Identification of sigma and chi phases in duplex stainless steels

Núria Llorca-Isern [a,*], Héctor López-Luque [a], Isabel López-Jiménez [a], Maria Victoria Biezma [b]

[a] Departament de Ciència dels Materials i Enginyeria Metal·lurgica, Facultat de Química, Universitat de Barcelona, Marti-Franqués 1, 08028 Barcelona, Spain
[b] Department of Earth, Materials Science and Engineering, University of Cantabria - UC, Gamazo, 1, 39004 Santander, Spain

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ABSTRACT

The aim of this work is to find out the most suitable method for detecting and analyzing accurately the formation conditions of secondary phases, particularly Sigma-phase (σ-phase) and Chi-phase (χ-phase) in duplex stainless steels (UNS S32205 and UNS S32750). The microstructure was characterized after a solution annealing at 1080 °C followed by an isothermal heating at 830 °C for different time ranges, ranging from 1 min to 9 h, in order to enlighten the controversial point concerning the mechanism of χ-phase nucleation in relation with the σ-phase. Etched samples were observed using optical microscopy (MO), and scanning electron microscopy (FESEM) with a backscattered electron detector (BSE) was used on unetched samples. Compositional microanalysis (EDS) was carried out for identifying the different phases present in the steels. Sigma phase was easily observed using different etching procedures, whereas χ-phase was only clearly detected with FESEM–BSE on unetched samples. The compositional analyses showed that the molybdenum content in χ-phase almost doubles the content of this element in σ-phase, and as a result the kinetics of nucleation and growth were also found to be remarkably faster when the alloy content in the steel is higher. In addition, chromium nitrides and carbides were also observed to precipitate as a result of the heat treatments and, in the case of the chromium nitrides, they act as a favorable site for the nucleation of σ-phase and χ-phase.

1. Introduction

The microstructure of duplex stainless steels presents a beneficial banded mixture of austenitic (γ) and ferritic (δ) phase properties. High strength and corrosion resistance come from the ferrite, whereas the austenite phase increases ductility and resistance to uniform corrosion. Superduplex stainless steels possess a PREN (Pitting Resistance Equivalent Number) greater than 40 and therefore are extremely resistant to pitting [1,2]. However, the exposure of these steels to high temperatures between 600 °C and 1000 °C results in the precipitation of different compounds, with σ-phase, χ-phase, chromium nitrides and carbides being the most frequently found in them [1,3–5].

Sigma phase is a non-magnetic intermetallic based in the system of iron and chromium. It has a tetragonal crystallographic structure with 32 atoms per unit cell [6] that increases the hardness and decreases the toughness, as well as the elongation of the steel [7], and even changes the fracture type from transgranular to intergranular as the quantity of σ-phase increases [8]. Chi-phase belongs to the topologically close-packed (TCP) phases and precipitates as a ternary compound containing Fe, Cr and Mo [9] with a wide range of stoichiometry extending from the ternary χ-phase $Fe_{36}Cr_{12}Mo_{10}$ to $Fe_{36}Cr_{12}Mo_3Ti_7$ [10]. Chi-phase and

σ-phase usually are found simultaneously, thus it is difficult to study their individual effect on impact properties and corrosion resistance [11].

The precipitation of these new phases causes a matrix impoverishment in alloying elements, i.e. chromium, molybdenum and niobium that leads to deterioration in toughness and corrosion resistance in the steel [1,3,12]. Several authors [13–15] have studied the microstructural evolution in these steels following isothermal treatments, but further information is still needed to enlighten when, where and how the formation of the secondary precipitates takes place inside these steels is necessary in order to prevent the problems related to these relevant microstructural changes.

2. Material and methods

The samples used in the present study were stainless steel plates provided by Outokumpu (Finland) from duplex stainless steel grade 2205 (UNS S32205, in this study DSS 2205) and from superduplex stainless steel grade 2507 (UNS S32750, in this study SDSS 2507). The chemical composition of both stainless steels was provided by the manufacturer and is shown in Table 1.

All the samples were first solution-treated at 1080 °C for 30 min and water quenched. Subsequently, thermal annealing was conducted at 830 °C, followed by water quench. Temperature fluctuations did not exceed 5 °C in any case. The aging periods ranged from 1 min to 9 h. Metallographic conventional sample preparation has been carried out

* Corresponding author.
 E-mail addresses: nullorca@ub.edu (N. Llorca-Isern), hlopezlu7@alumnes.ub.edu (H. López-Luque), ilopezji9@alumnes.ub.edu (I. López-Jiménez), maria.biezma@unican.es (M.V. Biezma).

Table 1
Chemical composition of DSS 2205 and SDSS 2507 (%wt, balance Fe).

	C	Si	Mn	P	S	Cr	Ni	Mo	N	Cu	Ce
2205	0.015	0.40	1.5	0.018	0.001	22.49	5.77	3.21	0.184	0.18	0.002
2507	0.018	0.26	0.84	0.019	0.001	25.08	6.88	3.82	0.294	0.17	–

by grinding (P320, P600, P800 and P1200) and polishing with diamond pastes (6 μm and 1 μm).

Different etching solutions were used by previous researchers, including acid-basic and electrochemical etchings [2,16]. The etching conditions performed in the present study are indicated in Table 2 for acid reagents and in Table 3 for electrochemical reagents.

