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Microstructural changes in SAF 2507 superduplex stainless steel produced by thermal cycle.

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ABSTRACT

This research work studies the microstructural changes in SAF 2507 superduplex stainless steel after thermal cycle in the range from 200 to 900°C for 20 minutes. The results showed there is no microstructural change in the temperature range of 200-700°C. However, over 800°C the sigma phase precipitates; the percentage of this phase increases with temperature. Sigma phase precipitates at the boundaries of δ/δ and δ/γ. The experimental results also showed precipitation of small particles of sigma phase at 900°C all over the microstructure showing the initial stages of formation.

Keywords: SAF 2507 superduplex stainless steel, sigma phase, thermal cycle.

1 INTRODUCTION

Duplex stainless steel consists of approximately 50 per cent ferrite and 50 per cent austenite allowing a combination of excellent mechanical properties and high corrosion resistance. These alloys have a corrosion resistance similar to the ferritic stainless steels, although its toughness is inferior to that of austenitic steels but superior to ferritic stainless steels, while their mechanical strength is greater than that of austenitic stainless steels. These properties mean than duplex stainless steels are excellent materials for industrial applications and their use has increased in the oil, chemical, petroleum and electric power industries. As an example, these alloys find its application in the pumps for fuel gas and desulfurization plants, which have high corrosion and corrosion-erosion resistance requirements [1].

The high mechanical properties and corrosion resistance of duplex stainless steel depends on adding Cr, Mo, Ni and N. However, this alloy elements, also promotes the precipitation of secondary phases in duplex stainless steels such as sigma phase, chi phase, chromium nitrides or secondary austenite. Since secondary phases are dependent on time and temperature, the mechanical properties and corrosion resistance of duplex stainless steel decrease significantly in the temperature range of 600-900°C [2] where sigma phase and other secondary phases precipitates. The sigma phase is not only the phase that most precipitates in duplex stainless steel, but also it is the most detrimental for corrosion resistance and therefore mechanical properties.

Several researchers have studied secondary phase precipitation in duplex stainless steel and its effect on corrosion resistance and mechanical properties. Kim and Kwon reported the degradation of pitting and stress corrosion resistance in ageing of 25% Cr duplex stainless steel at 850°C. They suggested that the decrease of resistance to localized corrosion of the alloy results from the sigma phase at δ/δ or δ/γ boundaries [3].

Steigerwald in his excellent review of the effects of second phases in stainless steels addressed the complex relationship between sigma and other phases. Since the sigma phase contains more Cr than ferrite, its presence also could affect either the local or general corrosion resistance of duplex stainless steel [3].

Despite the existence of studies about secondary phases, previous research mostly focused to explain the influence on corrosion resistance and mechanical properties, especially on SAF 2205 duplex stainless steel, which belongs to an earlier generation of duplex stainless steels than the superduplex alloy studied in this work. So far, there is little information about the secondary phases on SAF 2507 superduplex stainless steel.

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SAF 2507 superduplex stainless steel has marine and petrochemical applications. Materials working in these environments need good corrosion resistance and mechanical properties, reason why they are replacing SAF 2205 duplex stainless steel. However, in certain applications, the superduplex stainless steels will experience thermal cycles, as result, a microstructural change can occur by reason of secondary phase formation.

Such phases, due to chemical composition, can decrease the mechanical properties and corrosion resistance of the material, avoiding a good performance in-service. Therefore, this research work focuses on studying microstructural changes with time and temperature of a SAF 2507 superduplex stainless steel subjected to thermal cycles. The goal is to find out the temperature range where microstructural change occurs in the alloy.

2 MATERIALS AND METHODS

This research examines the SAF 2507 superduplex stainless steel in the as-received and thermal cycle conditions, supplied as pipe SCH 40. The thermal cycle of the alloy samples involves a single cycle comprising heating, holding and a rapid cooling (water quenching) at temperatures from 200 to 900°C and a holding time after temperature homogenization as shown in Table 1. The sectioned samples were of 1 cm^2. The thermal cycle has a heating rate of 10°C/s. After remaining at constant temperature for the holding time, the samples were water quenched. The objective of the thermal cycle is to promote secondary phase formation and keep the final microstructure at room temperature.

