at any metallography laboratory. On the other hand, automatic image analysis - ASTM E1245 (ASTM, 2018) is an alternative technique that can be also used for achieving the same type of results, however, requires the existence of special software and image acquisition capabilities to perform the analysis allied with expertise and trained technicians, for this reason the technique practical application is not available at a large number of laboratories. Consequently, manual point counting technique is kept as the conventional specified method for determination of the ferrite volume fraction on d2s steels.

In theory, both quantitative methods will give good results, if they are well applied for measuring volume fraction in metals, nevertheless, practice and interlaboratory analysis comparison show that quantification errors exist, based on the application of two different ASTM standards. This fact justifies the urgency of the present study.

2. MATERIALS AND METHODS

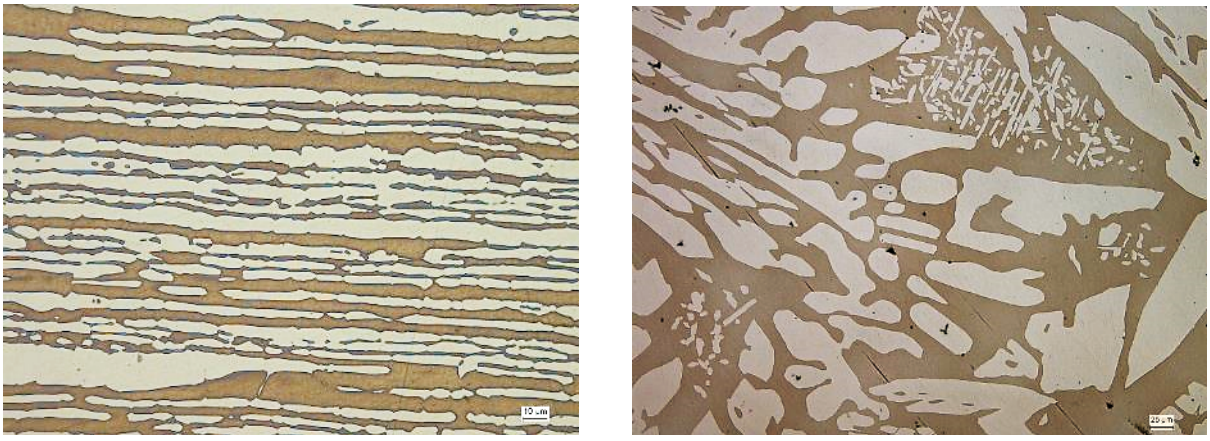
2.1. Materials

Standard duplex stainless steels and super duplex stainless steels were used for performing the ferrite content measurements corresponding to the cast and wrought heat-treated grades shown in Table 1.

Material condition	Duplex	Superduplex
Cast	ASTM A995 4A	ASTM A995 5A ASTM A995 6A
Wrought	EN 1.4462	EN 1.4410 SA 790 UNS S32750

Table 1. Analysed materials.

Typical obtained microstructures for casting and wrought samples are shown in Figure 1.



a) b)

Fig 1. Optical micrographs of a typical microstructure after electrolytic attack with aqueous NaOH solution; Fig. 1 a) Wrought d2s; Fig. 1 b) Cast d2s.

2.2. Preparation of samples for analysis

Ferrite volume fraction measurements were made according to the above standards using a metallographic analytical technique (optical microscopy using reflected light). The evaluated surface of the sample contains the longitudinal cross section with respect to the rolling direction (wrought material) or any given direction (cast material).

The most common sample preparation procedure for this type of observation is mechanical preparation with final electrolytic etching. This technique is based on cutting the samples, most commonly by sawing or cutting discs. The sample thus obtained is subsequently roughed and mirror polished, initially using abrasive sandpapers of different grain sizes, successively finer as the preparation progresses, removing material from the surface of the sample, and subsequently using polishing cloths impregnated with abrasive diamond particles of successively finer sizes (6 and 1 μm) until the desired mirror result, free of scratches and dirt, is achieved.

