University POLITEHNICA of Bucharest
Doctoral school Materials Science and Engineering

PhD thesis

ABSTRACT

Specific phenomena occurring during thermomechanical processing of super-duplex stainless steel (SDSS) alloys

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Table of content

Abstract

Super duplex stainless steel (SDSS) alloys are designated as a subdivision of duplex stainless steel (DSS) alloys, showing a PRE value greater than 40, which guarantees high resistance to pitting corrosion. To achieve this high PRE value in the SDSS alloys chemical composition a high weight-fraction of Cr, Mo and N is necessary, which can increase the tendency of deleterious secondary phase precipitation in the ferrite phase, due to the increased diffusivity and decreased solubility of the main alloying elements in the ferrite phase in comparison with the austenite phase. Careful and precise control of the microstructure evolution during thermomechanical (TM) processing, by hot-deformation and subsequent heat treatments, is necessary to achieve optimum mechanical properties, including toughness and corrosion resistance.

Based on the identified knowledge gap, the general objective of the PhD thesis was to study the *specific phenomena occurring during thermomechanical processing of super-duplex stainless steel (SDSS) alloys*, which gives the title of the PhD thesis. In order to achieve the general objective, all research was performed on a *EN 1.4410 / UNS S32750 / F53* SDSS alloy, which was TM processed in two stages. Firstly, by hot rolling deformation at 1100°C, with a total applied deformation degree (thickness reduction) of approximately $\varepsilon_{total} \approx 65\%$, in six rolling steps. Aster hot deformation, a solution treatment at 1050°C, with a treatment duration of 30min and water quenching was applied, to obtain a pristine defect-free microstructure. Secondly, by different heat treatments, such as: isothermal / isochronal solution treatments and short-duration / long-duration ageing treatments, to study the influence of TM processing conditions on the microstructural evolution and the exhibited mechanical behaviour.

Keywords: super duplex stainless steel; thermomechanical processing; microstructural analysis; mechanical characterisation

Rezumat

Oțelurile inoxidabile de tip super duplex sunt desemnate ca o subdiviziune a oțelurilor inoxidabil de tip duplex, prezentând o valoare a parametrului PRE (*Pitting Resistance Equivalent*) mai mare de 40, ceea ce garantează o rezistență ridicată la coroziunea de tip pitting. Pentru a obține valori ridicate ale parametrului PRE, în compoziția chimică a oțelurilor de tip SDSS este necesară o fracție masică ridicată de Cr, Mo și N, care poate crește tendința de precipitare a fazelor secundare în masa de ferită, din cauza difuzivității crescute și a solubilității reduse a principalelor elemente de aliere în masa de ferită în comparație cu masa de austenită. Controlul atent și precis al evoluției microstructurii acestor oțeluri în timpul procesării termomecanice (TM) prin deformare la cald și tratamente termice, este necesar pentru a obține proprietăți mecanice optime (inclusiv tenacitate și rezistență la coroziune). Prelucrarea termomecanică a oțelurilor de tip SDSS poate fi o sarcină dificilă din cauza riscului crescut / tendinței ridicate de a forma faze secundare dăunătoare în timpul încălzirii.

Pe baza lacunelor de cunoștințe identificate, obiectivul general al tezei de doctorat a fost reprezentat de studierea *fenomenelor specifice care apar în timpul prelucrării termomecanice a oțeluri inoxidabile super-duplex (SDSS)*, obiectiv ce dă și titlul tezei de doctorat. Pentru atingerea obiectivului general, toate cercetările au fost efectuate pe aliajul / oțelul *EN 1.4410 / UNS S32750 / F53*, care a fost procesat TM în două etape. Prima etapă de procesare a constat într-o deformare prin laminare la cald, la temperatura de 1100°C, cu un grad total de deformare aplicat de aproximativ $\varepsilon_{total} \approx 65\%$, în șase pași de laminare. După deformarea la cald, s-a aplicat un tratament de călire de punere în soluție la temperatura de 1050°C, cu o durată de tratament de 30min și răcire în apă. Scopul tratamentului de călire de punere în soluție a fost acela de a obține o microstructură curată, fără defecte de microstructură. A doua etapă de procesare a constat într-o serie de tratamente termice diferite, cum ar fi: tratamente izoterme / izocronale de călire de punere în soluție și tratamente de îmbătrânire de scurtă și lungă. Scopul acestor tratamente a fost acela de a studia influența condițiilor de procesare TM asupra evoluției microstructurale și a comportamentului mecanic.

Cuvinte cheie: oțeluri inoxidabile de tip super duplex; procesare termomecanica; analiza microstructurală; caracterizare mecanică.

Introduction

Super duplex stainless steel (SDSS) alloys are designated as a subdivision of duplex stainless steel (DSS) alloys, showing a PRE value greater than 40, which guarantees high resistance to pitting corrosion. To achieve this high PRE value in the SDSS alloys chemical composition a high weight-fraction of Cr, Mo and N is necessary, which can increase the tendency of deleterious secondary phase precipitation in the ferrite phase, due to the increased diffusivity and decreased solubility of the main alloying elements in the ferrite phase in comparison with the austenite phase. Careful and precise control of the microstructure evolution during thermomechanical (TM) processing, by hot-deformation and subsequent heat treatments, is necessary to achieve optimum mechanical properties, including toughness and corrosion resistance.

Based on the above considerations, the research carried out in the PhD thesis aimed to investigate the effects induced by the thermomechanical processing conditions on both the microstructure evolution and the mechanical behaviour of super duplex stainless steel alloys.

* * *

The PhD thesis is structured in three parts, describing the research carried out to achieve the main objectives.

The first part is devoted to the literature overview of the field under investigation and includes the research objectives, concepts and employed methods. The literature overview covers different aspects, such as:

- Fe-based stainless alloys (stainless steels);
- role of alloying elements in stainless steel alloys;
- classification of stainless steels;
- secondary phases and precipitates in duplex stainless steel alloys;
- general considerations regarding stainless steel alloys crystallography;
- general data on EN 1.4410 / UNS S32750 / F53 super-duplex stainless steel alloy.

The PhD thesis assumed five research objectives, which were as following:

1. investigation of microstructural evolution during hot deformation of EN 1.4410 / UNS S32750 / F53 super-duplex stainless steel alloy;
2. investigation of isochronal treatment effects induced on the microstructure and the mechanical properties of EN 1.4410 / UNS S32750 / F53 super-duplex stainless steel alloy;

3. investigation of isothermal treatment effects induced on the microstructure and the mechanical properties of EN 1.4410 / UNS S32750 / F53 super-duplex stainless steel alloy;
4. investigation of ageing treatment effects induced on the hot-deformation microstructure and the mechanical properties of EN 1.4410 / UNS S32750 / F53 super-duplex stainless steel alloy;
5. investigation of ageing treatment effects induced on the solution treated microstructure and the mechanical properties of EN 1.4410 / UNS S32750 / F53 super-duplex stainless steel alloy.

The second part is dedicated to the presentation of the published research articles in extenso. The most important research results were disseminated in high-impact ISI indexed journals, such as:

- JOURNAL OF ADVANCED RESEARCH (FI 2022 – 10.7);
- JOURNAL OF MATERIALS RESEARCH AND TECHNOLOGY (FI 2022 – 6.4);
- MATERIALS (FI 2022 – 3.4);
- METALS (FI 2022 – 2.9).

The third part presents general conclusions and personal contributions resulting from the performed research. The PhD thesis concludes with the reference section, consisting of 335 references.

1. Presentation of the doctoral theme. Concepts and methods

1.1. Literature overview: *Specific phenomena occurring during thermomechanical processing of super-duplex stainless steel (SDSS) alloys*

1.1.1. Fe-based stainless alloys (stainless steels)

Stainless steels are a category of steels that, over the more than 100 years since their discovery, have seen a great deal of interest, due both to their excellent corrosion resistance properties in increasingly aggressive, highly oxidising and high-temperature environments, and to their various combinations of improved mechanical strength, ductility and toughness, thus finding their use in the most diverse applications, from the simplest, such as kitchen utensils, to the most complex, such as space vehicles [1,2].

According to the standards [3], the notion of stainless steel means an iron (Fe) and carbon (C) alloy, in which the chromium (Cr) content in the alloy's composition must exceed the value of 10.5wt%. The ability of chromium to produce a tightly adherent oxide layer on the surface of stainless steels in relatively mild environments, sufficiently enriched in oxygen to maintain this layer, has led to their improved corrosion resistance compared to other categories of steels, thus becoming their most important property. In order to guarantee an increase in corrosion resistance in more hostile environments, higher chromium contents must be added, together with other alloying elements, so that stainless steels have a complex, multicomponent chemical composition, containing high amounts of substitutional and interstitial alloying elements, such as: (10 ÷ 30)wt% Cr, (1 ÷ 25)wt% Ni, (1 ÷ 8)wt% Mo, $\leq$ 1wt% C, Mn, Cu, W, Ti, N, etc., which also have a particular influence on the mechanical properties, deformability, weldability and heat treatment stability [4-7].

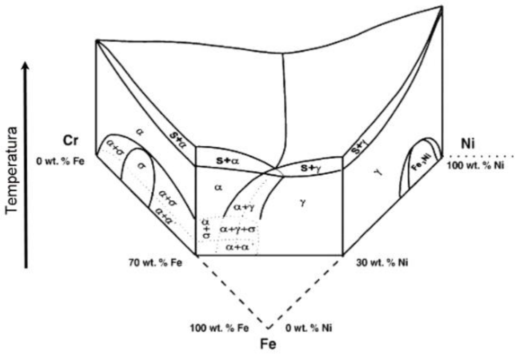

Figure 1. *Fe-Cr-Ni phase diagram [8,9].*

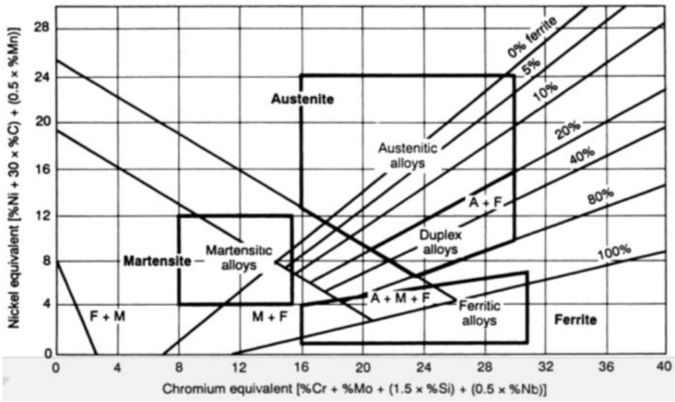

Figure 2. *Schaeffler's structural diagram [11,12].*

The compositional base of stainless steels is the constituted by the Fe-Cr-Ni ternary system (Figure 1) [8,9] which also determines both the number and types of present phases and their compositional range.

In the case of Fe-based stainless alloys, the stability of the constituent phases, ferrite (α/δ) and austenite (γ), depends on the content of alloying elements. Thus, alloying elements can be divided into alpha/delta stabilising-elements (Cr, Mo, Si, Nb), which stabilise the ferrite phase – exhibiting a *body-centred cubic* crystal lattice (BCC), and gamma stabilising-elements (Ni, Mn, N, Cu), which stabilise the austenite phase – exhibiting a *face-centred cubic* crystal lattice (FCC). In view of the effects of these elements on the phase balance, in practice the chromium equivalent (Cr_{ech}) content for ferritic-phase stabilising elements and the nickel equivalent (Ni_{ech}) content for austenitic-phase stabilising elements are used as standards [10].

Using the Schaeffler diagram (Figure 2) [11,12], defined in chromium equivalent and nickel equivalent coordinates, the alloy microstructural type can be predicted according to relations (1) and (2):

$$Cr_{ech}[\%wt.] = \%Cr + \%Mo + (1.5 \cdot \%Si) + (0.5 \cdot \%Nb) \tag{1}$$

$$Ni_{ech}[\%wt.] = \%Ni + (30 \cdot \%C) + (0.5 \cdot \%Mn) + (30 \cdot \%N) \tag{2}$$

From the Schaeffler diagram (Figure 2) [11,12], it can be observed that the type of structure obtained after air quenching of stainless steel is a function of the chemical composition and the existing ratio of alpha/delta and gamma stabilising-elements. The Schaeffler diagram is often used for welded microstructures predictions, being very helpful to approximate the microstructure stability ranges of different stainless steels [13].

Depending on the presence of the predominant phase in the microstructure at room temperature, the stainless steels are classified into four main classes: martensitic, austenitic, ferritic and duplex. There is a fifth class of stainless steels, represented by steels that are not characterized by microstructure, but rather by a special hardening mechanism that leads to the formation of precipitates in the microstructure, constituting the precipitation hardenable stainless steel class. [14].

Due to both their high corrosion resistance in various environments (wet, oxidising, acidic, etc.) and their favourable combination of mechanical properties (strength, toughness, ductility, etc.), stainless steels can be successfully used as structural and protective materials, usually at temperatures up to 800°C, in a wide range of industrial applications, from the food industry to the oil, gas, chemical and nuclear industries [15]. Also, stainless steels usually possess good machinability and weldability properties, making them easy to process and use [1,2].

1.1.2. The role of alloying elements in stainless steel alloys

Under particular environmental conditions, e.g. acidity, salinity, etc., the stainless steels are not completely immune to corrosion, they may be susceptible to localized corrosion, the most important forms of localized attack being spot/pitting corrosion, crevice corrosion, intergranular corrosion, mechanical stress corrosion [16]. To increase the corrosion resistance, large amounts of expensive alloying elements (Cr, Ni, Mo) have to be introduced into their composition, but this increases the production cost of stainless steels [17]. Other elements can be added to increase, for example, corrosion resistance in acidic, aggressive environments (Mo, Cu), hot oxidation resistance (Si, Al) and to improve mechanical characteristics at low and high temperatures (Ti, Nb, Co) [18].

Since corrosion resistance is of particular importance in stainless steel applications, a *corrosion protection factor/coefficient* has been introduced for spot corrosion (corrosion known as pitting) and defined as a local penetration of the passive layer in typical chloride solutions, the chloride ions being some of the most aggressive ions against these steels, but also ubiquitous in the environment [19]. This coefficient has the acronym PRE (*Pitting Resistance Equivalent*) and depends on the composition of the alloy, mainly on key elements such as Cr, Mo and N [20], which over the years showed several computation formula (Table 1) [21], the most commonly used being:

$$PRE = Cr[\%] + 3.3\ Mo[\%] + 16\ N[\%] \tag{3}$$

Tabel 1. *Evolution of computation formula for the PRE (Pitting Resistance Equivalent) coefficient* [21].

PRE	***Source***
Cr[%] + 3.3 Mo[%]	Lorenz (1969)
Cr[%]+ 3.3 Mo[%] + 16 N[%]	Truman (1978)
Cr[%]+ 3.3 Mo[%] + 30 N[%]	Herbsleb (1982)
Cr[%] + 3.3 Mo[%] + 1 N[%]	Gysel (1987)
Cr[%] + 3.3 Mo[%] + 15 N[%] + 2 Cu[%]	Heimgartner (1988)
Cr[%] + 3.3 Mo[%] + 30 N[%] - 1 Mn[%]	Rondelli (1995)
[Cr(%) -14.5 C(%)] + 3.3 Mo[%] + 2 Cu[%] + 2 W[%] + 16 N[%]	API Standard 610/ ISO 13709 (2003)

The higher the value of the PRE index, the higher the resistance of stainless steel to pitting corrosion. This number does not apply to all corrosive media and does not represent the absolute value of corrosion resistance. However, this parameter is often taken into account because it provides a general estimate of the resistance to spot/pitting corrosion in a chlorinated aqueous solution [22].

1.1.3. Classification of stainless steel alloys

Since the microstructure has a decisive effect on exhibited properties, stainless steels can be classified according to their microstructure at room temperature into the following categories (Figure 3): martensitic stainless steels (their microstructure consisting of martensite phase), ferritic stainless steels (their microstructure consisting of ferrite phase), austenitic stainless steels (their microstructure consisting of austenite phase) and ferritic-austenitic stainless steels (their microstructure consisting of a mixture of ferrite and austenite phases) [1].

Ferritic-austenitic stainless steels, containing a two-phase microstructure, are also called duplex stainless steels. Usually, in this class of steels, the amount/mass fraction of phases present in the microstructure is approximately equal (50 austenite / 50 ferrite) [27]. Depending on the chemical composition and the pitting resistance equivalent number (PRE_N – for nitrogen-containing stainless steels), they are further classified into four subcategories: lean duplex, standard duplex, super duplex and hyper duplex.

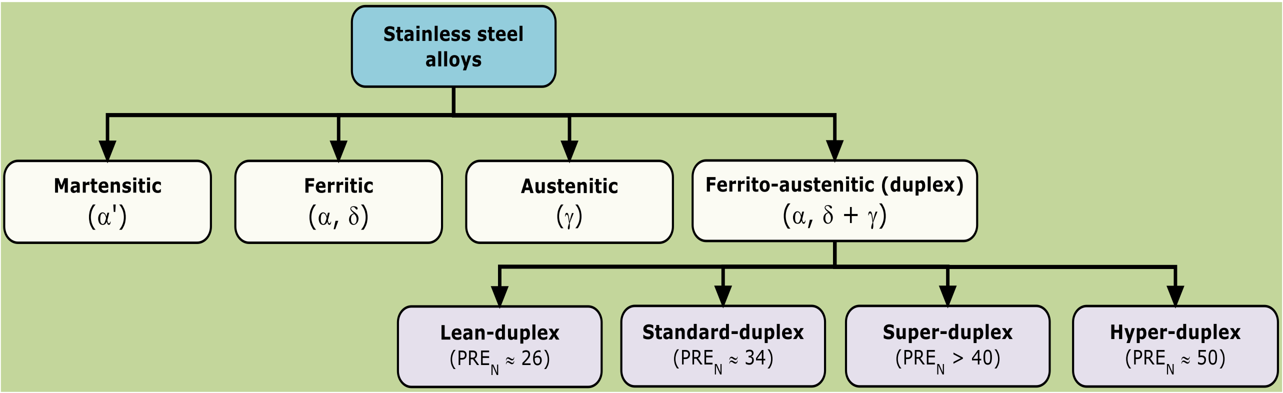

Figure 3. *Classification of stainless steel alloys.*

1.1.3.1. Martensitic stainless steels

Martensitic stainless steels contain martensite as the basic phase at room temperature. Also, at room temperature, the phase structure of these steels may contain residual phases, such as ferrite (α, δ) and/or austenite (γ). Martensitic stainless steels are obtained by applying an appropriate heat treatment, which involves heating the alloy in the austenitic range (γ) and rapidly cooling it [14].

In the microstructure of these steels, the martensitic phase is largely responsible for the properties manifested by these steels. In general, martensitic stainless steels possess high hardness, strength and toughness, but they are characterized by low ductility (high brittleness). These steels are also resistant to corrosion in mild environments and are ferromagnetic [53].

In the chemical composition of these steels there is a limited amount of Cr, normally between (11.5 ÷ 18)wt% and a C content among the highest of the stainless steels, generally between (0.1 ÷ 1.2)wt%, which makes these steels hardenable in various media, from air cooling to cooling in various liquid media (water, oils, emulsions, etc.). Also, after the quenching heat treatment, these steels can undergo tempering heat treatments, at different temperatures, to finally produce favourable combinations of mechanical properties (strength, toughness, etc.) and plasticity (ductility) [54].

Usually, these steels are subjected to a softening annealing treatment, at temperatures between 750°C and 900°C, followed by slow cooling (in a furnace or in air), ensuring good machinability. In order to obtain the final mechanical properties, these steels are subjected to an enhancement heat treatment (quenching followed by tempering), undergoing heating at temperatures between 950°C and 1050°C, followed by quenching (in water/oil or air), while tempering is performed at temperatures between 600°C and 750°C, followed by cooling in air [55]. In these steels, at elevated temperature, the microstructure is austenitic, but following the enhancement treatment martensitic-type microstructures are obtained. Alloys with increased Cr (≥ 16wt%) and C (0.6 ÷ 1.2wt%) contents, in the quenched and tempered state have a yield strength that can reach almost 1900 MPa and a high hardness, almost 60 HRC, making them suitable for wear-resistant machine parts, such as for example grade EN 1.4125 / UNS S44004 / AISI 440C [56].

