

*-Article

Sigma Phase: Nucleation and Growth

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Abstract

Duplex Stainless Steels (DSS) and Superduplex Stainless Steels (SDSS) are an important class of stainless steels because they combine the benefits of austenite and ferrite phases, resulting in steels with better mechanical properties and higher corrosion resistance. Due to these characteristics are widely employed in various industries. However, the appearance of deleterious phases in their microstructure impairs the properties of DSS and SDSS. Among the deleterious phases, the main one is the sigma phase (σ), which can be nucleated when the steel is exposed to the temperature range between 650 °C and 900 °C, reducing its toughness and resistance to corrosion. In a previous work, Fonseca and collaborators used two descriptors of the microstructural path to analyze the formation of sigma phase (σ), S_V , interfacial area per unit volume between sigma phase and austenite, and $\langle \lambda \rangle$, mean chord length of sigma, both in function of the V_V , volume fraction of sigma, known in the literature as microstructural partial path (MP). In this work, the contiguity ratio is applied for the first time to describe the microstructural path in the study of sigma phase precipitation in SDSS. The contiguity ratio showed that the distribution of the ferrite/sigma boundaries is homogeneous. Thus, it is reasonable to infer that one has a uniform distribution of sigma phase nuclei within the ferrite. About the kinetics of sigma phase formation, the DSS can be described by the classical JMAK equation, whereas for the SDSS, the kinetics tends to follow the Cahn model for grain edge nucleation. Finally, we present the 3D reconstruction of the sigma phase in SDSS. The results demonstrate that the sigma phase nucleates at the edges of the ferrite/austenite interfaces. Moreover, the sigma phase grows consuming the ferrite, but it is not fully interconnected.

Keywords: Sigma Phase, Contiguity, Kinetics, Cahn models, 3D Reconstruction

1. Introduction

Duplex stainless steel (DSS) and superduplex stainless steels (SDSS) favorably combine the properties of ferritic and austenitic stainless steels. They possess a high mechanical strength, good tenacity, adequate corrosion resistance in various media, and excellent resistance to stress corrosion cracking. These steels are widely used in the chemical industry and in offshore applications that require high corrosion resistance and great mechanical strength [1–10]. The continuous development of DSS resulted in the composition of complex steels containing considerable amounts of alloying elements. The substantial alloying element content of these steels aims at obtaining better mechanical properties and superior resistance to corrosion. As usual, the benefits of such additions invariably come with unavoidable drawbacks, the most important being thermodynamic microstructural instability [3,11].

As a consequence of this microstructural instability, during processing (heat treatment, welding) or in use (isothermal aging), precipitation of undesirable intermetallic phases such as chi (χ), alpha prime (α'), sigma (σ), carbides and nitrides, can happen. The precipitation of phase σ is of significant interest for DSS and SDSS. The presence of sigma phase worsens the mechanical properties and the corrosion resistance of these steels [1–3]. The sigma phase presents the most significant volume when compared to the other intermetallic phases observed in the DSS/SDSS microstructures. Therefore, in

many cases, it is common for other phases precipitated in these steels to be disregarded in the analysis of the properties of the material, choosing the sigma phase as the main responsible for the degradation of such properties [1–10]. It is of great importance to understand the conditions that lead to the formation of the sigma phase to avoid it during processing or use, and thus preserve the properties of the steel.

These phase transformations, which occur through the nucleation of the new phase and its subsequent growth, are often studied with the support of theories of formal kinetics. The basis of formal kinetic studies is the Johnson-Mehl, Avrami, and Kolmogorov (JMAK) theory. According to JMAK theory, the nuclei are uniform randomly within the matrix. JMAK theory determines the overall rate of phase transformation, that is, the volume fraction as a function of time of the transformation [12–16]. Using JMAK theory, one can study the kinetics of nucleation and growth of sigma phase. Cahn in his classic work [17] proposed another useful model, which expands JMAK theory. In his work, Cahn models nucleation on the grain boundary, on the grain edges, and the grain corners. In this work, we are going to make use of Cahn's equations extensively. Our study is, to the best of our knowledge, the first study of sigma phase precipitation in SDSS to use Cahn's equations.

Using JMAK's equations only it is difficult to pinpoint the preferential locations of nucleation. The microstructural path (MP) suggested by Gokhale and Dehoff [18] relates interfacial area density between parent and product phases, S_V , and volume fraction transformed, V_V . Later MP was extended by Vandermeer and co-authors [19–23]. In recent work by Fonseca and co-authors [2], used the JMAK theory and the microstructural path with the objective of analyzing the formation, kinetics and microstructural evolution of the sigma phase in the SDSS. Our previous results indicated that the nucleation of the sigma phase occurs by site saturation with anisotropic linear impingement, i.e., the sigma phase nucleated at the edges. However, the microstructure contains further information that can help to characterize the phase transformation. Measuring microstructural quantities in addition to S_V and V_V such as the contiguity ratio [23], C , can reveal further microstructural characteristics. The contiguity ratio is the interfacial area between the new phase divided by the total interfacial area. The contiguity ratio ranges from zero to 1. Zero in the untransformed condition and 1 in the fully transformed condition. Vandermeer showed that when the contiguity is approximately equal to the volume fraction of the new phase, the nuclei distribution within the matrix is random. A positive deviation from this equality would indicate nucleation in clusters.

The application of this parameter is common in recrystallization studies when new nuclei arise in a deformed matrix, but until now it has not been used in the studies of sigma phase precipitation. For the use of the contiguity ratio in this work, we show a new equation, since the microstructures analyzed in this work involve the transformation of the matrix (austenite and ferrite) to sigma phase or to sigma phase more secondary austenite [2]. Thus, in our steels austenite, ferrite, sigma phase, and secondary austenite may be present. In contrast, the usual case discussed in the literature normally involves the decomposition of the parent phase into a new single phase [23]. Recently, Alves and coauthors [24] deduced contiguity equations for the case of simultaneous and sequential reactions. The authors obtained several equations for contiguity, but still, not treating the sigma phase precipitation. Here it has a greater degree of difficulty because it involves a greater possibility of combining the interfaces.

Therefore, in this work, we intend to analyze the microstructural changes in a DSS treated at 800°C and SDSS treated at 750°C. The temperatures used here a lower than 850°C regarded by several authors as the maximum kinetics temperature of sigma phase formation [4,8,25]. We used a lower temperature because we considered it to be most suitable to study nucleation and growth of sigma phase.

Finally, this work presents a 3D reconstruction by serial sectioning [26–28] of an SDSS sample treated to reach the thermodynamic equilibrium. Based on this 3D reconstruction it is possible to analyze the interconnectivity of the sigma phase and how it grows consuming ferrite.

2. Materials and Methods

2.1. Duplex Stainless Steel (DSS) and Superduplex Stainless Steel (SDSS)

Two commercial stainless steels were studied, they are: DSS 2205 and SDSS 2507; the DSS 2205 was hot rolled and annealing, and the SDSS 2507 was hot rolled. Table 1 shows the chemical compositions. Pieces were cut from as delivery plate with 10mm of thickness to obtain samples with 20 x 20 x 10 mm.

Table 1 - Chemical Composition of Duplex Stainless Steel (DSS) and Superduplex Stainless Steel (SDSS) (wt. (%))

SAF	C	Si	Mn	P	S	Cr	Ni	Mo	N	Cu
2205	0.023	0.320	1.85	0.030	0.001	22.50	5.30	2.90	0.166	0.030
2507	0.020	0.328	0.85	0.027	0.0009	24.89	6.82	3.72	0.278	0.156

Duplex stainless steel samples were treated at 800 °C for different heat treatment times (up to 79200 s (22h)). Superduplex stainless steel samples were treated at 750 °C for different heat treatment times (up to 180000 s (50h)) and air-cooled. These two samples groups were used for kinetic studies. Since the kinetics of the sigma phase formation is faster in SDSS [2], the temperature of 750 °C, lower than 800 °C for DSS, was chosen. It was an attempt to study the kinetics under the condition of slower sigma phase growth velocity. Another set of SDSS samples was treated at 800 °C up 108000 s (30 h). The sample treated for 30 h was chosen for 3D reconstruction.

After the heat treatments (HT) the specimens were ground with emery paper down to 2500 mesh. The samples were metallographic polished with 6 µm, 3 µm and 1 µm diamond abrasive. Finally, to reveal the microstructure of the steels, two chemical etchings were carried out. The first etching was for austenitic grain boundaries, the composition of which is 10 mg of picric acid diluted in 10 ml of hydrochloric acid (HCl) for 60 seconds [29]. The second etching to reveal the sigma phase used a modified Behara solution, made up of 20 ml of hydrochloric acid (HCl), 80 ml of distilled water (H₂O) and 0.3 g of potassium metabisulphite (K₂S₂O₅), this etching was carried out by immersion during the 1 minute and 30 seconds for sigma phase revelation [1-2].