Table 1: Holding time for each temperature testing

Temperature (°C)	200	300	400	500	600	700	800	900
Holding time	30 s	5 min	10 min	15 min	20 min	25 min	30 min	35 min

The tested pieces were examined through optical microscopy (OM) to calculate phase percentage using commercial software for image analysis SigmaScan™. Scanning electron microscope (SEM) was used with secondary electrons (SE) to observe the morphology microstructure and with backscattering electrons (BSE) to phase identification where a good contrast between areas with different chemical compositions can be observed especially when the average atomic number is quite different and thus, the different phases in the sample are observed. Samples for SE were prepared by grinding and polishing; the microstructure was revealed with Beraha reagent at room temperature which consists in 20mL HCl, 40mL H_2O, 0.5g $K_2S_2O_5$. Samples for BSE were prepared by polishing. Punctual chemical analysis and mapping were carried out on each phase to get the composition and element distribution on every phase.

3 RESULTS AND DISCUSION

The material was supplied with a PREN (Pitting Resistance Equivalent Number) of 43, calculated using equation 1, which estimates the alloying elements influence such as Cr, Mo and N on corrosion resistance in Fe-Cr-Ni alloys. Table 2 shows the chemical composition of SAF 2507 superduplex stainless steel. Figure 1 shows the microstructure formed by austenite and ferrite with a ferrite percent of 56%.

$$PREN: \%Cr + 3.3\%Mo + 16\%N \qquad 1)\ [4]$$

Table 2: Chemical composition of SDSS SAF 2507 (wt%)

C	Si	Mn	Ni	Cr	Mo	N
0.019	0.353	0.420	6.57	24.86	4.272	0.27

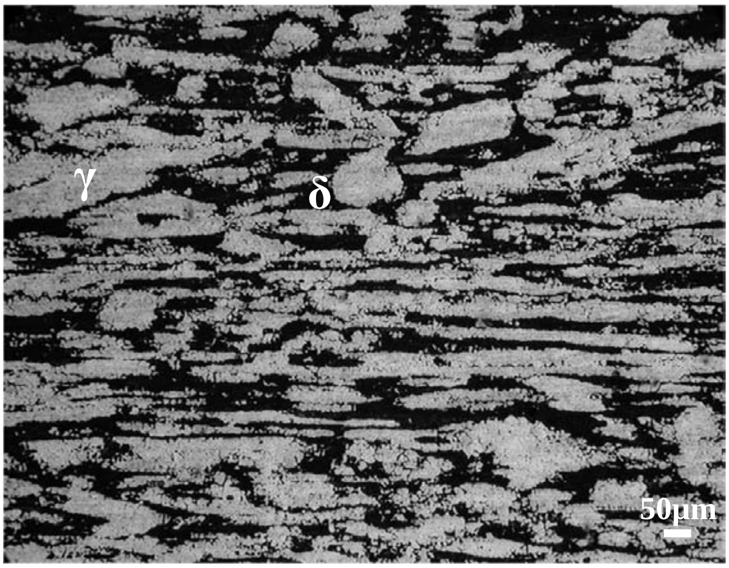


Figure 1: Microstructure of SAF 2507 superduplex stainless steel in the as-received condition.

The pieces that were subject to a thermal cycle with temperatures in the range of 200-700°C, showed no changes in microstructure. With SEM in backscattering electrons mode at 3000x, only a biphasic microstructure of austenite + ferrite was identified in the superduplex stainless steel. The percentage of ferrite remained in nearly 56%.

In the pieces subjected to 800 and 900°C, there is a significant microstructural change due to precipitation of sigma phase.

