Phase analysis in duplex stainless steel: comparison of EBSD and quantitative metallography methods

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Abstract. The purpose of the research was to work out the qualitative and quantitative analysis of phases in DSS in as-received state and after thermal aging. For quantitative purposes, SEM observations, EDS analyses and electron backscattered diffraction (EBSD) methods were employed. Qualitative analysis of phases was performed by two methods: EBSD and classical quantitative metallography. A juxtaposition of different etchants for the revealing of microstructure and brief review of sample preparation methods for EBSD studies were presented. Different ways of sample preparation were tested and based on these results a detailed methodology of DSS phase analysis was developed including: surface finishing, selective etching methods and image acquisition. The advantages and disadvantages of applied methods were pointed out and compared the accuracy of the analysis phase performed by both methods.

1. Introduction

Duplex stainless steels (DSS) represent an important and expanding class of stainless steels with an attractive combination of properties related to the fact that their microstructure allows a beneficial mixture of austenite (γ) and ferrite (α). However, the ferritic matrix in duplex stainless steels undergoes a variety of decomposition processes when aged in the temperature range 650 - 900 °C. Undesirable phases such as intermetallic phases, carbides and nitrides may exist in the steel if the manufacturing processes are not carefully controlled. High levels of elements stabilising ferrite, such as chromium, molybdenum and silicon, can promote the formation of sigma-phase (σ). σ-phase is a hard and brittle intermetallic phase which is generally formed between 600 and 950 °C with rapid formation kinetics [1-3]. Additional phases found in duplex stainless steels can include chi (χ), R, and α’ [4, 5]. χ-phase belongs to the topologically close-packed (TCP) phases. It frequently occurs in steels, as a ternary compound containing Fe, Cr and Mo, according to the composition Fe$_{30}$Cr$_{12}$Mo$_{10}$ [6]. The nucleation sites for σ- and χ-phases are grain boundaries, incoherent twin boundaries and dislocations. It is well established that the precipitation of these phases leads to a reduction of the creep ductility. It has also a reverse effect on the toughness and corrosion properties [7, 8]. A substantial depletion of solid solution strengtheners (like Cr, Mo, C and N) mainly due to a copious precipitation of the σ- and χ-phases beyond one hundred hours results in a strong decrease of the yield strength [9]. Therefore, it is very useful to be able to identify correctly the quantity of σ- and χ-phases in the DSS.
There are a lot of contradictions in the literature regarding the correct identification of \( \sigma \)- and \( \chi \)-phases, mainly due to the similar chemical composition of these phases. Electron backscatter diffraction (EBSD) can be used to distinguish the various phases within the DSS [10-13] and may solve these problems. The ability to rapidly analyse large areas of samples and easier specimen preparation when compared to transmission electron microscopy (TEM) is a major advantage promoting its use. However, selection of sample preparation method for EBSD studies is a crucial point and may lead to significant impediment.

In the present work, EBSD phase analysis was employed to detect and evaluate the quantity of basis balance phases and intermetallic precipitations in 2205 DSS. The results of EBSD analyses were compared with quantitative metallography methods. A brief review of sample preparation methods for EBSD analysis was presented.

2. Experimental procedure

2.1. Material

The material used in this investigation was 2205 DSS (plate of 25 mm in thickness and rod of 25 mm in diameter) with its chemical composition shown in Table 1. All the specimens were water-quenched for 30 min at 1100 °C in order to homogenize the structure. Afterwards, isothermal heat treatments were performed: 30 min at 900 °C, 2 h at 750 °C, and 5 h at 750 °C.

2.2. SEM observations and EDS analysis

Microstructural observations were carried out using a Hitachi S-3400 scanning electron microscope (SEM). The individual phases were analysed with a Thermo Noran energy-dispersive X-ray spectrometer system (EDS) with Six System software coupled to the SEM.

2.3. Quantitative metallography

For the metallographic research, specimens were cut out from the as-rolled steel plate in the longitudinal (L) direction of rolling and in the transverse (T) direction from the rod. Grinding was performed using water-cooled silicon carbide papers of 120-, 280-, 500- and 1200-grit size. After being ground to a 1200-grit finish, the samples were polished to produce flat, scratch-free surfaces. Coarse polishing was performed in two steps, using 6 \( \mu \)m and 3 \( \mu \)m diamond pastes; for the fine polishing step 1 \( \mu \)m diamond paste was used. Specimens were cleaned properly after each grinding and polishing step. Electrolytic etching was performed just after examination of the as-polished specimen. To maximize the contrast among different phases, 1 N KOH aqueous solution was used. In the electrolytic system, stainless steel was used as the cathode material.