2.2. Stereological Measures

The samples were examined with Nikon Eclipse LV150 Optical Microscope (Nikon, Tokyo, Japan). Micrographs were analyzed by public domain software Image J. Volume fractions (V_V) and interfacial areas per volume (S_V) of ferrite, austenite and sigma phase were carried out by conventional quantitative metallography techniques [30]. Equations 1 and 2:

$$V_V = P_P \quad (1)$$

$$S_V = 2P_L \quad (2)$$

where P_P is the average number of points falling on phase divided by a total number of points applied and P_L is the average number of intersections per unit length of interfaces with a test (L) line. In this work, 10 lines per micrographs were used with $L = 63.6 \mu\text{m}$ for each isolated line.

Contiguity equations will be deduced in the next chapter.

The volume fraction of ferrite, as well as measured by stereology, was also checked after each time of heat treatment with a Ferritescope (FERITSCOPE® FMP30, Helmut Fischer GmbH, Sindelfingen, Germany) used to determine the volume fraction of ferrite in DSS. The measurement is non-destructive, fast and can be performed in situ. The operational principle of the Ferritescope is based on the determination of the magnetic permeability of the material [31].

2.3 Computational Thermodynamics

The calculation of the mass quantity of the main elements (Fe, Cr, Ni, and Mo) at 800 °C for the SDSS was performed using the Thermo-CalC software (Thermo-CalC Software, Solna, Sweden) with

database TCFE7. Also, the mass composition of the previously mentioned elements was measured experimentally, in SDSS samples treated at 800 °C, by Energy Dispersive Spectrometry (EDS), (EDAX, Mahwah, New Jersey USA), analysis on a Scanning Electron Microscope (SEM). The Zeiss scanning electron microscope, model EVO MA10 (Carl Zeiss, Stuttgart, Germany), which operates with lanthanum hexaboride (LaB6) filaments. The sample treated at 800 °C for 108000 s (30h) presented the composition of the sigma phase closest to that presented by Thermo-Calc. So, it was chosen for 3D reconstruction. The idea was to reconstruct the sigma phase as close to thermodynamic equilibrium as possible.

2.4 3D Reconstruction

For the 3D reconstruction of the sigma phase, the serial section technique [26-28] was used. This 2D plane sectioning method comprises serial steps such as proper sample preparation by polishing, etching, microhardness indents, and image acquisition. After a metallographic preparation, like section 2.1, a field of the sample was randomly chosen to guarantee the continuity of two-dimensional images of the same field and also to measure the distance between consecutive sections accurately. For this step, it was necessary to perform Vickers micro-impressions with a load of 980.7mN for 15 seconds. The microhardness indents were performed by Shimadzu HMV Vickers Hardness Tester (Shimadzu, Kyoto, Japan). Final polishing took place using a Buehler EcoMet™ 250 Grinder Polisher (Buehler, Lake Bluff, Illinois, USA). After final polishing care should be taken to ensure that the hardness indent is not completely polished, as it would be impossible to align the images and also the knowledge of the amount of material removed. The idea was to analyze a field where it shows the sigma phase, in 2D, consuming the ferrite/austenite boundary and analyze how it is in 3D. What is your interconnection? Does the sigma phase consume the entire ferrite/austenite boundary? These are questions that need to be answered. For this, between each 2D plane, there was a distance around 0.035 µm. It took 100 sections. Thus, a total of 3.5 µm in depth was removed. The reconstructed volume was 127 µm x 68 µm x 3.5 µm. This amount was enough to visualize the sigma phase in 3D and answer the previous questions. Recalling, that the value of the mean chord length of sigma $\langle\lambda\rangle$ at 800 °C between 1 and 10 µm [2]. With the reconstructed volume, you have a lot of information. To analyze the sigma phase in detail, the sigma phase that consumed the 2D boundary was reconstructed. Only the first 20 sequential images were used. Thus, a small depth of analysis was chosen so as not to lose microstructural information. To calculate the quantity to be removed (Δh), the differences between the diagonals ($D_1 - D_2$) of the microhardness indenter pyramidal was used, with D_1 being the diagonal before polishing and D_2 the diagonal measured after polishing, using Equation 3, it is possible to estimate Δh :

$$\Delta h = \frac{D_1 - D_2}{2 \tan\left(\frac{\varphi}{2}\right)} \quad (3)$$

Where φ is the angle formed between the opposite faces of the pyramid and the square base of the indenter, φ is equal to 136°. NIH Image J public domain software, version 1.46r, was used for the three-dimensional process of images. Two consecutive sections are aligned through common points (such as Vickers micro-impressions in the present study). Sigma phase was reconstructed by cropping and editing images to contain only the sigma phase of interest. The sequence of manipulations in the micrographs was: micrographs transformed into 8-bits; apply enhanced image, contrast, and brightness to differentiate the sigma phase from the other phases; manual alignment using the Align Slice plug-in; correction of the micrographs by making the cut and rendering the volume with the Volume viewer plug-in.

3. Results and Discussion

3.1. Microstructural characterization

Figure 1 shows an optical micrograph of samples in the as received (AR) condition for the DSS and the SDSS. In Figure 1a, notice the microstructure with equiaxial austenite grains in a ferritic

matrix. This microstructure is a result of the industrial annealing after hot rolling. Figure 1b shows the microstructure containing grains that comprise ferrite and austenite lamellae. This lamellar arrangement is commonly found in the literature [1-4, 7, 8]. The volume fraction of ferrite and austenite for DSS (AR) is 0.55 ± 0.05 and 0.45 ± 0.05 , respectively. For SDSS (AR), the volume fraction of ferrite is 0.47 ± 0.03 and for austenite 0.53 ± 0.04 .

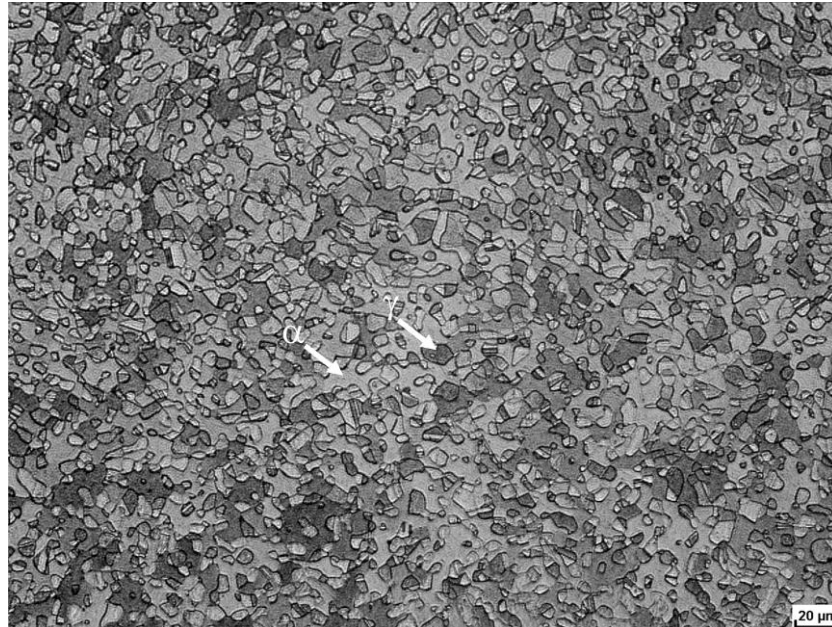


Figure 1a) AR Micrograph of a duplex stainless steel (DSS) showing α -ferrite and γ -austenite. One can see equiaxial austenite grains embedded in the ferritic matrix.

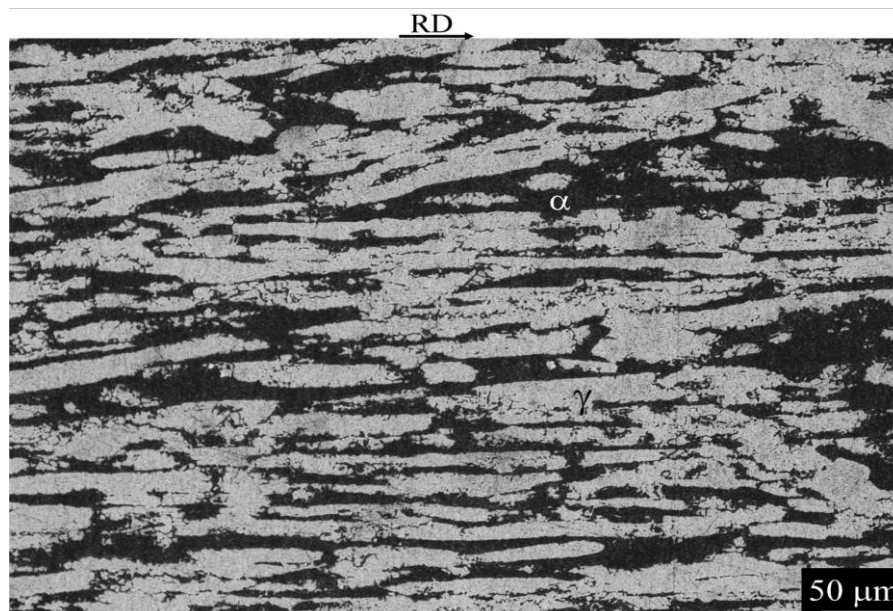


Figure 1b) AR Micrograph from superduplex stainless steel (SDSS). α -ferrite (black) and γ -austenite (white). One can see elongated grains of both phases. RD - Rolling Direction.