The microstructural analysis was conducted using an optical microscope Zeiss Axiovert 100 A, and scanning electron microscope FESEM JEOL J-7100F with a coupled Robinson BSE detector. The composition of the different phases was determined using the energy-dispersive X-ray spectroscopy system (EDS) INCA PentaFETx3. In addition, a JEOL JXA-8230 microprobe (with five WDS spectrometers) allowed us to obtain a higher chemical composition accuracy.

3. Results and discussion

Both optical microscope and FESEM observation of the etched samples were performed in order to analyze the microstructural changes that occurred in the annealed DSS 2205 and SDSS 2507 samples for the different thermal treatment lengths.

3.1. Optical microscopy characterization

Satisfactory results were obtained with some of the etching reagents referred in the literature, but others were not considered satisfactory and therefore were rejected for optical microscope and FESEM characterization (Table 3).

Glyceregia reagent (Fig. 1a and b) provides the best contrast between ferrite phase and σ-phase when the latter occupies a low percentage in the microstructure, but the etching time step, close to 2 min, could be considered too high in particular cases if a significant number of samples have to be observed. It is worth mentioning that this reagent is the only one in which σ-phase is observed as a white phase in the optical microscope. Grosbeck's reagent (Fig. 1c and d) has the advantage of differentiating nitrides (darkest phase), but requires an imprecise time

Table 2
Acid and electrochemical reagents and etching conditions used to reveal the microstructure of DSS and SDSS [2,16].

Chemical reagent	Etching conditions
Glyceregia	Time of etching: 2 min Temperature: 20 °C
Grosbeck's	Time of etching: 1–10 min Temperature: 60–90 °C
Marble's	Time of etching: 3–10 s Temperature: 20 °C
Murakami's (modified)*	Time of etching: 3–5 s Temperature: 20 °C
Villela's	Time of etching: 1 min Temperature: 20 °C
Electrochemical NaOH	Time of etching: 10 s Potential: 3 V Cathode: Pt
Electrochemical HCl/ethanol	Time of etching: 3–5 s Potential: 1.5 V Cathode: Pt

* KOH was replaced by NaOH.

Table 3
Summary of the ability to reveal the microstructure in optical microscopy for the different etching reagents used.

Etching	Current study observation
Glyceregia	Grain boundaries and σ-phase
Grosbeck's	Selective etching for σ-phase and nitrides
Marble's	Unsatisfactory performance obtained
Murakami's (modified)	Reveals ferrite and σ-phase
Villela's	Unsatisfactory performance obtained
Electrochemical NaOH	Reveals ferrite and σ-phase, nitrides are visible but not completely revealed
Electrochemical HCl/ethanol	Unsatisfactory performance obtained

of etching (1–10 min). Between the different chemical etching reagents, Murakami reagent (Fig. 1e and f) was found to be the most convenient due to its short time of etching needed and sufficient contrast between the different phases. However, it is difficult to identify ferrite phase when present in small quantities. If an electrochemical etching has to be employed, the 20% NaOH solution (Fig. 1g and h) provided good results as long as the operation conditions are appropriately controlled, and also it is fast etching, easy to prepare and it does not produce any toxicity problem, but again distinguishing between ferrite phase and σ-phase when the amount of σ-phase outnumbers the amount of ferrite phase becomes complicated.

The specific microstructure, the time of etching and the sensitivity to the reagents concentration are important to achieve a good identification of the phases hence there is not a general ideal reagent for duplex and superduplex stainless steels. Examples of this fact can be observed when χ-phase or carbides are known to be present in the microstructure but could not be seen in optical microscopy of etched samples, due to the detachment from the matrix or to their small size.

3.2. Scanning electron microscopy characterization

The samples were also characterized by FESEM, firstly on etched samples since previous studies used this procedure [2,15]. Unfortunately, the results were unsatisfactory due to the formation of oxide layers which complicated the compositional analysis. Also, certain phase boundaries are initially dissolved as can be seen in Fig. 2; if any phase is formed close to or in this interphase it may be lost by etching. Therefore, unetched samples were imaged in the FESEM and a back-scattered electron detector was used due to its ability to differentiate between phases according to their mean atomic number without need of chemical etching. Since σ-phase and specially χ-phase contain a higher percentage of molybdenum, a heavier element than the other present in these steels, the greyscale contrast of these phases should be significant compared to that of ferrite and austenite (Fig. 3). In Fig. 3, the different phases can be clearly identified as ferrite (darkest phase), austenite (dark gray), σ-phase (light gray) χ-phase (brighter phase), and some dark spots which can be observed at the interphase between ferrite and austenite and will be studied further on. These dark spots are also detected by other authors using BSE on unetched samples [1,17], hence SEM–BSE would be the recommended characterization technique in order to clearly differentiate between the intermetallic phases. Furthermore, if carbides and nitrides are also present, a high resolution microscope would be needed, hence FESEM–BSE is the best combination to study secondary phases in DSS and SDSS.

Energy-dispersive X-ray spectroscopy (EDS) was used in order to identify from compositional information the different microstructural phases and compounds in the samples. The results obtained for DSS 2205 and SDSS 2507 are shown in Table 4. Initially only two phases are present in the microstructure: Austenite, which contains a higher relative percentage of nickel (gammagen element) and ferrite, which is richer in chromium (alphagen element). The intermetallic phases