Figure 2 shows SEM micrographs of the pieces subjected to 800 and 900°C. The microstructure consists of ferrite, austenite and sigma phase delimiting ferritic grain boundaries. The sigma phase percentage in both pieces is different. At 800°C, there is an 8% of sigma phase. At 900°C, the sigma phase percentage is about 31%. As it can be observed, at 900°C the sigma phase consumed nearly all ferritic grains in the microstructure showing that at high temperature, ferrite phase becomes more unstable promoting sigma phase formation in SAF 2507 superduplex stainless steel. Besides the percentage difference between the sigma phase at 800 and 900°C, the grain size of the sigma phase is larger at 900°C than at 800°C. An explanation could be that at 900°C solute atoms diffuse faster making grain size of the sigma phase larger [5].

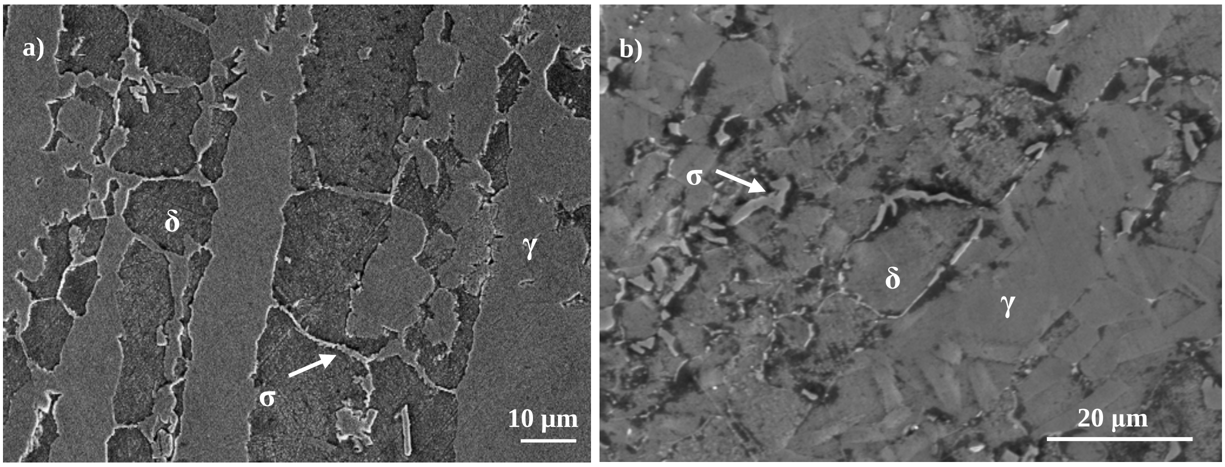


Figure 2. Microstructure of SAF 2507 superduplex stainless steel: a) at 800°C, b) at 900°C.

Preferential growth of the sigma phase into the ferrite is mainly the result of higher Cr and Mo concentrations in the ferrite phase [5]. An explanation is that sigma phase grows into the ferrite, because this phase is thermodynamically metastable at the temperature of sigma phase formation. As result, ferrite should decompose into an equilibrium state. The evidence for this comes from researches which have shown that an equilibrium microstructure is a mixture of sigma and austenite phases in the temperature range 650-900°C [5]. However, this will also depend on the chemical composition of the alloy, because a high percentage of N will cause a concentration of N into the ferrite, promoting chromium nitrides formation. At the same way, high percentages of Ni possibly increase the temperature where sigma phase is stable, having a high susceptibility of sigma phase formation at temperatures higher than 900°C. In both cases, the equilibrium can be a mixture of austenite, sigma phase (in larger proportion) and chromium nitrides.

Results show that SAF 2507 superduplex stainless steel is susceptible to sigma phase formation at 800 and 900°C. Also, sigma phase forms preferentially at ferrite grain boundaries being this phase nearly consumed at 900°C due to sigma phase formation. The high susceptibility of the duplex stainless steels to sigma phase formation is often credited to ferrite composition. The ferrite is rich in sigma forming elements as Cr, Mo, and Si, and poor in C, N and Ni which are less soluble in the sigma phase than in austenite [6].