Figure 2 shows the micrographs of the samples heat-treated at $800\text{ }^{\circ}\text{C}$ for 79200 s (22h) for the DSS and $750\text{ }^{\circ}\text{C}$ for 180000 s (50h) for the SDSS. Figure 2a displays depleted ferrite,

austenite, and sigma phase of DSS, Figure 2b exhibits austenite, sigma and secondary austenite of SDSS.

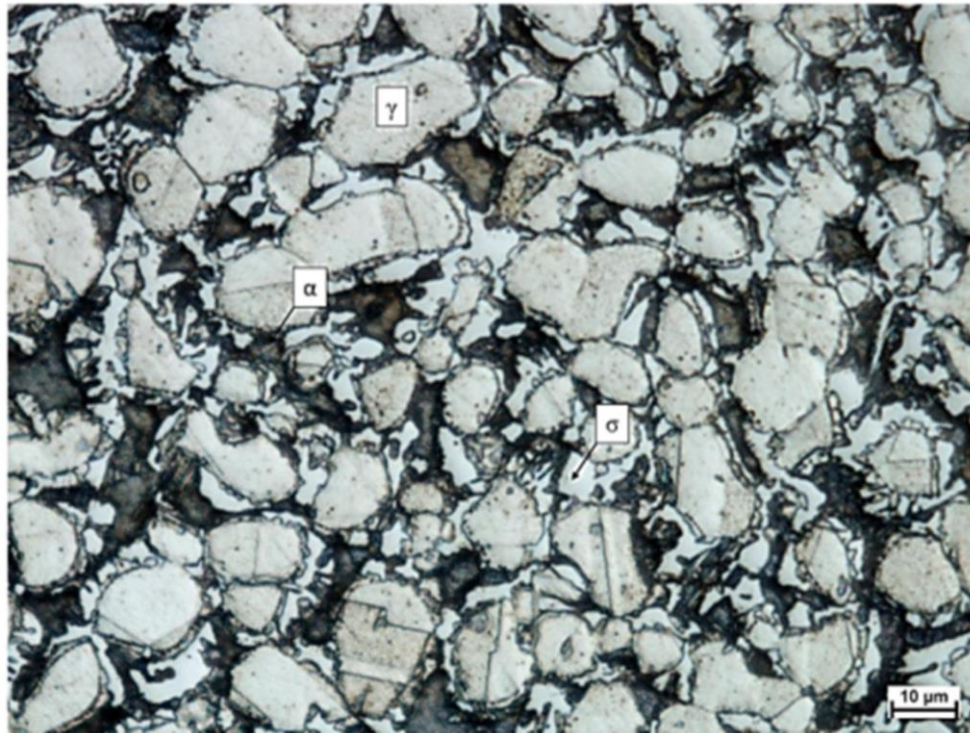


Figure 2a) Micrograph of DSS aged 79200 s (22h) at 800 °C. One can see grains of austenite (γ), depleted ferrite (black) (α) and sigma phase (white) (σ).

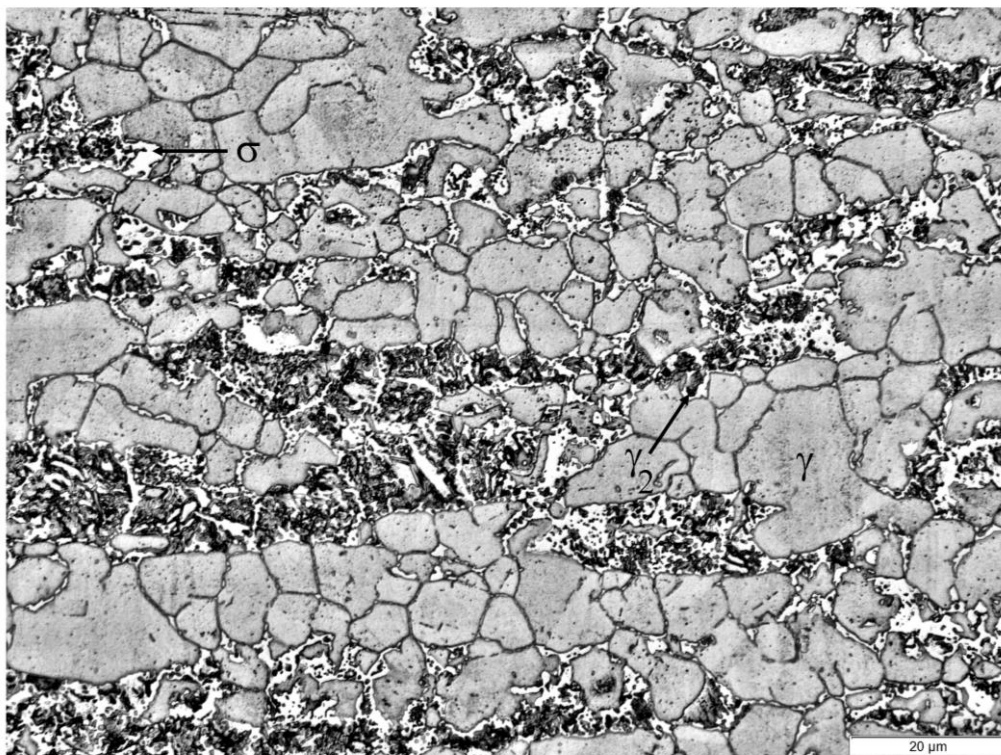


Figure 2b) Micrograph SDSS aged 180000 s (50h) at 750 °C. One can see austenite (γ), secondary austenite (black) (γ_2) and sigma phase (white) (σ).

The volume fraction of ferrite and austenite for the treated samples, shown in Figure 2a, are 0.10 ± 0.01 of ferrite and 0.45 ± 0.01 of austenite in DSS. The sigma phase presented a continuous morphology. The volume fraction of sigma phase was about 0.45. Thus, ferrite decomposition is given by $\alpha \rightarrow \alpha^* + \sigma$, where α^* is depleted ferrite. The literature of superferritic steels [7] also contains examples of the decomposition of ferrite into depleted ferrite plus sigma phase. Ferritescope measurements confirmed that the volume fraction of ferrite phase remained around 0.10 at the end of the treatment. For the SDSS, the volume fraction of ferrite and austenite for the treated samples, shown in Figure 2b, is around 0.0 for ferrite and 0.55 ± 0.02 for austenite. Ferritescope measurements confirmed that the ferrite phase was entirely consumed. The eutectoid transformation of ferrite to secondary austenite (γ_2) plus sigma phase took place in the SDSS. This agrees with several published papers [2, 6-8]. The volume fraction of the sigma phase was 0.28 ± 0.02 and the volume fraction of the sigma phase plus secondary austenite was 0.48 ± 0.03 . These values were a result of aging at 750 °C for 180000s (50h).

3.1.1 DSS kinetics

As shown by Magnabosco [4], the kinetics of the sigma phase precipitation in DSS in the 700-850 °C range can be represented by the JMAK equation, Equation 4.

$$V_V = 1 - e^{-kt^n} \quad (4)$$

Where k and n are constants that depend on the nucleation rate, growth rate, and shape of the precipitates. Magnabosco found n equal to 0.92 for the sample aged at 800 °C. The initial microstructure showed by Magnabosco was a lamellar morphology. In this work, the initial microstructure of the DSS has equiaxed austenite grains, see Figure 1a. One measured the volume fraction of the sigma phase as a function of time aging at 800 °C up to 79200 s (22 h). Figures 3a and 3b depict the precipitation kinetics of sigma phase. Figure 3a shows that the maximum volume fraction of sigma phase is around 0.45. Figure 3b displays normalized data obtained dividing the volume fraction of the sigma phase by the maximum volume fraction found at the end of the heat treatment. Equation 4 fitted the data displayed in Figure 3b.

