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Trabajo Final de Grado

State-of-the-art of the new alloys in the duplex stainless steel family. Alloy design, manufacturing, post treatments and applications.

Estado actual de las nuevas aleaciones en los aceros inoxidables dúplex. Diseño de la aleación, fabricación, tratamientos posteriores y aplicaciones.

Iván Ferré Adán

Junio de 2021

"Pienso, luego existo".

René Descartes

Este trabajo va dedicado a todas las personas que me han estado apoyando durante toda mi trayectoria académica:

A mis padres, por haberme apoyado siempre y por haberme permitido labrarme un futuro mejor. Gracias por confiar siempre en mí, vuestro orgullo es mi mayor recompensa.

A todos los profesores que he tenido durante el transcurso del grado, con especial mención al Dr. Josep María Chimenos y a la Dra. Núria Llorca-Isern. Gracias por haberme acompañado durante toda mi trayectoria académica y por haberme ayudado a potenciar todas mis capacidades.

A mis amigos, por haber estado siempre ahí y por entender todas esas veces que no he podido hacer planes con ellos por tener que estudiar.

REPORT

CONTENTS

1. GLOSSARI

Argon Oxygen Decarburization (AOD): Highly alloyed steel refining process that allows selective desulfurization and oxidation of carbon by injecting argon, nitrogen and oxygen into the liquid metal.

Alphagen: Alloying element of steel that stabilizes the ferritic phase.

Basic Oxygen Furnace (BOF): Pig iron refining process by injecting oxygen and adding magnesium to reduce the carbon, sulfur, phosphorus and silicon content, resulting in low-carbon steel.

Native copper: Ore with high copper content discovered in prehistoric times.

Critical pitting temperatura (CPT): Temperature above which pitting corrosion begins.

Chromium equivalent (Cr_{eq}): Parameter which considers the stabilizing elements of the ferritic phase in steels, allowing interpretation of the X axis of the WRC diagram. These elements are chromium, molybdenum and niobium.

DSS: Abbreviation for Duplex Stainless Steel.

Gammagen: Alloying element of steel that stabilizes the austenitic phase.

Heat Affected Zone (HAZ): Zone around the molten pool generated during welding processes which is thermally affected due to heat diffusion from the pool to the base metal.

Sponge iron: A metallic product of porous character due to the direct reduction of oxidized iron ore.

Wrought iron: Iron with a surface carburization process that allows steel to be obtained on surfaces exposed to CO/CO2 flow. These irons could contain more layers of steel inside by repeating the operations of surface carburizing, bending and drawing by forging.

Nickel equivalent (Ni_{eq}): Parameter which considers the stabilizing elements of the austenitic phase in steels, allowing interpretation of the Y-axis of the WRC diagram. These elements are nickel, carbon, nitrogen and copper.

Pitting Resistance Equivalent Number (PREN): Empirical expression that allows quantifying the resistance to pitting corrosion from the chromium, molybdenum, tungsten and nitrogen composition of stainless steels.

Stress Corrosion Cracking (SCC): Corrosion phenomenon induced by the combined action of stresses and an aggressive environment. Materials affected by SCC eventually fail by brittle fracture due to the growth without plastic deformation of the cracks generated in this corrosive process.

Vacuum Oxygen Decarburization (VOD): Highly alloyed steel refining process that allows selective desulfurization and oxidation of carbon by injecting argon, nitrogen and oxygen into the liquid metal under a vacuum atmosphere.

2. SUMMARY

Duplex stainless steels have been a big revolution mainly in the offshore oil industries. These alloys have become a very good alternative for dealing very efficiently with stress corrosion cracking (SCC) with a much lower associated cost than nickel base alloys. From their discovery in the late 1920's to the present day, these alloys have been evolving in the form of new duplex alloys which have offered increasingly better corrosion resistance and improved mechanical properties.

This paper offers a brief journey through time from the beginning of the Iron Age to the present day, narrating the evolution of the use of iron in the different stages of humanity. Subsequently, all the theoretical principles associated with duplex stainless steels are described, as well as the associated technologies for obtaining and processing them. Finally, the state-of-the-art of the most recent duplex alloys, the super duplex and hyper duplex stainless steels, has been elaborated.

3. RESUMEN

Los aceros inoxidables dúplex han supuesto una gran revolución principalmente en las industrias petroleras de alta mar. Estas aleaciones se han convertido en una muy buena alternativa que permite hacer frente de manera muy eficiente a la corrosión bajo tensión (SCC) con un coste asociado mucho menor que las aleaciones base níquel. Desde su descubrimiento a finales de los años 20 hasta la actualidad, estas aleaciones han ido evolucionando en forma de nuevas aleaciones dúplex las cuales han ofrecido cada vez más resistencia a la corrosión y mejores propiedades mecánicas.

En el presente trabajo se ofrece al lector un breve viaje en el tiempo desde el inicio de la edad de Hierro hasta nuestra época actual, narrando la evolución del uso del hierro en las distintas etapas de la humanidad. Posteriormente, se describen todos los fundamentos teóricos asociados a los aceros inoxidables dúplex, así como las tecnologías asociadas para su obtención y procesado. Por último, se ha elaborado el estado del arte de las más recientes aleaciones dúplex, los aceros inoxidables super dúplex e hiper dúplex.

4. INTRODUCTION

When we talk about metallic materials, it is likely that one of the first materials that comes to mind is steel. This alloy had a worldwide production of 1,869.9 million tons (Mt) in 2019, with an annual growth of 3.4% compared to 2018[1]. It was the third material with the highest production worldwide[2], as shown in Figure 1.

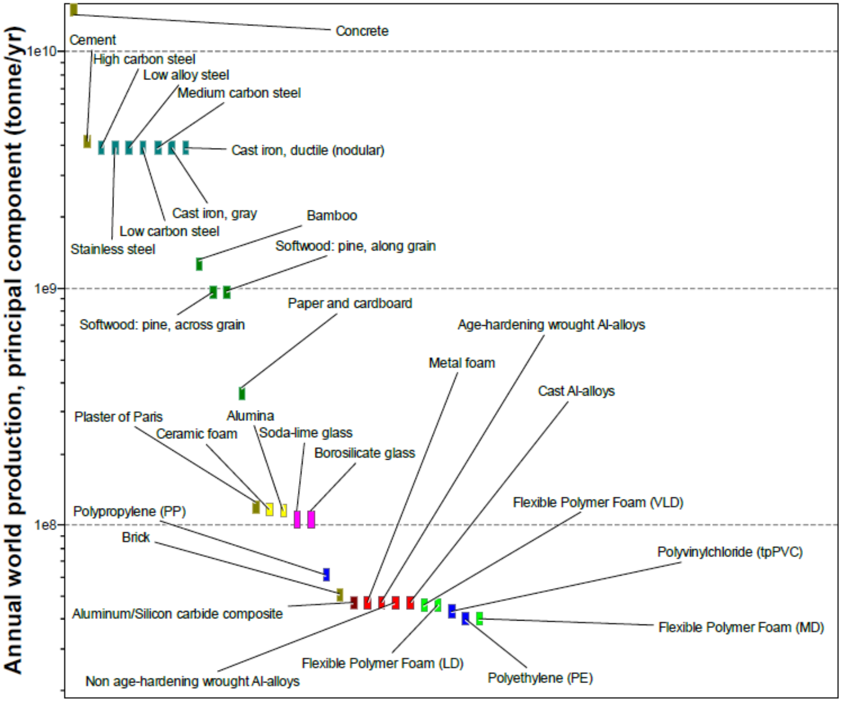

Figure 1: Top 30 annual world production (tonnes/year) of materials[2].

This alloy has been extensively studied over the last centuries, allowing for great versatility in terms of applications, chemical compositions, manufacturing methods, geometries, properties, etc.

Despite all this knowledge acquired by mankind, it would be ignorant to think that little remains to be discovered. One of the most recent lines of research on this alloy is that of duplex stainless steels. This is the reason why the present work will focus on the analysis of these new alloys, offering a new vision of the state of these alloys and the new horizons present today.

In order to follow a solid argumentative thread, this chapter will briefly describe the evolution of iron up to the steels of today. The chronology associated with the different stages of history may be different depending on the criterion of each author. That is why in the following points a chronology will be constructed based on books and articles of different authors collected on page 49, being able to differ this chronology with any other provided by different sources. Another point to mention is the possibility that several eras have a chronological overlap. Again, this is due to the difficulty of obtaining an exact chronology describing the different stages of history.

It is necessary to add that the different populations of mankind have progressed at different rates in the various stages of history depending on their geographical location. It is for this reason that the most premature findings of each stage will be mentioned without assuming that these findings can be generalized to all populations.