Martensitic stainless steels are typically alloyed with Ni and Mo to achieve, after enhancement treatment, high strength and improved corrosion resistance in certain environments. Alloying elements such as V, W and Nb are added to improve temper strength by forming stable carbides. Also, the chemical composition of these alloys can contain an amount of Ni, up to 8wt%, necessary to inhibit the occurrence of ferrite, which can have a detrimental role on mechanical properties [57]. They can also be additionally alloyed with S or Se to improve machinability, as in the case of EN 1.4005 / UNS S41600 / AISI 416.

Tabel 2. *Chemical composition of some martensitic stainless steel alloys [61].*

Grade (standard) EN / UNS / AISI	***Chemical composition, wt%***											
	C	***Mn***	***Si***	***P***	***S***	***Cr***	***Mo***	***Ni***	***Nb***	***Al***	***Cu***	***N***
1.4006 / S41000 / 410	0.08 - 0.15	<1.5	<1.0	<0.04	<0.03	11.5 - 13.5	-	<0.75	-	-	-	-
1.4021 / S42000 / 420	0.16 - 0.25	<1.5	<1.0	<0.04	<0.03	12.0 - 14.0	-	-	-	-	-	-
1.4104 / S43020 / 430F	0.10 - 0.17	<1.5	<1.0	<0.04	0.15 - 0.35	15.5 - 17.5	0.2 - 0.6	-	-	-	-	-
1.4109 / S44002 / 440A	0.60 - 0.75	<1.0	<0.7	<0.04	<0.03	14.0 - 16.0	0.4 - 0.8	-	-	-	-	-
1.4112 / S44003 / 440B	0.75 - 0.95	<1.0	<1.0	<0.04	<0.03	16.0 - 18.0	<0.75	-	-	-	-	-

The stainless steels are symbolized according to international standards (*European Standard* - EN, *American Iron and Steel Institute* - AISI) [58-60], each type of steel being identified by name or number (*European Number* - EN, *Unified Numbering System* - UNS). The chemical compositions of some martensitic stainless steels are shown in Table 2 [61].

Typical applications in which martensitic stainless steels are used include a multitude of fields, ranging from machine building (moulds, work tools, etc.) to food (kitchen utensils, etc.), e.g. [61]:

- ***EN 1.4006 / UNS S41000 / AISI 410***: mechanical components working in aqueous environments: bolts, valves, water pump parts, blades for steam and hydraulic turbines, etc;
- ***EN 1.4021 / UNS S42000 / AISI 420***: mechanical components working in aqueous and weak acid environments: steam and water turbine blades, bolts, medical instruments, springs, civil construction / architectural facades, etc;
- ***EN 1.4125 / UNS S44004 / AISI 440C***: mechanical components working in aqueous and weakly acidic/corrosive environments, mainly from the food and chemical industries: household items, valves, bolts, pumps, rollers, bearing balls, etc.

1.1.3.2. Ferritic stainless steels

Ferritic stainless steels contain ferrite, α/δ (BCC), as the base phase, with chromium being the major alloying element, added in sufficient quantities to completely stabilise the ferrite. In the chemical composition of these steels, the amount of Cr is, generally, between (10.5 ÷ 30)wt%. Also, in the composition small amounts of gamma-stabilising elements, such as C (usually less than 0.1wt%), N, Mn, sometimes Ni can also be found. They are ferromagnetic and do not undergo structural transformations on heating and cooling [62]. Usually, in order to increase their machinability, after mechanical processing by hot or cold plastic deformation, these steels are heat treated by annealing at temperatures between 680°C and 850°C, followed by cooling in water or air (e.g. EN 1.4003 / UNS S40977 / AISI 410L, EN 1.4016 / UNS S43000 / AISI 430, EN 1. 4512 / UNS S40900 / AISI 409L, EN 1.4521 / UNS S44401 / AISI 444) [63]. In some cases, following rapid cooling from the austenitic range (γ), an amount of residual austenite may be present in the microstructure of these steels, which may contribute to an increase in both weldability, machinability and ductility characteristics and corrosion resistance [64].

These steels possess low toughness and machinability and are susceptible to embrittlement due to the possibility of precipitation of secondary phases (R, G, μ, ε, σ, χ, etc.) in the ferrite mass, which are dangerous/deleterious to ductility, toughness and corrosion resistance [65]. They also exhibit ductile-fragile transition, which leads to decreased toughness of these steels when stressed at negative temperatures [66].

Ferritic stainless steels have good corrosion resistance (e.g. in aqueous environments containing chloride ions, alcohols, organic acids, nitric acid, nitrates, etc.), superior to martensitic stainless steels, but inferior to austenitic stainless steels [67]. In order to increase the corrosion resistance, toughness, ductility and weldability of these steels, the content of interstitial alloying elements should be reduced to amounts of less than 0.03wt% for each of these elements, but it should be kept in mind that a much-reduced content of these interstitial elements favours the exaggerated growth of ferrite grains, with harmful consequences on the mechanical properties [68]. Thus, a fine grain size, a low content of interstitial elements and the elimination or reduction as far as possible of secondary phases by a well-controlled heat treatment contribute to improve the ductility, toughness and corrosion resistance of these steels [69].

To give the steels particular characteristics, some marks/grades are alloyed with Mo (to improve corrosion resistance in chloride environments), S or Se (to improve machinability, e.g. EN 1. 4105 / UNS S43020 / AISI 430F), with Al and Si (to increase the stability of the ferritic structure and to improve hot oxidation resistance), with Ti and/or Nb (to help improve intergranular corrosion resistance and weldability, e.g. EN 1.4509 / UNS S43940 / AISI 441) [70,71].

In the case of ferritic stainless steels possessing a Cr content above 18wt% (super ferritic stainless steels), the carbon content is very low (< 0.025wt%) and, in order to increase corrosion and oxidation resistance, higher amounts of Mo (1.5 ÷ 2.5)wt% and Ti (0.2 ÷ 0.8)wt% are introduced in their chemical composition, e.g. EN 1.4521 / UNS S44401 / AISI 444 [72]. Nickel can also be added without destabilizing the ferrite, usually between (2 ÷ 4)wt%, to increase toughness, but also for its positive effect on corrosion resistance in reducing pitting and crevice corrosion [73,74]. Chemical compositions of some ferritic stainless steels are given in Table 3 [75].

Tabel 3. *Chemical composition of some ferritic stainless steel alloys [75].*

Grade (standard) EN / UNS / AISI	***Chemical composition, wt%***											
	C	***Mn***	***Si***	***P***	***S***	***Cr***	***Mo***	***Ni***	***V***	***Ti***	***Nb***	***N***
1.4000 / S41008 / 410S	<0.08	<0.08	<0.1	<0.04	<0.03	12.0 - 14.0	-	<0.6	-	-	-	-
1.4003 / S40977 / 410L	<0.03	<1.5	<1.0	<0.04	<0.03	10.5 - 12.5	-	0.3 - 1.0	-	-	-	<0.03
1.4016 / S43000 / 430	<0.08	<1.0	<1.0	<0.04	<0.015	16.0 - 18.0	-	-	-	-	-	-
1.4105 / S43020 / 430F	<0.08	<1.5	<1.5	<0.04	0.15 - 0.35	16.0 - 18.0	0.2 - 0.6	-	-	-	-	-
1.4512 / S40900 / 409L	<0.08	<1.0	<1.0	<0.04	<0.03	10.5 - 11.7	-	<0.5	-	<0.75	-	-
1.4509 / S43940 / 441	<0.03	<1.0	<1.0	<0.04	<0.02	17.5 - 18.5	-	-	-	0.1 - 0.6	0.3 - 1.0	-
1.4510 / S43035 / 430TI	<0.05	<1.0	<1.0	<0.04	<0.03	16.0-18.0	-	<0.75	-	0.15-0.80	-	-
1.4521 / S44401 / 444	<0.025	<1.0	<1.0	<0.04	<0.02	17.0-20.0	1.8-2.5	-	-	0.15-0.80	-	<0.03

Typical applications in which ferritic stainless steels are used range from food (utensils, household items, etc.) to architectural (load-bearing structures, facades, etc.), where these alloys are usually used in medium aggressive environments, e.g. [75]:

- ***EN 1.4003 / UNS S40977 / AISI 410L***: mechanical and decorative components working in non-aggressive environments: bolts, civil constructions, architectural facades, etc;
- ***EN 1.4000 / UNS S41008 / AISI 410S***: mechanical components working in aqueous and mildly corrosive, acid or alkaline environments: columns and reaction vessels in the chemical industry, heat exchangers, pipes, etc;
- ***EN 1.4016 / UNS S43000 / AISI 430***: mechanical components working in aqueous and weakly corrosive, acidic or alkaline environments, as well as environments with chlorine, nitrogen ions, etc.: columns and reaction vessels in the oil industry, heat exchangers, pipes, etc;
- ***EN 1.4512 / UNS S40900 / AISI 409L***: mechanical components working in aqueous media containing chlorine ions (with a concentration < 200ppm), especially in the marine industry: desalination plants, heat exchangers, pipes, etc.

1.1.3.3. Austenitic stainless steels

Austenitic stainless steels, at room temperature, contain austenite phase - γ (FCC) as a base phase. The chemical composition of these steels usually contains a quantity of Cr between (16 ÷ 25)wt%, Ni between (8 ÷ 27)wt%, a C content, usually < 0.1wt%, and other alloying elements (Mo, Nb, V, Ti, Cu, N, etc.) [76]. They are non-magnetic and, like ferritic stainless steels, cannot be hardened by heat treatment and can only be hardened by cold-working to achieve high mechanical strengths [77]. Usually, in order to increase their machinability, after the plastic forming operation, these steels are heat treated by solution annealing at temperatures between 1050°C and 1160°C, followed by cooling in water or air (e.g. EN 1.4361 / UNS S30600 / AISI 306, EN 1.4401 / UNS S31600 / AISI 316, EN 1.4438 / UNS S31703 / AISI 317L) [78].

Austenitic stainless steels have the advantage of high weldability, machinability, ductility and toughness properties and, are not susceptible to embrittlement because the possibilities of precipitation of secondary phases (R, G, μ, ε, σ, χ, etc) in the austenite mass are limited [79]. This behaviour is mainly due to the crystallographic characteristics of γ austenite (specific to FCC crystal lattice materials), but also to the fact that these steels exhibit a low tendency to overgrow austenite grain size during their heating/thermal processing. In some cases, following rapid cooling from the austenite range, an amount of residual ferrite may be present in the microstructure of these steels, which may contribute to an increase in both strength characteristics (ultimate strength, yield strength) and corrosion resistance in chloride ion-rich environments [80]. Austenitic stainless steels do not exhibit the ductile-fragile transition, which leads to increased toughness, performing very well under shock/dynamic loading, even at low temperatures [81].

An important effect of alloying with a high content of gamma stabilising-elements (Ni, Mn) is represented by the increased austenite stability on cooling. The structure of these steels at low temperatures containing austenite, regardless of the cooling rate. The addition of nickel improves the mechanical properties at high temperatures and cold workability; thus, these steels have superior corrosion resistance and weldability in comparison to other classes of stainless steels [82].

The high Cr and Ni contents make these steels expensive. In addition, they have a susceptibility to stress corrosion cracking, especially in environments containing chloride solutions and at high temperatures, i.e. AISI 200 series, which typically contain >12wt% Cr, < 7wt% Ni and (4 ÷ 15.5)wt% Mn [83].

Depending on the conditions imposed by the various fields of use, around the classical composition, containing around 18wt% Cr and 8wt% Ni (18 - 8 steels), a large number of steel grades have been developed. The most common are austenitic Fe-Cr-Ni stainless steels, known as the AISI 300 series, containing (16 ÷ 26)wt% Cr, < 24wt% Ni, < 3wt% Mo, such as: EN 1.4301 / UNS S30400 / AISI 304 and EN 1.4401 / UNS S31600 / AISI 316, being used in the manufacture of parts in the automotive, aero and naval industries, elements of machinery and installations in the chemical industry, medical devices, implants and prostheses, in the food industry, and in the manufacture of household equipment [84].

Grades containing more than 0.03wt% C, when heated to temperatures between 500 ÷ 800°C and cooled slowly, show a high susceptibility to precipitation of metallic carbides at the grain boundary, which increases the risk of *sensitisation*, a phenomenon that increases the susceptibility to intergranular corrosion, with precipitation of Cr-enriched carbides at the grain boundary, depleting adjacent areas of Cr [85]. This type of corrosion can be prevented either by lowering the carbon content of the steel to its austenite solubility limit, usually < 0.03wt% (e.g. EN 1.4306 / UNS S30403 / AISI 304L and EN 1. 4404 / UNS S31603 / AISI 316L) [86], either by applying a solution quenching treatment, heating the steel to temperatures above 800°C until the chromium carbides dissolve in the solid solution, then cooling it rapidly, thus preventing the carbides from forming again, or additional alloying with strongly carburising elements, such as Ti and/or Nb, which form stable carbides with the carbon not dissolved in austenite (e.g. EN 1. 4541 / UNS S 32100 / AISI 321 and EN 1.4550 / UNS S 34700 / AISI 347) [87].

In the case of austenitic stainless steels with a high Cr content, usually between (18 ÷ 28)wt%, known as super austenitic stainless steels, in order to maintain the austenitic character it is necessary to increase the content of gamma stabilising-alloying elements (Ni, Mn, N), so that on cooling the phase transition $\gamma \rightarrow \delta$ is inhibited [88]. Therefore, in these steels, the amount of Ni is between (20 ÷ 30)wt%, with significant additions of Cu (0.5 ÷ 1.8)wt% and N up to 0.9wt%. In order to improve weldability, Mn is added to these steels, which also partially replaces nickel and is an element that stabilises austenite and helps to increase nitrogen solubility [90].

Also, super austenitic steels can contain up to 8wt% Mo, to improve corrosion resistance in environments containing chloride ions. An example of such a steel is EN 1.4652 / UNS S32654 / AISI 654 SMo, which exhibits an excellent combination of mechanical properties (yield strength of ~ 450 MPa, tensile strength of ~ 750 MPa and elongation of 40%) and corrosion resistance (PREN ≈ 35), competing with high-alloyed super duplex stainless steels [91,92]. The chemical compositions of some austenitic stainless steels are shown in Table 4 [93]. Due to their advantageous properties, high ductility and mechanical strength, weldability, toughness even at very low temperatures, as well as corrosion resistance in highly corrosive environments (oxidizing acids, non-oxidizing acids, halogens, etc), austenitic stainless steels remain the most popular, being appreciated in many fields, from the food industry (tableware and houseware, food furniture, etc.) to the chemical and energy industry (refineries, combustion boilers, etc.), examples of such steel grades being the following [93]:

- ***EN 1.4301 / UNS S30400 / AISI 304,*** used in almost all industries, in the construction of components and parts working in aqueous, corrosive environments and environments rich in chlorine, fluorine, nitrogen ions, etc.: columns and reaction vessels in the chemical and oil industry, storage tanks, heat exchangers, plumbing, water pipes, etc;

Tabel 4. *Chemical composition of some austenitic stainless steel alloys [93].*

Grade (standard) EN / UNS / AISI	***Chemical composition, wt%***											
	C	***Mn***	***Si***	***P***	***S***	***Cr***	***Mo***	***Ni***	***V***	***Nb***	***Cu***	***N***
1.4301 / S30400 / 304	<0.07	<2.0	<1.0	<0.04	<0.02	17.5 - 19.5	-	8.0 - 10.5	-	-	-	<0.11
1.4305 / S30300 / 303	<0.15	<2.0	<1.0	<0.20	>0.15	17.0 - 19.0	-	8.0 - 10.0	-	-	<1.0	<0.11
1.4306 / S30403 / 304L	<0.03	<2.0	<1.0	<0.45	<0.03	17.5 - 20.0	-	8.0 - 13.0	-	-	-	<0.10
1.4303 / S30500 / 305	<0.06	<2.0	<1.0	<0.45	<0.03	17.0 - 19.0	-	10.5 - 13.0	-	-	-	<0.11
1.4361 / S30600 / 306	<0.02	<2.0	3.7 - 4.5	<0.02	<0.01	16.5 - 18.5	<0.2	14.0 - 16.0	-	-	<0.5	<0.11
1.4401 / S31600 / 316	<0.07	<2.0	<1.0	<0.45	<0.02	16.5 - 18.5	2.0 - 2.5	10.0 - 13.0	-	-	-	<0.11
1.4404 / S31603 / 316L	<0.03	<2.0	<1.0	<0.45	<0.03	16.5 - 18.5	2.0 - 2.5	10.0 - 13.0	-	-	-	<0.11
1.4438 / S31703 / 317L	<0.03	<2.0	<1.0	<0.45	<0.03	17.5 - 19.5	3.0 - 4.0	13.0 - 17.0	-	-	-	<0.11
1.4466 / S31050 / 310MoLN	<0.02	<2.0	<0.7	<0.25	<0.01	24.0 - 26.0	2.0 - 2.5	21.0 - 23.0	-	-	-	0.10 - 0.16
1.4652 / S32654 / 654 SMo	<0.02	2.00-4.00	<0.50	<0.3	<0.01	24.0 - 25.0	7.00 - 8.00	21.0 - 23.0	-	-	0.3 - 0.6	0.45 - 0.55
1.4550 / S 34700 / 347	<0.08	<2.0	<1.0	<0.45	<0.03	17.0 - 20.0	-	9.00 - 13.00	-	<1.10	-	-
1.4563 / N08028 / Alloy 28	<0.02	<2.0	<0.7	<0.3	<0.01	26.0 - 28.0	3.0 - 4.0	30.0 - 32.0	-	-	0.7 - 1.5	<0.10
1.4570 / S30330 / 303Cu	<0.08	<2.0	<1.0	<0.04	0.15 - 0.30	17.0-19.0	<0.6	8.0 - 10.0	-	-	1.4 - 1.8	<0.11
Nitronic 50 / S20910 / XM-19	<0.06	4.0 - 6.0	<0.75	<0.04	<0.03	20.5 - 23.5	2.0 - 3.0	11.5 - 13.5	0.1 - 0.3	0.1 - 0.3	-	0.2 - 0.4
Nitronic 60 / S21800 / Alloy 218	<0.1	7.0 - 9.0	3.5 - 4.5	<0.06	<0.03	16.0 - 18.0	<0.75	8.0 - 9.0	-	-	-	0.08 - 0.18

- ***EN 1.4361 / UNS S30600 / AISI 306,*** used in almost all industries, in the construction of machine elements and parts working in highly acidic environments (sulphuric, nitric, hydrochloric acid, etc.): columns and reaction vessels in the chemical industry, storage tanks, heat exchangers, pipes, etc;
- ***EN 1.4401 / UNS S31600 / AISI 316 și EN 1.4404 / UNS S31603 / AISI 316L,*** used in almost all industries, in the construction of components and parts working in highly corrosive environments (phosphoric acid, nitric acid, formic acid, acetic acid, lactic acid, salts, etc.): marine installations, petrochemical plants, refineries, cryogenic plants, food industry equipment, boilers, heat exchangers, burners, autoclaves, etc;
- ***EN 1.4547 / UNS S31254 / AISI 254 SMO,*** used in the construction of elements of machinery and installations working in highly corrosive environments (chlorides and non-oxidizing acids):

petrochemical plants, refineries, in the pulp and paper industry, for storage tanks, cryogenic installations, aviation and aeronautical components, bolts, screws, valves, boilers, burners, etc;

- ***Nitronic 50 / UNS S20910 / XM-19** și **Nitronic 60 / UNS S21800 / Alloy 218,*** used in applications requiring both high corrosion resistance and high working temperature, such as: reaction vessels, storage tanks, chemical extraction columns, heat exchangers, etc.