Figure 3 and Table 3 shows microstructure and microanalysis of ferrite and austenite phases in the as-received condition, respectively. Chemical composition of the austenite phase differs significantly from that of the ferrite phase due to the presence of ferrite promoting elements (Cr, Mo, and Si). When the alloy solidifies, they concentrate into the ferrite phase, while austenite promoting elements (C, Ni, and N) are part of the austenite phase.

Figure 4 shows the microstructure at 900°C, with a strong presence of sigma phase. Punctual microanalysis in Table 4 shows a great quantity of Cr and Mo in sigma phase compared with austenite and ferrite. So, sigma phase forms with strong ferrite promoting elements. However, the sigma phase is also rich in austenite promoting elements such as Ni. The sigma phase easily forms nuclei in the δ/δ and δ/γ grain boundaries. The more the time increases, the more the quantity of sigma phase increases, growing gradually through ferrite phase until, eventually, consume the entire ferritic grain.

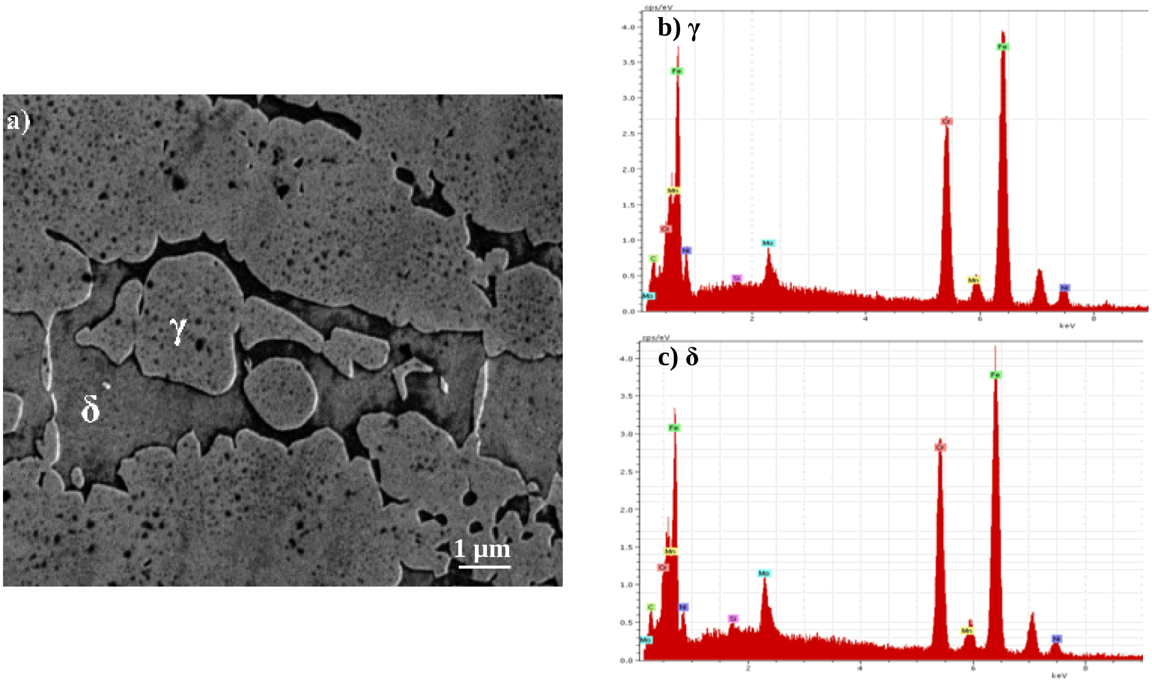


Figure 3: SAF 2507 superduplex stainless steel in the as-received condition: a) Microstructure, b) Spectrum of austenite phase and c) Spectrum of ferrite phase.