4.1 TIMELINE OF THE STEEL

4.1.1. Prehistory: The road to the Iron Age

Before the beginning of the Iron Age, mankind used naturally occurring materials such as wood, bones, stones, gold, meteoric iron, and copper. These materials were processed by rudimentary carving techniques, except for metals. The latter group was shaped by cold plastic deformation by beating, due to the certain degree of purity with which they were found in nature. Metallurgy was born out of the need to obtain pure metals, this being one of the most important moments in the history of humanity[3].

The first metal to be treated with metallurgical technology was copper due to its known malleability, as well as the fact that it was easier to melt than iron. Therefore, this period is known as the Copper Age or Chalcolithic. The beginning of the use of copper obtained by metallurgical means was not homogeneous around the world. The first indications of a chronological beginning of the Copper Age have been found in what is nowadays Anatolia and Iran in the form of clearly documented evidence and archaeological findings such as copper tools and mines, metallurgical furnaces and slag remains. These findings are estimated to date back to the beginning of the 5th millennium B.C. and can thus be considered the beginning of the Copper Age[4].

The successor to the Copper Age is the Bronze Age. Archaeological findings show that in Egypt at the end of the 4th millennium B.C. objects were already being produced with this alloy for decorative purposes. It was not until the middle of the 3rd millennium BC when the use of this alloy began to spread due to its superior hardness compared to copper, significantly improving the performance of weapons and tools of the societies of the time. Bronze definitively replaced copper on the coasts of the Aegean Sea during the 2nd millennium B.C., and this date can be defined as the beginning of the Bronze Age. This practice had a later heterogeneous extension, mainly in Europe and Asia[5].

Again, to establish a transition from the Bronze Age to the Iron Age, historians rely on archaeological findings in different regions of the world. Some of these findings show how in eastern Anatolia at the end of the 3rd millennium BC, isolated iron objects were made from meteoric iron[6].

4.1.2. Ancient history: Discovery and consolidation of wrought iron

The Ancient history is understood generically as the historical period from the beginning of writing (approximately 4,000 B.C.) to the fall of the Roman Empire (476 A.D.)[7].

It can be seen how, based on the above chronology, there is an overlap between the Iron Age and the Ancient history, with the Iron Age being contained within the Ancient history. To date, the various historians who are experts on the subject are unable to agree on the chronology of each historical stage, as indicated on page 9. Consequently, this chronological development will validate the historical overlap that has occurred based on the archaeological findings according to the sources consulted.

Initially, the iron obtained by metallurgical way was of considerable purity. This iron is currently called sponge iron due to the porosity generated during the obtaining process of the time. This process involved a softening of the iron ore by direct contact with the embers generated from firewood. These embers provided the ore with carbon monoxide, thus allowing a partial reduction of the iron, in addition to generating a porosity in the metal that implied the accumulation of slag in the porous areas. The deposits of the time indicate that the sponge iron had contents of less than 0.1wt% in alloying elements and slag trapped in the pores of less than 3wt%. It was not until 1,200 B.C. that carburizing techniques began to be used, which consisted of burying wrought iron objects in ground charcoal obtained from firewood. The metal workers observed how, after this process, the hardness of the iron increased notably. These workers were completely unaware that they were applying a process known today as surface carburizing. Due to this discovery, mankind began to produce the predecessor of steel, wrought iron. It is necessary to point out that these objects were not made entirely of steel, they were objects of high purity iron with an outer layer of steel due to the carburization process[8].

The first wrought iron productions with certain regularity did not occur until approximately 900 B.C. in the eastern Mediterranean, coinciding with the Greek geometric period, thus defining this date as the beginning of the Iron Age. The transition from the Bronze Age is the most difficult to define due to the state of oxidation and deterioration in which objects of the period are found, making it very difficult to date them. The production of this new metal was not so simple for the bronze smiths converted into blacksmiths of the time. Wrought iron required processes for which the metal workers had no experience: carburization of the iron, tempering, forging and elimination of impurities. Some archaeological finds show how these techniques were not yet properly mastered in the second Iron Age (400 BC). Despite its production for more than half a millennium, there were still difficulties in obtaining and processing it, giving us to understand that mankind required a long process of adaptation to achieve a certain mastery of this metal. The main reason for this slow technological progress was the lack of knowledge of the science behind the processes of obtaining and shaping iron. The advances that were made over the centuries were the result of trial and error by the blacksmiths[9].

4.1.3. Middle Ages: Development of forging techniques and first blast furnaces

The Middle Ages lasted from the fall of the Roman Empire in 476 to the fall of the Byzantine Empire in 1453 or to the discovery of America in 1492, depending on the historian's point of view[7].

From the beginning of this era, iron was still obtained in the form of sponge iron. Forging and surface carburizing continued to be used as a process for shaping the material. As the centuries progressed, the blacksmiths of the time developed different forging techniques, mainly for the manufacture of sword blades and tools. These techniques consisted mainly of carburizing the surface of the blades and then, by means of plastic deformations, increasing the length and folding the blade over itself. This process was repeated often depending on the blacksmith's technique. With this it was possible to introduce steel inside the iron blades, increasing the performance much more than blades with a single external carburization[8].

These techniques could be very different from each other depending on the society that manufactured the wrought iron. Some examples to highlight that allowed a greater geographical expansion of the societies that used them are the ill-named Damascus steel and the Japanese sabers[10].

It was not until the 14th century that the first blast furnaces appeared in Central Europe. These furnaces allowed the introduction, by means of bellows, of humid air which greatly improved the combustion kinetics of the coal. As a result of these improvements, if sufficient coal were used during combustion, a cast iron with a carbon concentration of around 4wt% could be obtained. This molten alloy is what we call pig iron today, melting at around 1,154 ºC. Thanks to the liquid state of the alloy, it could be cast in ingot molds with geometries close to that of the final product. This technological implementation was the forerunner of today's large-scale foundries[11].

Solidified pig iron is a brittle alloy due to the high presence of carbon, which forms iron carbides or graphite. Blacksmiths of the time increased the toughness of the cast iron by introducing the objects into horizontal furnaces, heating the metal by means of hot air flows. The contact of the air at high temperatures with the surface of the metal allowed the oxidation of the carbon, thus reducing the concentration of carbon on the surface by the formation of carbon monoxide. This refining process was long and difficult because it required sufficient skill to form steel on the surface of the metal without oxidizing it excessively. This refining process was accompanied by the typical forging processes to introduce layers of steel into the interior of the metal[11].

4.1.4. Modern history: Discovery of Crucible Steel

This stage lasted from the end of the Middle Ages until the independence of the United States of America in 1776 or the beginning of the French Revolution in 1789[7].

This technique consisted of introducing pieces of wrought iron from pig iron, with its characteristic layers of steel, into a crucible to later melt the whole. Although Huntsman was unaware of the phenomena of atomic diffusion, this process made it possible to homogenize the carbon in the steel layers, thus obtaining steel throughout the volume. Although it was not possible to obtain steel in large quantities by this process, this discovery was of great importance since it made it possible for the first time to obtain steel from the liquid state[12].

Some sources suggest that this practice was already known to some blacksmiths around the world, such as, for example, ancient Indian blacksmiths[8]. Nevertheless, Huntsman's rediscovery was a precedent for all the technological improvements that have occurred in the contemporary age.

In addition to the discovery of crucible steel, at this time charcoal was replaced by coke, improving the efficiency of blast furnaces, and consequently increasing pig iron production[11].

4.1.5. Contemporary history: The era of alloy steels

The Contemporary history began at the end of the Modern history and is the historical stage in which we find ourselves today [7].

Initially, steel was expensive to obtain due to the low productivity of Huntsman's method. Therefore, this alloy was mainly used to manufacture weapons, since structural elements were made of wrought iron due to its lower cost, as it was obtained from pig iron[8].

Due to the higher mechanical properties of steel compared to wrought iron, the main objective at the beginning of this era was to find an economical method of production that would allow large-scale production of this alloy

In 1820, Kersten made a first theoretical approach to the effects of carbon on iron. Subsequently, Leibig followed Kersten's theory and developed in 1831 the first accurate carbon measurement method[8,12]. At this point, it was known that pig iron had higher carbon concentrations than steel, thus requiring an efficient refining process to remove the excess carbon from the pig iron.

It was not until 1856 that Henry Bessemer developed a converter system to obtain steel from liquid pig iron. Bessemer's system was able to obtain 30 tons of steel from pig iron in just a few minutes. Initially, this system failed because of the need for basic refractory walls, a technology that did not exist at the time of Bessemer's invention. The solution to this problem came from Thomas and Gilchrist in 1878 when they introduced refractory magnesia walls in the Bessemer converter[11,12].