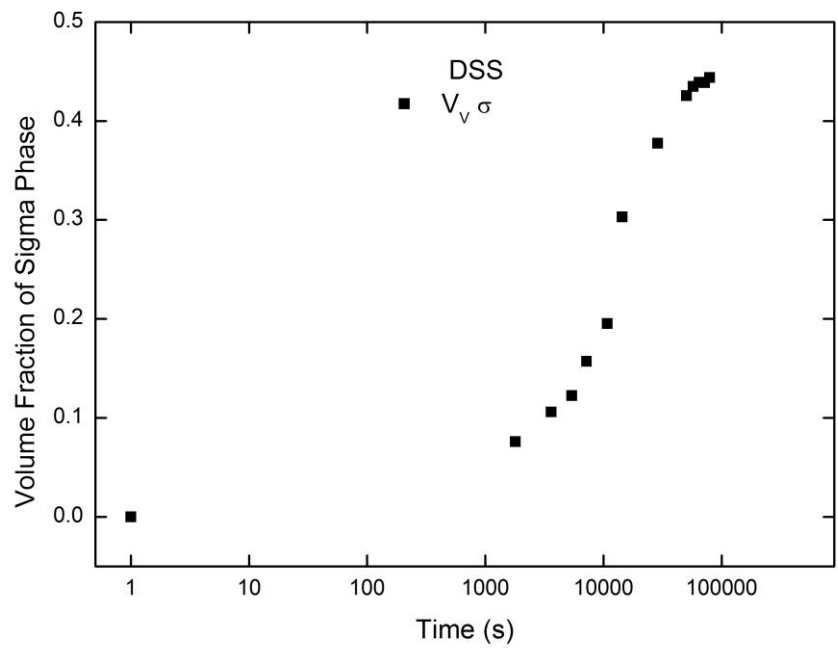


Figure3. a) Volume fraction of the sigma phase as a function of the aging time, at 800 °C.

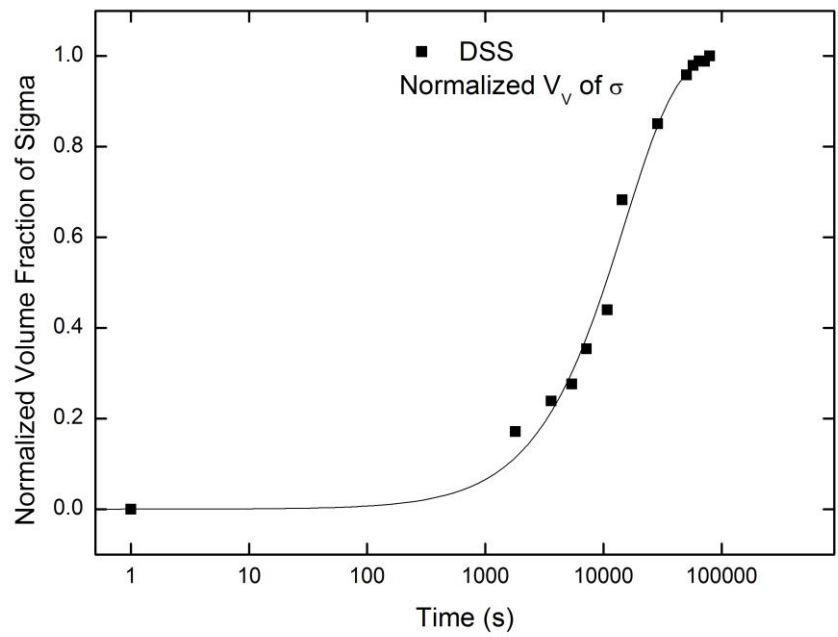


Figure3. b) Normalized volume fraction of the sigma phase as a function of the aging time, at 800 °C. The solid line represents the fit of the experimental data to Equation 4 (JMAK)

The fitting parameter obtained using JMAK was $n = 1.0$, with a high coefficient of determination, $R^2 = 0.99$. The value of $n = 1.0$ is very close to 0.92 found by Magnabosco at the same aging temperature. Thus, concerning the initial grain morphology, lamellar [4] or equiaxed, does not appear to influence the kinetics. The value of n near 1 indicates diffusion control, probably of Cr [2,4]. Performing the same procedure for the SDSS and applying the JMAK model did not yield satisfactory results, as also shown by Magnabosco [4] in treated DSS at 900 °C and by Fonseca and co-authors in SDSS [2]. Fonseca and co-authors proposed two mechanisms, interface control and diffusion control, to explain the poor agreement of JMAK with the kinetic data.

3.2. SDSS

Nucleation of the sigma phase needs examination in greater depth. First, would it arise in the ferrite/austenite boundaries? If so where would nucleation take place: on the grains face, the grains edges or the grains corners? In previous work, Fonseca and co-authors [2] suggested that the sigma phase would nucleate on the grain edges and grow consuming the ferrite phase. Thus, analyzing the contiguity of the phases becomes paramount to understand how the sigma phase nucleates and grows. We need to know whether nucleation takes place uniformly or in clusters. Recrystallization studies often employ the contiguity ratio. But the contiguity ratio can also be useful to understand any solid phase transformation [23]. It would also be of fundamental importance to visualize the sigma phase in 3D and see their interconnections and how it takes up space in 3D. Reconstruction could provide solid experimental evidence regarding the nucleation site. For readers' clarification, since the main aim was to study the individual interfaces, the contiguity ratio of the ferrite/sigma phase, measured by stereology, plots against the volume fraction of sigma phase. Figure 2b shows that at during aging ferrite decomposes into sigma and secondary austenite resulting in a typical coral-like morphology [32]. Thus, to interpret the kinetic data, we considered that the amount of ferrite consumed during the transformation was equal to the amount of sigma phase plus secondary austenite formed. Measuring the quantity of $\sigma + \gamma_2$ was possible employing the Ferritescope. The Ferritescope showed the amount of ferrite after each treatment time. Therefore, the total initial amount of ferrite less the final amount of ferrite was equal to "sigma plus secondary austenite" formed after each treatment time.

3.2.1 Contiguity, Interfacial Migration Rate, Cahn Models

The contiguity ratio is a stereological parameter, which relates the spatial distribution of new grains, for example, recrystallized in a deformed matrix. One can define the contiguity of the new grains in a deformed matrix as [23]

$$C_{aa} = \frac{2(S_V)_{aa}}{2(S_V)_{aa} + (S_V)_{ab}} \quad (5)$$

where $(S_V)_{aa}$ is the interfacial area between two new grains and $(S_V)_{ab}$ is the interfacial area between the new grain and the matrix. Thus, the contiguity (C_{aa}) is the fraction of the boundary area of the new grains shared between the new grains. Therefore, the ratio varies from 0, when there is no transformation to the maximum value of 1, with the complete transformation. Vandermeer showed that when there is a random distribution of new grains, the contiguity value, (C_{aa}), would be approximately equal to the transformed volume fraction and that a positive deviation of this equality would signify nuclei clusters. Recently, Alves and co-authors [24] deduced an equation for contiguity considering a matrix that transforms into two other phases. Therefore, Alves and co-authors extended the concept of contiguity to more than two constituents. Alves and co-authors took into account simultaneous and sequential reactions obtaining Equation 6

$$C_1 = \frac{2(S_V)_{11} + (S_V)_{12} + (S_V)_{1M}}{2(S_V)_{11} + 2(S_V)_{22} + 2(S_V)_{12} + (S_V)_{1M} + (S_V)_{2M}} \quad (6)$$

where $(S_V)_{11}$ is the interfacial area between phase 1 and phase 1. $(S_V)_{22}$ is the interfacial area between phase 2 and phase 2. $(S_V)_{12}$ is the interfacial area between phase 1 and phase 2. $(S_V)_{1M}$ and $(S_V)_{2M}$ are the interfacial areas between phases 1 and 2 with the matrix, respectively. In the present case, it is necessary to present a new expression for contiguity, since we have a matrix of ferrite and austenite and part of the matrix transforms into the sigma phase and secondary austenite. It is, therefore, possible to have the following interfaces in the microstructure: ferrite-ferrite ($\alpha\alpha$), austenite-austenite ($\gamma\gamma$), ferrite-austenite ($\alpha\gamma$), sigma-sigma ($\sigma\sigma$), ferrite-sigma ($\alpha\sigma$), austenite-sigma ($\gamma\sigma$), secondary austenite-sigma ($\gamma_2\sigma$) and secondary austenite-ferrite ($\gamma_2\alpha$). Numerous combinations of interfaces are possible. In the present study, we assume that the sigma phase nucleates at the ferrite/austenite interface and grows in conjunction with the secondary austenite consuming ferrite. Figure 2b illustrates this point. Equation 7 defines the ferrite/sigma contiguity, $C_{\alpha\sigma}$,

$$C_{\alpha\sigma} = \frac{S'_{V\alpha\sigma}}{2S_{V\alpha\alpha} + S_{V\alpha\gamma} + S'_{V\alpha\sigma}} \quad (7)$$

where, $S_{V\alpha\gamma}$ is the interfacial area between ferrite and austenite, $S_{V\alpha\alpha}$ is the interfacial area between ferrite and ferrite and $S'_{V\alpha\sigma}$ is the interfacial area between ferrite and sigma phase (values of the interfacial area between secondary austenite/sigma ($S_{V\gamma_2\sigma}$) and interfacial area between secondary austenite/ferrite ($S_{V\gamma_2\alpha}$), were added to this $S_{V\alpha\sigma}$). Thus, we have Equation 8:

$$S'_{V\alpha\sigma} = S_{V\alpha\sigma} + S_{V\gamma_2\sigma} + S_{V\gamma_2\alpha} \quad (8)$$

During aging, the nucleation and growth of the sigma and secondary austenite phases cause the disappearance of the ferrite/austenite interface and also of the ferrite/ferrite interface. Figure 4 shows the contiguity of the ferrite/sigma phases obtained by equation 7 as a function of the volume fraction of sigma. Figure 4 shows SDSS aged at 750 °C. The sigma phase did not consume all other phases present. Consequently, the total volume fraction of sigma was around 0.30 at the end of aging. Thus, it is necessary here to modify Vandermeer's original idea that the contiguity is approximately equal to the volume fraction transformed when random nucleation occurs. Thus, the model presented in Figure 4 considers that $C_{\alpha\sigma} = 3 V_{V\sigma}$. The 100% transformation presented for the case of the complete transformation of a deformed matrix to new grains, in the case of the present work, would be around (1/3) transformation.

