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PHASE TRANSFORMATIONS AND MODELLING OF THERMAL STRESSES IN A CAST SUPER DUPLEX STAINLESS STEEL

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Abstract

Metal casting is an old manufacturing process that involves the melting and solidification of an alloy to make a product with a simple or complex shape. Despite the fact that metal casting is one of the most economical routes to transform raw materials into finished metal products, it is also one of the most challenging manufacturing processes. In the past, to control the quality of final products a trial-and-error approach was typical. Nowadays, the traditional methods of manufacturing have been replaced by advanced production systems capable of managing the small batch production of complex products and short lead times. Furthermore, computation is currently an essential tool because it displays new methods of modelling and simulation to optimize the design and manufacturing processes.

In metal casting, there are several physical phenomena that affect the quality of the final products, such as solid-phase transformations of the material, heat transfer between the hot metal and the cold mold and thermal stresses generated during cooling. In this regard, for any current advanced production system, modelling plays an important role in describing quantitatively the relationships among the aforementioned physical phenomena. This methodology can be applied to solve complex problems associated with casting technology.

In this context, the objective of the present thesis is focused on creating a model that describes the main parameters affecting the formation of residual stresses in cast parts with complex geometries. In particular, the specific objectives are 1) to determine the solid-phase transformations occurring in 25Cr-7Ni-Mo-N super duplex stainless steel, as a function of temperature and cooling rate, 2) to understand the kinetics of formation of secondary phases and the distribution of phases across the thickness of the cast parts, and 3) to create numerical models to predict the residual stresses of 25Cr-7Ni-Mo-N super duplex stainless steels parts. Through the development of numerical models, the effects of temperature distribution, mechanical constraints, and solid-phase transformations on the residual stresses of cast parts are effectively predicted.

To understand the solid-phase transformations occurring in 25Cr-7Ni-Mo-N super duplex stainless steel, an initial study was made on the microstructural characterization of the as-cast components. Subsequently, the secondary phases formed at temperatures between 700 °C and 1000 °C were identified and their kinetics of formation were assessed. With this information, a sequentially coupled thermo-mechanical model was developed in Abaqus™, using empirical descriptions of the thermophysical properties of the materials.

The accuracy of the models was evaluated by measuring the residual stresses using the contour method. A close agreement between the predicted and measured residual stresses was achieved, showing the importance of defining the interfacial heat transfer coefficient, which strongly depends on the specific setup.

In summary, this thesis greatly contributes to improve the quality of cast super duplex stainless steel components. In addition, the methodology developed can be extrapolated to other materials and manufacturing processes. This work fosters future developments within the field of casting, in particular to predict the microstructure evolution along the thermal processing cycle.

Resumo

A fundição é um dos mais antigos processos de fabrico, que envolve a fusão e a solidificação de uma liga metálica numa moldação, cerâmica ou metálica, permitindo obter componentes de geometria mais ou menos complexa. Apesar de ser descrito como um dos processos mais económicos para o fabrico de componentes metálicos, a fundição também se apresenta como um dos processos mais desafiantes. Relativamente à garantia da qualidade, no passado, esta era controlada com base em metodologias “tentativa-erro”; contudo, os métodos tradicionais têm vindo a ser substituídos por sistemas de produção avançados, capazes de garantir o fabrico de pequenas séries de produtos complexos e com tempos de entrega reduzidos. Além disso, os métodos numéricos tornaram-se ferramentas poderosas e essenciais para modelar e simular os processos de fabrico, com vista à sua otimização.

No processo de fundição, a qualidade final das peças é afetada por vários fenómenos físico-químicos, tais como transformações de fase no estado sólido, transferência de calor entre o metal e a moldação e a geração de tensões residuais originadas durante o arrefecimento. Perante esta diversidade de fatores que condicionam a qualidade final das peças, os métodos numéricos tornaram-se absolutamente essenciais para descrever quantitativamente as relações entre os diversos parâmetros e, assim, resolver problemas complexos associados à tecnologia da fundição.

Neste contexto, o objetivo desta tese é estabelecer um modelo que descreve os principais parâmetros que afetam a formação de tensões residuais em peças fundidas com geometrias complexas. Em particular, os objetivos específicos são: 1) caracterizar as transformações no estado sólido que ocorrem no aço inoxidável super duplex 25Cr-7Ni-Mo-N, em função da temperatura e velocidade de arrefecimento; 2) compreender a cinética de formação das fases secundárias, bem como a sua distribuição em função da secção das peças; 3) criar modelos numéricos que permitam prever as tensões residuais em componentes de aço inoxidável super duplex 25Cr-7Ni-Mo-N. Desta forma, será possível prever o efeito da distribuição de

temperaturas, constringimentos mecânicos e transformações de fase no estado sólido, nas tensões residuais das peças.

De forma a compreender as transformações de fase no estado sólido no aço inoxidável super duplex 25Cr-7Ni-Mo-N, foi realizado um estudo da microestrutura de componentes fundidos na condição as-cast. Posteriormente, estudou-se a formação de fases secundárias no intervalo de temperatura de 700 °C a 1000 °C, incluído a caracterização da respetiva cinética de formação. Com esta informação, foi desenvolvido um modelo termo-mecânico em ABAQUS™, que utiliza as descrições empíricas das propriedades termofísicas dos materiais.

A validação da simulação das tensões residuais foi realizada através da sua medição na peça, utilizando-se o método de contorno. Obteve-se uma boa aproximação entre os resultados da previsão e da medição, demonstrando a importância de se definir corretamente o coeficiente de transferência de calor, que depende das características do processo, no modelo termo-mecânico.

Em resumo, o trabalho apresentado nesta tese é uma contribuição para a melhoria da qualidade final de componentes em aço inoxidável super duplex, podendo a metodologia apresentada ser extrapolada para outros materiais e processos de fabrico. Pretende-se que este estudo sirva de catalisador para outros desenvolvimentos na área da fundição, nomeadamente a previsão da evolução da microestrutura em função do processamento térmico.

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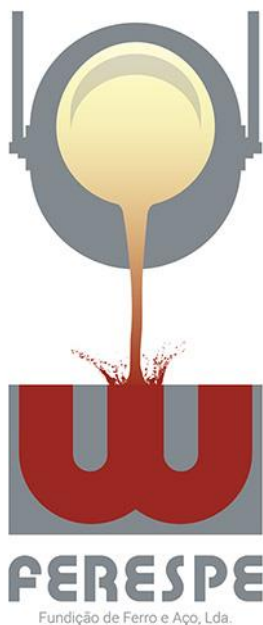
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Acronyms and Symbols

Acronyms

ASTM	American society for testing and materials
BSE	Backscattered electron
CAE	Computer aided engineering
CALPHAD	Computer coupling of phase diagrams and thermochemistry
CCT	Continuous-cooling-transformation
CMM	Coordinate measuring machine
DSS	Duplex stainless steel
EBSD	Electron backscattered diffraction
EDS	Energy dispersive X-ray spectroscopy
FIB	Focused ion beam
JMAK	Johnson-Mehl-Avrami-Kolmogorov
LCF	Low cycle fatigue
LSP	Laser shock processing
HCF	High cycle fatigue
IHTC	Interfacial heat transfer coefficient
NT	Nodal temperature
OM	Optical microscopy
OR	Orientation relationship
PRE	Pitting resistance equivalent
PRE _N	Pitting resistance equivalent (considering the N effect)

PRE _w	Pitting resistance equivalent (considering the W effect)
SAED	Selected area electron diffraction
SCC	Stress corrosion cracking
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TTT	Time-temperature-transformation
UNS	Unified numbering system
WEDM	Wire electro discharge machining

Symbols

A	Area
Cr _{eq}	Chromium equivalent
Ni _{eq}	Nickel equivalent
ρ	Density
C_p	Specific heat
d	Distance
ΔT	Temperature difference
ε	Total strain
ε^{el}	Elastic strain
ε^{th}	Thermal strain
ε^{p}	Plastic strain
ε^{cr}	Creep strain
ε^{v}	Volumetric strain
ε^{tr}	Transformation plasticity strain
f	Fraction of the new phase formed
G	Temperature gradient
k	Thermal conductivity
k	Reaction constant sensitive to temperature
k^2	Constant determined from the uniaxial tension test
n	Avrami exponent

$\dot{Q}$	Rate of heat generated per unit volume
q	Rate of heat transfer
S_{11}	Normal stresses
S_y^2	Yield stress
T	Temperature
t	Time
τ	Stress tensor
τ_y^2	Pure shear stress tensor
τ_v^2	von Mises criterion
V	Volume percentage
$V_{\sigma,t}$	Volume percent of σ -phase measured at aging time t
$V_{\chi,T}$	Maximum volume percent of χ -phase measured at aging temperature T
$V_{\chi,t}$	volume percent of χ -phase measured at aging time t
δ -phase	Ferrite
γ -phase	Austenite
γ_2 -phase	Secondary austenite
γ_3 -phase	Tertiary austenite
σ -phase	Sigma phase
χ -phase	Chi Phase
.odb	Output database file

Chapter 1 Introduction

1.1 General Context and Motivation

Metal casting is a widely used manufacturing process. This technology is based on the principle of pouring liquid metal into a mold cavity, to obtain a near net shape product. Despite the oldest metallic casting dating to 5000 to 3000 B.C., metal casting has been considered an art, governed by a trial-and-error approach. Nonetheless, in the last hundred years, metal casting has been developed significantly, through improvements in casting processes and materials.

As expected, one of the most important priorities in the metal casting industry is to match the fast-growing market requirements and demands. Therefore, flexibility and agility are essential for responding and adapting quickly to market demands, and consequently to guarantee the success of the companies. In this context, manufacturers must undergo a process of reinvention in which traditional methods of manufacturing are replaced by advanced production systems capable of managing small production batches of complex products and short lead times. Such production systems require, in addition to new manufacturing technologies, new modelling methods and simulations that allow the optimization of new designs and manufacturing processes.

In this context, it is critical to simulate many physical phenomena, such as the flow of the liquid metal, heat transfer between the hot metal and the cold mold, thermal stresses arising from distinct cooling rates and different geometries, as well as the formation of defects and microstructural evolution. Thus, modelling plays an important role in describing quantitatively, the relationships among geometry, processing variables, microstructure, bulk properties, and service performance. Hence, it can be applied to solve complex problems arising in casting technology. In this regard, the type and occurrence of defects in metal casting is a central topic for casting processing engineers, because defects affect the reliability and properties of the cast component and increase

the production costs. Among these defects, porosity due to shrinkage, gas porosity, distortions, and cracking are critical.

To mitigate the formation of defects, modelling has been providing an adequate framework to build a virtual cast component, which includes only the relevant physical phenomena for the process, thus reducing the computational costs. From an engineering perspective, to build a model which describes the physical phenomena of metal casting is technically challenging and costly. This includes heat transport, phase transformations, thermal contraction, and elastic deformation. In general, each casting process involves a distinct set of factors that affect the final product quality. Therefore, an effective model requires an understanding of the dominating mechanisms and factors to simulate the proper conditions and to produce effective cast designs.

Prior to this thesis, a systematic methodology capable of predicting residual stresses and distortions induced by phase transformations in casting parts with complex geometries was not available. It is well known that the distribution of residual stresses and deformation of the final parts are a consequence of the correlations between the temperature gradients and the mechanical constraints imposed by the mold to a free contraction. Apart from these factors, the stress-induced solid-phase transformations that occur must be also considered when assessing the residual stresses, because they may have a great impact on the level of the generated residual stresses. This is particularly critical for those materials that undergo phase transformations within the cooling temperature range or during the subsequent thermal processing, such as the solutionizing or welding processes. This is the case of the super duplex stainless steel (DSS) studied in this project, which is prone to the formation of complex phases at temperatures ranging from 700 °C to 1000 °C.

Duplex stainless steels are advanced steels used in many applications due to their high strength, toughness and corrosion resistance [1-3]. The resistance of DSS to localized forms of corrosion, such as pitting and crevice corrosion, is strongly dependent on the alloy content, in particular, Cr, W, Mo and N [4]. These alloying elements play an important role on the stabilization of the duplex microstructure and improvement of the corrosion resistance, although, as the concentration of the alloying elements increases, the risk of precipitation of secondary phases is raised. Several phases may form, among which, brittle intermetallic phases. [5-10]. In the literature, there is significant work concerning this topic on wrought alloys [6, 8, 11-16], yet the number of studies dedicated to cast alloys is very reduced [17, 18]. This distinction is important because the kinetics

of secondary phases formation and the solid phase transformation mechanisms are strongly affected by the processing route.

Cast parts with complex shapes and wide range of thicknesses (from thin to thick cross-sections) will solidify at different times. As expected, faster cooling rates are found in thinner cross-sections. Under these circumstances, the impact of differential cooling must be addressed, in particular, its effect on phase distribution and non-uniform shrinkage [19, 20]. Both effects can act together as the root cause for the creation of stress fields during cooling, which may result in cracking. So, metallurgical aspects, mechanical constraints, and temperature distributions during the solidification of a cast part will cause the creation of residual stresses that may compromise the reliability of the part. Despite the amount of research work published concerning residual stresses in castings, an effective methodology relating the main processing parameters affecting the residual stresses and ultimately the quality of super DSS castings is lacking. In this regard, this research work provides a methodology to correlate the geometry of the cast part with the temperature distribution, microstructural phase evolution, and the consequent residual stresses generated. In particular, the research work focuses on developing an understanding of the occurrence of geometric defects, such as distortions and/or cracking, which are induced by residual stresses, on sand castings of super DSS. These defects have a negative impact on the production of advanced stainless steels.

1.2 Objectives and Main Contributions

To address the aforementioned issues, the main objectives of this research work are:

1. To identify the phases and constituents of the 25Cr-7Ni-Mo-N super DSS, which is one of the highest alloyed standard cast grades and more prone to the precipitation of secondary intermetallic phases that affect, among other things, the residual stresses in the cast components.
2. To understand the kinetics of formation of secondary phases within the temperature range 700 °C to 1000 °C, where the precipitation of secondary phases is likely to occur.
3. To address the effect of the cooling rate on the distribution of phases, thus allowing us to predict the microstructure across the thickness of the cast parts.

4. To develop and validate experimentally a numerical model to simulate the thermal residual stresses of 25Cr-7Ni-Mo-N super DSS parts, which were cast in furan-bonded sand molds.

The main contributions of this thesis are as follows:

1. Combining optical microscopy, scanning electron microscopy and transmission electron microscopy, to unambiguously identify the secondary phases and to determine the time-temperature-transformation (TTT) diagram for the high alloyed DSS cast grade.
2. The development of a numerical thermal model, capable of efficiently predicting the cooling curves across the thickness of 25Cr-7Ni-Mo-N super DSS cast parts. This model uses calibrated curves of interfacial heat transfer coefficients (IHTCs) as a function of temperature, determined by an inverse methodology that uses the experimental cooling curves. Such curves obtained by temperature measurements with thermocouples positioned inside the mold and the metal, also permit to correlate the cooling rates with the microstructural phase distribution across the thickness of the cast parts.
3. The development of a numerical model to predict the residual stress distributions of the 25Cr-7Ni-Mo-N super DSS cast parts, built upon the thermal model mentioned above. In addition, the approach used in this thesis uses the elasto-plastic properties obtained from the composition of phases, as a function of the temperature.
4. The validation of the numerical models against the experimental results obtained from the cooling curves and residual stresses measurements by the contour method.

1.3 Organization of the Thesis

This thesis is organized into six main chapters. A brief summary of the contents is given here. Chapter 1 describes the general context and motivation for this thesis. The objectives and main contributions are also summarized.

Chapter 2 is divided into five sections. It starts by presenting the DSS grades based on the pitting resistance equivalent number and proceeds with a description of the applications of these alloys. The following section details the solid-phase transformations, the fundamentals and the effect of alloying elements on the kinetics of phase transformations. A discussion about the kinetics of secondary phases formation

is given for several DSS grades fabricated by different processing routes. The third section introduces the topic of residual stresses in the casting process. This section also discusses the effect of residual stresses on fatigue strength, stress corrosion cracking and dimensional stability of the components. The fourth section presents the fundamentals of residual stress modelling and ends with a literature review of the proposed models on sand casting process. Finally, the fifth section provides the theoretical framework of the contour method, which was selected to measure the residual stresses on the cast parts.

Chapter 3 is divided into six sections that provide an in-depth description of the materials and experimental methods. The first section provides the chemical composition of the studied 25Cr-7Ni-Mo-N super DSS. The second section describes the geometry of the specimens produced and the procedure to measure the temperature in the specimens. In the third section, the solution and aging heat treatments are described, and in the fourth section, the microstructural characterization techniques are detailed. The fifth section enumerates the pre-processing operations to model thermal residual stresses in cast components. This section also depicts the determination of the thermophysical properties to include in the numerical models. In the end, the sixth section is devoted to the experimental procedure selected to measure the residual stresses.

Chapter 4 discusses the experimental results from the microstructure characterization. The first section focuses on thermodynamic simulations. The second and third sections are dedicated to the characterization of the as-cast and solutionized microstructures, respectively. Finally, the fourth section reports the solid phase transformation of the 25Cr-7Ni-Mo-N super DSS within the temperature range of 700 °C to 1000 °C. The mechanisms of formation of secondary phases are discussed here as well as the JMAK model proposed to describe the transformation kinetics.

Chapter 5 is divided into three sections, covering the numerical models developed to simulate the cooling and the residual stresses distribution of the 25Cr-7Ni-Mo-N super DSS cast parts. The first section provides the results of the temperature measurements in different regions of the specimens which were the basis of the development of the thermal model. In the second section, the development of mechanical analysis is given. Additionally, the effect of the thermal gradients in residual stresses of the produced specimens is detailed. Finally, in the third section, the numerical results are compared to the residual stress measurements by the contour method.

Chapter 6 presents the main conclusions along with a discussion of future work.

Chapter 2 State of Our Understanding

2.1 Duplex Stainless Steels

Duplex stainless steels are advanced materials for high corrosion applications that require both strength and corrosion resistance. These alloys belong to the family of stainless steels, which exhibit a two-phase microstructure, with approximately equal volume fractions of ferrite (δ -phase) and austenite (γ -phase). This duplex structure is obtained by designing the chemical composition and the heat treatment conditions. As a result, these duplex stainless steels exhibit high mechanical resistance, high toughness and high corrosion resistance [1, 21]. Recently, the development of new stainless steel grades for acidic environments, containing high concentrations of chloride ions, have been the driving force to develop highly alloyed duplex stainless steels grades [22].

According to the ASTM A890 standard [23], the duplex stainless steels contain Cr ranging from 21% to 27%, which forms a passive oxy-hydroxide film, protecting the alloy against corrosion. Despite the positive effect of Cr in the corrosion resistance, the addition of this element is limited because it needs to be balanced with the austenite stabilizing elements, in order to obtain a good balance of δ -phase and γ -phase. Furthermore, the Cr enrichment of the ferrite may enhance precipitation of intermetallic phases, such as sigma, which affect the toughness, ductility, and corrosion resistance [24]. Thus, Mo may be added to improve the corrosion resistance by extending the passive potential range, therefore reducing the corrosion current density of the passive layers and improving the stability of the oxy-hydroxide layer [25]. As these two elements are δ -phase stabilizers, it is required to add γ -phase stabilizers to balance the microstructure. The essential γ -phase stabilizer is Ni, which contributes to a typical ratio of 50/50 [24]. Perhaps, the great achievement during the development of duplex stainless steels has been the addition of N, which defines the second generation of

duplex stainless steels. This element is a strong γ -phase stabilizer and despite the limited amount added to duplex stainless steels (0.33%), according to ASTM A890 standard [23]), N significantly improves the pitting corrosion resistance and the mechanical strength [26]. Finally, the additions of W or Cu also enhance the corrosion resistance of some specific duplex stainless steels [23]. In the case of W, this element is added up to 2% and improves the pitting corrosion resistance [24]. On the other hand, the addition of Cu enhances the galvanic corrosion resistance in environments containing sulphuric acid, even at temperatures near 60 °C. However, this element is restricted (3.3%, according to ASTM A890 standard [23]) due to the increased risk of precipitation of intermetallic phases [24, 27]. Nevertheless, all of the benefits associated with a high alloy content also bring about an increased risk of destabilization of the duplex microstructure, in particular for temperatures below 1000 °C. This topic will be later covered, in section 2.2.

The wide range of chemical compositions present in duplex stainless steels demands a straightforward definition of the pitting corrosion resistance for these materials. According to [21, 28], in 1969, Lorenz defined the Pitting Resistance Equivalent (PRE) value to rank the pitting corrosion resistance of the duplex stainless steels grades. This is expressed as:

$$PRE = \%Cr + 3.3 \times \%Mo \quad (\text{Eq. 1})$$

The PRE formula in Eq. 1 highlights the positive effects of the Cr and Mo additions, yet it does not consider the effect of other elements, such as N. According to [21, 28], in 1982, Herbsleb discussed the role of N in the corrosion resistance of duplex stainless steels and purposed a modified version of the PRE_N formula expressed as:

$$PRE_N = \%Cr + 3.3 \times \%Mo + k \times \%N \quad (\text{Eq. 2})$$

for which different authors used different values of k [5, 29, 30].

Due to the positive effect of W on pitting corrosion resistance, the formula was modified to include its effect [31, 32]. Therefore, the PRE_W formula is considered [33]:

$$PRE_W = \%Cr + 3.3 \times (\%Mo + 0.5 \times \%W) + k \times \%N \quad (\text{Eq. 3})$$

Despite the positive effect of the alloying elements considered in Equation 3, it is worthwhile mentioning their differential partitioning into the γ -phase and δ -phase. According to several authors [2, 21], Cr, Mo, and W are preferentially dissolved in the δ -phase, while N is mostly dissolved in the γ -phase. According to Garfias-Mesias *et al.* [3], the calculation of PRE value from the chemical composition of duplex stainless steels

provides a considerable simplification of the pitting corrosion resistance determination. Instead, they purposed that the PRE value should be calculated for each phase, considering the chemical composition of each one.

As mentioned above, duplex stainless steels exhibit a microstructure with nearly equal proportions of γ and δ . On this basis, the solutionizing heat treatment, followed by quenching in water is necessary to adjust the proportion of these phases, as well as to avoid the precipitation of secondary phases. Although this procedure is designed to achieve a γ/δ ratio of 50:50, it is possible to further adjust the γ/δ ratio in order to obtain the same PRE value for both phases. The increase of the solutionizing temperature leads to a decrease in the volume percent of γ -phase, whereas the PRE value of this phase increases. On the other hand, the PRE value of the δ -phase decreases, as the volume percent of this phase increases as well [2, 3, 34]. The changing of the proportions of the two phases and the element partitioning between phases affect the chemical composition of the individual phases. For this reason, matching the PRE value of the two phases may be more meaningful than establishing a ratio of 50:50. The crossover point of the two PRE value curves permits to determine the solutionizing temperature that enhances the pitting corrosion resistance of the duplex stainless steels, as shown in Figure 1.

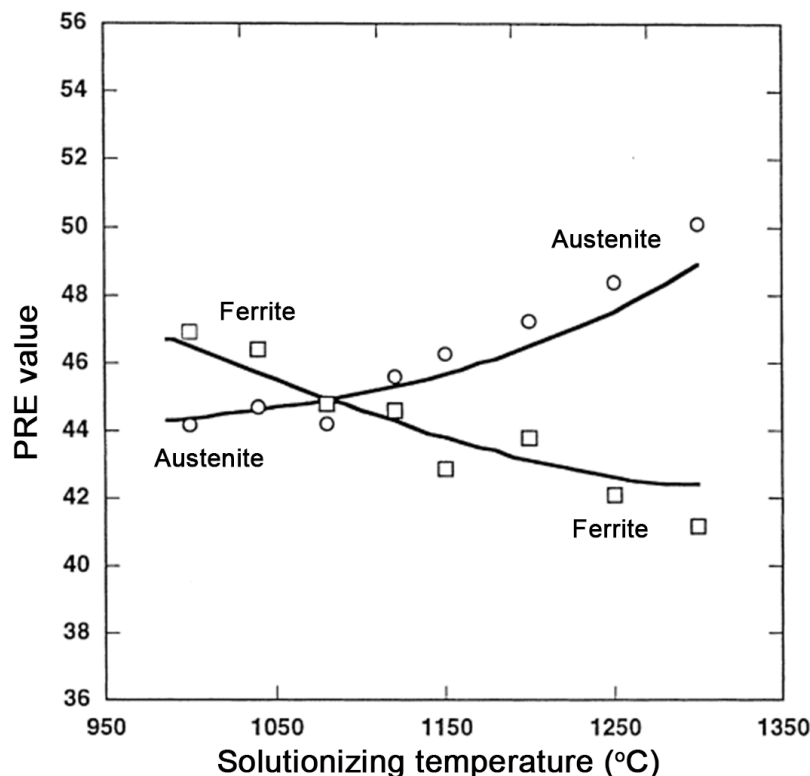


Figure 1 - Effect of the solutionizing temperature on the PRE value of the single phases in a duplex stainless steel. Modified from [2].

2.1.1 Duplex Stainless Steel Grades

As discussed before, the alloying elements affect the pitting corrosion resistance of duplex stainless steels. Thus, the PRE value has been used by industry and in research as an index to rank the various alloys with different compositions [1, 24]. Consequently, duplex stainless steels are conveniently classified into four grades, as follows:

- Lean duplex – low alloyed duplex stainless steels, with low content on Mo and Ni and a PRE value less than 30. As a result, these are the least expensive duplex grades. Some examples of these lean duplex stainless steels are UNS S32101 and UNS S82441 alloys [35-37].
- Standard duplex – these alloys have higher Ni and N contents and an addition of Mo, which improves the PRE value up to 30. The UNS S32205 alloy is one of the most applied duplex stainless steels [7, 37-39].
- Super duplex – In these alloys, as UNS S32750 and UNS S32760, W is added to improve the pitting corrosion resistance. Therefore, it is needed to consider the PRE_w value, which ranges between 40 and 50, due to the higher content on W, Cr (the minimum is 25%), Mo and N [37, 40, 41].
- Hyper duplex – these alloys are characterized by their PRE_w above 50, which is a consequence of an increased content in Cr, Mo, W, and N. Also, the hyper DSS may have additions of Cu and rare-earth elements to improve the corrosion resistance in specific environments. The UNS S33207 and UNS S32707 references are the most produced hyper alloys, providing superior pitting corrosion resistance among the duplex stainless steels [22, 42-44].

2.1.2 Applications

Duplex stainless steels exhibit an exceptional performance when subjected to pitting corrosion, but also to crevice corrosion and stress corrosion cracking. In terms of mechanical properties, the yield strength can be twice as higher as the strength of the austenitic grades. As an example, the yield strength of the duplex UNS S32205 (450 MPa) is more than twice that of the austenitic grade UNS S30400 (210 MPa) [1]. In these cases, the application of duplex stainless steels allows thinner sections to be used and, consequently, lighter structures and cost savings.

The pulp and paper industry is one of the oldest fields that uses duplex stainless steels. This industry uses chemical processes that combine temperature (up to 170 °C), pressure (6.5 to 8.5 bar), alkali solutions (sodium hydroxide and sodium sulfide), acid solutions and chloride media. Such harsh conditions require high-performance duplex stainless steels to be used in structures and equipment. In 1930, the grades 453E and 453S were used on pumps, valves and circulation systems in these industries. Nowadays, the duplex stainless steels are selected for bleaching reactors, tanks and vessels, as well as pipe cooling systems, heat exchangers, pumps and valves [24, 37, 45, 46].

Oil and gas industries have been probably the main fields for duplex stainless steels due to the superior performance of these alloys on aggressive environments containing CO₂ and H₂S, combining with boiling water. In addition, the exploration of deeper waters with pressure above 1000 bar, requires stronger and tougher materials to resist the external pressure and to support the own weight of large structures [22]. Thus, super and hyper duplex grades have been used, for example, on umbilicals to connect the sub-sea equipment to off-shore platforms, pump casings and pipes for flowlines [37]. The grades UNS S32507, UNS S32707 or UNS S33207 are some examples of super and hyper duplex stainless steels developed to use on such harsh conditions.

Desalination units are another relevant application of duplex stainless steels, due to their high corrosion resistance on saline environments. So, duplex stainless steels have been used on pressure piping systems, evaporator shells, condensers, vent systems and storage tanks [37, 47].

Moreover, it is worth to mention the significant impact of duplex stainless steels in the construction sector. The structural applications made of these alloys benefit from the combination of high yield strength and corrosion resistance, enabling a significant weight reduction of the structures. Additionally, the low maintenance requirements and low life-cycle cost are strong arguments in favor of the selection of duplex stainless steels, particularly on bridges [37, 48].

In recent years, due to the high cost of Ni, the lean grades of duplex stainless steels have attracted more interest because they use Mn and N to substitute Ni. Therefore, these low-Ni lean duplex stainless steels, such as UNS S32101 or UNS S32304 could be an alternative to the UNS S30400 or UNS S31606 austenitic grades, particularly in high strength-to-weight ratio applications [18, 48-50]. The reservoirs used to transport chemical products are one application in which lean duplex stainless steels emerge as an alternative to austenitic grades. In this sense, the selection of duplex stainless steels

could reduce the weight of the reservoir by 10%. Also, duplex stainless steels exhibit adequate ductility and weldability [24], which are essential requisites for this particular application.

2.2 Solid-Phase Transformations in Duplex Stainless Steels

As described in the previous section, duplex stainless steels have a significant impact on various engineering applications that require a combination of high mechanical resistance, high toughness, and high pitting corrosion resistance. The combination of these properties results from the duplex microstructure consisting of nearly equal proportions of δ -phase and γ -phase, obtained from designing the chemical composition and selecting the appropriate thermal processing conditions.

When exposed to specific thermal cycles, duplex stainless steels may undergo solid phase transformations, which disrupt the balance between the δ -phase and the γ -phase. This destabilization of the duplex microstructure also depends on the chemical composition of the alloy and may occur quite rapidly in high alloyed grades, such as the super and hyper grades. In this section, we discuss the effect of the chemical elements on the solid phase transformations, as well as the kinetics of the phase transformations.

Phase diagrams are useful to predict the stable or metastable equilibrium phases. However, in the case of duplex stainless steels, the phase diagrams are complex because these alloys are composed of at least five different components. As a result, distinct phases can precipitate during the decomposition of a supersaturated δ -phase or γ -phase.

The solidification path of duplex stainless steels depends on the content of δ -phase stabilizer elements (Cr, Mo, Si, and W) and γ -phase stabilizer elements (Ni, Mn, N, C). Typically, the first phase to solidify is the δ -phase, directly from the liquid ($L \rightarrow \delta$), because of the high content of δ -phase stabilizer elements in duplex stainless steels. As the reaction takes place, the liquid becomes depleted in δ -phase stabilizer elements and the concentration of γ -phase stabilizers increases. Because of this, the phase equilibrium moves towards the $L + \delta + \gamma$ phase field, as the γ -phase crystals form from the melt ($L \rightarrow \gamma$). The progress of the γ -phase formation will lead to the consumption of the liquid phase until the solidification is completed [21, 37]. Both the δ -phase and γ -phase are the only phases that are thermodynamically stable at temperatures above 1000 °C. Upon further cooling, the amount of γ -phase increases because of the diffusion-controlled transformation of δ -phase into γ -phase.

In industry, it is common to employ empirical methods to predict the amounts of δ -phase and γ -phase formed. Among these methods, the most frequently used approach is to consider the Ni and Cr equivalent numbers (Ni_{eq} and Cr_{eq} , respectively), which reflect the effect of γ -phase stabilizing elements (Equation 4) and δ -phase stabilizing elements (Equation 5) [51], according to the expressions:

$$Ni_{eq} = \%Ni + 30 \times \%C + 30 \times \%N + 0.5 \times \%Mn \quad (\text{Eq. 4})$$

$$Cr_{eq} = \%Cr + \%Mo + 1.5 \times \%Si + 0.5 \times \%Nb \quad (\text{Eq. 5})$$

The combination of both equivalent numbers enables the use of another tool, known as the Schaeffler-DeLong diagram. This method was developed to predict the phases of welding microstructures, but it is also applied to estimate the amount of δ -phase and γ -phases formed at high temperatures on cast alloys quenched from the liquid. As described in [51], the first version of this diagram was developed by Schaeffler, in 1948, and modified by DeLong, in 1960, to take into account the effect of N addition on the δ + γ domain. Figure 2 shows the Schaeffler-DeLong diagram [52], where the phases formed by rapid cooling from the liquid are represented over a broad chemical composition range. However, The Schaeffler-DeLong diagram must be seen as a rough prediction of the phases of the microstructure because it does not address kinetics considerations.

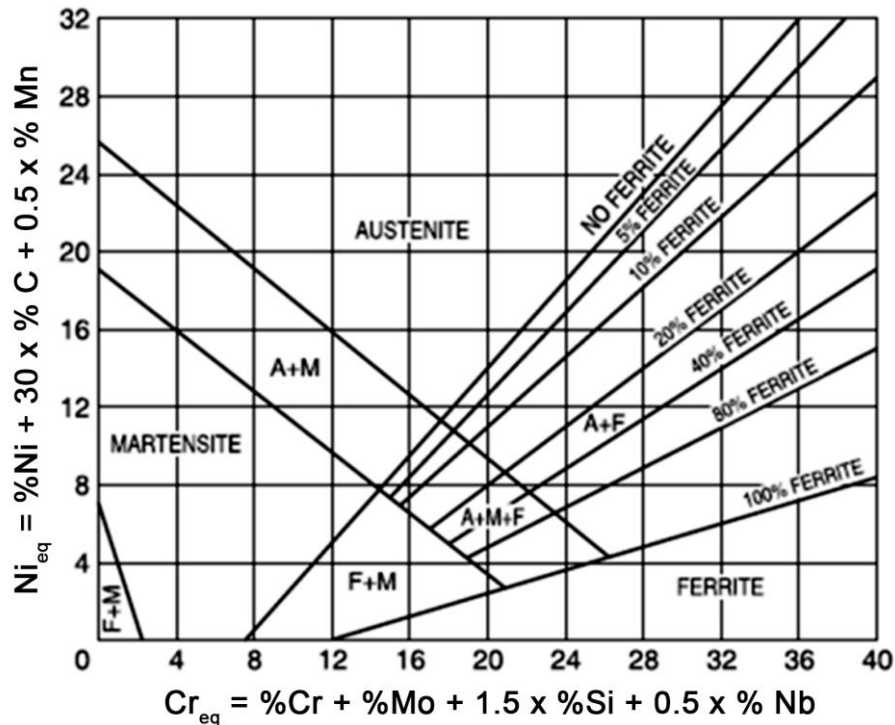


Figure 2 – Schaeffler-DeLong diagram showing the solidified microstructure a function of Ni_{eq} and Cr_{eq} . Modified from [52].

The development of highly alloyed duplex stainless steels led to the production of grades with enhanced corrosion resistance and mechanical properties, such as the super and hyper grades. During the thermal processing or even under service, duplex stainless steels are prone to several phase transformations, at temperatures ranging from 300 °C to 1000 °C, which must be avoided or, at least, should be mitigated [1, 21].

The balanced ferrite/austenite microstructure is thermodynamically unstable at temperatures below 1000 °C, due to the large amount of alloying elements. Therefore, various secondary phases may form, concomitant with the fact that their mechanisms of precipitation are complex and not well understood. Given this, the chemical composition and thermal processing conditions are key parameters that affect the nature and amount of the secondary phases that may form. The following sub-sections will present an overview of the secondary phases, with an emphasis on kinetic studies.

2.2.1 Kinetics of Secondary Phases Formation

As previously described, the tendency to form secondary phases increases proportionally with the alloying content. Additionally, slow cooling rates enhance the risk of the formation of secondary phases. These are undesirable phases with a negative impact on both corrosion resistance and mechanical properties.

To understand the relation between the cooling rate and the solid phase transformations, it is useful to have at the disposal of the continuous-cooling-transformation (CCT) and time-temperature-transformation (TTT) diagrams. These diagrams provide information about the final microstructure obtained at a fixed cooling rate (CCT diagram), and the effect of an isothermal stage at a fixed temperature (TTT curve). In this context and as shown in Figure 3, an increase of alloying content enlarges the temperature range where the secondary phases are stable. Also, for higher alloying contents, the time to form secondary phases is shorter, which means that it is necessary to impose faster cooling rates from the solutionizing heat temperature to avoid the disruption of the duplex structure. Figure 3 also highlights the secondary phases which are possible to form on duplex stainless steels [53].

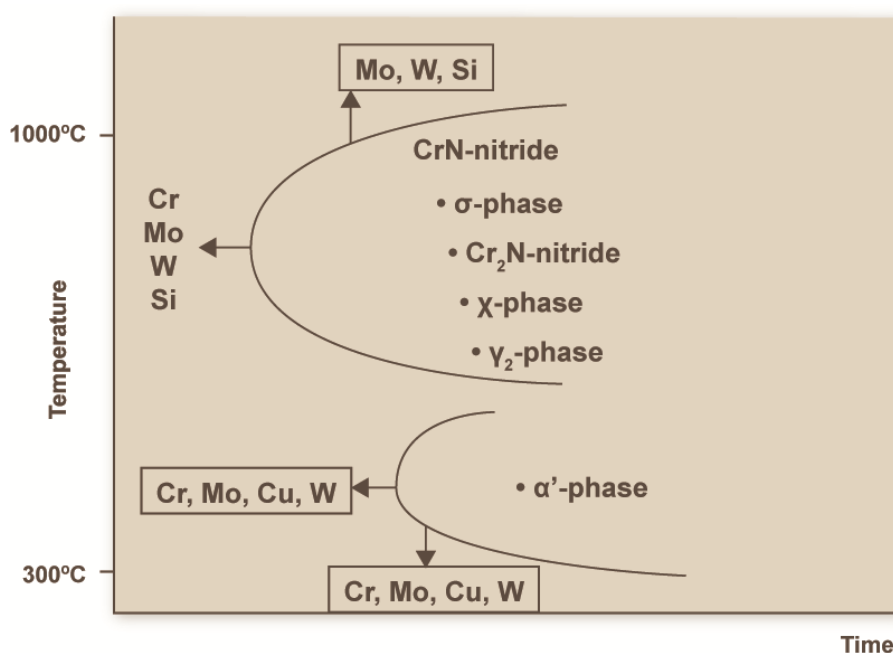


Figure 3 –TTT curves representing the effect of alloying additions on the precipitation kinetics of secondary phases on duplex stainless steels. Adapted from [53].

As previously described, the extension and nature of secondary phase formation are closely linked with the chemical composition of the duplex stainless steels and their thermal process. Regarding the CCT or TTT diagrams, it is worth to mention that these tools can only describe the kinetics of solid phase transformations for specific chemical composition. In other words, any CCT or TTT diagram determined for a lean duplex (for example UNS S32101 and UNS S82441) will fail to describe the kinetics for a super duplex (for instance UNS S32750 and UNS S32760), because, for higher alloyed grades, the kinetics of secondary phases formation is considerably faster. For this reason, a brief review is provided below, with particular emphasis on the kinetic studies of wrought and cast alloys.

Nilsson *et al.* [6] assessed the time-temperature-transformation (TTT) diagram for a 29Cr-6Ni-2Mo-0.38N super DSS (equivalent to UNS S32906) in the extruded condition. Several aging conditions were tested, at temperatures ranging between 700 °C to 1000 °C and times ranging from 1 min to 72 h. The σ -phase was the only secondary phase detected. The authors concluded that the lack of χ -phase due to the low content of Mo, was the leading cause of the retarded precipitation of intermetallic phases.

Escriba *et al.* [12] investigated the effect of aging treatments at 700 °C and 750 °C from 1 h to 8 h, on the formation of secondary phases. The studied alloy was a wrought

22Cr-6Ni-3Mo-0.2N lean DSS (equivalent to UNS S31803). A combined analysis of micrographs obtained by optical microscopy and scanning electron microscopy detected both the χ -phase and σ -phase. This study concluded that the χ -phase occurred before the σ -phase, yet in lower amounts. Thus, longer aging dwelling times supported the disappearance of χ -phase, which transformed into σ -phase.

Akisanya *et al.* [8] studied the effect of aging temperature from 600 °C to 900 °C holding times from 1 min to 240 min, on the microstructure and mechanical properties of a 25Cr-6.7Ni-0.32N-3.0Mo-2.5W super DSS (equivalent to UNS S39274), in the extruded conditions. The microstructural characterization performed by SEM revealed the formation of χ -phase and σ -phases. While the σ -phase preferentially formed at δ/γ and δ/δ interfaces, the χ -phase occurred mainly on δ/δ interfaces. Moreover, the authors concluded that the χ -phase was metastable, disappearing for longer exposure times at the aging temperatures. Additionally, they found that the higher content on W was beneficial to delay the beginning of the formation of secondary phases. Finally, the tensile tests demonstrated that for a fraction of secondary phases less than 7%, the mechanical performance was not affected.

Isern *et al.* [14] carried out a study on two wrought grades, namely the UNS S32205 (22Cr-6Ni-3Mo-0.17N) DSS and the UNS S32507 (25Cr-7Ni-4Mo-0.2N) super DSS, which were aged at 830 °C for periods from 1 min to 9 h. The electron backscattered SEM images showed submicrometer sized phases, such as chromium nitrides and carbides for shorter aging periods. After comparing the two grades, the authors concluded that the UNS S2507 super DSS exhibited higher kinetics of secondary phases formation, due to the significant content of Cr and Mo elements.

Örnek and Engelberg [15] analyzed a wrought UNS S32205 DSS (22Cr-6Ni-3Mo-0.17N), under aging treatment at 750 °C for 5 h. Amongst possible secondary phases formed at the aging temperature, chromium nitrides, χ -phase and σ -phase were detected by EBSD. The authors also used scanning Kelvin probe force microscopy (SKPFM) to characterize the corrosion processes in each phase. They concluded that the σ -phase and chromium nitrides had a cathodic behavior, which means that these phases had a high propensity to be corroded. On the other hand, the χ -phase exhibited an anodic behavior, among the detected secondary phases.

Wan *et al.* [16] studied the kinetics of σ -phase precipitation at the temperature range of 750 °C to 950 °C, in a wrought 15Cr-2Ni-2Al-11Mn DSS, with a reduced content on Ni compensated by the addition of Mn. The authors concluded that the maximum volume fraction of σ -phase occurred for aging at 850 °C. Also, at this temperature, the

precipitation rate was found to be the highest. By increasing the additions of Mo to 0.5 wt% and 1 wt%, the formation rate and volume fraction of σ -phase increased, and the χ -phase was not observed. Finally, the authors concluded that raising the content on σ -phase up to 4%, significantly reduced the pitting corrosion resistance of the studied DSS.

Several studies [17, 54, 55] investigated the secondary phases formation on a lean grade CD3MN (22Cr-5Ni-5.5Mo-0.2N), and super grade CD3MWCuN (25Cr-7Ni-7.5Mo-0.25N) cast DSS. The alloys were aged for 1 min to 30 days at temperatures from 700 °C to 900 °C. The authors compared the formation kinetics of secondary phases between the two grades and concluded that the kinetics was faster for the super grade. In the first study [54], the secondary phases were not characterized because the authors only used optical microscopy to measure the volume fraction of secondary phases. However, in a later study [17], TEM was used to reveal the different phases based on their crystal diffraction patterns. As a result, the authors corrected the previous TTT diagram, with the addition of individual curves for each secondary phase. Finally, in a later work [55], the authors provided CCT diagrams which were constructed based on two different approaches: using experimental data from metallographic sample preparations and theoretical calculations from previously determined TTT curves. Therefore, the authors proved the convergence of the two methods and provided the final CCT diagram to assess the amount of sigma phase formed at different cooling rates.

Yang *et al.* [56] discussed the effect of Ag additions on a cast UNS S2205 DSS (22Cr-6Ni-3Mo-0.17N). This research work provided the first description of the effect of Ag doping on the solid phase transformations at 800 °C. As the main conclusion, there is no evidence of changes in the kinetics of secondary phases caused by Ag additions. Finally, the authors proposed the sequence $\delta \rightarrow \chi + \gamma_2 \rightarrow \chi + \sigma + \gamma_2$ to describe the formation of secondary phases.

2.3 Residual Stresses

The prediction, prevention or delay of failures in components or assemblies has been a devoted topic of research studies, given the considerable impact on the safety of structures and longer life cycle of tools and appliances. The failure of components may occur by many mechanisms, including brittle failure mode, plastic collapse, fatigue, creep, or stress corrosion cracking.

With the use of modern analytical and computational techniques, it is possible to predict, with reasonable accuracy, where and when the failure may occur. Additionally, it is possible to consider the influence of the microstructure [57-60] or defects [61-63] on the developed models to predict the failure mechanisms. Thus, the application of the theories of elasticity and plasticity have been frequently used to understand the effect of the microscopic features on the failure mechanisms of metallic components. Despite the critical effect of the microstructure and defects, residual stresses constitute another factor that contributes to the failure mechanism. However, the residual stresses have received less attention on the prediction of the failure mechanisms. This fact may result from the difficulties of measuring or predicting their evolution under in-service conditions [64]

Residual stresses are those which are maintained within a body when no external forces or temperature gradients are acting upon them [64, 65]. Furthermore, they are self-equilibrating, which means that the resultant force and the resultant moment produced by them must be zero [66]. They are a consequence of the interaction between the following dominant parameters: temperature/time, stress/strain and microstructure (Figure 4). Thus, the variation of any of the parameters will have an impact another. The role of these interactions on the residual stresses of a cast component can be summarized as follows: a non-uniform temperature distribution within the component will create stresses and strains due to differential thermal contraction. Moreover, temperature-dependent phase transformations will lead to heterogeneous microstructural changes due to the variation on the cooling rate associated with the geometry of the component. These phase transformations will lead to local expansions or contractions and will create stresses. In turn, the mechanical work done by internal stresses can generate heat, which alters the temperature distribution. Also, phase transformations may occur by stress induced transformation, which leads to the generation of latent heat and changes in the temperature distribution [67].

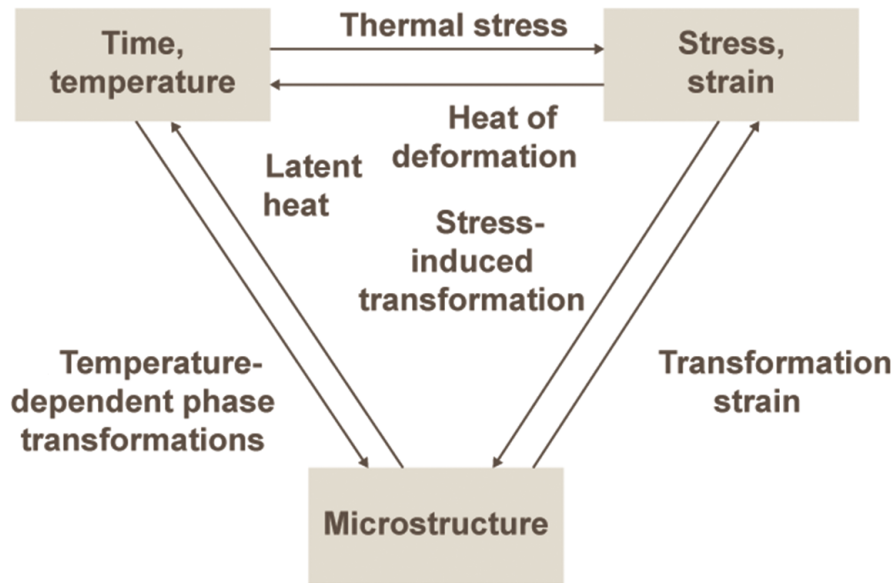


Figure 4 – Schematic diagram showing the interaction between time and temperature, stress and strain, and microstructure on the origin of residual stresses. Adapted from [67].

It is impossible to have a component or structure free from residual stresses because they are inherent to almost all of the manufacturing processes [68]. On the other hand, residual stresses can be developed during the service life due to local strains or temperature gradients in the component. On practical applications, the performance of the components is reduced by the combination of residual stresses and applied stresses. So, the understanding of the development of residual stresses is a topic with a remarkable interest [69].

Although residual stresses are an important issue concerning the prevention of unexpected failures during service, there are applications where residual stresses are introduced to improve the performance of the components. For instance, shot peening, hammer peening or laser peening, introduce compressive stresses that improve the surface properties of components, exposed to fatigue loads or wear mechanisms [65, 70]. Alternatively, surface chemical treatments, such as carburizing and nitriding, also create compressive stresses in the modified layer to enhance the performance of the components [71].

The residual stresses within a body may be categorized by different criteria: by their cause, by their effect on the mechanical behavior and by the length scale over which they self-equilibrate [64, 72, 73]. The length scale criterion is the most adopted, and there are three types of residual stresses:

- Type I is also referred to as macrostresses because they are nearly homogeneous across large regions comparable to the size of the component. If the equilibrium forces are changed, the component or structure will change dimensions.
- Type II is also known as microstresses or intragranular stresses because they occur at the scale of the size of grains. If the equilibrium is locally disturbed, changes in macroscopic dimensions may happen.
- Type III is also classified as microstresses. However, their extension is limited to submicrometer dimensions, over distances comparable to the size of some atoms. Microstresses of type III are caused by line defects, such as dislocations and interfaces or point defects resulting from doping with atoms of different size. If the equilibrium is disturbed, no changes at macroscopic dimensions are observed.