The phase area fraction A was measured for each sample by MetIlo [14]. As many as 10 fields were measured at 500x magnification. The procedure of the measurements is illustrated in figure 1.
Figure 1. The measurement procedure in Metillo software for the quantitative evaluation of phases in 2205 DSS: a) uploading of the image; b) putting the median filter 3x3 in aim to smooth of the grey image; c) manual binarisation of the chosen phase in the image; d) selection of the objects (> 200 pixels); e) closing (with a step: 3); f) manual correction - filling of large holes; and g) measurement of the detected surface.
2.4. EBSD analysis

Specimens were cut from the DSS, mounted in conductive bakelite and were prepared using standard metallographic procedures, followed by prescribed method. Specimens were ground and polished using a diamond suspension with grit sizes of 9, 3, 1, and 0.25 µm, then a colloidal silica suspension of 0.05 µm grit size. The last stage of specimen preparation consisted of vibratory polishing using a colloidal silica suspension with 0.05 µm grit size for 20 hours to obtain the lowest possible surface roughness. Several methods of surface finishing for EBSD analysis were studied.

The crystallographic orientation were characterized with a scanning electron microscope (SEM, Hitachi S-3400N) equipped with an electron backscatter diffraction (EBSD) detector INCA HKL Nordlys II (Channel 5). The primary SEM electron beam for imaging and EDS analyses was 15 keV. EBSD analyses were done with a 20 keV primary electron beam and a 0.3 µm step size. Because the indexation was better than 90 %, raw maps were submitted to the standard cleaning procedure as per the manufacturer’s user instructions (Oxford Instruments HKL Technology, 2006). The cleaning procedure consisted of first removing wild spikes (isolated points that were incorrectly indexed) and then removing zero solutions (low-level extrapolation). Finally, we applied the 3×3 orientation-averaging filter (Kuwahara filter).

In Table 2 the list of phases and their crystallographic information is shown, which were supposed to exist in the 2205 DSS alloy.

Table 2. List of phases investigated in the DSS alloy using EBSD.

| Phase | Crystal structure | Lattice parameters, Å |
|-------|-------------------|-----------------------|
| ferrite | body centred cubic (bcc) | a = 2.87 |
| austenite | face centred cubic (fcc) | a = 3.66 |
| σ | tetragonal | a = 8.80, c = 4.56 |
| χ | body centred cubic (bcc) | a = 8.92 |

The orientation relationships between the phases are clearly seen in the inverse pole figures shown in figure 6. The austenite and ferrite phases were found to have the Kurdjumov-Sachs relationship, i.e., (110)Ferrite|| (111)Austenite. The σ- and χ-phases can be seen to have an orientation relationship with the ferrite phase, (001)σ||(110)ferrite, (110)χ||(110)ferrite.

3. Results and discussion

3.1. SEM observations and EDS analyses

Electrolytic etching (3 V, 2 - 15 s) in 1 N KOH solution was used to reveal the microstructure of the steel. The respective microstructures of DSS in the as-received state and after heat treatment are shown in figure 2. As can be seen in these micrographs, the austenite phase (light grey phase) was embedded in the semi-continuous ferrite matrix (dark phase). Precipitation of intermetallic phases were coloured bright and were found at the expense of the ferrite with the increase in time of heat treatment. The chemical composition of the phases given by energy-dispersive X-ray spectrometry (EDS) was applied to preliminary identification. The results of EDS analyses of phases depicted in figure 2 are presented in Table 3. The EDS analyses confirm the correct detection of main balance phases: austenite and ferrite. In case of intermetallic precipitates, the analysis did not reflect any constant relation in the chemical composition. Some of precipitates are characterized by the higher content of Mo and Cr, while most of precipitates possess similar composition to the ferrite. These divergences in chemical composition of intermetallic phases raise doubts regarding the proper detection of phases in thermally aged DSS.
Figure 2. Microstructure of 2205 DSS: a) as-received (rod); b) heat treated at 900 °C for 30 minutes (rod); c) heat treated at 750 °C for 2 hours (plate); d) heat treated at 750 °C for 5 hours (plate).