Table 3: Chemical composition of ferrite and austenite phases in the as-received condition

	ELEMENT (wt%)						
PHASE	Cr	Mo	Mn	Fe	Ni	Si	Partition coefficients δ / γ
γ	22.3	3.4	1.4	63	8.2	0.2	2.6
δ	23	7.4	1.1	50	7.5	0.3	3.5

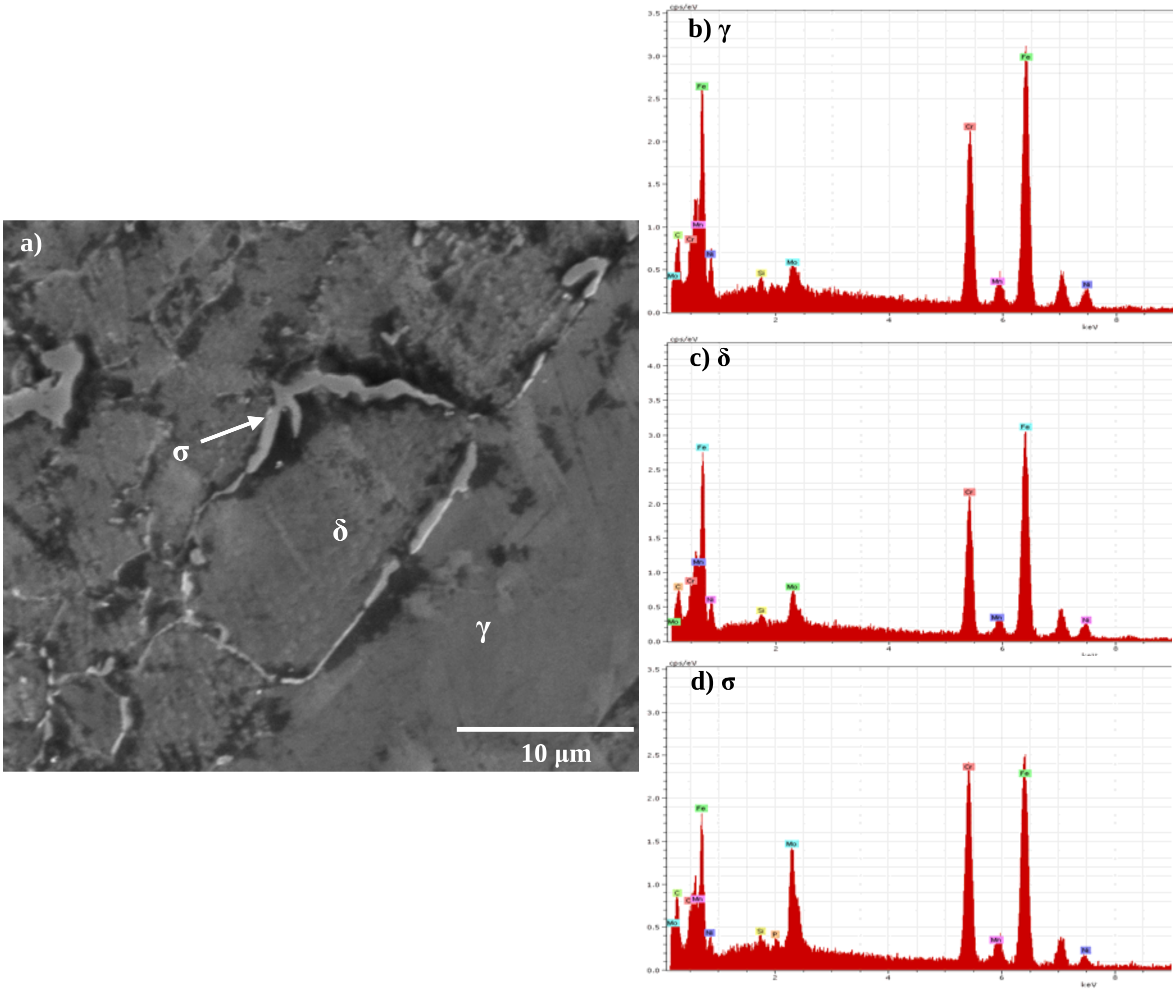


Figure 4: SAF 2507 superduplex stainless steel at 900°C: a) Microstructure, b) Spectrum of austenite phase, c) Spectrum of ferrite phase and d) Spectrum of sigma phase.