Usually, the sum of residual stresses of type I, II and III determines the total amount of residual stresses acting at a particular region on the material. Furthermore, the occurrence of many misfits at a particular scale will have a cumulative effect, such as those that give rise to residual stresses at a longer scale. For example, the existence of a single edge dislocation adds a half-plane of atoms into a crystal resulting in microstresses (type III). However, if the number of dislocations in a single grain increases, intergranular misfits between neighbor grains may occur, which cause intergranular microstresses (type II). Then, the accumulation of intergranular misfits may impose misfits at a longer scale, that originate macrostresses gradients (type I) [64].

2.3.1 Effects of Residual Stresses

Despite the importance of applied stresses on the performance of engineering components and structures, residual stresses also have a significant impact on fatigue behavior, fracture strength, and corrosion resistance [74]. Moreover, since almost all manufacturing processes introduce residual stresses, it is critical to understand their origin and effect for the design of engineering parts.

The fatigue mechanism is categorized into two regimes, regarding the level of involved stress and the number of cycles required until failure occurs: low cycle fatigue (LCF) and high cycle fatigue (HCF). They are differentiated by the number of cycles to failure using 10,000 cycles as the definition limit [64]. The effect of residual stresses on the failure depends on the applied regime. For instance, the effects of introducing superficial compressive residual stresses are less beneficial in the LCF regime because

the large amplitude of the oscillating plastic strains causes a fast relaxation of the compressive stresses.

For the HCF regimes, residual compressive stresses may enhance the fatigue strength as much as 50%, compared to the base material without any surface treatment [74]. The fatigue performance of a UNS S32205 wrought DSS in the HFC regime was improved by laser shock processing (LSP). The LSP induces residual compressive stresses in the surface that eliminate the effect of residual tensile stresses resulting from the manufacturing process. The authors reported an enhancement of fatigue limit up to 79% after LSP [75].

Stress corrosion cracking (SCC) is another critical issue for the engineering design of components, which is also affected by residual stresses. Therefore, the surface residual stresses introduced in some machining operations, such as grinding, milling or rolling are the leading cause for the initiation of pits (cracks precursors) and the formation of micro-cracks and their propagation until cracking [76-78]. In the literature, it is reported that the grinding operations degrade the SCC resistance of the UNS S22304 DSS because induce tensile residual stresses that lead to micro-cracks formation [79]. Thus, the residual compressive stresses, which can be induced by appropriate surface modification, are desirable to enhance the SCC resistance of the components.

Residual stresses can also affect the dimensional stability of the engineering components. Actually, residual stresses can affect the shape and dimensions of components, leading to geometrical distortions and, consequently, additional operations to correct them. Casting, machining, welding, or heat treatments are operations in which residual stresses may cause severe deformations of the components [74, 80-83]. This problem is particularly difficult to solve in the casting process because the components exhibit complex shapes and thicknesses from thin to thick cross-sections that solidify at different times. Therefore, temperature gradients are created. Additionally, the mechanical constraints imposed by the mold to the free contraction and the stress-induced by solid phase transformations must be addressed when assessing the residual stresses state [19, 20].

2.4 Modeling the Distribution of Residual Stresses in Cast Components

The casting process has broad applicability, allowing the production of structural components on different materials with a wide variety of dimensions and shapes. Despite

this versatility, the casting design deals with several physical phenomena, such as fluid flow, heat transfer, thermal residual stresses, formation of defects and microstructural evolution. The complex interaction of these physical phenomena may affect the conformity of the end cast components and, consequently, the productivity of the casting process. So, an essential activity of a design engineer is to control the most critical physical phenomena to guarantee that the final cast components meet the conformity requirements. In the context of design and project of cast components, modeling enables the design engineer to build virtual cast parts and to study the effect of relevant physical phenomena, and, consequently, to establish the most appropriate conditions for casting. In other words, modeling is an indispensable tool for enhancing the quality of the products and processes, promoting the cost and lead-time reduction and eliminate trial-and-error approaches [84].

Modeling the residual stresses from casting involves the simulation of temperature distribution, phase transformations, and mechanical constraints acting on the cast component.

2.4.1 Generation of Residual Stresses in Cast Components

The residual stresses in cast parts may arise during different processing steps, namely solidification and cooling, mold removal, machining, and heat treatment. As the scope of the present research work focuses on simulating the thermal residual stresses on cast parts, it is crucial to understand their origin. According to Chandra and Ahmed [85], the principal causes of residual stresses from casting lie in mechanical constraints of the mold, temperature gradients and volumetric changes. These causes are briefly described as follows:

- Mechanical constraints of the mold. The mold material presents a negligible contraction during cooling, and it is more rigid than the hot metal. The rigidity of the mold inhibits the shrinkage of the cast part, causing stresses.
- Temperature gradients in the cast part, cause differential shrinkage. Significant stresses are generated when adjacent regions present different cooling rates.
- Volumetric changes associated with solid-state phase transformations are a result of different crystal structures and atomic packing between the parent phase and the product phases. Under these circumstances, tensile and/or compressive stresses might appear.

2.4.2 Modelling of Residual Stresses

Residual stresses in the cast components are usually modeled through two sequential steps: a non-linear thermal analysis and an elastic-plastic stress/displacement analysis. This strategy is labeled as sequentially coupled thermal-mechanical analysis.

The results of the thermal analysis are used as input for the stress/displacement analysis. The thermal analysis is first performed at many increments of time from the pouring to the room temperature. These temperatures establish the initial and final conditions of the numerical model, respectively. The initial condition can be either defined from the mold-filling analysis or assumed to be constant and equal to the pouring temperature, through the cast part model [85-87].

Regarding the boundary conditions necessary for the thermal analysis, several types should be considered and carefully defined. For instance, the interface could be exothermic or insulating. Additionally, there are three possible mechanisms of heat transfer between the cast part and the mold: convection, radiation, and conduction. At this point, it is critical to highlight the importance of the interfacial heat transfer coefficient (IHTC). The selection of the IHTC has a direct effect on the results of thermal analysis, and consequently, on the results of the mechanical analysis. The IHTC characterizes the thermal fluxes from the hot metal to the mold. This parameter is extremely complex to set because it depends on several parameters: the gap between the metal and the mold, surface roughness and contact pressure, temperature-dependent properties of the cast part and mold materials and pouring temperature [88]. In essence, the IHTC is different at each step and changes as the cooling of the cast part proceeds.

The casting process is time-dependent, which means that the heat-transfer equation must be solved for each time increment, which is expressed as:

$$\rho C_p \frac{\partial T}{\partial t} = k \left[\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right] + \dot{Q} \quad (\text{Eq.6})$$

where ρ is the density of the alloy, C_p is the specific heat, T is the temperature at an arbitrary location in the system at time t , k is the thermal conductivity of the material and $\dot{Q}$ is the rate of heat generated per unit volume [85, 87]. It should be emphasized that the accuracy of the thermal model depends significantly on the material properties data available.

The transient elastic-plastic stress/displacement analysis (also referred to mechanical analysis) provides the stress and displacement for each element point of the model and for each time step from the pouring to room temperature. Briefly, the underlying theory of mechanical analysis is described by:

$$\varepsilon = \varepsilon^{el} + \varepsilon^{th} + \varepsilon^p + \varepsilon^{cr} + \varepsilon^v + \varepsilon^{tr} \quad (\text{Eq. 7})$$

where ε is the total strain and ε^{el} , ε^{th} , ε^p , ε^{cr} , ε^v and ε^{tr} represent the components of strain: elastic, thermal, plastic, creep, volumetric change, and transformation plasticity, respectively [85]. However, only the first three components of the strain are well documented in the literature and, usually, the commercial solvers could not handle the other components [87, 89-91]. Therefore, it is frequent to use an elastic-plastic stress thermal model. Finally, we should consider the transmitted forces between the cast part and the mold. To address this issue, specific contact conditions are applied: conventional elastic-plastic contact, rigid mold contact, and virtual mold contact [87].

When performing the sequentially coupled thermal-mechanical analysis, the temperature distribution is first calculated without considering the thermal contraction that occurs during the cooling of the metal. As expected, in the casting process, the metal shrinks away from the mold cavity during cooling, which creates a gap at the metal-mold interface, while, in other regions, the metal permanently contacts with the mold. The existence of gaps and contact points locally affects the temperature distribution [85].

One way to overcome this limitation is to apply a fully coupled thermal-mechanical analysis, solving the thermal and mechanical equations simultaneously. Thus, the temperature, stress, and displacement are found at each time step, which enables the determination of the gap thickness between the metal and the mold. As a result, the rate of heat transfer (q) between the metal and the mold is calculated at each time step increment, as follows:

$$q = \frac{k A (T_{metal} - T_{mold})}{\delta} \quad (\text{Eq. 8})$$

where, k is the thermal conductivity at the interface metal-mold, A is the area of the contact surface, $T_{metal} - T_{mold}$ is the temperature drop across the interface and δ is the thickness of the gap between the metal and the mold. The ratio k/δ corresponds to the heat transfer coefficient at the interface (IHTC) [85].

Both sequentially coupled and fully coupled thermal-mechanical analyzes have been successfully used to predict residual stresses in sand casting. Therefore, an overview of the strategies currently used in residual stresses modeling is given.

Farhangi *et al.* [92] evaluated the effect of several process parameters, including melting and pouring superheat temperatures, chemical composition and geometry on the magnitude of residual stresses on Ni-based superalloys cast components. The authors found a positive correlation between the level of residual stresses and the superheat temperature, independently of the geometry of the cast part.

Lee *et al.* [93] developed a numerical model to calculate the thermal deformation of a large marine propeller, made on a bronze cast alloy, and produced in a sand casting process. The software ProCAST™ was used to predict the effect of the shakeout temperature on the deformation, through a coupled thermo-elastic-plastic model. The authors proposed a longer shakeout time made in a sequential manner to reduce the deformation of the cast propeller. The strategy consisted of removing the lower sand mold some hours after removing the upper sand mold.

Gustafsson *et al.* [86] studied the thermal residual stresses formed during the solidification and cooling of a grey cast iron specimen (a three-bar frame with two thin outer bars and a thick inner bar). The numerical model was built in Abaqus™, using a sequentially coupled thermal-mechanical analysis. Although the model did not take into account the gap formation, the results showed a good agreement with experimental stress measurements.

Johnson *et al.* [94] developed a fully coupled thermal-mechanical model using MAGMASOFT™, to simulate the solidification and cooling of ductile iron cast parts. The authors reported slight differences between the experimental stress evaluation, through neutron diffraction and the numerical results. To discuss the differences in numerical and experimental results, the authors highlighted that the model did not take into account the solid-phase transformations, in particular, the formation of iron carbides, which is the phase with higher elastic modulus and would affect the overall results.

Afazov *et al.* [95] developed two models to simulate thermal residual stresses in a Ni-superalloy produced by investment casting. The models were developed in two different solvers, namely Abaqus™ and ProCAST™. In general, both solvers predicted the same location and magnitude of residual stresses peak, yet differences in the residual stresses distribution were observed. Additionally, the authors concluded that the pouring step did not influence the final results, and the pouring temperature could be used as an initial condition for the thermo-mechanical model.

Afazov *et al.* [96] developed a sequentially coupled thermo-mechanical model in Abaqus™ to predict the thermal residual stresses of a high-pressure turbine blade obtained through directional solidification Bridgman process. The authors concluded that the magnitude of residual stresses increased with the withdrawn rate.

Motoyama *et al.* [97] built a thermal-elastic-plastic model to calculate the residual stresses on grey cast iron parts, using the sequentially coupled thermo-mechanical analysis in Abaqus™. The authors concluded that the residual stresses were overestimated when compared to the experimental measurements. According to them, the application of the mechanical melting temperature improved the accuracy of the numerical model. The mechanical melting temperature (coincident with A₁ transformation temperature) permitted to relax the residual stresses created above this temperature.

Motoyama *et al.* [98] discussed the effect of the element type applied to build the finite element mesh, on the results of a sequentially coupled thermo-mechanical analysis, using Abaqus™. The authors showed that the second-order elements were more appropriate to model the deformation of grey cast iron parts, so the agreement between the numerical and experimental results was improved. The authors also showed that an increasing of the shakeout temperature from 80 °C to 600 °C increased the residual stresses of the cast parts.

Baghani *et al.* [87] investigated the effect of the stiffness of the mold on calculated residual stresses of steel parts produced by the sand casting process. For this purpose, a fully coupled thermo-mechanical model was implemented in Abaqus™, to simulate the residual stresses distribution. The authors concluded that the rigid mold condition originated excessive residual stresses, showing poor agreement with the results of the hole-drilling method. Alternatively, employing the elastic-plastic condition for the sand mold allowed the transfer of the forces from the cast part to the mold and the shrinkage of the cast part, which improved the accuracy of the numerical results.

Kang *et al.* [99] proposed a sequential thermo-phase transformation-mechanical model to predict the deformations on heavy (16.5 tons) hydro turbine blade castings made of martensitic stainless steel. The numerical model was implemented in two software: the thermal analysis was performed on FT-STAR™, and the mechanical analysis was executed in Abaqus™. The authors discussed the effect of the transformation from austenite to martensite on the deformation of the cast hydro turbine blades and concluded that the thermo-phase transformation–mechanical model was more accurate than the thermo-mechanical model in predicting the stresses and displacement evolution with time.

Palumbo *et al.* [90] simulated the evolution of residual stresses during the cooling of DSS castings. To accomplish this purpose, the authors implemented a fully coupled thermo-mechanical model in Abaqus™, and the numerical results were compared with the displacement measurements. The authors also compared the results from solving the elasto-visco-plastic equations with those from the elasto-plastic equations and observed that incorporating the viscous strain would lead to more accurate predictions. Additionally, the authors concluded that excluding the sand mold from the mechanical model did not affect the accuracy of results, in addition to reduce the computational cost.

Keste *et al.* [100] simulated the formation of residual stresses in a shifter obtained by precision casting, using ANSYS™. The model explored the sequentially coupled thermo-mechanical analysis to calculate the residual stresses and, consequently, the shape of the component was modified to reduce the residual stresses while keeping its functionality.

In summary, an unique solution to model the residual stresses in cast parts does not exist. However, all the authors agree on the point that the prediction of the temperature distribution is a key factor to obtain a robust and accurate stress/displacement model for residual stresses prediction in the casting process. Although the majority of the numerical models agree with the experimental measurements, the proposed approaches differ in the analysis of the interactions with the sand mold. Some of the proposed models incorporate the elastic-plastic properties of the sand mold to improve the accuracy of the results. On the other hand, other models neglect the sand mold in the mechanical analysis. In addition to the thermal-mechanical models, the thermo-phase transformation-mechanical models are also proposed to improve the accuracy of the numerical solutions.

2.5 Measurement of Residual Stresses

There are several methods to measure the residual stresses, which are commonly classified as non-destructive, semi-destructive, and destructive [101]. They may also be classified in stress relaxation-based or diffraction-based methods [72]. The stress relaxation-based methods rely on the measurement of deformations due to the release of stresses upon removal of material from the specimen. On the other hand, the diffraction-based methods rely on the measurement of the interplanar spacing of the microstructure, the speed of sound or the magnetic domain on the material [72, 73, 101].

The various techniques for measuring residual stresses are summarized in Table 1, which provides the main differences in terms of penetration depth and spatial resolution.

Table 1 – Summary of the methods for residual stresses measurements [72, 102].

	Method	Residual stresses type	Penetration depth	Spatial resolution	Principle	Comments
Destructive methods	Hole drilling	Type I	<hole diameter	50 µm depth ~1 mm laterally	Measures in plane stresses from distortion caused by stress relaxation	The procedure is regulated by the ASTM E837 standard [103]
	Curvature	Type I	Few mm	1/20 of thickness No lateral resolution	Measures in plane stresses by changes in curvature of strip	Accuracy limited by minimum measurable curvature
	Contour	Type I	Full plane of interest	Dependent on measurement technique and FEM mesh used	Bueckner's superposition principle	Only suitable for measuring stresses normal to the plane of interest
Non-destructive methods	X-ray diffraction	Type I, II and III	< 50 µm (Al) < 5 µm (Ti)	20 µm depth 1 mm laterally	Measures the interplanar spacing	Requires layer removal for depth sensitivity
	Neutron diffraction	Type I, II and III	100 mm (Al) 4 mm (Ti)	500 µm	Atomic strain gauge	Availability, low acquisition rate and costly
	Ultrasonics	Type I, II and III	< 10 cm	5 mm	Stress-related changes in elastic wave velocity	Microstructure sensitive

The contour method will be detailed in the next subsections because it was the method used to measure the residual stresses of the cast specimens produced in this study.

2.5.1 Contour Method

In the contour method, the part is cut into two halves using an electric discharge machine, causing the relaxation of the residual stresses normal to the cutting plane. The height profile of each newly created surface is measured to determine the original residual stresses. In this sense, any deviation from planarity of the cut surface is caused by the elastic relaxation of the residual stresses [104, 105]. So, the output of the contour method is a two-dimensional map of residual stresses normal to the cutting plane.

The contour method was developed by Prime [104] to solve problems for other methods. For instance, the access to diffraction facilities is limited and costly [106]. Another example is the curvature method which exhibits low spatial resolution and technical complexity [104]. The main disadvantage of the contour method is that only the normal component of residual stresses is determined. Nevertheless, equipment required for this method is readily available in many machine shops, making the contour method more affordable.

The contour method is based on the Bueckner's superposition principle. This principle is illustrated in Figure 5, where a specimen (see A) contains the residual stresses. After cutting, the specimen is divided into two halves (see B). Each half will deform as the residual stresses are released by the cut. At this point, the deformation of both surfaces is measured, and displacement is applied to force the deformed shape back to a planar shape (see C), in a finite element model. Therefore, superimposing the relax stress state in B with the change in stress in C will give the residual stresses acting in the specimen before cutting [64, 107, 108].

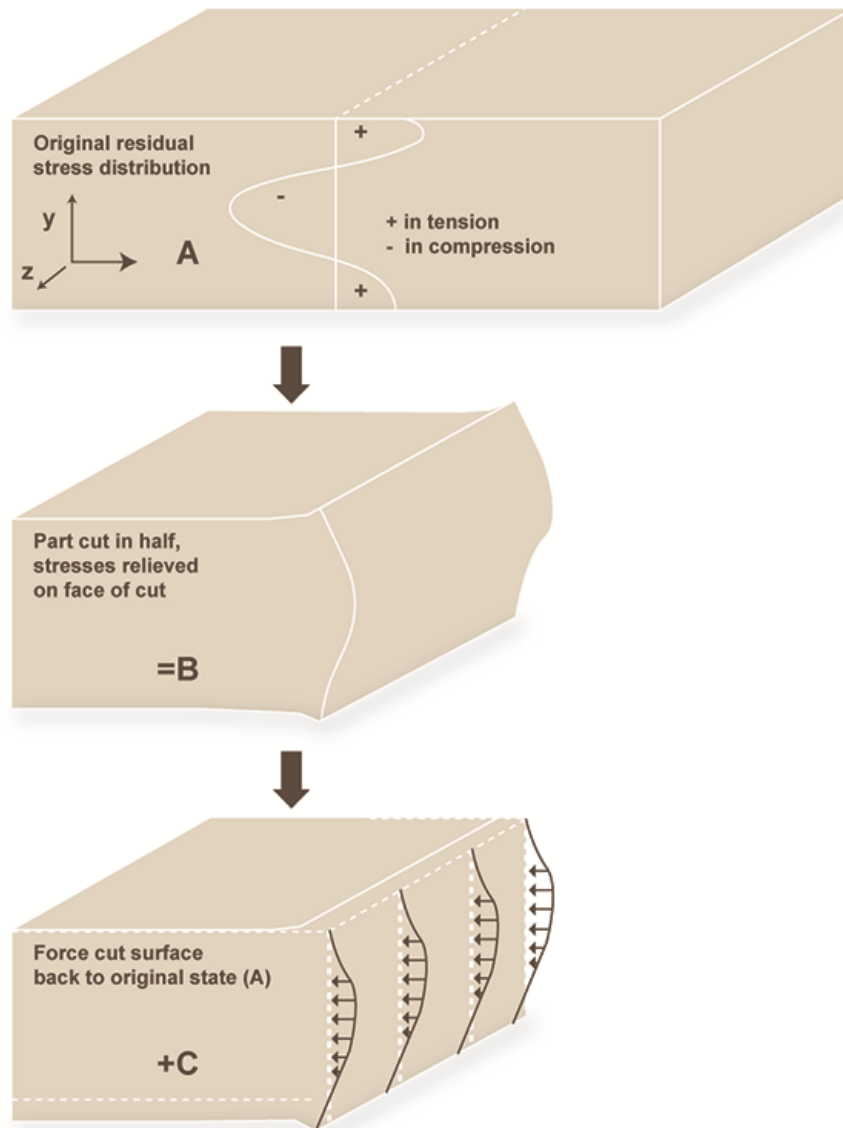


Figure 5 – Scheme of the Bueckner's superposition principle. Adapted from [109, 110].

The implementation of the contour method relies on the proper application of a few assumptions and approximations [105], that allow the determination of the residual stresses, in particular:

- the superposition principle assumes that the material behaves elastically during the relaxation of the residual stresses; this assumption is common to other relaxation methods, such as hole drilling or curvature techniques;
- in a finite element solver, the deformed cut surface represented in C (see Figure 5) is modeled as a flat surface and a displacement boundary condition to force the flat

surface into the deformed shape is applied to calculate the stresses; this modeling strategy is more straightforward;

- averaging the measurements of the two cut surfaces removes any anti-symmetric cutting errors that can be originated from the wandering effect and movement of the specimen during cutting;
- averaging the contours of the two cut halves requires that the stiffness is the same on the two sides and this condition is only observed in homogenous materials and when a symmetric part is cut through a symmetry plane.

2.5.2 Practical Procedure for Contour Method

The contour method is considered to be accurate and reliable, proving repeatable results [111, 112], even compared to other methods, such as neutron and X-ray diffraction [110, 113, 114]. Although the contour method is quite simple in principle, some aspects must be considered to ensure the reliability of the measurements. Making the cut is probably the most critical experimental aspect because it may introduce stresses and deformations, which would affect the results. To avoid these issues, the recommended cutting method is by wire electro discharge machining (WEDM) [104, 109]. The cut surface quality is another factor that affects the accuracy of the contour method. Therefore, one should select the proper wire size to reduce the anti-symmetric errors. The smallest wire diameters are recommended, although undesirable wire breakage may happen, and the cutting time will increase [105].

Another important aspect that affects the accuracy of the results is the configuration selected that fixes and constraints the movement of the part during cutting. Any movement would affect the relaxation of the residual stresses. Thus, the part must be clamped on both sides of the cutting plane. In general, more clamping constraints close to the cut surface will improve the accuracy of the results [115].

After the WEDM process, the height profile of both cut surfaces must be measured. It is worth to mention that the spatial resolution of the contour method is affected by the resolution of the metrology technique applied. Moreover, the process needs to be reliable and accurate in terms of both position and height measurements. Typically, a coordinate measuring machine (CMM) is used. Alternatively, the optical techniques, such as laser triangulating, provide adequate accuracy, however the higher amount of data will increase the computational time [105, 116].

The contour data processing is divided into several steps. First, the data from the two cut surfaces should be aligned to the same coordinate frame, appearing as mirror images. Thus,

the measurement points must be coincident on the two surfaces. Secondly, data from the two surfaces should be averaged, using the matching points defined on the first step. Up to this point the surface measurement data will contain some undesirable noise that results from the measurement error and roughness of the cut surface. This noise will significantly affect the resultant stresses. Therefore, it must be removed from the data. A method to eliminate the noise consists of fitting the data to a smooth surface, using bivariate splines [105, 116, 117]. After averaging and removing the noise, the final displacements are imported to a finite element solver as displacement boundary conditions. The final results of the contour method are the resulting stresses on the plane of the cut in the normal direction, which correspond to the residual stresses present in the material before cutting [105].

Chapter 3 Materials and Methods

3.1 Materials

In this research work, the material studied is a 25Cr-7Ni-Mo-N super DSS (CD3MWCuN grade, according to the ASTM A 890 [23]) produced by sand casting. The alloy was prepared at FERESPE facilities by induction melting, and it was poured into furan-bonded sand molds. Three batches of 25Cr-7Ni-Mo-N super DSS were prepared to produce the necessary samples for the investigation of phase transformations and analysis of residual stresses. The pouring temperature varied between 1620 °C to 1640 °C for the three casting experiments. Table 2 shows the nominal chemical composition of the alloy, determined by optical emission spectroscopy, using a SPECTROLAB™ SPECTROMAXx.

Table 2 – Nominal chemical composition of the 25Cr-7Ni-Mo-N super DSS (wt %).

C	Mn	Si	Cr	Ni	Mo	Cu	W	N
0.015	0.5	0.5	25.0	7.5	3.5	0.75	0.75	0.25

3.2 Specimens Preparation

The selection of the appropriate specimen geometry is of significant concern to carry out the microstructural and residual stress studies. For this reason, we have chosen the C-ring geometry, which is shown in Figure 6. Because of its unique shape, the cooling rates differ throughout the geometry, causing a non-uniform distribution of phases and thermal residual stresses, thus simulating the real casting conditions of a complex component with differential cross-section. To account for the effect of the wall thickness on the distribution of phases and residual stresses, we have designed two C-rings: one with a prong thickness of 8 mm

(C-ring-8) and another with a prong thickness of 12 mm (C-ring-12). The dimensions of the two C-rings are given in Figure 6.

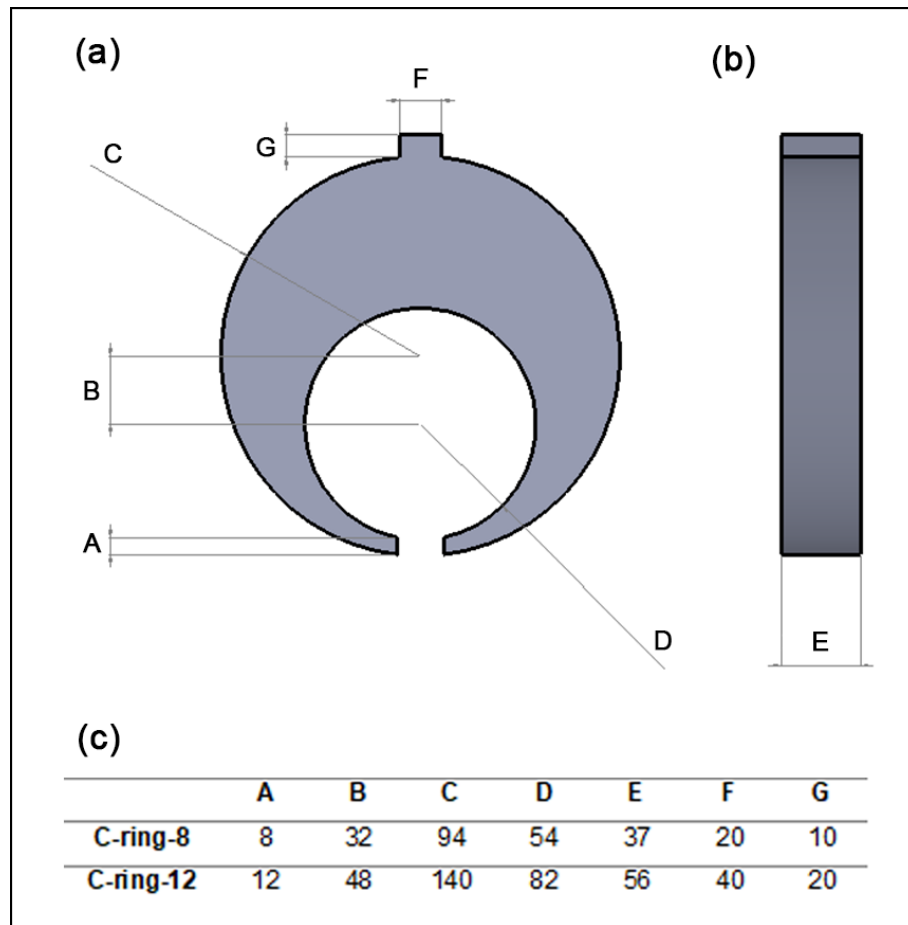


Figure 6 – Front (a) and side view (b) of the C-ring specimen. The dimensions (c) are given in millimeters.

3.2.1 Temperature Acquisition During the Casting Experiments

The temperature was measured during the solidification and cooling of the C-rings using four R-type (PtRh – 13%Pt) thermocouples which are appropriate for the working temperature range of 0 °C to 1600 °C. The thermocouples were placed at two positions inside the mold cavity (corresponding to the thick and thin cross-sections of the C-ring specimens). Four holes were drilled on the sand mold at the positions where the temperature had to be measured. Figure 7 shows the drag and cope molds with the thermocouples installed. The positions are marked by red circles (see Figure 7b).

The temperature acquisition was carried out during the casting of two batches of 25Cr-7Ni-Mo-N super DSS. Once the liquid metal was poured into the molds, the acquisition temperature data logger was turned on to record the temperature with a frequency of 1.1 Hz

for 12000 s. After the solidification and cooling of the metal, the shakeout of the sand molds was performed on a vibratory system, and the thermocouples were removed.

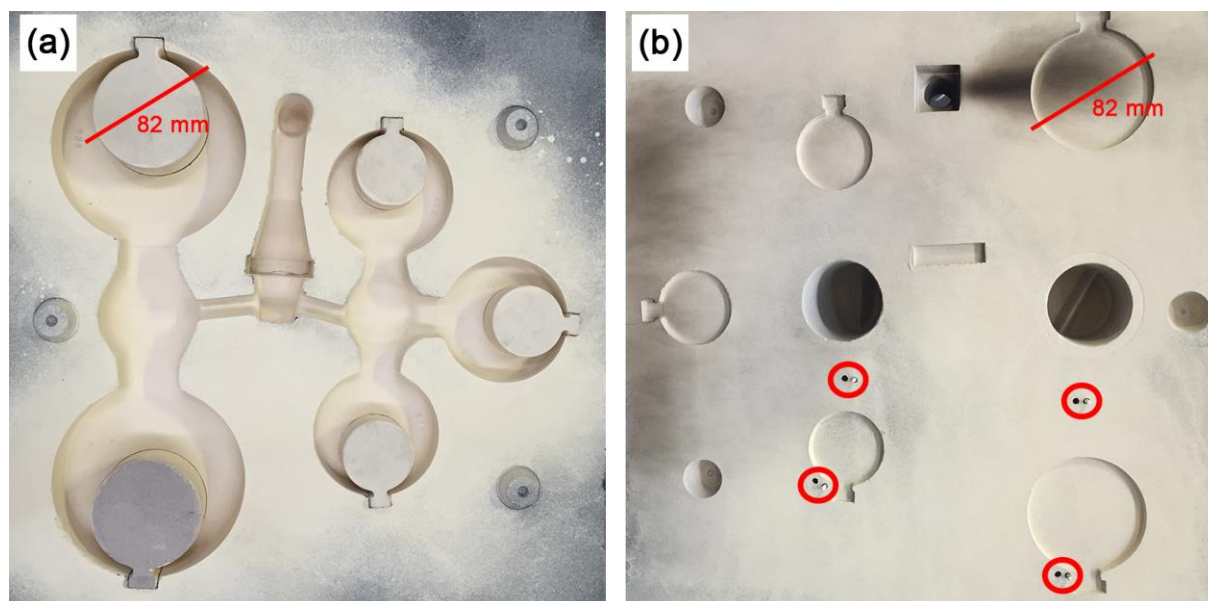


Figure 7 – Furan-bonded sand mold for casting the C-ring specimens; a) drag mold with cores placed to create the inner circle of the C-ring; b) cope mold where the tips of the R-type thermocouples are visible and marked by red circles; the thermocouples were positioned 10 mm inside the mold cavity.

3.3 Solid-Phase Transformations

3.3.1 Solution Heat Treatment

The solution heat treatment is a required step to achieve a γ -phase/ δ -phase ratio of 50:50 and to dissolve the secondary phases that may form during the casting of DSS. Consequently, the C-rings were solutionized, at FERESPE facilities, using a chamber furnace at 1120 °C for 3 h followed by water quenching.

3.3.2 Aging Treatments

To study the formation of secondary phases, samples from the solutionized condition were cut and subsequently were isothermally aged at temperatures ranging from 700 °C to 1000 °C, for aging times varying from 1 min to 72 h. For aging times between 1 and 8 min and to achieve greater accuracy, a furnace with low thermal inertia and very small cylinder samples (2 mm diameter and 12 mm length) was used. For aging treatments longer than 16 min, samples with dimensions of 15 x 15 x 10 mm³ were isothermally aged in a chamber furnace.

3.4 Microstructural Characterization

The C-rings were divided into six regions, labelled from A (thin cross-section) to F (thick cross-section), as shown in Figure 8. To study the as-cast and solutionized microstructures, samples were taken from those regions.

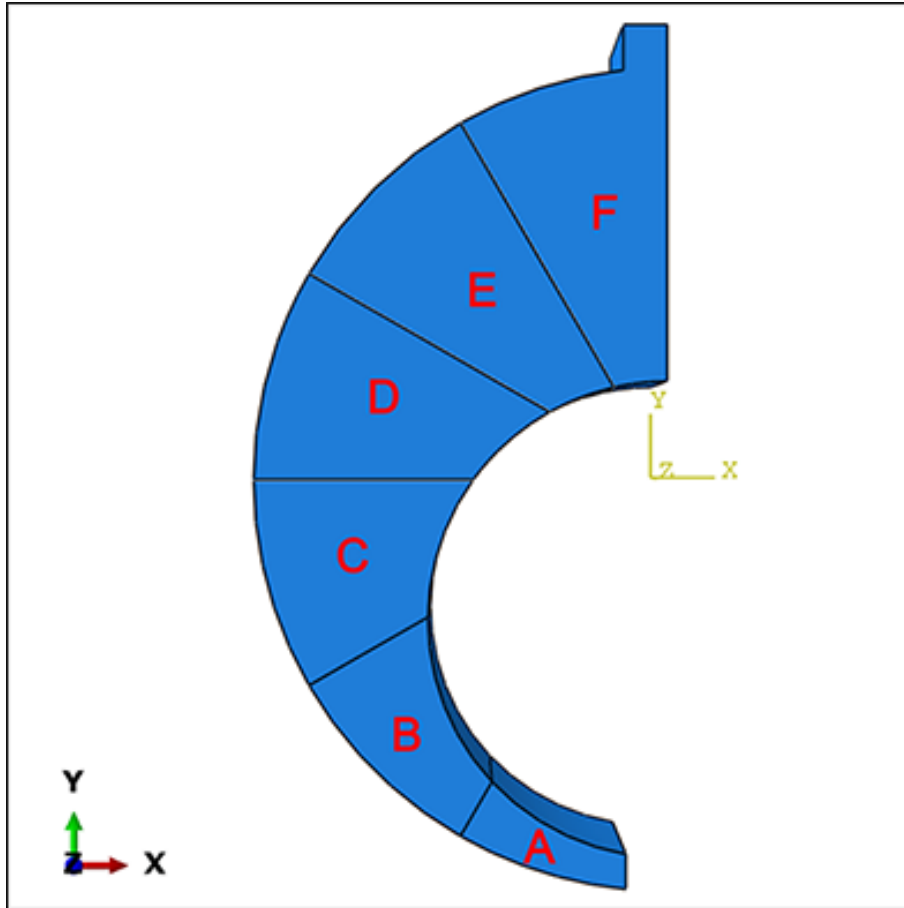


Figure 8 – C-ring 3D model with six regions for microstructural characterization.

The metallographic samples were prepared using standard techniques of cutting, grinding and polishing, using 0.6 μm diamond paste during the final stage. Samples for optical microscopy (OM) analysis were etched electrolytically in a solution of 20% NaOH (2 V, 1.5 A, and 45 s) to reveal the various phases in the microstructure, using a LEICATM DM4000 M.

To study the formation of secondary phases, the aged samples were investigated by scanning electron microscopy (SEM), using a FEITM Quanta 400FEG ESEM in backscattered electron (BSE) imaging mode. Energy dispersive X-ray spectroscopy (EDS) coupled to the SEM was used to analyze the chemical composition of the phases formed during the aging treatments, using the ZAF correction method.

A detailed characterization of the different phases was performed in a JEOL™ 2100 transmission electron microscope (TEM) operated at 200 keV, using thin foils extracted from specific regions of the SEM samples and prepared in a dual-beam focused ion beam (FIB) FEI™ Helios G2 NanoLab 450S.

3.4.1 Quantification of Phases

The volume percent of the phases present on the microstructure was calculated by image segmentation, using ImageJ, an open-source image analysis software. Both optical and SEM/BSE micrographs were segmented using a thresholding-based histogram algorithm to separate objects (phases) from the background (matrix). Among possible approaches for image segmentation, the brightness histogram was used to assign each pixel to a group having the same brightness level, corresponding to a particular phase. In Figure 9, an example of this segmentation process is shown, where an optical micrograph was subjected to a thresholding-based histogram algorithm to separate both the grains of γ -phase (brighter phase) and the precipitates (darker phases) from the background. The thresholding algorithm converts the optical grey image into binary images where black areas correspond to the group of pixels having the highest brightness level, and white areas correspond to the pixels with the lowest brightness level. The δ -phase volume percent is the difference between 100% and the combined sum of γ -phase and precipitates.

In each sample, the volume percent of the phases was found by analyzing 30 optical images with a magnification of 200X. To study the formation of secondary phases, 10 SEM/BSE images with a magnification of 4000X per sample were also analyzed.



Figure 9 – Segmentation of optical micrographs using a thresholding-based histogram algorithm; a) Optical micrograph showing brighter γ -phase, middle-grey δ -phase and dark precipitates of secondary phases; b) binary image where black areas correspond to γ -phase; c) binary image where black areas correspond to precipitates of secondary phases.

3.4.2 Modelling of phase transformations

In this work, we used JMatProTM v.11.2 to simulate the equilibrium phase diagram of the super DSS using the Stainless Steel module.

The thermodynamic software packages, such as JMatProTM or Thermo-CalcTM, are specialized tools designed to calculate the thermodynamic properties of multicomponent systems, just as duplex stainless steels. These software uses the CALPHAD approach to calculate the equilibrium phases diagram and may be used to predict the solution temperature that permits to achieve the δ -phase/ γ -phase ratio of 1:1. Also, these software packages may be used for prescreening new chemical compositions and predicting the transformation temperatures, as well as to understand the effect of the alloying elements on the phases formed.

3.5 Modelling of Residual Stresses

With the objective of analyzing the effect of the processing parameters on the final residual stresses of super DSS cast specimens, the software AbaqusTM/CAE v. 6.13 was used to develop a numerical model to predict the residual stresses by finite element method (FEM). This software allows us to model the sand cast process (through pre-processing operation), to solve the numerical model equations (using processing operation) and to analyze the results (by means of post-processing operation).

In this research work, we used a sequentially coupled thermal-mechanical analysis procedure. The first task was the creation of the thermal model to predict the temperature distribution in the sand cast part, and the second one was the development of the model to simulate the stress/strain state of the cast part during the cooling.

3.5.1 Thermal Model for Casting

In order to obtain the numerical model for the temperature distribution in the sand cast part, first, we 1) constructed the FEM model and the mesh of the cast part and the sand mold, 2) defined the thermophysical material properties varying along with temperature, 3) set the cooling conditions before shakeout and 4) after shakeout. The shakeout is an important factor to consider in the modelling because at this step (extraction of the metallic specimen from the sand mold) there is a change in the heat transfer mechanism.

The C-ring and sand mold models are shown in Figure 10. The symmetry condition was used because this simplification represents considerable computational time savings. Additionally, Figure 10 shows the mesh built with 4-node linear tetrahedron elements (DC3D4).

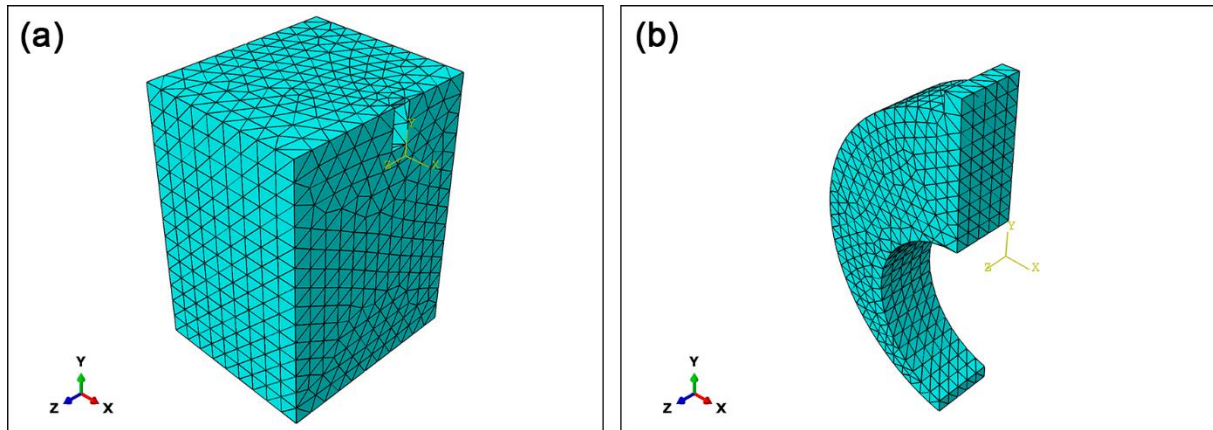


Figure 10 – FEM model and mesh of the a) half of the mold and b) half of the C-ring specimen.

With respect to the thermophysical material properties, which are temperature-dependent, we have included the thermal conductivity, density and specific heat of the super DSS and the furan-bonded sand. The latent heat of the super DSS was also included. The properties of the super DSS were obtained from JMatPro™, using Stainless Steel module. As explained in section 3.4.2, this software calculates the equilibrium phase diagrams. Then, JMatPro™ uses the individual properties of each phase to predict the properties of the bulk alloy. Firstly, the distribution of phases from liquid to room temperature were calculated, using the “temperature step” function. Having the thermodynamic results, the thermal conductivity, density, and specific heat were accessed in the “physical properties” option. The properties are shown in Figure 11. The latent heat (150000 J/kg), liquidus temperature (1185 °C), and solidus temperature (1445 °C) for the super DSS were also obtained from JMatPro™ and included in the model. Finally, the properties of the furan-bonded sand were obtained elsewhere [86] (Figure 12).

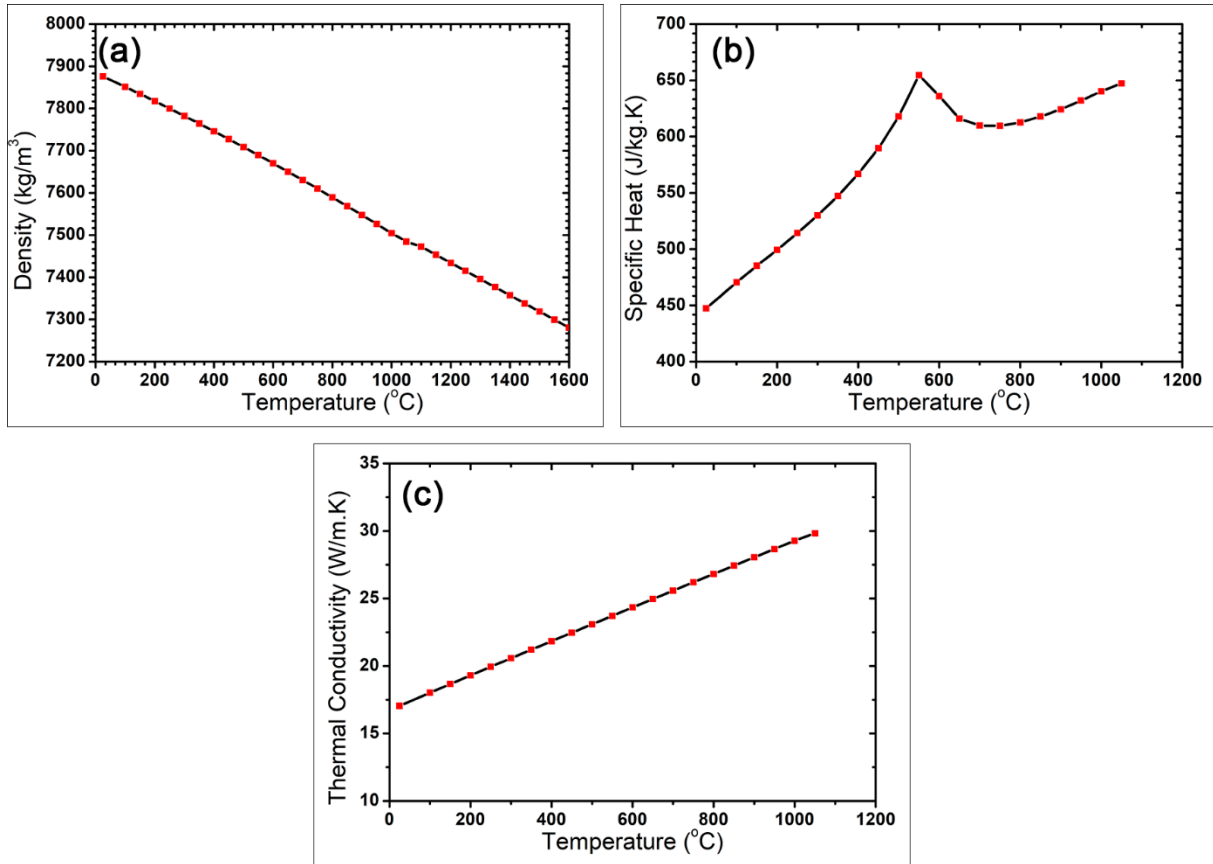


Figure 11 – Thermophysical properties of the 25Cr-7Ni-Mo-N super DSS as a function of the temperature: a) density; b) specific heat; c) thermal conductivity.

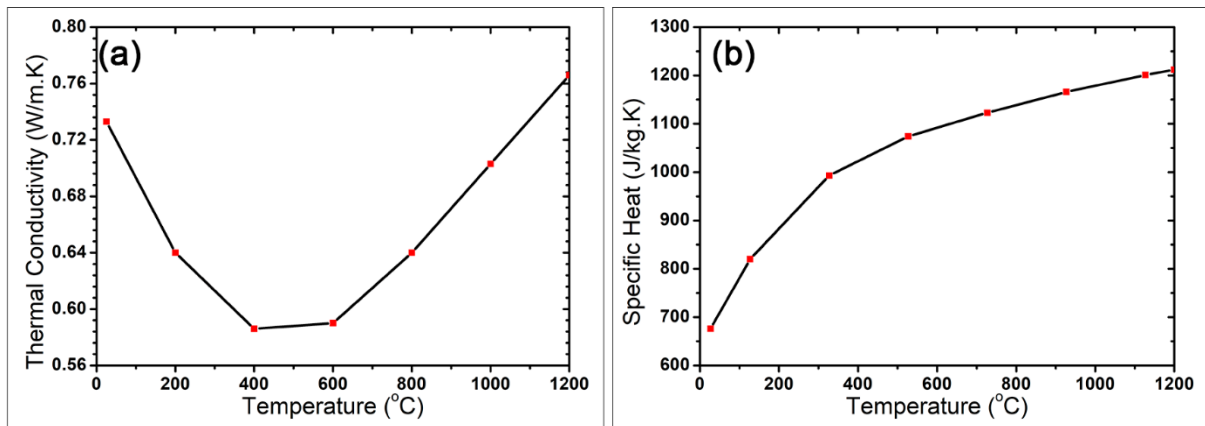


Figure 12 – Thermophysical properties of the furan-bonded sand as a function of temperature: a) thermal conductivity and b) specific heat. Adapted from [86].

To set the cooling conditions before shakeout, we should consider that the heat transfer from the hot metal to the sand mold occurs mainly through conduction. As the shakeout

occurred 12000 s after pouring the liquid metal in the sand mold, a “heat transfer” step was created with the same duration. The time increment was automatically set in order to have temperature variations smaller than 50 °C in all nodes of the mesh. This was done by setting “maximum allowable temperature change per increment equal to 50 °C”. The initial temperature in the “before shakeout” step was set for the mold (25 °C), for the C-ring-8 (1415 °C at thick cross-section region and 1100 °C at thin cross-section region) and the C-ring-12 (1425 °C and 1300 °C for thick and thin cross-sections regions, respectively). These values correspond to the average maximum temperature of each location, which were obtained by the thermocouples placed inside the mold cavity during casting, as described in section 3.2.1. The distinction between thick and thin cross-section regions was made based on the calculation of the casting modulus (defined by Chvorinov cited in [118] as the ratio of the melt volume and the mutual cooling surface area). We can see in Table 3 that the thick cross-section region shows a modulus approximately 30% higher than the thin cross-section region in both C-rings. The two regions are represented with different colors in Figure 13.

Table 3 – Geometric characteristics of thin and thick cross-sections regions of the C-rings.