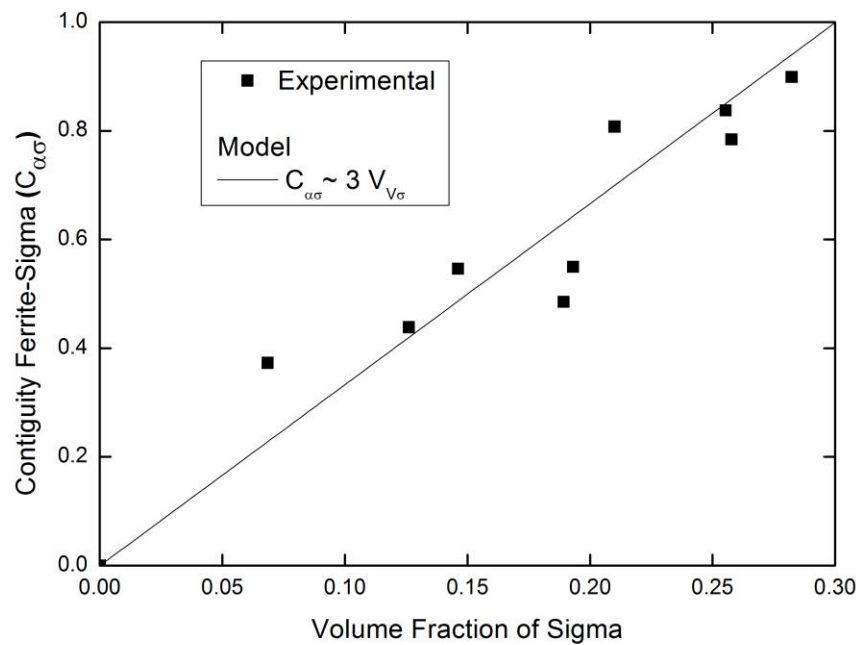


Figure 4. Contiguity between the ferrite/sigma phases as a function of the volume fraction of sigma phase. In the case of random nucleation $C_{\alpha\sigma} = 3V_{V\sigma}$. The straight line represented by this equation is also presented

Figure 4 reveals that the points are close to the model. Therefore, Figure 4 implies a random distribution of the nuclei of the sigma phase within the ferrite. The data do not have a positive linear deviation in relation to the volume fraction of sigma phase. This in Vandermeer [23] previously studied the austenite decomposition to ferrite in hypoeutectoid steel that exhibits a positive deviation thus implying that nucleation took place in clusters. In contrast, here one obtained a random distribution of nuclei in space. Such a conclusion, here reported for the first time, was suggested the contiguity between the sigma and ferrite phases in superduplex stainless steel. To calculate the kinetics of formation and growth of the sigma + secondary austenite and to apply models different of JMAK, in the case of the present work, the Cahn models [17], to find the interfacial migration rate (G) of these phases is of fundamental importance. We now derive G taking into account that the precipitation of sigma plus secondary austenite consumes the ferrite/austenite interface. Figure 5 shows the $S_{V\alpha\gamma}$ variation as a function of time.

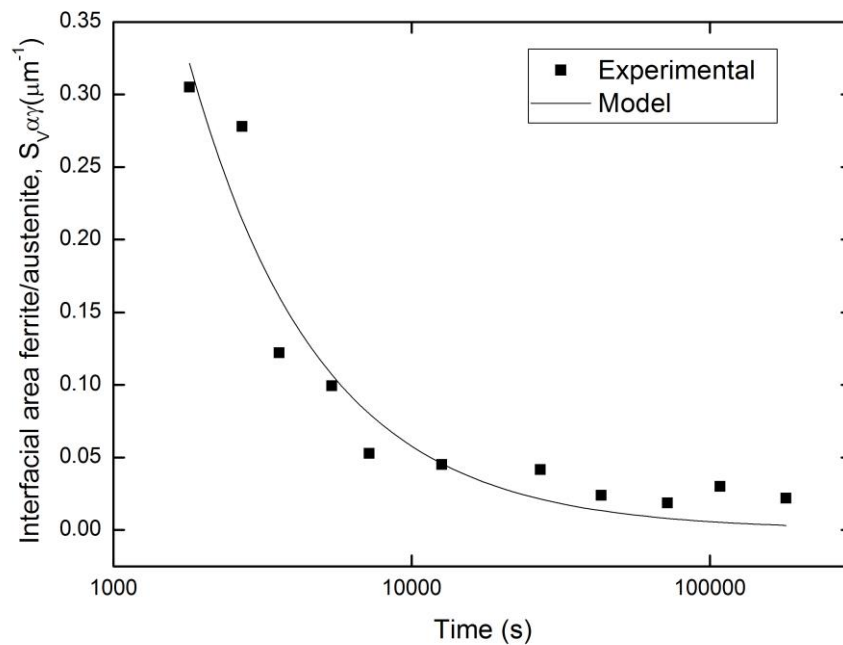


Figure 5. Interfacial area ferrite/austenite ($S_{v\alpha\gamma}$) as a function of the aging time, at 750 °C.

Figure 5 demonstrates that during aging the interfacial area of ferrite with austenite is consumed. Equation 9 corresponds to the model fitted to the experimental data

$$S_{v\alpha\gamma} = Kt^n \quad (9)$$

where K and n are constants. Applying Equation 9, we obtain: $S_{v\alpha\gamma} = 582t^{-1}$ and $R^2 = 0.92$, a good fit. In addition to analyzing the decrease in the interfacial area ferrite/austenite during the transformation, one measured the volume fraction of ferrite as a function of time, indicating that, as expected, the ferrite volume fraction is decreasing during aging. Figure 6 shows the volume fraction of ferrite, measured by the Ferritoscope, as a function of time.

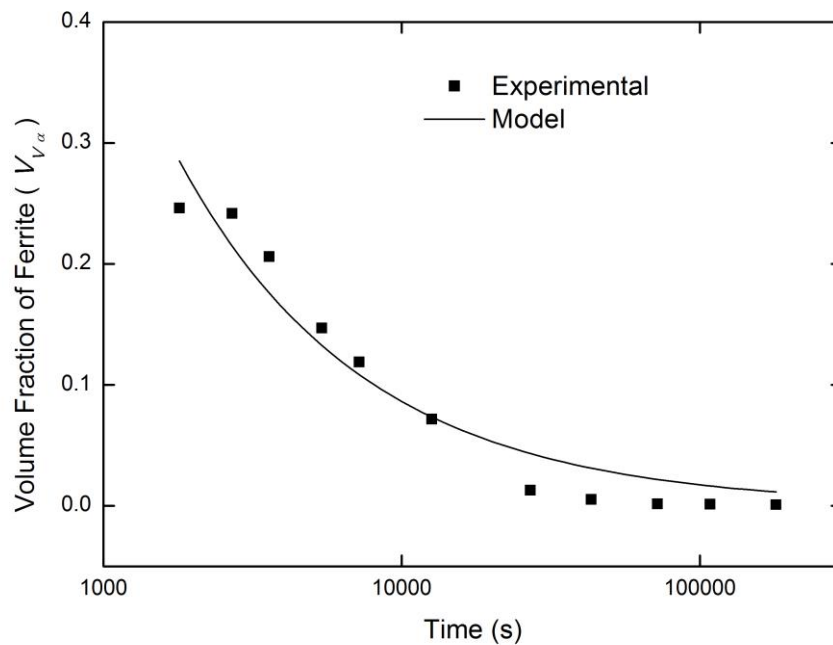


Figure 6. Volume fraction of ferrite as a function of the aging time, at 750 °C

Figure 6 shows that the volume fraction of ferrite decreases during aging. The final microstructure at the end of the aging comprises the sigma phase plus secondary austenite, see Figure 2b. The model fitted to the experimental data is presented in Equation 10:

$$V_{V\alpha} = Ct^m \quad (10)$$

Where C and m are constants. Applying Equation 10, one obtains $V_V = 52.56t^{-0.7}$ and $R^2 = 0.94$. Therefore, there is good agreement between model and experimental data. With the data obtained from Equations 9 and 10, it is possible to find the interfacial migration rate, G . The hypothesis raised here is that the rate of appearance of the sigma + secondary austenite is equal to the speed of ferrite consumption. The interfacial migration rate, G , can be estimated by Equation 11, Cahn and Hagel equation [33]

$$G = \frac{1}{S_{V\alpha\gamma}} \frac{dV_{V\alpha}}{dt} \quad (11)$$

Combining the results obtained by Equations 9 and 10 and equation 11 gives $G = -0.063t^{-0.7}$. Assuming that the growth rate of the sigma plus secondary austenite is equal to the value of G with opposite sign, that is, positive, it is possible to obtain Figure 7, interfacial migration rate as a function of aging time