Table 4: Chemical composition of ferrite, austenite and sigma phases at 900°C.

	ELEMENT (wt%)					
PHASE	Cr	Mo	Mn	Fe	Ni	Si
γ	19.1	2.4	1.7	66.5	6.1	0.2
δ	20.5	3.2	0.3	68.6	3.3	0.8
σ	23.1	7.1	0.9	59.3	5.3	0.5

As mentioned before, sigma phase forms by strong elements promoters of ferrite (Cr and Mo). This is why during back scattering electrons (BSE) examination; a mapping was done to identify the chemical composition and element distribution in the sigma phase. Figure 5 shows the mapping of a piece heated at 900°C where the distribution of Cr and Mo on sigma phase is observed. Distribution of sigma phase is uniform.

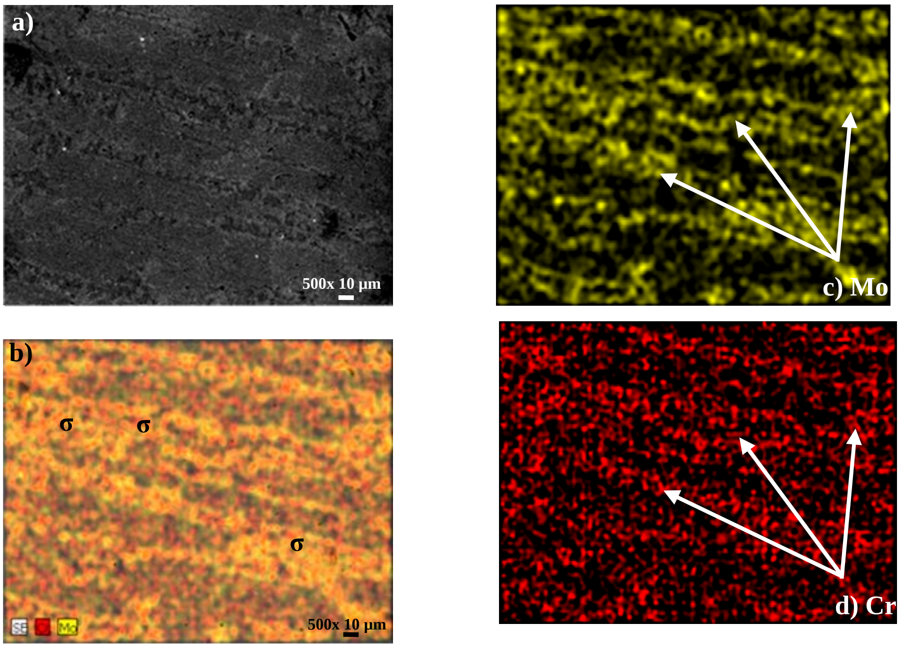


Figure 5: a) BSE image, b) Mapping of SAF 2507 superduplex stainless steel at 900°C in function of c) Mo and d) Cr.

In the present study, at 800°C the morphology of sigma phase is in form of little clusters which delimitates the δ/δ o δ/γ grain boundaries. At 900°C, Figure 6 shows the sigma phase with a butterfly like morphology, which is larger and compact.