C-ring	Cross-section region	Melting volume (mm³)	Cooling surface area (mm²)	Casting modulus (mm)
8 mm	Thin	107681	15218	7.1
	Thick	236589	23504	10.1
12 mm	Thin	363358	33233	10.9
	Thick	808647	53841	15.0

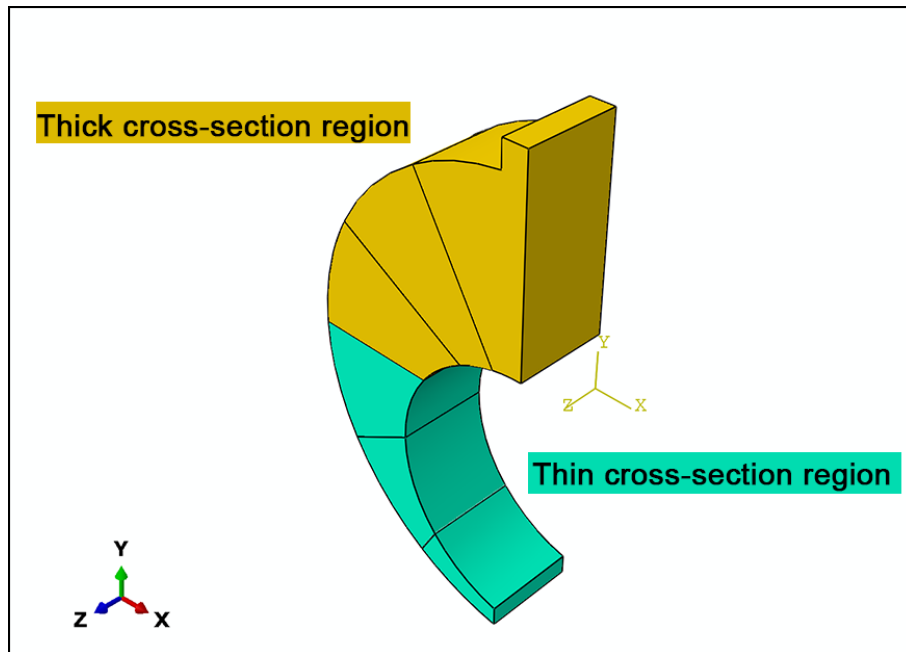


Figure 13 – FEM model of the C-ring showing the thin and thick cross-section regions.

The conductive heat transfer mechanism between the C-ring and the inner surfaces of the mold was modeled by selecting a contact interaction of the type “surface-to-surface”. The default parameters of the discretization method and small sliding formulation were used since it is expected little relative sliding of one surface along the other. Finally, the IHTC values were specified using the “thermal conductance” property. For the first simulations, we used the values reported in the literature [88] for super DSS (grade CE3MN according to the ASTM A 890 [23]) and silica sand.

Although several authors [119-121] have reported the IHTC as a function of time for simple geometries, such as plates [122, 123], bars or cylinders [88, 119, 124], the available data do not apply to different set of conditions. Nevertheless, to our best knowledge, the IHTC values for 25Cr-7Ni-Mo-N super DSS (CD3MWCuN grade) and furan-bonded sand system are not available from the literature.

Therefore, the IHTC values were also determined using an inverse methodology based on experimental temperature measurements. The inverse methodology relies on the minimization of the difference between experimental and numerical cooling curves. In this procedure, the numerical curve was calibrated by employing the least squares method to minimize the differences between the predicted and experimental temperature data.

For each C-ring, two sets of IHTC values were determined, one for the thin and one for thick cross-section region. The use of this method is based on the Chvorinov's rule, which states that sections with lower casting modulus are the first to solidify. Therefore, we may expect higher cooling rates in these regions. So, the determination of one set of IHTC values for each region seemed to be a logical method to employ.

In the “after shakeout” step, the mold is not considered, as expected, and the heat transfer from the hot metal surface to the ambient atmosphere is governed by radiation and convection. The heat transfer mechanisms were modeled through the “heat transfer” step with a duration of 7200 s, in accordance with the experimental process. The time increment was automatically set to have temperature variations smaller than 20 °C in all nodes of the mesh. This specification was done by setting “maximum allowable temperature change per increment equal to 20 °C”. The final nodal temperatures calculated in the previous step (“before shakeout”) were used as the input temperature for this step (“after shakeout”).

In order to model the convection and radiation modes of heat transfer, the following conditions between the C-ring surfaces and the atmosphere were considered: 1) “surface film condition” interaction - the convection heat transfer was set at 15 W/m² [125] and 2) “surface radiation” interaction - the emissivity was set at 0.50 and the ambient temperature at 25 °C. The calculated temperature distribution was visualized in AbaqusTM/VIEWER and exported to a datasheet. The output database file was used as input for the mechanical analysis.

3.5.2 Mechanical Model for the Residual Stresses Analysis

To model the residual stresses in the sand cast process we have 1) created the FEM model and the mesh of the C-ring, 2) defined the thermophysical material properties along with temperature, 3) set the boundary conditions and 4) employed the thermal history obtained from the previous thermal analysis.

The FEM model and the mesh of the C-ring are shown in Figure 14. Concerning the mechanical properties of the sand, there are authors that defend the need to address this topic because an excessive rigid mold would exaggerate the simulated residual stresses [87, 91]. On other hand, we have found a wide diversity of mechanical properties for the furan-bonded sand, that may result from the percentage of recycled sand, water and clay contents, sand particle size and distribution, and catalyst type [126]. However, contrary to what is desirable, databases containing mechanical properties for different types of furan-bonded sand are not available. Moreover, there are studies that have employed the elastic-plastic model for the sand mold and others did not consider the sand mold. Even so, both approaches exhibited

accurate predictions of residual stresses. Under these circumstances, the proposed mechanical model does not consider the furan-bonded sand mold. The mesh (see Figure 14) was built with 10-node modified quadratic tetrahedrons (C3D10M) elements.

For the mechanical boundary conditions, three nodes of the symmetry plane were fixed to prevent the rigid body motion (Figure 14 highlights the selected nodes). For that, the displacement (U) of these nodes over the three directions (X , Y and Z) was restricted to zero ($U_x = U_y = U_z = 0$).

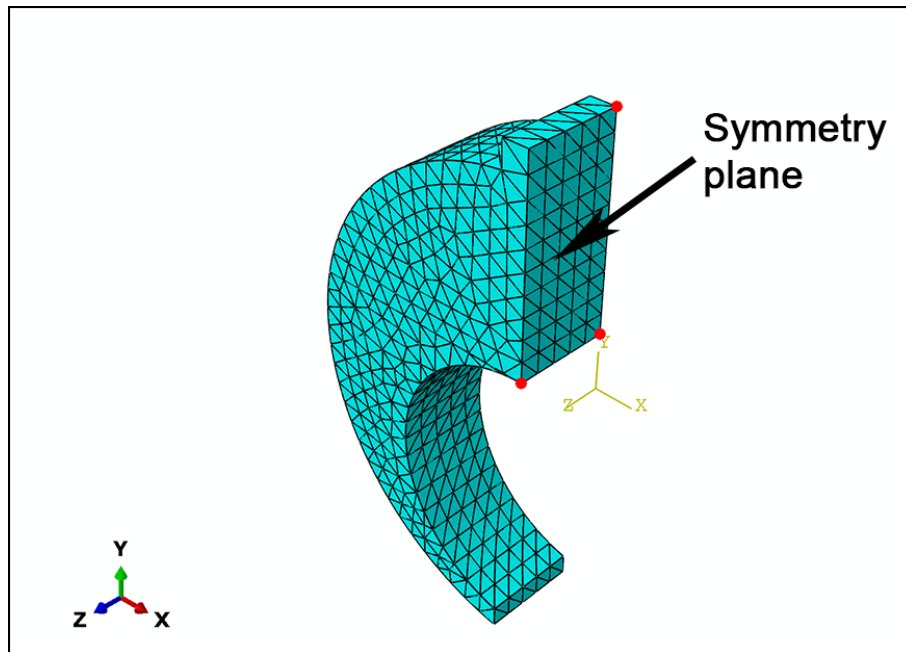


Figure 14 – FEM model and mesh of the C-ring and selected nodes that prevent the rigid body motion.

The necessary thermophysical material properties as a function of the temperature were calculated with the Stainless Steel module from JMatPro™. Firstly, the distribution of phases from liquid to room temperature were calculated using the “temperature step” function. Then, the true stress versus strain curves were obtained from the “flow stress analysis”. Finally, the density, Young’s modulus and Poisson’s ratio were accessed in the “thermo-physical and physical properties” option. The properties are shown in Figure 15.

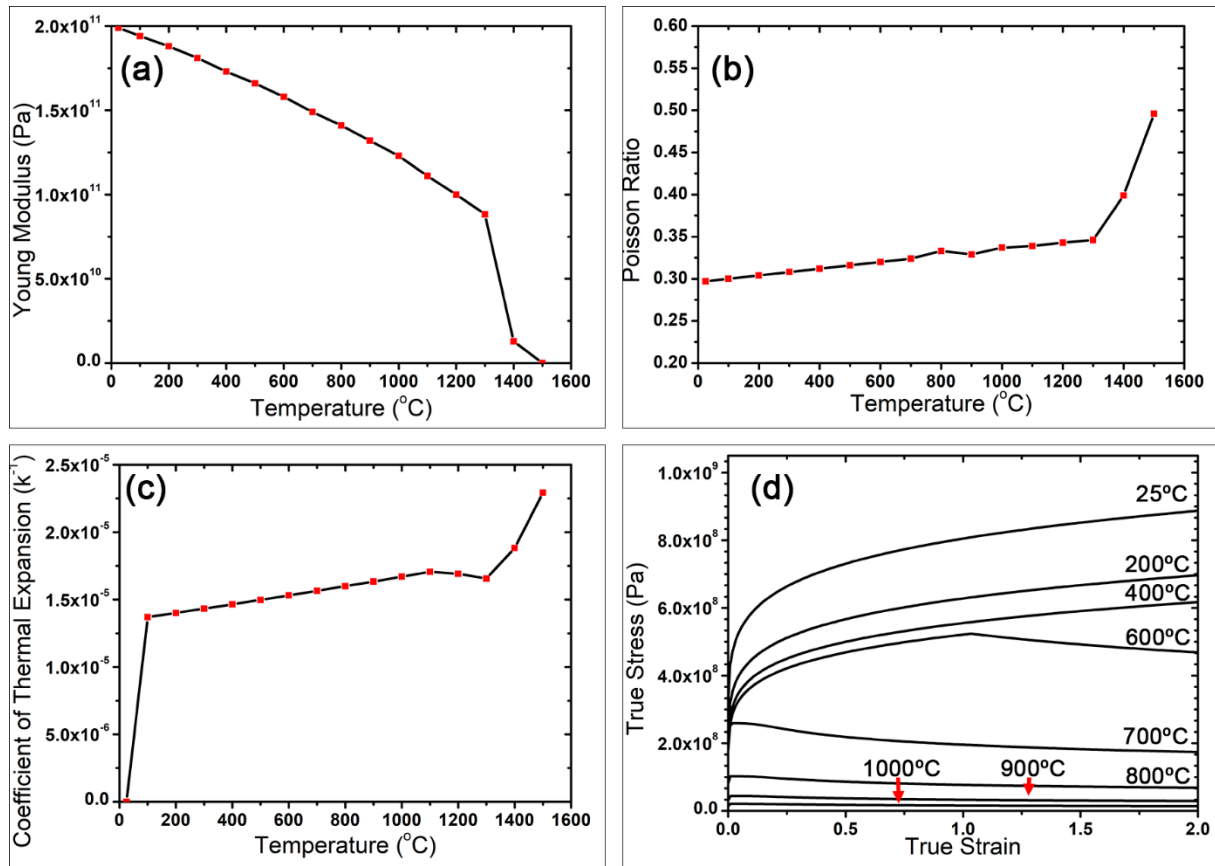


Figure 15 – Thermophysical properties of the 25Cr-7Ni-Mo-N super DSS as a function of the temperature used on the mechanical model: a) Young's modulus; b) Poisson's ratio; c) coefficient of thermal expansion; d) true stress-strain curves.

As previously described, the shakeout occurred 12000 s after pouring the liquid metal in the sand mold. Therefore, two “static, general” steps were defined, corresponding to the “before shakeout” step and “after shakeout” step. The temperature history was employed as a thermal input in each mechanical step.

Finally, the mechanical model was solved, and the maps of residual stresses were analyzed in AbaqusTM/Viewer.

3.6 Residual Stresses Measurements by the Contour Method

The results of the numerical model were verified in order to evaluate its reliability since one of the objectives in this study was the development of a numerical model capable of predicting the residual stresses in large cast components. So, the results of the sequential coupled thermal-mechanical analysis done with AbaqusTM/CAE were compared with the measurements of the residual stresses by the contour method.

First, the C-ring-8 was cut through the symmetry plane (Figure 14). The cutting was performed by a wire electrical discharge machining (WEDM) in a FANUC ROBOCUT α -C400i with an HBZ-U brass wire (JIS C2800) of 0.25 mm diameter. During the operation, the C-ring specimen was clamped on both sides of the cutting plane and submerged in temperature-controlled deionized water.

After cutting the C-ring-8, the two halves were measured in a coordinate measuring machine (CMM), using a DEA Global Performance Silver Edition, equipped with the HP-S-X1 touch probe head with stylus length 20 mm and tip diameter 3 mm. The nominal resolution of this system is 0.039 μm , and the room temperature was controlled at $20\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$. The cut surfaces were scanned using a regular grid of 1 mm x 1 mm.

Before using the measured coordinates on the calculation of residual stresses, it was necessary to calculate the mean of the measurements from the two halves into a unique grid. This was done using MatlabTM, according to the steps detailed in the work of Braga [127]. Then, the stresses were calculated on the symmetry plane by the application of a displacement boundary condition in the normal direction of that plane. This operation was done in AbaqusTM/CAE. At the end, the results of the contour method were compared with the numerical model.

Chapter 4 Solid-Phase

Transformation of 25Cr-7Ni-Mo-N super DSS

The high alloy content of the super DSS enhances the precipitation of secondary phases at slow cooling rates and temperature below 1000 °C, leading to the destabilization of the required duplex microstructure. In this context, it is therefore essential to characterize the microstructure of the C-rings and to understand the kinetics of secondary phase formation.

4.1 Thermodynamic Calculations

JMatPro™ v.12. was used to calculate the equilibrium phase diagram of the super DSS studied. Therefore, the Stainless Steel module was selected and the chemical composition was used as input into the thermodynamic algorithm of JMatPro™. The calculated equilibrium diagram is shown in Figure 16.

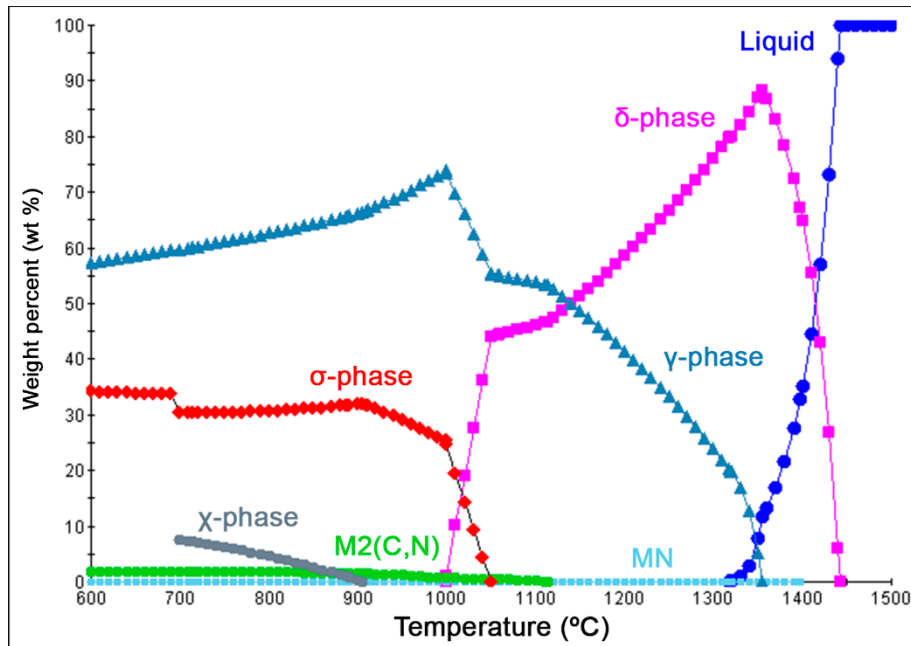


Figure 16 – Prediction of the equilibrium phases of the 25Cr-7Ni-Mo-N super DSS by JMatPro™ v.11.2.

From the equilibrium phase diagram, the solidification of the 25Cr-7Ni-Mo-N super DSS begins with the formation of primary δ -phase down to 1354 °C (88.3 wt.% of δ -phase and 11.7 wt.% of liquid phase). On further cooling, the formation of γ -phase takes place, and the full solidification of the liquid occurs at 1318 °C. Within the temperature range 1354 °C to 1318 °C, the phases at equilibrium are the liquid phase, δ -phase, γ -phase, and also the MN phase. Less attention has been paid to the MN phase, because its content is restricted to less than 0.004 wt.%. The above solidification path is in agreement with previous studies related to the solidification mode of duplex stainless steels [21, 128], which has been explained by the high content of δ -phase stabilizer elements (Cr, Mo, W, Si) as previously discussed in section 2.2. The formation of the γ -phase occurs for temperatures below 1354 °C, following a nucleation and growth mechanism. The δ -phase/ γ -phase ratio of 1:1 is reached at 1140 °C.

The equilibrium phase diagram also provides information about the secondary phases that may form on super DSS. In addition, the M2(C,N) phase is predicted for temperatures below 1113 °C, in an amount less than 1.8 wt.%. This phase may be described as a chromium nitride, as it is documented in the literature [41, 53, 129-131]. Other secondary phases which are found below 1050 °C, are described as σ -phase and χ -phase. These two secondary phases may be present in a high volume percent: the σ -phase is stable below 1050 °C, with a maximum content of 34.2 wt.% , while the χ -phase is stable between 900 °C and 700 °C, with a maximum content of 7.6 wt.%.

The thermodynamic results indicate that the σ -phase and χ -phase are the predominant secondary phases stable at temperatures below 1000 °C. The section 4.4 covers the methods used to distinguish each phase as well as to determine the kinetics of their formation in the 25Cr-7Ni-Mo-N super DSS.

4.2 As-Cast Microstructures

The microstructure of the six regions of each C-ring (A to F) is shown by the optical micrographs displayed in Figures 17 and 18. The etching procedure produced different levels of contrast for the various phases. A bright γ -phase, a light-grey δ -phase, and dark-grey particles corresponding to secondary phases (labeled S) can be observed.

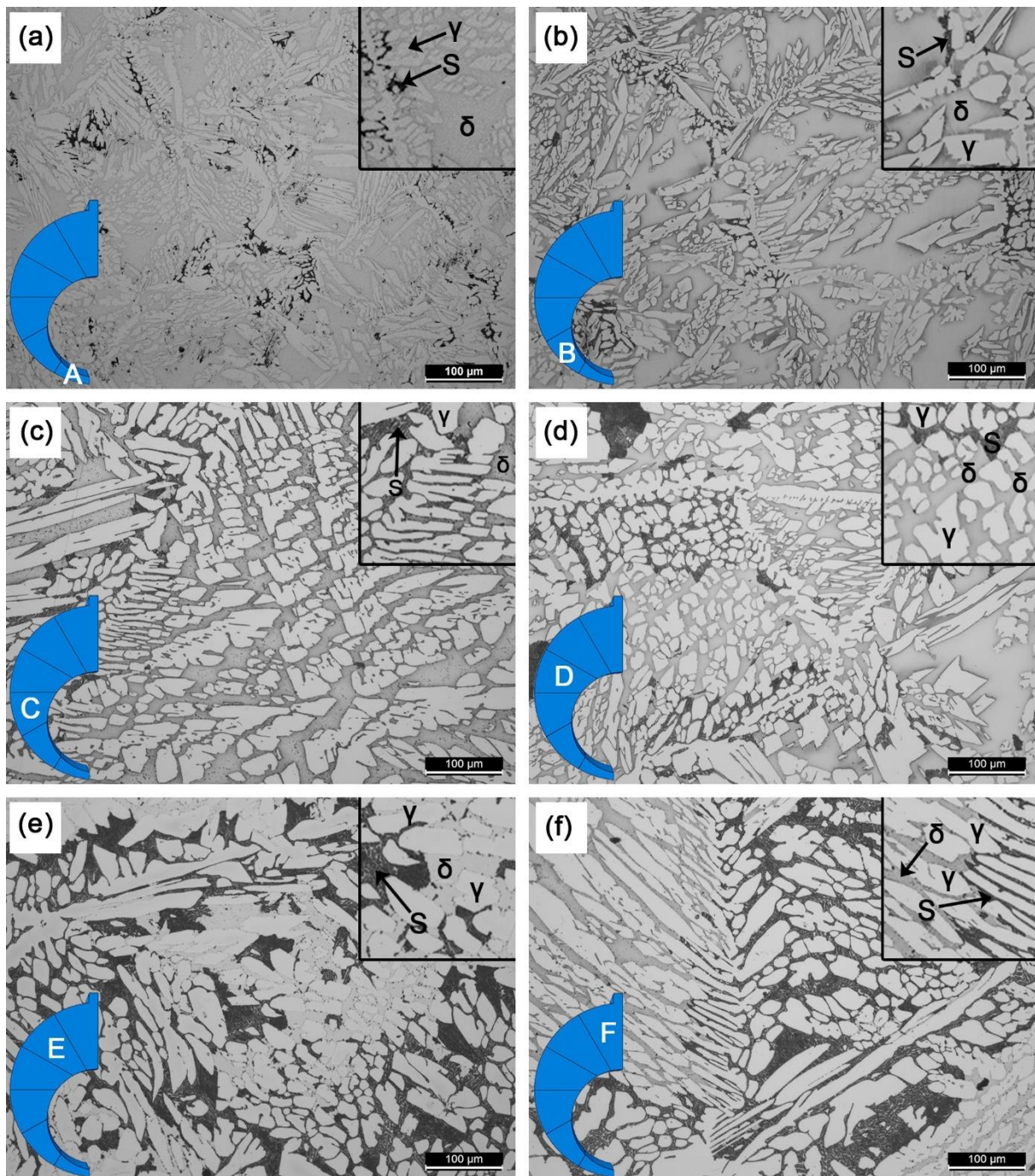


Figure 17 – OM micrographs of six regions from C-ring-8. Secondary phases (S) are darker than the δ -phase, whereas the γ -phase is the brightest phase. No secondary phases are observed inside the γ -phase grains.

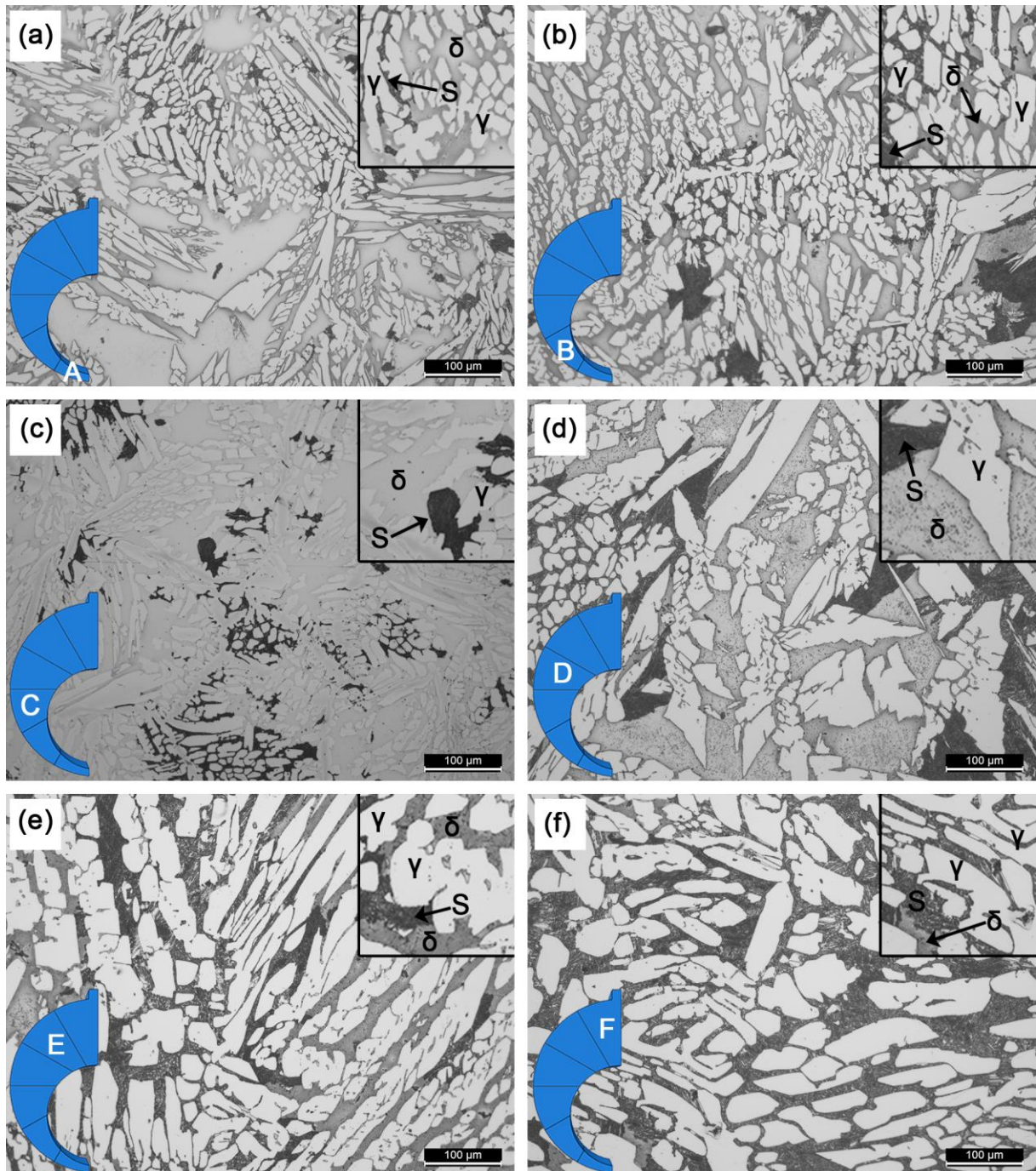


Figure 18 – OM micrographs of six regions from C-ring-12. Secondary phases (S) are darker than the δ -phase, whereas the γ -phase is the brightest phase. No secondary phases are observed inside the γ -phase grains.

In general, the secondary phase particles precipitate at the δ/γ grain boundaries and within the δ -phase. In regions with low precipitation, it is possible to observe small round particles (see for example Figure 17d). On the other hand, some precipitates that form within the δ -phase seems to have a plate-like shape (see for example Figure 18f).

The OM analysis also shows that the island-shaped γ -phase is coarser on the thick cross-sections of the C-rings (see Figures 17c-17f and Figures 18d-18f) than the γ -phase islands in the thin cross-sections (see Figures 17a and 17b and Figures 18a and 18c). In fact, the size of the γ -phase islands is affected by the cooling rate. The thick regions remain at a higher temperature for a longer time and under these conditions, the diffusion assists the grain coarsening.

In addition, OM analysis permits to conclude that during the cooling of the solid metal, the secondary phases grow at the expense of the δ -phase. In fact, OM shows that the primary γ -phase did remain stable because no secondary precipitation occurred within the γ -phase grains. This indicates the stability of this phase during the slow cooling of the sand casting process. The volume percent of phases formed in the six regions of C-ring-8 and C-ring-12 is shown in Figures 19 and 20, respectively.

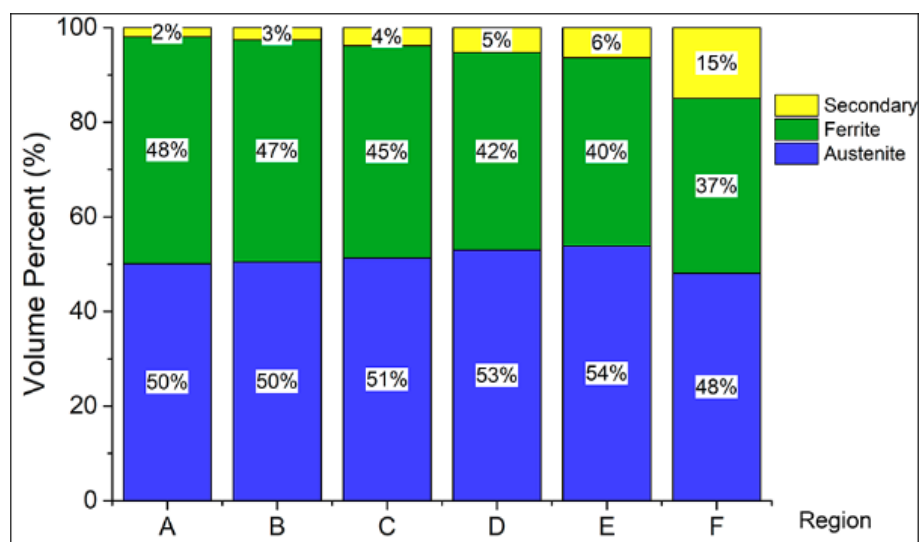


Figure 19 – Distribution of the volume percent of phases in the six regions of C-ring-8.

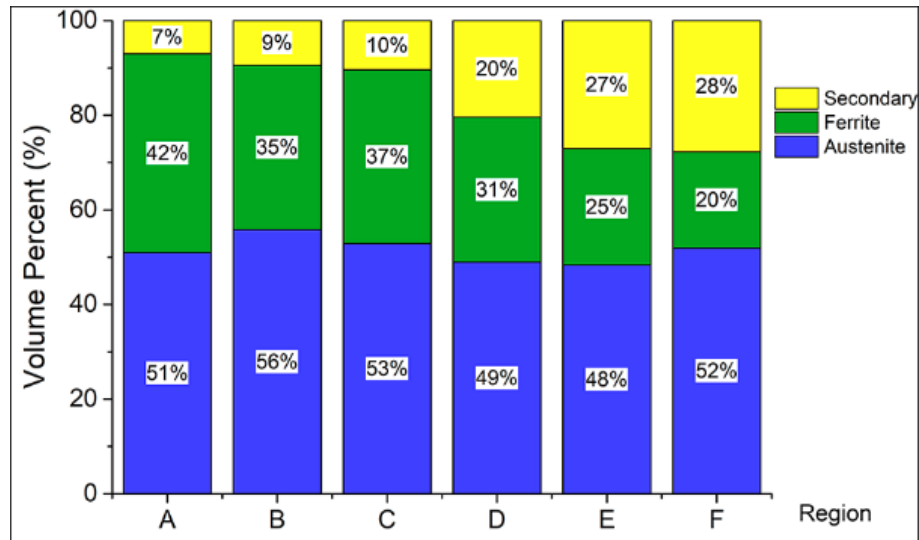


Figure 20 – Distribution of the volume percent of phases in the six regions of C-ring-12.

It is known that the destabilization of the δ -phase with the formation of secondary phases is greatly affected by the cooling rate [6, 132]. Thus, in order to understand the effect of the cooling rate on the microstructure, we have plotted the volume percent of secondary phases as a function of the cross-section area of each C-ring, which is shown in Figure 21. As explained in section 3.2, the C-ring specimen exhibits a variable cross-section from region F to region A, causing an increase of the cooling rate from regions F to A. The cross-section area at midsection of each region can be found in Table 4.

Table 4 – Cross-section area of the six regions considered in each C-ring.

Region	A	B	C	D	E	F
C-ring-8	347 mm ²	816 mm ²	1527 mm ²	2146 mm ²	2506 mm ²	2656 mm ²
C-ring-12	780 mm ²	1836 mm ²	3436 mm ²	4838 mm ²	5639 mm ²	5975 mm ²

Figure 21 suggests that the higher cross-section area leads to an increase amount of secondary phases, which is related with the cooling rates at different regions. Assuming the cooling rates at 950 °C, the increase of the cross-section area represents a decrease in the cooling rate, from 128 °C/min (region A) to 7 °C/min (region F), in C-ring-8 (black). The same trend is observed in C-ring-12 (red), for which the cooling rate decreases from 56 °C/min (region A) to 5 °C/min (region F). As a consequence, the volume percent of the secondary phases was raised from 2% $\pm$ 1% to 15% $\pm$ 9% in C-ring-8 and from 7% $\pm$ 2% to 28% $\pm$ 7% in C-ring-12. There is scarce information about the relationship of the cooling rate and the percentage of secondary phases formed. However, it is relevant to mention that Kim *et al.* [55]

expressed the percentage of σ -phase as a function of the average cooling rate and estimated a percentage above 3% for a rate of 5 °C/min, for a similar DSS.

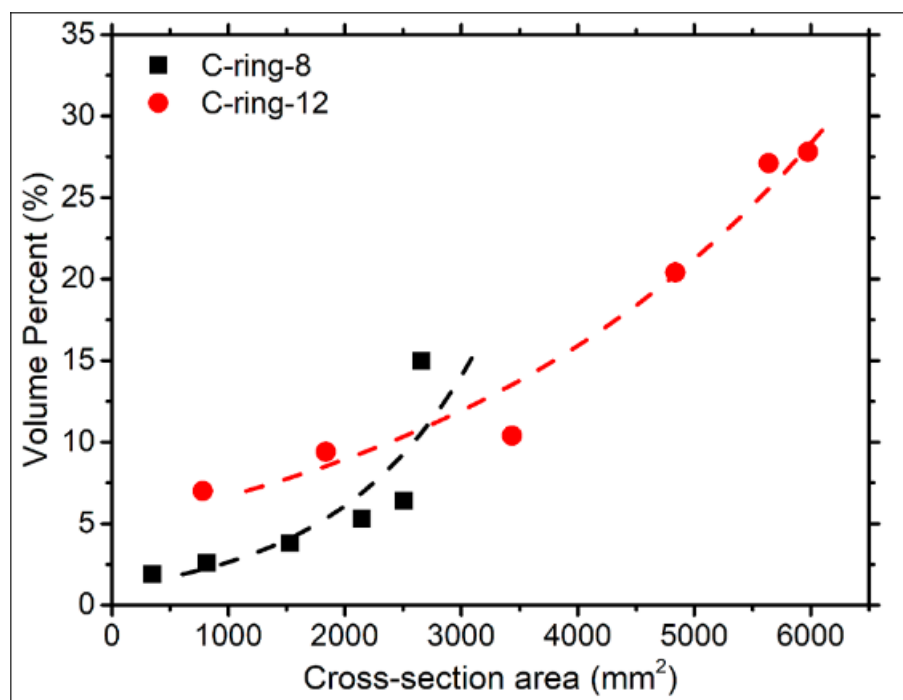


Figure 21 – Evolution of the volume percent of secondary phases of C-ring-8 (black) and C-ring-12 (red) as a function of cross-section area.

As described in section 2.2.2., several secondary phases are possible to form on duplex stainless steels, such as σ -phase, χ -phase, chromium nitrides (CrN or Cr_2N), alpha-prime (α') or R-phase, among others [1, 5, 40, 133]. All of these phases are detrimental to the performance of the duplex stainless steels, in particular, to the corrosion resistance [35, 36, 133, 134] and impact toughness [1, 40, 135-137]. To study the formation of these phases from the duplex structure, the C-rings were first solutionized to obtain a structure containing similar δ -phase and γ -phase proportions. The solutionized microstructures are described in section 4.3, whereas the secondary phases formed in the aging treatment are discussed in section 4.4.

4.3 Solutionized Microstructures

After the solution heat treatment, the six regions of both C-rings were prepared and characterized through OM. The electrolytic etching in a solution of NaOH revealed white grains of γ -phase surrounded by dark grey δ -phase, indicating that the solution temperature

effectively promoted the dissolution of the secondary phases. The microstructure of the solutionized C-rings is shown in Figure 22 and 23.

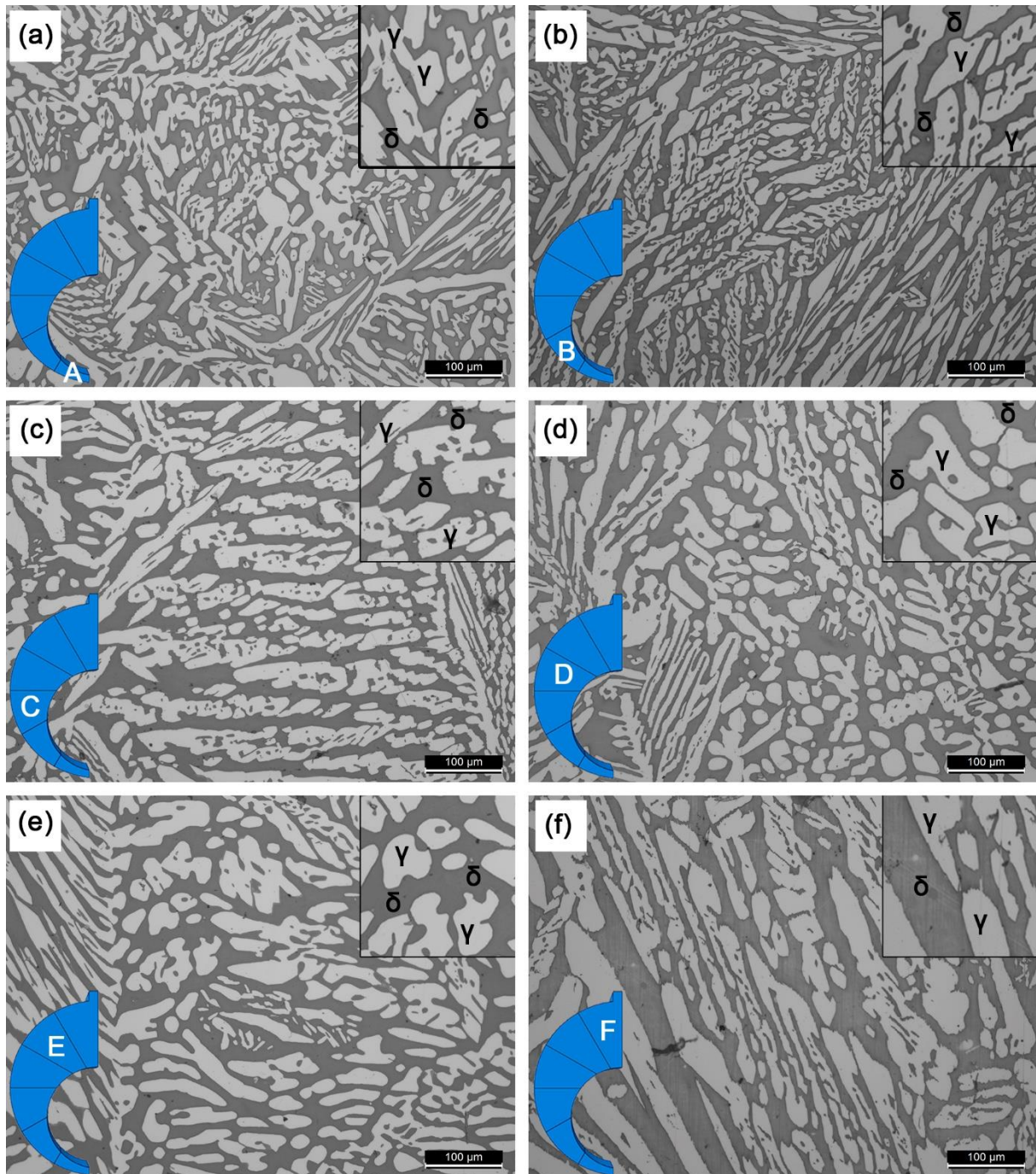


Figure 22 – OM micrographs from C-ring-8. The brighter phase is γ -phase, and δ -phase is the light grey phase.

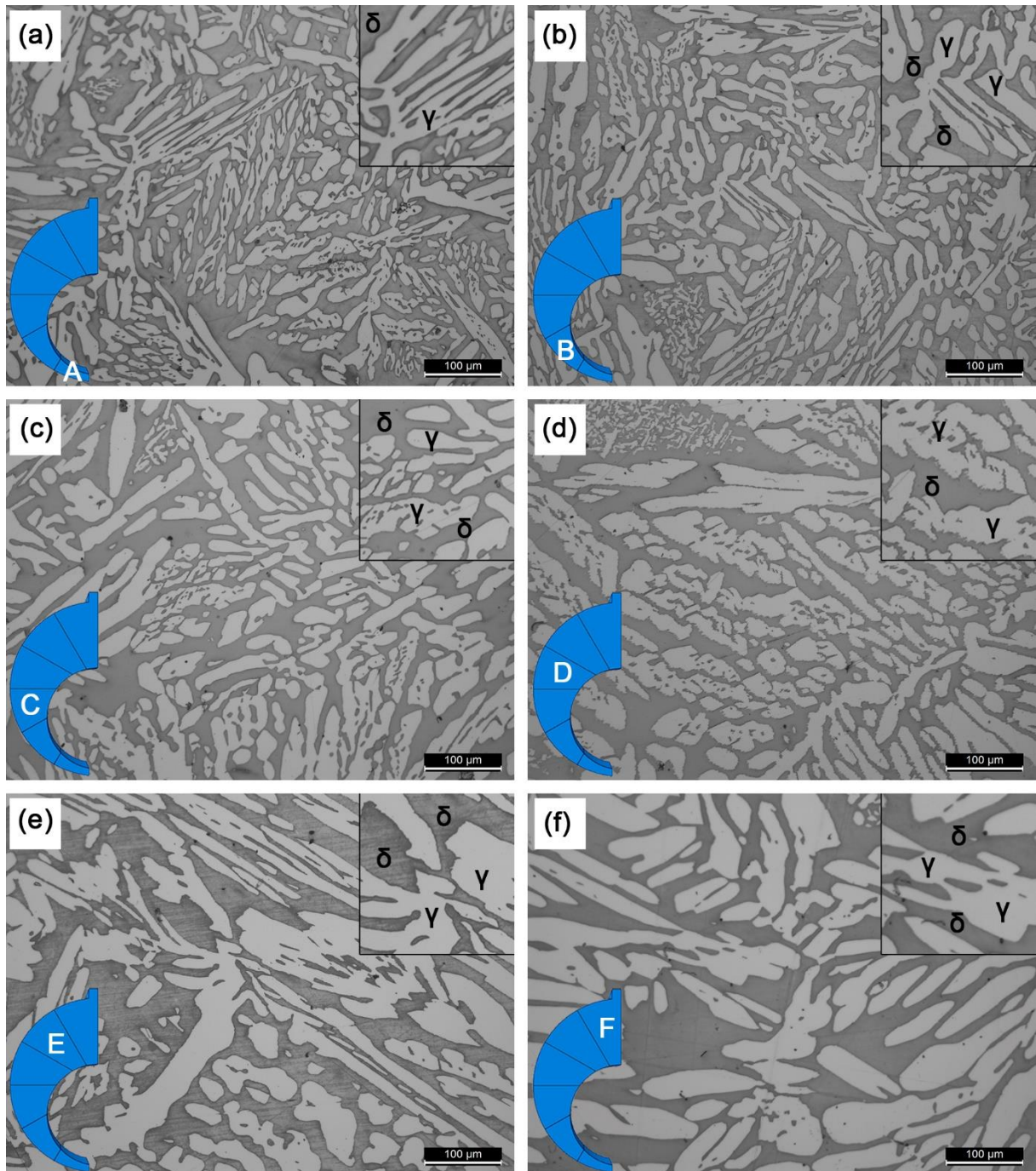


Figure 23 – OM micrographs from C-ring-12. The brighter phase is γ -phase, and δ -phase is the light grey phase.

The OM analysis revealed that the solution heat treatment homogenized the microstructure thereby leading to a uniform distribution of the two phases. A slight spheroidization of the γ -phase is also observed. The volume percent of the γ -phase and δ -phase in the six regions of the C-rings is shown in Figure 24 and 25. It is observed that for both C-rings, the volume percent of each phase varied slightly from the 50% value, independently of the prior as-cast microstructure. It is clear that an increase of δ -phase has

occurred with the dissolution of secondary phases. As previously discussed in the literature, temperatures above 1000 °C favor the dissolution of secondary phases into δ -phase [6, 132], which is in line with our results. Also, this duplex microstructure is in good agreement with that one predicted by the equilibrium phase diagram from JMatPro™ (see Figure 16). As a summary, these results indicate that the dwelling time (3 h) at 1120 °C is sufficient to promote the dissolution of secondary phases and to obtain a microstructure composed of γ -phase and δ - in almost equal proportions.

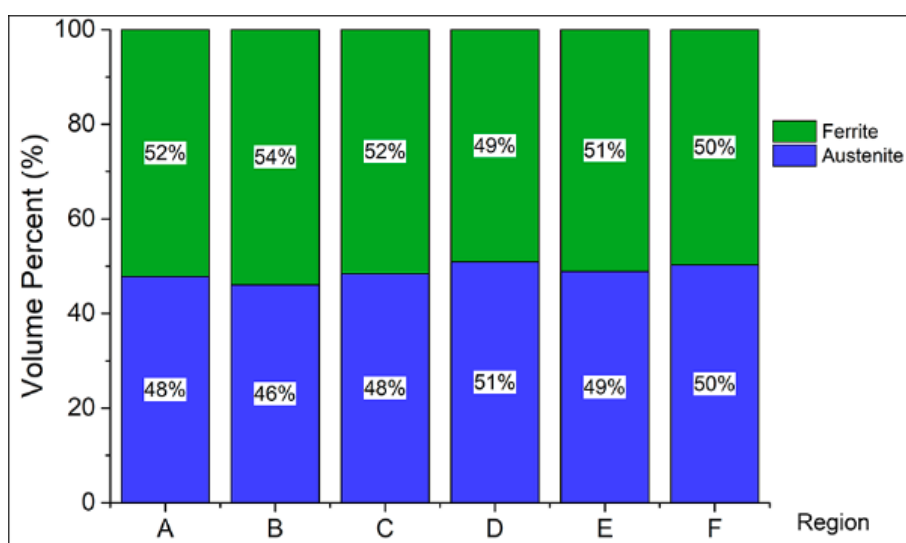


Figure 24 – Distribution of the volume percent of phases in the six regions of C-ring-8 after the solution heat treatment.

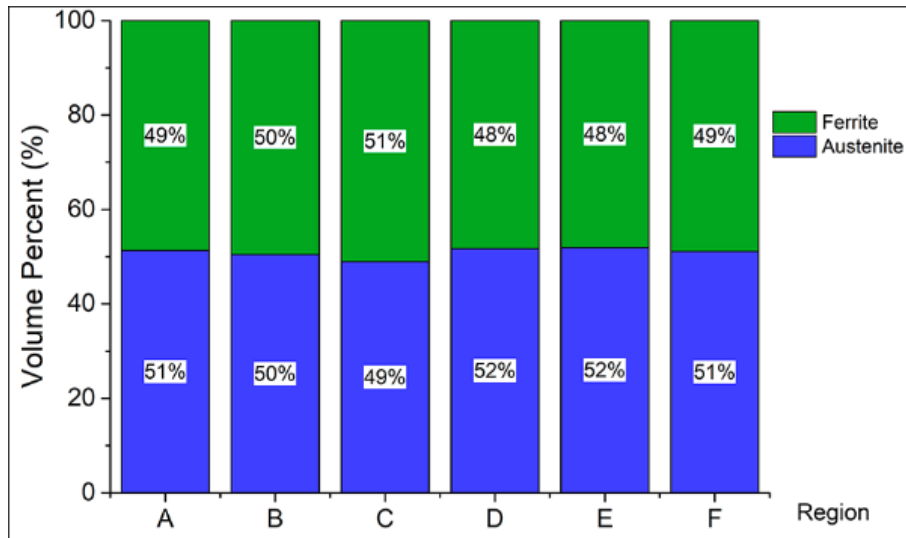


Figure 25 – Distribution of the volume percent of phases in the six regions of C-ring-12 after the solution heat treatment.

4.4 Precipitation of σ -phase and χ -phase

As previously discussed, super duplex stainless steels are prone to the formation of secondary phases at slow cooling rates. The secondary phase formation can be a serious problem in the casting process because of the slow continuous cooling condition over the temperature range of precipitation. In this context, it is therefore fundamental to understand the mechanisms and kinetics of secondary phase formation in cast super DSS. In particular, we have investigated the effect of aging time and temperature on the formation of secondary phases and determined the time-temperature-transformation (TTT) diagram for the cast super DSS subjected to our study. One key issue associated with the presence of secondary phases is the fact that it is very challenging to identify and distinguish the σ -phase from the χ -phase by using OM, as the available etchants produce the same contrast for both phases [13, 14, 17, 54, 56] (sections 4.2 and 4.3).

Nevertheless, these limitations are reduced using SEM coupled with EDS analysis, which allows semi-quantitative analysis of elements, facilitating the identification of phases that exhibit distinct chemical composition. As an alternative, electron backscattered diffraction (EBSD) has emerged as a promising technique for mapping the various phases by using the crystallographic features to identify the phases among the possible candidates. This technique was applied by a couple of research groups [15, 138] to identify the χ -phase and σ -phase on wrought 2205 DSS. However, difficulties associated with sample preparation have been reported because of the influence of the preparation method on the accuracy of the results. Another relevant aspect to take into account when using EBSD on duplex stainless steels is

an effect known as “ferrite shredding” that causes the wrong indexation of the δ -phase particularly on samples with high content on σ -phase [138].

To overcome the aforementioned issues, we combine OM, SEM, and TEM, such that we can correlate imaging, chemical composition, and electron diffraction at various scales to identify the secondary phases unambiguously and to understand their formation in the cast super DSS under study. OM is an essential technique for the microstructural evaluation of duplex stainless steels as it permits the identification of both the δ -phase and γ -phase. However, it is not able to distinguish the various secondary phases. Therefore, SEM/BSE is also used, as the secondary phases are expected to have distinct chemical compositions, thus providing different levels of mass-thickness contrast. Yet, to correlate these variations in chemical composition with a specific phase, thus allowing unambiguous identification of the secondary phases, TEM coupled with SAED is required to analyze the crystallographic information. As a result, this combination of imaging, chemical analysis, and electron diffraction through various microscopy techniques allow us to identify the secondary phase and to study their kinetics of precipitation.