1.1.3.4. Duplex stainless steels

The emergence of numerous innovative brands of steels, in which the main alloying element is chromium, is due to the wide variety of working conditions to which stainless steels are subjected and the need to use a steel that is suitable for the technological purpose and at the same time as cheap as possible. Ferritic-austenitic (duplex) stainless steels are a category of steels that has been developed to solve these problems and to meet certain requirements, particularly those of the oil extraction and refining industry, and are now used in a wide range of applications [94].

Duplex stainless steels are two-phase (ferrite – austenite) alloys at room temperature, belonging to the Fe-Cr-Ni system (Figure 1) [8], in which the constituent elements generally provide a balanced balance of the volume fractions of the two phases, ferrite δ (BCC) and austenite γ (FCC), often in a ratio close to 50 : 50, without undesirable secondary phases, in order to achieve excellent mechanical and corrosion resistance properties [95,96]. To achieve this ratio, ferrite-stabilising elements (Cr, Mo, Si, W, Nb, Ti) are balanced by austenite-stabilising elements (Ni, N, C, Mn, Cu), the exact proportions of ferrite and austenite being also determined by the applied heat treatments [27,97]. Partitioning of alloying elements between the two phases takes place by a controlled diffusion process and is strongly determined by the cooling rate to which the steel is subjected [98].

Duplex microstructure is formed during the solidification. Starting from the liquid state, a duplex stainless steel solidifies into a fully ferritic microstructure (δ) and, as it cools, the transformation of ferrite (δ) to austenite (γ) occurs [99]. This austenite is formed from the ferrite matrix by a process of nucleation and growth [100], then developing as elongated lamellae (islands) uniformly distributed in the ferritic matrix, with its fraction mass increasing as the temperature decreases, transforming into a duplex microstructure [101].

During plastic deformation at high temperatures, usually in the (1200 ÷ 1050)°C temperature range, where ferrite δ and austenite γ are thermodynamically stable, a typical plastic deformation duplex microstructure with grains of austenite γ, elongated (islands) in the plastic processing direction, occurs in the ferrite δ matrix [102]. After hot plastic deformation, it is necessary to apply a solution treatment, usually at temperatures between 1050°C and 1100°C, followed by cooling in water or air, to obtain a microstructure with a phase balance of δ-ferrite and γ-austenite of about 50 : 50, which ensures an attractive combination of properties [103]. Thus, on the one hand, ferrite provides mechanical strength and *stress corrosion cracking* (SCC) and, on the other hand, austenite provides ductility and toughness, resulting in a fine-grained and corrosion-resistant steel [104].

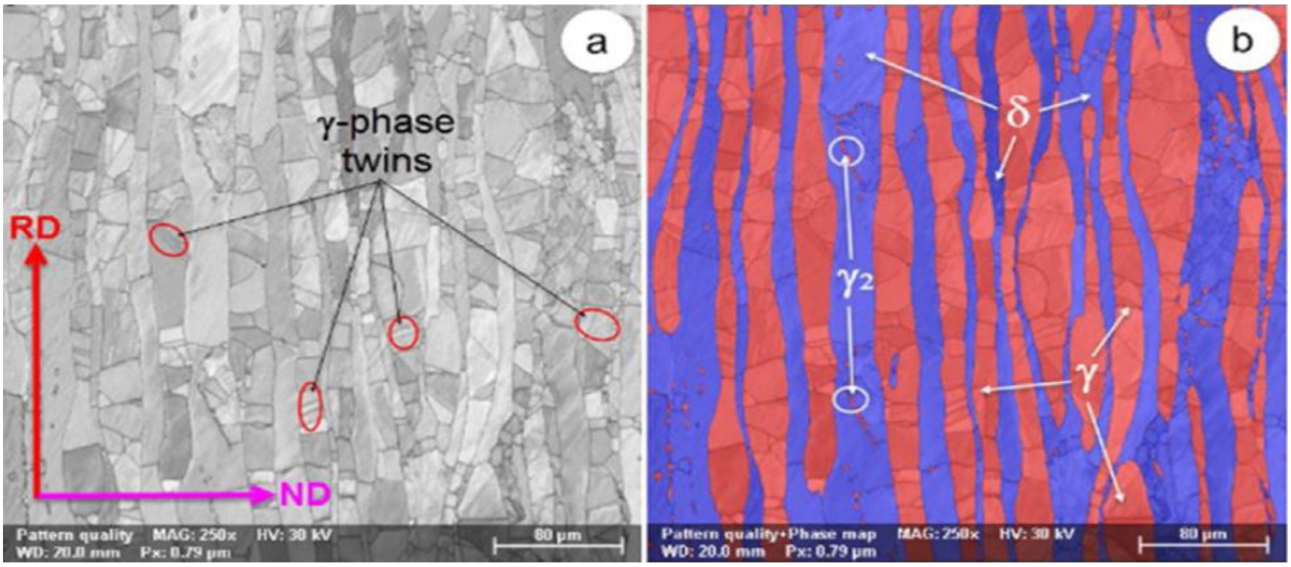

Figure 4. *SEM-EBSD microstructural images of super duplex stainless steel EN 1.4410 / UNS S32750 / F53 alloy, hot deformed (1100 °C) and solution treated (1050°C, 30min water quenched), showing elongated austenite γ islands within ferrite δ matrix (a); phase distribution map: austenite γ (coloured in red) and ferrite δ (coloured in blue) (b) [105].*

Scanning Electron Microscopy (SEM) images using the Electron Backscattered Diffraction (EBSD) technique are shown in Figure 4. These images are typical of a duplex microstructure obtained after hot plastic deformation followed by solution treatment, showing elongated islands of γ austenite (coloured red) in a matrix of δ ferrite (coloured blue) [105].

Thanks to this duplex microstructure, almost double yield strength values can be achieved, giving the opportunity to reduce the weight of the steel without compromising its quality and performance, as well as better resistance to pitting, crevice corrosion and stress induced corrosive cracking in environments containing chloride solutions (*Chloride Stress Corrosion Cracking* - CSCC) compared to conventional austenitic stainless steels such as AISI 304 (UNS S30400 / EN 1. 4301) and AISI 316 (UNS S31603 / EN 1.4401) [106,107]. The main difference between such austenitic stainless steel and duplex stainless steels is that the last have higher Cr contents, (20 ÷ 30)wt%, higher Mo contents, up to 5wt%, lower Ni contents, up to 8wt%, N up to 0.5wt%, Mn up to 5wt%, C maintained between (0.01 ÷ 0.08)wt%, and other alloying elements (Cu, Si, W, Nb, Ti, etc.) [108,109]. Duplex stainless steels have better toughness and plasticity, are easier to weld and do not present serious embrittlement problems, compared to ferritic stainless steels, such as AISI 430 (UNS S43000 / EN 1.4016) [107,110].

Table 5 shows the values of the minimum mechanical properties, at room temperature, of duplex stainless steels compared to those of other categories of stainless steels [111].

Tabel 5. *Minimum mechanical properties of duplex stainless steels processed by plastic deformation compared to other categories of stainless steels [111].*

Type of stainless steel	***Mechanical characteristics***			
	***Ultimate tensile strength**, MPa*	***Yield strength**, MPa*	***Elongation to fracture**, %*	***Hardness**, HB*
Ferrito-austenitic (duplex)	650–750	450–550	15–25	105
Austenitic (AISI 200-300)	485–655	170–260	40	88–96
Feritic (AISI 400)	380–515	170–275	21	88–96
Martensitic	415–485	205–275	21	89–96
Precipitation hardenable	895–1620	655–1520	6–16	105–116

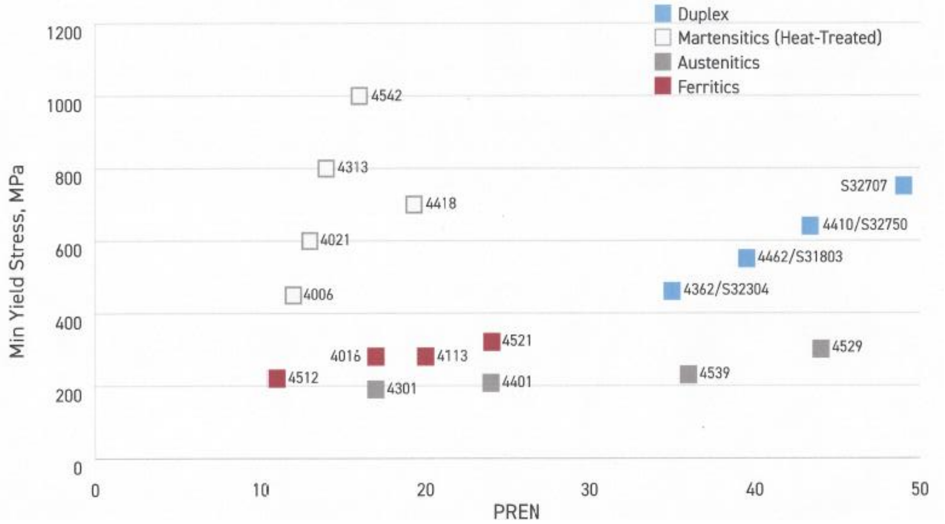

Figure 5. *Positioning of duplex stainless steels in relation to other categories of stainless steels in terms of PRE_N values and minimum yield strength (MPa) [114].*

Having a lower Ni content than austenitic stainless steels for the same level of corrosion resistance, due to the presence of approximately 50wt% ferrite in the microstructure, makes duplex stainless steels much more cost competitive, which favours their use for a wide range of industrial applications, such as equipment for the oil and gas industry, shipbuilding and marine platforms, elements for machinery and plants in the chemical industry, pulp and paper industry, etc., even replacing conventional austenitic stainless steels where they may have problems related to pitting corrosion and fatigue corrosion in wet chloride environments [112,113]. Figure 5 [114] shows the positioning of duplex stainless steels in relation to the other categories of stainless steels, taking into account their corrosion resistance, by the value of the PREN parameter, calculated with relation (3), and their minimum yield strength (MPa).

Duplex stainless steels have high Cr and Mo contents, which have a higher diffusivity in ferrite than in austenite. Thus, a number of phenomena can easily occur in their ferrite mass, such as: precipitation of secondary phases, spinodal decomposition of ferrite, phase transformations, with negative effects on properties [115-117]. Also, although having an attractive combination of corrosion resistance and mechanical properties, duplex stainless steels are used in the (-50 ÷ +300)°C temperature range, thus being restricted to be used above +300°C or below -50°C, due to the brittle behaviour of ferrite at these temperatures and the susceptibility to easily form different unwanted phase; in addition, presenting a ductile-brittle transition temperature, compared to austenitic stainless steels which are stable at cryogenic and higher temperatures [118-120].

In the duplex stainless steel family, the most intensively produced grade of steel, almost 80% of their total production, is EN 1.4462 / UNS S32205 / F51, marketed under the name 2205, with use in applications where austenitic AISI 300 series grades are more susceptible to CSCC [121]. It falls into the group of standard duplex stainless steels, having a nominal composition of 22wt% Cr, 5wt% Ni, 3wt% Mo and 0.17wt% N [121]. Continuous improvements have been made to this standard, leading to the emergence of new types and groups of modern duplex stainless steels, introduced on the market, either to produce an economical alternative to the well-known brand by reducing the expensive alloying elements, such as Ni and Mo, forming up the group of *Lean-Duplex* (LDX) stainless steels, such as the EN 1.4162 / UNS S32101 and EN 1 brands. 4362 / UNS S32304 [122-124], or to improve corrosion resistance, in more aggressive environments, by increasing the alloying Cr, Mo, Ni and N content and, sometimes with the addition of Cu and W, forming the *Super-Duplex Stainless Steels* (SDSS) group, such as EN 1.4501 / UNS S32760 / F55, EN 1.4410 / UNS S32750 / F53 and EN 1.4507 / UNS S32550 / F61 [125]. The latest were developed as an alternative to expensive super austenitic stainless steels, such as those containing 6wt% Mo, or even Ni-based superalloys, due to their high property-to-cost ratio, thus experiencing an increasing use/demand [119,126]. Super duplex stainless steels are used in marine applications, oil platforms in the offshore industry, where both high corrosion resistance in very severe, chlorine-rich corrosive environments and high mechanical and thermal stress properties are required [127,128].

New high-alloyed duplex stainless steels have been continuously developed, leading to the emergence of a new group, i.e. *Hyper-Duplex Stainless Steels* (HDSS), with much better corrosion resistance and mechanical strength than existing duplex steels, with higher Cr (> 25wt%) and N addition (around 0.5wt%), intended for use in applications in the oil and gas industry, in extremely severe corrosive environments, at high temperatures, pressures and depths [129]. Examples of such high-alloy duplex steels are EN 1.4658 / UNS S32707 and EN - / UNS S33207 [130,131].

Low alloyed duplex (LDX) steels show less corrosion resistant than the standard EN 1.4462 / UNS S31803/ S32205 grade [132], but still have a continuous yearly increase, due to use of lower contents of expensive alloying elements (Ni and Mo), being competitive with the AISI 304 and 316 austenitic stainless steel grades [133,134]. The production of high-alloyed duplex, super duplex and hyper duplex steels is less dynamic than that of low-alloyed duplex steels, accounting for less than 10% of the total production of duplex stainless steels [133,135].

Despite their small market share, with annual world production of duplex stainless steels accounting for less than 5% of total stainless steel production [136,137], they are nevertheless of increasing interest to researchers as well as stainless steel manufacturers, suppliers and users. They have shown concerns about the stability of the microstructure during thermomechanical processing and welding, the effects induced by various parameters on the evolution of microstructure and mechanical and corrosion resistance properties, concerns about machinability, weldability, etc.

Numerous studies have highlighted the importance of the manufacturing process of duplex stainless steels to improve their quality and performance [138-140], the effect of alloying elements on the phase balance [141], the effect of precipitation of various secondary phases on mechanical and corrosion properties in case of incorrect heat treatment [142, 143], recognition of the positive effect on mechanical and corrosion properties when adding N to the composition [144,145], and the effect of thermomechanical processing parameters on microstructure, microtexture and mechanical properties [146-148]. Thermomechanical processing technologies have been proposed, with heat treatments carried out at various temperatures and time intervals, reporting the precipitation of a variety of undesirable secondary phases in certain temperature ranges, causing serious degradation of mechanical and corrosion properties [149-153].

The precipitation mechanisms of secondary phases and compounds have been intensively studied in the case of both ferrite and austenite phases [154-156]. In duplex stainless steels, usually in the (600 ÷ 1000)°C temperature range, as a result of inadequate cooling, the following secondary phases and intermetallic compounds can precipitate: sigma phase (σ), chi phase (χ), secondary austenite phase (γ_2), R phase, carbides ($M_{23}C_6$, M_7C_3) and nitrides (CrN, Cr_2N) [157-160]. Of these, the most dangerous is the hard and brittle intermetallic σ phase, which on the one hand reduces toughness and on the other hand decreases corrosion resistance [161-164]. Thus, correct heat treatment procedures are essential for these types of alloys.

There are also important concerns about the difficulties that arise during hot deformation processing as a direct consequence of their two-phase microstructure, the hot workability of duplex stainless steels being still a critical point [165-167]. Due to the fact that these two phases (austenite and ferrite) exhibit different recrystallization mechanisms, accommodation of plastic deformation by these duplex microstructures has always been a challenge [168-170]. While austenite, which is softer, recrystallizes by extensive dynamic restoration or continuous dynamic recrystallization, ferrite, which is stiffer, undergoes conventional dynamic recrystallization, such as nucleation and growth [171-173].

However, the effect of thermomechanical processing parameters (type of mechanical processing and applied heat treatments) on the microstructure and exhibited mechanical behaviour of super duplex stainless steel alloys is not yet fully investigated [174-176], thus, the present work attempts to deeply investigate the specific phenomena occurring in EN 1.4410 / UNS S32750 / F53 alloy, processed under special conditions.

Classification of duplex stainless steels

The first duplex stainless steels, called *first-generation duplex steels*, were produced between the 1930s and 1960s. Initially, they were mainly aimed at solving the problem of intergranular corrosion to which austenitic high-carbon stainless steels were susceptible [177]. These new steels exhibited greatly improved intergranular corrosion resistance and high yield strength and were used, in particular, in the construction of machine and plant components in the pulp and paper industry, as well as in many applications in the dairy and food industries [178]. Then, grades with good resistance in acids were designed and clearly demonstrated that a phase-balanced, ferritic and austenitic microstructure provides better *CSCC* resistance than a fully austenitic microstructure [27]. However, these first-generation duplex steel grades had a high sensitivity to welding, due to the high ferrite content that was obtained in the heat affected zone, producing decreased toughness and significantly reducing corrosion resistance. These steels also had high values of residual impurities and inclusions [179].

In the late 1960s and early 1970s, with the introduction of new metallurgical steelmaking technologies with advanced *Argon-Oxygen Decarburization* (AOD) and *Vacuum Oxygen Decarburization* (VOD) processes, it was possible to produce steels with lower contents of C, S, O and other residual elements as well as better control of nitrogen content [180]. Also, the introduction of the continuous casting process for stainless steels has contributed to improved quality and lower production costs [181]. All these factors, together with the increasing price of austenitic stainless steels, in combination with an intense activity of the offshore oil industry, which demanded a stainless steel resistant to aggressive environments, as well as a better knowledge and understanding of duplex microstructure, led to the introduction of a new generation of more modern duplex stainless steels, whose properties control was much improved [182]. Thus, the controlled addition of N (0.14 ÷ 0.20)wt% led to the development of *second-generation duplex stainless steels* containing (22 ÷ 23)wt% Cr [183,184]. Their microstructure is usually composed of approximately equal volume fractions of the two phases, ferrite and austenite, giving the steels excellent resistance to intergranular corrosion, pitting and crevice corrosion, good resistance to stress corrosion cracking in chloride environments, and increased structural stability during welding, and these new steels are used extensively in oil and gas industry applications [185]. The alloy known as 2205 (EN 1.4462 / UNS S31803/ S32205), with a ferrite content typically ranging from (44 ÷ 55)wt%, has gained commercial importance in the production of natural gas pipelines for the oil and gas industry, oil vessels, chemical, petrochemical, pulp and paper industry applications [186,187]. It falls into the group of standard duplex stainless steels [188].

The increasing expansion of the offshore oil and gas industry, as well as demands from the chemical and petrochemical industries, have led to the need to produce high performance materials with higher mechanical strength and corrosion properties in more aggressive environments and with improved weldability. So, in the mid-1980s, a variety of high-alloy alloys were developed, generally having 25wt% Cr, 7wt% Ni, 3.5wt% Mo and (0.22 ÷ 0.3)wt% N, called super duplex stainless steels (*SDSS*) - *third-generation duplex stainless stee*ls [181]. Initially, they were in cast form, then in plastic deformable form (forged, rolled), being used for specific applications, especially in aggressive chlorinated environments, competing successfully with austenitic high performance stainless steels [189,190]. The EN 1.4410 / UNS S 32750 / F 53 super duplex steel grade, with a typical chemical composition: (24 ÷ 26)wt% Cr, (6 ÷ 8)wt% Ni, (3 ÷ 5)wt% Mo, (0.4 ÷ 0.32)wt% N, ≤ 1.2wt% Mn, ≤ 0.5wt% Cu, ≤ 0.03wt% C, ≤ 0.8wt% Si, ≤ 0.035wt% P, ≤ 0.02wt% S, is an example of this new generation duplex stainless steel and *is the material of study in this PhD thesis*.

For applications in very severe environments, such as those in the oil and gas industry, *hyper duplex stainless steels* (HDSS), much higher alloyed than *super duplex stainless steels* (SDSS), have recently been developed, showing superior mechanical and corrosion resistance properties, and can even replace Ni-based superalloys in applications that take into account effective corrosion protection and cost [191].