At the same time, Sir William Siemens developed the open-hearth furnace in 1857. The Frenchman Pierre-Émile Martin used this type of furnace for the first time to obtain steel from pig iron in 1865. Due to both contributions, this furnace became known as the Martin-Siemens furnace[13]. This furnace had a high fuel oil consumption and a low production capacity compared to the Bessemer converter, requiring 8 to 12 hours per casting. The main advantage of this method of production was the high quality of the steel obtained and the ability to precisely control the concentration of carbon in the alloy[11,14].

In 1882, Sir Robert Hadfield observed that by alloying steel with 12wt% manganese, the abrasion resistance of the alloy could be greatly increased. [15]. This discovery gave rise to the subsequent development of alloy steels. Faced with this new need, Paul Héroult designed and built in 1890[12] the first electric arc furnace to produce alloy steels [16].

4.1.6. The emergence of the stainless steels

Due to the corrosion problems presented by steels, metallurgist Harrey Brearley began a series of investigations to find a solution to the oxidation problems presented by the steels of that time. Brearley studied the effects of different carbon and chromium compositions on steel by metallographic analysis. On August 20, 1913, he observed the difficulties in revealing the microstructure with nitric acid (a common reagent for steels) of a martensitic steel with a composition of 0.24wt% carbon and 12.8wt% chromium. Brearley realized that this composition gave the steel a corrosion resistance that had never been seen before. Thus, the first stainless steel was born, which was characterized by a martensitic microstructure[17].

Although the first development of stainless steels is generally attributed to Brearley by most of the sources consulted, there are a few other personalities who also developed the first stainless steels independently and in parallel:

- Elwood Haynes (1912): Martensitic stainless steel[18].
- Benno Strauss and Eduard Maurer (1912): Austenitic stainless steel[19].
- Christian Dantsizen and Frederick Becket (1912): Ferritic stainless steel[17].

Later, in 1930, the British chemist Ulick Richardson Evans was able to provide the first description. Richardson proposed that the chromium of the steel surface, when in contact with the atmosphere, forms a passive layer of chromium (III) oxide which protects the steel and makes corrosion phenomena significantly more difficult[21].

After the discovery of the first stainless steels, this type of alloys continued to be studied until reaching the point of interest of the present work, the duplex stainless steels (DSS). The first reference to these alloys dates back to 1927 by Griffith and Bain. The authors explained how in some steels of the Fe-Cr-Ni system the coexistence of ferritic and austenitic phases in the microstructure can be observed[22]. In 1929, the foundry Avesta Jernverks AB produced one of the first commercial DSS castings under the name of 453E steel with a composition of Fe-25%wt Cr - 5%wt Ni[23].

Due to the Korean War conflict in the 1950s, the price of nickel rose. It was common to use nickel-based superalloys for environments in which stress corrosion cracking (SCC) occurs. As nickel became more expensive, the number of investigations related to

DSS increased. The duplex family exhibited some degree of SCC resistance with lower nickel content, thus making this alloy in need of further development to replace nickel-based superalloys[24,25].

At the end of the 1960s and the beginning of the 1970s, another increase in the price of nickel took place[26]. In addition, this increase in prices coincided with the 1973 oil crisis[27]. The high demand for SCC-resistant metal alloys for the construction of offshore oil platforms and the high price of nickel gave the final impetus to the ongoing research in which DSS alloys are currently immersed[23].

Thanks to this research, one of the major breakthroughs in the 1970s was the possibility of decarburizing steel under vacuum using oxygen and argon. These processes are known as Vacuum Oxygen Decarburizing (VOD) and Argon Oxygen Decarburization (AOD). The use of these techniques made it possible to obtain DSS by continuous casting, thus significantly reducing production costs. In addition, the compositional quality was improved by having a low carbon content and good nitrogen control. A low carbon content provides better corrosion resistance because this element forms carbides with chromium, molybdenum and tungsten, elements that protect the steel from corrosion. On the other hand, nitrogen is a stabilizing element of the austenitic phase. A correct proportion of this element makes it possible to stabilize this phase at higher temperatures without the need for slow cooling, which is favorable during the welding process since the heat-affected zone (HAZ) has faster cooling that favors greater ferrite formation[28].

In view of these improvements, the so-called second generation DSS began to be manufactured in the 1980s. These alloys had improved weldability (thanks to nitrogen additions) and corrosion resistance compared to the first generation. This improvement in properties made it possible to reduce costs by reducing the thickness of tubes, sections and plates (among other geometries) while maintaining the resistance to SCC[29].

An example of a conventional second generation DSS is the ASTM 2205 alloy. This alloy is formed by rolling and consists of 21 - 23%wt Cr, 4.5 - 6.5%wt Ni, 2.5 - 3.5wt% Mo and 0.08 - 0.20%wt N (Fe balance). Later developments brought to the market superduplex and hyperduplex stainless steels, based on higher additions of Cr, Ni, Mo and N which further improve of corrosion resistance. As a novelty to the conventional DSS, the superduplex alloys have small additions of W which also enhance the corrosion resistance of the material[30].

One of the great dilemmas in the world of DSS was how to quantify the corrosion resistance of each alloy. For this reason, an empirical expression called pitting resistance equivalent number (PREN) was devised. The PREN grade is obtained from the elements involved in the corrosion resistance by the following equation[31]:

$$PREN = \%wt\ Cr + 3{,}3 \cdot (\%wt\ Mo + 0{,}5 \cdot \%wt\ W) + 16 \cdot \%wtN$$

This expression is currently used today to evaluate the level of corrosion resistance of an alloy as a function of its composition.

4.2 MICROSTRUCTURE AND PROPERTIES

4.2.1. Solidification

The microstructure of duplex stainless steels is composed of two phases, a ferritic (δ) and an austenitic (γ) phase. As we can see in Figure 2 (in this image the ferritic phase has been represented as ferrite-α but in fact the ferritic phase is of the δ type), the percentage of chromium and nickel (fixing the composition of the rest of the stabilizing elements of the austenitic and ferritic phases) will influence the type of microstructure of the alloy. We can observe that it is possible to obtain a totally ferritic microstructure, totally austenitic or with a coexistence of both phases as it happens in the duplex stainless steels.

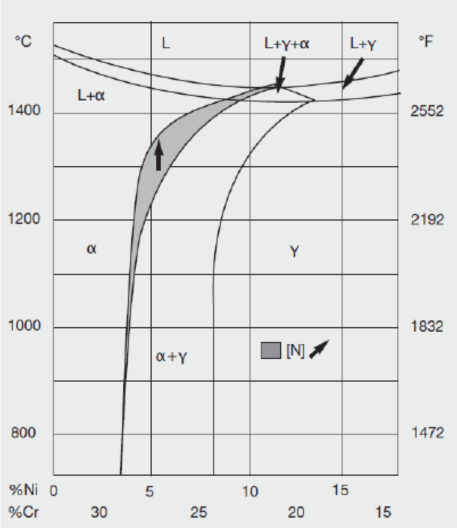

Figure 2:Ternary Fe-Cr-Ni constitution diagram at 70% Fe [86].

For an alloy with a chemical composition that allows to obtain a ferritic-austenitic microstructure at room temperature, the first nuclei generated in the solidification process correspond to the ferritic phase with a crystallographic structure type BCC. These nuclei grow until they reach total solidification, thus obtaining a fully ferritic polycrystalline microstructure.

4.2.2. Solid-state reactions

During the cooling of the solid, in the range of approximately 1200 and 1420 ºC (depending on the composition), the austenite begins to nucleate, which has a crystallographic structure of FCC type, at the ferritic grain boundaries. After this nucleation, a Widmanstätten-type growth of the austenitic phase takes place until the equilibrium state is reached, which corresponds to an austenitic phase enveloped by a ferritic phase matrix[32].

As the metal cools further, other reactions occur in the solid state between 970 and 500 °C involving the precipitation of intermetallic phases, carbides and nitrides. These reactions can take place as long as states close to thermodynamic equilibrium (slow cooling) are allowed or during processes involving working temperatures in the above-mentioned range[33]. These transformations are not of interest because they may embrittle and reduce the corrosion resistance of the alloy[34].

In the following, the range of precipitates that can be formed will be briefly described:

- **Sigma phase (σ):** This intermetallic phase has a BCT-type structure and is composed of Fe, Ni, Cr and Mo [$(Fe,Ni)_x(Cr,Mo)_y$]. It is formed from a divorced eutectoid-type reaction in which the grain boundaries of the ferritic phase decompose to form sigma phase and austenitic prime phase ($\delta \rightarrow \sigma + \gamma'$). This reaction occurs at the ferritic grain boundaries because of their higher Cr and Mo content. The transformation proceeds towards the interior of the ferritic grains until their complete decomposition.
  The reaction mechanism consists in a diffusion of the alphagene elements from the ferritic phase towards the grain boundaries for the formation of the sigma phase. The ferrite with a defect of alphagene elements loses its stability and is forced to transform into the austenitic raw phase, which differs from the austenite prior to this transformation due to the lack of elements favouring corrosion resistance.