2.2.1. Grinding

During roughing, the cut marks were removed, and the surface of the sample was cleaned. Scratches caused by sandpaper during roughing were eliminated having very little material removal during this operation.

Four silicon carbide sandpapers with successively finer grain sizes (180, 320, 600 and 1200 mesh, in this sequence) placed on rotating discs were used. The operation was carried out under running water

so that loose abrasive debris were immediately washed away. This kept the sample cooled during the entire grinding operation. The sample was successively rotated 90º between each grinding step, so that the elimination of scratches from the previous step was confirmed. The sample was carefully cleaned and dried at the end and before proceeding with the polishing operation.

2.2.2. Polishing

Polishing is the last operation to prepare the specimens in order to obtain a good surface finish free of marks or scratches (mirror finish). For this purpose, abrasives were sprayed onto the polishing cloth by applying a liquid solution containing diamond particles. The final polishing step was done with 1 μm diamond thus impregnating a very soft cloth.

2.2.3. Etching

Etching is probably the most variable step. Very often a trial-and-error experimental method is required to find the optimal parameters for this step. The goal is to obtain confident and repeatable results. After obtaining a mirror-smooth surface, both studied test methods require the analysis of a polished surface area of the sample either chemical or electrolytic etched using a metallographic (reflected light) microscope (ASTM, 2020).

The analysed cross sections were etched by using electrolytic means with NaOH 40% aqueous solution electrolyte providing contrast and distinguishability of constituents.

2.3. Determining volume fraction of ferrite in d2s

Determining volume fraction of ferrite can be performed either manually (ASTM E562) or automatically (ASTM E1245). In both methods the ferrite content in d2s was viewed with a light motorized inverted platinum Microscope Leica DMi8A and a Digital Camera Leica DMC 2900 using a suitable prepared metallographic specimen prepared as described above.

The image is detected using a tube camera and displayed on a high-resolution video monitor.

2.3.1. Manual determination of ferrite's volume fraction in d2s

In manual mode, the traditional one, ferrite was determined by using systematic manual point count whereby a clear plastic test grid consist of equally spaced points formed by the intersection of fine lines is superimposed over the image. The number of test points falling within the phase or constituent of interest were counted and divided by the total number of grid points yielding a point fraction, and expressed as a percentage, for that field. The average point fraction for n measured fields gave an estimate of the volume fraction of the ferrite.

The magnification of the micrographs (200x and 500x) was selected in order to give adequately resolution of the microstructure without resulting in adjacent grid points overlaying a single constituent feature.

Table 2, show up the guidelines for grid size selection representing an optimum for efficiency for the time spent counting and for the statistical information obtained per grid placement.

Visual Area Fraction Estimate Expressed as a Percentage	Grid Size (Number of Points, PT)
2 to 5 %	100
5 to 10 %	49
10 to 20 %	25
25 >20 %	16

Table 2. Guidelines for Grid Size Selection (ASTM, 2020).

The used grid size were 100 and 16 points. The 16 points grid was selected for the main number of analysis in agreement to the indications given in Table 2. The 100 points grid was used for measuring the fine structures in order to reduce errors arising from the coarser grid resolution associated with the lower point grid.

Table 3 gives an example to the number of fields or images to be counted as a function of the number of points, for 33% accuracy (statistical precision), and the magnitude of the volume fraction.

Amount of volume fraction, Vv in percent	**33 % Relative Accuracy**			
	Number of fields n for a grid of PT =			
	16 points	25 points	49 points	100 points
2	110	75	35	20
5	50	30	15	8
10	25	15	10	4
20	15	10	5	4

Table 3. Prediction of the number of fields (n) to be observed as a function of 33% accuracy and of the estimated magnitude of the volume fraction of the constituent amount of volume fraction (ASTM, 2020).