Also, another trend in the development of modern duplex stainless steels is towards the production of *low-alloyed duplex* (LDX) steels with high mechanical properties, being competitive with austenitic AISI 304 and 316 stainless steel grades, but less corrosion resistant than the standard EN 1.4462/UNS S31803/ S32205 grade, because they have lower Ni content and no or lower Mo content, presenting the advantage of a lower costs [192].

The development of duplex stainless steels is continuous and nowadays they can be classified according to their corrosion resistance, characterized by the value of the PRE parameter, empirically calculated based on the stainless steel chemical composition [193], either with relation (4), common to stainless steels containing N (PRE_N), or with relation (5), for stainless steels containing N and W (PRE_W) [194]:

$$PRE_N = Cr[\%] + 3.3\ Mo[\%] + 16\ N[\%] \text{ - oțeluri austenitice și duplex} \quad (4)$$

$$PRE_W = Cr[\%] + 3.3\ Mo[\%] + 1.65\ \mathrm{W}[\%] + 16\ N[\%] \text{ - oțeluri austenitice și duplex} \quad (5)$$

Depending on the value of the $\mathrm{PRE_N}$ parameter, duplex stainless steels can be divided into four distinct classes [195]:

- low-alloyed / lean-duplex stainless steels: $24 \leq \mathrm{PRE_N} \leq 30$;
- standard-duplex stainless steels: $30 < \mathrm{PRE_N} < 40$;
- super-duplex stainless steels: $40 \leq \mathrm{PRE_N} < 48$;
- hyper-duplex stainless steels: $48 \leq \mathrm{PRE_N} \leq 55$.

It can be seen that in order to obtain increased values of the PREN parameter, a continuous increase in the amount of Cr (or Cr_{ech}) is required, but it should be kept in mind that the Ni (or Ni_{ech})

content must also be continuously increased in order to achieve ferrite and austenite phase balance, and obtain the mechanical properties in the optimum range (Figure 2).

Lean-duplex stainless steels

Low-alloyed / lean-duplex stainless steels were developed with the aim of reducing the production cost of duplex stainless steels by decreasing the content of (Ni and Mo) expensive alloying elements and increasing the content of cheap (Mn and N) alloying elements, without substantially changing their phase structure and, hence, their corrosion resistance and mechanical strength properties [196]. Thus, the role of these additions is to replace the nickel and to stabilize austenite content, assuring a proper phase balance in the microstructure (~ 50% austenite: 50% ferrite) [197].

In the chemical composition of these steels, Cr is usually between (21 ÷ 24)wt%, Ni between (1.0 ÷ 5.5)wt%, Mo between (0.1 ÷ 0.8)wt%, N between (0.05 ÷ 0.26)wt%, Mn up to 2wt%, additionally with Cu, up to 0.8wt%, as well as other elements (Si, P, S, etc.), i.e. grades: EN 1.4062 / UNS S32202 , EN 1.4162 / UNS S32101 and EN 1.4362 / UNS S32304 [198]. These stainless steels can successfully replace austenitic stainless steels, having strength properties comparable or even superior to most austenitic stainless steels, due to both their duplex structure and lower cost price. A drawback of these steels lies in their low toughness at negative temperatures due to low Ni content [199]. Duplex low alloy stainless steels ($24 \leq PRE_N \leq 30$), possess both good resistances to localized intergranular, pitting or crevice corrosion and to high temperature oxidation, but due to embrittlement phenomena their use is limited up to 300°C [200]. Table 6 [198] shows the chemical compositions and PRE_N parameter values of some low alloy duplex grades.

Tabel 6. *Chemical composition and PRE_N value of some lean-duplex stainless steel alloys [198].*

Grade (standard) EN / UNS / ASTM A182	***Chemical composition, wt%***								
	C	***Cr***	***Ni***	***Mo***	***N***	***Mn***	***Cu***	***W***	***PRE_N****
1.4062 / S32202	<0.03	21.50-24.00	1.00-2.80	0.45	0.18-0.26	<2.00	-	-	26
1.4162 / S32101	<0.04	21.00-22.00	1.35-1.70	0.10-0.80	0.20-0.25	4.00-6.00	0.10-0.80	-	26
1.4362 / S32304 / F 68	<0.03	21.50-24.50	3.00-5.50	0.05-0.6	0.05-0.20	<2.50	0.05-0.60	-	26
$PRE_N = Cr[\%] + 3.3\, Mo[\%] + 16\, N[\%]$									

Usually, to increase their machinability, after the hot or cold plastic forming operation, these steels are heat treated by solution quenching at temperatures between 1000°C and 1080°C, followed by cooling in water or air (EN 1.4162 / UNS S32101 and EN 1.4362 / UNS S32304) [201]. Low-alloy duplex stainless steels are successfully used in a multitude of industrial applications where corrosion resistance requirements are less stringent but require high mechanical properties, such as [198]:

- ***EN 1.4162 / UNS S32101,*** in the construction of components and parts for the aircraft industry, marine construction: water treatment plants, storage and transport tanks and containers, etc;
- ***EN 1.4362 / UNS S32304 / F 68,*** in the construction of components and parts for marine construction, chemical industry: valves, pumps, mixers, water treatment and desalination plants, storage and transport tanks and containers, etc.

Standard-duplex stainless steels

The chemical composition of these steels usually contains Cr between (21 ÷ 23)wt%, Ni between (4.5 ÷ 6.5)wt%, Mo between (2.5 ÷ 3.5)wt%, N between (0.08 ÷ 0.20)wt%, Mn up to 2wt% and other elements (Si, P, S, etc.). The most known grades are EN 1.4462 / UNS S31803 / F51 and its improved variant, EN 1.4462 / UNS S32205 / F60, having a chemical composition optimized to increase corrosion resistance [198]. Table 7 [198] shows the chemical compositions and PRE_N parameter values corresponding to these grades, being symbolized according to international standards [202].

Standard duplex stainless steels ($30 < PRE_N < 40$), possess both good resistances to localised, intergranular, pitting or crevice corrosion and to corrosive cracking in acidic and chloride ion-rich environments, and are clearly superior to austenitic stainless steels for use at temperatures up to 250°C [203]. Usually, to increase their machinability, after the hot or cold plastic forming operation, these steels are heat treated by solution quenching at temperatures between 1020°C and 1100°C followed by cooling in water, oil or air [204].

Tabel 7. *Chemical composition and PRE_N value of some standard-duplex stainless steel alloys [198].*

Grade (standard) EN / UNS / ASTM A182	***Chemical composition, wt%***								
	C	***Cr***	***Ni***	***Mo***	***N***	***Mn***	***Cu***	***W***	***PRE_N****
1.4462 / S31803 / F51	<0.03	21.0-23.0	4.50-6.50	2.50-3.50	0.08-0.20	<2.0	–	–	33
1.4462 / S32205 / F60	<0.03	22.0-23.0	4.50-6.50	3.00-3.50	0.14-0.20	<2.0	–	–	35
$PRE_N = Cr[\%] + 3.3\, Mo[\%] + 16\, N[\%]$									

Typical applications in which duplex standard stainless steels are used include a multitude of fields such as chemical, petroleum, shipbuilding, aeronautics, etc., where both good corrosion resistance and high mechanical strength properties are required, such as the example marks [198]:

- ***EN 1.4462 / UNS S31803 / F51,*** in the construction of components and parts: bolts, screws, valves, pumps, coolers, storage and transport tanks and containers, etc;
- ***EN 1.4462 / UNS S32205 / F60,*** in the construction of components and parts: bolts, screws, valves, pumps, rotors, press rollers, mixers, coolers, etc.

Super-duplex stainless steels

In the chemical composition of these steels, the main alloying elements are usually found in amounts ranging from (24 ÷ 27)wt% Cr, (4.5 ÷ 8.0)wt% Ni and (2.9 ÷ 5.0)wt% Mo, higher amounts of alloying elements compared to low alloyed and standard duplex stainless steels [125]. These steels are also alloyed with N between (0.2 ÷ 0.35)wt%, Mn up to 1.5wt% and additionally with Cu (0.5 ÷ 2.5wt%.) [109]. Examples of super duplex stainless steel grades are given in Table 8 [198], together with their chemical compositions and corresponding PRE_N parameter values.

In comparison with the chemical compositions of duplex and standard duplex low alloyed stainless steels, the alloying element additions was based on the following considerations [206]: Cr to improve both corrosion resistance and mechanical strength; Ni to maintain the balance between the basic phases; Mo to improve corrosion resistance; N to maintain the balance between the base phases and improve corrosion resistance; Cu to improve corrosion resistance.

Super duplex stainless steels are characterized by superior corrosion resistance to low alloyed duplex and standard duplex steels, with a PRE_N parameter value > 40, which is why they are mainly used in applications with temperatures up to 300°C and where high resistance to localized intergranular, pitting or crevice corrosion and corrosive cracking in acidic and chloride ion-rich environments is also required [205]. Usually, to increase their machinability, after the hot or cold plastic forming operation, these steels are heat treated by solution quenching at temperatures between 1050°C and 1150°C, followed by cooling in water, oil or air [207].

Typical applications in which super duplex stainless steels are used include a multitude of fields such as chemical, petroleum, energy, nuclear, shipbuilding, civil construction, etc., where both high corrosion resistance and mechanical strength properties are required, such as [198]:

- ***EN 1.4410 / UNS S32750 / F53*** and ***EN 1.4501 / UNS S32760 / F55,*** in the construction of components and parts for the chemical industry, oil and gas industry, maritime, aeronautical, storage tanks, chemical reactors, extraction columns, boilers, pumps, coolers, pipes, desalination plants, etc;
- ***EN 1.4507 / UNS S32520 / F59*** and ***EN 1.4507 /UNS S32550 / F61,*** in the construction of components and parts for the chemical industry, oil and gas industry, maritime industry, aeronautics, mixers, water treatment and desalination plants, storage tanks, chemical reactors, etc.

Tabel 8. *Chemical composition and PRE_N value of some super-duplex stainless steel alloys [198].*

Grade (standard) EN / UNS / ASTM A182	***Chemical composition, wt%***								
	C	***Cr***	***Ni***	***Mo***	***N***	***Mn***	***Cu***	***W***	***PRE_N****
1.4410 / S32750 / F53	<0.03	24.0-26.0	6.00-8.00	3.00-5.00	0.24-0.32	<1.2	<0.50	–	43
1.4501 / S32760 / F55	<0.03	24.0-26.0	6.00-8.00	3.00-4.00	0.20-0.30	<1.0	0.50-1.00	0.50-1.00	42
$PRE_N = Cr[\%] + 3.3\,Mo[\%] + 16\,N[\%]$									

Hyper-duplex stainless steels

In the chemical composition of these steels, there are higher amounts of alloying elements compared to super duplex stainless steels, usually having (26 ÷ 33)wt% Cr, (5.5 ÷ 9.0)wt% Ni and (3.0 ÷ 5.0)wt% Mo [208]. These steels are also alloyed with Mn up to 1.5wt%, Cu up to 1.0wt% and an increased N content between (0.3 ÷ 0.6)wt%, in Table 9 [198] chemical compositions and PRE_N values corresponding to some grades of hyper duplex stainless steels are presented.

Hyper duplex stainless steels are characterised by a higher corrosion resistance than super duplex stainless steels, usually having a PRE_N value > 50, which is why they are mainly used in special applications where maximum corrosion resistance is required (intergranular, pitting, crevice, corrosive cracking, etc.). To achieve these values, it is necessary to increase the content of alloying elements, but these highly alloyed compositions make these steels more susceptible to precipitation of unwanted intermetallic secondary phases (σ, χ, etc.) during thermomechanical processing and welding [210].

Tabel 9. *Chemical composition and PRE_N value of some hyper-duplex stainless steel alloys [198].*

Grade (standard) EN / UNS	**Chemical composition, wt%**								
	C max.	**Cr**	**Ni**	**Mo**	**N**	**Mn**	**Cu**	**W**	**PRE_N***
1.4658 / S32707	0.03	26.0-29.0	5.50-9.50	4.00-5.00	0.30-0.50	<1.5	<1.00	–	49
- / S33207	0.03	29.0-33.0	6.00-9.00	3.00-5.00	0.40-0.60	<1.5	<1.00	–	50
$PRE_N = Cr[\%] + 3.3\, Mo[\%] + 16\, N[\%]$									

Hyper duplex stainless steels have been developed as an alternative to Ni-based superalloys, which have a much higher production cost [211]. Typical applications in which hyper duplex stainless steels are used include a multitude of fields such as chemical, petroleum, energy, nuclear, etc., where superior mechanical and corrosion resistance properties are required, thus [198]:

- ***EN 1.4658 / UNS S32707*** and ***- / UNS S33207,*** are used in the construction of components and parts in the chemical industry, oil and gas industry, maritime industry, nuclear industry, etc.: storage tanks, chemical reactors, extraction columns, boilers, pumps, coolers, pipes, valves, etc.

1.1.4. Secondary phases and precipitates in duplex stainless steel alloys

Duplex stainless steels are characterized as having a two-phase basic structure, composed of ferrite (α, δ) and austenite (γ), with a very close mass ratio between these phases of 50 : 50, which is necessary to achieve superior mechanical strength and corrosion characteristics [212]. So, in order to achieve these performances, this phase balance is very important parameter and is influenced by the way in which the alloying elements are partitioned. Depending on their phase-stabilizing character, they can be grouped into ferritic phase-stabilizing elements (Cr, Mo, Si, Nb, V, Al, etc.) and austenitic phase-stabilizing elements (Ni, Mn, N, etc.), their quantity ultimately determining the mechanical strength and corrosion characteristics [27]. It is also essential that a correct heat treatment to by applied to these duplex steels. Any change in the optimum phase balance fraction, as well as incorrect application of heat treatments after hot/cold working, can lead to a number of phenomena, such as spinodal decomposition of ferrite, precipitation of secondary phases and phase transformations (Figure 6) [213], with negative effects on the mechanical and the corrosion resistance properties [214].

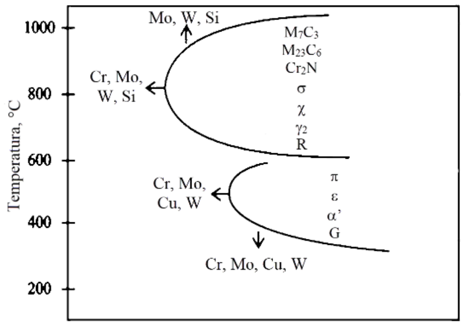

Figure 6. *TTT schematic diagram for duplex stainless steels [213].*

A schematic presentation of the main phenomena that can occur in ferrite mass, in which the alloying elements have a higher diffusivity and a lower solubility compared to austenite mass, is presented in Figure 6 [213]. From the analysis of the *Time-Temperature Transformation* (TTT) schematic diagram, it can be seen that there are two temperature ranges in which the appearance of secondary phases, intermetallic compounds, carbides and nitrides is possible, as follows:

- ***between 300°C and 600°C***: in this range the occurrence of ($\delta \rightarrow \alpha + \alpha'$) spinodal decomposition of ferrite and precipitation of (G, ε, π, τ, etc) secondary phases is possible;
- ***between 600°C and 1000°C***: in this range the precipitation of (R, χ, σ) secondary phases and precipitation of nitrides and metal carbides (CrN, Cr_2N; M_7C_3, $M_{23}C_6$, etc) is possible.

Also, from the analysis of the schematic TTT diagram (Figure 6) [213], it is observed that the kinetics of these transformations is substantially influenced by the concentration of the main alloying elements presented in the chemical composition of these steels, thus:

- for transformations/precipitations occurring at temperatures < 600°C, with increasing concentration of alloying elements there is a shift of the transformation/precipitation temperature ranges towards longer durations and lower temperatures;
- for transformations/precipitations occurring at temperatures > 600°C, as the concentration of alloying elements increases, the transformation/precipitation temperature ranges shift towards shorter durations and higher temperatures.

Research has shown that all these precipitates, phases and compounds, developed in the ferrite mass, have a negative effect on the mechanical and corrosion resistance properties of stainless steels, which is why in the design of thermomechanical processing technologies for these steels the thermomechanical processing in these temperature ranges is generally avoided [215-217].

1.1.4.1. Secondary phases and precipitates in the (300 ÷ 600)°C temperature range

Spinodal decomposition of ferrite

In the (300 ÷ 600)°C temperature range, in the Fe-Cr miscibility diagram (Figure 7a) [218], a decrease in miscibility is observed, leading to the appearance of adjacent crystallographically coherent (no boundary/separation boundary) Cr-rich/Fe-poor (α') and Cr-poor/Fe-rich (α) zones in the ferrite mass, either as a result of spinodal decomposition or via a nucleation and growth mechanism [219-222].

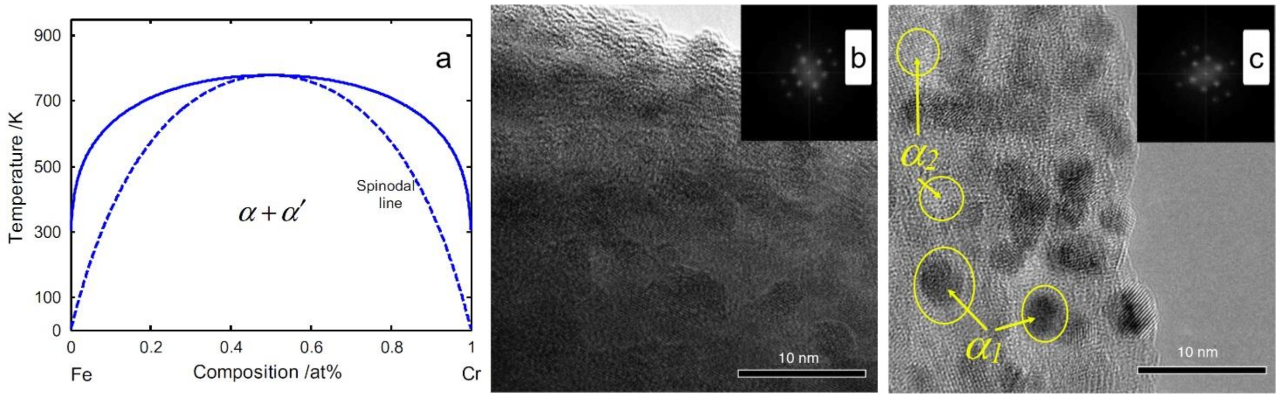

Figure 7. *Fe-Cr miscibility diagram: solid line - phase separation curve; broken line - spinodal decomposition curve (a) [218]; TEM images for Fe-40Cr alloy microstructure (%at) aged at 470°C for 50h (b) and 500h (c) [224], showing spinodal decomposition of ferrite in:* α_1 *- Cr-rich/Fe-poor zones and* α_2 *- Fe-rich/Cr-poor zones.*

This ferrite decomposition usually occurs at the nanometric level [223], with Cr-rich (α') and Fe-rich (α) zones/precipitates having sizes in the order of (10 ÷ 15)nm (Figures 7b and 7c) [224], leading to increased hardness and decreased toughness of the steel [225,115]. Due to the relatively low diffusivity of Cr in ferrite in this temperature range, a high holding time is required for ferrite decomposition to occur, which is why this decomposition occurs after high duration heat treatments, in the order of hours/tens/hundreds/thousands of hours, depending on the composition of the stainless steel under analysis [226,227]. This phenomenon is also known as *475°C embrittlement*, due to the maximum ferrite decomposition reaction occurring around 475°C [228,229].

G phase

The G phase can be precipitated in the microstructure of duplex stainless alloys as a result of holding at temperatures between 280°C and 500°C, in the same temperature range as spinodal decomposition ($\delta \rightarrow \alpha + \alpha'$), but for much longer holding duration, typically in the order of thousands of hours [230,231]. Precipitation of G phase has been observed predominantly around the δ/δ grain boundaries, as a result of enrichment of these zones in alloying elements such as Ni and Si [27].