Consequently, the resulting microstructure ($\sigma+\gamma+\gamma'$) is of lamellar type and will present corrosion-friendly zones at the boundary between the sigma phase and the austenite-prime phase. In addition, there is also a reduction in toughness due to the brittleness of the sigma phase[35].

- **Chi phase (χ):** The chi phase is another intermetallic compound which has a BCC-type structure and is composed of the same elements as the sigma phase [$Fe_{36}Cr_{12}Mo_{10}$, $(Fe,Ni)_{36}Cr_{18}Mo_4$]. The reaction mechanism for its formation is the same as that of the sigma phase, with the particularity that for its formation it is necessary for the molybdenum content present in the alloy to be higher than 2%wt. Its presence in the microstructure of the alloy also involves a loss of toughness and corrosion resistance. This phase can eventually transform into a sigma phase if the kinetic conditions allow it[36,37].

  Figure 3 shows the morphology associated to the presence of chi and sigma phase in an austenoferritic matrix. The image shown has been obtained by field emission scanning electron microscopy with a backscattered electron detector (FESEM-BSE).

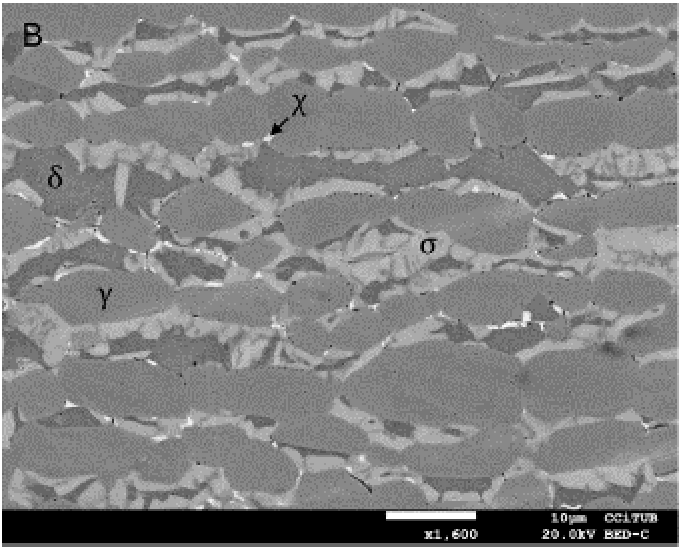

Figure 3: Image obtained by FESEM-BSE of a super duplex stainless steel 2507 heat treated for 10 minutes at 830 ºC[33].

- **Chromium carbides:** These carbides can appear in as little as half an hour at temperatures between 900 and 700°C and have an FCC-type crystallographic structure. They are formed by an eutectoid reaction in which the ferritic phase decomposes into chromium carbides and secondary austenite ($\delta \rightarrow Cr_{23}C_6+\gamma_2$). The austenitic phases have a higher carbon content, while the ferritic phases have a higher chromium content because chromium is an alphagenic element. It is for this reason that the nucleation of these carbides occurs at the boundaries between the ferritic and austenitic phases, since the diffusion of the elements involved in their formation is favoured in these areas. The secondary austenitic phase formed in this reaction is a phase with a lower chromium content than the austenitic phases prior to the reaction. For this reason, the presence of chromium carbides reduces the resistance to sensitization as the resulting microstructure contains phases with a tighter chromium content and therefore more susceptible to sensitization in shorter time ranges.[38].

- **Chromium nitrides:** Nitrogen is an element that is added to the duplex stainless steels to stabilize the austenitic phase, being able to generate in this phase the presence of chromium nitrides (Cr_2N) which have a hexagonal crystallographic structure. The appearance of chromium nitrides occurs simultaneously with the generation of chromium carbides during the cooling of the alloy after solidification. In addition, these nitrides can also occur during welding processes. The ferritic phases of HAZ are supersaturated with nitrogen, allowing for a higher solubility of nitrogen at the welding temperatures. In this situation, nitrogen can diffuse into the austenitic phases or can precipitate in the form of chromium nitrides if the HAZ is cooled rapidly. The presence of these nitrides leads to a loss of mechanical properties and corrosion resistance[39,40].

  Figure 4 shows the accumulation of chromium and nitrogen in localized zones of an austenoferritic matrix. These accumulations are associated with the presence of chromium nitrides. The images were obtained by scanning electron microscopy with a backscattered secondary electron detector (SEM-BSE) and wavelength dispersive spectroscopy (WDS).

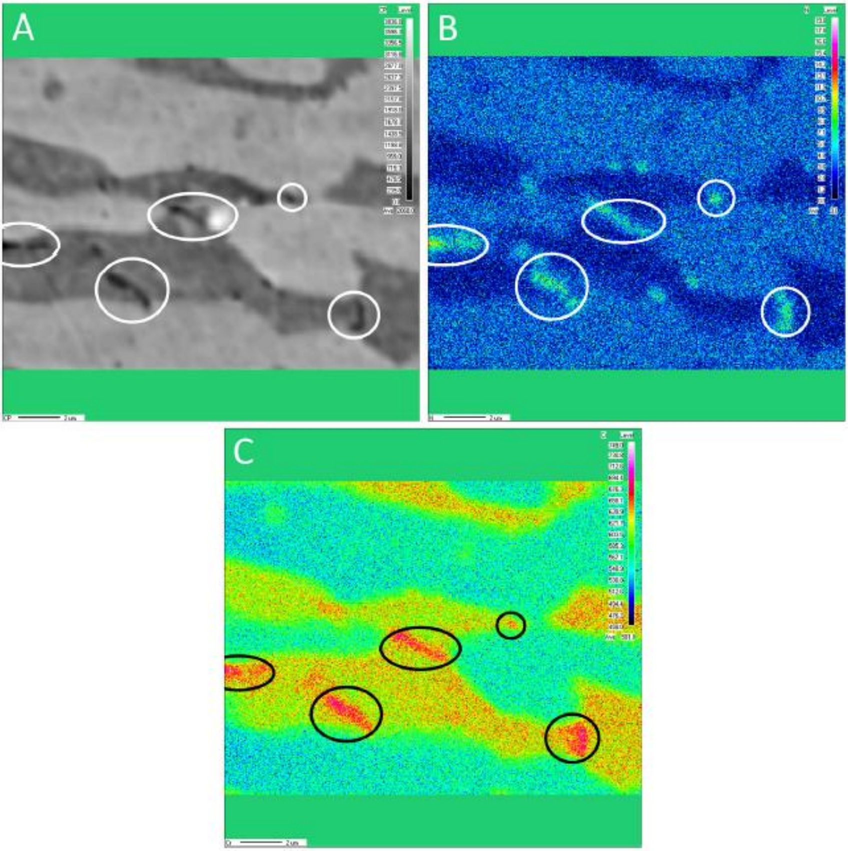

Figure 4: WDS of a super duplex stainless steel 2507 heat-treated 3 minutes at 830 ºC. A) SEM-BSE image showing chromium nitrides encircled. B) Chromium accumulations. C) Nitrogen accumulations[33].

Finally, the last solid state reaction that occurs under the same thermodynamic conditions as in the previous cases is the formation of the alpha-prime phase (α'). This phase occurs in the temperature range between 300 and 550°C and is generated from the spinodal decomposition of the ferritic phase[41]. The new phase generated also has a crystallographic structure of the BCC-type and its morphology is that of small precipitates coherent with the ferritic phase. The main consequences of this transformation are an increase in hardness, yield strength and tensile strength and a loss of elongation capacity and ductility. The reason for this change in properties is none other than the difficulty that the alpha-precipitates provide for the movement of dislocations of the ferritic phase[42,43]. The loss of toughness appears much earlier than the hardening, therefore, the presence of this phase induces an embrittlement of the alloy without any other benefit[44].

4.2.3. Ratio of ferritic and austenitic phases

To predict the percentage of each phase present in the equilibrium state, Kotecki and Siewert[45] made a modification of the Schaeffler diagram[46], empirically creating the WRC-1992 diagram (Figure 5).