4.4.1 Optical Microscopy Analysis

The effect of aging conditions (temperature from 700 °C to 1000 °C and holding time from 1 min to 4320 min) on the microstructure is shown in Figures 26 to 35. For all samples, the metallographic preparation produced different levels of contrast for the various phases, namely a bright γ -phase, a light grey δ -phase, and dark grey particles corresponding to secondary phases.

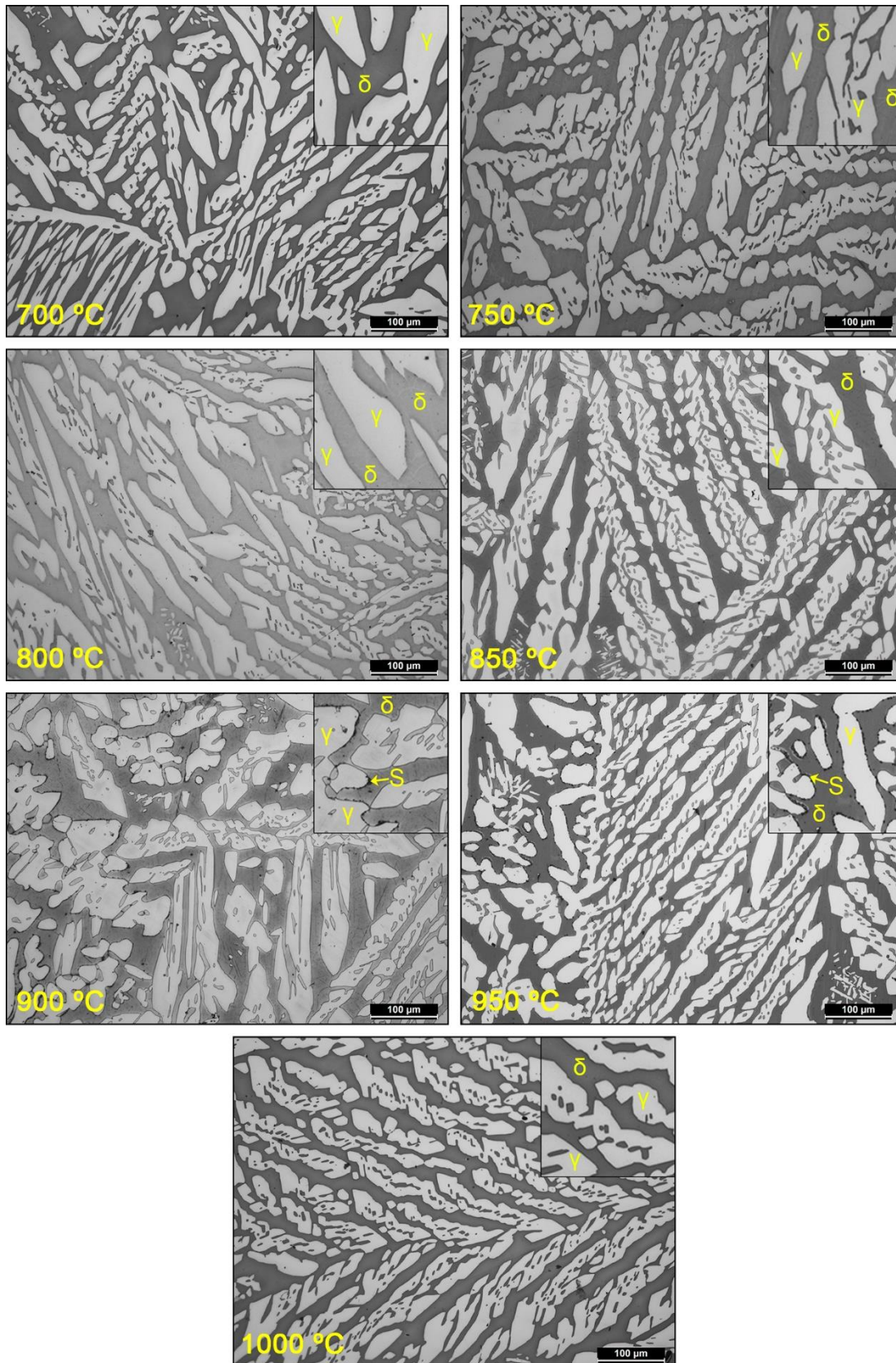


Figure 26 – Optical micrographs of samples aged for 1 min at temperatures ranging from 700 °C up to 1000 °C. Secondary phases (S) are observed at the δ/γ grain boundaries for aging temperatures of 900 °C and 950 °C.

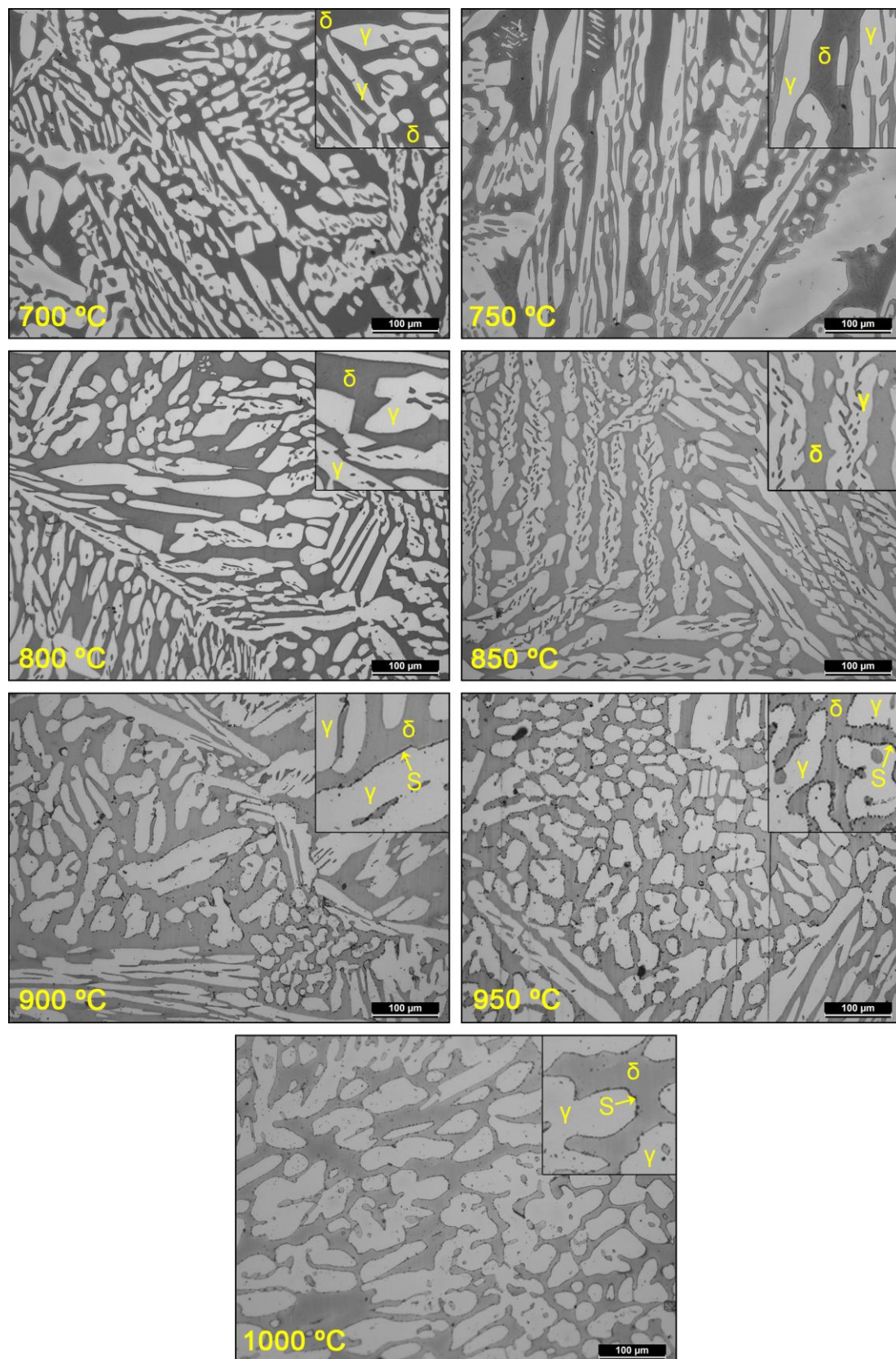


Figure 27 – Optical micrographs of samples aged for 2 min at temperatures ranging from 700 °C up to 1000 °C. Secondary phases (S) are observed at the δ/γ grain boundaries for 900 °C and higher aging temperatures.

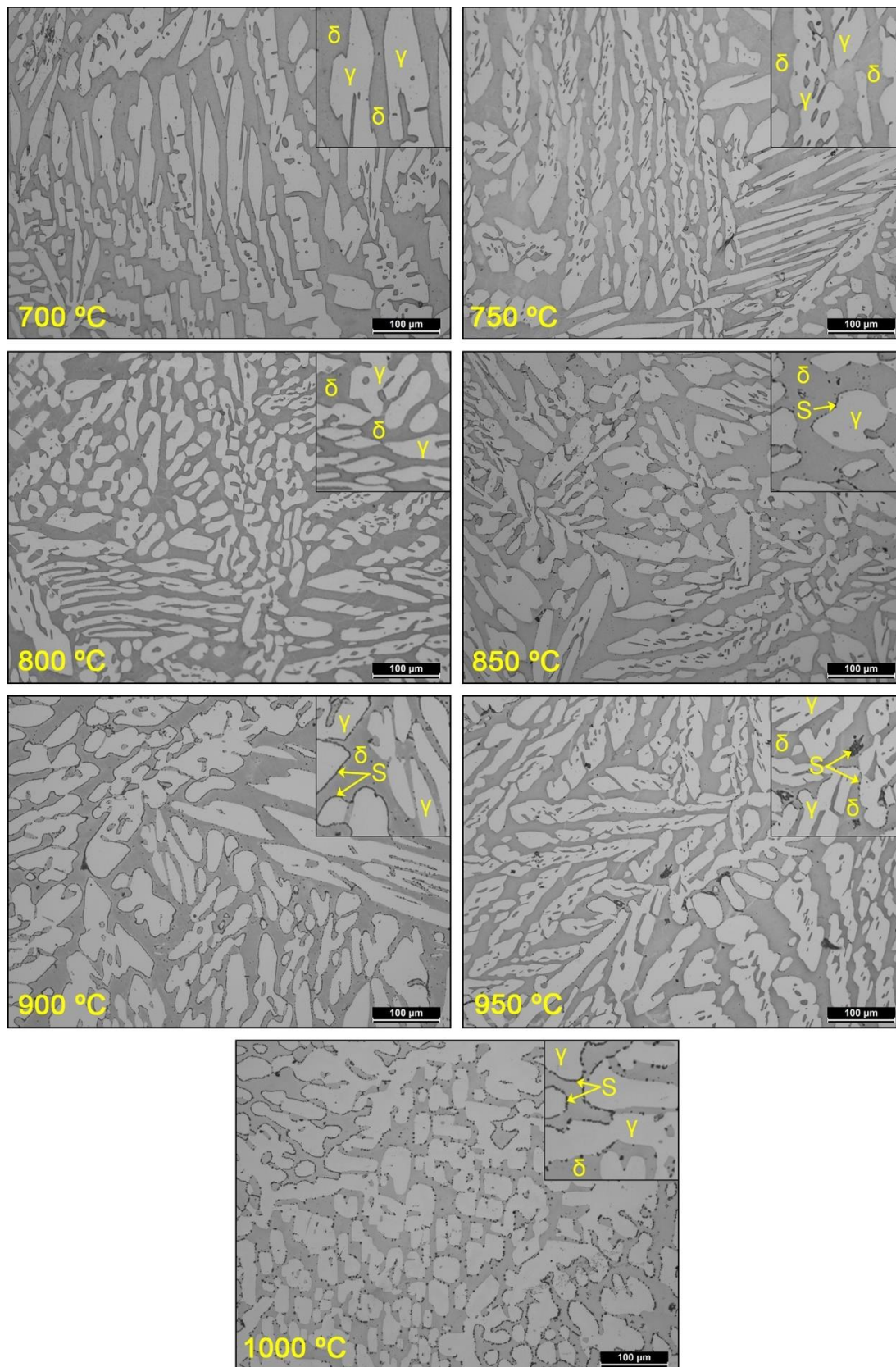


Figure 28 – Optical micrographs of samples aged for 4 min at temperatures ranging from 700 °C up to 1000 °C. Secondary phases (S) are observed at the δ/γ grain boundaries for 850 °C and higher aging temperatures and also within the δ-phase grains for 950 °C.

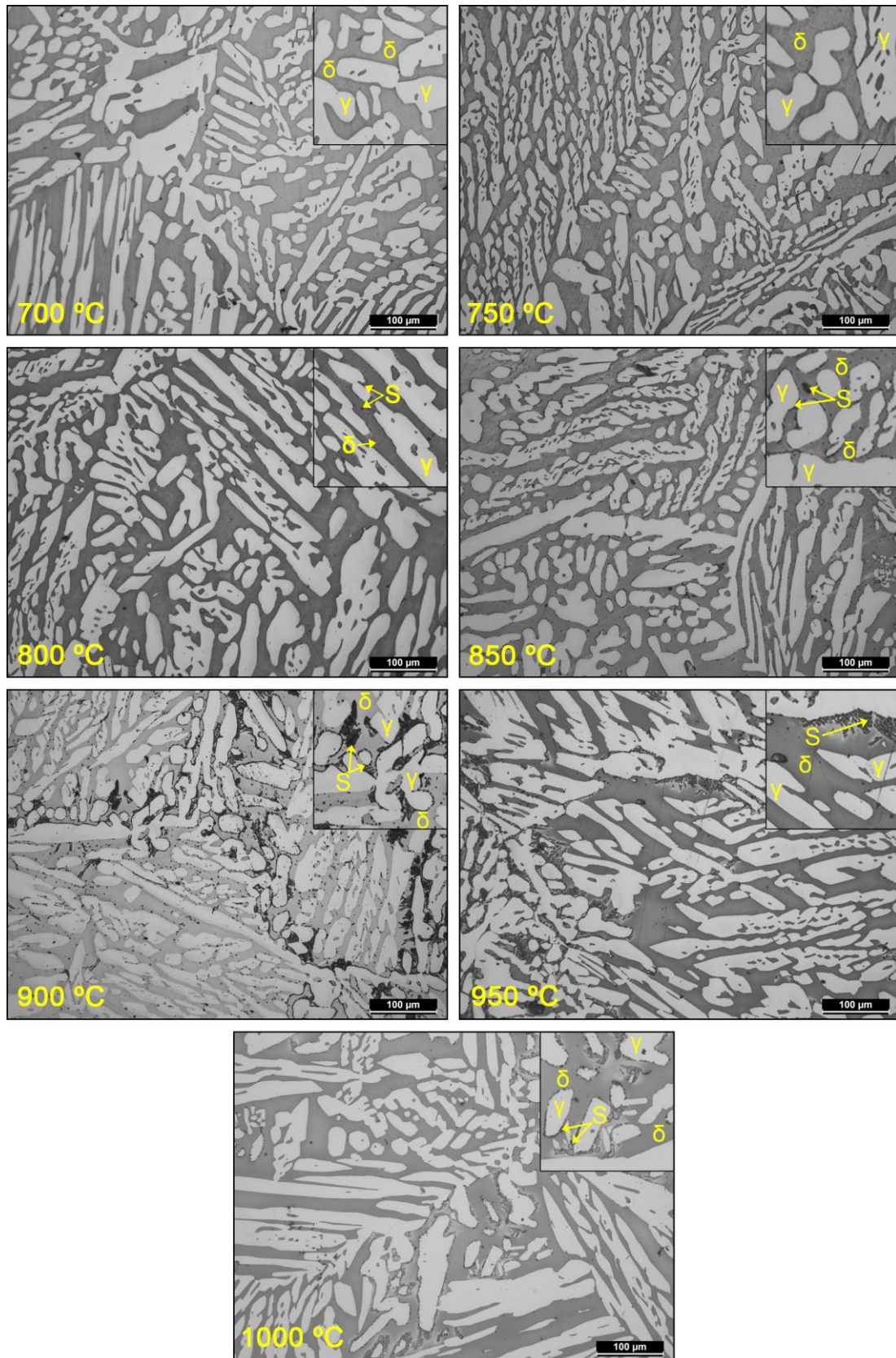


Figure 29 – Optical micrographs of samples aged for 8 min at temperatures ranging from 700 °C up to 1000 °C. Secondary phases (S) are observed at the δ/γ grain boundaries for 800 °C and higher aging temperatures. At 900 °C and 950 °C, the precipitates are also found within the δ -phase.

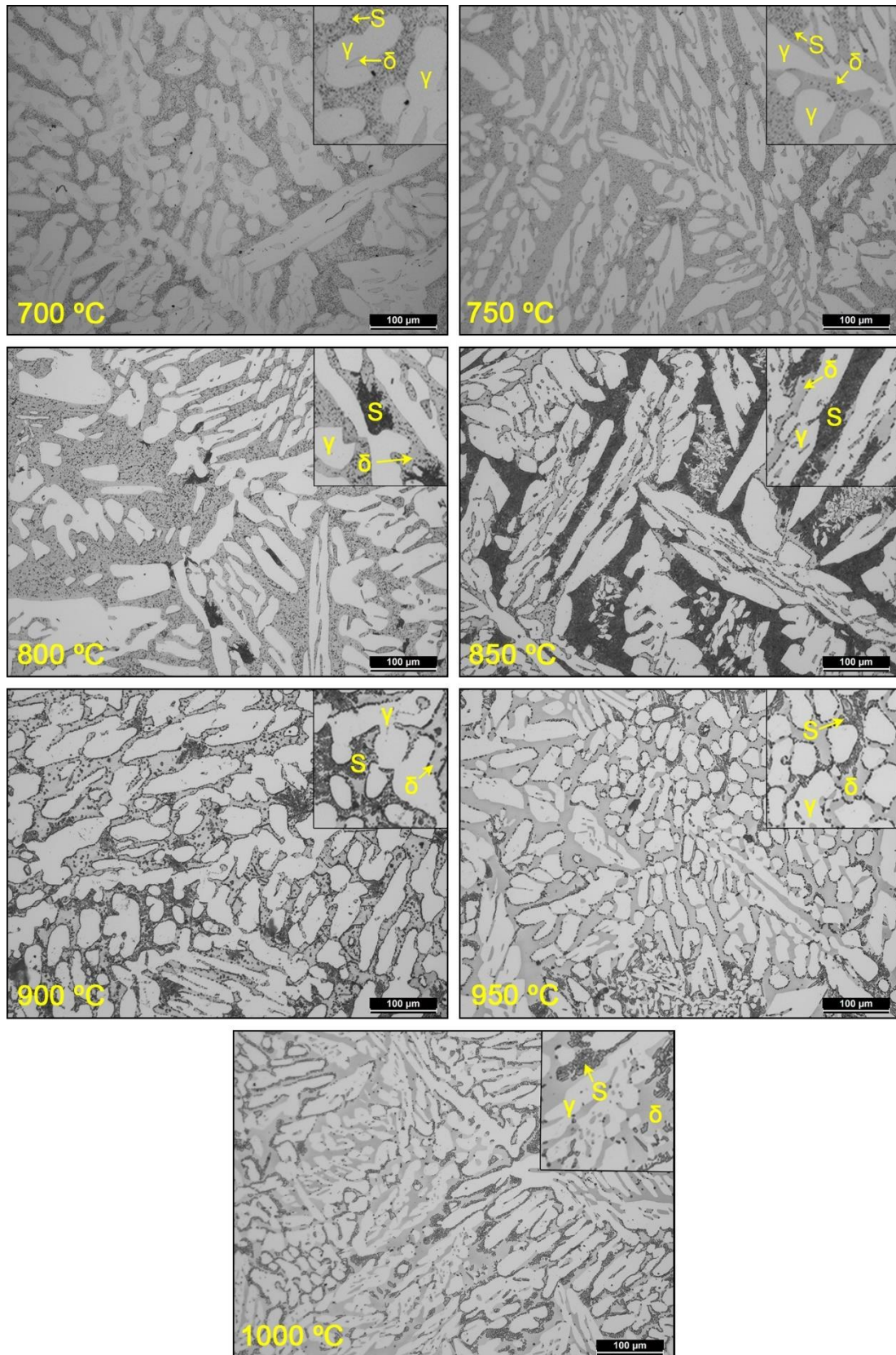


Figure 30 – Optical micrographs of samples aged for 16 min at temperatures ranging from 700 °C up to 1000 °C. Secondary phases (S) are observed within the δ -phase grains for all aging temperatures. Precipitates with an irregular shape in addition to round precipitates are observed for aging temperatures of 800 °C or higher.

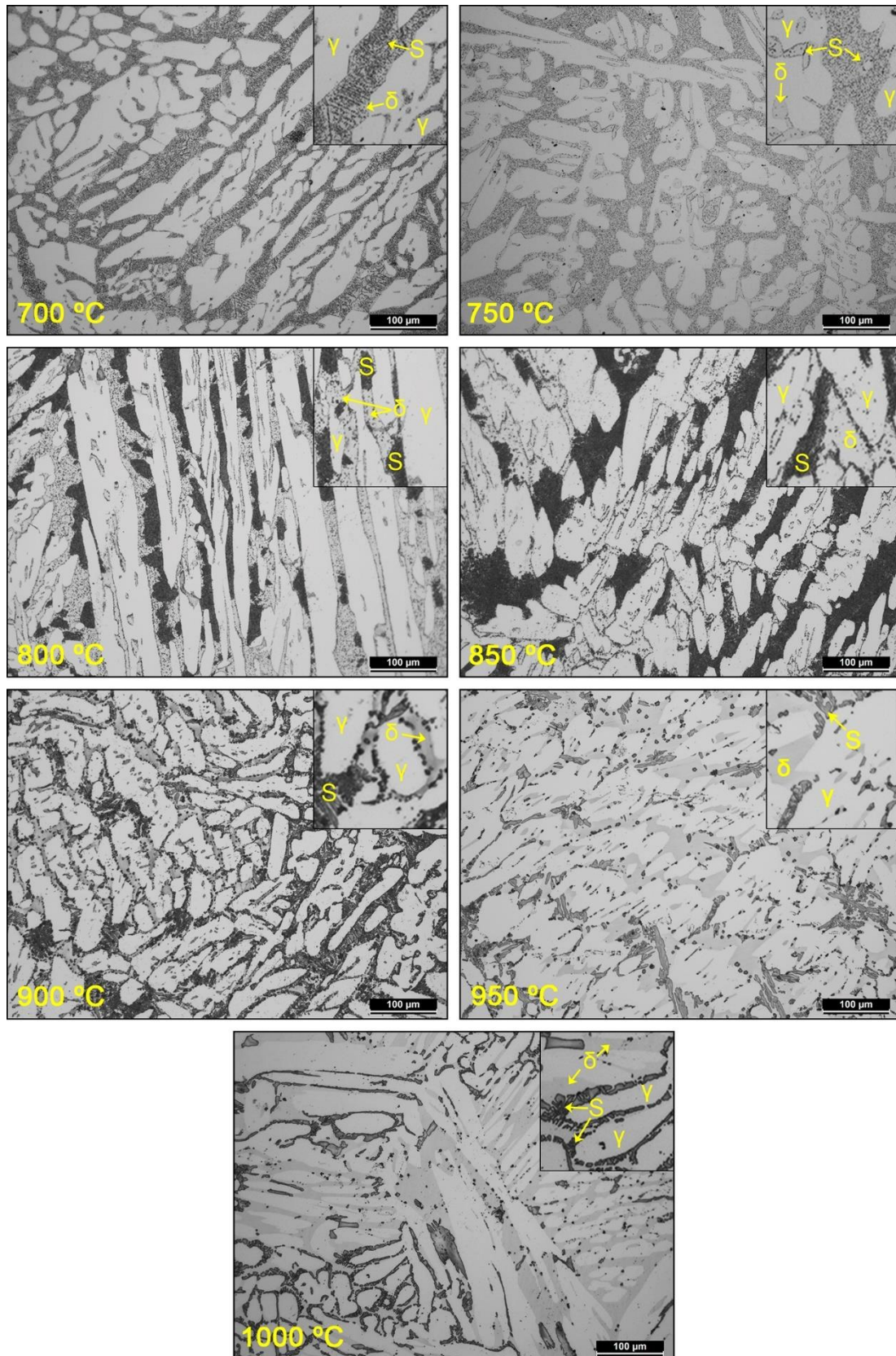


Figure 31 – Optical micrographs of samples aged for 32 min at temperatures ranging from 700 °C up to 1000 °C. No significant differences are observed in comparison to the aging time of 16 min, beyond the growth of the secondary phases (S), with an irregular shape, that is taking place.

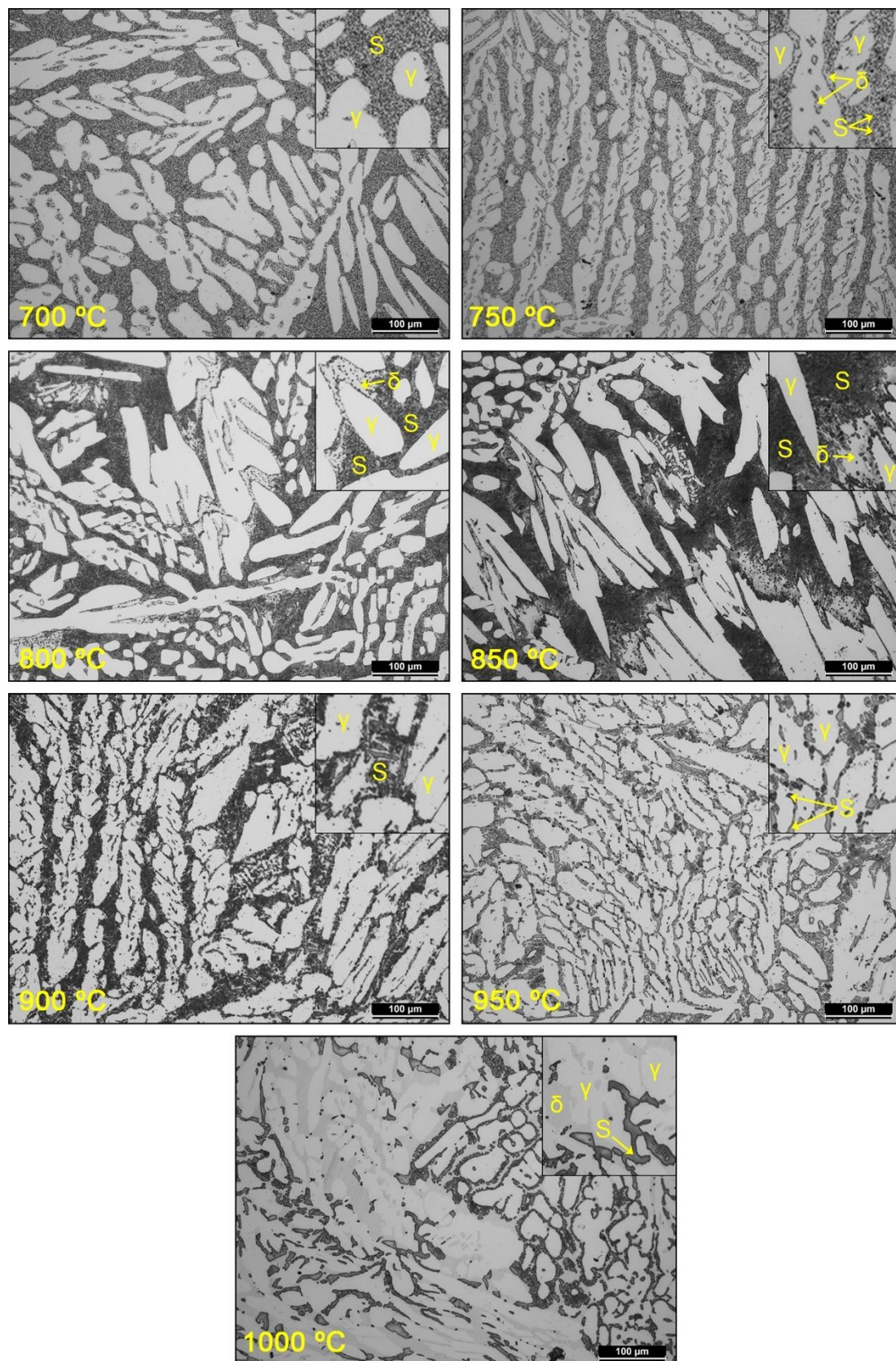


Figure 32 – Optical micrographs of samples aged for 64 min at temperatures ranging from 700 °C up to 1000 °C. No significant differences are observed in comparison to the aging time of 32 min, beyond the growth of the secondary phases (S), with an irregular shape, that is taking place.

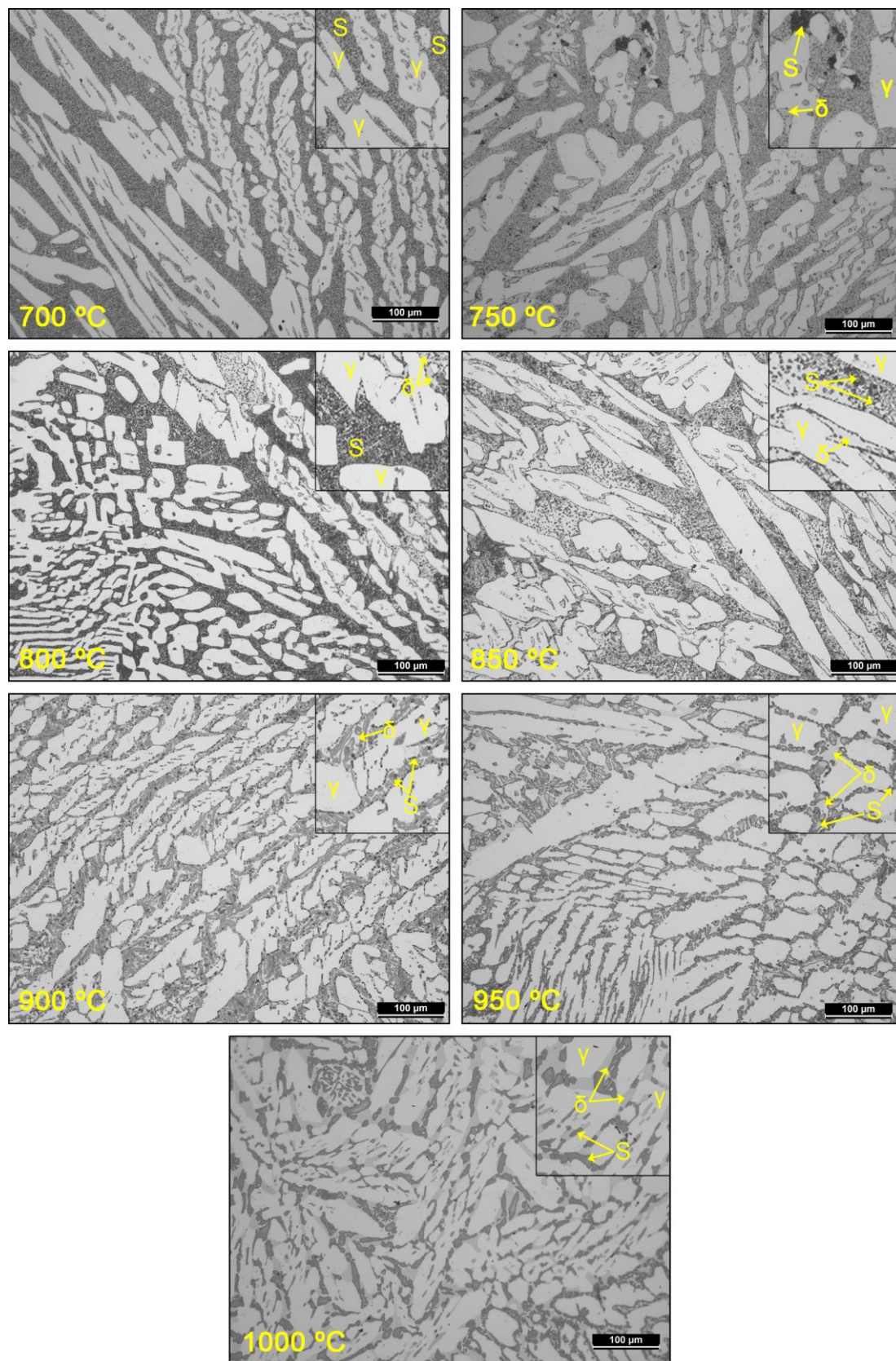


Figure 33 – Optical micrographs of samples aged for 128 min at temperatures ranging from 700 °C up to 1000 °C. Secondary phases (S) are observed within the δ -phase for all aging temperatures. Precipitates with an irregular shape are visible at the lower aging temperatures (750 °C).

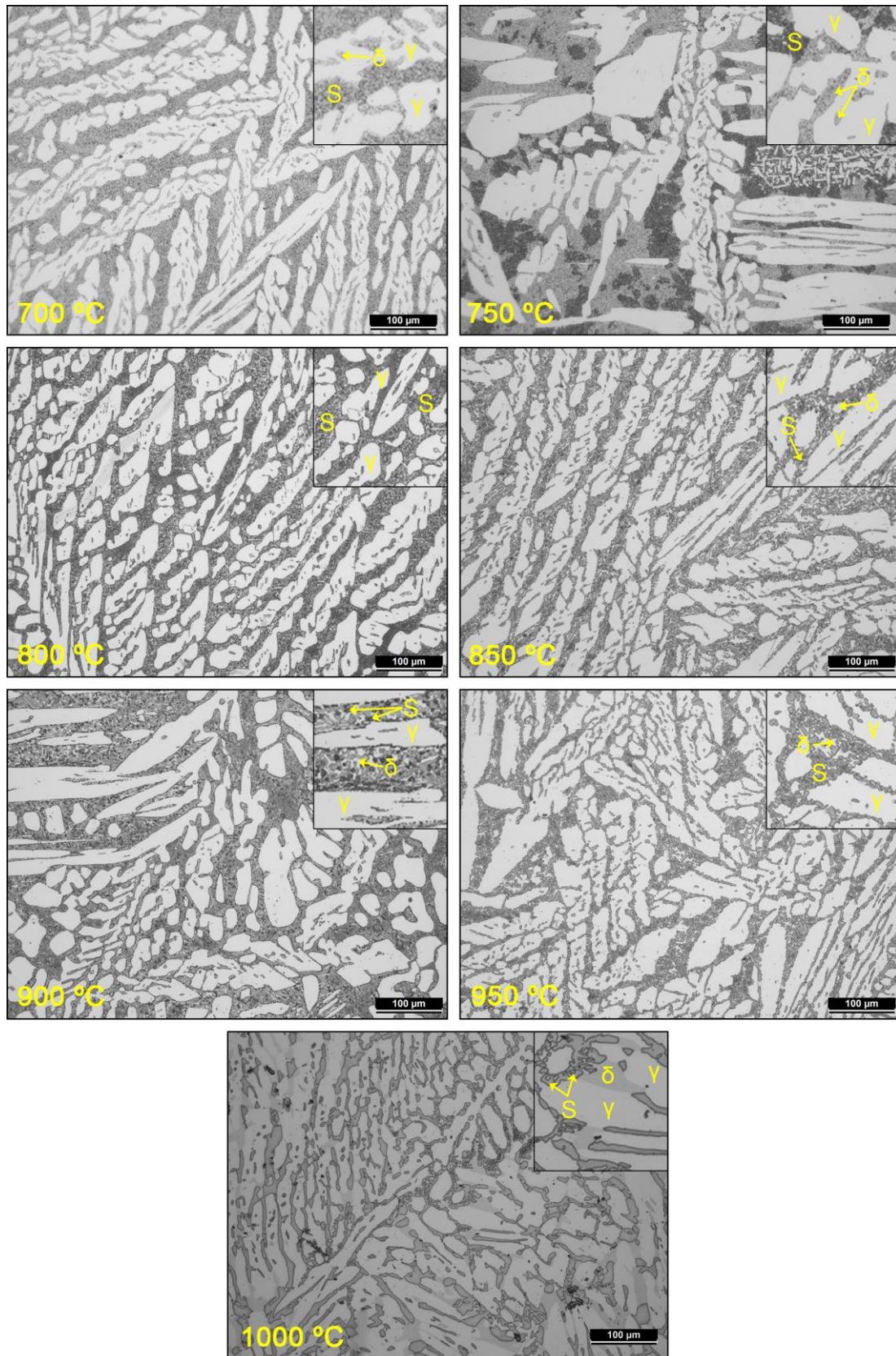


Figure 34 – Optical micrographs of samples aged for 384 min at temperatures ranging from 700 °C up to 1000 °C. No significant differences are observed in comparison to the aging time of 128 min, beyond the growth of the precipitates, with an irregular shape, that is taking place.

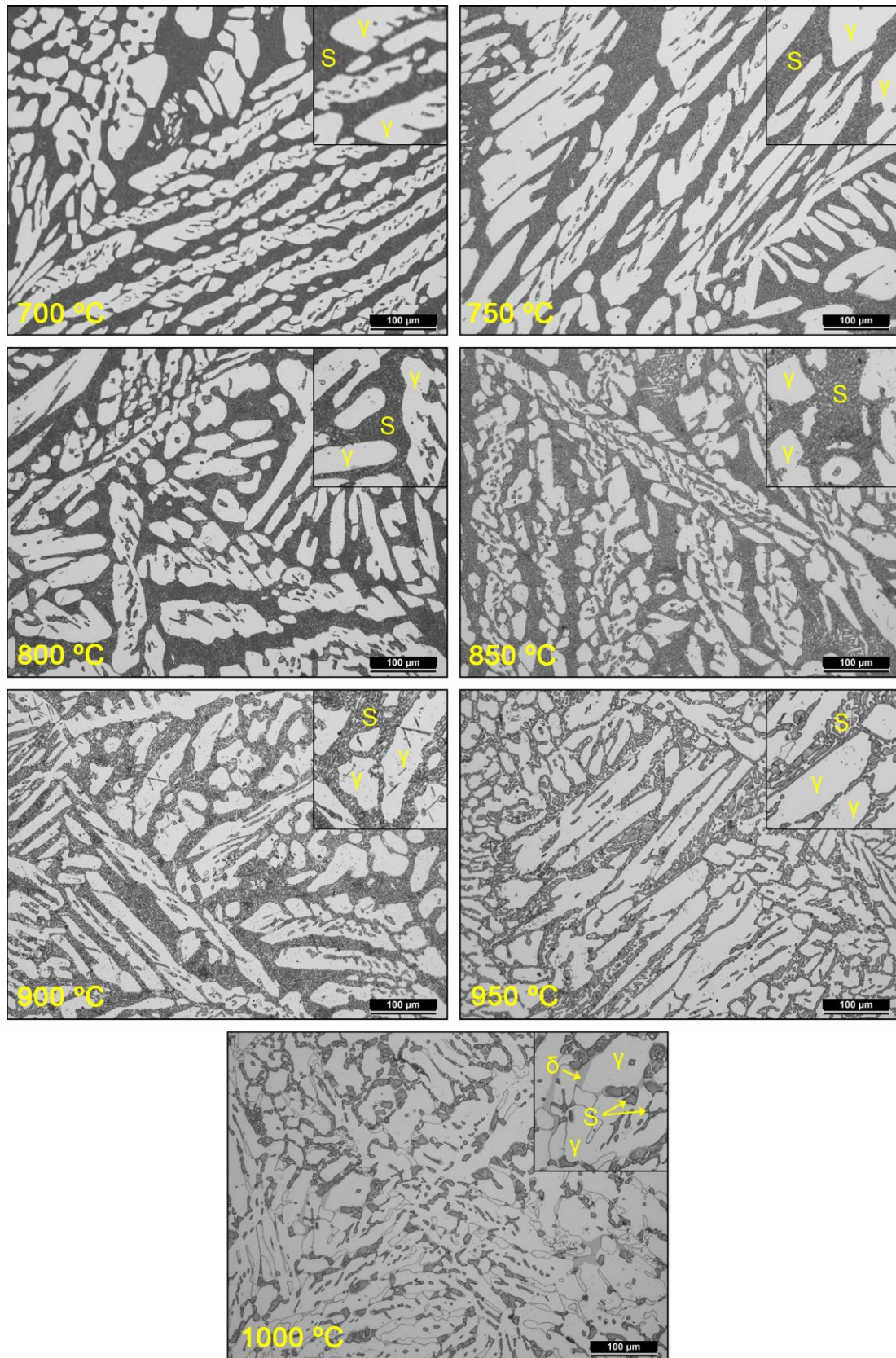


Figure 35 – Optical micrographs of samples aged for 4320 min at temperatures ranging from 700 °C up to 1000 °C. The secondary phases (S) nearly replaced the δ -phase grains for all aging temperatures.

Regarding the secondary phases, the onset of precipitation was affected by the aging temperature. The precipitation was faster between 900 °C and 1000 °C (1 min at 900 °C and 950 °C and 2 min at 1000 °C). For aging temperatures below 900 °C, the precipitation occurred more slowly as the temperature decreased (4 min at 850 °C, 8 min at 800 °C, and 16 min at 700 °C and 750 °C).

The precipitation sites and the morphology of secondary phase particles depend on the aging temperature. At 700 °C and 750 °C and for aging times up to 32 min, round sub-micrometer precipitates were found to be randomly distributed in the δ -phase (see Figure 26 to Figure 31). At 800 °C and higher temperatures, round particles randomly distributed in the δ -phase were observed, as well as the precipitation of coarser particles with an irregular outline (see Figure 30 and Figure 31). Furthermore, as the dwelling time is increased (see Figure 32 to Figure 35), the coarsening of secondary particles is noticeable for all temperatures studied. For the longest aging time (4320 min), it is possible to observe that the secondary phases nearly replaced the δ -phase.

The OM observations show that the secondary phases grow at the expense of the δ -phase. The increase in aging time leads to a decrease of the volume percent of δ -phase and an increase of secondary phases, while the volume percent of γ -phase remains approximately stable, as shown in Figure 36. That is valid for all temperatures studied based on the image segmentation results using ImageJ.

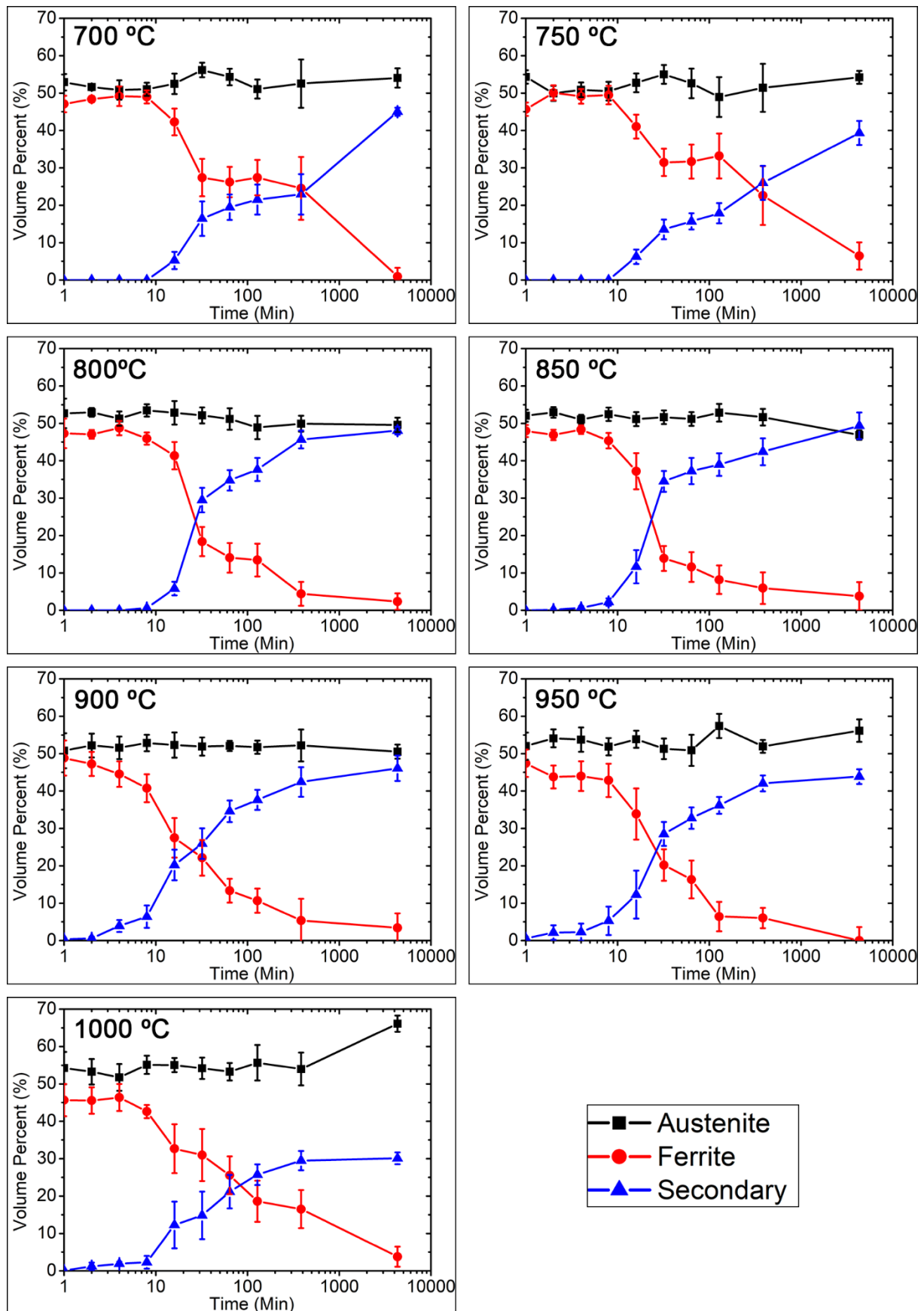


Figure 36 – Evolution of the volume percent of secondary phases, δ -phase, and γ -phase, as a function of aging time and temperatures ranging between 700 °C and 1000 °C.

Regarding the identification of secondary phases, OM does not provide the appropriate contrast for distinguishing between the various phases using the available etchants. This limitation of OM has been previously reported elsewhere [13, 14, 17, 54, 56]. So, the observation and identification of the secondary phases were performed by SEM/BSE imaging mode and TEM. The next sub-sections detail these analyses.

4.4.2 Scanning Electron Microscopy Observations

SEM/BSE imaging mode facilitates the identification of the various secondary phases exhibiting distinct chemical compositions because the contrast associated with this imaging mode is very sensitive to the average atomic number of the phases. As a result, the phases rich in heavy elements appear brighter in SEM/BSE images. Thus, SEM/BSE observations combined with EDS analysis are valuable to characterize the phases present. According to the literature [12, 13, 139-141], χ -phase is the richest phase in Mo and W, σ -phase is the richest in Cr, and γ -phase is the richest in Ni. Therefore, using the grey level scale of the SEM/BSE images, the brightest phase corresponds to the χ -phase; light grey areas are associated with the σ -phase, which are Cr-rich, while the medium grey regions are enriched in Ni and correspond to the γ -phase. The level of grayscale contrast of δ -phase is similar to that of γ -phase. Table 5 shows the relationship between SEM/BSE contrast, chemical composition, and the various phases formed during aging at 950 °C. In this fashion, it is thus possible to understand and discuss the mechanisms of secondary phase formation.

Table 5 – Chemical composition (weight percent) of the various phases of the super DSS obtained by SEM-EDS after aging at 950 °C.

Fe	Cr	Ni	Mo	W	Mn	Cu	Si	Phase	Grey level
47.7 ± 1.7	25.2 ± 0.9	3.8 ± 0.3	16.1 ± 1.7	5.1 ± 0.6	0.4 ± 0.1	0.3 ± 0.3	1.4 ± 0.1	X-phase	White
53.1 ± 2.0	29.3 ± 1.3	4.7 ± 0.6	8.0 ± 1.1	2.6 ± 0.4	0.4 ± 0.1	0.6 ± 0.3	1.2 ± 0.1	σ -phase	Light grey
60.0 ± 0.4	23.0 ± 0.2	9.3 ± 0.3	3.3 ± 0.1	1.3 ± 0.2	0.7 ± 0.1	1.6 ± 0.2	0.9 ± 0.1	γ -phase	Medium grey
59.8 ± 1.9	26.7 ± 0.4	5.1 ± 0.6	4.4 ± 1.1	1.6 ± 0.4	0.4 ± 0.2	1.0 ± 0.3	1.0 ± 0.1	δ -phase	Medium grey

The evolution of the χ -phase and σ -phase as a function of aging time was observed by SEM/BSE (Figures 37 to 46). The analysis of the aged samples revealed that for temperatures varying from 700 °C to 1000 °C, the balance between the δ -phase and γ -phase is disrupted.