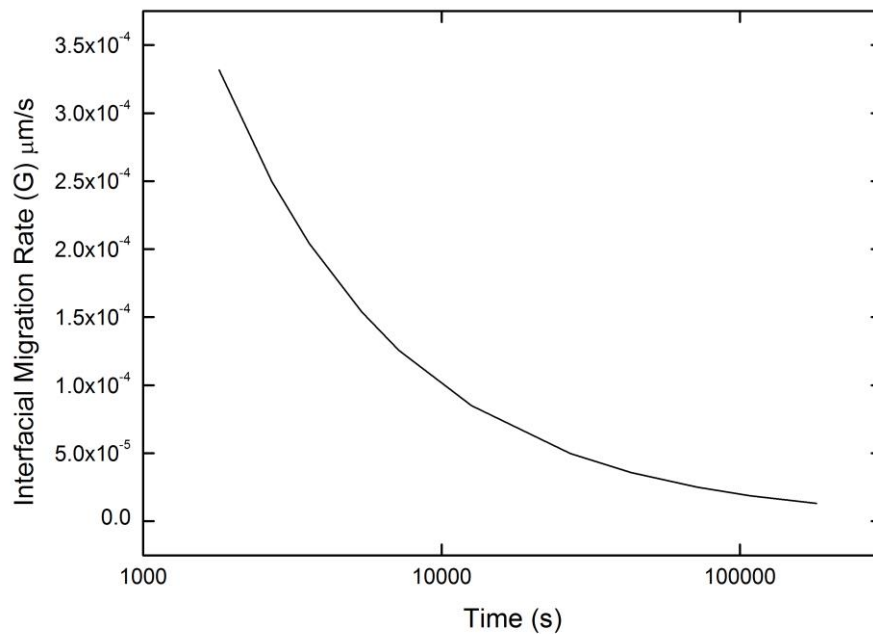


Figure 7. The growth rate of the sigma + secondary austenite as a function of the aging time, at 750 °C. In other words, the interfacial migration rate of sigma/secondary austenite consuming ferrite.

Analyzing Figure 7, a velocity of roughly 0.00035 μm/s occurs the concentration gradients overlapping of the elements, thus the velocity decreases [34]. Now with the knowledge of the interfacial migration rate, G , of the new phases, sigma plus secondary austenite, it is possible to analyze whether the phases nucleated on the grain boundary, grain edge or grain corner. For this, we used the classic Equations of Cahn [17]

$$V_V = 1 - e^{-2S_V r} \quad (12)$$

$$V_V = 1 - e^{-\pi L_V r^2} \quad (13)$$

$$V_V = 1 - e^{-\frac{4}{3}\pi C_V r^3} \quad (14)$$

where S_V , L_V e C_V are respectively the boundary area, edge length and grain corner number, all per unit volume and $r = Gt$. And Equations 12, 13 and 14 are for the case of grain boundary nucleation, grain edge nucleation, and corner nucleation, respectively. Since G is not constant, remembering that $G = 0.063t^{0.7}$, it is necessary to integrate Equation 15

$$\frac{dr}{dt} = G \quad (15)$$

Getting: $r = 0.21t^{0.3}$. Knowing that S_V , L_V e C_V can be obtained by Equations 16 to 18 [17]:

$$S_V = \frac{3.35}{D} \quad (16)$$

$$L_V = \frac{8.5}{D^2} \quad (17)$$

$$C_V = \frac{12}{D^3} \quad (18)$$

Cahn [17] made these considerations using space-filling tetrakaidecahedral grains. D is the distance between the square faces of a tetrakaidecahedron.

Replacing r by $r=0.21t^{0.3}$ and inserting the values of S_V , L_V e C_V , obtained by Equations 16 to 18, into Equation 12 to 14, it is possible to compare the volume fraction of sigma plus secondary austenite obtained experimentally, with the models presented in Equations 12 to 14. Using the initial S_V value of the as received sample, $0.272 \mu\text{m}^{-1}$, into Equation 16 one can find D . In this case D is equal to $12.3 \mu\text{m}$. With this value of D , it is possible to find L_V e C_V using Equations 17 and 18. Figure 8a shows the volume fraction of the phases ($\sigma + \gamma_2$) as a function of the aging time. Figure 8a shows that the maximum value of sigma + secondary austenite formed is around 0.48. We normalized the data of Figure 8a by dividing the volume fraction of sigma plus secondary austenite obtained at each aging time by the maximum value of V_V found at the end of the treatment. Thus, it was possible to compare the normalized data, shown in Figure 8b with Cahn's models, Equations 12 to 14.

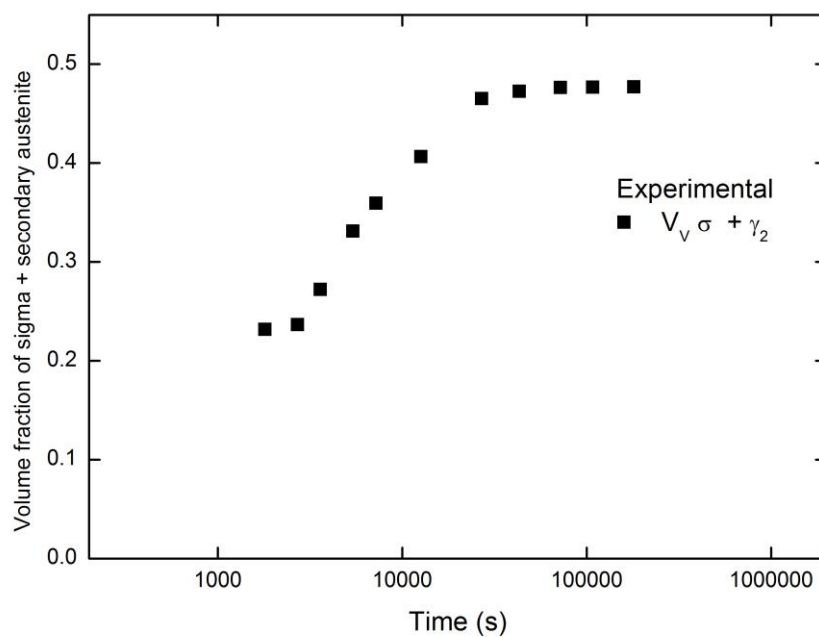


Figure 8. a) Volume fraction of sigma + secondary austenite as a function of the aging time, at 750 °C.

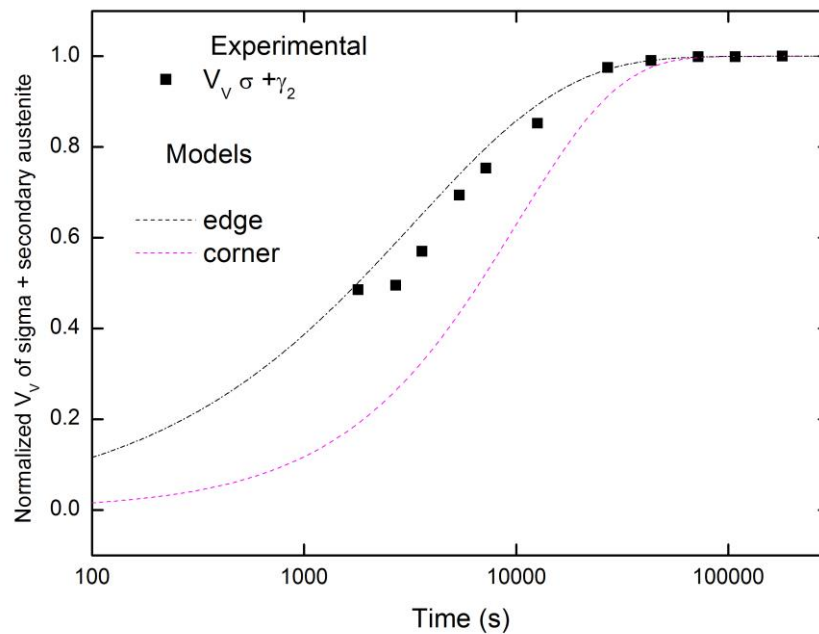


Figure 8. b) Normalized volume fraction of the sigma phase + secondary austenite as a function of the aging time, at 750 °C. The dashed lines represent the fit of the experimental data to Equations 13 and 14, respectively (Cahn Models)

Analyzing Figure 8b, it is clear the tendency of these phases, to first saturate the edges of the ferrite with austenite. The initial lamellar morphology (α/γ) seems to have great influence on the edge length, generating a large number of edges so that the total edge length was sufficient to provide the nucleation sites for the sigma phase. Figure 8b does not show the grain boundary nucleation model because of the poor fit.