The G phase belongs to the Ni-Nb-Si system ($Ni_{16}Nb_6Si_7$; $Ni_{15}Nb_6Si_7$), but in its composition there may also be substitutions with Cr, Fe, Mn, Mo, V, etc. [232]. The dissolution temperature of G-phase precipitates is located at values higher than 700°C, depending on the chemical composition of the stainless steel [233,234]. The G phase exhibits a FCC-type crystalline cell and is characterized by a lattice parameter a = (10.9 ÷ 11.1)Å [235]. It has also been observed that G phase has an important effect on ductility and hardness, increasing the fraction mass of G phase leading to decreased ductility [236] and increased hardness [237,238].

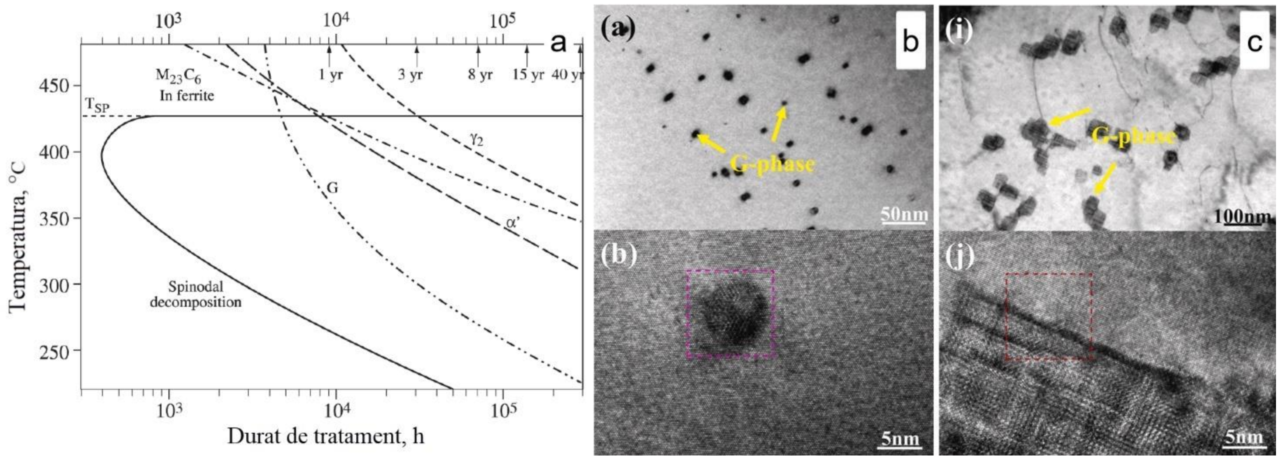

Figure 8. *TTT diagram for Fe-20Cr-9Ni duplex alloy (wt%) (a) [239]; TEM images for the microstructure of Fe-20Cr-9Ni duplex alloy (wt%) aged at 400°C for 20000h (b) and aged at 475°C for 3000h (c) [231], showing G-phase precipitates.*

As shown in Figure 8a [239], G phase kinetics is significantly influenced by temperature, with the size of G phase precipitates increasing strongly with increasing treatment temperature, from ~10nm at 400°C, with a treatment duration of 20000h (Figure 8b), to ~40nm at 475°C, with a treatment duration of 3000h (Figure 8c) [231]. Also, at the same time as the size of G phase precipitates increases, a change in their morphology from spherical to prismatic/cubic shape is observed [231,240].

ε (epsilon) and π (pi) phase

In duplex stainless steels containing Cu (i.e. EN 1.4410 / UNS S32750 / F53, EN 1.4501 / UNS S32760 / F55, EN 1.4507 / UNS S32520 / F59, etc) at temperatures < 500°C and treatment durations in the order of tens/hundreds of hours, precipitation of nanometric ε phase particles occurs inside the ferrite grains [241].

Also, for duplex steels (i.e. EN 1.4410 / UNS S32750 / F53, EN 1.4507 / UNS S32520 / F59, EN 1.4658 / UNS S32707, etc), at temperatures close to 600°C and treatment durations in the order of hours / tens of hours, inter-granular precipitation of nanometric Mo-enriched π phase particles (Fe-Mo/Cr-N precipitate) can occur in the ferrite [242].

1.1.4.2. Secondary phases and precipitates in the (600 ÷ 1000)°C temperature range

R phase

In duplex stainless steels heat treated in the (500 ÷ 700)°C temperatures range [243] and treatment durations in the order of hours / tens of hours, due to the decrease in solubility of the main alloying elements (Cr, Ni, Mo, Si, etc.) in the δ ferrite mass, usually in the δ / γ interfaces area, precipitation of fine R phase particles can occur (Figure 9) [244,105], The R phase precipitates belongs to Fe-Mo-Cr system [245], whose chemical composition varies between (16 ÷ 30)wt% Cr, (25 ÷ 40)wt% Mo, (3 ÷ 5)wt%. Ni and (25 ÷ 56)wt% Fe [246]. Other alloying elements such as Si, Mn, etc. can also be found in the composition of R phase precipitates [246].

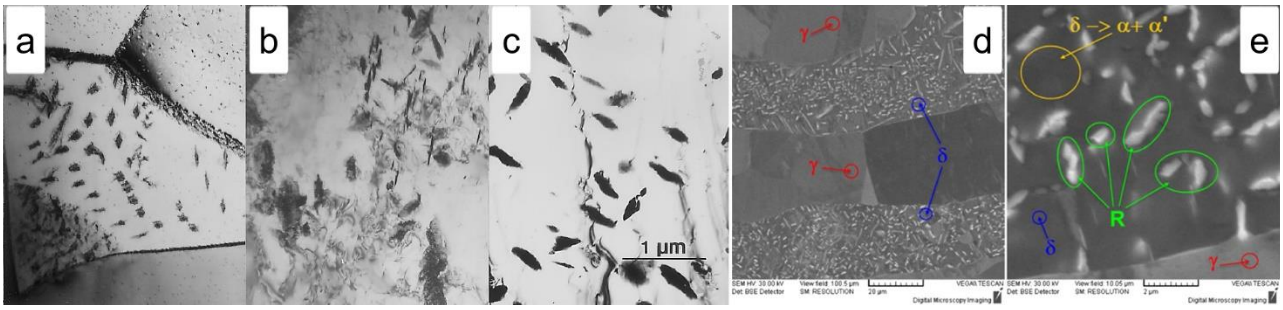

Figure 9. *TEM and SEM-EBSD images for the microstructure of super duplex alloy EN 1.4410 / UNS S32750 / F53 aged at 600°C for 3h (a), 5h(b) and 10h (c) [244] and aged at 600°C for 120h at various magnifications (d, e) [105], showing R phase precipitates.*

The R phase exhibits a trigonal or hexagonal crystalline cell, characterized by a lattice parameter a = (10.7 ÷ 10.9)Å and c = (19.3 ÷ 19.7)Å [27,247]. With increasing holding duration, especially at temperatures >550°C, due to the increased solubility and diffusivity of Mo in ferrite, the R phase can act as a precursor for the precipitation of the σ phase [248].

χ (chi)

The χ phase can be precipitated into the microstructure of duplex stainless alloys as a result of heating at temperatures between 700°C and 900°C, with treatment durations in the order of tens of minutes [243].

The χ phase belongs to the Fe-Cr-Mo system ($Fe_{36}Cr_{12}Mo_{10}$), having Cr (24 ÷ 28wt%), Mo (20 ÷ 22wt%) and Fe (50 ÷ 56wt%) in its composition [249], exhibiting a BCC-type crystalline cell and characterized by a lattice parameter a = (8.8 ÷ 8.9)Å [250]. Most of the time, the mass fraction of the χ phase presented in the microstructure of duplex stainless steels is small, since its formation involves a sharp local depletion in Mo and Cr of adjacent zones [250,251].

The χ phase was observed either in the δ / γ interface area (Figure 10a) [252] or in the δ ferrite mass, being induced as a result of the eutectoid decomposition reaction $\delta \rightarrow \chi + \gamma_2$ (Figures 10c and

10d) [253]. It has also been shown that χ phase precipitates can act as precursors for σ phase formation (Figure 10b) [252], especially for long treatment durations at temperatures between 700°C and 800°C [243,254,255].

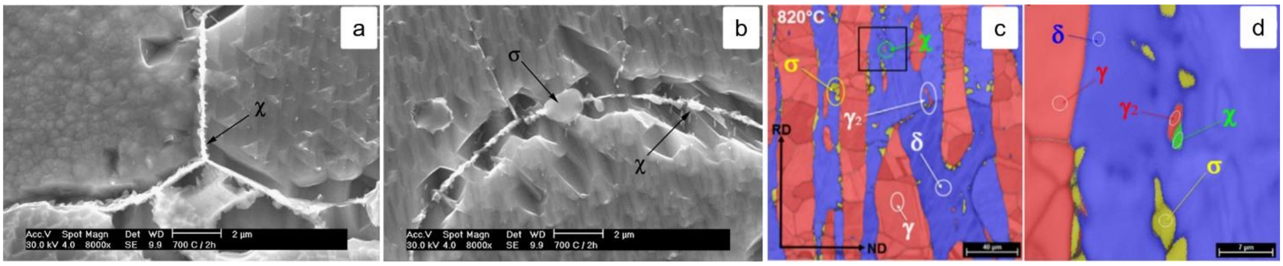

Figure 10. *SEM images for the microstructure of duplex alloy EN 1.4462 / UNS S31803 / F51 treated at 700°C for 2h: χ phase precipitated at the δ/γ interface (a) and the presence of the σ phase obtained by transforming the χ phase (b) [252]; SEM-EBSD images for the microstructure of super duplex alloy EN 1.4410 / UNS S32750 / F53 treated at 820°C for 15min, at different magnifications (c, d) [253].*

σ (sigma)

The σ phase can be precipitated into the microstructure of duplex stainless alloys as a result of heating at temperatures between 600°C and 1000°C, with treatment durations in the order of minutes [256,257]. Like the χ phase, the σ phase belongs to the Fe-Cr-Mo system, showing a content of Cr between (25 ÷ 40wt%), Mo between (11 ÷ 20wt%) and Fe between (35 ÷ 55wt%) [243]. Also, in the chemical composition of σ phase precipitates other alloying or substitutional elements can be found, such as: Ni, Si, Mn, etc [258]. The σ phase exhibits a hexagonal or tetragonal crystalline cell, characterized by a lattice parameter a = (8.7 ÷ 8.9)Å and c = (4.5 ÷ 4.6)Å [243], depending on its chemical composition [27].

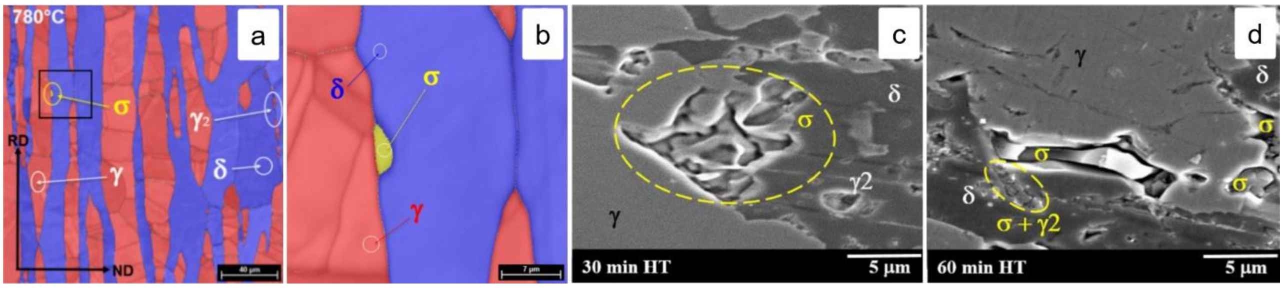

Figure 11. *SEM-EBSD images for the microstructure of super duplex alloy EN 1.4410 / UNS S32750 / F53 treated at 780°C for 15min at different magnifications (a, b) [253]: σ phase precipitated at the interface δ/γ; SEM images for the microstructure of duplex alloy EN 1.4462 / UNS S31803 / F51 treated at 850°C for 30min (c) and 60min (d) [260]: presence of σ phase due to eutectoid reaction* $\delta \rightarrow \sigma + \gamma_2$.

The σ phase was observed at lower temperatures (600°C÷800°C) in the δ / γ interfaces area [259] (Figures 11a and 11b) [253]. At higher temperatures (800°C ÷ 1000°C), the σ phase precipitates into the δ ferrite mass as a result of eutectoid decomposition $\delta \rightarrow \sigma + \gamma_2$, exhibiting a coral structure-like morphology [8] (Figure 11c), which gradually increases with increasing treatment duration (Figure 11d) [260], leading to a drastic decrease of the δ ferrite mass fraction.

In contrast to the χ phase, the σ phase can precipitate to a significantly higher mass fraction, due to both the wider temperature range over which its existence can be assured and the lower amount of Mo required for its nucleation, germination and growth [261,262]. Practically, in duplex stainless steels, when the treatment duration is sufficiently long, the δ phase can be fully transformed into a mixture of σ phase and γ_2 secondary austenite phase [263-265].

γ_2 *(secondary austenite)*

The γ_2 phase (secondary austenite) can be precipitated into the microstructure of duplex stainless alloys, in the δ ferrite mass as a result of heating these steels at temperatures between 700°C and 1000°C [243,275]. The γ_2 phase is characterized by a slightly different chemical composition in comparison with primary austenite (γ), showing an increased Ni and low Cr and Mo content [276,277].

At temperatures < 1000°C, the γ_2 phase co-precipitates in the microstructure of these alloys together with the χ phase and/or the σ phase and/or $M_{23}C_6$-type carbides, as a result of the eutectoid decomposition of ferrite: $\delta \rightarrow \chi + \gamma_2$; $\delta \rightarrow \sigma + \gamma_2$; $\delta \rightarrow M_{23}C_6 + \gamma_2$ [278-282]. At temperatures > 1000°C, similar to primary austenite (γ), secondary austenite (γ_2) undergoes a dissolution process in the ferrite mass as a result of $\gamma \rightarrow \delta$ phase transformation [8,283,284].

Carbides and nitrides

In the (700 ÷ 1050)°C temperature range, a number of carbides and nitrides can be generated in the microstructure of duplex stainless steels [285].

The most common carbides are $M_{23}C_6$ (Figure 12) [286] and M_7C_3 (Figure 13) [287] (where M = Cr, Fe, Mo), which are present in the microstructure of C-rich stainless steels in the (700 ÷ 1050)°C temperature range, both at the δ / γ and δ / δ grain boundaries [288,289]. The $M_{23}C_6$-type carbides (present at temperatures between 700°C and 950°C) are characterized by a cubic-type elemental crystalline cell, with lattice parameter $a = (10.5 \div 10.7)$Å [290,291], while M_7C_3-type carbides (present at temperatures between 950°C and 1050°C) show an orthorhombic elemental crystal cell, with lattice parameters $a = (4.5 \div 4.6)$Å, $b = (6.9 \div 7.1)$Å and $c = (12.1 \div 12.2)$Å [292,293]. It has also been shown that, following a suitable heat treatment, M_7C_3-type carbides can be transformed into $M_{23}C_6$-type carbides (Figure 13) [287].

Studies have shown that the growth process of $M_{23}C_6$-type carbides is a diffusive one, occurring after a eutectoid decomposition reaction of ferrite, similar to the case of the χ and σ phases, thus: $\delta \rightarrow M_{23}C_6 + \gamma_2$ [294,295] (Figure 12).

Typically, both $M_{23}C_6$ and M_7C_3 carbides, for the early growth stages, exhibit an initial blocky morphology (with equivalent size/diameter on the order of 30nm ÷ 80nm), which undergoes a change towards a lamellar morphology (with lamella thickness and length on the order of 40nm ÷ 100nm and 600nm ÷ 1000nm, respectively) as the treatment duration increases [296-299].

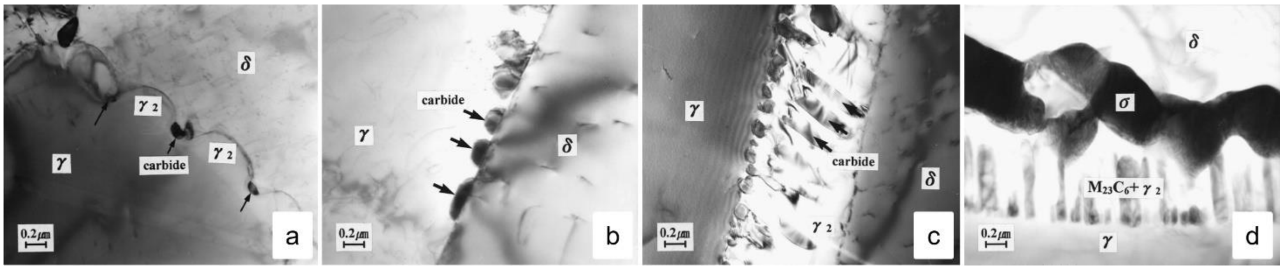

Figure 12. *TEM images for microstructure of duplex alloy EN 1.4462 / UNS S31803 / F51 treated at 800°C for 15min (a), 30min (b), 1h (c) and 2h (d) [286]:* $M_{23}C_6$ *carbides precipitated at the* δ/γ *grain boundary.*

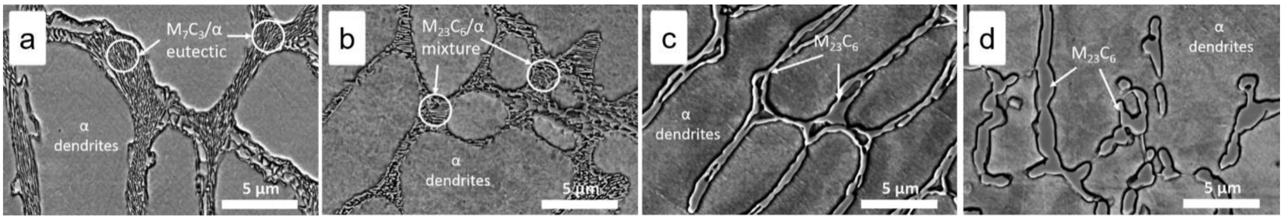

Figure 13. *SEM images for the microstructure of Fe-25Cr-0.8C duplex alloy in the cast state (a) and treated for 4h at 650°C (b), 850°C (c) and 1000°C (d) [287]:* M_7C_3 *carbides precipitated in the ferrite mass (α) and* $M_{23}C_6$ *carbides precipitated at the* α/γ *grain boundary.*

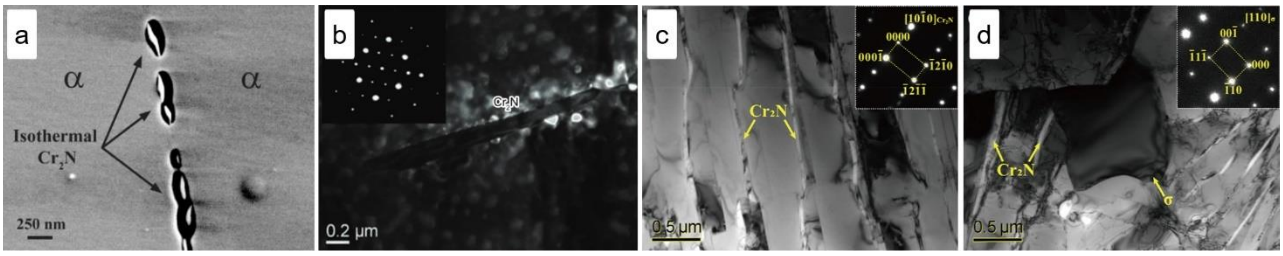

Figure 14. *SEM image for microstructure of duplex alloy EN 1.4462 / UNS S32205 / F60 in heat treated state at 950°C for 1min, cooled in water (a) [301]; TEM images for microstructure of duplex alloy Fe-18Cr-18Mn-0.63N (P550) treated at 850°C for 4h (b) [302], treated at 750°C for 3h (c) and 24h (d) [303], showing* Cr_2N *nitrides at the* α/α *grain boundary.*

In the microstructure of duplex stainless steels, the most common nitrides are Cr-based nitrides, which are particularly present in N-rich steels in the (700°C to 900°C) temperature range [243,300]. Thus, CrN- and Cr_2N-type nitrides can be encountered, these being precipitated mainly at the δ / δ boundaries and within δ-ferrite grains (Figure 14) [301-303], but also at the δ / γ boundaries, as a result of ferrite over-saturation with N [304,305]. Typically, CrN- and Cr_2N-type nitrides exhibit lamellar morphology, with lamella thicknesses and lengths on the order of 20nm ÷ 80nm and, 0.5μm ÷ 2μm respectively [306-308]. The CrN-type nitrides are characterized by a cubic-type crystalline cell, with lattice parameter a = (4.1 ÷ 4.4)Å [309,310], while Cr_2N-type nitrides have a hexagonal-type crystalline cell and lattice parameter a = (4.8 ÷ 4.9)Å and c = (4.4 ÷ 4.5)Å [309,311,312].