Thus, the duplex microstructure is transformed into a mixture of γ -phase, δ -phase, χ -phase, and σ -phase. As the precipitation of the χ -phase and σ -phase is the root cause for the degradation of the mechanical and corrosion performance of super DSS [1, 36, 142, 143], it is fundamental to understand the mechanisms and kinetics of secondary phases formation. It should be noted that for an aging time of 1 min, χ -phase was not observed for temperatures under 900 °C. Also, for an aging time of 2 min, χ -phase was not observed for temperatures under 800 °C. That is why the corresponding images were not included.

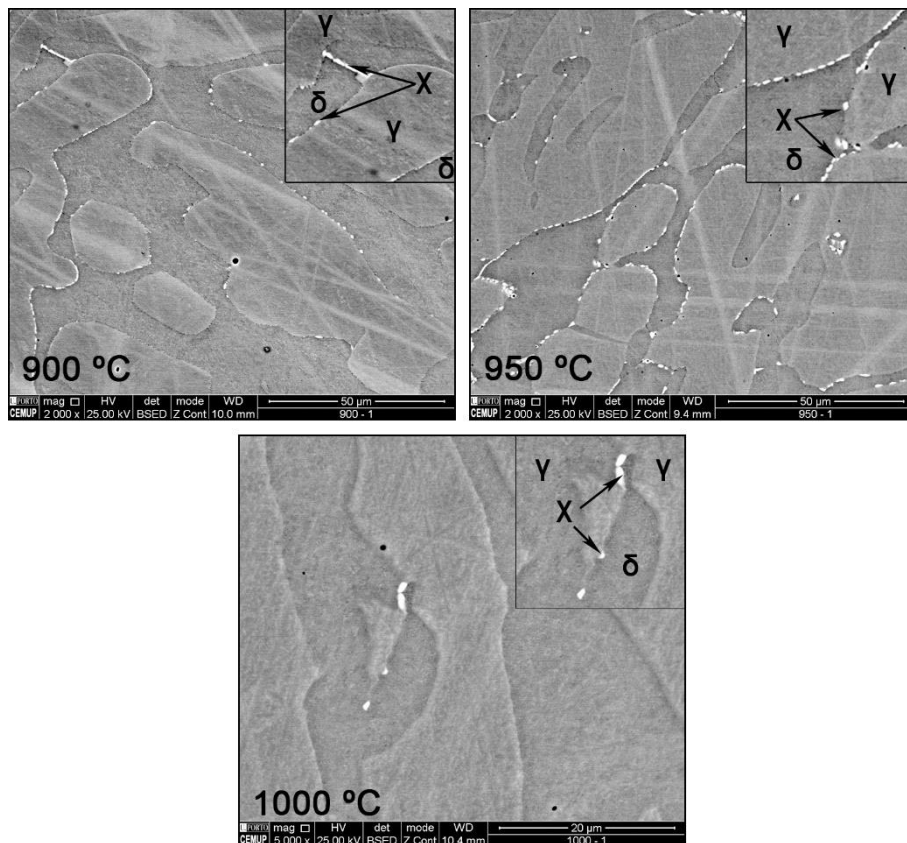


Figure 37 – SEM/BSE micrographs of samples aged for 1 min at temperatures ranging from 900 °C up to 1000 °C. The χ -phase is the white phase precipitated at the δ/γ grain boundaries.

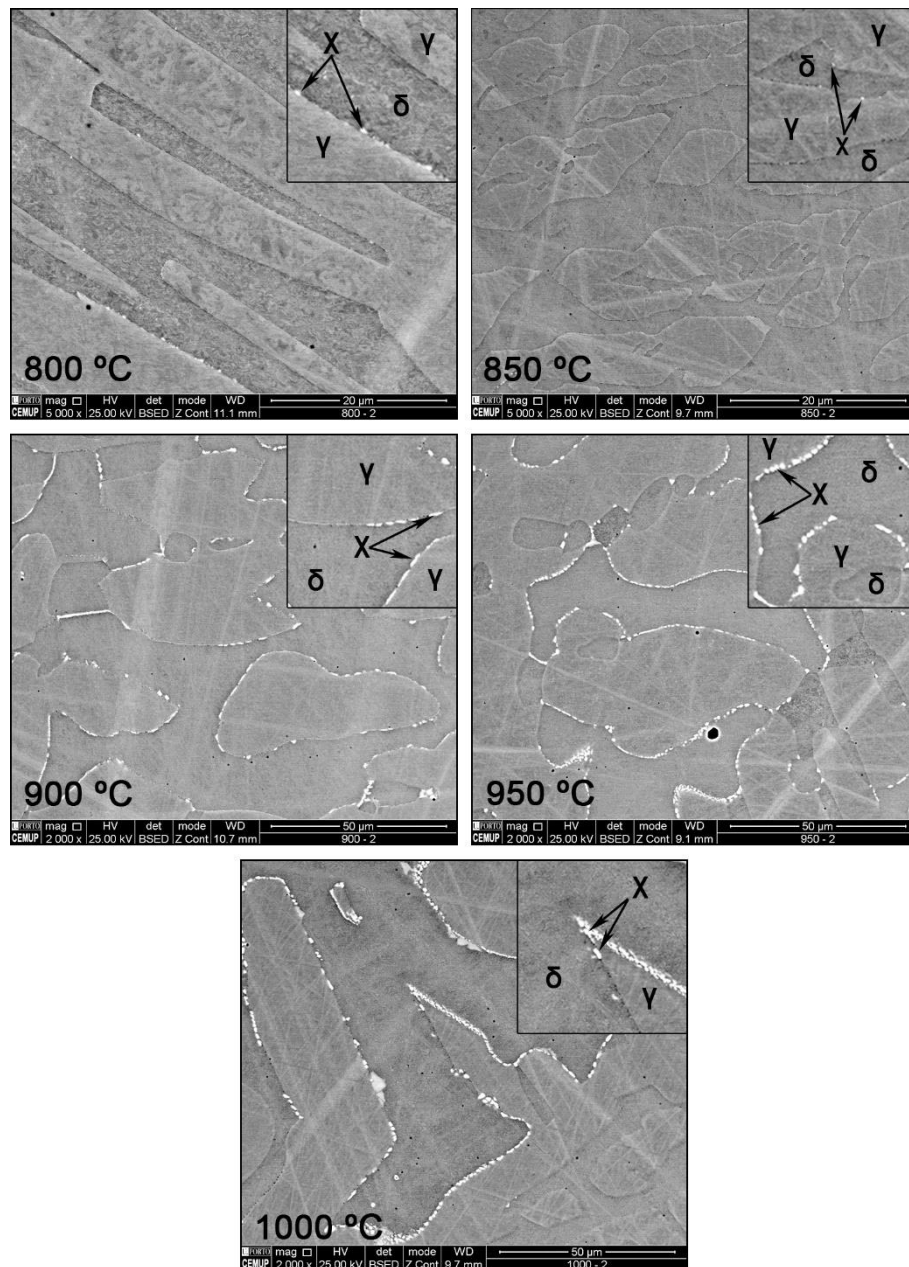


Figure 38 – SEM/BSE micrographs of samples aged for 2 min at temperatures ranging from 800 °C up to 1000 °C. The presence of χ -phase precipitates at the δ/γ grain boundaries at higher aging temperatures is more evident.

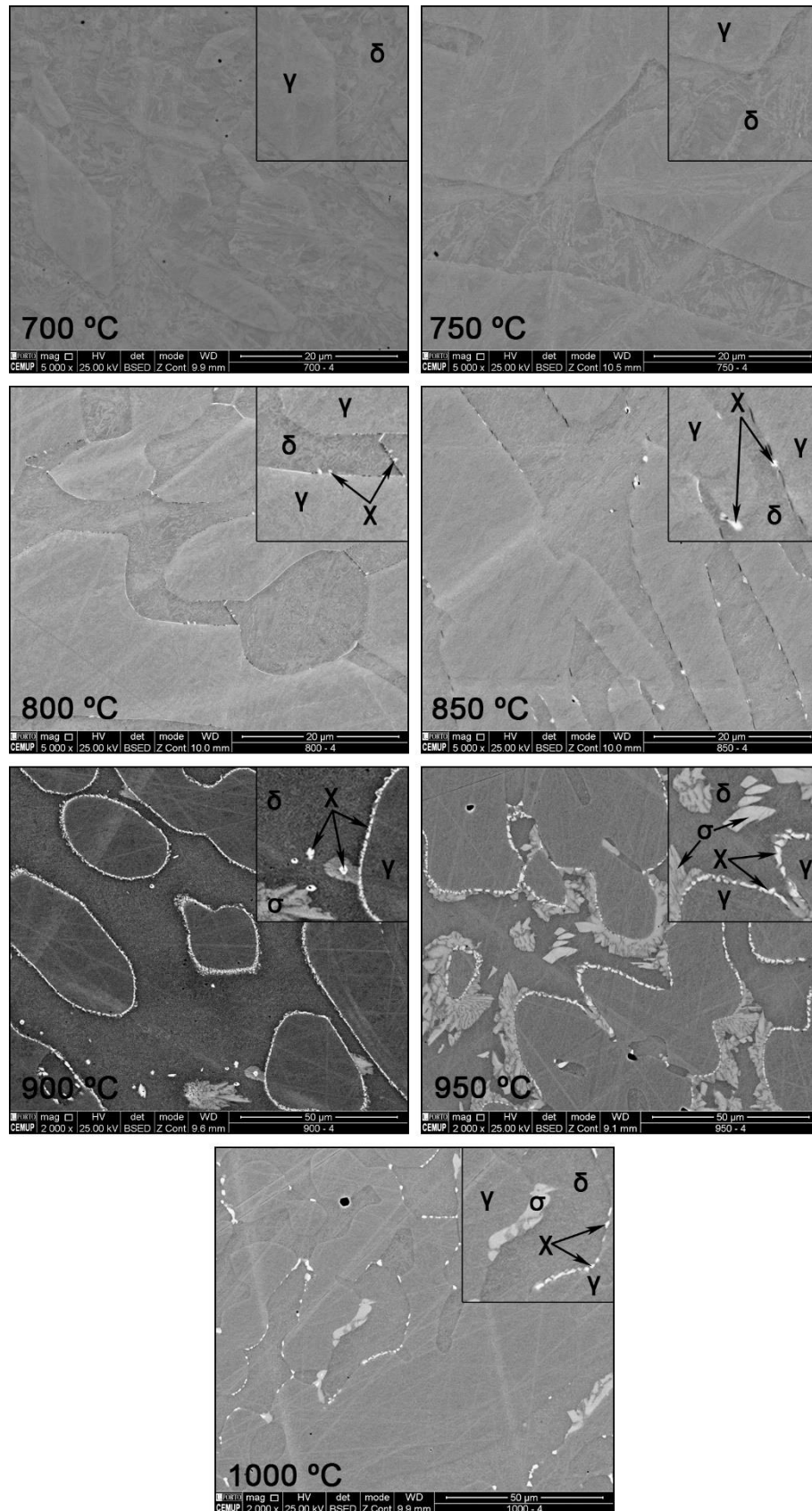


Figure 39 – SEM/BSE micrographs of samples aged for 4 min at temperatures ranging from 700 °C up to 1000 °C. The σ -phase is the light grey phase precipitated at the δ/γ grain boundaries and inside the δ phase, for 900°C and higher aging temperatures. Some particles of χ -phase are noticed within the σ -phase.

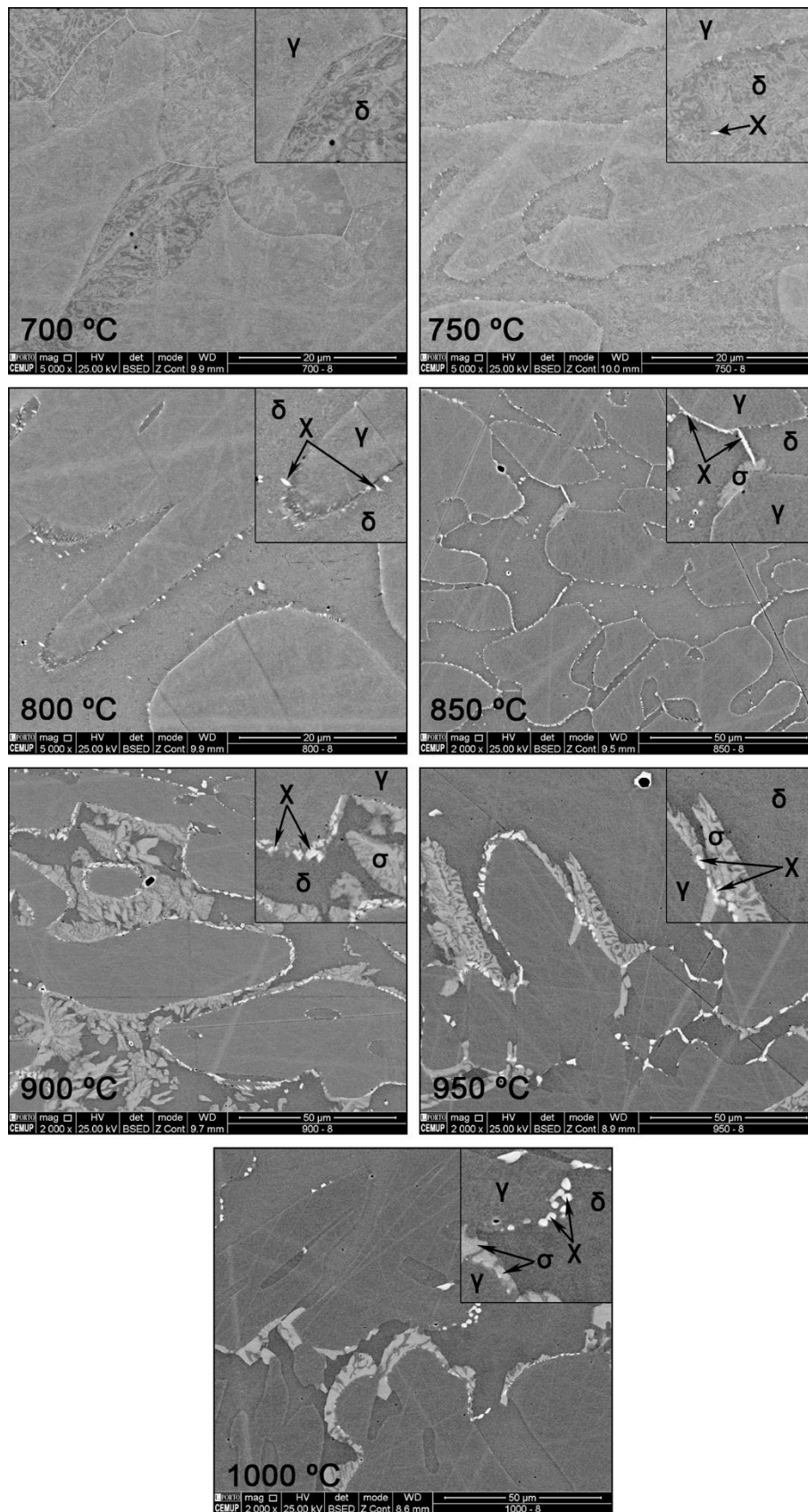


Figure 40 – SEM/BSE micrographs of samples aged for 8 min at temperatures ranging from 700 °C up to 1000 °C. There is significant precipitation of σ -phase (light grey phase) in the δ -phase grains for 900°C and higher aging temperatures.

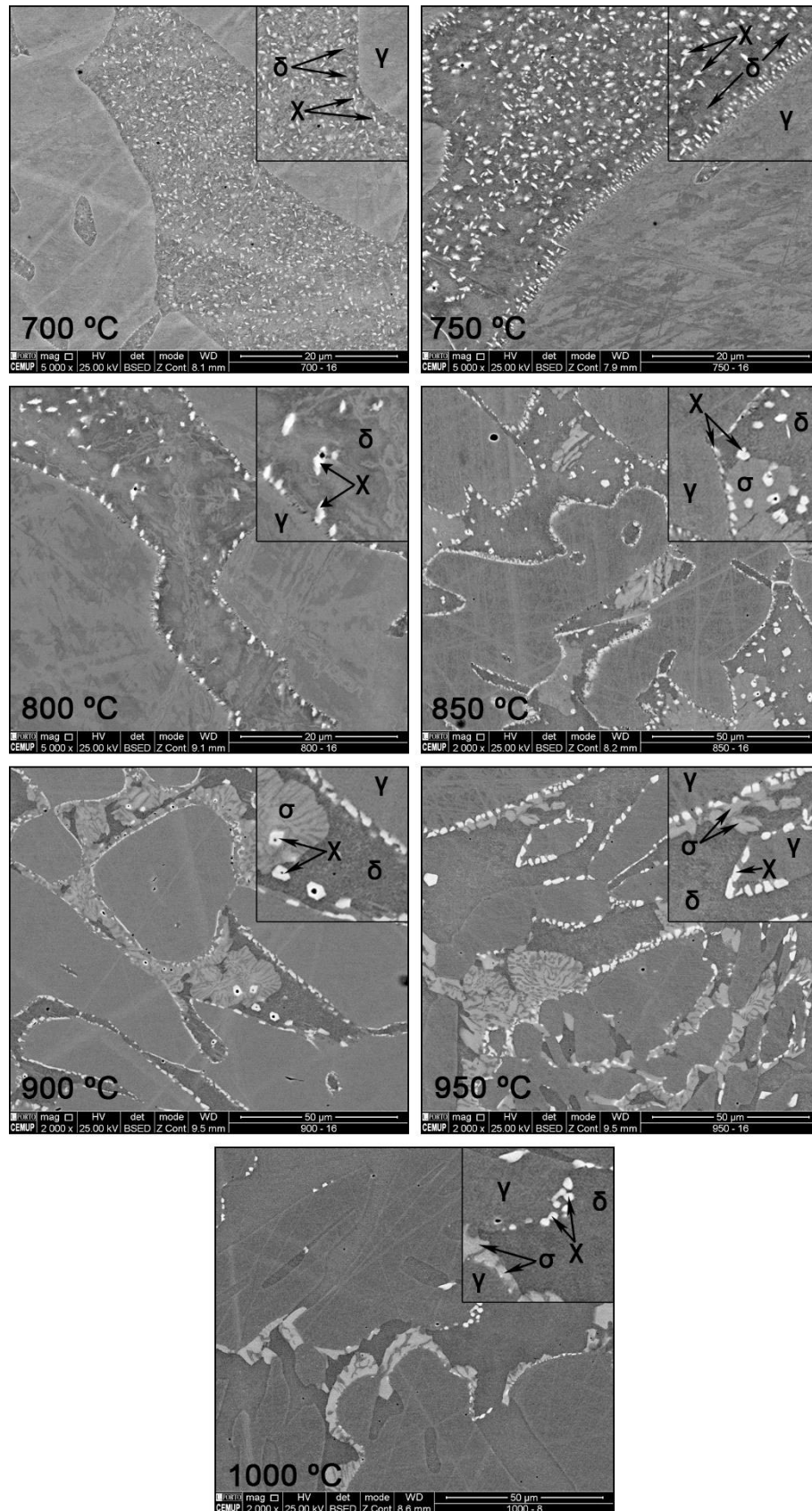


Figure 41 – SEM/BSE micrographs of samples aged for 16 min at temperatures ranging from 700 °C up to 1000 °C. The χ -phase is randomly distributed in the δ -phase for 700 °C and 750 °C. A lamellae structure of σ -phase is well observed at 900°C, and some particles of χ -phase are noticed inside the σ -phase.

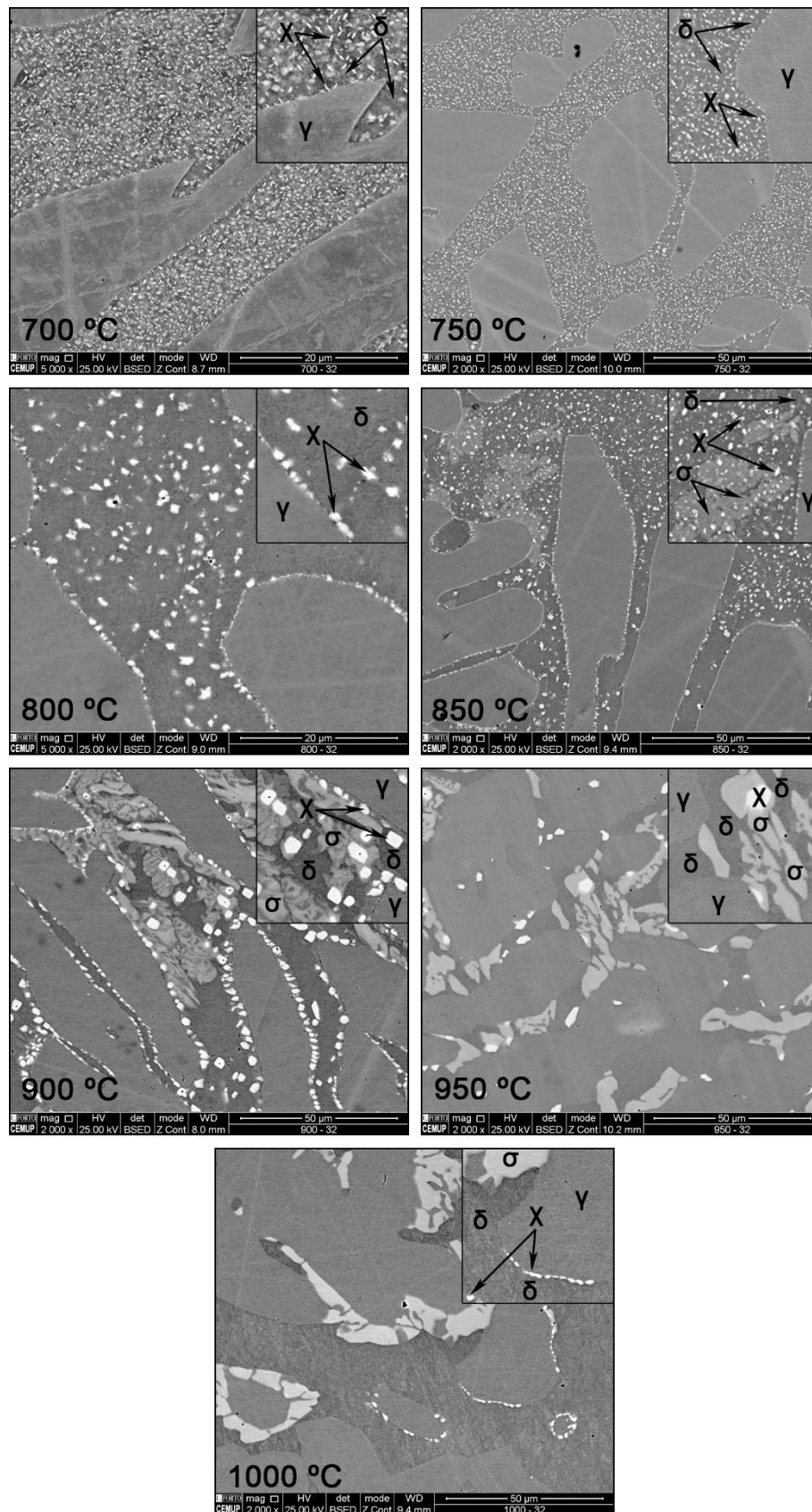


Figure 42 – SEM/BSE micrographs of samples aged for 32 min at temperatures ranging from 700 °C up to 1000 °C. The χ -phase is randomly distributed in the δ -phase for temperatures up to 850°. There is significant precipitation of σ -phase within the δ -phase for 900°C and higher aging temperatures.

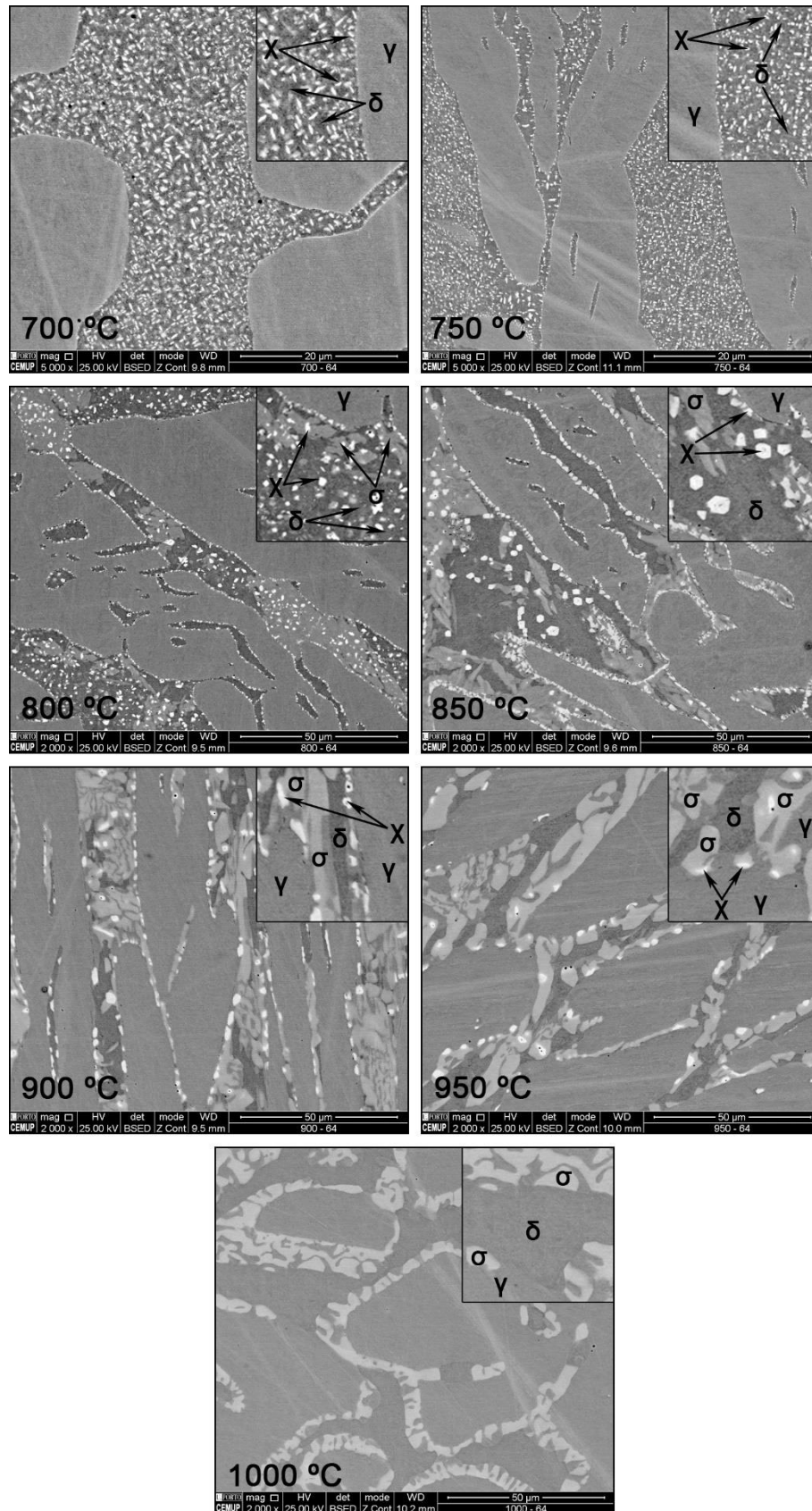


Figure 43 – SEM/BSE micrographs of samples aged for 64 min at temperatures ranging from 700 °C up to 1000 °C. The χ -phase is randomly distributed in the δ -phase for temperatures below 800 °C. There is significant precipitation of σ -phase within the δ -phase for 800°C and higher aging temperatures.

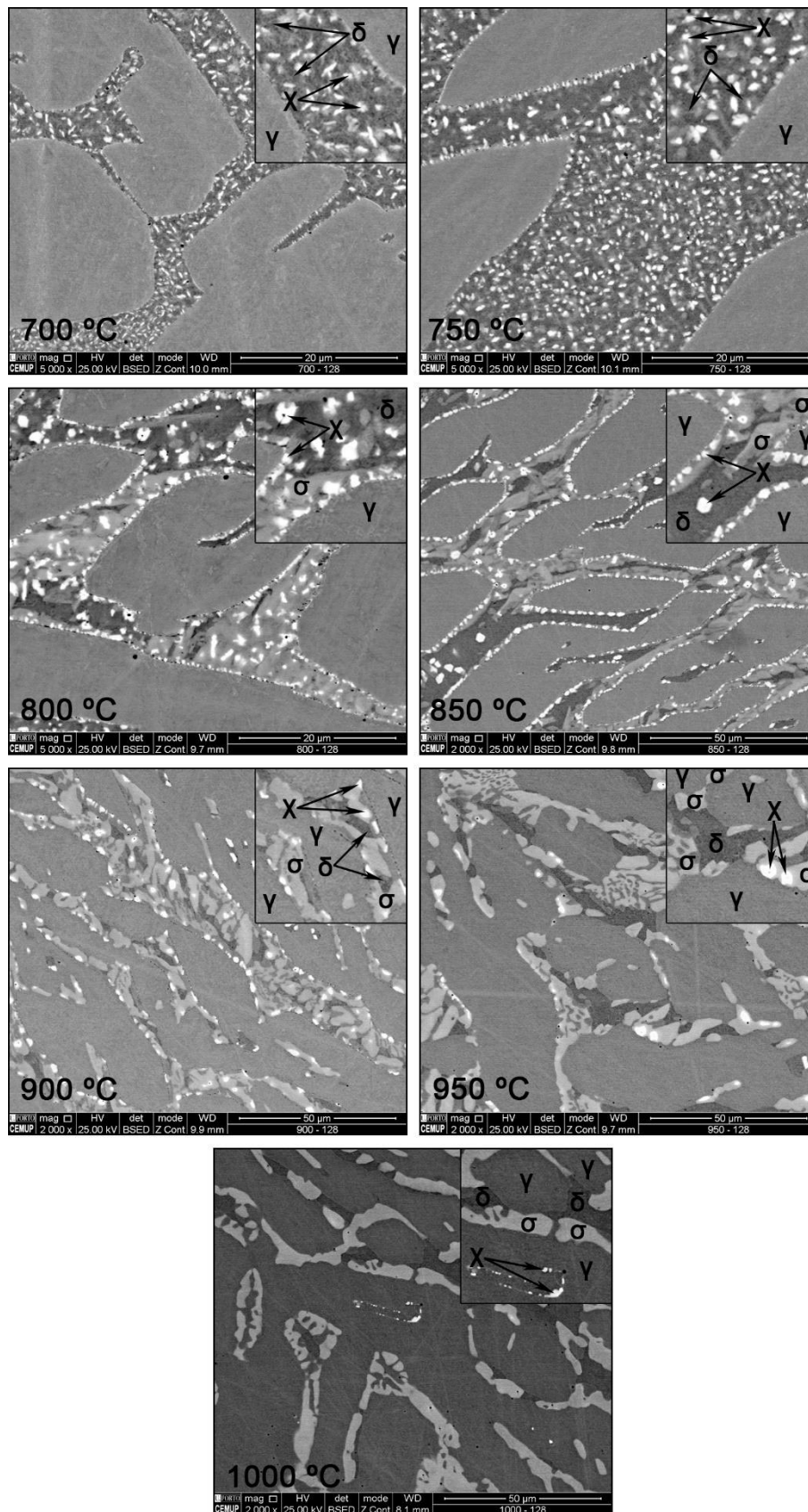


Figure 44 – SEM/BSE micrographs of samples aged for 128 min at temperatures ranging from 700 °C up to 1000 °C. For temperatures below 800 °C, the χ -phase is randomly distributed in the δ -phase. The precipitation of the σ -phase in the δ -phase increased significantly for 800 °C and higher temperatures.

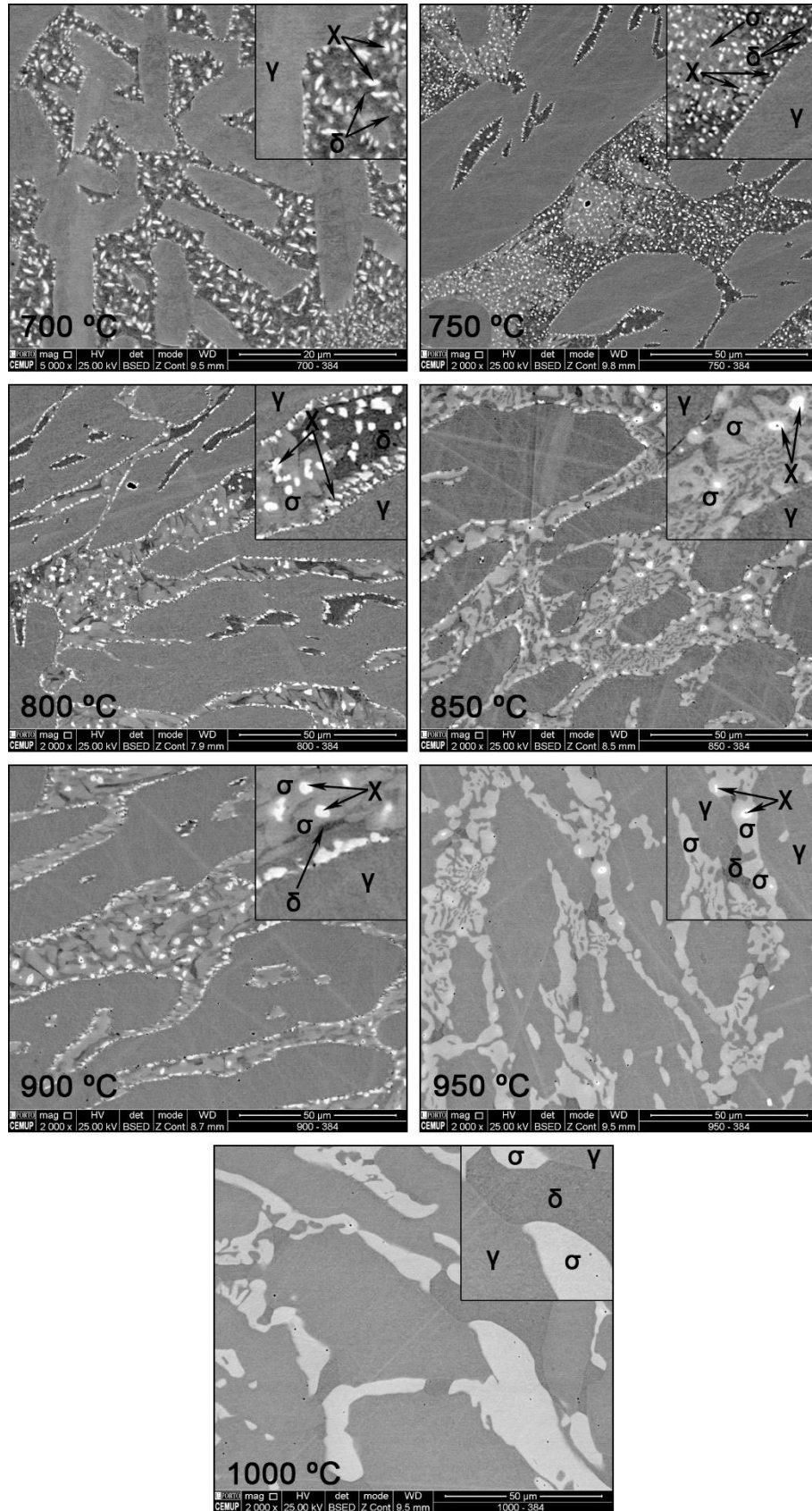


Figure 45 – SEM/BSE micrographs of samples aged for 384 min, at temperatures ranging from 700 °C up to 1000 °C. The χ -phase is randomly distributed in the δ -phase at 700 °C, and no σ -phase can be observed. There is significant precipitation of the σ -phase in the δ -phase for 750°C and higher aging temperatures.

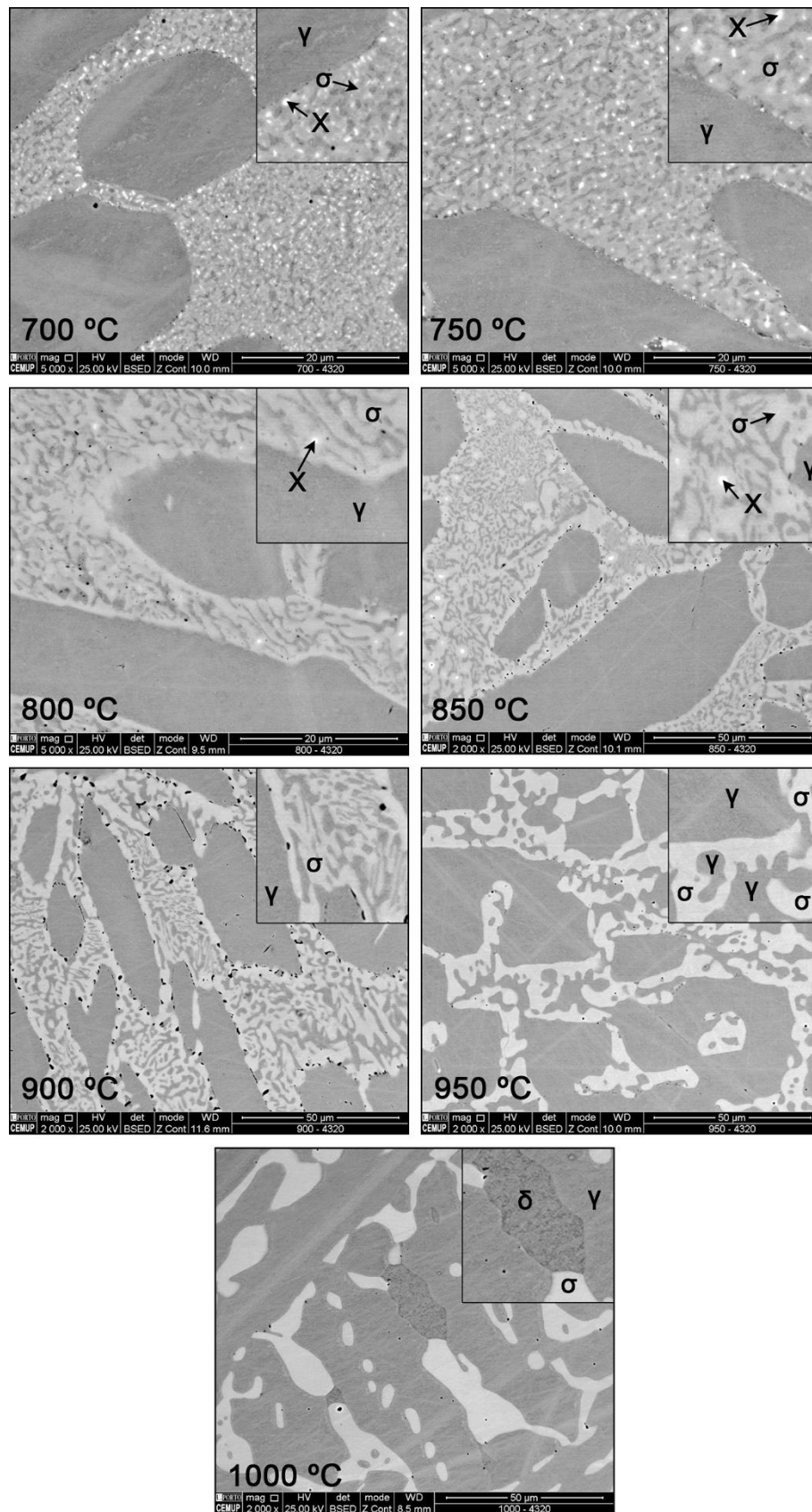


Figure 46 – SEM/BSE micrographs of samples aged for 4320 min at temperatures ranging from 700 °C up to 1000 °C. For all aging temperatures, it is clear the tendency of the σ -phase to grow until the complete consumption of the δ -phase.

For the lowest aging temperatures (700 °C and 750 °C), the χ -phase was the only secondary phase detected up to 128 min (see Figure 43), randomly dispersed within the δ -phase grains. This random distribution has not been previously documented, particularly on cast super DSS. As the aging temperature increased to 800 °C and 850 °C, the χ -phase appeared after only 2 min at the γ/δ grain boundaries (see Figure 38). At aging temperatures higher than 850 °C, the χ -phase particles were precipitated after 1 min (see Figure 37).

The SEM/BSE images show that the precipitation of χ -phase occurred earlier than the σ -phase. For the lowest aging temperatures (700 °C and 750 °C), the σ -phase was only detected after 384 min (see Figure 45), but for higher aging temperatures, σ -phase was observed on samples aged for 64 min at 800 °C (see Figure 43), 8 min at 850 °C (see Figure 40) and 4 min at 900 °C or higher (see Figure 39). These observations are in line with previous investigations [8, 12, 143]. It is interesting to note that at higher aging temperatures (between 850 °C and 1000 °C), the σ -phase exhibits a lamellar structure, which is clearly observed for 16 min or higher aging times (see Figure 41 to Figure 46). This structure is composed by σ -phase and γ -phase. This γ -phase is usually described in the literature as tertiary austenite (γ_3 -phase) to distinguish it from the primary austenite (γ -phase) that solidifies from the liquid phase, and secondary austenite (γ_2 -phase) formed by solid-state transformation from the ferrite [40].

It seems that aging at 800 °C or higher temperatures favors the precipitation of χ -phase and σ -phase at δ/γ grain boundaries (see Figure 38 to Figure 41). This means that the preferred precipitation sites depend on the aging temperature. As the aging temperature is closer to the solvus temperature, the more likely it is for χ -phase and σ -phase to precipitate at the δ/γ grain boundaries.

The SEM/BSE images allowed us to infer the tendency for the σ -phase to grow from the δ -phase, and to detect χ -phase particles within the σ -phase, which suggests that χ -phase particles are likely sites for nucleation of the σ -phase (see Figure 41 to Figure 46, relating to aging temperature of 850 °C or above). The detection of the χ -phase particles within the σ -phase was also observed by Isern [14], Yang [56] and Escriba [12]. The mechanism of σ -phase precipitation has been discussed in previous studies [14, 40, 132, 140, 144] and it is well accepted that it is a byproduct of the eutectoid decomposition $\delta \rightarrow \sigma + \gamma_3$. Another possibility involves the χ -phase as an intermediate precipitate in the transformation of the σ -phase [56].

As a result of the identification of the secondary phases by SEM/BSE, it was possible to obtain the quantification of the χ -phase and σ -phase by image segmentation using ImageJ. The result of this analysis is shown in Figure 47, where the volume percent of the χ -phase and

σ -phase are presented. At this point, the total volume percent of σ -phase formed (σ -phase from χ -phase and δ -phase) was compared to the volume percent of σ -phase formed from only the δ -phase. Accordingly, the volume percent of σ -phase formed from δ -phase was estimated as follows:

$$V_{\sigma,\delta} = V_{\sigma,t} - (V_{\chi,T} - V_{\chi,t}) \quad (\text{Eq. 9})$$

where $V_{\sigma,t}$ represents the volume percent of σ -phase measured at aging time t , and $(V_{\chi,T} - V_{\chi,t})$ represents the σ -phase formed from χ -phase, where $V_{\chi,T}$ is the maximum volume percent of χ -phase measured at aging temperature T , and $V_{\chi,t}$ is the volume percent of χ -phase measured at aging time t . As $(V_{\chi,T} - V_{\chi,t})$ is a significantly small value, only a reduced amount of σ -phase is formed from χ -phase. Figure 47 shows that the χ -phase formed earlier than the σ -phase, reached a maximum value and then decreased for longer aging times. On the other hand, the amount of σ -phase continued to increase as a function of time until an equilibrium is reached.

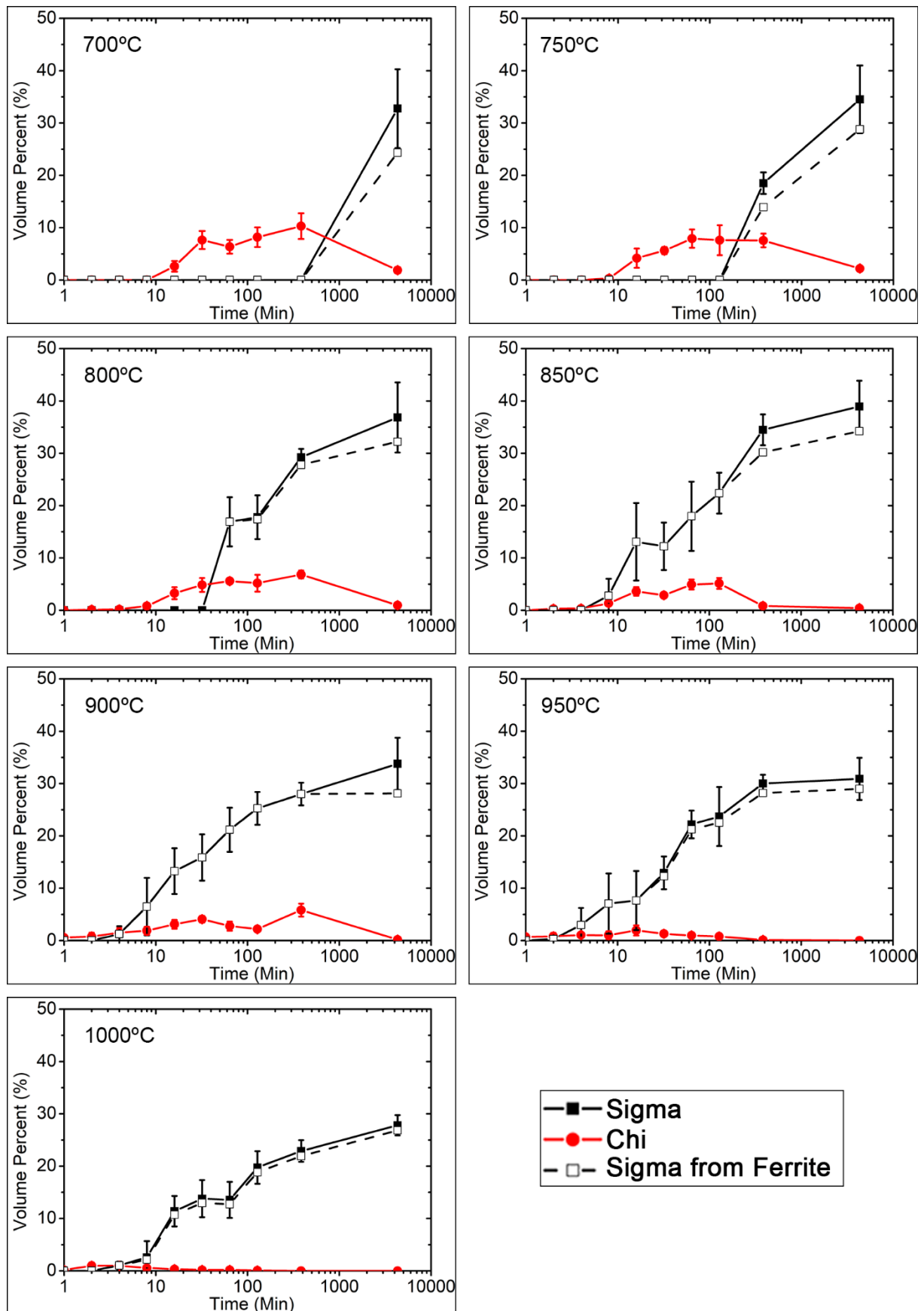


Figure 47 – Evolution of the volume percent of χ -phase and σ -phase as a function of aging time, for temperatures ranging from 700 °C up to 1000 °C.

A comparison between the volume percent of the χ -phase and σ -phase reveals that the maximum amount for the χ -phase was $10.2\% \pm 2.5\%$ at 700 °C after 384 min, while for the σ -phase was $38.9\% \pm 4.9\%$ at 850 °C after 4320 min of aging. Moreover, for temperatures below 800 °C the maximum content of the χ -phase was higher, in comparison to the maximum amount of χ -phase formed at 800 °C or above. This indicates lower stability of the χ -phase as the aging temperature was increased, which is in line with previous findings. Calliari *et al.* [7] showed that the χ -phase was the first phase to form, preferentially at the α/γ grain boundaries, during the aging of UNS S32205 steel samples. They also suggested that the χ -phase was gradually replaced by σ -phase as aging time increased. Similar conclusions were drawn [8, 12] for other wrought DSS.

4.4.3 Transmission Electron Microscopy Observations

Despite the previous description of both σ -phase and χ -phase, a complete confirmation of the secondary phases requires crystallographic information. Thus, given the complex precipitation behavior, a detailed characterization using TEM coupled with electron diffraction is necessary. However, to correlate the prior SEM data with the TEM observations, the chemical composition of each phase should match each other.

On this basis, Figures 48a and 48b show dark-field TEM images of a sample aged at 800 °C for 16 min, while characteristic diffraction patterns (SAED) obtained from this sample are shown in Figures 48c to 48e. In Figure 48a, dark particles of χ -phase dispersed within the δ -phase grains are observed. Additionally, Figure 48a shows an interface between γ -phase and δ -phase (pointed with yellow arrows). Figure 48b provides a higher magnification image of this region, where a γ/γ grain boundary is pointed with red arrows, and χ -phase precipitates embedded on γ -phase are seen. This phase distribution suggests that the formation of χ -phase may be associated with γ_2 -phase formation. Since the precipitation of χ -phase is via the diffusion of Mo, W or Cr and rejection of Ni or N, the δ -phase may become unstable and undergo a solid transformation into γ_2 -phase [40, 56].