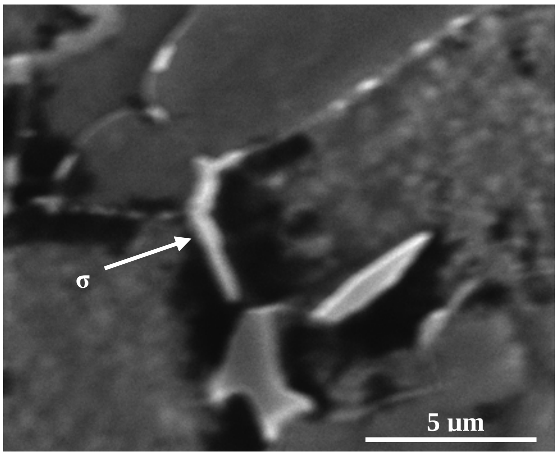
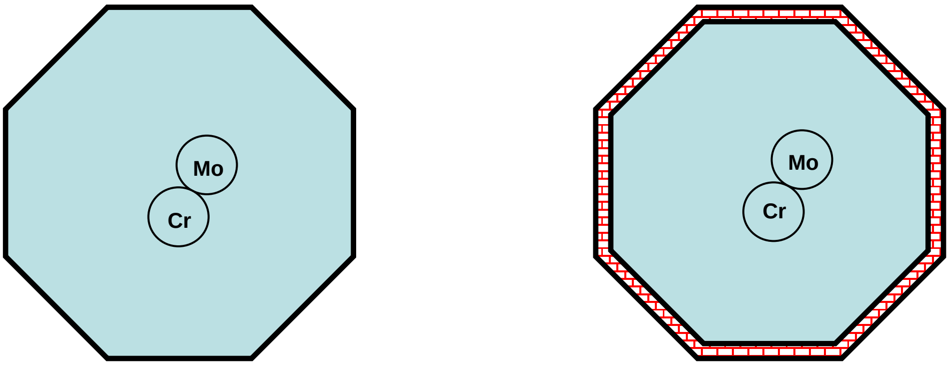


Figure 6: Morphology of sigma phase at 900°C in SAF 2507 superduplex stainless steel.

The sigma phase depends on diffusion range of Cr, Mo and other forming elements. Diffusion rate is higher in ferrite than in austenite because ferrite structure is less compact compared with austenite. During cooling, ferrite promoting elements displace towards the ferrite phase and austenite promoting elements, to the austenite phase. On account of the ferrite phase solidifies during cooling with a great quantity of Cr, means that Cr concentrates preferentially in the grain center and not in grain boundaries. The sigma phase formation in duplex alloys can be described by the eutectoid transformation of ferrite into the sigma phase plus austenite as follows: $\alpha \rightarrow \sigma + \gamma_2$ (where γ_2 is secondary austenite). The sigma phase particles nucleate on the δ/γ boundaries and growth into the ferritic phase, before the end of the transformation [7]. At some point of cooling, grain boundaries are high-energy zones, attracting the main ferrite promoting elements such as Cr and Mo. Due to the high cooling rate these elements stay trapped in the grain boundaries and promote sigma phase formation in δ/δ or δ/γ grain boundaries.

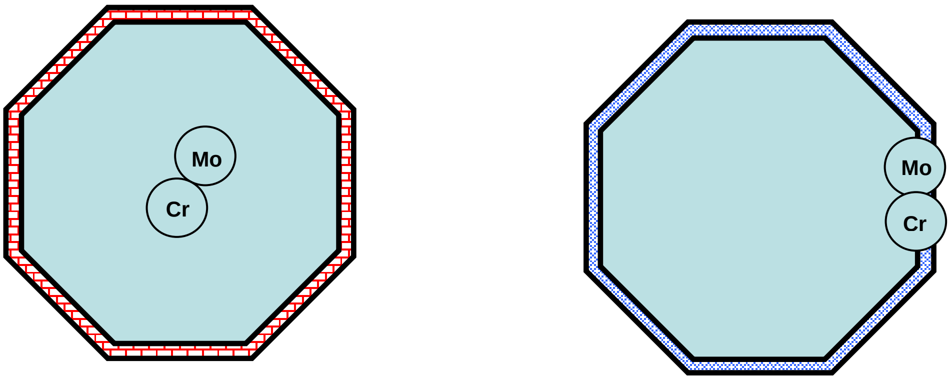
The previous mentioned transformation agrees to that occurring during cooling at room temperature. However, the samples with sigma phase experienced a thermal cycle with a fast cooling. An explanation is that sigma phase transformation would not follow this behavior because it forms isothermally in the material.