1.1.5. General crystallography of stainless steel alloys

1.1.5.1. Crystallography

The solid state of metal alloys is generated as a result of the melt solidification process (liquid state). In the liquid state, atoms move freely in the melt mass, not occupying fixed positions. As the melt temperature decreases, the degree of mobility of the atoms decreases until they occupy fixed spatial positions. If the spatial distribution of the fixed positions of the atoms in the structure of the solid body is regular and periodic, then the solid possesses a crystalline structure, otherwise the structure becomes amorphous. The smallest repeating crystallographic unit in the crystalline structure is called an elementary cell and contains all the information about the three-dimensional symmetry of the crystal structure (Figure 15) [313,314].

Crystalline elementary cells can be classified into seven types according to the spatial position of the atoms within them, a position defined by the elementary cell parameters: the relative length of the cell (the distance between atoms, i.e. the lattice sides denoted by a, b and c) and the angles between its sides (denoted by α, β and γ) (Figure 16) [313,314], as follows:

- cubic cell: $a = b = c$ și $\alpha = \beta = \gamma = 90°$;
- tetragonal cell: $a = b \neq c$ și $\alpha = \beta = \gamma = 90°$;
- orthorhombic cell: $a \neq b \neq c$ și $\alpha = \beta = \gamma = 90°$;
- monoclinic cell: $a \neq b \neq c$ și $\alpha = \gamma = 90°$; $\beta \neq 90°$;
- hexagonal cell: $a = b \neq c$ și $\alpha = \beta = 90°$; $\gamma = 120°$;
- rhombohedral cell: $a = b = c$ și $\alpha = \beta = \gamma \neq 90°$;
- triclinic cell: $a \neq b \neq c$ și $\alpha \neq \beta \neq \gamma \neq 90°$.

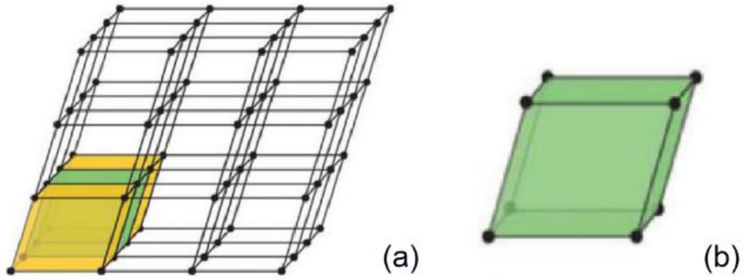

Figure 15. *Three-dimensional distribution of atoms in the crystal lattice (a), elementary cell (b) [313,314].*

At room temperature, iron grains/crystallites exhibit a cubic-type crystalline cell ($a = b = c$ și $\alpha = \beta = \gamma = 90°$), belonging to the *body-centred cubic* cell (BCC) subtype, with an additional Fe atom located in the centre of the elemental cell, which makes the degree of filling of the elemental cell about 68% (Figure 17) [313,314]. At high temperature another allotropic form of iron grains/crystallites is present, also characterized by a cubic-type crystalline cell ($a = b = c$ și $\alpha = \beta = \gamma = 90°$), but belonging to the *face-centred cubic* cell (FCC) subtype, with an additional Fe atom located in the centre of the six elementary cell faces, which makes the elementary cell approximately 74% full (Figure 17) [313,314], leading to a higher degree of atom mobility on the planes of maximum atomic density compared to the BCC-type cell.

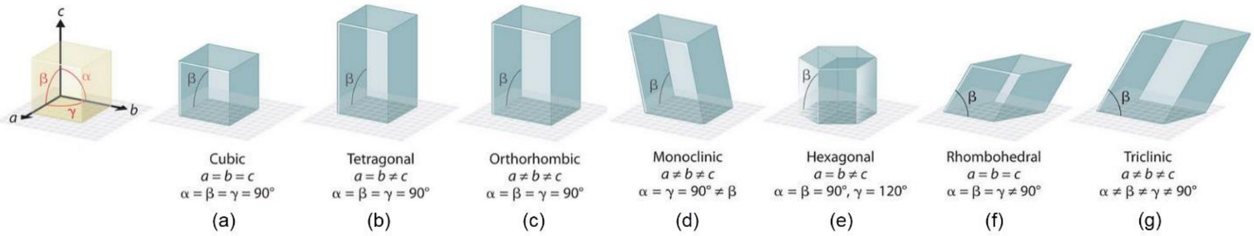

***Figure 16.** Crystalline cell types [313,314].*

In practice, in order to control the properties of metallic materials, their composition contains a series of elements, where one element is the base (having the highest mass fraction) and the rest are alloying elements. Iron-based alloys may contain a number of alloying elements (Cr, Ni, Mo, Mn, etc.), present in different mass fractions, making the crystal structure of the alloy either BCC or FCC, depending on the amount / weight-fraction of alloying elements and the thermomechanical processing history applied to it.

The alloying elements can be of substitutional or interstitial type, depending on their atomic size, chemical nature and position in the elemental crystal cell structure. In the case of iron-based alloys, metallic alloying elements, such as Cr, Ni, Mo, Mn, replace the Fe atoms within the elemental cell, they are substitutional elements (Figure 18) [314]. Non-metallic alloying elements, e.g. C, N, O, B, H, having atomic sizes much smaller than those of the base element atoms, occupy interstitial positions within the elemental crystal cell, leading to its distortion (Figure 18) [314]. When the chemical bond between the substituent and interstitial elements is energetically favourable, new crystal structures can form in which the interstitial atoms occupy fixed and periodic positions in the structure, as for example in the case of intermediate and intermetallic phases.

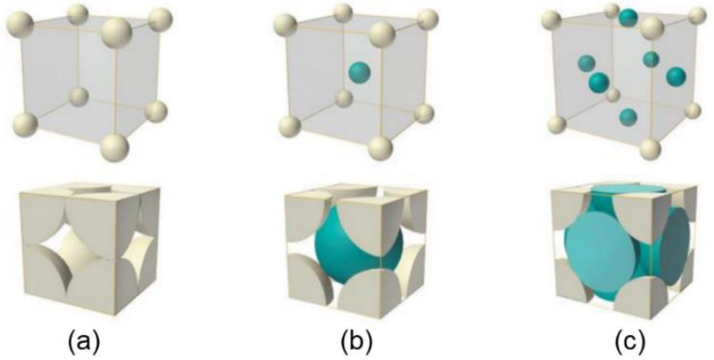

***Figure 17.** Simple cubic (a), body-centred cubic (b) and face-centred cubic (c) crystalline cells [313,314].*

In the case of iron-based alloys, the BCC-type crystalline structure phase is called ferrite and can be alpha (α) or delta (δ), while the FCC-type crystalline structure phase is called austenite and is gamma (γ). The stability of the phases on solidification (cooling from the liquid state) depends very much on the chemical composition of these alloys. For example, in the case of an iron-based alloy containing 25%Cr and 5%Ni, ferrite δ is first formed on solidification, which is further transformed into austenite γ, so that at the end of solidification, at room temperature, the microstructure of the alloy consists of a duplex mixture of δ ferrite and γ austenite [315].

The nature and quantity (mass fraction) of alloying elements can influence the existence ranges of the basic phases in metallic alloys. For example, in the case of Fe-Cr-Ni system alloys, the existence domains of ferrite and austenite phases strongly depend on the chemical composition of the alloy and the temperature (Figure 1) [8,9]. Since, in Fe-based stainless alloys, Fe constitutes the basic element of the crystalline matrix for both ferrite and austenite, the same alloying elements (substitutional and/or interstitial) may be present in the crystal structure of both phases, but in distinctly different mass fractions due to the different solubility limits of these basic phases [316].

1.1.5.2. Plastic deformation accommodation at crystalline level

The plastic deformation behaviour of iron-based alloys is determined by their crystalline structure, i.e. the phase constitution and morphology of the constituent phases. In general, the accommodation of plastic deformation at the crystalline level occurs through slip and twinning mechanisms. Depending on the nature of the constituent phases, slip and twinning occur on high atomic density planes, planes that depend on the crystalline system. The combination of the slip/twinning plane and the slip/twinning direction is called the slip/twinning system.

The mechanism of slip occurrence and propagation is governed by the mechanism of dislocation occurrence and displacement on the high-density atomic planes.

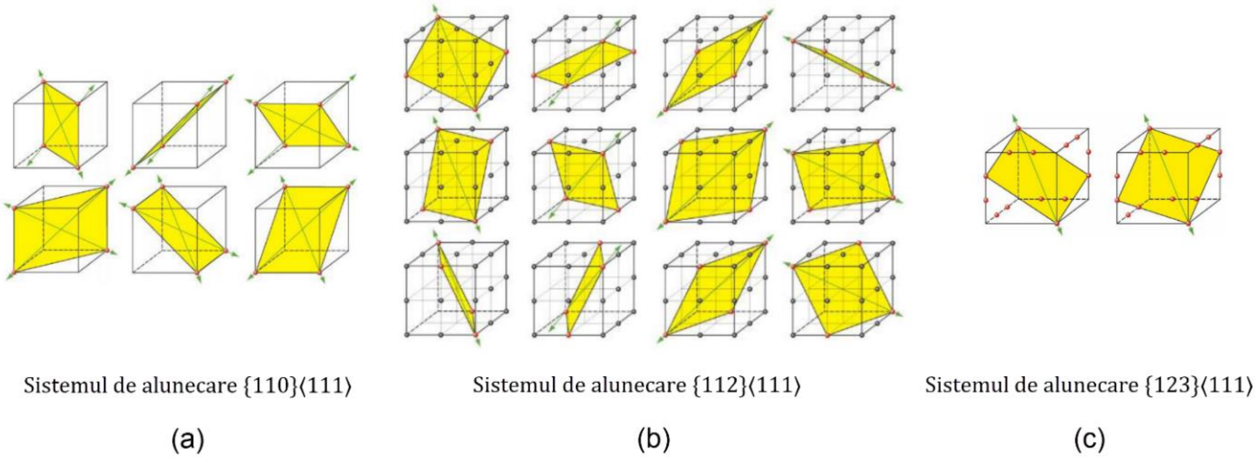

Figure 19. *Schematic representation of {110}⟨111⟩ (a), {112}⟨111⟩ (b) and {123}⟨111⟩ (c) slip systems in ferrite (BCC) [314].*

In the case of ferrite, having a BCC-type crystal structure, the accommodation of slip deformation occurs mainly on the {110}, {112} and {123} atomic plane, along the ⟨111⟩

crystallographic directions (Figure 19) [314]. Thus, the possible plane/slip direction combinations are constituted of 12 possible combinations belonging to the $\{110\}\langle 111\rangle$ system, 12 possible combinations belonging to the $\{112\}\langle 111\rangle$ system and, 24 possible combinations belonging to the $\{123\}\langle 111\rangle$ system (Table 10) [314].

Tabel 10. *Composition of {110}⟨111⟩, {112}⟨111⟩ and {123}⟨111⟩ slip systems in ferrite (BCC) [314].*

{110}⟨111⟩ slip system			***{112}⟨111⟩ slip system***			***{123}⟨111⟩ slip system***					
No.	***{110}***	***⟨111⟩***	***No.***	***{112}***	***⟨111⟩***	***No.***	***{123}***	***⟨111⟩***	***No.***	***{123}***	***⟨111⟩***
1	(011)	$[1\bar{1}1]$	***1***	(211)	$[\bar{1}11]$	***1***	(123)	$[11\bar{1}]$	***13***	(231)	$[1\bar{1}1]$
2	(011)	$[\bar{1}\bar{1}1]$	***2***	$(\bar{2}11)$	$[111]$	***2***	$(\bar{1}23)$	$[1\bar{1}1]$	***14***	$(\bar{2}31)$	$[11\bar{1}]$
3	$(0\bar{1}1)$	$[111]$	***3***	$(2\bar{1}1)$	$[11\bar{1}]$	***3***	$(1\bar{2}3)$	$[\bar{1}11]$	***15***	$(2\bar{3}1)$	$[111]$
4	$(0\bar{1}1)$	$[\bar{1}11]$	***4***	$(21\bar{1})$	$[1\bar{1}1]$	***4***	$(12\bar{3})$	$[111]$	***16***	$(23\bar{1})$	$[\bar{1}11]$
5	(101)	$[\bar{1}11]$	***5***	(121)	$[1\bar{1}1]$	***5***	(132)	$[1\bar{1}1]$	***17***	(312)	$[\bar{1}11]$
6	(101)	$[\bar{1}\bar{1}1]$	***6***	$(\bar{1}21)$	$[11\bar{1}]$	***6***	$(\bar{1}32)$	$[11\bar{1}]$	***18***	$(\bar{3}12)$	$[111]$
7	$(\bar{1}01)$	$[111]$	***7***	$(1\bar{2}1)$	$[111]$	***7***	$(1\bar{3}2)$	$[111]$	***19***	$(3\bar{1}2)$	$[11\bar{1}]$
8	$(\bar{1}01)$	$[1\bar{1}1]$	***8***	$(12\bar{1})$	$[\bar{1}11]$	***8***	$(13\bar{2})$	$[\bar{1}11]$	***20***	$(31\bar{2})$	$[1\bar{1}1]$
9	(110)	$[\bar{1}11]$	***9***	(112)	$[11\bar{1}]$	***9***	(213)	$[11\bar{1}]$	***21***	(321)	$[\bar{1}11]$
10	(110)	$[\bar{1}1\bar{1}]$	***10***	$(\bar{1}12)$	$[1\bar{1}1]$	***10***	$(\bar{2}13)$	$[1\bar{1}1]$	***22***	$(\bar{3}21)$	$[111]$
11	$(\bar{1}10)$	$[111]$	***11***	$(1\bar{1}2)$	$[\bar{1}11]$	***11***	$(2\bar{1}3)$	$[\bar{1}11]$	***23***	$(\bar{3}21)$	$[11\bar{1}]$
12	$(\bar{1}10)$	$[11\bar{1}]$	***12***	$(11\bar{2})$	$[111]$	***12***	$(21\bar{3})$	$[111]$	***24***	$(\bar{3}21)$	$[1\bar{1}1]$

In the case of austenite, having a FCC-type crystalline structure, the accommodation of slip deformation occurs mainly on the $\{111\}$ atomic planes, along the $\langle 110\rangle$ crystallographic directions (Figure 20) [314]. Thus, the possible plane/slip direction combinations are: 12 possible combinations belonging to the $\{111\}\langle 110\rangle$ system (Table 11) [314]. The existence of slip on 4 planes: (111), $(\bar{1}\bar{1}1)$, $(1\bar{1}\bar{1})$ and $(\bar{1}1\bar{1})$, in 3 possible directions is observed, resulting 12 combinations (Figure 20).

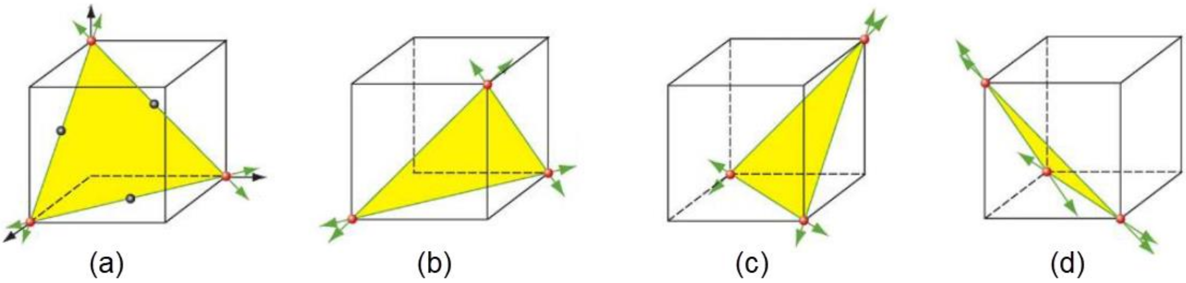

Figure 20. *Schematic representation of {111}⟨110⟩ slip system in austenite (FCC):* $(111)\langle 110\rangle$ *sub-family (a),* $(\bar{1}\bar{1}1)\langle 110\rangle$ *sub-family (b),* $(1\bar{1}\bar{1})\langle 110\rangle$ *sub-family (c),* $(\bar{1}1\bar{1})\langle 110\rangle$ *sub-family (d) [314].*

In addition to slip, plastic deformation can also be accommodated by twinning. Energetically, the activation of the twinning mechanism requires a higher local energy than the activation of slip. For this reason, the twinning occurs after the slip has been blocked on the higher-density atomic planes and the defect density has reached a critical value that makes the activation energy of the slip (on the less favourably oriented atomic planes in respect to the applied deformation stress direction) to be higher than the critical activation energy of the twinning. The increase in crystal fault density, due to internal slip, can lead to *stacking faults*, which in turn lead to fragmentation of the slip planes and, as a result, to slip hindrance, but may lead to local crystallographic re-orientations (*twinning faults*) which can favours the occurrence of twinning [317].

Tabel 11. *Composition of {111}⟨110⟩ slip system in austenite (FCC) [314].*

No.	***1***	***2***	***3***	***4***	***5***	***6***	***7***	***8***	***9***	***10***	***11***	***12***
{111}	(111)	(111)	(111)	$(\bar{1}\bar{1}1)$	$(\bar{1}\bar{1}1)$	$(\bar{1}\bar{1}1)$	$(1\bar{1}\bar{1})$	$(1\bar{1}\bar{1})$	$(1\bar{1}\bar{1})$	$(\bar{1}1\bar{1})$	$(\bar{1}1\bar{1})$	$(\bar{1}1\bar{1})$
⟨110⟩	$[01\bar{1}]$	$[\bar{1}01]$	$[1\bar{1}0]$	$[0\bar{1}\bar{1}]$	$[101]$	$[\bar{1}10]$	$[0\bar{1}1]$	$[\bar{1}0\bar{1}]$	$[110]$	$[011]$	$[10\bar{1}]$	$[\bar{1}\bar{1}0]$

Considering both the crystallographic characteristics of ferrite (BCC-type crystalline cell) and austenite (FCC-type crystalline cell) and the level of energy barrier induced by packing faults, activation of twinning in austenite requires lower energy in comparison with the one required for activation of twinning in ferrite. In the case of ferrite, exhibiting a BCC-type crystal structure, the accommodation of deformation by twinning occurs mainly on the {112} atomic planes, along the ⟨111⟩ crystallographic directions (Table 12) [317]. Thus, the possible plane / twinning direction combinations are represented by 12 possible combinations belonging to the {112}⟨111⟩ system. In the case of austenite, exhibiting a FCC-type crystal structure, the accommodation of deformation by twinning occurs mainly on the {111} atomic plane, along the ⟨111⟩ crystallographic directions (Table 13) [317]. Thus, the possible plane / twinning direction combinations are represented by 12 combinations belonging to the {111}⟨112⟩ system.