Table 3. EDS analysis results of phases in 2205 DSS (average values for 5 analyses per each phase).

| no. | Phase    | Cr  | Ni  | Mo  | Mn  | Fe  |
|-----|----------|-----|-----|-----|-----|-----|
| 1   | ferrite  | 24.4| 4.7 | 3.7 | 2.0 | 65.2|
| 2   | austenite| 21.2| 7.0 | 1.6 | 2.1 | 68.0|
| 3   | ferrite  | 25.5| 2.6 | 1.9 | 1.7 | 68.3|
| 4   | austenite| 21.8| 6.4 | 1.9 | 1.9 | 67.8|
| 5   | precipitate| 28.9| 2.9 | 6.4 | 1.8 | 60.0|
| 6   | ferrite  | 25.4| 3.8 | 3.1 | 1.9 | 65.7|
| 7   | austenite| 21.5| 5.9 | 2.0 | 1.9 | 67.9|
| 8   | precipitate| 22.2| 4.3 | 3.9 | 1.6 | 66.4|
| 9   | ferrite  | 24.4| 3.3 | 4.1 | 1.5 | 68.4|
| 10  | austenite| 21.6| 6.4 | 2.1 | 1.8 | 68.2|
| 11  | precipitate| 21.8| 4.2 | 2.4 | 1.9 | 68.4|
3.2. Quantitative analysis of phases
The quantitative analysis results of phases in DSS in the as-received state and after ageing are shown
in Table 4. The results were obtained on the basis of measurements performed on SEM images
(magnification 1000x, 10 images per one sample condition) by means of Mettlo software. With the
measurement methodology applied, the relative error of the volume fraction evaluation of phases and
structural components in the steel did not exceed 5 %.

Table 4. Quantitative phase evaluation results for precipitates in 2205 DSS.

| Sample          | Phase | A, %  |
|-----------------|-------|-------|
| as-received     |       |       |
| ferrite         | 53.5  |       |
| austenite       | 46.5  |       |
| 900 °C / 30 min |       |       |
| ferrite         | 26.0  |       |
| austenite       | 58.5  |       |
| precipitate     | 15.5  |       |
| 750 °C / 2 h    |       |       |
| ferrite         | 23.9  |       |
| austenite       | 57.9  |       |
| precipitate     | 18.2  |       |
| 750 °C / 5 h    |       |       |
| ferrite         | 8.5   |       |
| austenite       | 69.7  |       |
| precipitate     | 21.8  |       |

3.3. EBSD analysis - selection of preparation method
The preparation methods tested for EBSD purposes in this study are listed in Table 5. All the methods
were tested on as-received DSS.

Table 5. Preparation methods for EBSD sample preparation for DSS.

| no. | Procedure                                                                 | Indexation       | Quality of Kikuchi lines |
|-----|---------------------------------------------------------------------------|------------------|--------------------------|
| 1   | Vibratory polishing (Al₂O₃ suspension 0.05 µm), time: 4 h                 | ~ 85 %           | good                     |
| 2   | Vibratory polishing (Al₂O₃ suspension 0.05 µm), time: 8 h                 | 82 - 86 %        | good                     |
| 3   | Vibratory polishing (Al₂O₃ suspension 0.05 µm), time: 4 h, Electrolytic polishing (70 % ethanol, 20 % HClO₄, 10 % ethyleneglycol monobuthyl ether), 20 °C, 28 V, time: 10 s | 84 - 87 %        | good                     |
| 4   | Vibratory polishing (OP-S* 0.04 µm, pH = 10), time: 15 mins              | 50 - 60 %        | poor                     |
| 5   | Vibratory polishing (OP-S 0.04 µm, pH = 10), time: 4 h                   | 90 - 95 %        | very good                |
| 6   | Vibratory polishing (OP-S 0.04 µm, pH = 10), time: 8 h                   | 90 - 95 %        | very good                |
| 7   | Vibratory polishing (OP-S 0.04 µm, pH = 10), time: 3x8 h (3 days with intervals) | 90 - 92 %        | very good                |
| 8   | Vibratory polishing (OP-S 0.04 µm, pH = 10), time: 20 h (constant polishing) | 94 - 96 %        | very good                |
| 9   | Electrolytic polishing (10 % HClO₄, 90 % ethylene glycol monobuthyl ether), 6 °C, 30 V, time: 30 mins | < 50 %           | -                        |

*colloid silica suspension
Among the tested methods, the best results of sample preparation were obtained using vibratory polishing. Alumina suspension did not work well for a final polishing; the best for EBSD pattern quality is colloidal silica. Constant long term vibratory polishing (no. 8) assures good quality of sample finishing and reliable OIM data (figure 3a). The solution polishes and slightly etches the specimen, removing most of the surface deformation layer. It was also reported that a key role in this method plays time of polishing. Shorter periods of polishing or using intervals during polishing cause the adverse effect of “ferrite shredding” (figure 3b). This effect was also observed for other methods tested in this study.