Theoretically an explanation is that during heating at 800 and 900°C, the superduplex stainless steel increases its internal energy due to temperature. This increase of energy promotes diffusion of atoms in the alloy, moving them from one side to another, concentrating ferrite promoting elements in ferrite and austenite promoting elements in austenite. Since, these elements are phase stabilizers; they concentrate preferentially in grain centers, leaving grain boundaries without related elements to accommodate by diffusion, storing high energies. The explanation is that there is a moment where the system begins seeking equilibrium to remove high-energy zones, attracting ferrite promoting elements such as Cr and Mo to ferritic grain boundaries, forming the sigma phase preferentially in δ/δ or δ/γ grain boundaries, consuming almost all the ferrite phase. In this moment, the system is on equilibrium with stable phases by reason of the decreasing of high-energy zones. Later, with fast cooling it is possible to freeze the current microstructure as schematized in Figure 7.



1. High temperature

2. Grain boundaries: high-energy zones



3. System seeking equilibrium

4. Sigma phase formation

Figure 7: Schematization of sigma phase formation in isothermally conditions.

Figure 8 shows the ferritic grain delineated by sigma phase. All over the microstructure, there are bright round particles surrounding the grain boundaries. Microanalysis was performed to identify the principal elements of the unknown particle.

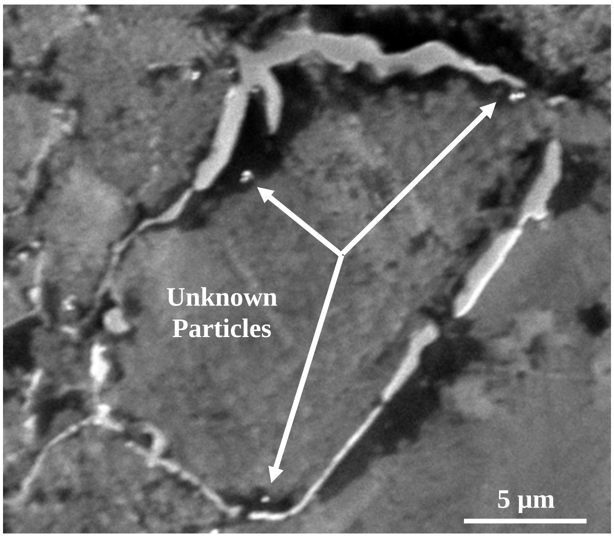


Figure 8: Particles observed at 900°C in SAF 2507 superduplex stainless steel.

The examined particle contains huge quantities of Cr and Mo, as can be seen in Table 5, with the possibility of being particles of sigma phase showing its initial stages as reported by Elmer *et al*. [8]. Due to the particle size and chemical composition, carbides, nitrides and carbonitrides are discarded. The relationship between chromium nitrides and secondary austenite precipitation in commercial duplex stainless steel was studied by Ramirez *et al.* [9]. They reported the chemical composition of chromium nitrides found in SAF 2205 duplex stainless steel with higher contents of Cr (78.97% ±2.47) and Mo (7.49%±0.69). This result differs significantly with percentages in the particle observed in the superduplex stainless steel studied in this work.

Table 5: Chemical composition of unknown particle.

	ELEMENT (wt %)						
PHASE	Cr	Mo	Mn	Fe	Ni	Si	C
Particle unknown	25.78	5.28	---	59.18	4.57	0.39	4.8

An explanation for Mn depletion in sigma phase is probably the presence of secondary austenite. However, it should be noted that the characterization methods used in this work may not fully identify the secondary austenite.

4 CONCLUSIONS

- Biphasic microstructure of ferrite + austenite of SAF 2507 superduplex stainless steel remains without changes after a thermal cycle in the range of temperatures from 200 to 700°C during 20 minutes at a constant temperature and fast cooling.
- Sigma phase formation occurs about 800°C in SAF 2507 superduplex stainless steel.
- Sigma phase percentage increases with temperature in the range from 800 to 900°C. At 800°C ferritic phase coexist with the sigma phase in the microstructure.
- At 900°C, formation of the sigma phase almost consumes the ferritic phase.

5 ACKNOWLEDGEMENTS

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