The number of fields or images measured depends on the desired degree of precision for the measurement. In accordance with Table 3, 30 measurements were made by using 16 points grid and 5 measurements were done under a 100 points grid.

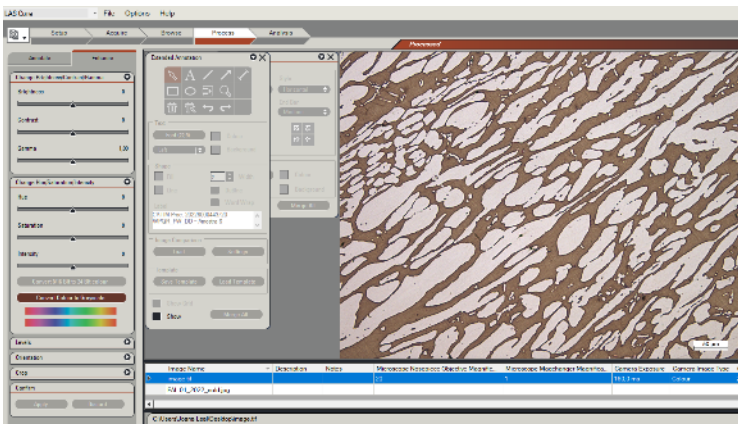
2.3.2. Automatic determination of ferrite's volume fraction in d2s

An automated solution allows fully automatic analysis of multiple samples. A careful sample preparation is a requirement for a reproducible analysis of whole samples. The results are impartial and the automated analysis methods are compliant with the chosen international standards already mentioned above. The overall time for analysis and reporting of a large number of results would be faster and more reliable with an automated solution (Leica Microsystems, 2020), eliminating individual technician variability and human error associated with the task performance.

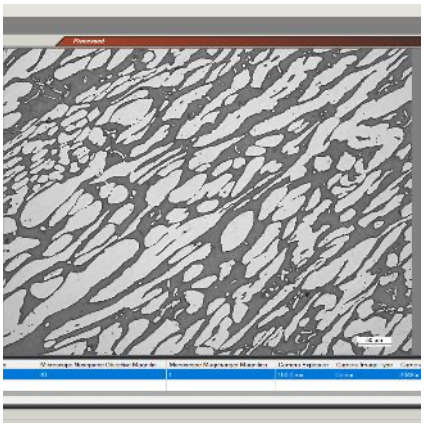
For this analysis the Leica Application Suite Version 4.13 software (LAS V4.13) with Phase Expert module was used together with a motorised Inverted Platinum Microscope Leica DMi8A and a Digital Camera Leica DMC 2900 to automatically acquire images for further processing, in order to also automatically determine the volume fraction of ferrite in d2s samples microstructures identified by their distinctive color or contrast in materials and thus produce an automatic report, minimizing human interaction and associated human error.

The results obtained by computerised analysis generated reports with automatic calculation, which were measured, according to ASTM E1245 standard. The images and results obtained for each field of view were automatically stored, allowing re-analysis and reprinting of the same. Both automatic and manual analysis were performed over the same field images.

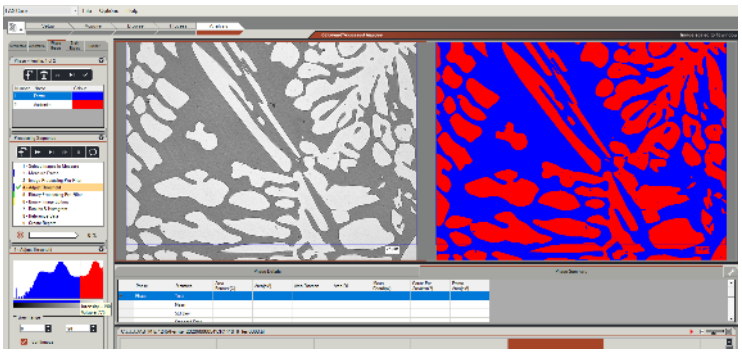
The automatic analysis steps (Figure 2) consisted in acquire the microstructures field of view images, converting them into greyscale format with further adjusting threshold (defining grey level limit) and transforming it into a binary color image. A last image processing was done by applying borders phase contrast filters. The phases are detected and discriminated based on their grey-level intensity differences.