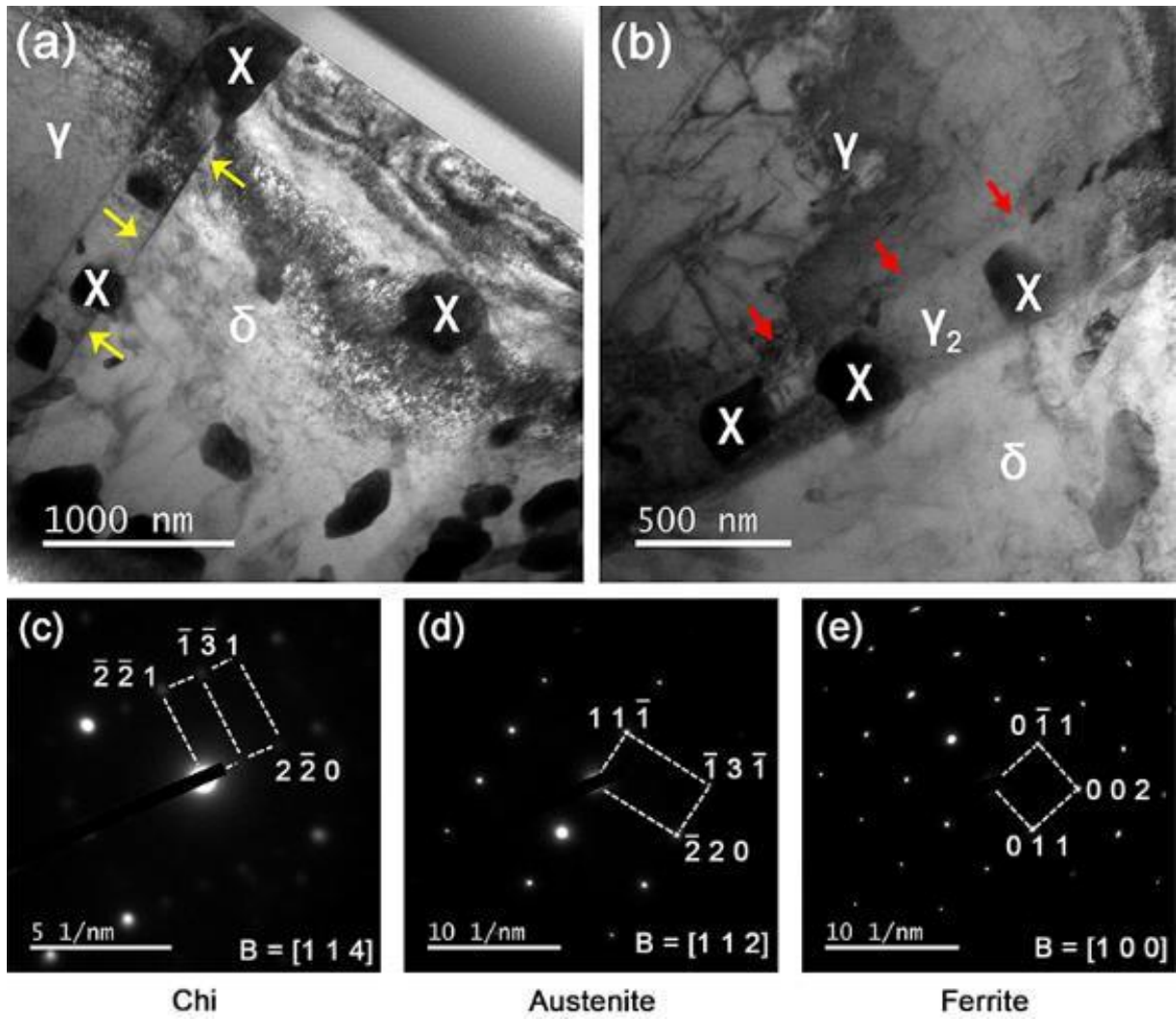


Figure 48 – Dark-field TEM image of sample aged at 800°C for 16 min showing a) interface between δ -phase and γ -phase and dark χ -phase particles and b) higher magnification of χ -phase and γ_2 -phase structure formed on γ/δ interface. The identification of phases was concluded by means of SAED with c) $[1\ 1\ 4]$ zone axis of χ -phase; d) $[1\ 1\ 2]$ zone axis of γ -phase and γ_3 -phase; e) $[1\ 0\ 0]$ zone axis of δ -phase.

Figure 49a shows a lamellar structure consisting of alternating lamellae of σ -phase and γ -phase of a sample aged at 900 °C for 32 min. This morphology has already been observed in OM and SEM/BSE images and may have resulted from the eutectoid decomposition of the δ -phase. Figure 49a also shows a χ -phase particle on the vicinity of the σ/γ lamellae structure (observed at higher magnification in Figure 42b), which is in accordance with previous SEM observations (see Figure 50 - aging temperatures between 850 °C and 1000 °C), where it was possible to detect χ -phase particles within the σ -phase. On the other hand, Figure 49b shows a δ - χ - σ triple point junction.

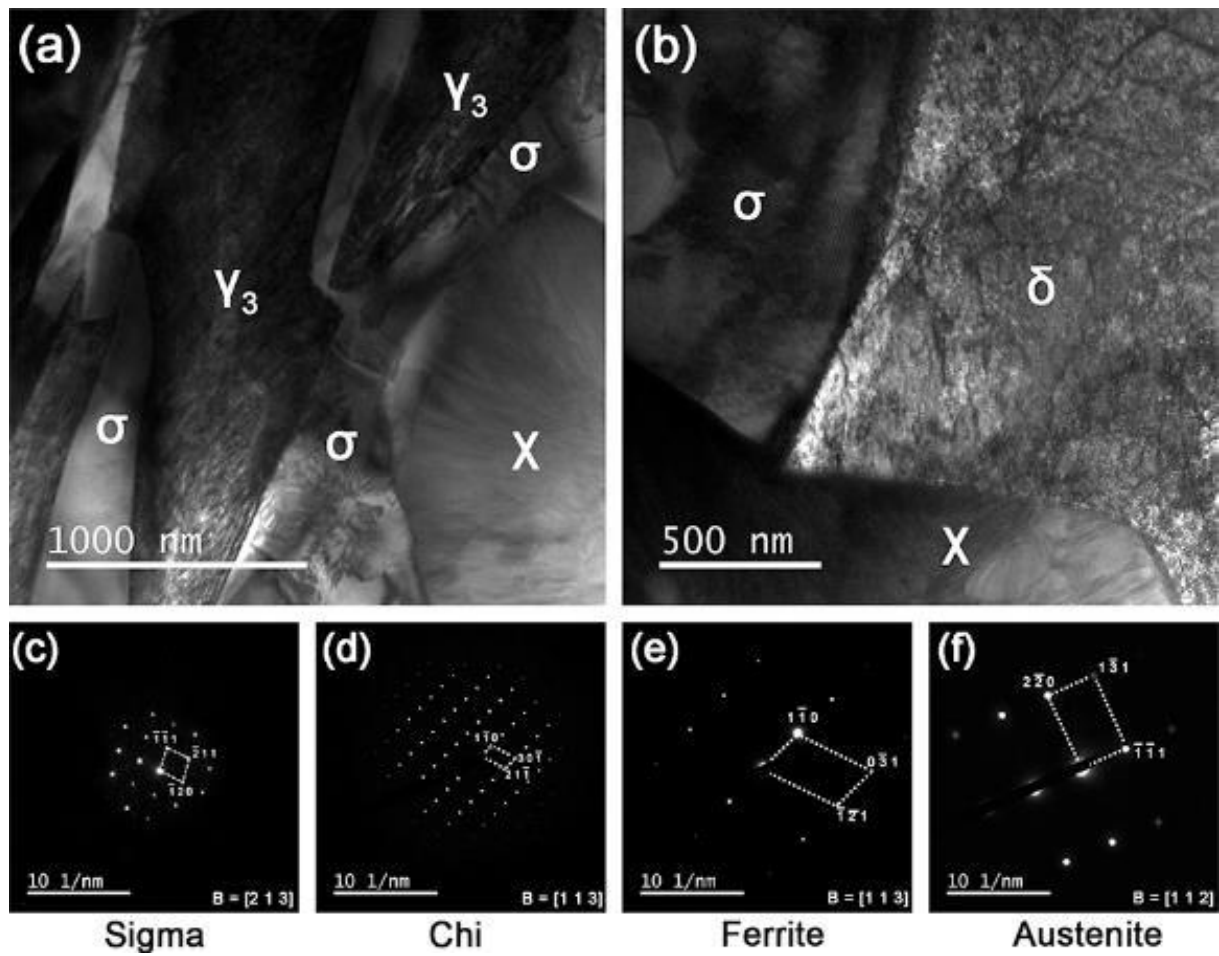


Figure 49 – Dark-field TEM image on sample aged at 900°C for 32 min showing a) the eutectoid structure of σ -phase and γ_3 -phase, as well an isolated particle of χ -phase and b) a triple point junction of δ -phase, σ -phase and χ -phase. The identification of phases was confirmed by SAED, as shown in c) by the $[2\ 1\ 3]$ zone axis of σ -phase; d) $[1\ 1\ 3]$ zone axis of χ -phase; e) $[1\ 0\ 0]$ zone axis of δ -phase and f) $[1\ 1\ 2]$ zone axis of γ -phase.

Up to this point, we have been able to detect and identify the various secondary phases, which allows us further to assess the formation kinetics of the σ -phase and χ -phase. This is an important step as there has been a lack of information concerning the quantification of both secondary phases as a function of temperature and/or time of aging, particularly for cast super DSS. This limitation is mostly due to the difficulty and time-consuming sample preparation required, as well as the combination of microscopy techniques to fully characterize the complex microstructure.

One important issue regarding the kinetics of the formation of secondary phases is the diffusion of substitutional solute elements such as Cr, Mo, and W, which are present in the χ -phase and σ -phase. In this regard, the formation of secondary phases is favored in δ -phase due to the enrichment of Cr, Mo, and W, which exhibit higher diffusion rates in this phase when compared to γ -phase. It was observed that the χ -phase nucleates first for all aging temperatures tested (Figure 47), even if it requires a significant partitioning of Mo and W. This apparent contradiction can be explained by the crystallographic similarity between the χ -phase and δ -phase, with a cubic-to-cubic orientation relationship (OR), despite the difference in lattice parameters of χ -phase ($a = 0.892$ nm) to that of δ phase ($a = 0.287$ nm) [38, 143, 145-147]. This OR, which can be analysed in the diffraction patterns obtained from χ/δ interphase boundaries, was $[111]_{\chi} \parallel [111]_{\delta}$, as shown in Figure 50.

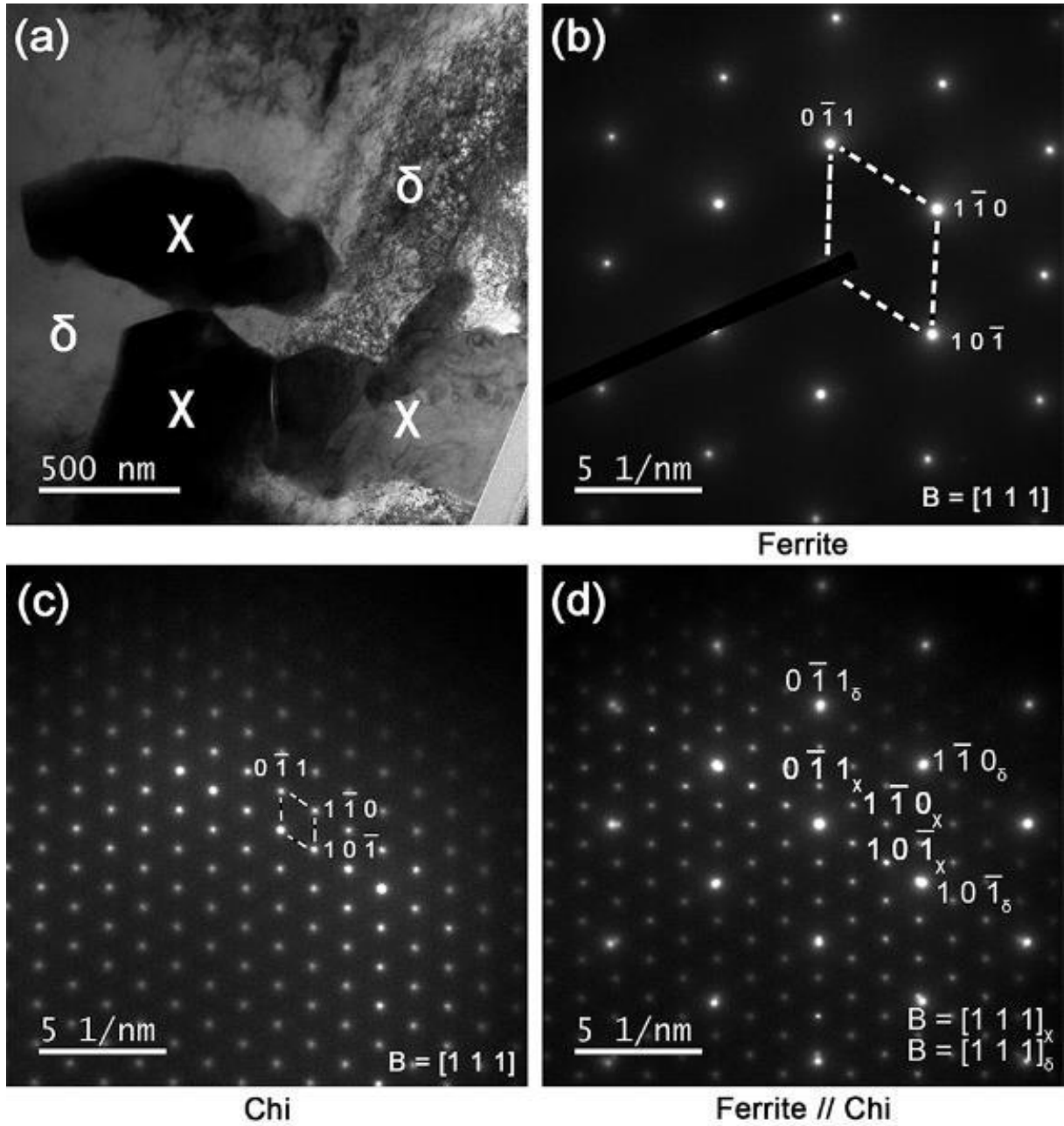


Figure 50 – Dark-field TEM image on sample aged at 800°C for 16 min showing a) dark χ -phase particles dispersed within δ -phase. The identification of phases was confirmed by SAED shown by b) $[1\ 1\ 1]$ zone axis of δ -phase and c) $[1\ 1\ 1]$ zone axis of χ -phase. The cubic-to-cubic OR was recorded on d), with diffraction spots of χ -phase and δ -phase at $[1\ 1\ 1]$ zone axis.

Although the χ -phase formed prior to the σ -phase, it disappeared after a given dwelling time, depending on the aging temperature (see Figure 47). This means that the χ -phase is metastable and undergoes a dissolution process for the aging temperatures tested. Particularly, for temperatures of 700 °C and 750 °C, the dissolution of the χ -phase is related to the growth of the σ -phase. This dissolution of metastable χ -phase precipitates may be a

consequence of the change in the δ -phase chemical composition as the σ -phase formation progresses by removing solute from the parent phase. This change in the chemical composition of the parent phase inhibits the growth of the χ -phase. The transformation from the cubic δ -phase to the equilibrium tetragonal σ -phase may assume an unconventional pathway, as it was formulated by Ni *et al.* [148], who divided it into two stages. In the first stage, the δ -phase undergoes a transformation into a metastable cubic χ -phase dispersed in the δ -phase matrix. In the second stage, the growing χ -phase particles transform into the tetragonal σ -phase. Yang *et al.* [56] proposed the following transformation mechanism $\delta \rightarrow \gamma_2 + \chi \rightarrow \gamma_2 + \sigma$, until the complete dissolution of χ -phase. Similar conclusion was drawn by Escriba *et al.* [12] and Akisanya *et al.* [8], which agrees with our observations. Besides, the kinetics of σ -phase formation within the temperature range studied would not be significantly affected by the χ -phase particles, given its little amount in the microstructure.

4.4.4 Transformation Kinetics of Secondary Phases

Following the discussion of the transformation mechanisms, the experimental data allowed us to develop a model for the transformation kinetics of σ -phase. Therefore, the Johnson-Mehl-Avrami-Kolmogorov (JMAK) approach [6, 8, 11, 54, 149] was considered, to describe the kinetics of precipitation of σ -phase. As discussed previously, the χ -phase disappears after a specific time depending on the aging temperature. Thus, the variation of the volume fraction of χ -phase with time exhibits a deviation from the sigmoidal shape. Hence, it is not surprising that the JMAK model failed to describe the formation of χ -phase.

The JMAK model is given as follows:

$$f = 1 - e^{-kt^n} \quad (\text{Eq. 10})$$

where f is the fraction of new phase formed, normalized by the amount of the new phase present at equilibrium after an isothermal treatment for a period t , k is a reaction constant sensitive to temperature, and n is the Avrami exponent, which is a dimensionless constant depending on particular nucleation and growth conditions [11, 150]. Because the volume fraction of σ -phase formed from δ -phase is very close to the total volume fraction of σ -phase formed (σ -phase formed from χ -phase and δ -phase), we have considered only the JMAK curve for the σ -phase formed from δ -phase. In our model, the volume percentage of the σ -phase at the most prolonged aging durations (4320 min) has been considered the equilibrium amount of σ -phase.

The Avrami exponent n and the constant k were experimentally determined, using data from the isothermal σ -phase transformations. The constants n and k were obtained as follows:

$$\ln(-\ln(1-f)) = \ln k + n \ln t \quad (\text{Eq. 11})$$

Thus, a plot of $\ln(-\ln(1-f))$ versus $\ln t$ gives a straight line with a slope of n , while the y-intercept can be defined by $\ln k$. This procedure was applied to all aging temperatures, considering the volume percentage of the σ -phase formed from δ -phase measured from the SEM/BSE images. The results obtained are shown in Table 6. As expected, k and n are sensitive to temperature. Higher values of k are associated with faster transformations of σ -phase during isothermal aging between 850 °C and 1000 °C. In what concerns the n parameter, similar values of n were obtained for the higher aging temperatures (800 °C to 1000 °C) and lower from those obtained for the lower temperatures (700 °C and 750 °C). The n values obtained were statistically analyzed using a t-test. The results can be approximated to $n = 1$ for the higher aging temperatures (800 °C to 1000 °C) and $n > 1$ for the lower temperatures (700 °C and 750 °C), with a 95% confidence level. The variation of this exponent n can be related to different nucleation and growth conditions involved for each temperature [151].

Table 6 – Values of the parameters n and k of JMAK equation.

Temperature (°C)	700	750	800	850	900	950	1000
k	1.0×10^{-7}	8.3×10^{-5}	3.1×10^{-3}	1.9×10^{-2}	3.1×10^{-2}	2.3×10^{-2}	2.0×10^{-2}
n	2.1	1.4	1.0	0.8	0.8	0.8	0.8

The calculated JMAK curves for σ -phase formation and the experimental points at 900 °C are shown in Figure 51. The curves indicate that the nucleation (at the plateau onset) is faster at temperatures ranging from 850 °C to 1000 °C, which results in faster kinetics for the σ -phase formation.

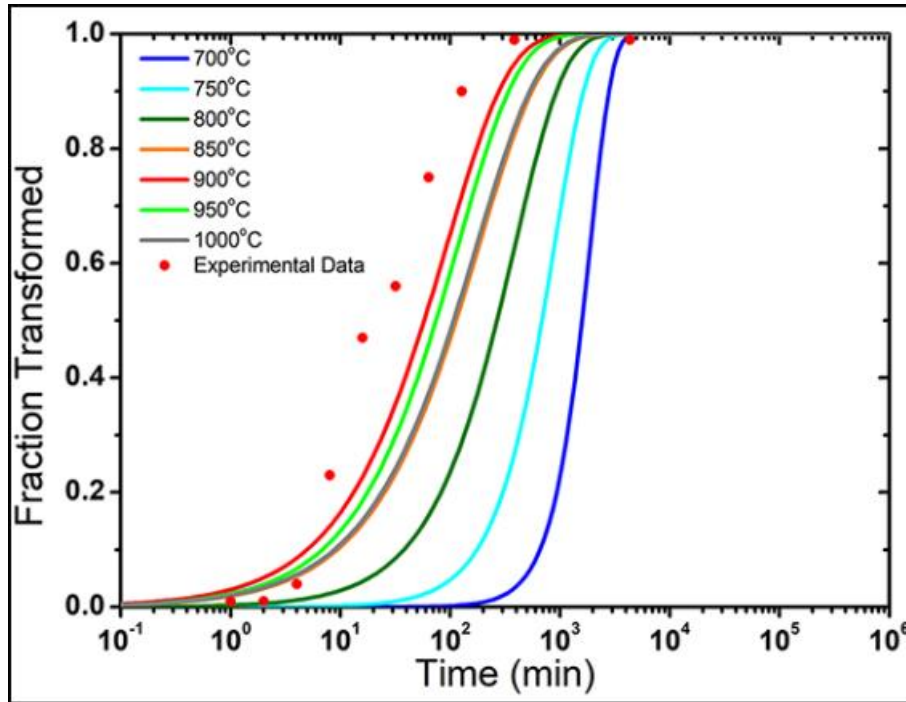


Figure 51 – JMAK curves for the σ -phase formed from δ -phase for aging temperatures ranging from 700°C to 1000°C. Experimental data for 900°C are shown on the graph.

Considering the kinetic model developed, the isothermal transformation of δ -phase into σ -phase can be represented by plotting f as a function of time and temperature as exhibited by the diagram in Figure 52. This time-temperature-transformation diagram (TTT) for σ -phase formation, between 700 °C and 1000 °C shows that the nose of the C-curve is located at 950 °C, which means that the σ -phase starts to precipitate after 30 s at this temperature. The nose of the C-curve obtained for the 25Cr-7Ni-Mo-N super DSS is located at higher temperatures and shorter times, when compared with previous studies for wrought materials [6, 150] or grades with lower alloying content [17, 54]. This difference may be a result of small variations in chemical composition between the studied stainless steels, as well as metallurgical defects that commonly occur in castings, such as chemical segregation [43], inclusions [139], and differences in grain size [54], which affects the number and distribution of nucleation sites.

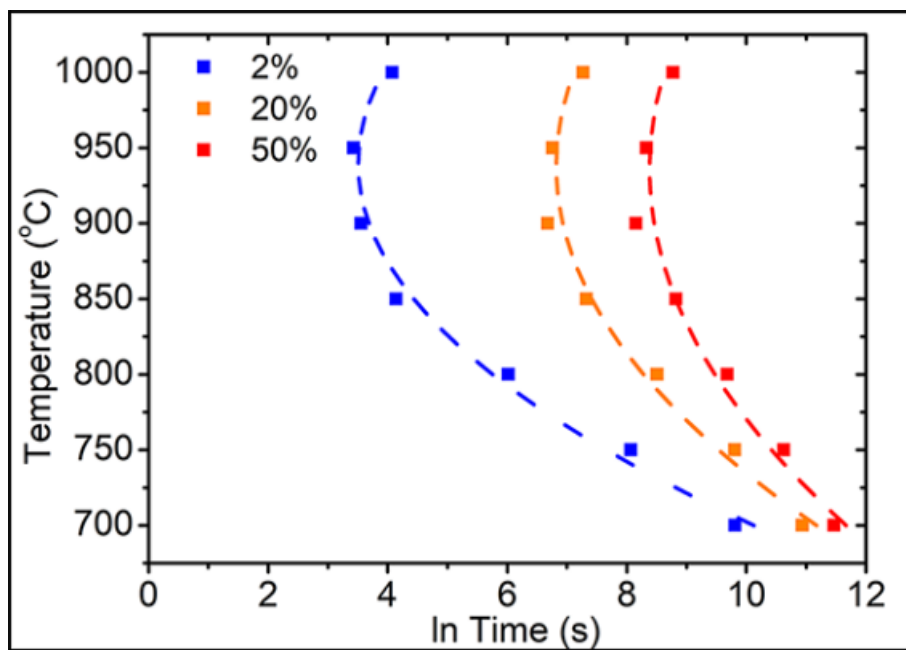


Figure 52 – Calculated TTT curves for σ -phase formed from δ -phase.

Chapter 5 Modelling the Residual Stresses of 25Cr-7Ni-Mo-N super DSS

The prediction of the residual stresses in the casting processes is an essential procedure to guarantee the structural integrity of the final parts. In this sense, this chapter discusses the results of the residual stresses simulations.

The chapter is divided into three sections. It starts by presenting the results of the thermal analysis. After having the temperature fields, the next task was to solve the mechanical model. This topic is discussed in the second section. The chapter ends with a comparison between the predicted residual stresses with measured ones, using the contour method.

5.1 Thermal Model

In this work, the numerical calculations for the residual stresses were carried out through two sequential steps (mentioned in section 3.5.1), using a methodology known as sequentially coupled thermal-mechanical analysis. Firstly, the thermal model is created. Subsequently, the stresses and deformations, which depend on temperature, are simulated. In this fashion, the temperature fields are found independently of stresses and deformations analyses.

The thermal model was developed for two stages of cooling: “before shakeout” and “after shakeout”. So, the results of these steps will be separately analysed in the next sub-sections.

5.1.1 Thermal Model for the First Stage of Cooling “Before Shakeout”

For the first simulations, the IHTC values reported in the bibliography were used, as described in section 3.5.1. These values were reported by Palumbo *et al.* [88], and are shown in Table 7.

Table 7 – Values of IHTC determined by Palumbo *et al.* [88].

Temperature (°C)	IHTC (W/m ² K)
300	194
1000	194
1200	360
1447	905
1600	905

In this way, all the material properties of the super DSS and furan-bonded sand, such as thermal conductivity, density, specific heat, as well as the initial temperature of the C-rings and the boundary conditions are defined to get a numerical solution and solve the thermal problem. The calculated temperature distribution for the C-ring-8 and C-ring-12 is shown in Figure 53 and Figure 54.

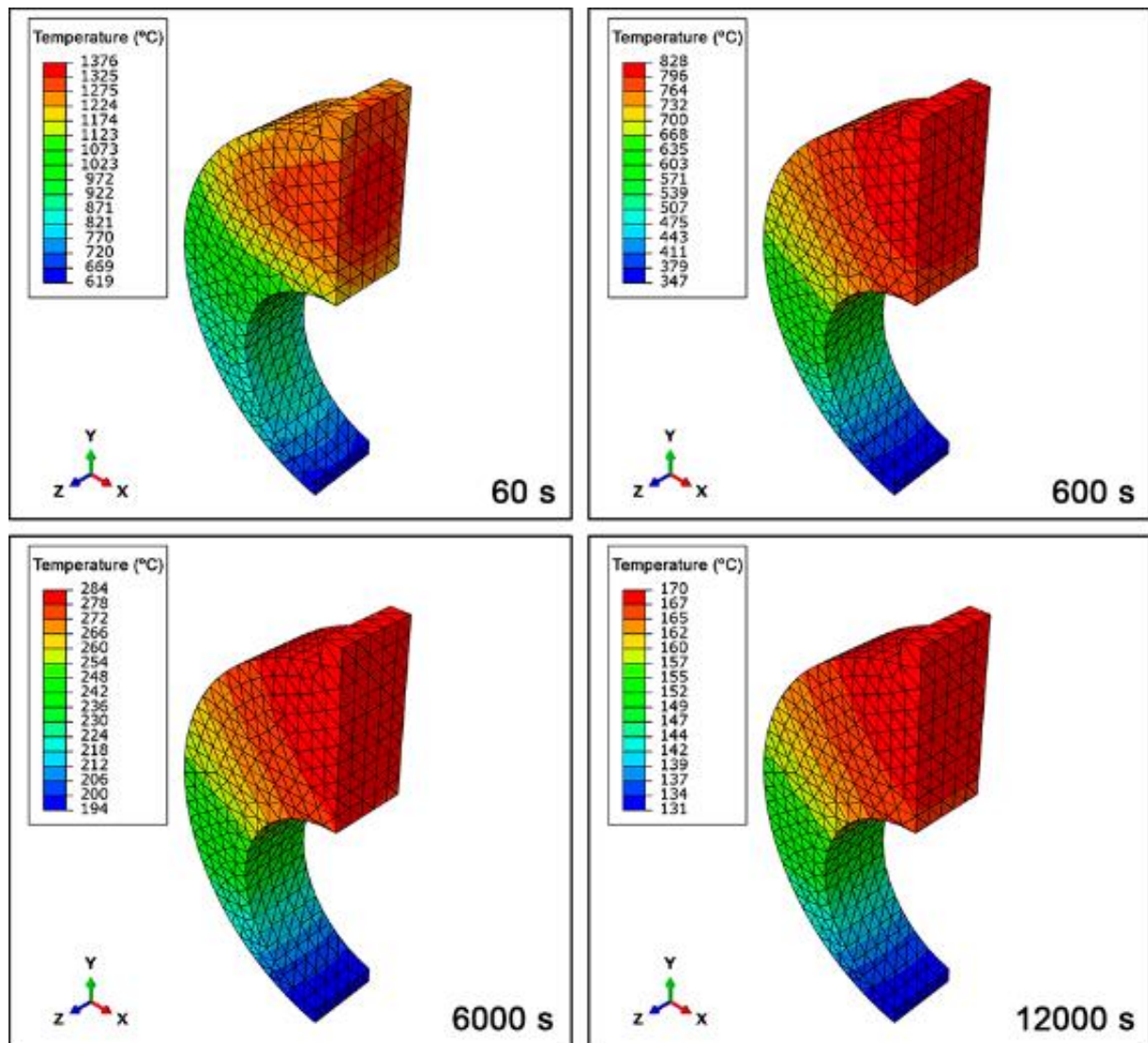


Figure 53 – Temperature distribution using the IHTC values from the literature at a) 60 s, b) 600 s, c) 6000 s, and d) 12000 s for the C-ring-8.

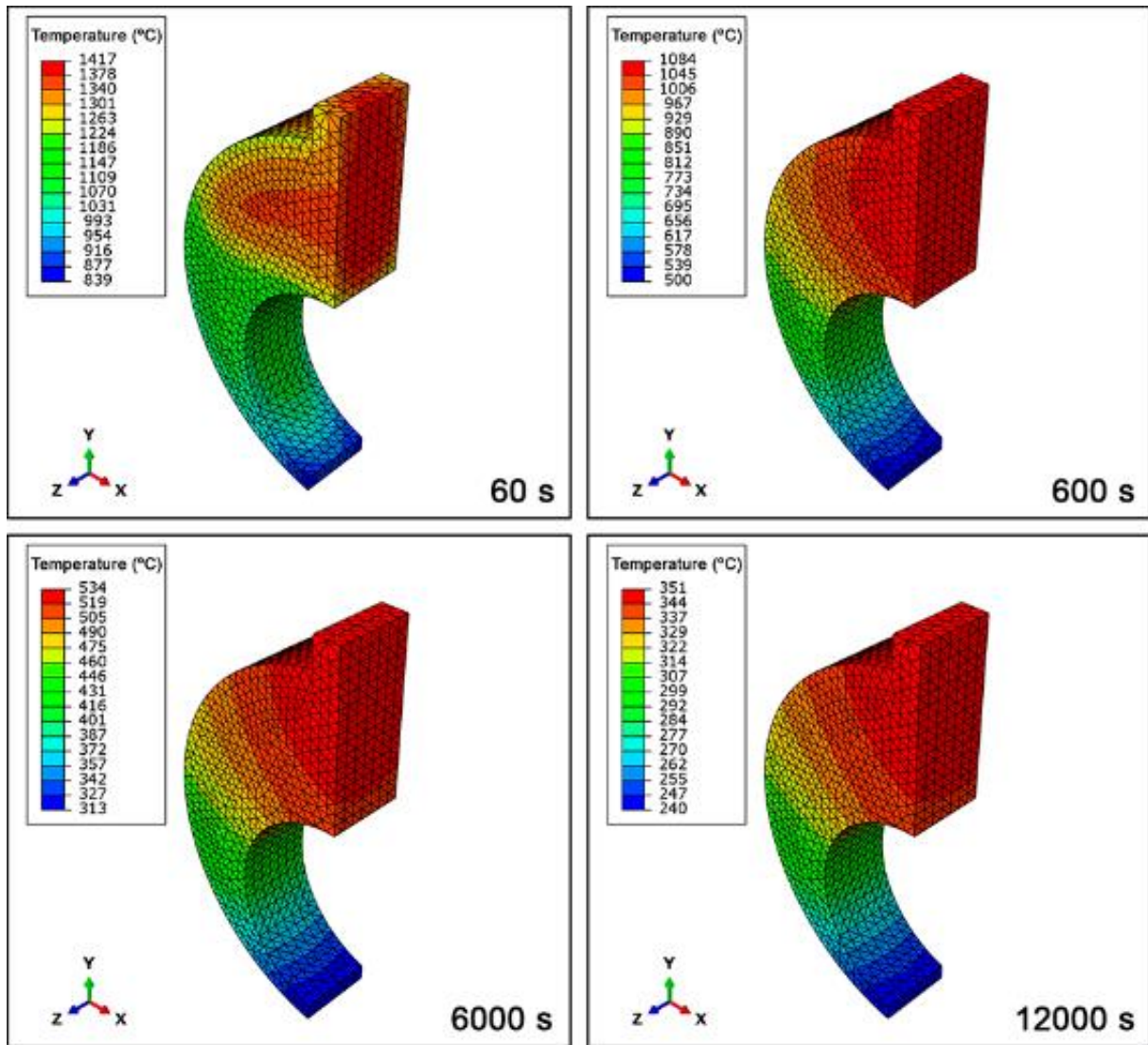


Figure 54 –Temperature distribution using the IHTC values from the literature at a) 60 s, b) 600 s, c) 6000 s, and d) 12000 s, for C-ring-12.

5.1.2 Experimental Cooling Curves of the C-rings

The experimental cooling curves obtained, as explained in section 3.2.1, are shown in Figure 55 and Figure 56, for C-ring-8 and C-ring 12, respectively. For the C-ring-8, the maximum temperature measured was 1462 °C at the thicker cross-section and 1106 °C at the thinner cross-section (see Figures 55a and 55b). In the case of the C-ring-12, the maximum temperature was 1489 °C and 1346 °C, for the thick and thin cross-section, respectively (see Figures 56a and 56b). One can conclude that the R-type thermocouples placed at the thin cross-sections were not able to record the temperature of the liquid metal during the filling of the mold cavities, as the temperature at that beginning of the pouring was around 1625 °C. In the particular case of the C-ring-8, the first value measured at the thin cross-section corresponds to the metal already solidified. This can be explained by the heating inertia of the

thermocouples, due to the outer ceramic sheaths that are embedding the hot junction. Two sheaths are necessary to ensure the functionality of the thermocouple, yet they increase the response time, estimated at around 150 s.

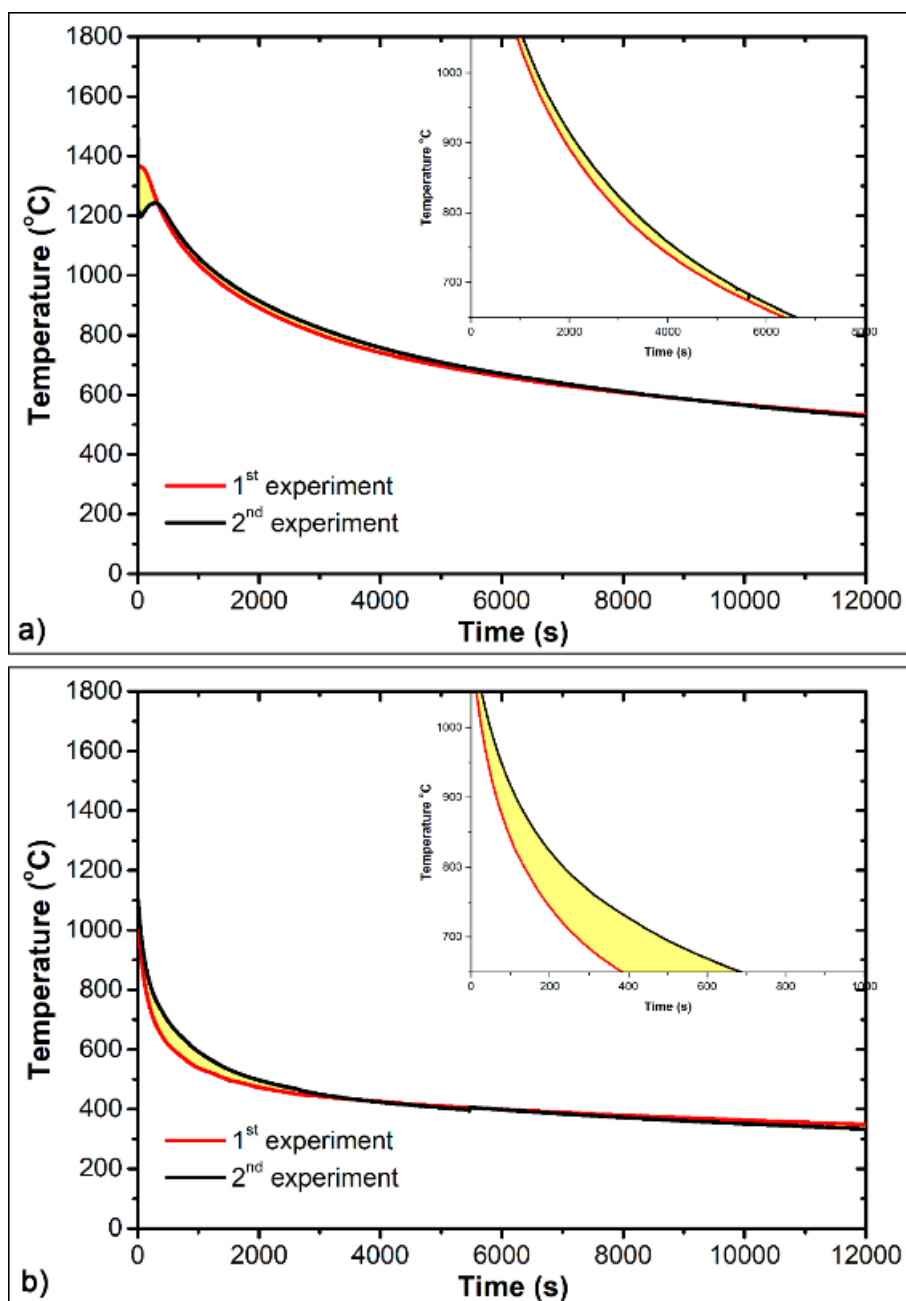


Figure 55 – Experimental cooling curves for a) thick and b) thin cross-section of C-ring-8. The zoom details the cooling curves at the temperature range of 1000 °C to 700 °C, in which the secondary phases are formed in the super DSS.

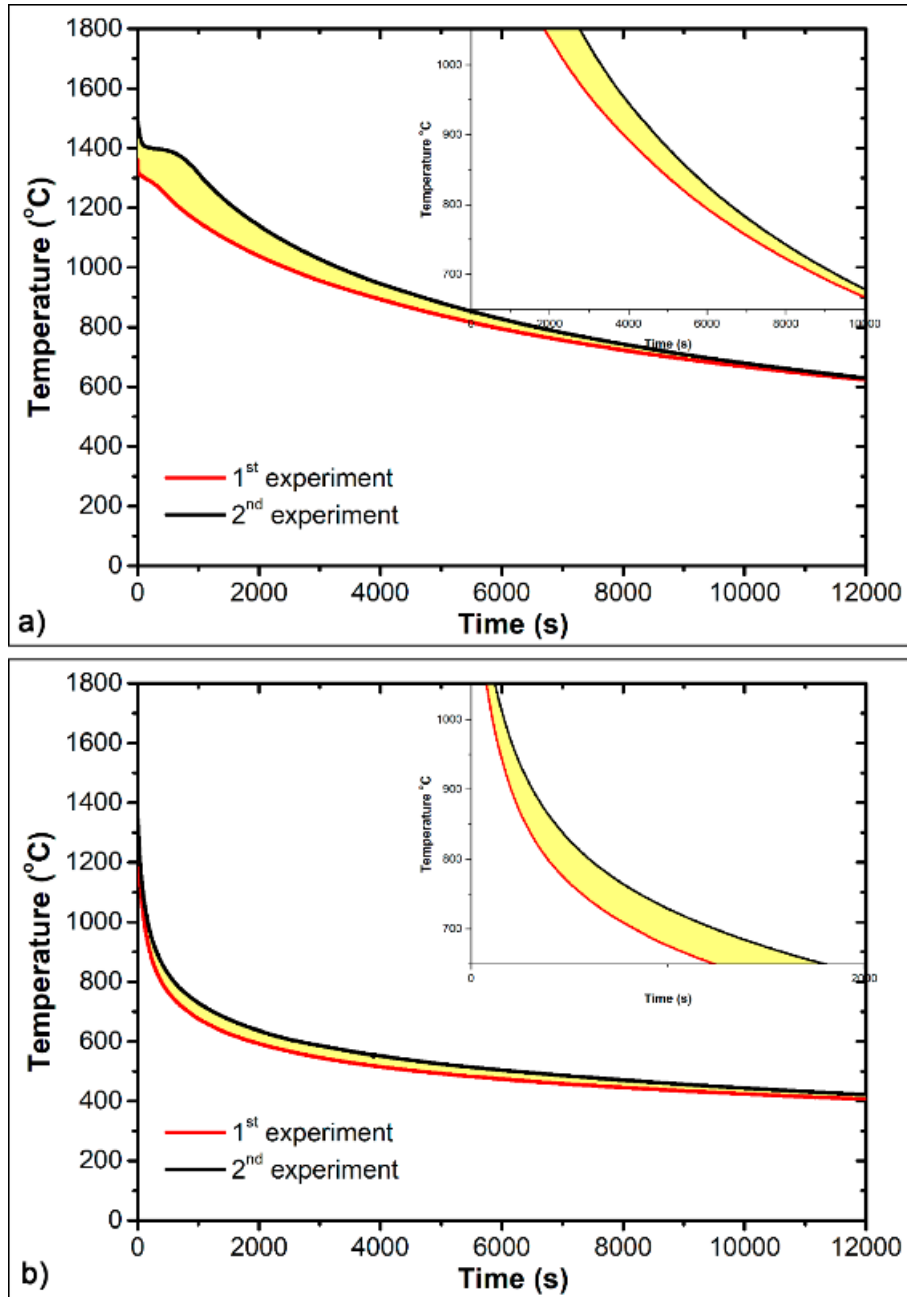


Figure 56 – Experimental cooling curves for a) thick and b) thin cross-section of C-ring-12. The zoom details the cooling curves at the temperature range of 1000 °C to 700 °C, in which the secondary phases are formed in the super DSS.

The agreement between the two experimental curves in each C-ring is generally good, except for a slight deviation at the beginning of the measurement. This deviation may be a consequence of a displacement of the thermocouples caused by the pressure of the liquid metal when entering the mold cavity. In what concerns the C-ring-12, there was the rupture of the ceramic sheath in the first experiment, which affected the measurements. Even so, it can

be concluded that the implemented procedure for temperature acquisition inside the sand molds permitted to obtain consistent temperature measurements.

The extraction of the cast parts from the sand mold occurred 12000 s after pouring the liquid metal. The temperature measured at that moment in each position of the C-rings is shown in Table 8.

Table 8 – The C-ring temperature measured at the shakeout time.

	Cross-section	1 st experiment	2 nd experiment
C-ring-8	Thick	527 °C	533 °C
	Thin	333 °C	349 °C
C-ring-12	Thick	627 °C	616 °C
	Thin	420 °C	397 °C

The results show quite different temperatures at the shakeout time. The difference between the thin and thick cross-section is 194 °C (and 184 °C) for the C-ring-8, and 207 °C (and 219 °C) for the C-ring-12. The combination of thermal gradients and dimensions of the cast part may induce a wide range of cooling rates, after the shakeout. Since distinctive cooling rates are one of the leading causes of thermal residual stresses [85, 100], the accurate prediction of residual stresses is highly dependent on the accurate calculation of the temperature distribution. So, in this work, the experimental cooling curves were used to determine the IHTC values by the inverse method.

5.1.3 Comparison Between the Numerical and the Experimental Cooling Curves

The numerical cooling curves were compared with the experimental ones before the shakeout cooling stage. At this point, the thermocouples had to be removed, so any more data was collected after the shakeout time.

The comparison between the numerical and experimental cooling curves (of the second experiment) is shown in Figure 57. It is evident that the temperature profile of the thick and thin sections is quite different on both C-rings, where the predicted temperatures are considerably lower than the measured ones. For example, at the shakeout time, the difference between the predicted and the measured temperature, shown in Table 9, allows us to conclude that the thermal model, using the IHTC values from the literature, provides results that do not match with real values.

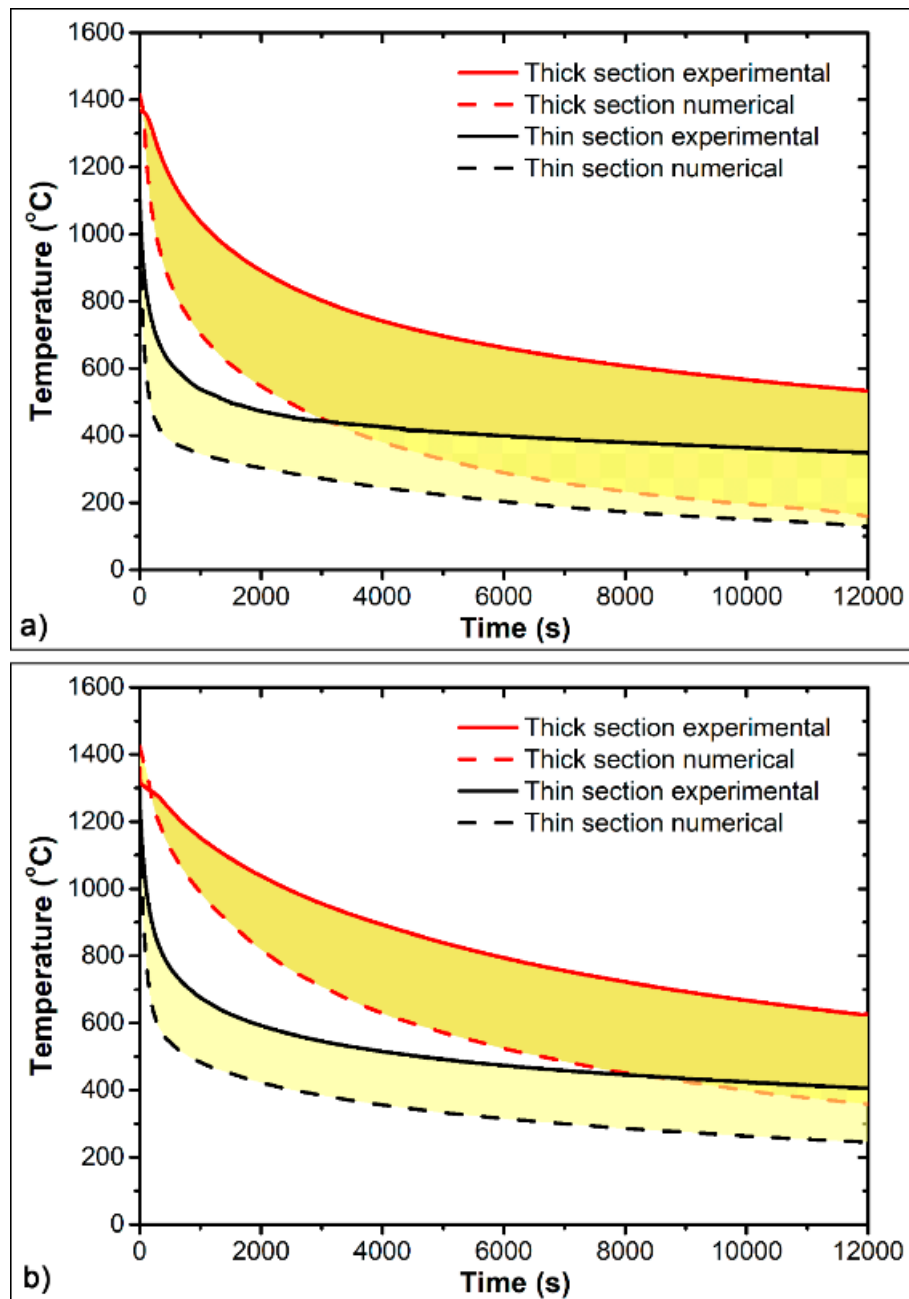


Figure 57 – Comparison of experimental (solid) and numerical (dash) cooling curves for the thick and thin sections
a) C-ring-8 and b) C-ring-12.

Table 9 – Predicted and experimental temperatures at the shakeout time.

	Cross-section	Experimental	Numerical
C-ring-8	Thick	533 °C	160 °C
	Thin	349 °C	128 °C
C-ring-12	Thick	616 °C	343 °C
	Thin	397 °C	239 °C

Another relevant issue is the difference between the cooling rate calculated from the numerical model and from the experimental cooling curve at the temperature range in which the σ -phase precipitates. At 950 °C (the nose of the σ -phase precipitation curve - see section 4.4.4), the numerical model predicts a faster cooling rate than that one measured experimentally, as shown in Table 10.

Table 10 - Comparison between the cooling rate at 950 °C solved numerically and experimentally measured.