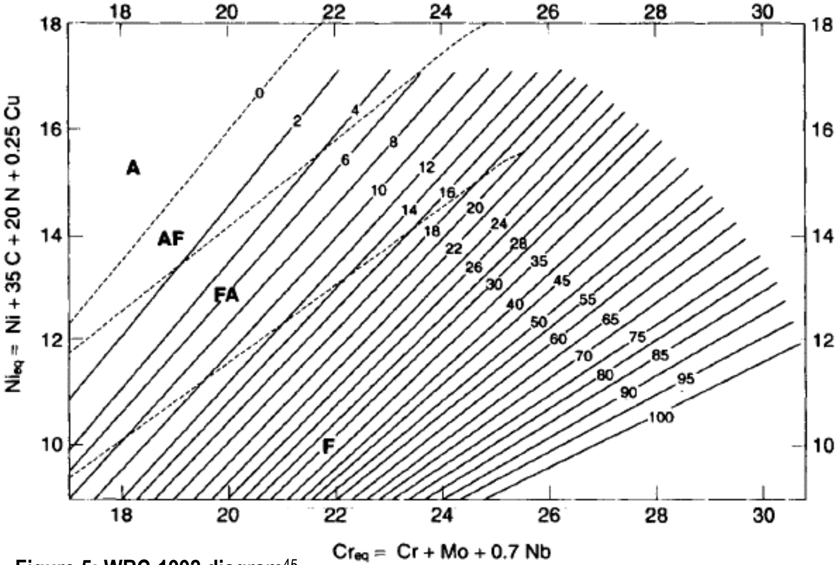

Figure 5: WRC-1992 diagram[45].

With this diagram, the percentage of ferrite present in the microstructure can be obtained from the equivalent chromium (Cr_{eq}) and equivalent nickel (Ni_{eq}) values. The equivalent chromium considers in its expression all the stabilizing elements of the ferritic phase. Similarly, the expression for nickel equivalent considers all stabilizing elements of the austenitic phase. Both expressions can be seen in the WRC-1992 diagram. It should be added that this diagram was created to predict the microstructure obtained in welds as a function of the composition of the filler metal. Nevertheless, the diagram gives a good prediction of the resulting microstructure during solidification and cooling of duplex alloys.[45].

A stainless steel can be considered duplex when its ferritic phase content is in the range of 30-70%[47,48]. Ideally, the presence of each phase should be 50% as this maximizes the effect of the binding properties provided by each phase[49].

4.2.4. Properties of DSS

The mechanical properties of the duplex stainless steels are an average of the mechanical properties of the austenitic stainless steels and the ferritic stainless steels. This is logical since the microstructure of the duplex stainless steels is composed of ferritic and austenitic phases, each providing its own properties. The austenitic stainless steels are generally harder due to their higher carbon content, tougher, with higher mechanical strength, and with a higher yield strength and elongation. On the other hand, ferritic stainless steels are much cheaper due to the absence of nickel in their composition, they have good weldability and can have a higher corrosion resistance in some of their alloys.

If we analyse the corrosion resistance of the duplex stainless steels, they have a higher resistance than most of the austenitic and ferritic stainless steels. This is the main advantage of this alloy that makes it interesting for its use as they offer a higher PREN grade. As these steels can be alloyed with higher contents of alphagens (Cr, Mo and W) and gammagens (N) elements at the same time, the corrosion resistance is more favourable compared to the other families of stainless steels without an excessive increase of their cost per unit mass (except in some alloys with a much higher PREN grade which have a much higher cost). Annex 1 shows a set of graphs allowing a comparison of all the above mentioned properties of duplex, ferritic and austenitic stainless steels[2].

4.3 PRODUCING DSS

The production of steel from primary sources involves the processes of blast furnaces and subsequent refining of the pig iron using Basic Oxygen Furnace (BOF) converters. The injection of oxygen into the pig iron by means of a torch promotes the refining by oxidation and slagging of the typical elements of the pig iron such as C, P, S, Si and Mn. If the liquid contained other alloying elements typical of duplex stainless steels, these would also oxidize and be lost as they would be retained in the slag. This is why BOF converters, although highly efficient for carbon steels, show low productivity for high alloy steels[50].

For this reason, DSS are obtained, with few exceptions, by electric arc furnaces or induction furnaces, since they are more efficient when working with alloyed steels. The charge used in these furnaces can be material with high purity in the elements of interest or highly alloyed steel scrap with a chemical composition close to the alloy to be obtained. In the case of needing to increase the composition of some alloying element, the addition of ferroalloys is used, since this type of alloys present a great variety of commercial compositions, being able to select the most suitable one according to the compositional situation of the liquid. Subsequently, refining is carried out using AOD and VOD converters. These refining methods make it possible to obtain high quality alloys. On the one hand, the carbon composition can be adjusted by injecting oxygen with a torch, as in the BOF converter. The main difference of this refining process is the preferential oxidation of the carbon to the other elements thanks to the vacuum atmosphere generated in the process. On the other hand, the concentration of nitrogen is increased thanks to the injection of this element together with argon from the lower part of the furnace, also favoring in this process the degassing of the molten metal due to the drag-out effect of the argon and the nitrogen that does not solubilize in the liquid metal. However, the previous stage of selection of the materials to be melted contributes significantly to the final compositional quality, especially in the sulfur and phosphorus contents, which have an impact on the mechanical and corrosion properties of the material. [51,52].

The next stage in the process of obtaining DSS consists of further refining by adding deoxidizing agents and inoculants. These compounds consist mainly of SiCaMn, SiCaCe, Al, Ti, Mg, Nb, Zr and rare earth metals (REM). The higher thermodynamic tendency of these compounds to oxidize facilitates the deoxidation of other elements in the liquid such as Fe, Cr, Mo, W, V and C. These additions allow the precipitation in the liquid of microscopic particles of oxides which favor the nucleation of ferrite during solidification. To eliminate the excess oxides generated, slagging compounds such as CaO are added.

Slagging agents, as their name suggests, allow a slag layer to form on top of the liquid and are easily extractable due to their higher viscosity[53,54].

4.4 FORMING PROCESSES

Once all the refining operations described above are completed, the liquid metal is suitable for the forming processes. Depending on the forming process, DSS stainless steels are called cast or wrought[47,48]. The main wrought and cast alloys can be found in Annex 2.

4.4.1. Cast DSS

In these forming methods, the liquid metal is cast directly into a mold which has a cavity with the final shape of the desired part. These processes are mainly used when the geometry of the parts makes it impossible or expensive to obtain them by plastic deformation processes[11]. Most of the parts obtained by casting are pumps and valves intended for corrosive environments and may or may not be under pressure[55.]

The main molding methods are as follows [2,56]:

- **Sand-casting processes:** This type of molding has a very limited productivity due to the need to manufacture a mold for each part. It allows obtaining very complex geometries with a great variety of dimensions. The sand used can be recycled to make another mold. A large grain microstructure is obtained due to the low thermal conductivity of the sand.
- **Permanent mold processes:** In general terms, these processes have a higher cost associated with the manufacture of the mould. The main advantage is the possibility of reusing these moulds many times, allowing the higher cost to be amortised in the long run compared to sand moulds. These processes allow to obtain a better surface finish and less porosity retained in the metal. The microstructure obtained is finer due to the high thermal conductivity of the metal mould. Permanent mould processes can be classified into the following techniques:
    - *Gravity die casting*: A moulding process in which liquid metal fills the mould by the action of gravity.

- *Die casting*: A permanent mold process which employs a permanent mold and injects the liquid metal under pressure (low or high pressure). This technique produces isotropic and superior mechanical properties compared to traditional molding. The main disadvantage of this process is the high cost associated with machinery and molds.
- *Centrifugal casting*: This moulding process consists of solidifying a layer of metal on the walls of the mould by means of the centrifugal action of the mould. Centrifugal casting can be horizontal or vertical depending on the direction of the axis of rotation with respect to the ground. This technique is used to obtain highly symmetrical products such as pipes and tubes.
- *Hybrid process*: These processes are characterised by a combination of casting and other processing techniques. The main hybrid processes to highlight are squeeze casting, semi-solid metal casting and osprey process. Squeeze casting consists in solidifying the liquid metal in the die of a forging while simultaneously exerting pressure. This method minimises casting defects such as shrinkage. On the other hand, semi-solid metal casting (also known as rheocasting) allows casting under pressure from a metal in a semi-solid state (approximately 60% solidity), obtaining a metal with very low porosity, good surface finish and good dimensional accuracy. Finally, the osprey process allows the liquid metal to be sprayed, using nitrogen and argon, and then deposited as a spray on the surface of the mould. This process makes it possible to obtain densities close to theoretical densities, fine-grained microstructures, isotropic mechanical properties and the absence of macro-segregations.
- *Vacuum casting*: This technique involves bringing the inlet channel at the bottom of the mould into contact with the surface of the liquid metal. Subsequently, a vacuum is generated from an orifice at the top of the mould allowing the liquid metal to penetrate into the mould against gravity.