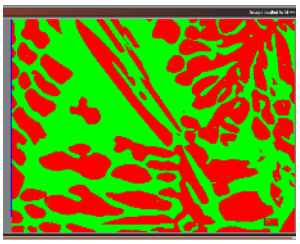
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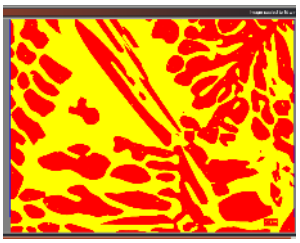
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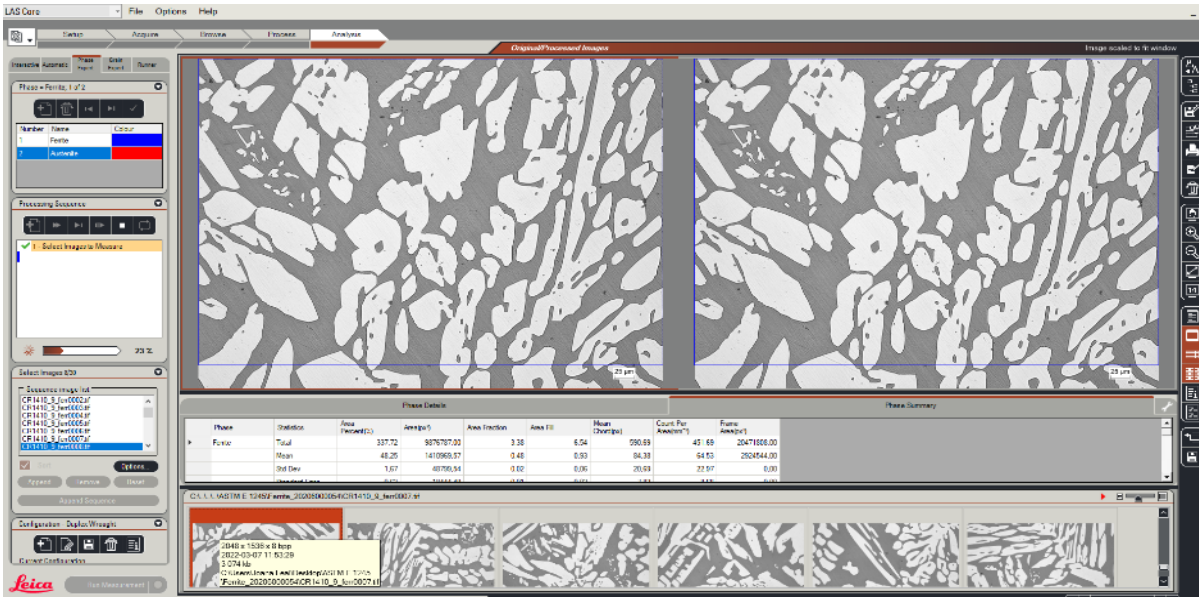
c)



d)



e)



f)

Fig 2. Continuous scan imaging with LAS V4.13 software and Processing Sequence of the Phase Expert module a) image acquired in color mode; b) conversion of color image to grayscale image; c) adjust threshold; d) binary processing pre-filter menu: e) binary image editing menu; f) running measurement in previously selected images

3. RESULTS

In the present work two different methods were used for determining ferrite content in d2s. Obtained results for the same sample corresponding to the different techniques used are shown in Figure 3. It is observed in Figure 3 that there is a tendency for having somehow higher ferrite content values when automatic image analysis is used. This occurs by measuring the same sample field images. A continuous slope can be apparently highlighted from the obtained results, as illustrated by the green scattering area shown in the Figure 3.