	Cross-section	Experimental cooling curve	Numerical model
C-ring-8	Thin	2.14 °C/s	7.89 °C/s
	Thick	0.11 °C/s	0.72 °C/s
C-ring-12	Thin	0.93 °C/s	3.59 °C/s
	Thick	0.08 °C/s	0.19 °C/s

This difference could lead to inaccurate predictions of residual stresses because the thermal field affects the mechanical response of the component. So, if the thermal model is inaccurate, the design engineers cannot correctly solve the residual stresses problem and improve the quality of the castings. For example, Kang *et al.* [19] reduced the deformation in large cast components by imposing uniform cooling rates. Furthermore, solid-phase transformations affect the residual stresses. Since the predicted cooling curves are different from the experimental ones, the thermal model would not be reliable to predict secondary precipitation.

To obtain accurate numerical thermal results, it is fundamental to determine the IHTC as a function of temperature and/or time. However, the IHTC values are not easily determined by direct measurements, since they are dependent on several factors, such as the geometry of the component, existence of air gaps and contact pressure at the metal/mold interface, roughness of the mold and chemical composition of both the metal and mold materials [90, 120, 152, 153]. To overcome these issues, the inverse method based on experimental temperature measurements can be a solution for predicting the IHTC values. This topic will be explained in greater detail in the next section.

5.1.4 Prediction of the Temperature Distribution using IHTC Determined by the Inverse Method

The determination of IHTC values by the inverse method was made taking into account the experimental measurements performed before the shakeout time. As described in section 3.5.1, the inverse method consists of setting values of IHTC, solving the cooling curve and comparing it with the experimental one. This procedure was repeated until achieving the best agreement between the two curves. We have employed the technique of least squares to minimize the differences between the predicted and the measured temperatures.

Since the measured temperatures were performed at two locations for each C-ring, we set two series of values of IHTC as a function of temperature. One should mention that the best agreement between the predicted and the measured temperatures was obtained by taking IHTC values for the thin and for the thick cross-section instead of setting a single series of values for the whole C-ring. If more thermocouples were used to measure the temperature at more locations in the C-ring, then a greater number of values could be applied in the inverse method. At the end of the iteration, the best possible agreement between the experimental and numerical cooling curves was obtained with the IHTC values shown in Table 11.

Table 11 – IHTC values determined by the inverse method.

Temperature (°C)	IHTC (W/m ² K)			
	C-ring-8		C-ring-12	
	Thin cross-section	Thick cross-section	Thin cross-section	Thick cross-section
25	30	2	150	2
300	30	2	150	2
350	110	2	150	2
400	110	2	150	2
500	110	2	150	2
550	20	2	150	2
600	20	7	150	2
700	20	20	10	2
800	20	20	250	10
850	20	20	250	25
1100	20	20	250	25
1200	20	50	250	30
1300	20	250	250	30
1400	20	250	250	100
1500	20	250	250	500
1600	20	250	250	500

Table 11 highlights that IHTC varies with temperature, geometry and the cross-section area of the C-rings. The dependence of IHTC with temperature and the region of the cast specimen indicates that the heat transfer mechanisms change during the cooling process. The formation of air gaps at the metal/mold interface, separating the metal from the mold in some regions during the cooling, also contributes to the variation of the IHTC, although this characterization is hardly achieved. In fact, most of the research work assumed so far no spatial variation in the air gap formation. Yet, Arunkumar *et al.* [122] have demonstrated that the formation of air gaps varies spatially and changes the heat flux at the metal/mold interface. In addition, any displacement of the cast part due to shrinkage may change the distribution of the air gaps at the metal/mold interface, as well as the heat transfer mechanisms at the metal/mold interface during the cooling.

The calibration of the thermal model through an inverse analysis is essential to obtain accurate values of IHTC. Otherwise, the thermal model would fail to predict the cooling curves of the cast components. Figure 58 and Figure 59 show the numerical and experimental cooling curves using the IHTC from the inverse method, for C-ring-8 and C-ring-12, respectively.

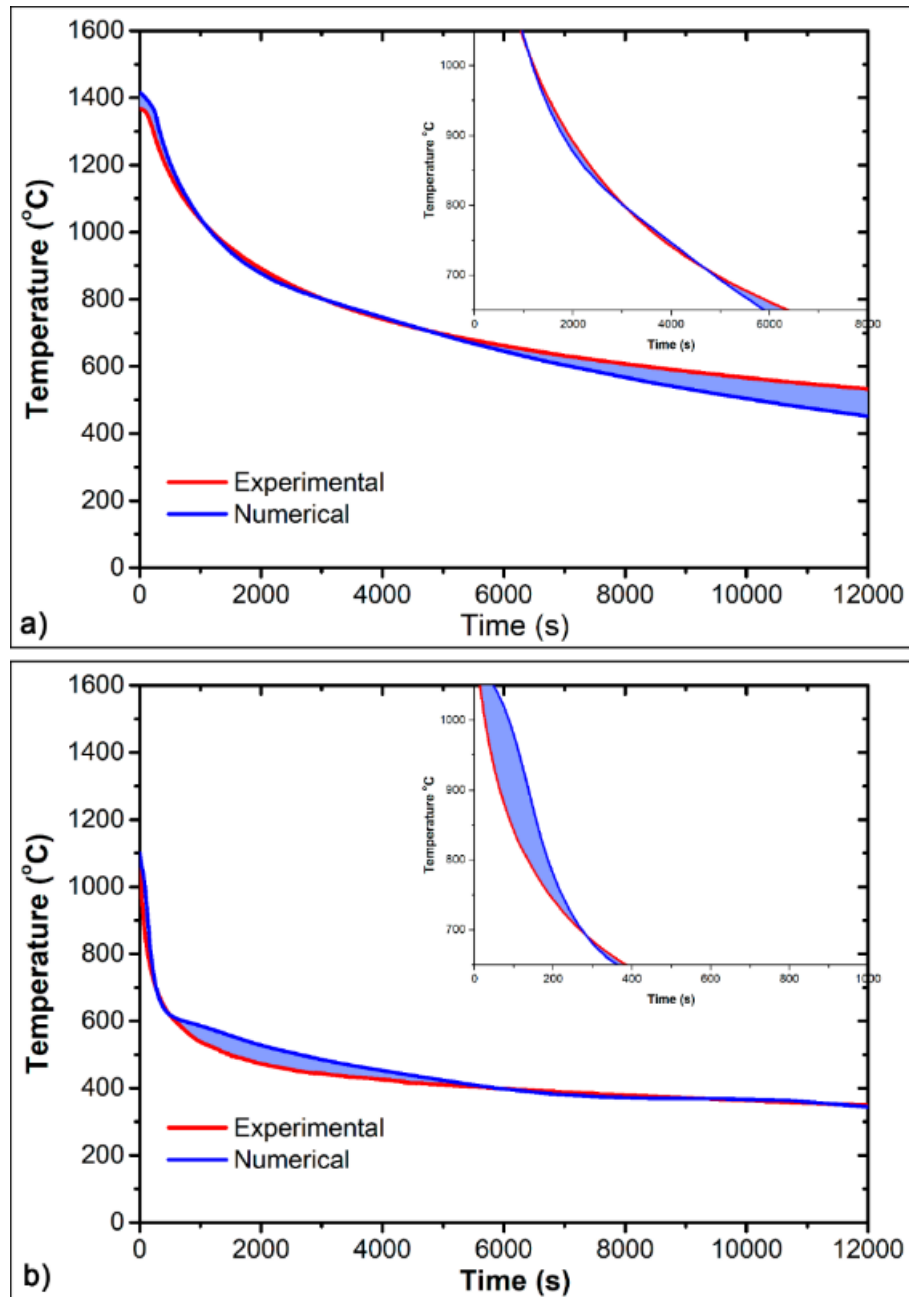


Figure 58 – Comparison of experimental (red) and numerical (blue) cooling curves for a) thick and b) thin cross-sections of C-ring-8. The zoom shows the cooling curve in the temperature range 1000 °C - 700 °C, in which the secondary phases are formed in super DSS.

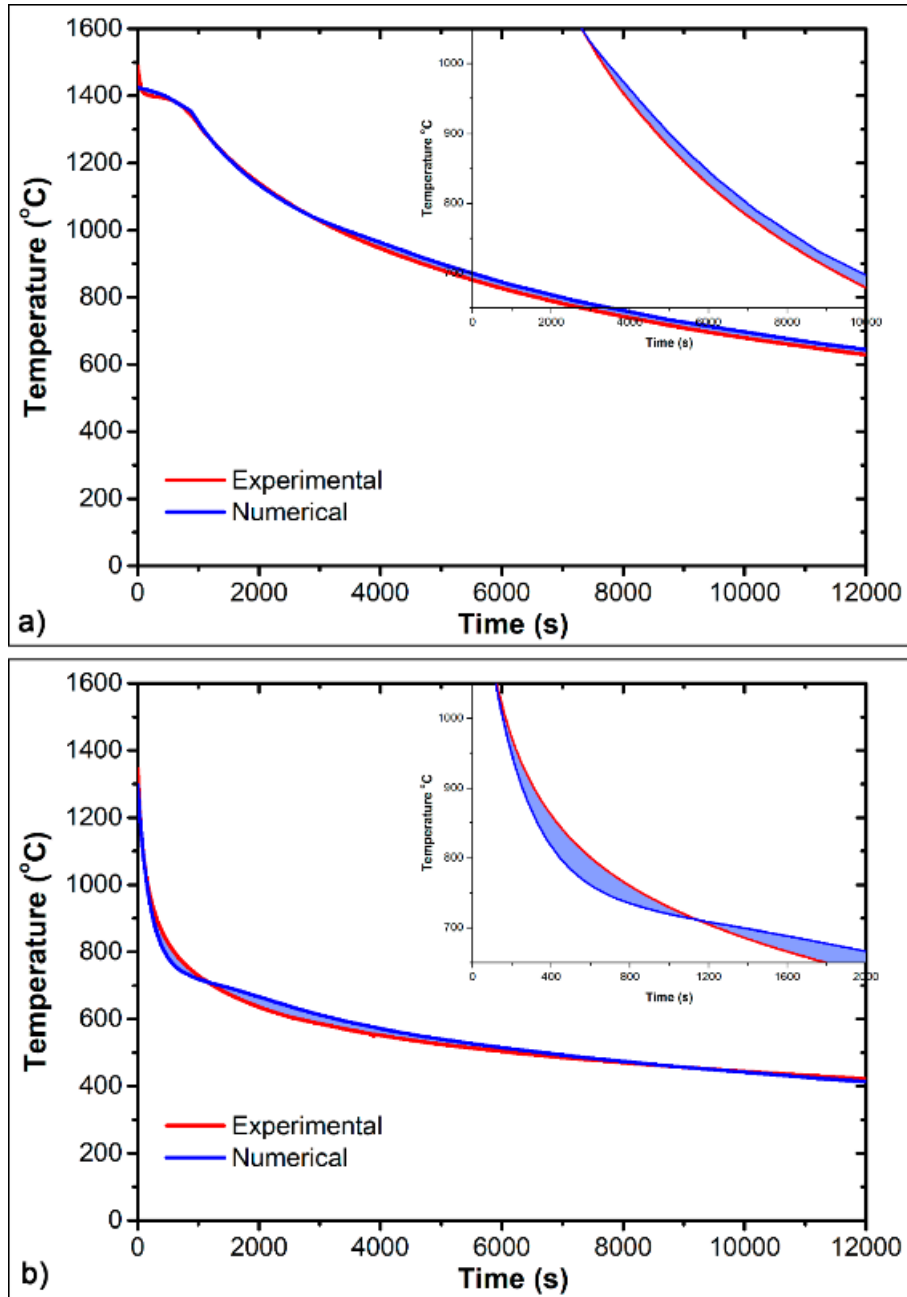


Figure 59 – Comparison of experimental (red) and numerical (blue) cooling curves in a) thick and b) thin cross-sections of C-ring-12. The zoom shows the cooling curve in the temperature range 1000 °C - 700 °C, in which the secondary phases are formed in super DSS.

The evolution of the temperature distribution in C-ring-8 and C-ring-12 is shown in Figure 60 and Figure 61.

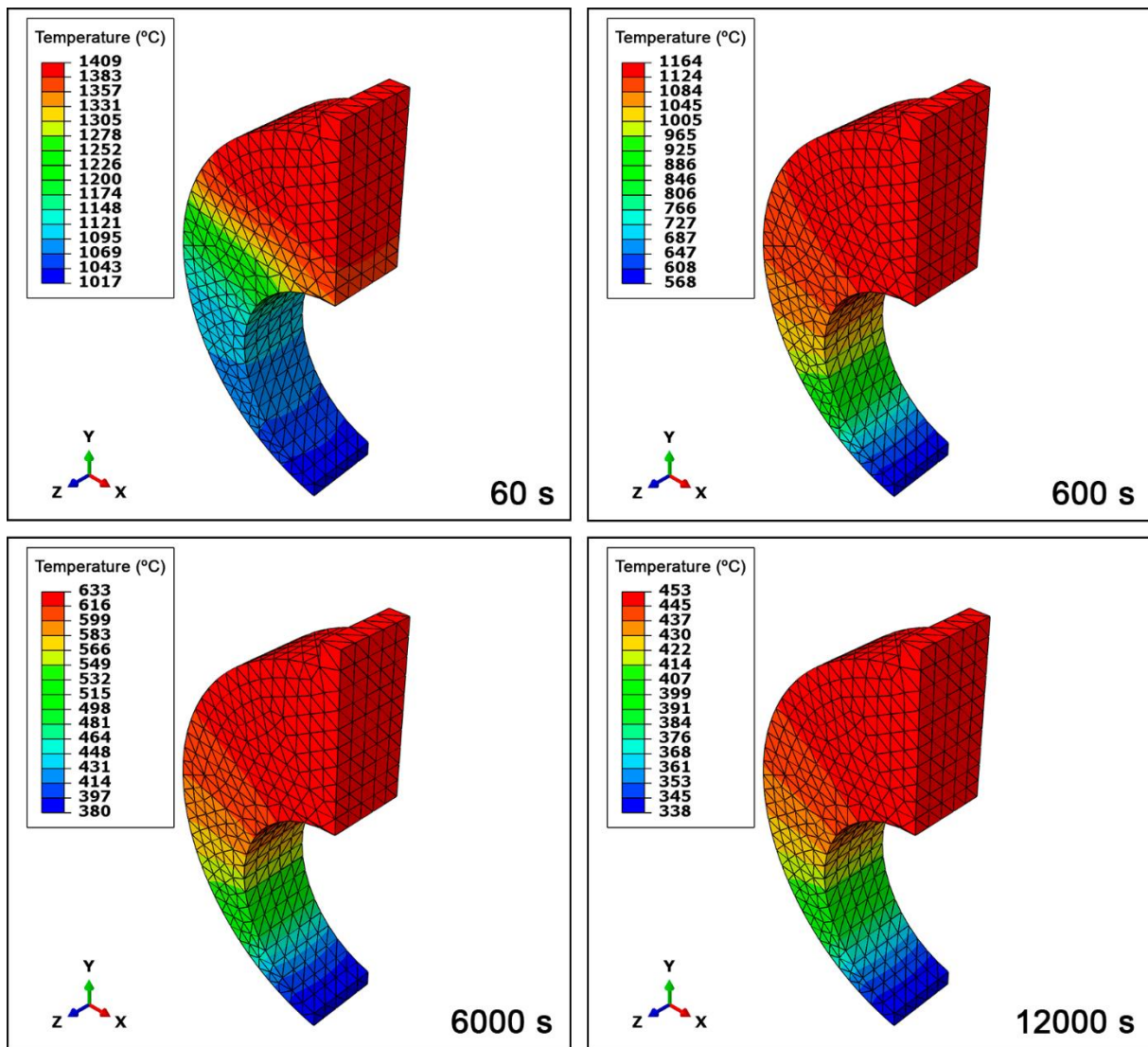


Figure 60 – Temperature distribution in C-ring-8 at a) 60 s, b) 600 s, c) 6000 s, and d) 12000 s.

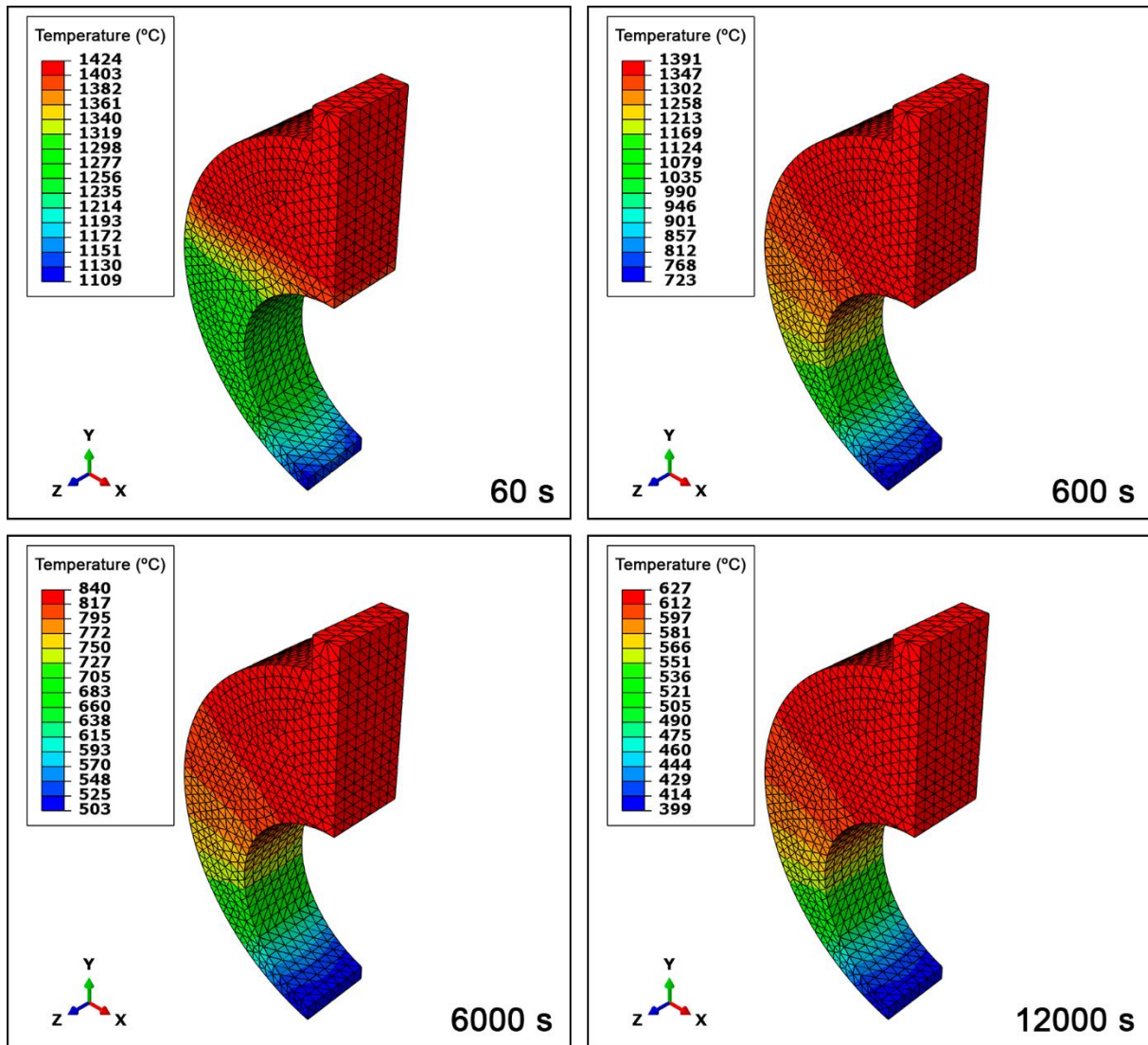


Figure 61 – Temperature distribution in C-ring-12 at a) 60 s, b) 600 s, c) 6000 s, and d) 12000 s.

Figure 60 and Figure 61 show that the minimum temperature predicted at the shakeout time (12000 s) in C-ring-8 was 338 °C, while in the C-ring-12 was 399 °C. After the shakeout, the final cooling stage to room temperature occurred outside of the mold.

The predicted temperatures at the shakeout time were compared to those that were measured and are shown in Table 12. The simulated values are very close to the measurements, thus considered sufficiently accurate.

Table 12 – Predicted and experimental temperatures at the shakeout time.

	Cross-section	Experimental	Numerical
C-ring-8	Thick	533 °C	453 °C
	Thin	349 °C	338 °C
C-ring-12	Thick	616 °C	625 °C
	Thin	397 °C	399 °C

5.1.5 Thermal Model for the Second Stage of Cooling “After Shakeout”

As described in section 3.5.1, the “after shakeout” cooling stage represents the cooling conditions after the extraction of the C-ring from the sand mold. The cooling curves for the thick and thin cross-sections are shown in Figure 62, where the cooling “after shakeout” is plotted as an extension of the “before shakeout” cooling.

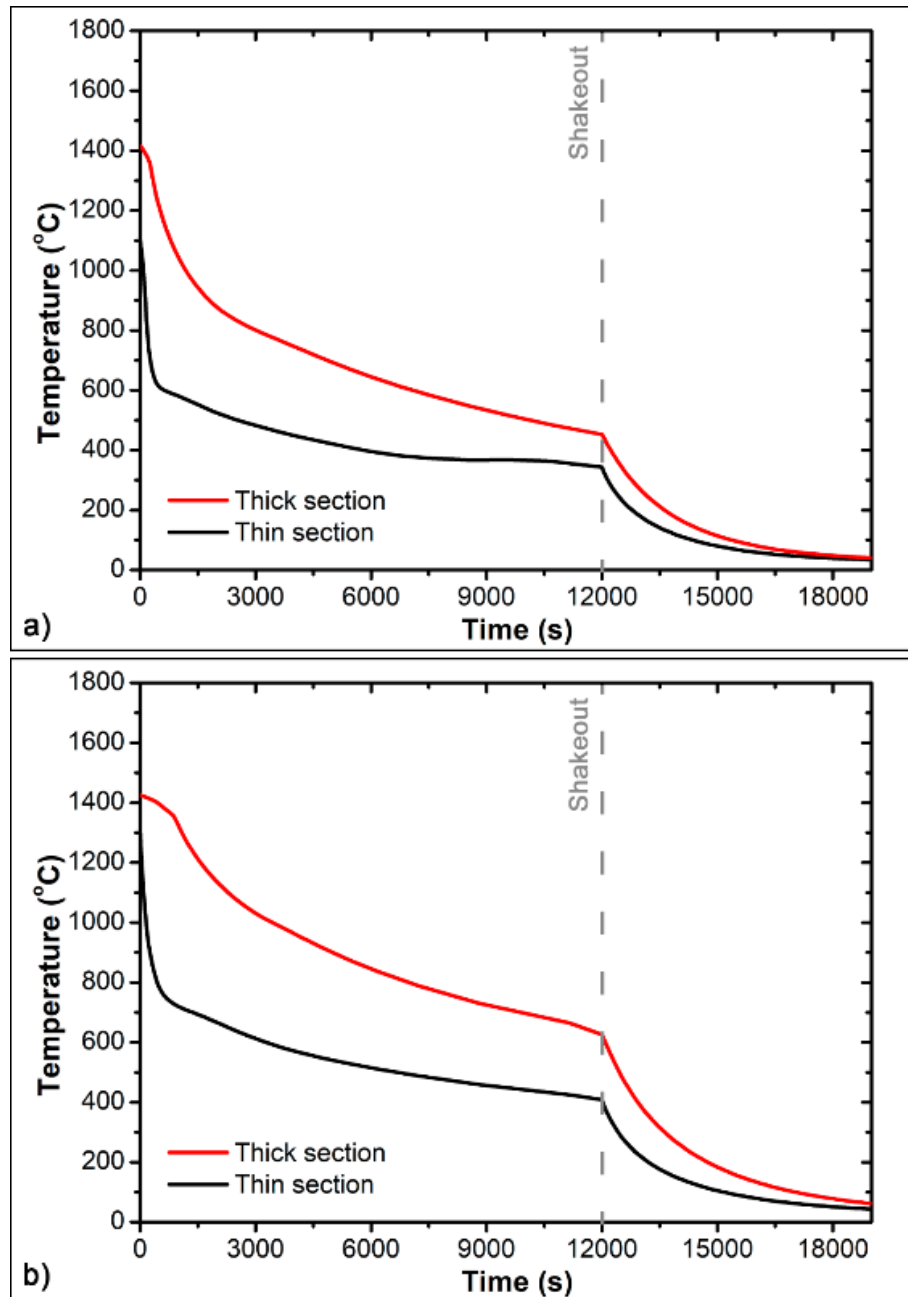


Figure 62 – Numerical cooling curves for the thick cross-section (red) and thin cross-section (black) of the a) C-ring-8 and b) C-ring-12.

According to the simulation, the C-rings reached room temperature after 7200 s of shakeout time (19200 s after the pouring). Figure 63 and Figure 64 give the temperature distribution at several time periods until the end of cooling. In the case of the C-ring-8, the calculated temperature varied between 35 °C and 31 °C, whereas for the C-ring-12, the calculated temperature varied from 64 °C to 43 °C.

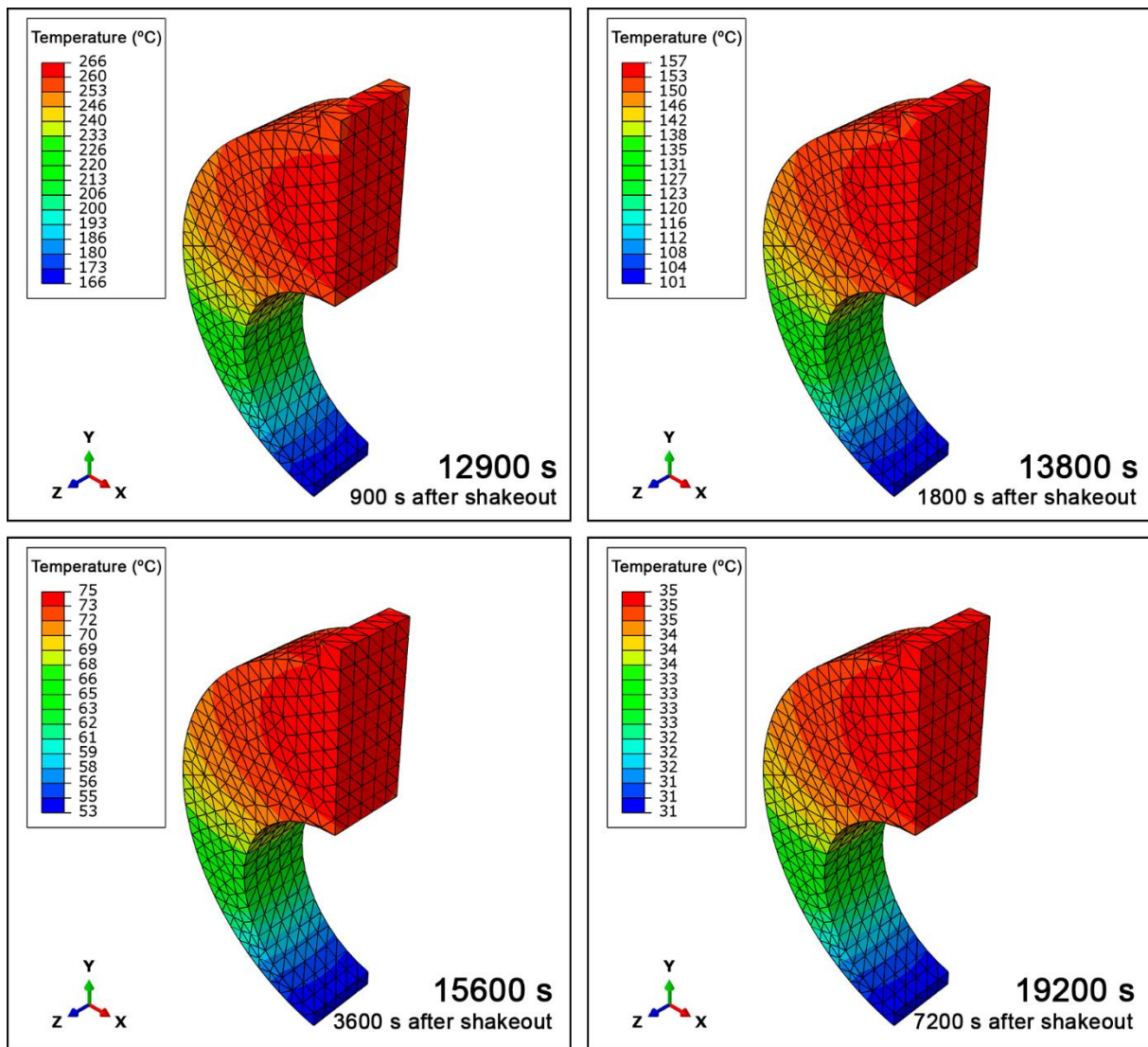


Figure 63 – Temperature distribution in C-ring-8 after shakeout at a) 900 s, b) 1800 s, c) 3600 s, and d) 7200 s.

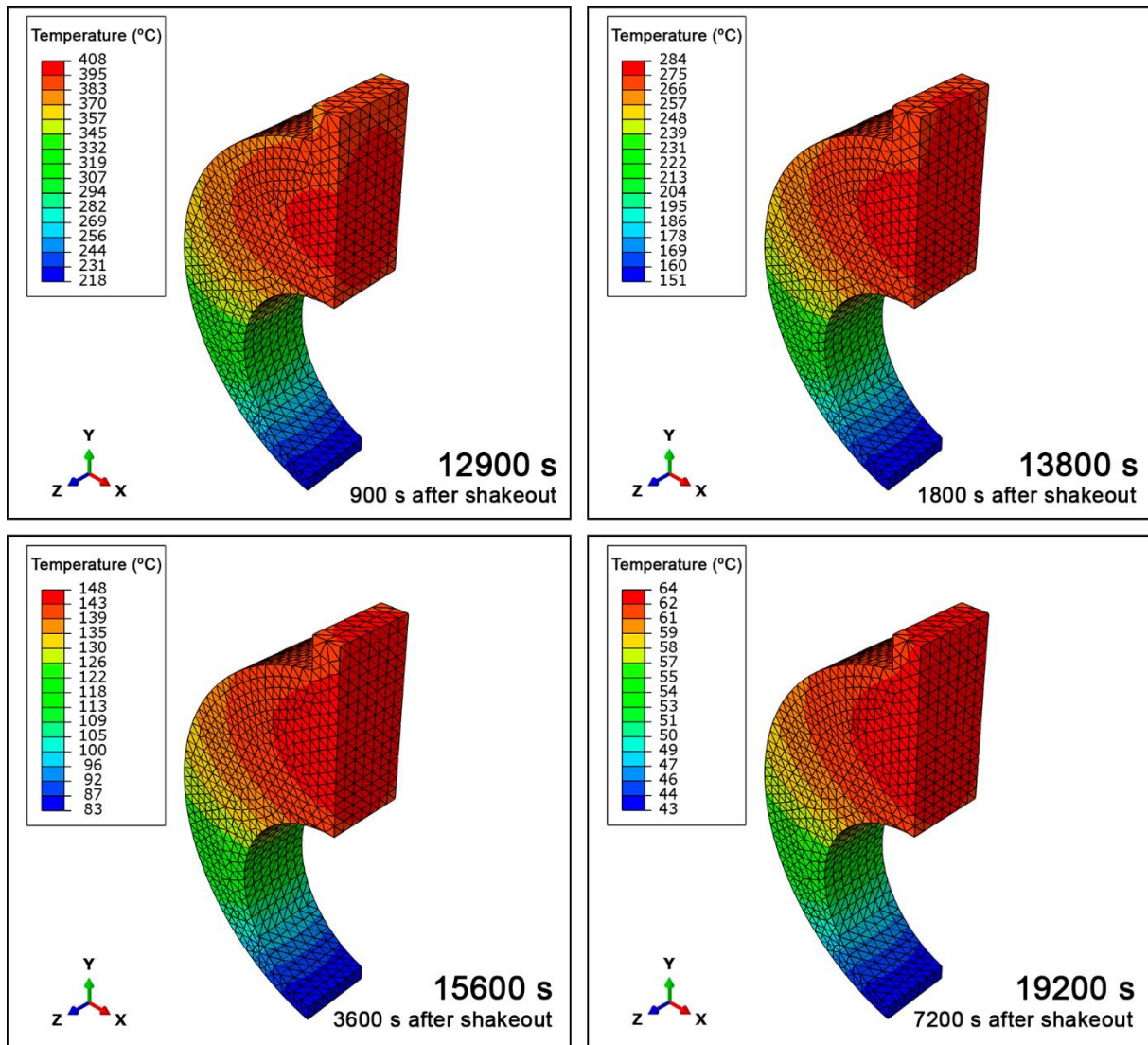


Figure 64 – Temperature distribution in C-ring-12 after shakeout at a) 900 s, b) 1800 s, c) 3600 s, and d) 7200 s.

The results from the thermal model were exported to the mechanical model, and this topic is covered in section 5.2.

5.2 Mechanical Model

For the mechanical simulation it is necessary to take the temperature distribution previously calculated and the thermophysical properties of the DSS. The next subsection details the procedure followed to calculate the thermophysical properties of the material which depend on the composition of phases present as a function of temperature.

5.2.1 Definition of the Thermophysical Material Properties as a Function of Temperature

The thermal-mechanical model should consider the solid-phase transformations that occur during cooling of super DSS, which were discussed in chapter 4. This is because the precipitation of secondary phases, which is affected by the cooling rates, may cause residual stresses due to differences in the CTE and elastic-plastic properties of the phases. In addition, the distribution of phases at the microscale should be considered by the thermal-mechanical model. The aforementioned issues were not directly considered in the sequentially coupled thermal-mechanical model developed. Yet, an alternative procedure, which relies on determining the thermophysical properties from predicting the phases fraction as a function of temperature, was implemented according to the scheme of Figure 65. The creation of the material properties database started with the construction of the equilibrium phase diagram, as it provides information about the phases that form as function of temperature. Subsequently, the quantification of phases was estimated for the temperature range 1500 °C to 700 °C with a step of 50 °C. For temperatures lower than 700 °C the microstructure remained unchanged. So, next, the material properties were determined for each temperature step and stored in the database. It should be highlighted that JMatPro™ gives the properties of the phases formed. This procedure enabled us to get the macroscopic material properties for a specific temperature, using the rule of mixtures.

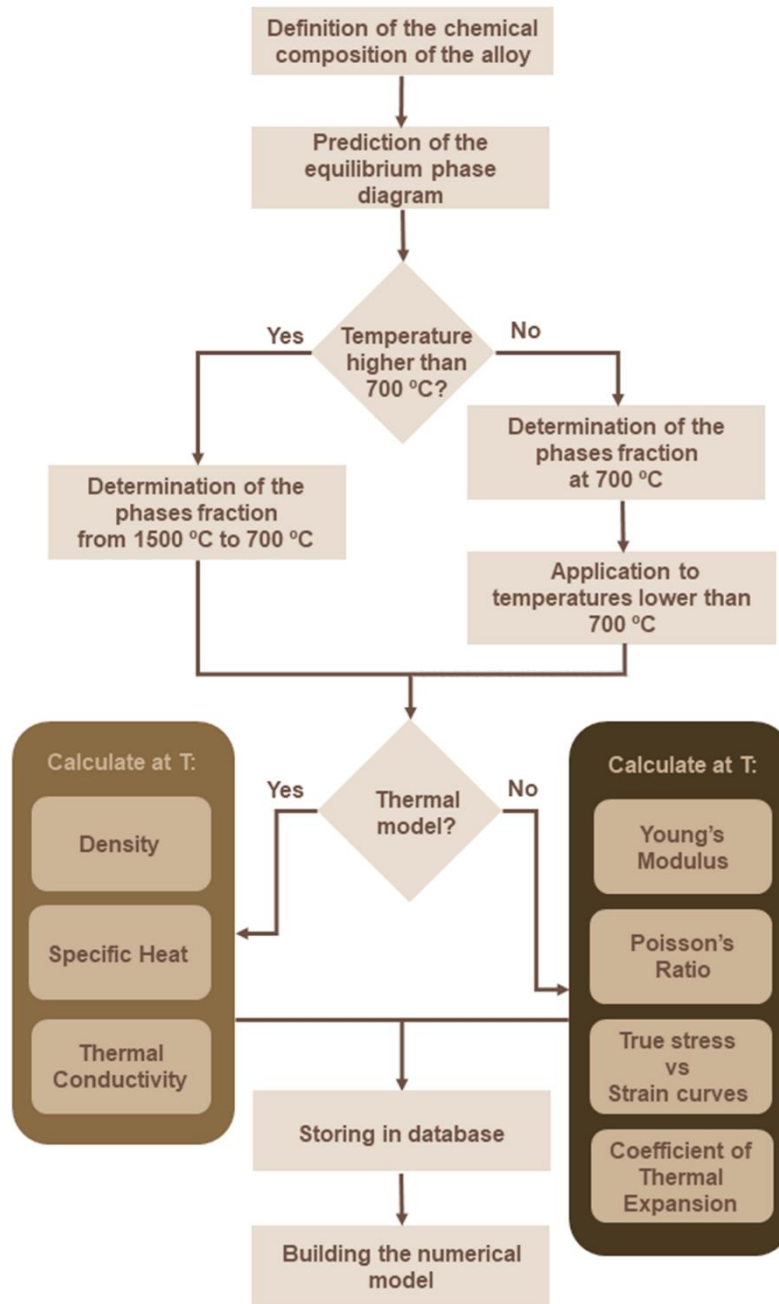


Figure 65 – Methodology for the construction of the material properties database.

Finally, AbaqusTM/CAE computes the temperature of each node of the mesh with the thermophysical properties at that temperature. One can state that this procedure increases the reliability of the thermal-mechanical model developed because it uses detailed thermophysical descriptions of super DSS.

5.2.2 Effect of Phase Distribution on Residual Stresses

The distribution of phases in the C-ring in the as-cast condition is heterogeneous because the precipitation of secondary phases is dependent on the cross-section dimensions and the corresponding cooling rates. As discussed in section 2.3, the distribution of phases influences the residual stresses at the micro and macroscales. In other words, the stresses at the grain scale (microstresses) may lead to residual stresses across large regions, that are comparable to the size of the component (macrostresses). However, modelling the residual stresses based on real microstructures is rarely found in the literature. Alternatively, it is common to generate numerical models representative of the microstructure that capture the main characteristics to be analyzed, such as grain size, grain shape, and/or phase distribution. In order to understand how the secondary phase precipitation affects the residual stresses at the microscale, we have created simple models based on microstructures collected from thick and thin cross-section regions (regions A and F, from C-ring-12). The regions A and F (C-ring-12 in as-cast condition) were selected because the size of the γ -phase islands and the volume percent of secondary phases are significantly different in these two regions. The models of the microstructures were created using the software OOF2TM. This finite element software is specialized in creating meshes directly from real images. From each OM micrograph (Figure 66a and Figure 67a), a representative zone was taken and uploaded to OOF2TM (Figure 66b and Figure 67b). Then, the meshes were constructed in OOF2TM and exported to AbaqusTM/CAE (Figure 66c and Figure 67c).

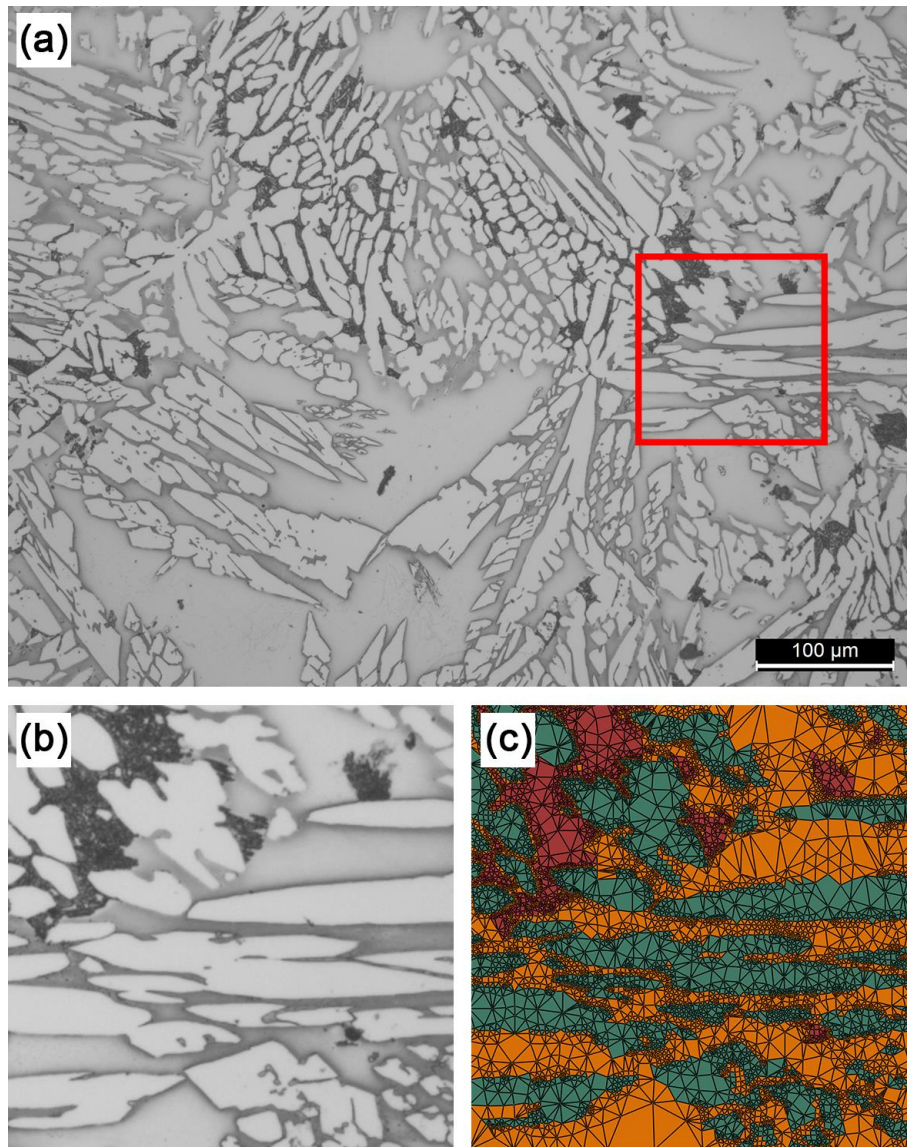


Figure 66 – Construction of the mesh based on a) OM micrograph from region A of C-ring-12. A representative zone (red-square) in higher magnification (b) and the corresponding mesh created in OOF2™ (c). The δ -phase is represented in orange, γ -phase in green and the σ -phase in red.

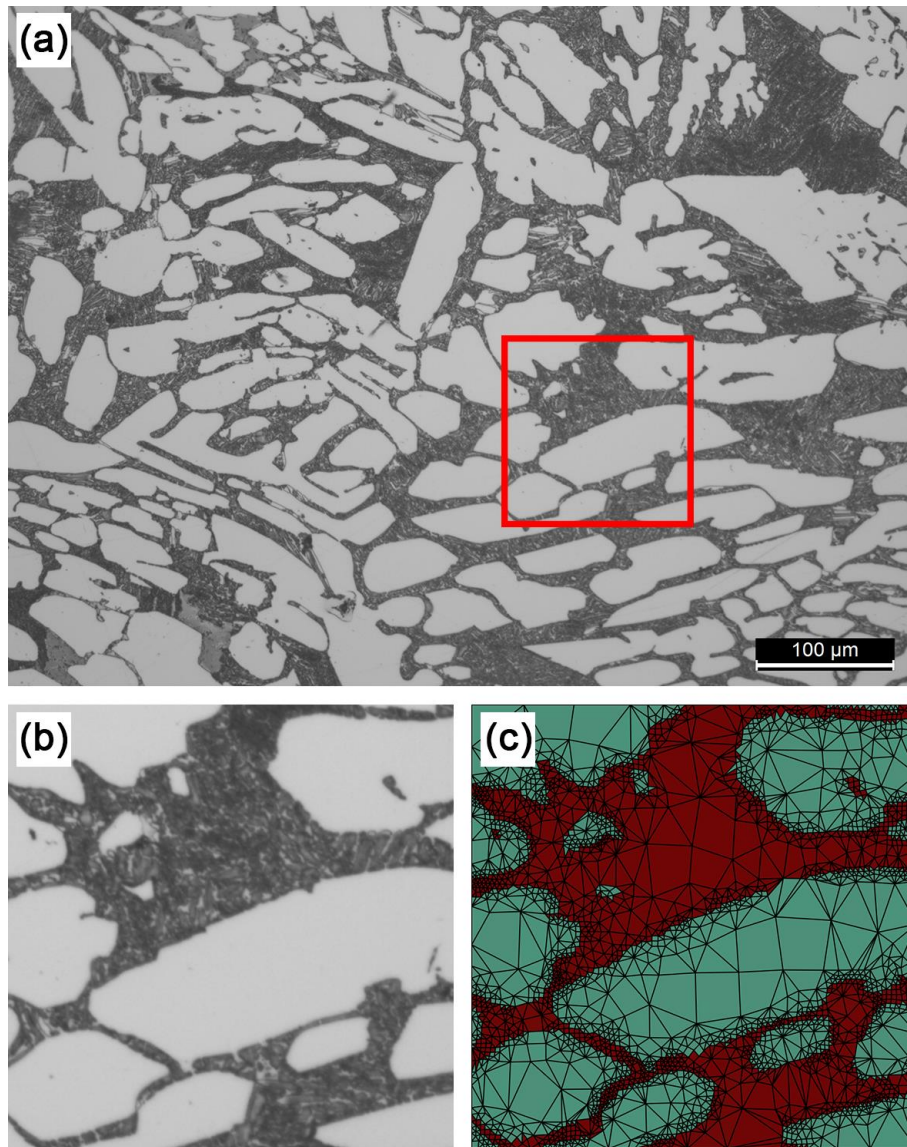


Figure 67 – Construction of the mesh based on a) OM micrograph from region F of C-ring-12. A representative zone (red-square) in higher magnification (b) and the corresponding mesh created in OOF2™ (c). The γ -phase is represented in green and the σ -phase in red.

After exporting the meshes to Abaqus™/CAE, the elastic properties and the coefficient of thermal expansion (CTE) obtained from JMatPro™ (Table 13) were assigned to each phase. Then, the cooling procedure from 700 °C to 25 °C was simulated. In this case, a fully coupled thermal-mechanical analysis was performed, and beyond rigid body motion prevention there were no boundary conditions set, so the models of the microstructures were free to contract. The von Mises stress maps for both models are shown in Figure 68.

Table 13 – Physical Properties for the various phases in the microscale model.

Phase	Young Modulus	Poisson's ratio	CTE
γ	$189 \times 10^9 \text{ Pa}$	0.33	$1.72 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$
δ	$220 \times 10^9 \text{ Pa}$	0.29	$1.04 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$
σ	$234 \times 10^9 \text{ Pa}$	0.31	$1.76 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$

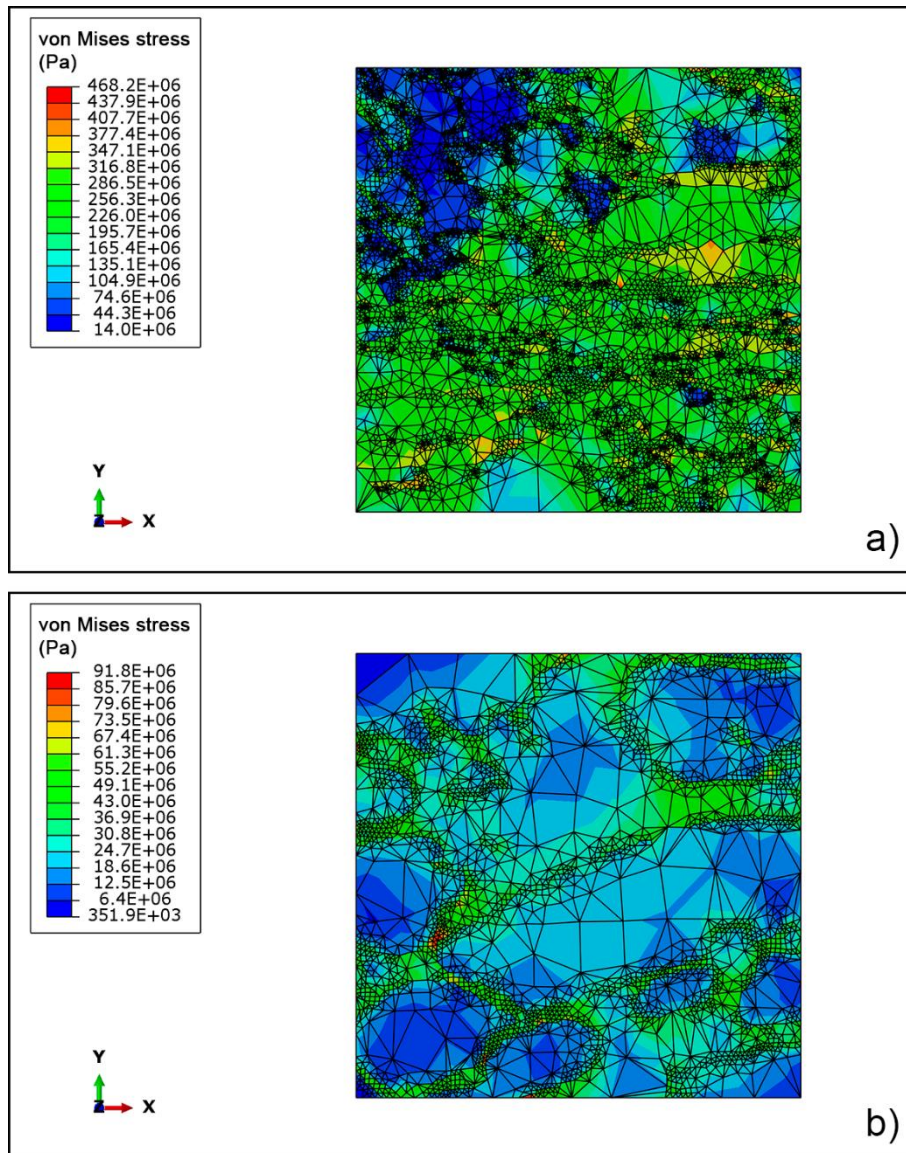


Figure 68 – Von Mises stress map after cooling from 700 °C to room temperature on a) region A and b) region F of C-ring-12.