Among these techniques, the sand-casting technique is the most used because of its low cost. Another advantage of this method over the others is that it allows slow cooling rates. As already mentioned, the DSS stainless steels can embrittled during cooling due to the formation of intermetallic or secondary phases, such as the sigma phase. This embrittlement reduces the thermal shock resistance of the alloy, resulting in cracks if cooling occurs too rapidly.

4.4.2. Wrought DSS

Plastic deformation forming operations start with a continuous casting process in which the liquid metal is introduced into a bottomless mold. The geometric shape of the cross section of this mold corresponds to the cross section of the semi-product to be obtained. From this semi-product, the various forming operations are carried out in the solid state[56].

The DSS steels are more complex to form in the solid state than other alloy steels. This is mainly due, as already mentioned, to the presence of embrittling intermetallic phases in some temperature ranges. The most used forming operation is rolling, since the main applications of these alloys are tanks and pipes in contact with corrosive media and under pressure. However, operations such as forging can be carried out on a very occasional basis.

Very generically, DSS stainless steels require temperatures between 1230 and 900 ºC to be hot formed without risk of embrittlement cracking. It is important to maintain the working temperature throughout the part because embrittlement can occur at local points where the temperature is below the working range. In the case that the forming process is carried out as a warm process, it is necessary to consider that working temperatures above 315 ºC and for a prolonged period of time, can lead to a loss of toughness and corrosion resistance. Cold forming gives good results since these alloys have minimum elongations of between 15 and 30%. In addition, the risk of embrittlement is avoided due to working at room temperature and a high degree of strain hardening is obtained[44].

4.4.3. Joining techniques for DSS

In the industrial environment, the need to join the parts obtained after forming with other elements or sections is common. It is also very common to carry out repairs on pieces obtained from casting techniques due to the presence of casting defects or aesthetic defects. To carry out these tasks, different welding techniques are used. Each technique is adapted to the needs of the joint or repair to be carried out, thus allowing this process to be as efficient as possible while trying to minimize all the effects associated with the heat input into the HAZ[57].

The main welding techniques used in DSS are as follows[2]:

- **GTAW (Gas Tungsten Arc Welding):** The electrode used is tungsten and the filler material is added manually. The pool and electric arc are enveloped by argon, helium or carbon dioxide. These gases protect the pool from corrosion by preventing contact with the atmosphere.
- **GMAW (Gas Metal Arc Welding):** This technique follows the same principles as the GTAW technique with the main difference that the electrode acts as a carrier material, which is consumed during the welding process.
- **SMAW (Shielded Metal Arc Welding):** As in the GMAW technique, the electrode used in this technique acts as a filler material. In this case, the pool is protected by a flux coating which generates a slag layer on the surface of the pool, protecting it from the atmosphere. No protective gases are used as the slag satisfies this need to protect the pool.
- **FCW (Flux-Cored Arc Welding):** This technique uses a consumable tubular rod as an electrode. A flux is introduced inside the rod which, during its consumption, provides protective gases. In addition, these fluxes also generate protective slag from the liquid pool.
- **PAW (Plasma Arc Welding):** Plasma arc welding is considered an evolution of the GTAW technique. The electrode used in this technique is made of tungsten and is non-consumable. The gases used to protect the pool from corrosion are in the plasma state, thus allowing a greater penetration capacity of the weld.
- **SAW (Submerged Arc Welding):** This welding technique uses unshielded consumable electrodes. Once the electric arc (and consequently the pool) is generated, a layer of flux is deposited on the surface of the liquid metal while the welding is in progress. In this way, both the electrode tip and the pool are protected by the flux.
- **EBW (Electron Beam Welding):** By using an electron gun, a beam is generated which is focused on the surface to be welded. The kinetic energy associated with the

electrons is transformed into thermal energy due to the collisions of the electrons with the surface to be welded. This allows temperatures to be reached which locally melt the metal. This technique requires vacuum conditions and that the material to be welded is conductive. The main advantage associated with this technique is the high penetration capacity, which allows for very deep welds with high precision.

- **LW (Laser Welding):** This technique allows joints to be made by means of a monochromatic light beam which locally melts the joint area. Unlike the EBW technique, the laser beam does not require vacuum conditions, but it does require the use of protective gases. It has a lower penetration capacity than the electron beam, but it also has a lower associated cost.

4.4.4. Machining processes

Forming processes can be completed by the application of machining techniques. These techniques are used to give the parts a good surface finish and correct dimensioning. The main techniques are briefly described below[2]:

- **Band sawing:** Cutting by use of a saw which moves in a cyclically in one direction.
- **Circular sawing:** Cutting by a circular blade which rotates on its own axis at high speeds.
- **Cropping and guillotining:** Cutting by using a moving blade which is forced to pass through a lower blade. It is used to cut laminated metals.
- **Drilling:** Technique that allows making holes of different diameters by using a rotating cutting tool.
- **Flame cutting:** Cutting using oxyfuel gas flame. The flame makes it possible to cut very thick sheets.
- **Milling:** This technique allows metal to be extracted from a surface by a rotating milling cutter, making it possible to obtain surface machining with a wide range of possible orientations.
- **Punching, perforating, blanking and nibbling:** Punching and profiling of sheet metal through fracture induced by shear forces.
- **Shaping and planing:** Technique for removing metal from the surface of components in horizontal, vertical and angular planes.

- **Turning/boring/parting:** Obtaining surfaces of revolution from the removal of metal from a piece due to the rotation of the piece in front of the cutting tools.

4.5 HEAT TREATMENTS

The main objective of the heat treatments after forming and/or welding, both for cast and wrought forming, is to eliminate all the intermetallic phases, carbides and nitrides that may have been generated, thus eliminating the embrittlement present in the alloy. To achieve this purpose, it is necessary to carry out an isothermal treatment at a temperature that allows the alloy to be in solid solution. This temperature is known as the annealing temperature and is determined by the different manufacturing regulations currently in use[58].

An example can be the ASTM A480 standard which contains the general specification standards for the fabrication of stainless steels by rolling. This standard indicates that the minimum annealing temperature for duplex stainless steels is between 980 and 1125 ºC depending on the alloy. After keeping the alloy at the isothermal temperature, it is necessary to carry out a quenching (generally in water) to avoid that during the cooling the transformation reactions in the solid state described above occur, generating again an embrittlement and a reduction of the corrosion resistance of the alloy[44,59].

The temperature set in the heat treatment, in addition to generating a solid solution, has a direct influence on the proportion of austenitic and ferritic phases resulting after annealing. Higher annealing temperatures selected will lead to a higher proportion of the ferritic phase in the microstructure. This effect can be justified by the Fe-Cr-Ni ternary constitutional diagram in Figure 2. This diagram shows how, as the temperature of the alloy increases, the transformation of austenite into ferrite can occur. For this reason, it is necessary to avoid heat treatments with annealing temperatures excessively higher than the minimum temperatures established by the standards. In this way, it will be possible to obtain the best properties because the alloy has a microstructure close to 50% ferritic and austenitic phases (provided that the chemical composition is appropriate according to the criteria of the WRC-1992 diagram)[60].

After quenching, it is common to temper most low alloy steels to remove stresses generated by quenching. In the case of duplex stainless steels, tempering above 300 ºC is not carried out due to the ease of the alloy to form the embrittlement phases[61]. For this reason, once the quenching has been carried out, the duplex stainless steels finish their manufacturing process and are put into service.

5. NEW ALLOYS FOR DUPLEX STAINLESS STEELS

From the discovery of DSS to the present day, studies and research related to these alloys have been increasing over the years due to the great interest they generate in the scientific and industrial fields.

One way to reflect this growing interest may be the evolution of the number of scientific publications related to these alloys. A clear example can be found in the ScienceDirect database, which is estimated to contain a quarter of the world's content of textbooks, journals and scientific articles (among other things). A search for all content associated with DSS shows an increasing trend in the number of annual publications[62], as compiled in Figure 6.