Tabel 12. *Composition of {112}⟨111⟩ twinning system in ferrite (BCC) [317].*

No.	***1***	***2***	***3***	***4***	***5***	***6***	***7***	***8***	***9***	***10***	***11***	***12***
{112}	(211)	$(\bar{2}11)$	$(2\bar{1}1)$	$(21\bar{1})$	(121)	$(\bar{1}21)$	$(1\bar{2}1)$	$(12\bar{1})$	(112)	$(\bar{1}12)$	$(1\bar{1}2)$	$(11\bar{2})$
⟨111⟩	$[\bar{1}11]$	$[111]$	$[11\bar{1}]$	$[1\bar{1}1]$	$[1\bar{1}1]$	$[11\bar{1}]$	$[111]$	$[\bar{1}11]$	$[11\bar{1}]$	$[1\bar{1}1]$	$[\bar{1}11]$	$[111]$

Tabel 13. *Composition of {111}⟨112⟩ twinning system in austenite (FCC) [317].*

No.	***1***	***2***	***3***	***4***	***5***	***6***	***7***	***8***	***9***	***10***	***11***	***12***
{111}	(111)	(111)	(111)	$(\bar{1}\bar{1}1)$	$(\bar{1}\bar{1}1)$	$(\bar{1}\bar{1}1)$	$(1\bar{1}\bar{1})$	$(1\bar{1}\bar{1})$	$(1\bar{1}\bar{1})$	$(\bar{1}1\bar{1})$	$(\bar{1}1\bar{1})$	$(\bar{1}1\bar{1})$
⟨112⟩	$[\bar{2}11]$	$[1\bar{2}1]$	$[11\bar{2}]$	$[2\bar{1}1]$	$[\bar{1}21]$	$[\bar{1}\bar{1}\bar{2}]$	$[\bar{2}\bar{1}\bar{1}]$	$[12\bar{1}]$	$[1\bar{1}2]$	$[21\bar{1}]$	$[\bar{1}\bar{2}\bar{1}]$	$[\bar{1}12]$

1.1.6. EN 1.4410 / UNS S32750 / F53 super-duplex stainless steel alloy

The super duplex stainless steel EN 1.4410 / UNS S32750 / F53, known generically as 2507, was chosen as a study material to investigate the specific phenomena that may occur in the thermo-mechanical processing of super duplex stainless alloys, being a representative alloy for this class of stainless steels.

Super duplex stainless steel EN 1.4410 / UNS S32750 / F53 was targeted for use in aggressive environments containing high amounts of chloride ions, acids, etc [318]. It has a high resistance to localised pitting, crevice and intergranular corrosion, as well as to stress field-induced corrosive cracking in highly chlorinated solutions and is characterised by a $\mathrm{PRE_N}$ parameter value > 40 [319].

In the chemical composition of super duplex stainless steel EN 1.4410 / UNS S32750 / F53 there is a significant amount of Cr, Ni, Mo and N, which makes the balance between the basic phases approximately 50% ferrite δ : 50% austenite γ (Table 14) [320,321].

In addition to high corrosion characteristics, also super duplex stainless steel EN 1.4410 / UNS S32750 / F53 possesses high mechanical strength characteristics (Table 15) [320,321], having both a maximum strength limit > 750MPa and a minimum toughness (resilience) > 100J at room temperature.

Tabel 14. *Chemical composition of EN 1.4410 / UNS S32750 / F53 alloy [320,321].*

Grade (standard) EN / UNS / ASTM	***Chemical composition, wt%***								
	C	***Cr***	***Ni***	***Mo***	***N***	***Mn***	***Si***	***Cu***	***W***
1.4410 / S32750 / F53	<0.03	24.0-26.0	6.00-8.00	3.00-5.00	0.24-0.32	<1.2	<0.80	<0.50	–

Tabel 15. *Minimum mechanical properties for EN 1.4410 / UNS S32750 / F53 alloy [320,321].*

Grade (standard) EN / UNS / ASTM	***Mechanical characteristics***					
	***Ultimate tensile strength**, MPa*	***Yield strength**, MPa*	***Elongation to fracture**, %*	***Absorbed energy**, [J]*		***Hardness**, HB*
				-40°C	***20°C***	
1.4410 / S32750 / F53	> 750	> 550	> 25	> 40	> 100	< 310

Due to the optimal combination of high corrosion resistance and mechanical strength properties, the EN 1.4410 / UNS S32750 / F53 super duplex stainless steel can be successfully used in a number of applications, such as: oil, gas, marine installations, desalination plants, hydraulic turbines, pressure vessels, storage tanks, reaction vessels and tanks, etc [322,323].

1.2. Objectives, concepts and methods employed in the original research: *Specific phenomena occurring during thermomechanical processing of super-duplex stainless steel (SDSS) alloys*

Super duplex stainless steels have been and are intensively investigated, as they show a favourable combination of high mechanical properties and corrosion resistance in oxidative, acidic, chloride-ion-rich environments, etc. [324,325]. Compared to high-alloyed nickel alloys, which show similar properties, super duplex stainless steels have the advantage of much lower cost, for this reason they are experiencing increasing development and use [326-329]. Considering the presence of the basic phases (ferrite and austenite), as well as the particular compositional specificity of these steels, special attention should be paid to the transformations that may occur in ferrite, both for thermomechanical processing at temperatures below 700°C and above 700°C, as they lead to worsening of the mechanical and corrosion resistance properties [330-332]. Based on these considerations, the objectives of the PhD thesis are as follows:

Objective 1: The investigation of microstructural evolution during hot deformation of EN 1.4410 / UNS S32750 / F53 super-duplex stainless steel alloy.

To achieve this objective, samples of as-received (AR) EN 1.4410 / UNS S32750 / F53 alloy were hot plastic deformed at temperatures between 1000°C and 1275°C (*hot deformation*) with the same total degree of deformation (ε_{total}) of 30% in 25°C steps using the *up-setting* method [333]. The schematic representation of the thermomechanical processing route applied to this alloy is shown in Figure 21.

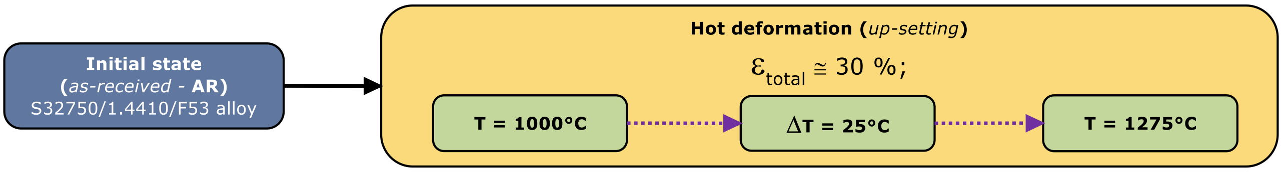

Figure 21. *Schematic representation of the thermomechanical processing route applied to achieve objective 1.*

All thermomechanically processed samples were microstructurally investigated. Microstructural analysis was performed by *Scanning Electron Microscopy* (SEM) using *Energy Dispersive Spectroscopy* (EDS) and *Electron Backscatter Diffraction* (EBSD) techniques. The following investigations were performed: chemical composition, phase structure evolution, phase morphology, phase mass fraction, phase grain size, structural homogeneity and dynamic recrystallization process. A full description of employed research concept and methodology is presented in the following publication:

E.M. Cojocaru, A. Nocivin, D. Raducanu, M.L. Angelescu, I. Cinca, I.V. Balkan, N. Serban, V.D. Cojocaru. *Microstructure evolution during hot deformation of UNS S32750 Super-Duplex Stainless Steel alloy*; MATERIALS, 2021, 14, 3916; 10.3390/ma14143916.

Objective 2: The investigation of isochronal treatment effects induced on the microstructure and the mechanical properties of EN 1.4410 / UNS S32750 / F53 super-duplex stainless steel alloy.

To achieve this objective, samples of EN 1.4410 / UNS S32750 / F53 alloy in the initial state (*as-received* - AR) were *hot-deformed by rolling* (HR) at 1100°C by a total deformation degree of 65% ($\varepsilon_{total} \approx 65\%$), in six equal rolling steps. All deformed samples were subjected to a first *solution treatment* (ST) at 1050°C for 30 min and water quenching (WQ). The second treatment stage continued with *isochronal solution treatments* (IT) carried out at temperatures between 700°C and 1060°C, in steps of 20°C, with a fixed treatment duration of 15min and water quenching [253]. The schematic representation of the applied thermomechanical processing route is shown in Figure 22.

All thermomechanically processed samples were microstructurally and mechanically investigated. Microstructural evolution analysis of thermomechanically processed samples was performed by SEM electron microscopy using EDS and EBSD techniques. Data on chemical composition, phase structure evolution, phase morphology, phase mass fraction, phase grain size and structural homogeneity was obtained. Analysis of the mechanical behaviour was carried out using tensile and resilience/impact tests. The following mechanical properties were determined: ultimate strength, yield strength, elongation at break and energy absorbed at break (resilience). A full description of employed research concept and methodology is presented in the following publication:

> ***E.M. Cojocaru***, D. Raducanu, S.S. Alturaihi, A. Nocivin, G. Coman, V.D. Cojocaru. *Influence of isochronal treatments on microstructure and mechanical properties of solution treated UNS S32750 SDSS alloy specimens*; JOURNAL OF MATERIALS RESEARCH AND TECHNOLOGY, 2020, 9, 7870–7879; 10.1016/j.jmrt.2020.05.056.

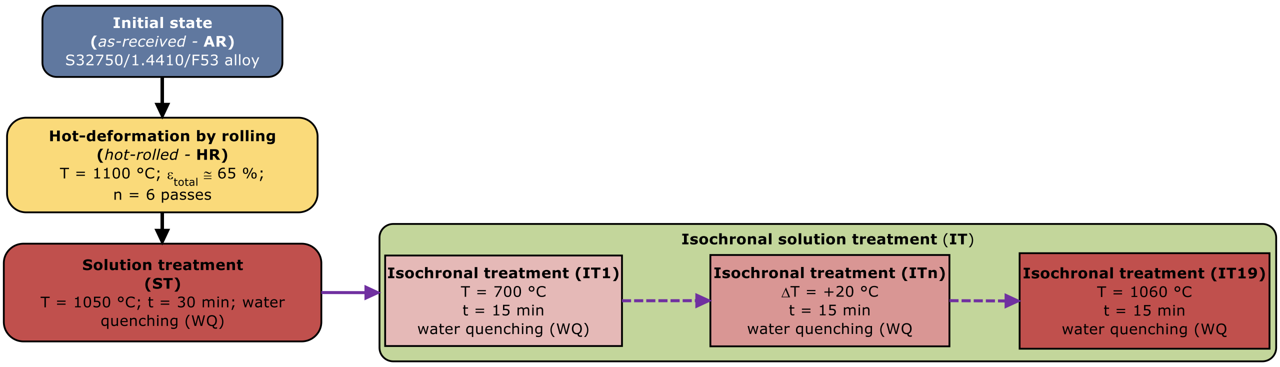

Figure 22. *Schematic representation of the thermomechanical processing route applied to achieve objective 2.*

Objective 3: The investigation of isothermal treatment effects induced on the microstructure and the mechanical properties of EN 1.4410 / UNS S32750 / F53 super-duplex stainless steel alloy.

To achieve this objective, samples of EN 1.4410 / UNS S32750 / F53 alloy, in the *initial state* (AR), were hot *deformed by rolling* (HR) at 1100°C with the same total deformation degree of 65% ($\varepsilon_{total} \approx 65\%$), in six rolling steps. The deformed samples were subjected to a first *solution treatment* (ST) at 1050°C for 30 min and water quenching (WQ). The second treatment stage continued with *isothermal solution treatments* (A) carried out at temperatures of 780°C, 850°C and 920°C, with holding times between 5min and 90min and cooling in water. The schematic representation of the applied thermomechanical processing route is shown in Figure 23 [334].

All thermomechanically processed samples were microstructurally and mechanically investigated. Microstructural evolution analysis of thermomechanically processed samples was performed by SEM electron microscopy using EDS and EBSD techniques. Data on chemical composition, phase structure evolution, phase morphology, phase mass fraction, phase grain size and structural homogeneity was obtained. Analysis of the mechanical behaviour was carried out using tensile and resilience/impact tests. The following mechanical properties were determined: ultimate strength, yield strength, elongation at break and energy absorbed at break (resilience). For all samples isothermal solution treated at 850°C, the compositional evolution of the constituent phases as a function of the treatment time was analysed in detail. A full description of employed research concept and methodology is presented in the following publication:

> **E.M. Cojocaru**, D. Raducanu, A. Nocivin, V.D. Cojocaru. *Influence of ageing treatment temperature and duration on σ-phase precipitation and mechanical properties of UNS S32750 SDSS alloy*; JOURNAL OF ADVANCED RESEARCH, 2021, 30, 53-61; 10.1016/j.jare.2020.11.005.

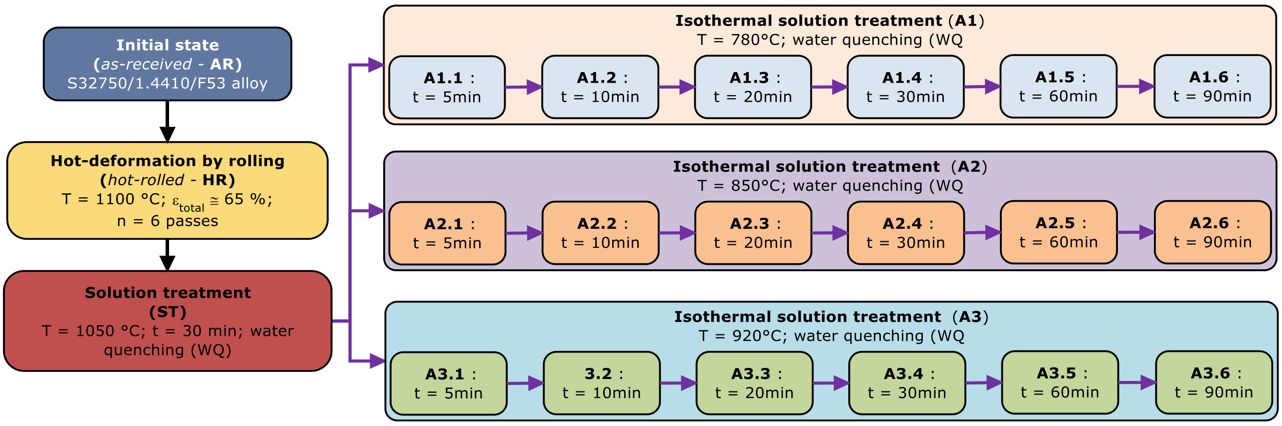

Figure 23. *Schematic representation of the thermomechanical processing route applied to achieve objective 3 [334].*

Objective 4: The investigation of ageing treatment effects induced on the hot-deformation microstructure and the mechanical properties of EN 1.4410 / UNS S32750 / F53 super-duplex stainless steel alloy.

To achieve this objective, samples of EN 1.4410 / UNS S32750 / F53 alloy, in the *initial state* (AR), were hot *deformed by rolling* (HR) at 1100°C with the same total deformation degree of 65% ($\varepsilon_{total} \approx 65\%$), in six rolling steps. After the hot plastic deformation step, the samples were subjected to an *ageing treatment* (A) carried out at temperatures of 400°C, 500°C and 600°C, with treatment durations of 3h (*short-duration ageing treatment*) and 120h (*long-duration ageing treatment*) and cooling in air. The schematic representation of the applied thermomechanical processing route is shown in Figure 24 [335].

All thermomechanically processed samples were microstructurally and mechanically investigated. Microstructural evolution analysis of thermomechanically processed samples was performed by SEM electron microscopy using EDS and EBSD techniques. Data on chemical composition, phase structure evolution, phase morphology, phase mass fraction, phase grain size and structural homogeneity was obtained. Analysis of the mechanical behaviour was carried out using tensile and resilience/impact tests. The following mechanical properties were determined: ultimate strength, yield strength, elongation at break and energy absorbed at break (resilience). A full description of employed research concept and methodology is presented in the following publication:

> **E.M. Cojocaru**, D. Raducanu, A. Nocivin, I. Cinca, A.N. Vintila, N. Serban, M.L. Angelescu, V.D. Cojocaru. *Influence of aging treatment on microstructure and tensile properties of a hot*

deformed UNS S32750 Super Duplex Stainless Steel (SDSS) alloy; METALS, 2020, 10, 353; 10.3390/met10030353.

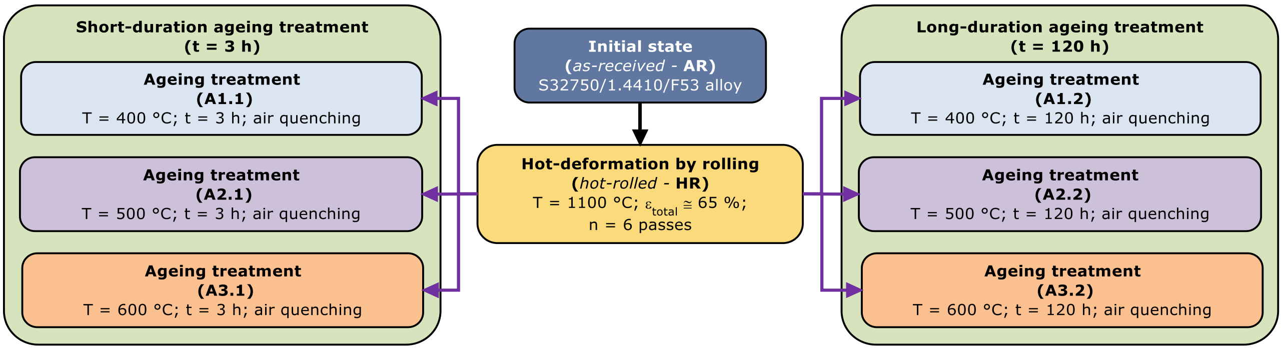

Figure 24. *Schematic representation of the thermomechanical processing route applied to achieve objective 4 [335].*

Objective 5: The investigation of ageing treatment effects induced on the solution treated microstructure and the mechanical properties of EN 1.4410 / UNS S32750 / F53 super-duplex stainless steel alloy.

To achieve this objective, samples of EN 1.4410 / UNS S32750 / F53 alloy, in the *initial state* (AR), were hot *deformed by rolling* (HR) at 1100°C with the same total deformation degree of 65% ($\varepsilon_{total} \approx 65\%$), in six rolling steps. The deformed samples were subjected to a first *solution treatment* (ST) at 1050°C for 30 min and water quenching (WQ). The second treatment stage continued with an *ageing treatment* (A) carried out at temperatures of 400°C, 500°C and 600°C, with treatment durations of 3h (*short-duration ageing treatment*) and 120h (*long-duration ageing treatment*) and cooling in air. The schematic representation of the applied thermomechanical processing route is shown in Figure 25 [105].