The von Mises stress map of region A (Figure 68a) reveals that the areas composed of γ -phase and σ -phase exhibit lower residual stresses than the areas comprising γ -phase and δ -phase, although the greater stiffness of the σ -phase. Furthermore, a microstructure entirely composed of σ -phase and γ -phase shows lower residual stresses, as depicted in region F (Figure 68b). Despite the fact that the von Mises stresses do not allow to highlight if the material is in tension or compression, the two main components (X and Y directions) permit to distinguish the positive and negative stresses for each region (Figure 69 and Figure 70).

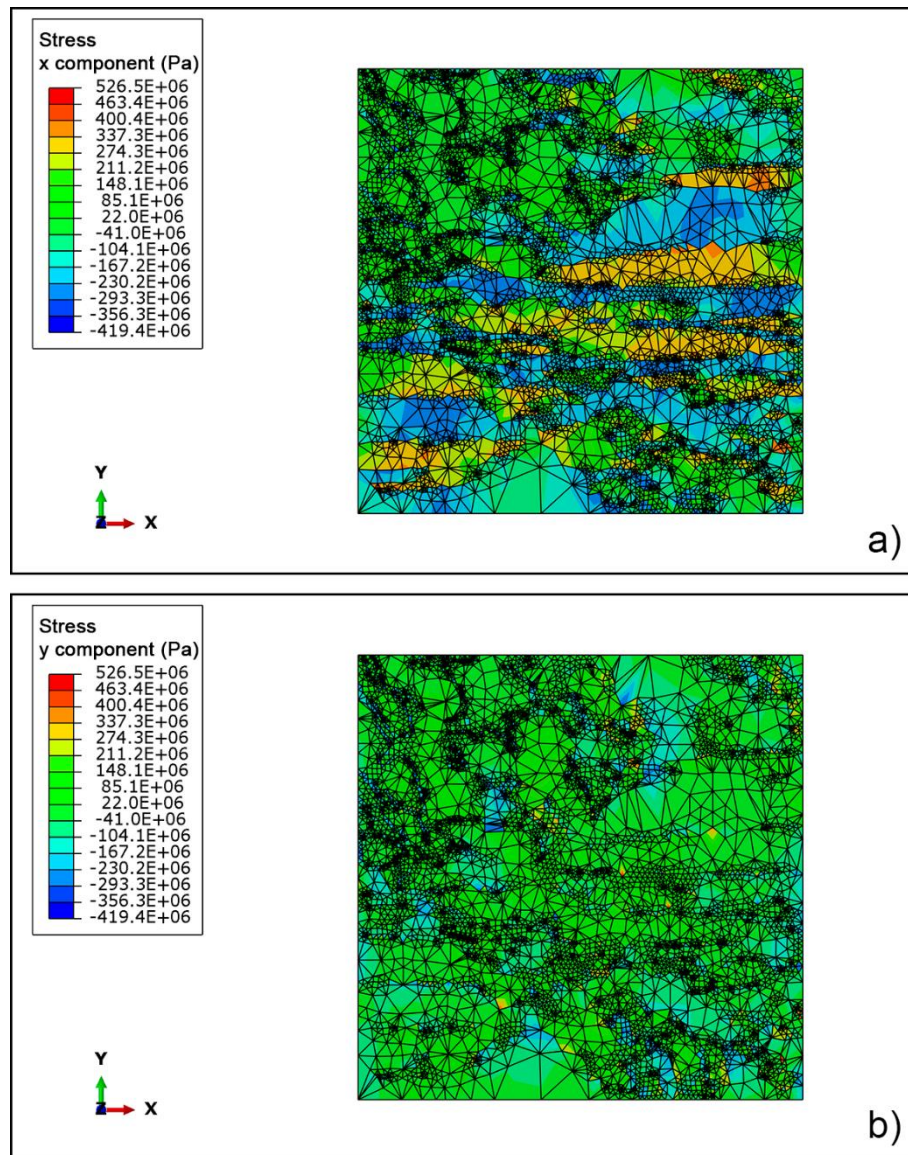


Figure 69 – Tensile and compressive stresses at region A of C-ring-12 in a) x component and b) y component.

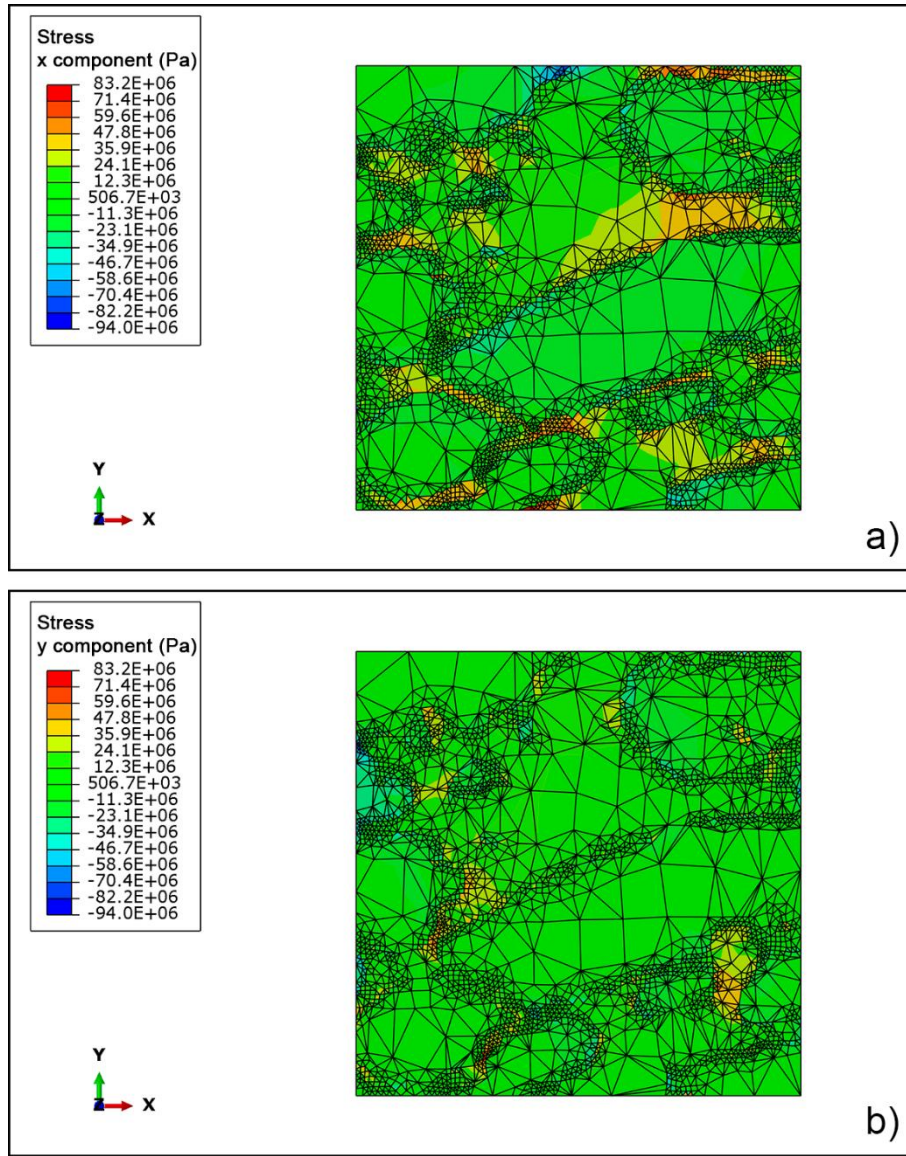


Figure 70 – Tensile and compressive stresses at region F of C-ring-12 in a) x component and b) y component.

In region A (Figure 69), the tensile stresses are associated with the γ -phase and σ -phase, whereas the compressive stresses are associated with the δ -phase. Moreover, the magnitude of stresses is higher along the growth direction of the γ -phase islands. In region F (Figure 70), the distribution of stresses is similar in both x and y directions and higher residual stresses are found in the σ -phase. These results can be explained in terms of the CTE of the phases. As the γ -phase and σ -phase have higher CTEs than the other phases, the thermal contraction of these phases is also higher. Therefore, tensile stresses are expected to be associated with the γ -phase and σ -phase, while the δ -phase will experience compressive stresses. When the microstructure is composed of σ -phase and γ -phase, tensile stresses are created in the σ -phase and compressive stresses appear in γ -phase. These results are in accordance with the results from the simulations developed by Johansson *et al.* [154] and demonstrate that the

heterogenous distribution of phases affects the stresses of the super DSS cast parts. We will discuss the residual stresses in C-rings in the next section.

5.2.3 Determination of Residual Stresses in C-rings

The von Mises stresses was applied to evaluate the residual stresses in C-rings as depicted in Figure 71 and Figure 72.

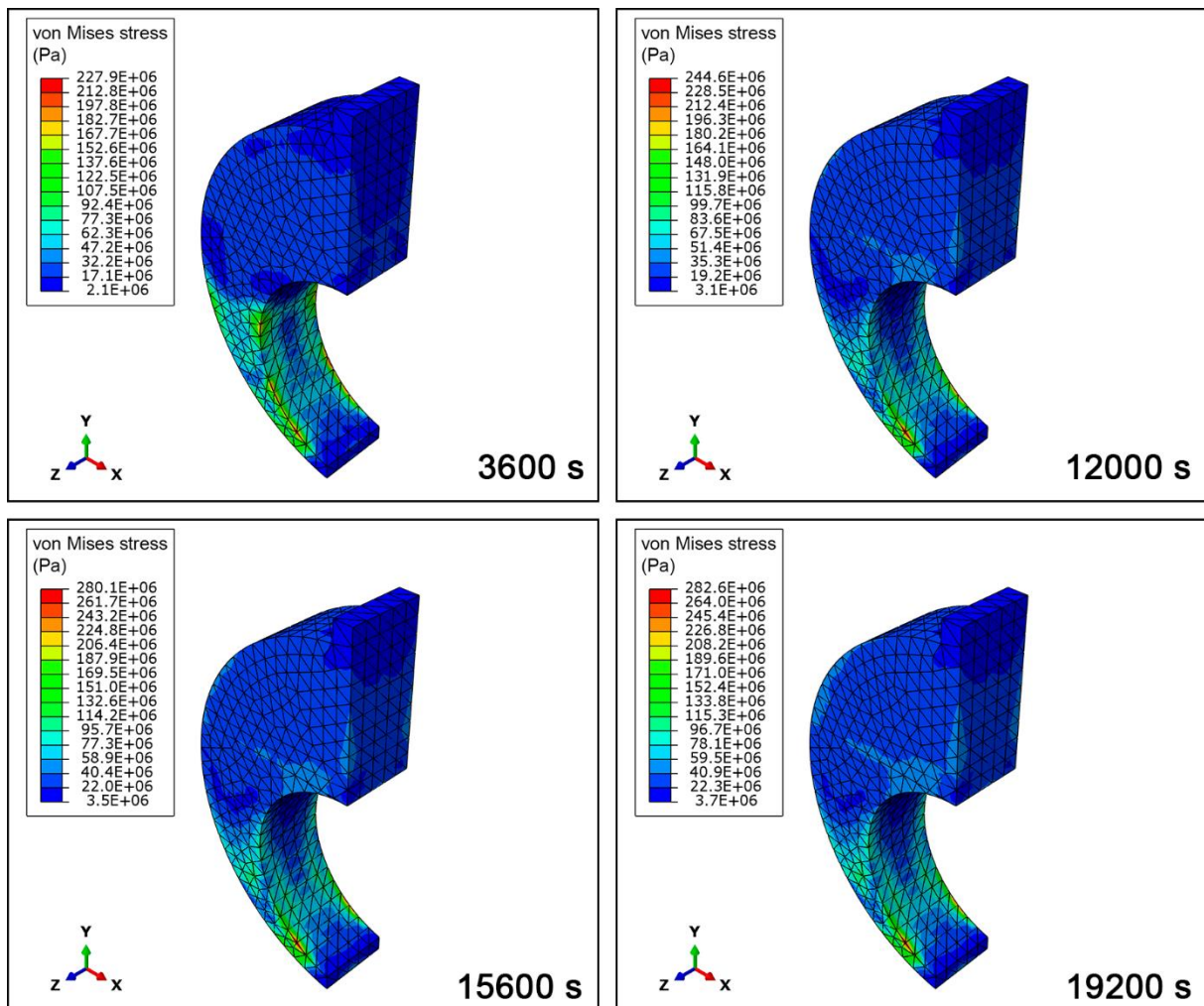


Figure 71 – Von Mises stress map in C-ring-8 at a) 3600 s, b) 12000 s (shakeout), c) 15600 s and d) 19200 s (end of cooling).

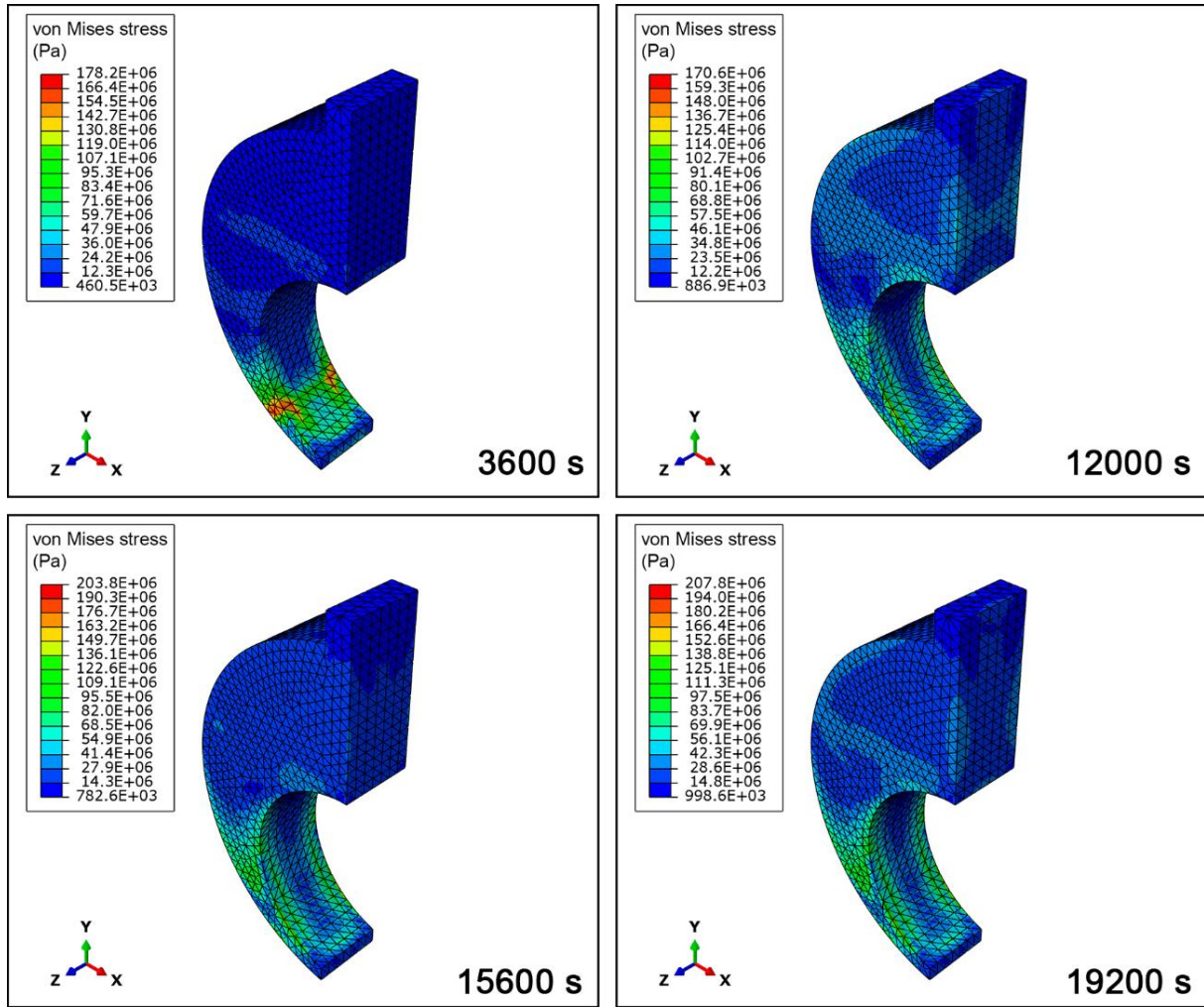


Figure 72 – Von Mises stress map in C-ring-12 at a) 3600 s, b) 12000 s (shakeout), c) 15600 s and d) 19200 s (end of cooling).

The von Mises stress maps show that the stresses are higher at the C-ring-8. This can be explained by faster cooling rates (see Figure 62) and higher temperature gradients at the C-ring-8. The temperature gradient can be expressed as the temperature difference (ΔT) between two points over a known distance (d), as the follows:

$$G = \frac{\Delta T}{d} \quad (\text{Eq. 12})$$

If we consider two positions (at thick cross-section and thin cross-section) then we can compare the thermal gradients for the two C-rings as it is shown in Figure 73.

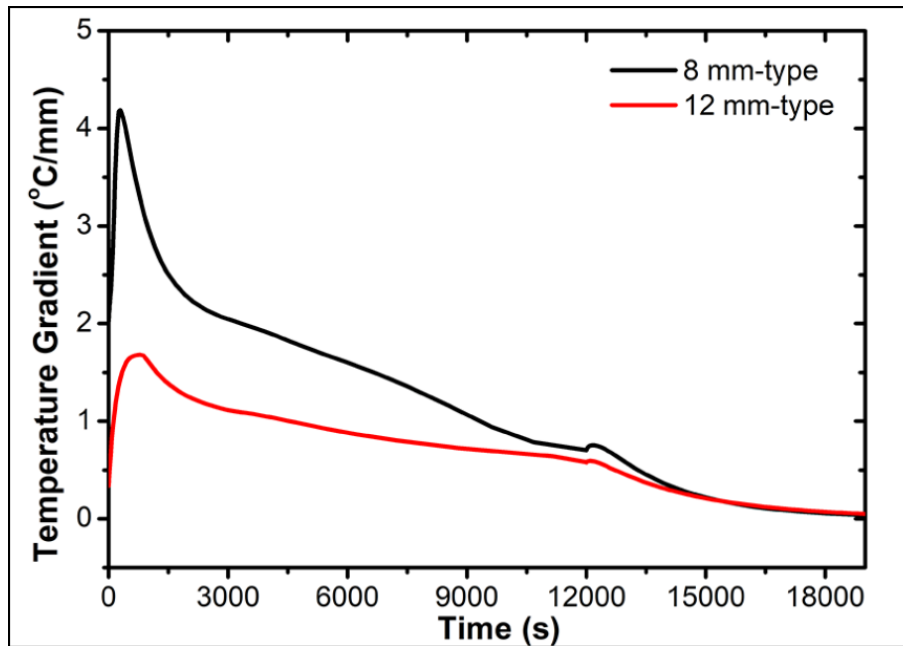


Figure 73 – Evolution of the temperature gradient for the C-ring-8 (black line) and C-ring-12 (red line).

It is well known that the residual stresses are created as a result of the factors cited above. However, the maximum residual stresses were lower than the yield strength of the super DSS at 350 °C. This is the temperature at the shakeout, for which the yield strength estimated for the super DSS is 464 MPa. The maximum von Mises stresses for both C-rings is detailed in Table 14, at the shakeout, and at the end of cooling.

Table 14 – Von Mises stress calculated for the two C-rings at the shakeout moment (12000 s after pouring the metal) and at the end of the cooling (19200 s after pouring the metal).

	12000 s (at the shakeout)	19200 s (at the end of cooling)
C-ring-8	244.6 MPa	282.6 MPa
C-ring-12	212.9 MPa	256.8 MPa

The increase in the residual stresses after the extraction of C-ring from the mold is due to the temperature gradients that are established during the cooling at the ambient atmosphere.

As mentioned above, the thermal-mechanical model applied the rule of mixtures to obtain the material properties for a specific temperature. However, as discussed in section 2.3, the microstresses that are influenced by the distribution of phases can affect the stresses at the macroscale. The results of the micromechanical models indicated there were higher stresses at the zones composed of γ -phase and δ -phase. So, if the distribution of phases had been considered in the macro mechanical models, a rather different results could be obtained.

Regarding the deformation of the C-rings, the magnitude of displacement is shown in Figure 74 and Figure 75.

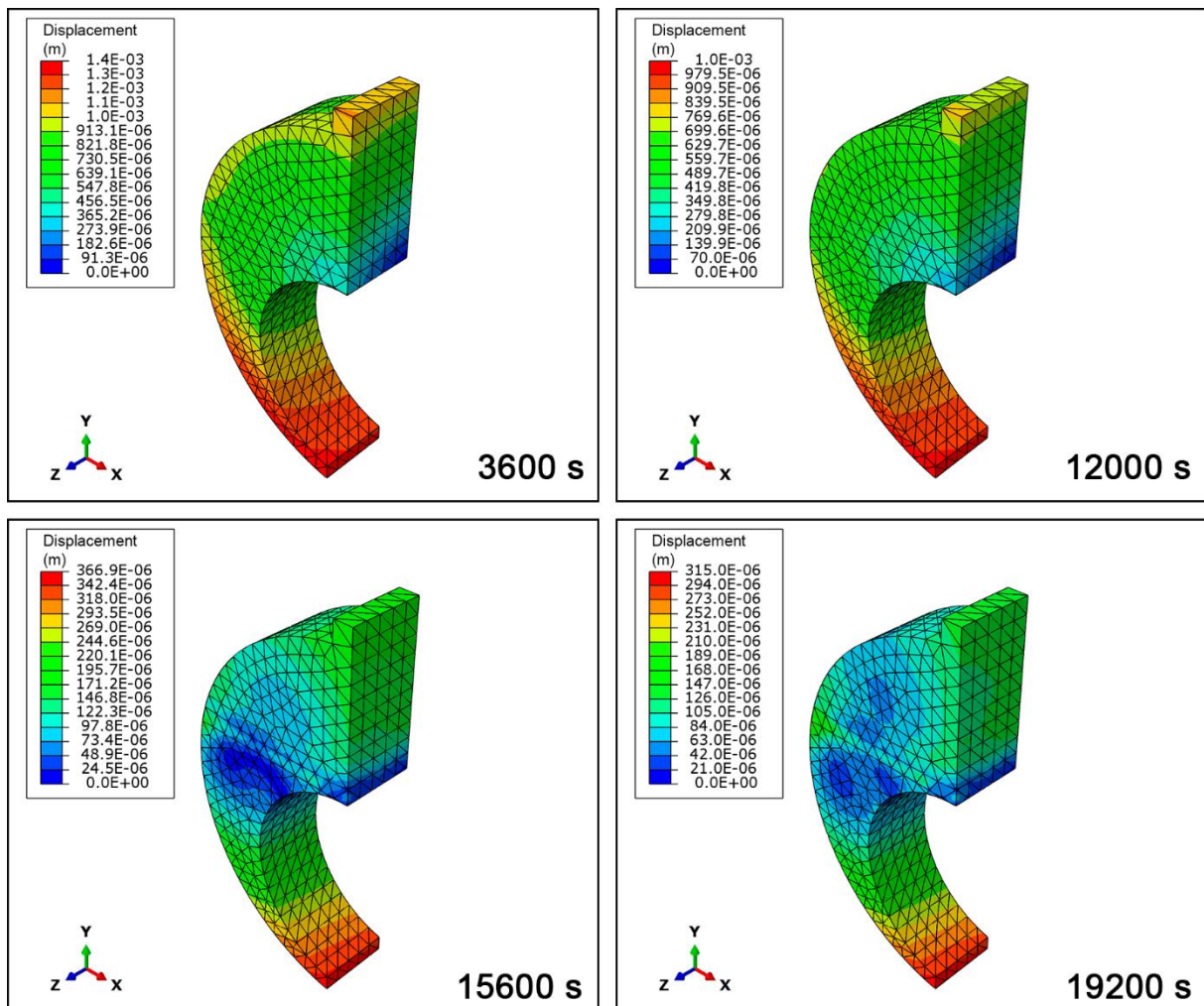


Figure 74 – Deformation map in C-ring-8 at a) 3600 s, b) 12000 s (shakeout), c) 15600 s and d) 19200 s (end of cooling).

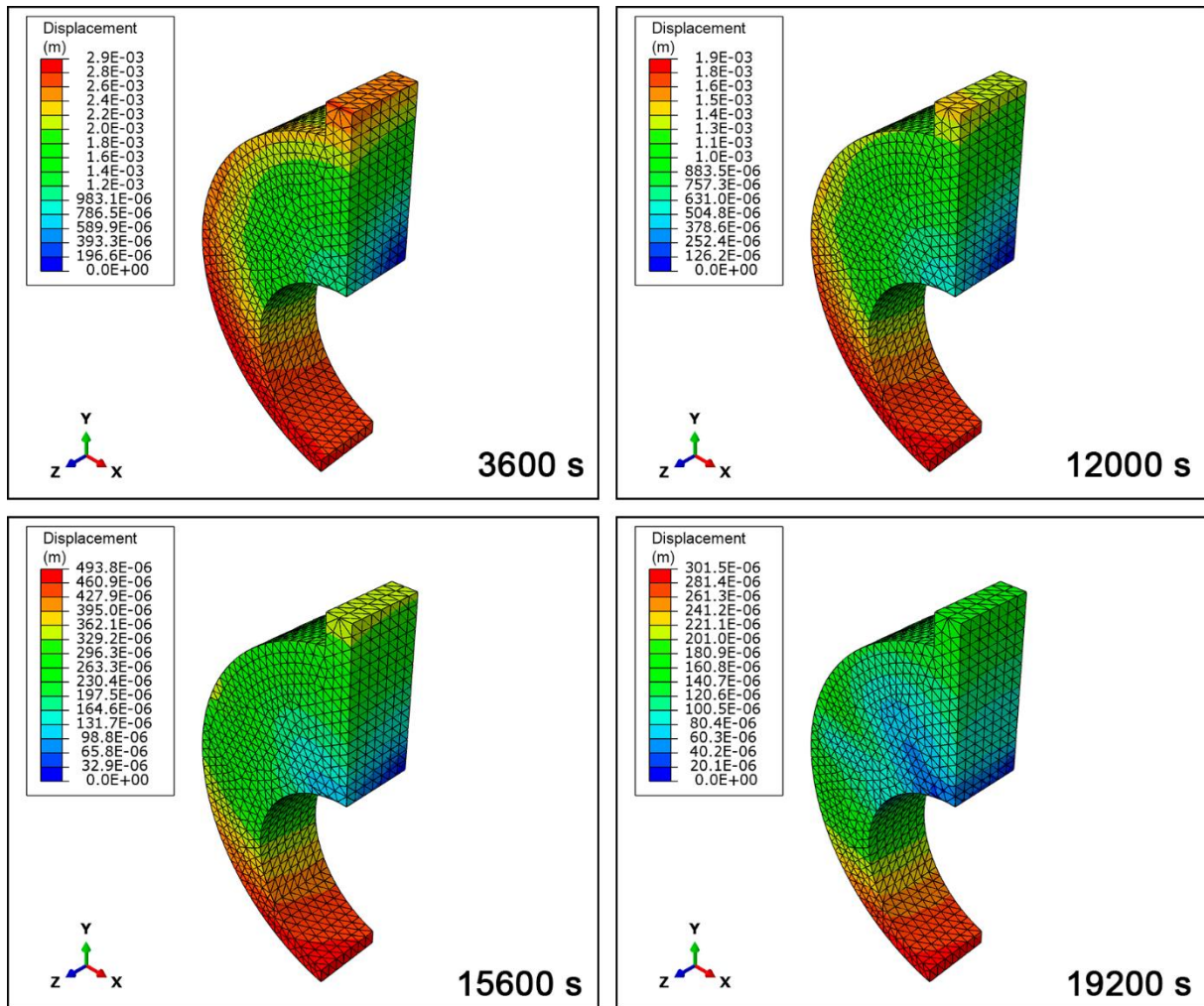


Figure 75 – Deformation map in C-ring-12 at a) 3600 s, b) 12000 s (shakeout), c) 15600 s and d) 19200 s (end of cooling).

In the macroscale models, the highest residual stresses are found in the thin cross-sections. So, the higher deformations were found at the prongs, which are also the least constrained regions in the C-rings.

Furthermore, the predicted deformation of the prong tips was compared to the measured displacement in real C-rings and the results were used to evaluate the accuracy of our mechanical model. In particular, Figure 76 shows the superposition of the geometry after cooling and the original geometry of both C-rings. The deformations are multiplied by a factor of 5, to help visualization. Also, the FEM model was mirrored to better visualize the deformation of the C-ring at the prongs. The mechanical analysis shows that the deformations are superior in the thinner regions (prong tips) when compared with the thicker regions. Moreover, the distance between the prong tips increased at the end of the cooling, compared to the original geometry.

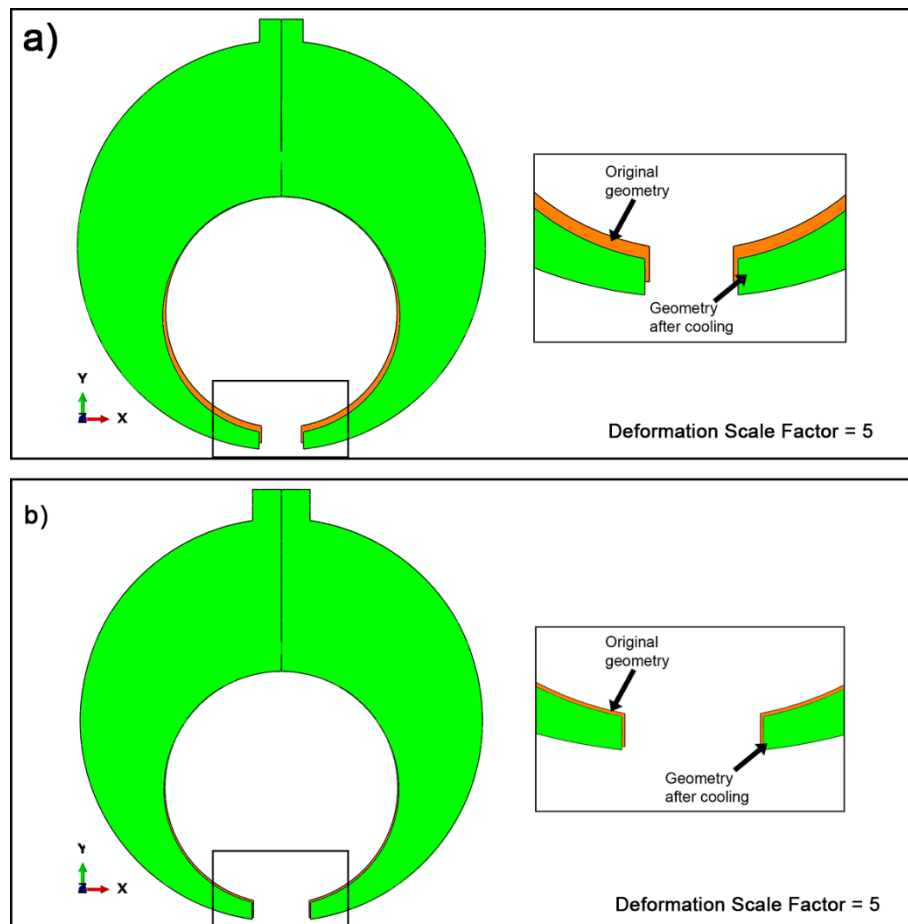


Figure 76 – Deformation of the C-rings after cooling. The original geometry (orange) is superposed with the deformed geometry (green) on a) C-ring-8 and b) C-ring-12.

Table 15 shows the distance between the prong tips of the C-rings, measured with a caliper. Also, this table provides the calculated distance by the mechanical model.

Table 15 – Measured and estimated values of the distance between the prong tips of the C-rings.

	C-ring-8	C-ring-12
Measured	21.6 mm	30.9 mm
Calculated	19.1 mm	28.5 mm

The numerical model predicted the opening of the C-rings prongs, which is in accordance with the dimensional measurements. So, the numerical model gives a reasonable prediction of the final distortion of the C-rings.

5.3 Residual Stresses Measurement by the Contour Method

The residual stresses created in C-ring-8 as a result of its constrained thermal contraction and microstructural transformation were measured by the contour method, as explained in section 3.6. Figure 77 shows the measured coordinates on the two halves surfaces, which give information about the relaxation of the residual stresses normal to the cutting plane.

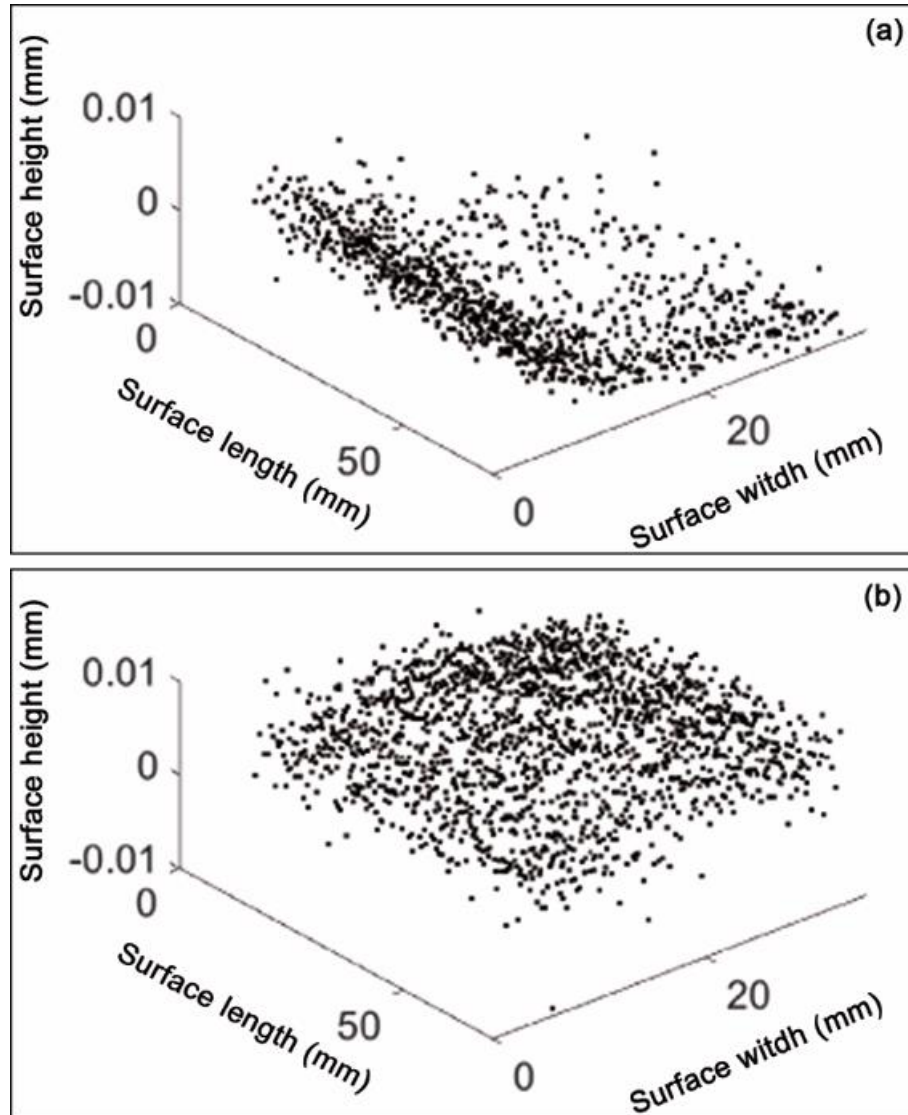


Figure 77 – Measured coordinates of cut surfaces of C-ring-8. The data was computed using MATLAB™.

The measured coordinates from the two halves were aligned and averaged to obtain the contour of the cut plane. The result of this procedure is shown in Figure 78. The surface noise was removed by smoothing the surface profile. The result of this operation is shown in Figure 79.

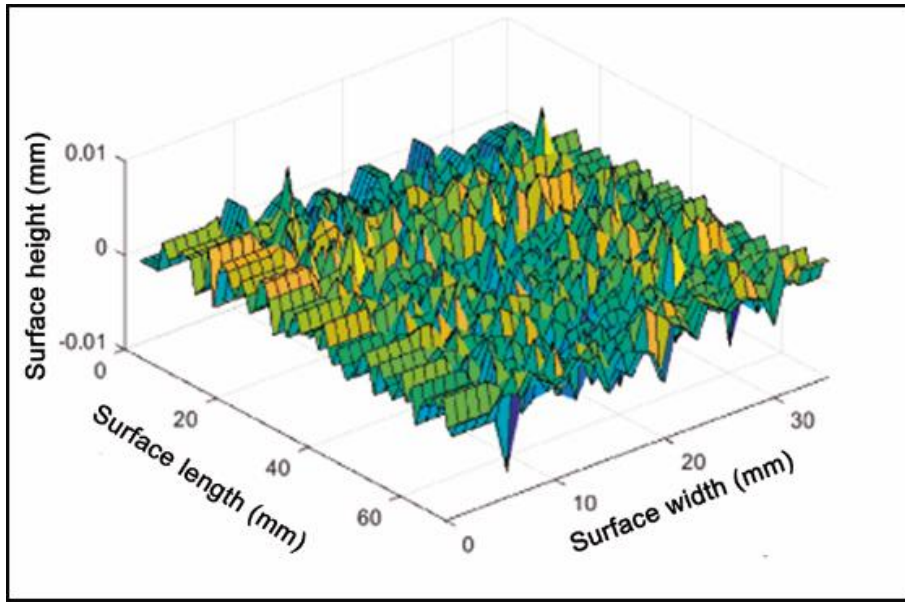


Figure 78 – Averaged contour of the cut plane of C-ring-8.

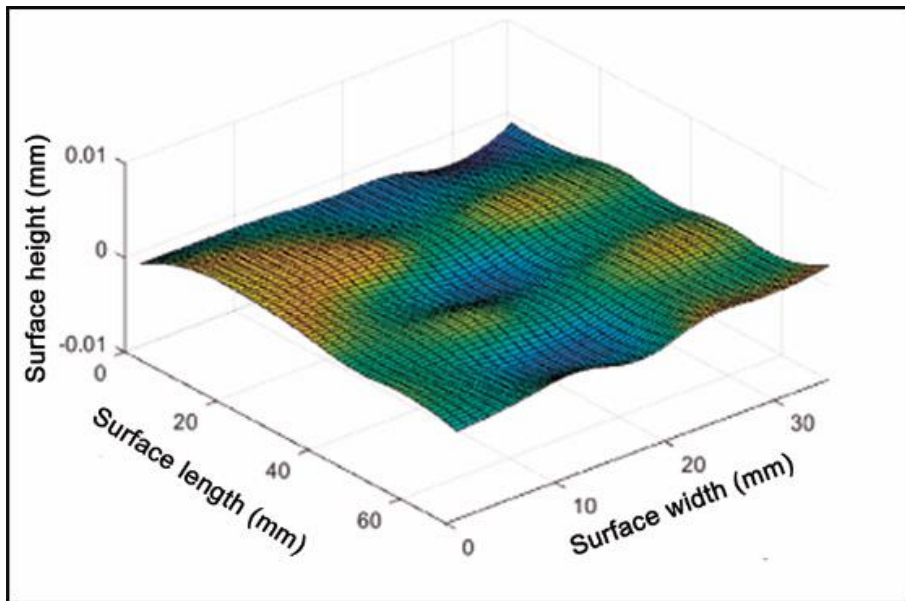


Figure 79 – Averaged smoothed contour of the cut plane of C-ring-8.

The residual stresses normal to the cut plane are shown in Figure 80a. In Figure 80b the residual stresses predicted by the numerical model are shown.

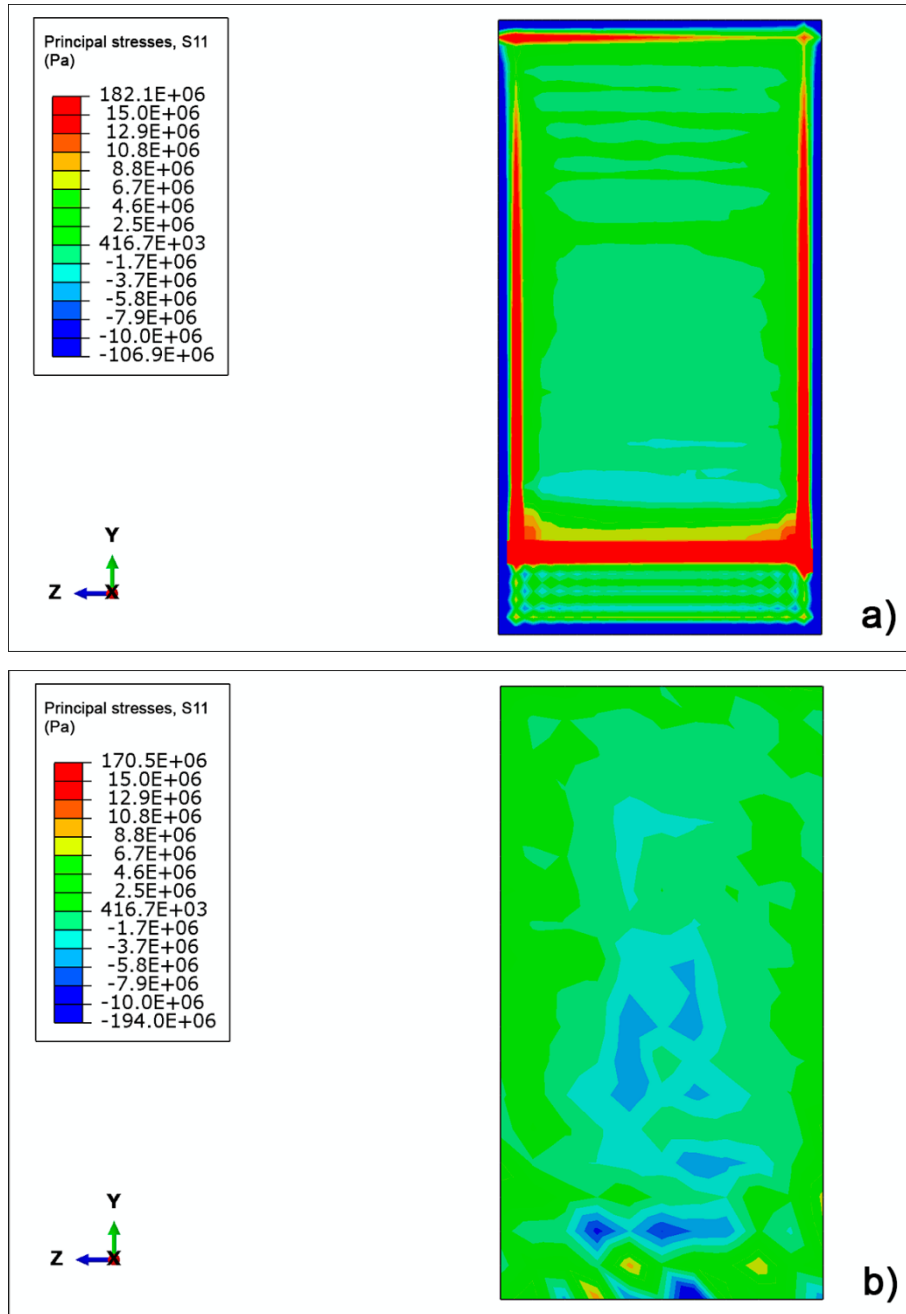


Figure 80 – Tensile and compressive stresses on symmetry plane of C-ring-8 in x component. Residual stresses a) measured by the contour method and b) calculated by the mechanical analysis.

There is a good agreement between the results obtained from the numerical calculations and the measurements performed in the selected cut surface of C-ring. However, the selected cut surface used in this study was not the best choice to assess the stresses across the C-rings, particularly at the thin regions. To overcome this issue, the symmetry plane across the longitudinal section of the C-ring should be cut. This alternative would be the ideal strategy to evaluate the residual stresses from thin to thick cross-section regions. However, the cut

operation would be burdensome and costly. Additionally, the fact that the contour method can only be executed on a symmetry plane, precludes its application on complex shapes.

Chapter 6 Conclusions and Future Work

6.1 Concluding Remarks

The high alloy content of the 25Cr-7Ni-Mo-N super DSS enhances the precipitation of secondary phases during cooling from solidification temperature, leading to the destabilization of the required duplex microstructure. We concluded that the cooling rate correlates to the volume percent of secondary phases with increased secondary phases at lower cooling rates. Additionally, we found that the secondary phases grow at the expense of the δ -phase.

We have also concluded that to provide an unequivocal and unique identification of the secondary phases, a combination of different imaging techniques is required. In particular, OM, SEM, and TEM need to be combined to provide the morphological, chemical, and crystallographic characterization of the secondary phases. As a result, we were able to identify the χ -phase and σ -phase. These phases are prone to form when the super DSS is exposed to temperatures between 700 °C and 1000 °C. Within this temperature range, the χ -phase nucleates on the δ -phase before the nucleation of the σ -phase, which is explained by the cubic-to-cubic OR between the χ -phase and δ -phase. However, the χ -phase showed metastability and underwent dissolution as the formation of the σ -phase proceeds. The formation of σ -phase was well modeled by the JMAK equation for the temperatures tested, between 700 °C and 1000 °C. Moreover, the kinetics of σ -phase isothermal formation is fastest at 950 °C, starting after 30 s at this temperature.

The volume percent of secondary phases formed depends on the holding time at the temperature range 700 °C to 1000 °C. In the case of cast parts with complex shapes and differential wall thickness, differential cooling rates are responsible for a differential microstructure. This fact needs to be taken in consideration when a numerical model is developed to simulate the thermal residual stresses of a cast part.

The distribution of residual stresses at the macroscale was carried out through two sequential steps: the thermal analysis and the mechanical analysis. In the case of the thermal analysis, we have found that the accurate prediction of the temperature distribution depends on the characterization of the IHTC at the metal/mold interface. In particular, the descriptions of the IHTC available in the literature cannot be widely applied. Instead, the IHTC must be characterized for each cast geometry, alloy chemical composition and sand mold composition. In this regard, the inverse method was successfully employed to determine the IHTC for the two C-rings of super DSS produced in furan-bonded sand molds.

The calibrated thermal model was used as input for the calculations of the residual stresses of the two C-rings with different sizes. The smaller C-ring showed higher residual stresses due to faster cooling rates and higher thermal gradient between the thick and thin cross-sections, confirming that avoiding high cooling rates, as well as high thermal gradients are essential rules for good quality cast components.

The effect of phase distribution on the residual stresses at the microscale was evaluated using models based on real images of the microstructure. The results show that differences on the distribution of phases cause different distribution on residual stresses. Higher stresses were found at the zones composed of γ -phase and δ -phase due to differences of the coefficient of thermal expansion between those phases. Furthermore, as demonstrated in the microstructural characterization of the C-ring, the γ -phase and δ -phase are found in the regions where the cooling rates from the solidification temperature were fast, particularly on thinner regions

Finally, the contour method was successfully applied to measure residual stresses of C-ring-8. On the symmetry plane across the thick cross-section, the experimental measurements agreed with the numerical results.

6.2 Future Work

The main research questions raised in chapter 1 were addressed through the present thesis. Yet, additional questions have appeared during this work. In this regard, suggestions for future work are proposed:

- Determine the kinetics of solid-phase transformations for higher alloyed grades, such as hyper DSS. To the best knowledge of this author, such studies have never been published.

- Conduct real-time imaging and elemental mapping of the formation of secondary phases through in situ TEM, to fully support the precipitation scenario of the 25Cr-7Ni-Mo-N super DSS.
- Implement an optimization algorithm to set the IHTC, using the temperature recorded in the experiment and the temperature estimated by thermal analysis. An automated approach would improve the convergence between the numerical and experimental temperatures, while reducing the time to obtain an accurate solution.
- Apply the sequentially coupled thermal-mechanical analysis to real cast components. Other variables associated with the sand casting process should be studied, and the geometry is an obvious extension of the current work. Additionally, the proposed methodology can be applied to other cast materials.
- Implement the kinetics of solid-phase transformation in the micromechanical analysis, to predict the phase distribution. As a starting point, the user subroutine UMAT on ABAQUS™ can provide data of the microstructural evolution during the cooling of cast parts. So, the uncoupled thermal-mechanical analysis will evolve into a phase-transformation-thermal-mechanical analysis.
- Measure the residual stresses in the C-rings through neutron diffraction. This non-destructive method provides in-depth measurements of the strain maps. In addition to this characteristic, some specialized facilities can accommodate real cast components, with weight up to 500 kg.

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