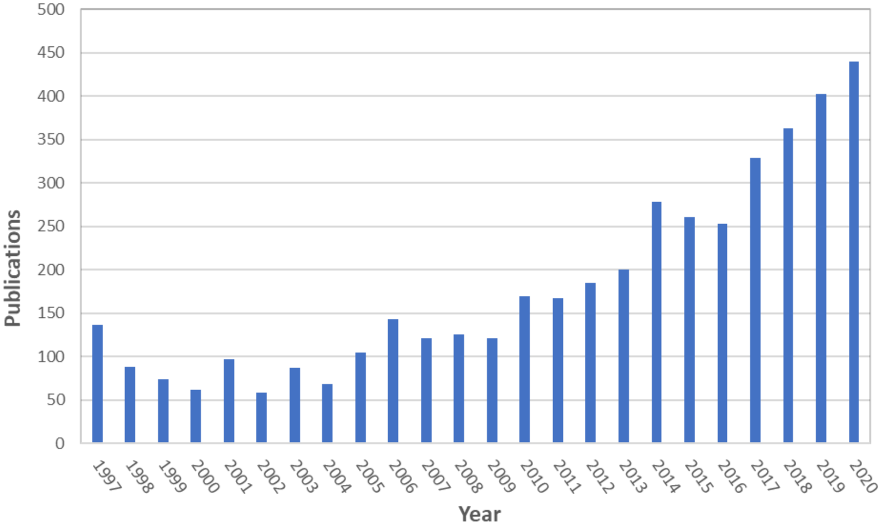

Figure 6: Number of scientific publications per year related to duplex stainless steels by ScienceDirect[62].

So far this year, the number of publications associated with 2021 at the time of the consultation was 360. With this data, and assuming that the number of publications throughout the year grows linearly, it can be estimated that the total number of publications this year will be 864, thus complying with the aforementioned growing trend.

This increasing trend is more noticeable in the last decade, which can be related to the development of new duplex alloys. These new alloys are commonly known as super duplex and hyper duplex stainless steels. Although the first research on super duplex alloys was published in the late 1980s[63], it was not until around 2010 that the generalization and growth of studies related to this alloy could be seen[62]. On the other hand, the development of hyper duplex alloys dates back to 2015 by the Swedish company Sandvik, being this company directly responsible for the growing worldwide interest in this new alloy[64].

Since these two alloys mentioned above are the main lines of research related to DSS, this chapter will describe the state of the art of these alloys.

5.1 DRIVING FORCE FOR DEVELOPMENT

The super duplex stainless steels can be considered an evolution of the conventional second generation DSS. These alloys began to be studied, as already mentioned, at the end of the 80[63]. Theoretically (according to the calculation of the PREN grade) it was possible to obtain alloys with a corrosion resistance higher than that of conventional duplex alloys and closer to that of nickel base alloys with a lower associated cost[2], establishing that a duplex alloy could be called super duplex when it had a PREN grade higher than 40[65]. The fact of being able to obtain chemical compositions which endowed a duplex alloy with a higher corrosion resistance made these alloys more interesting, this being the main driving force for the development of these new alloys.

From the first publications related to super duplex alloys up to the present day, it has been possible to verify how these alloys meet the service performance expected according to the studies carried out. As a direct consequence of this, these alloys have been able to replace the use of other alloys such as 300 series stainless steels, super austenitic steels and nickel base alloys because they show a better performance in service in environments related to the chemical and petrochemical industry. In these working environments, the materials must have a high resistance to acids, bases and halogens (halogen elements induce pitting corrosion), in addition to showing good mechanical properties[66,67].

Although super duplex alloys were a great advance in coping with the most corrosive operating environments, the current global scenario related to petroleum energy resources requires alloys with ever-increasing in-service performance. The exploitation and use of renewable energies and other energy sources will increase in the coming years, however, the use of hydrocarbons will continue to play an important role for at least the next two decades.[68].

This fact represents a real challenge for the oil and gas industry, since, in view of the increasing scarcity of oil fields exploitable with current technologies, it is necessary to locate and exploit new fields with geological and operational difficulties, such as deepwater or ultra-deepwater oil wells. The operating conditions in these wells located at high depths are characterized by high pressure, high temperature and extreme corrosion environments, thus requiring alloys that resist SCC more efficiently and economically. In addition to the limitations imposed by the service environment, the operation of deeper wells may require increasing the thickness of the tubing used, as well as the use in some cases of other coating materials for increased corrosion protection. The increase in the thickness of the pipes will be associated with an increase in the stress in the material itself generated by its own weight. This fact implies a limitation in terms of the maximum length of the pipes, being in some cases this length insufficient to be able to exploit a reservoir of a certain depth[64].

It is for this reason that super duplex alloys have continued to develop, giving rise to hyper duplex alloys. Service requirements are increasing and these alloys have improved corrosion resistance compared to their predecessors. In addition, these alloys offer superior mechanical properties compared to austenitic stainless steels for the same PREN grade value, thus allowing safe operation at greater depths while offering high corrosion resistance[69]. The cost associated with these new alloys remains lower compared to nickel base alloys, therefore, these alloys remain highly competitive in the markets[2].

5.2 CHEMICAL COMPOSITION

5.2.1. Super duplex stainless steel

The chemical composition of super duplex steels has some similarities to conventional DSS. Table 1 shows a couple of examples of conventional DSS and wrought super duplex stainless steels. It can be seen how the carbon contents remain at a maximum of 0.03%wt in order to minimize sensitization effects[28] and the sulfur and phosphorus contents are still kept low to avoid embrittlement of the steel[70]. The main compositional novelties in super duplexes are a higher chromium, nickel, molybdenum and nitrogen content, thus achieving a higher PREN grade and consequently better corrosion resistance. Increasing the contents of alphagen elements such as chromium and molybdenum implies the need to increase gammagen elements such as nickel and nitrogen, thus making it possible to maintain a correct ratio of ferritic and austenitic phases. Small additions of copper were already typical in conventional DSS and allow improved corrosion resistance in contact with sulfuric acid (selected examples of conventional DSS do not contain this element)[71]. Finally, tungsten is incorporated for the first time as an alloy in super duplexes, favoring the formation of the ferritic phase while increasing the PREN grade and thus improving corrosion resistance[72].

Table 1: Nominal chemical composition and PREN values of some wrought conventional duplex and super duplex stainless steels (%wt)[44].

Grade	UNS	C max	Si	Mn	P max	S max	Cr	Ni	Mo	N	W	Cu	PREN
Standard duplex													
2205	S31803	0.03	1.0	2.0	0.030	0.020	21-23	4.5-6.5	2.5-3.5	0.08-0.20	-	-	33-35
2205	S32205	0.03	1.0	2.0	0.030	0.020	22-23	4.5-6.5	3.0-3.5	0.14-0.20	-	-	35-36
Super duplex													
2507	S32750	0.03	0.8	1.20	0.035	0.035	24-26	6.0-8.0	3.0-5.0	0.24-0.32	-	0.50	40-43
-	S32506	0.03	0.9	1.0	0.040	0.015	24-26	5.5-7.2	3.0-3.5	0.08-0.20	0.05-0.30	-	40-42

Table 2 shows a couple of examples of conventional DSS and super duplex cast stainless steels. As in the wrought super duplex alloys, there is an increase in chromium, nickel, molybdenum and nitrogen composition with respect to the conventional duplex alloys, and these increases have a direct impact on the PREN grade.

Table 2: Nominal chemical composition and PREN values of some cast conventional duplex and super duplex stainless steels (%wt)[44].

Grade	UNS	C max	Si	Mn	P max	S max	Cr	Ni	Mo	N	W	Cu	PREN
Standard duplex													
3A	J93371	0.06	1.0	1.0	0.040	0.040	24-27	4.0-6.0	1.75-2.5	0.15-0.25	-	-	35-37
4A	J92205	0.03	1.0	1.50	0.040	0.020	21-23.5	4.5-6.5	2.5-3.5	0.10-0.30	-	-	35-37
Super duplex													
5A	J93404	0.03	1.0	1.50	0.040	0.040	24-26	6.0-8.0	4.0-5.0	0.10-0.30	-	0.50	43-45
6A	J93380	0.03	0.9	1.0	0.040	0.015	24-26	6.5-8.5	3.0-4.0	0.20-0.30	0.5-1.0	0.50-1.00	40-42

5.2.2. Hyper duplex stainless steel

Hyper duplex alloys did not start to be developed until about a decade ago. The Swedish company Sandvik succeeded in developing two new high wrought alloy DSS, Sandvik SAF 2707HD and Sandvik SAF 3207HD, which had a chromium content of up to 27%wt and 32%wt respectively, as well as increasing the nitrogen content to 0.5%wt in Sandvik SAF 3207HD, thus achieving a PREN value above 50 as can be seen in Table 3[64]. Sandvik SAF 3207HD alloy also incorporates 1%wt of cobalt in its chemical composition. This alloying element allows an improvement in pitting resistance as it is able to increase the repassivation ratio while reducing the corrosion current density of the alloy[73].

Table 3: Nominal chemical composition and PREN values of some wrought super duplex and hyper duplex stainless steels (%wt)[44,74,75].