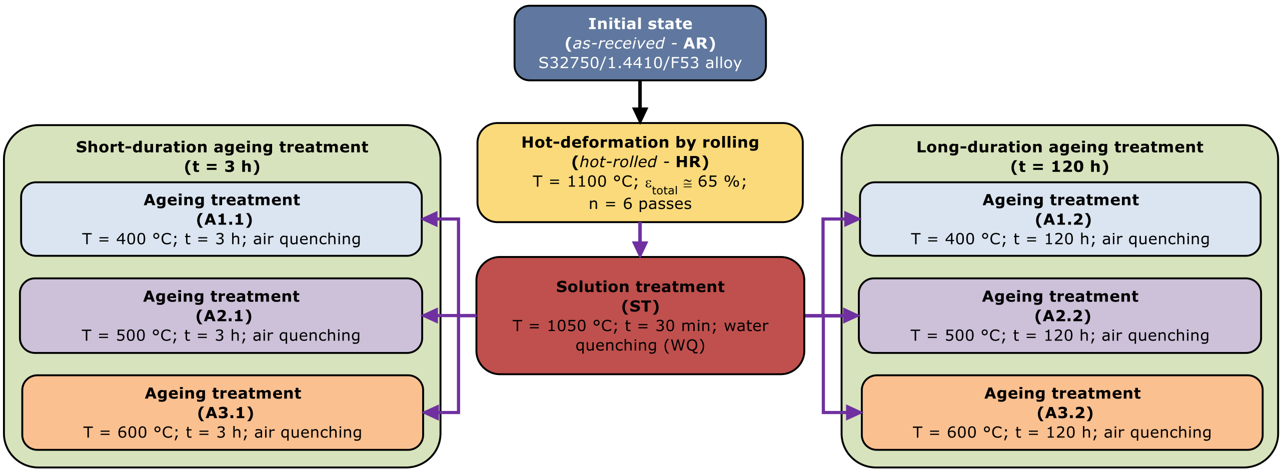

Figure 25. *Schematic representation of the thermomechanical processing route applied to achieve objective 5 [105].*

All thermomechanically processed samples were microstructurally and mechanically investigated. Microstructural evolution analysis of thermomechanically processed samples was performed by SEM electron microscopy using EDS and EBSD techniques. Data on chemical composition, phase structure evolution, phase morphology, phase mass fraction, phase grain size and structural homogeneity was obtained. Analysis of the mechanical behaviour was carried out using tensile and resilience/impact tests. The following mechanical properties were determined: ultimate strength, yield strength, elongation at break and energy absorbed at break (resilience). A full description of employed research concept and methodology is presented in the following publication:

> ***E.M. Cojocaru***, D. Raducanu, A.N. Vintila, S.S. Alturaihi, N. Serban, A.C. Berbecaru, V.D. Cojocaru. *Influence of ageing treatment on microstructural and mechanical properties of a solution treated UNS S32750/EN 1.4410/F53 Super Duplex Stainless Steel (SDSS) alloy*; JOURNAL OF MATERIALS RESEARCH AND TECHNOLOGY, 2020, 9, 8592–8605; 10.1016/j.jmrt.2020.05.127.

2. Published research articles in extenso

The following scientific articles have been published as a result of the experimental programmes carried out to achieve the objectives of the PhD thesis:

Objective 1: The investigation of microstructural evolution during hot deformation of EN 1.4410 / UNS S32750 / F53 super-duplex stainless steel alloy:

E.M. Cojocaru, A. Nocivin, D. Raducanu, M.L. Angelescu, I. Cinca, I.V. Balkan, N. Serban, V.D. Cojocaru. *Microstructure evolution during hot deformation of UNS S32750 Super-Duplex Stainless Steel alloy*; MATERIALS, 2021, 14, 3916; 10.3390/ma14143916 (***FI 2022 – 3.4***).

Objective 2: The investigation of isochronal treatment effects induced on the microstructure and the mechanical properties of EN 1.4410 / UNS S32750 / F53 super-duplex stainless steel alloy:

E.M. Cojocaru, D. Raducanu, S.S. Alturaihi, A. Nocivin, G. Coman, V.D. Cojocaru. *Influence of isochronal treatments on microstructure and mechanical properties of solution treated UNS S32750 SDSS alloy specimens*; JOURNAL OF MATERIALS RESEARCH AND TECHNOLOGY, 2020, 9, 7870–7879; 10.1016/j.jmrt.2020.05.056 (***FI 2022 – 6.4***).

Objective 3: The investigation of isothermal treatment effects induced on the microstructure and the mechanical properties of EN 1.4410 / UNS S32750 / F53 super-duplex stainless steel alloy:

E.M. Cojocaru, D. Raducanu, A. Nocivin, V.D. Cojocaru. *Influence of ageing treatment temperature and duration on σ-phase precipitation and mechanical properties of UNS S32750 SDSS alloy*; JOURNAL OF ADVANCED RESEARCH, 2021, 30, 53-61; 10.1016/j.jare.2020.11.005 (***FI 2022 – 10.7***).

Objective 4: The investigation of ageing treatment effects induced on the hot-deformation microstructure and the mechanical properties of EN 1.4410 / UNS S32750 / F53 super-duplex stainless steel alloy:

E.M. Cojocaru, D. Raducanu, A. Nocivin, I. Cinca, A.N. Vintila, N. Serban, M.L. Angelescu, V.D. Cojocaru. *Influence of aging treatment on microstructure and tensile properties of a hot deformed UNS S32750 Super Duplex Stainless Steel (SDSS) alloy*; METALS, 2020, 10, 353; 10.3390/met10030353 (***FI 2022 – 2.9***).

Objective 5: The investigation of ageing treatment effects induced on the solution treated microstructure and the mechanical properties of EN 1.4410 / UNS S32750 / F53 super-duplex stainless steel alloy:

E.M. Cojocaru, D. Raducanu, A.N. Vintila, S.S. Alturaihi, N. Serban, A.C. Berbecaru, V.D. Cojocaru. *Influence of ageing treatment on microstructural and mechanical properties of a solution treated UNS S32750/EN 1.4410/F53 Super Duplex Stainless Steel (SDSS) alloy*; JOURNAL OF MATERIALS RESEARCH AND TECHNOLOGY, 2020, 9, 8592–8605; 10.1016/j.jmrt.2020.05.127 (***FI 2022 – 6.4***).

3. General conclusions and original contributions

3.1. General conclusions

The following general conclusions can be drawn on the evolution of microstructural and mechanical properties during thermomechanical processing of super duplex stainless steel EN 1.4410 / UNS S32750 / F53 alloy:

Objective 1: The investigation of microstructural evolution during hot deformation of EN 1.4410 / UNS S32750 / F53 super-duplex stainless steel alloy:

- plastic deformation by up-setting, at temperatures between 1000°C and 1275°C, with a total degree of deformation of about 30%, does not significantly influence the ratio/mass fraction between the basic phases (ferrite δ / austenite γ). Practically, the ratio/mass fraction between the phases is approximately identical before and after the hot plastic deformation process;
- as a result of the plastic deformation process, the morphology of the basic phases is typical of plastically deformed microstructures, showing signs of strain-hardening. In the (1000 ÷ 1275)°C temperature range, for a total degree of deformation of about 30%, no major microstructural defects, such as cracks, micro-cracks, fissures, etc. are developed within the volume of the deformed samples, which indicates that in this temperature range the EN 1.4410 / UNS S32750 / F53 alloy can be deformed with high degrees of plastic deformation;
- during hot plastic deformation, precipitation of secondary phases in the microstructure of EN 1.4410 / UNS S32750 / F53 is observed at temperatures below 1025°C. The sigma phase (σ) is observed in the microstructure particularly in the δ / γ boundary/interface area, in the δ-ferrite mass. At plastic deformation temperatures above 1050°C, the σ phase is completely dissolved in the ferrite mass;
- in the (1200 ÷ 1275)°C deformation temperature range, an increase in the secondary austenite (γ_2) amount of is observed, precipitated particularly at the δ / δ boundaries / interfaces due to the increased kinetics of the dynamic recrystallisation process of the δ phase grains (in this temperature range the GROD analysis for the δ phase shows a sharp decrease from 49°C to 21°);
- in the (1200 ÷ 1275)°C deformation temperature range, the dynamic recrystallisation process of plastically deformed grains is observed only in the case of ferrite grains;

- the hot plastic deformation process of EN 1.4410 / UNS S32750 / F53 alloy can be successfully performed in the temperature range (1050 ÷ 1275)°C, at least with total deformation degrees between successive deformation stages of 30%.

***Objective 2: The investigation of isochronal treatment effects induced on the microstructure and the mechanical properties of EN 1.4410 / UNS S32750 / F53 super-duplex stainless steel alloy*:**

- in the (700 ÷ 1060)°C temperature range, for a treatment duration of 15min, in the microstructure of the EN 1.4410 / UNS S32750 / F53 alloy, precipitation of the sigma (σ) and chi (χ) secondary phases takes place, starting at 780°C for the σ phase and 820°C for the χ phase, respectively;
- the maximum σ phase mass fraction, approximately 13.3%, is precipitated following isochronal treatment at 920°C. Complete dissolution of the σ phase is observed following the treatment performed at 1020°C;
- the secondary phase σ has a maximum negative influence on the elongation at break and the energy consumed at break (resilience). The elongation at break reaches minimum value - close to 9% and, energy consumed at break (resilience) – close to 3.3J, for a σ phase fraction mass between (11 ÷ 13)%.

***Objective 3: The investigation of isothermal treatment effects induced on the microstructure and the mechanical properties of EN 1.4410 / UNS S32750 / F53 super-duplex stainless steel alloy*:**

- precipitation kinetics of the σ secondary phase is strongly influenced by both temperature and treatment duration. Thus, at 780°C, the incubation time required for the precipitation of the σ phase is about 20min, while at 850°C and 920°C, the σ phase is detected as early as 5min;
- the maximum precipitation kinetics of the secondary σ phase is recorded at 850°C, when the maximum mass fractions of the σ phase is obtained, for the same holding time compared to those recorded at 780°C and 920°C;
- the maximum precipitation kinetics of the secondary austenite phase (γ_2) is recorded at 920°C, when the maximum γ_2 phase mass fractions are obtained in comparison with the ones obtained for 780°C and 850°C treatments;
- σ phase has a maximum negative influence on elongation at break and energy consumed at break (resilience) and a minimum influence on maximum yield strength and yield strength. Increasing the σ phase mass fraction lead to drastic decreases in elongation at

break and energy consumed at break (resilience) and minimum increases in maximum yield strength and yield strength;

- in addition to influencing the mass fraction of precipitated secondary phases, increasing the treatment duration, also, significantly influences their chemistry. Thus, increasing the treatment duration leads, in the case of the σ phase, to its enrichment in Cr and Mo and depletion in Ni and, respectively, in the case of the γ_2 phase to its enrichment in Ni, Cr and Mo.

***Objective 4: The investigation of ageing treatment effects induced on the hot-deformation microstructure and the mechanical properties of EN 1.4410 / UNS S32750 / F53 super-duplex stainless steel alloy*:**

- in the hot plastic deformed EN 1.4410 / UNS S32750 / F53 alloy, heating at temperatures between 400°C and 600°C, has a major influence on two categories of phenomena, namely: the phenomenon of stress relief of the deformed microstructure and the precipitation of secondary phases. These phenomena, in addition to temperature, are also strongly influenced by the treatment duration;
- the average size of the δ ferrite grains and the dynamically recrystallised fraction of these grains, can be controlled by varying both the temperature and the duration of the ageing treatment;
- at short-duration ageing treatment (3h), an increase in strength properties (maximum strength limit, yield strength and elongation at break) and a decrease in resilience properties (energy consumed at break) is observed, since in the hot plastic deformed microstructure, the stress-relieving phenomenon plays the main role. At the same time, precipitation phenomena that may occur should not be ignored. Thus, the decrease in resilience properties is caused by the occurrence of α/α' spinodal decomposition/precipitation, which contributes substantially to the embrittlement of the alloy microstructure;
- at long-duration ageing treatment (120h), a decrease in strength properties (maximum strength limit, yield strength and elongation at break) and also a substantial decrease in resilience properties (energy consumed at break) is observed, because in the hot plastic deformed microstructure, precipitation phenomenon plays the main role. Precipitation phenomena that can occur in the (400 ÷ 600)°C temperature range are strongly influenced by the increase of the treatment duration. Thus, the decrease in strength and toughness properties is caused both by the increased intensity of the α/α' spinodal decomposition/precipitation and by the precipitation of other secondary phases, such as G

and R, which contribute substantially to the intensification of the embrittlement phenomena.

Objective 5: The investigation of ageing treatment effects induced on the solution treated microstructure and the mechanical properties of EN 1.4410 / UNS S32750 / F53 super-duplex stainless steel alloy:

- in EN 1.4410 / UNS S32750 / F53 alloy, hot deformed and annealed at 1050°C for 30min and water quenched, the application of a ageing treatment at temperatures between 400°C and 600°C, with treatment durations of 3h (short-duration) and 120h (long-duration), has a major influence on its mechanical behaviour;
- the ageing treatments does not induce major changes in the mass fraction of the basic phases, the morphology of the phases, the average size of the crystalline grains and their modal orientation;
- at short-duration ageing treatment (3h), an increase in strength properties (maximum strength limit and yield strength) and a decrease in ductility properties (elongation at break and energy consumed at break) are observed, because in the annealed microstructure the phenomenon of stress relief plays the main role. In this situation too, the precipitation phenomena that may occur should not be ignored. Thus, the decrease in ductility properties is caused by α/α' spinodal decomposition/precipitation, which contributes substantially to the embrittlement of the alloy microstructure;
- at long-duration ageing treatment (120h), an increase in strength properties (maximum strength limit and yield strength) and, also, a substantial decrease in ductility properties (elongation at break and energy consumed at break) are observed, since in the annealed microstructure precipitation plays the main role. Thus, a substantial increase in α/α' spinodal decomposition/precipitation is observed, as well as the precipitation of other secondary phases, such as G and R, which contribute substantially to the worsening of toughness / resilience properties.

3.2. Original contributions

Personal contributions to the field addressed in this PhD thesis are as follows:

- to carry out an extensive documentary study (literature overview) on the role of alloying elements, classification, microstructural characteristics, component phases, properties and use of stainless steels;

- design of complex experimental programs for thermomechanical processing of the super duplex stainless steel EN 1.4410 / UNS S32750 / F53 alloy, meeting the requirements necessary to achieve the objectives of the PhD thesis;
- design and development of specific sample preparation procedures for advanced characterisation of the super duplex stainless steel EN 1.4410 / UNS S32750 / F53 alloy;
- use of modern sample preparation methods for advanced characterisation of the super duplex stainless steel EN 1.4410 / UNS S32750 / F53 alloy:
    - a metallographic preparation procedure by grinding - polishing - super-polishing (vibro-polishing) of samples for microstructural characterisation;
    - the use of "standardised" samples for mechanical characterisation: dog-bone samples for tensile testing and V-notch samples for impact testing;
- use of modern methods for advanced characterisation of the super duplex stainless steel EN 1.4410 / UNS S32750 / F53 alloy:
    - chemical composition: Scanning Electron Microscopy (SEM) technique - *Energy Dispersive Spectroscopy* (EDS);
    - microstructural features (phases, constituents, morphology, fracture surfaces, etc.): SEM technique for imaging *Secondary Electrons* (SE) and *Backscattered Secondary Electrons* (BSE);
    - microstructural features (phases, constituents, grain size, modal orientation, identification of slip/ staining systems, etc.): SEM electron microscopy technique - *Electron Backscatter Diffraction* (EBSD);
    - mechanical properties (ultimate tensile strength, yield strength, elongation at break, energy consumed at break): tensile testing and impact testing (*Charpy impact testing*);
- advanced investigation of secondary phase precipitation phenomena in the ferrite mass of the super duplex stainless steel EN 1.4410 / UNS S32750 / F53 alloy, for temperatures below 700°C and above 700°C;
- establishment of specific correlations between microstructural observations and mechanical behaviour as a result of specific applied thermomechanical processing routes for the super duplex stainless steel EN 1.4410 / UNS S32750 / F53 alloy.

List of disseminated scientific results
(*in the doctoral theme field*)

A – Papers published in ISI journals
- as main-author

1. ***Elisabeta Mirela Cojocaru***, A. Nocivin, D. Raducanu, M.L. Angelescu, I. Cinca, I.V. Balkan, N. Serban, V.D. Cojocaru. *Microstructure evolution during hot deformation of UNS S32750 Super-Duplex Stainless Steel alloy*; MATERIALS, 2021, 14, 3916; DOI:10.3390/ma14143916; WOS:000676365200001 (***FI 2022 – 3.4***).

2. ***Elisabeta Mirela Cojocaru***, D. Raducanu, S.S. Alturaihi, A. Nocivin, G. Coman, V.D. Cojocaru. *Influence of isochronal treatments on microstructure and mechanical properties of solution treated UNS S32750 SDSS alloy specimens*; JOURNAL OF MATERIALS RESEARCH AND TECHNOLOGY, 2020, 9, 7870–7879; DOI:10.1016/j.jmrt.2020.05.056; WOS:000560697600002 (***FI 2022 – 6.4***).

3. ***Elisabeta Mirela Cojocaru***, D. Raducanu, A. Nocivin, V.D. Cojocaru. *Influence of ageing treatment temperature and duration on* σ*-phase precipitation and mechanical properties of UNS S32750 SDSS alloy*; JOURNAL OF ADVANCED RESEARCH, 2021, 30, 53-61; DOI:10.1016/j.jare.2020.11.005; WOS:000652682400005 (***FI 2022 – 10.7***).

4. ***Elisabeta Mirela Cojocaru***, D. Raducanu, A. Nocivin, I. Cinca, A.N. Vintila, N. Serban, M.L. Angelescu, V.D. Cojocaru. *Influence of aging treatment on microstructure and tensile properties of a hot deformed UNS S32750 Super Duplex Stainless Steel (SDSS) alloy*; METALS, 2020, 10, 353; DOI:10.3390/met10030353; WOS:000530137000057 (***FI 2022 – 2.9***).

5. ***Elisabeta Mirela Cojocaru***, D. Raducanu, A.N. Vintila, S.S. Alturaihi, N. Serban, A.C. Berbecaru, V.D. Cojocaru. *Influence of ageing treatment on microstructural and mechanical properties of a solution treated UNS S32750/EN 1.4410/F53 Super Duplex Stainless Steel (SDSS) alloy*; JOURNAL OF MATERIALS RESEARCH AND TECHNOLOGY, 2020, 9, 8592–8605; DOI:10.1016/j.jmrt.2020.05.127; WOS:000560698600007 (***FI 2022 – 6.4***).

- as co-author

6. F. Khoshnaw, C. Marinescu, A. Sofronia, C. Munteanu, M. Marcu, L.E. Barbulescu, C. Ciobota, ***Elisabeta Mirela Cojocaru***, S. Tanasescu, A. Paraschiv. *Microstructural and thermoanalytical characterization of super duplex stainless steel - UNS S32760-F55*; MATERIALS TODAY COMMUNICATIONS, 2021, 28, 102644; DOI:10.1016/j.mtcomm.2021.102644; WOS:000697030000002 (***FI 2022 – 3.8***).

7. M.L. Angelescu, ***Elisabeta Mirela Cojocaru***, N. Serban, V.D. Cojocaru. *Evaluation of hot deformation behaviour of UNS S32750 Super Duplex Stainless Steel (SDSS) alloy*; METALS, 2020, 10,673; DOI:10.3390/met10050673; WOS:000540220000121 (***FI 2022 – 2.9***).

8. N. Serban, V.D. Cojocaru, M.L. Angelescu, D. Raducanu, I. Cinca, A.N. Vintila, ***Elisabeta Mirela Cojocaru***. *High temperature deformation behaviour of an industrial S32760/1.4501/F55 super duplex stainless steel (SDSS) alloy*; METALLURGIA ITALIANA, 2019, 5, 41-48; WOS:000491966800004 (***FI 2022 – 0.3***).

9. M.L. Angelescu, V.D. Cojocaru, N. Serban, ***Elisabeta Mirela Cojocaru***. *Evaluation of optimal forging temperature range for an industrial UNS S32750 SDSS alloy using SEM-EBSD analysis*; METALS, 2018, 8, 496; DOI:10.3390/met8070496; WOS:000445096800026 (***FI 2022 – 2.9***).

10. V.D. Cojocaru, N. Serban, M.L. Angelescu, ***Elisabeta Mirela Cojocaru***, I. Cinca, D. Raducanu, A.N. Vintila. *Effect of short duration solution treatment at temperatures below 1000 degrees C on sigma-phase precipitation in a super duplex stainless steel alloy*; MATERIALWISSENSCHAFT UND WERKSTOFFTECHNIK, 2018, 49, 530-537; DOI:10.1002/mawe.201700280; WOS:000433499500004 (***FI 2022 – 1.1***).

11. V.D. Cojocaru, N. Serban, M.L. Angelescu, M.C. Cotrut, ***Elisabeta Mirela Cojocaru***, A.N. Vintila. *Influence of solution treatment temperature on microstructural properties of an industrially forged UNS S32750/1.4410/F53 Super Duplex Stainless Steel (SDSS) alloy*; METALS, 2017, 7, 210; DOI:10.3390/met7060210; WOS:000404056600027 (***FI 2022 – 2.9***).

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