3.3. Computational Thermodynamics / Scanning Electron Microscopy / Energy Dispersive Spectrometry

Thermo-Calc software with database TCFE7 calculated the SDSS equilibrium diagram with the chemical composition presented in Table 1. Figure 9 shows the diagram. Through this diagram, it is possible to extract the mass percentage of the elements at any desired temperature. Table 3 contains the mass percentage of the following elements: Fe, Cr, Mo, and Ni, at 800 °C, in the sigma phase, obtained by the diagram of Figure 9.

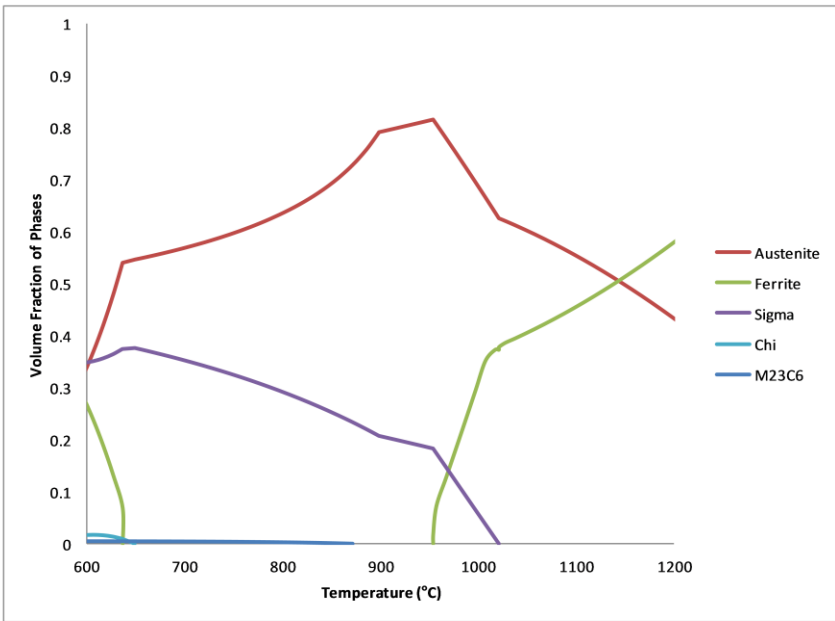


Figure 9. SDSS equilibrium phase diagram calculated thermodynamically with the aid of Thermo-calc software

Table 3 - Chemical Composition of the Sigma Phase (wt. (%)) - Thermo-calc 800 °C

Elements	Fe	Cr	Mo	Ni
	53.7	34.5	8.3	3.0

SEM coupled to EDS, determined the mass percentage of the sigma phase (Fe, Cr, Mo, Ni) in the samples treated at 800 °C until 108000 s (30h) for comparison with the data provided by Thermo-Calc, Table 3. Figure 10 shows two micrographs obtained using SEM of the sample treated at 800 °C for 108000 s (30h). These micrographs show the locations of the EDS analysis. Each line in the micrograph had an average of 10 reading points. Twenty lines were measured. Thus, measuring a total of 200 points generating the average values presented in Table 4. The sample treated at 800 °C for 108000 s (30h) was the one that was closer to the equilibrium values shown in Table 3

Table 4 - Chemical Composition of the Sigma Phase (wt. %) - Experimental – 800 °C – 108000 s

Elements	Fe	Cr	Mo	Ni
	53.2 ± 1.0	30.2 ± 0.5	10.5 ± 0.4	6.0 ± 1.0

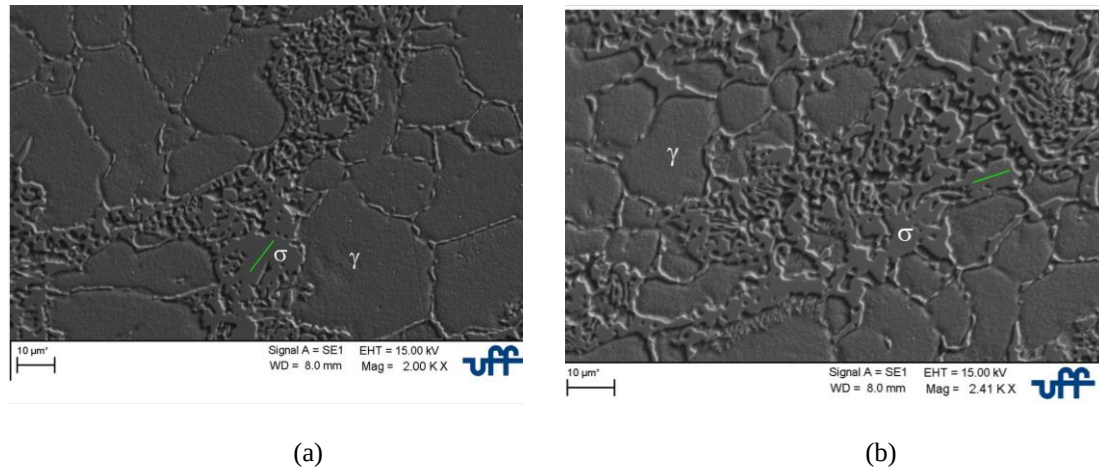


Figure 10. (a) e (b) Micrographs of the sample treated at 800 °C for 108000 s (30h), presenting austenite (γ) and sigma (σ) at different positions of the sample. The green line shows the position of the line of EDS scanning.

The values found by EDS analysis, Table 4, are in agreement with the composition calculated with the aid of Thermo-Calc software, table 3. The experimental sample, treated at 800 °C for 108000 s (30h), is closer to thermodynamic equilibrium. Hence, one chose this sample for the 3D reconstruction, representing the SDSS under equilibrium conditions.

3.4. 3D Reconstruction

First, one can see the 3D reconstruction of the volume of $127\ \mu\text{m} \times 68\ \mu\text{m} \times 3.5\ \mu\text{m}$ of a sample. Figure 11 shows the rendering of the volume. Figure 11 contains too much information. Therefore, it is necessary to specify a smaller region to analyze in detail.

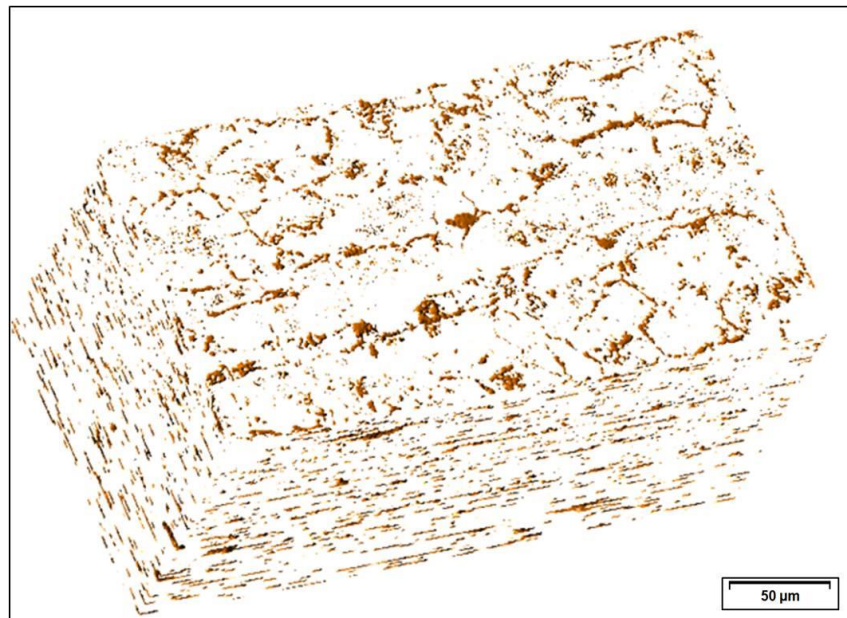


Figure 11. Micrograph of the surface-rendered reconstructed 3D microstructure. The micrograph depicts the sigma phase in brown.