It can be also seen that measurements of ferrite content fall in a variation range of ± 4% when the two methods are compared (ferrite content measurement deviation for a certain fixed automatic result).

For automatic image analysis method, maximum obtained error was ± 1,5% and average error found was ± 0,6%. For manual measurements, maximum error observed was ± 5,7% and average one of ± 3,9%. These techniques present standard deviation according to their measurement precision, meaning that manual grit counting method show a larger result variation over the automatic image analysis, as can be observed in the graphic shown in Figure 4.

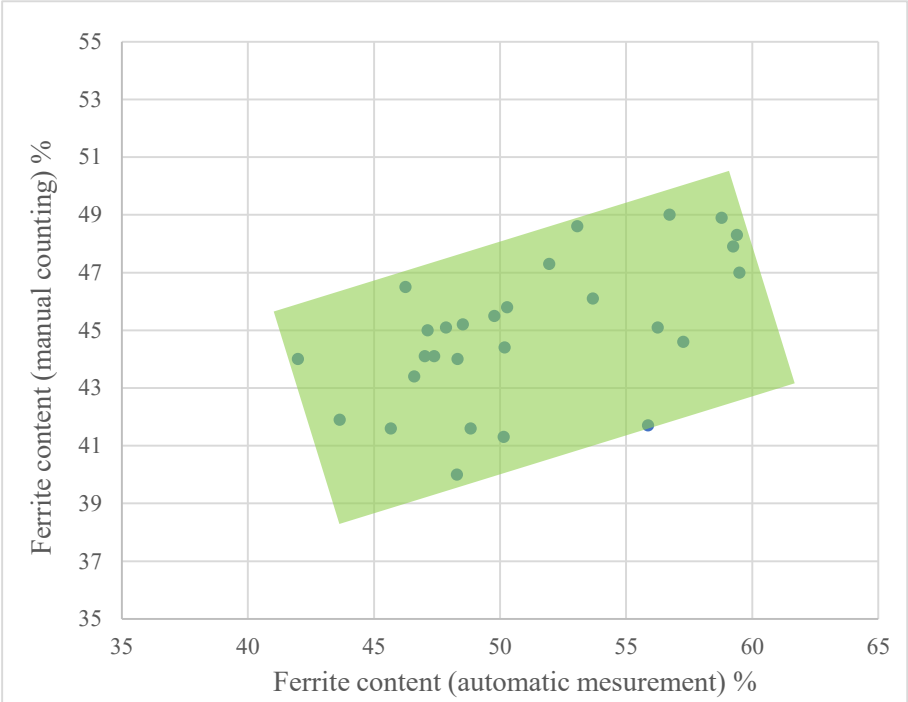


Fig 3. Comparison between automatic and manual ferrite content measurement

Table 4 lists the distribution of the obtained difference between final resulted measurements, coming from manual and automatic ferrite determination. 50% of the automatic measurements fall inside those of the manual method, meaning that results are within the associated error, calculated for each average final value, determined by the later technique. The higher differences corresponding to 21% of the obtained results, comes from the measurement of fine microstructures as those shown in Figure 5a. The fine microstructures were further analysed using high point-grits, being the results shown in Table 5.