3.4. EBSD phase analysis
For the chosen preparation method (no. 8), samples in the as-received state and after heat treatment were studied for the phase quantification. Figure 4 shows the EBSD phase maps for all the samples tested in this study.

**Figure 3.** EBSD phase maps for 2205 DSS in the as-received state: a) well prepared sample (method no. 8; rod); b) poorly prepared sample (method no. 7; plate).

**Figure 4.** EBSD phase maps for 2205 DSS: a) as-received (rod); b) heated at 900 °C for 30 minutes (rod); c) heated at 750 °C for 2 hours (plate); d) heated at 750 °C for 5 hours (plate). Ferrite (blue), austenite (red), sigma (green).
The maps clearly show the distribution of the different phases in DSS. In the case of heat treated sample, the existence of the $\sigma$-phase was confirmed, while there was no evidence of $\chi$-phase. The $\sigma$-phase was formed at the expense of the ferrite phase with the increase in time of the heat treatment. Unfortunately, in samples with higher content of the $\sigma$-phase re-calling of adverse effect of “ferrite shredding” on the phase map was observed. This phenomenon causes incorrect analysis of ferrite area fraction in favour of the austenite in DSS. No effect on $\sigma$-phase identification was observed.

Identification of $\sigma$-phase in DSS by EBSD method is poorly presented in the literature. Only few authors showed results concerning the quantification of $\sigma$-phase. However, the preparation method for EBSD measurements is usually has been neglected. Souza et al. [15] mentioned the difficulties with a proper quantitative analysis of $\sigma$-phase in DSS. The number of wrongly indexed points strongly increased with the work hardening produced before aging. This was the main limitation of the quantification by EBSD – cold rolled and aged (800 °C / 1 h) samples were very difficult to obtain good pattern. They also proved that the increase of the amount of $\sigma$-phase in DSS changes the austenite texture [15]. Probably, it could also influence the ferrite texture what may result in wrong indexation of ferrite. Up to the present, it has not been unequivocally proved and requires further investigations.

The area fractions measured from EBSD results are shown in Table 6. The area fractions of the $\sigma$-phase increased from 1 % to 15 % and the ferrite phase decreased from 41 % to 19.1 %, as the heat treatment time increased. Comparison of these results unequivocally depicts that identification of $\sigma$- and $\chi$-phases should be performed on the basis of crystallographic data only.

| Sample            | Phase | $A$, % |
|-------------------|-------|--------|
| as-received       | Ferrite | 45.3  |
|                   | austenite | 54.7  |
| 900 °C / 30 min   | Ferrite | 41.0  |
|                   | austenite | 57.5  |
| 750 °C / 2 h      | Ferrite | 22.8  |
|                   | austenite | 73.0  |
| 750 °C / 5 h      | Ferrite | 19.1  |
|                   | austenite | 67.8  |
|                   | Sigma  | 4.2   |

### 4. Conclusions
EBSD has been shown to be a useful tool for phase identification in DSS, which is particularly evident in the analysis of the $\sigma$ and $\chi$ intermetallic phases. The following conclusions can be drawn:

1. Standard metallographic polishing followed by a final colloidal silica polish, results in strain free surfaces suitable for EBSD studies assuring high level of indexation and good quality of Kikuchi lines.
2. This study clearly shows that evolution of EBSD patterns is dependent not only on surface polishing but also on the phases present in the sample. Higher content of sigma phase (> 2 %) in DSS disrupts correct identification of phases by the effect of “ferrite shredding”. New improved method should be developed for thermally treated DSS.
3. Significant differences in the phase area fraction (A) values for the σ-phase between quantitative metallography and EBSD methods show that identification of this intermetallic phase should not be performed on a basis of microstructural observation only. Identification of the σ-phase based on the analysis of crystallographic orientation is absolutely necessary!

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