Figure 12 shows the region chosen for 3D reconstruction. To analyze the sigma phase in detail, one reconstructed the sigma phase that consumed the 2D boundary. One used

only the first 20 sequential images. Despite a reduced number of layers, the 3D analysis was sufficient to indicate the preferred nucleation site.

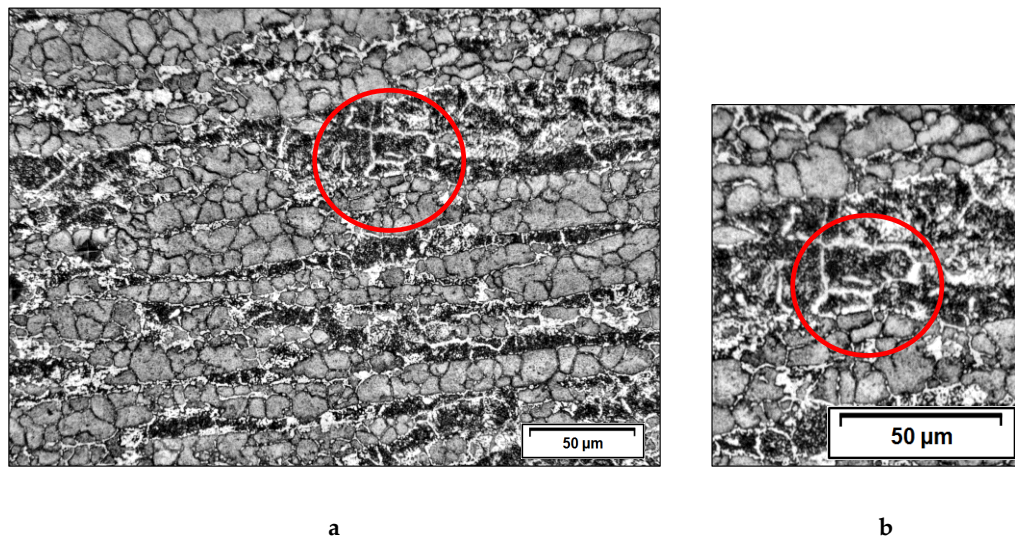


Figure 12. a) Micrograph of the sample treated at 800 °C for 108000 s (30h), presenting the region of interest for reconstruction within the red circle b) boundary that will be reconstructed, shown in detail.

Figure 13 shows the region analyzed from several angles. The sigma phase consumes the edges of the ferrite/austenite interface and grows into the ferrite boundary. However, the boundary is not fully consumed; but the edge is almost entirely consumed. This finding agrees with Figure 8b, that is, the sigma phase first saturates the edges of the ferrite with austenite. The sigma "wets" the edge but it is absent in some points interrupting the interconnection of the boundary. This is similar to Kral and coauthors [27] reconstruction of proeutectoid ferrite. Here, we present the first experimental evidence that the sigma phase nucleates at the edges of ferrite/ austenite. The 3D reconstruction corroborates the findings from the kinetic data, see Figure 8b. So, the grain boundaries, i. e., the faces, are not preferred sites for sigma phase nucleation. The grain edges are the preferred sites for sigma phase nucleation.

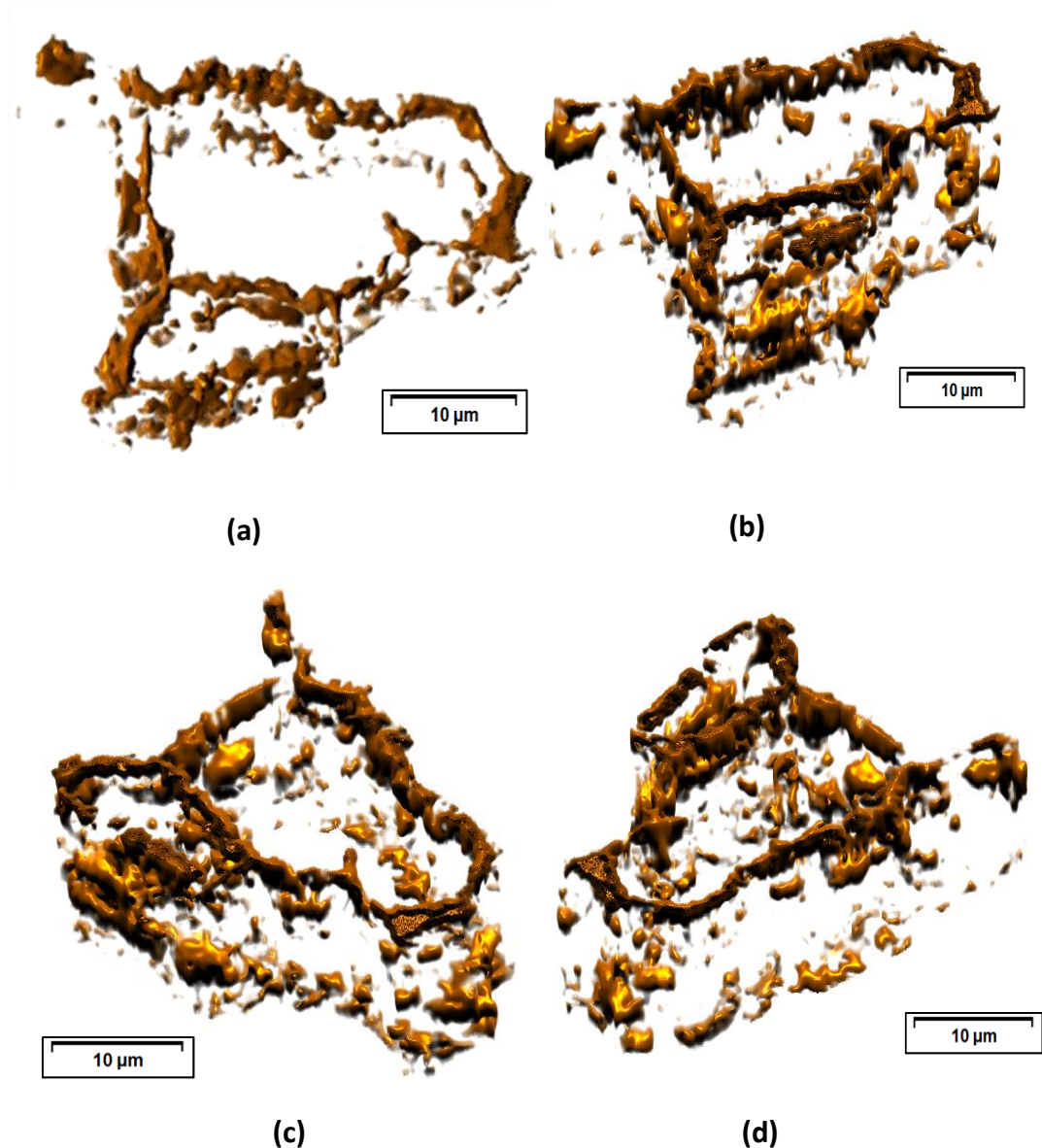


Figure 13. Sigma phase reconstructed in 3D, (a) - (d) Different viewing angles of the reconstructed region, shown in Figure 12.

4. Conclusions

The main conclusions of the investigation of precipitation kinetics of the sigma phase in duplex stainless steel and superduplex stainless steel were:

- Classical JMAK equations can adjust the kinetics of sigma phase precipitation in DSS with equiaxial morphology of the austenite grains. Ferrite decomposition during aging generated depleted ferrite plus sigma, as found in superferritic stainless steels. Ferrite decomposition during aging in SDSS generated as expected sigma phase more secondary austenite.
- For the first time, one studied the microstructure of SDSS with the help of the contiguity of ferrite/sigma. According to the contiguity, the distribution of the nuclei of the sigma phase is random and $C_{\alpha\sigma} = 3 V_{V\sigma}$.

- Cahn's equation for grain edge nucleation fitted well the kinetics of precipitation of the sigma phase + secondary austenite in SDSS.
- Computational thermodynamics indicated that the sigma phase aged at 800 °C for 108000 s (30h) had the composition close to equilibrium.
- The 3D Reconstruction, using the sample close to the equilibrium composition, verified that the sigma phase occupies the edges of the ferrite/austenite interfaces and grows around the austenite. The sigma phase loses the interconnection at some points on the grain boundary. For the first time, the one provided experimental evidence of the sigma phase nucleation at the ferrite/austenite edges. In other words, the edges are preferred sites for the nucleation of the sigma phase.

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Author Contributions:

Gláucio Soares da Fonseca conceived and designed the experiments; Priscila Sousa Nilo Mendes performed the SDSS experiments; Ana Carolina Martins Silva performed the DSS experiments and Computational Thermodynamics; Gláucio Soares da Fonseca analyzed the data and wrote the paper.

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