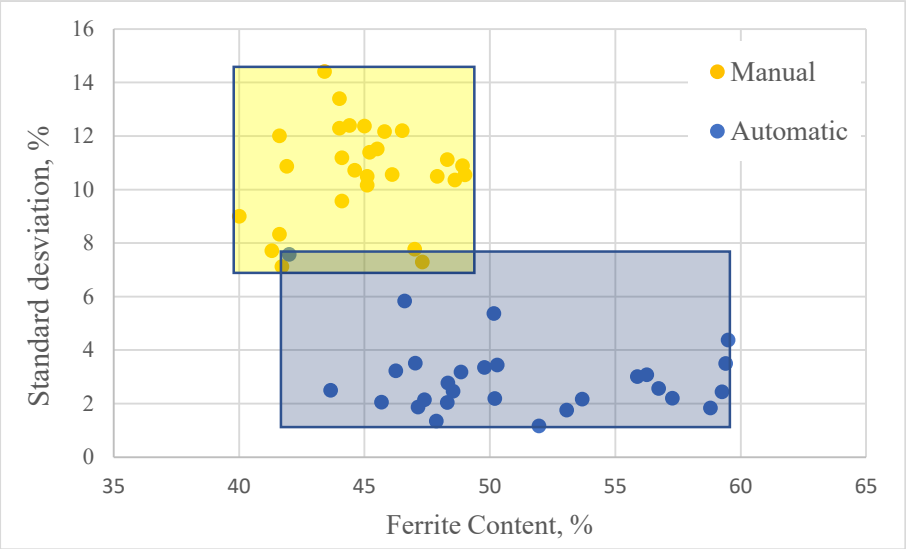


Fig 4. Standard deviation between ferrite content measurements obtained by manual point counting and automatic image analysis.

Results difference	Quantity	Relevance	Cumulative Sum
Acceptable results	14	50%	50%
≥ 4, < 6	2	7%	57%
≥ 6, < 8	3	11%	68%
≥ 8, < 10	3	11%	79%
≥ 10	6	21%	100%

Table 4. Error distribution obtained when performing manual counting and automatic image measurement.

In Figure 5 are represented the typical field images used for the measurements and those considered has being limits used in terms of respective grain dimensions. They correspond to better images captions using 200x and 500x magnifications to better suit representative analysis. Finer microstructures were measured using magnification of 500x. Higher enlargement was not used in order not to introduce distortion or wrong phase contrast (focusing problem), so the obtained microstructures better well reveal the duplex constituents.

It was used a 100-point grit over a fine microstructures sample in order to study if the determination deviation between techniques could be reduced. Attained results are given in Table 5. It was found that smaller standard deviation was obtained in ferrite content determination, but higher error was obtained, when comparing both techniques.

16-point grit		**100-point grit**	
Results difference	**Standard Deviation**	**Results difference**	**Standard Deviation**
≥ 12%	9,6%	≥ 18%	3,5%

Table 5. Comparison between 16- and 100-point grits. Average results.



a) b)

Fig. 5 a) Optical microstructure of a Fine Microstructure: 1.4410 Wrought d2s, after electrolytic attack with aqueous NaOH solution. **Fig. 5 b)** Optical microstructure of a Coarse Microstructure: 1.4410 Wrought d2s, after electrolytic attack with aqueous NaOH solution

4. DISCUSSION

Both manual point-counting and automatic image analysis are valid and recognized techniques for determining volume fractions of constituents of metals and alloys. Their use for a large number of measurements, over the same sample, should in principle give good and accurate results of constituent volume content. Available standards, for determining ferrite volume content in d2s, define analytical procedures to be used for using both manual and automatic methods in quantitative volume fraction analysis, however measurement errors exist, and several experimental observations were made and are discussed below.

A large number of the obtained values of the automatic image analysis measurements fall inside the range of the error associated to manual counting method. It can be considered that 50 % of the obtained results by any of these two techniques can be acceptable, considered valid and independent analysis by any of the two techniques for determining ferrite content in d2s. This observation is in agreement with expected use of both techniques supra mentioned.

Of the results, 21% presented a deviation of more than 10% between techniques. All this deviation is attributed to the fine microstructure existing on the field of view images used for quantification. If we remove this type of wrong interpretation microstructures from the analysis, it can be said that 64% of the automatic image analysis final results fall inside the manual counting error, and 73% of them are similar or have minor deviation when compared with result uncertain.

Manual point counting method present from around 7% up to 14% standard deviation for 30 different field measurements made over the same sample. The final average value has an error in determination of about $\pm$ 4%. This can be attributed to the technique precision, namely, referred to the 6% error in grit precision and the probability of grit points not being evenly distributed (positioned) over the constituent proportion. This give rise to significant dispersion over measurements made in the same sample, that are counterbalanced by the large number of fields measured, however not always leading to precise final result. On the other hand, automatic image analysis if done over a material well representative microstructure images, give accurate results, since all image pixels of the well contrasted images are considered for counting. By this way high accuracy is reached. This can be observed by significantly smaller standard deviation obtained by the automatic image method as shown in Figure 4.

By global analysis of results can be said that automatic image analysis is a more accurate method for measuring good contrast microstructures, since every single image pixel is considered on the ferrite

volume fraction content determination. By using manual point count technique, precision is reduced since relatively few points are being considered for points proportion analysis. This is clearly seen by comparing the standard deviation obtained for the two quantitative methods used in this work, as above discussed. By seeing less standard deviation, the automatic image analysis converges faster to a more precise value, giving also better results beside the fact of having better proportional point counting in a single field. The number of fields also can be thought to be reduced if microstructure, at associated magnification, is able to supply consistent succeeding evenly distributed austenite/ferrite proportion images. Therefore, automatic image analysis is the recommended practice to be used.

Errors arrive between the image automatic and manual point count techniques, mainly for fine microstructures (band spacing below 1,5 mm) manual counting differs from automatic method over 10%, this means that manual point counting technique fails to give good results. New analysis was made using a higher point grit (100 points), however, errors still persisted high (beside showing a lower standard deviation than 16-point grit previously used) since with banding microstructures, points locations, over successive orientation induce systematic single phase counting tendency introducing higher error. For this reason, automatic pixel image analysis is the recommended technique for determination of ferrite content in fine microstructures, if they are well magnified to represent and resolve the microstructure of the steel.

5. CONCLUSIONS

In this work, manual count point and automatic pixel image counting quantitative methods, were used to determine the ferrite content of the same d2s steels micrographs. A large number of samples and measurements were considered in the study, allowing the redraw of the following conclusions.

- Automatic image analysis and manual count point quantitative methods, when performed over the same micrographs, give similar ferrite determination results (within the manual counting error) for 64% of the well resolved microstructures (when fine microstructures are excluded).
- Band spacing below 1,5 mm provides a difference, between the results obtained by each one of the two techniques (larger than 10%). This observation comes from the orientation of the microstructure that induce the prevalence presence of a single phase over the other, on the manual point counting. A large number of points will fall aligned within the same phase, not respecting proportional distribution, basis of the quantitative technique.
- Automatic image analysis is a high precision quantitative technique, since it measures all the pixels present on the micrographs, so it corresponds to a more extensive counting over a reduced number of points existing in manual counting. Aiming a good proportional volume fraction estimation, sampling gives a better final result if a more representative analysis is performed by counting the all the number of points available in the sample field.
- Standard deviation is reduced if a higher number of points are considered in the analysis of representative magnified fields. This means that the sequence to be consider for decreasing deviation in the analysis, goes from 16-grit point counting to 100 points grit to automatic image analysis. If the analysis is performed over well representative sampling, point counting method, will give more consistency to the final result, being the analysis done in order to obtain more precise results with smaller standard deviation.
- Expertise and trained technicians are a key point in reducing error and enhancing the quality of the achieved results never forgetting the relevance of the expertise in transferring standards into daily laboratory procedures and practices.
- Experimental work, such as the one we present are the base for grounding good practices and for transferring knowledge into industrial ecosystems, raising practice allied with science.

ACKNOWLEDGMENTS

This research was funded by POR NORTE2020, under the Portugal2020 Partnership Agreement, through the European Regional Development Fund (ERDF); Grant Number: NORTE-01-0246-FEDER-000049.

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