Grade	UNS	C max	Si	Mn	P max	S max	Cr	Ni	Mo	N	W	Cu	Co	PREN
Super duplex														
2507	S32750	0.03	0.8	1.20	0.035	0.035	24-26	6.0-8.0	3.0-5.0	0.24-0.32	-	0.50		40-43
-	S32506	0.03	0.9	1.0	0.040	0.015	24-26	5.5-7.2	3.0-3.5	0.08-0.20	0.05-0.30	-		40-42
Hyper duplex														
SAF 2707HD	S32707	0.03	0.3	1.0	0.035	0.010	27	6.5	4.8	0.4	-	-	1.0	49.24
SAF 3207HD	S33207	0.03	0.8	1.5	0.035	0.010	32	7	3.5	0.5	-	-	-	51.55

In 2012, prior to Sandvik's market introduction of the first hyper duplex alloys, a new alloy called grade 7A was introduced in ASTM A890, this alloy being the first hyperduplex that could be formed by casting[76]. Compared to its predecessors, hyperduplex grade 7A presents a considerable change in its chemical composition and, therefore, a significant variation in its properties and characteristics.

As can be seen in Table 4, grade 7A has a lower chromium composition than compared to Sandvik's hyperduplex alloys. This lack of chromium can lead to a reduction in the percentage of the ferritic phase in the microstructure, but to avoid this effect, tungsten is added as a compensatory element. This element, in addition to being a stabilizer of the ferritic phase, contributes to a greater extent than chromium to increasing corrosion resistance according to the PREN expression.

Table 4: Nominal chemical composition and PREN values of some cast super duplex and hyper duplex stainless steels (%wt)[65].

Grade	UNS	C max	Si	Mn	P max	S max	Cr	Ni	Mo	N	W	Cu	PREN
Super duplex													
5A	J93404	0.03	1.0	1.50	0.040	0.040	24-26	6.0-8.0	4.0-5.0	0.10-0.30	-	0.50	43-45
6A	J93380	0.03	0.9	1.0	0.040	0.015	24-26	6.5-8.5	3.0-4.0	0.20-0.30	0.5-1.0	0.50-1.00	40-42
Hyper duplex													
7A	J93379	0.030	1.0	1.0-3.0	0.030	0.020	26-28	6-8	2-3.5	0.30-0.40	3-4	1 max	42.4-52.5

Extra additions in grade 7A:
Ba: 0.0010-0.0100
B: 0.0010-0.0100
Ce + La: 0.005-0.030

A novelty that can be appreciated in grade 7A is the presence of elements such as barium, cerium and lanthanum. These elements allow to increase the range of potentials in which the self-passivation of ferritic and austenitic surfaces is generated while reducing the current density of the passive layer, thus slowing down the corrosion rate. In addition, these elements allow the passive film to have greater stability at slightly higher than typical temperatures and delay the formation of embrittling intermetallic phases by hindering the diffusion of chromium[77]. On the other hand, some studies suggest that the addition of boron with typical grade 7A compositions can be detrimental by slightly reducing the resistance to intergranular corrosion[78], therefore, a first conclusion can be made questioning the content of this element in hyperduplex alloys.

Today, although there are current lines of research associated with hyper-DSS grade 7A steel, only wrought hyper duplex alloys obtained by extrusion are being marketed[79]. We are therefore at a point where we may witness in the not too distant future the beginning of the commercialization of hyper duplex alloys obtained by casting and their subsequent in-service evaluation.

5.3 PROPERTIES

5.3.1. Mechanical properties

Due to the large number of alloying elements contained in the super and hyper duplex alloys, they far exceed the mechanical properties of their predecessor alloys. Figure 7 shows the yield strength and mechanical strength for a set of duplex, super duplex and hyper duplex alloys, showing how these properties increase the more alloyed the DSS. In addition, the much higher yield strength of SAF 3207HD hyper duplex steel with respect to the other alloys can be highlighted.

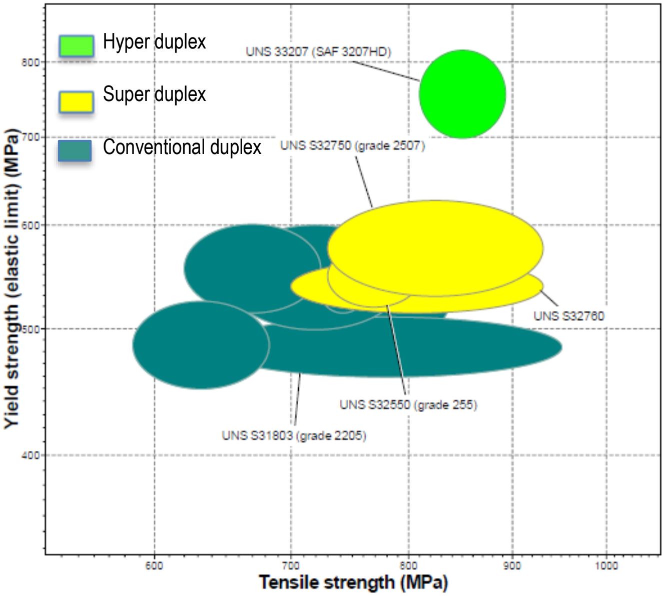

Figure 7: Tensile strength and yield strength for a set of duplex, super duplex and hyper duplex stainless steels[2].

Another example that demonstrates the proportionality between the increase in mechanical properties and the increase in alloying elements can be seen in Figure 8. This image shows how the yield strength varies as a function of temperature in the hyper duplex alloys SAF 3207HD and SAF 2707HD and in the super duplex alloy SAF 2507. As can be seen, the yield strength for the hyper duplex alloys is higher than that of the super duplex alloy in all temperature ranges tested. Other properties such as fatigue strength and impact strength are also superior to the super duplex alloys[80].

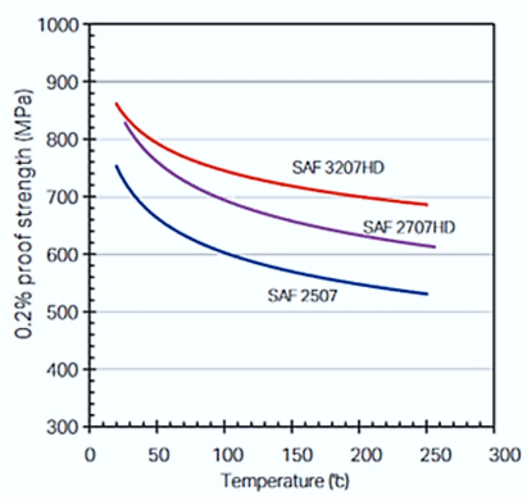

Figure 8: Influence of temperature on super and hyper duplex stainless steels tube materials[80].

5.3.2. Chemical properties

If we analyze the chemical properties, the super and hyper duplex alloys have a higher critical pitting temperature (CPT) than their predecessors. CPT is defined as the temperature at which pitting begins, thus limiting the maximum service temperature at which the alloys can work efficiently[67]. Figure 9 shows the CPT for some fully austenitic, duplex, super duplex and hyperduplex alloys, as well as a correlation between this property and the PREN grade. The study from which these data were obtained was carried out using a 6%wt aqueous solution of FeCl3 according to ASTM G48A[80,81].

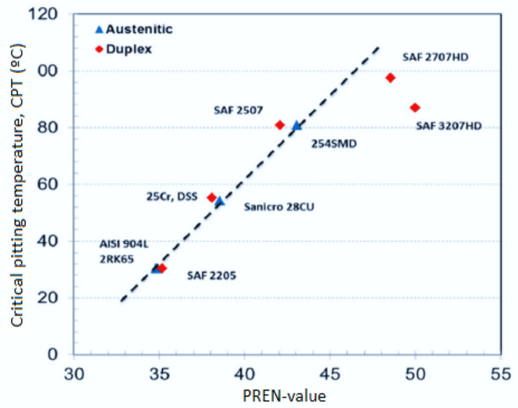

Figure 9: Correlation between critical pitting temperature and PREN-value for some austenitic, duplex, super duplex and hiper duplex stainless steels[80].

This study, in addition to proving that the hyper duplex alloys have the highest in-service temperature with respect to the rest of the duplex alloys, also reaffirms that the higher additions of alloying elements such as chromium, molybdenum, nickel and nitrogen (among others) have a great impact on corrosion resistance. On the other hand, it can be observed how the PREN grade shows a certain correlation with the CPT, thus corroborating the validity of this empirical expression as a reliable indicator to quantify the corrosion resistance of stainless steels[80].

The CPT can vary with the concentration of halogen ions present in the medium which is in contact with the metal surface. Figure 10 shows the results of another study which shows the variation of the CPT as a function of the concentration of chloride ions in the electrolyte medium for the SAF 2507 super duplex alloy with respect to two conventional duplex alloys.

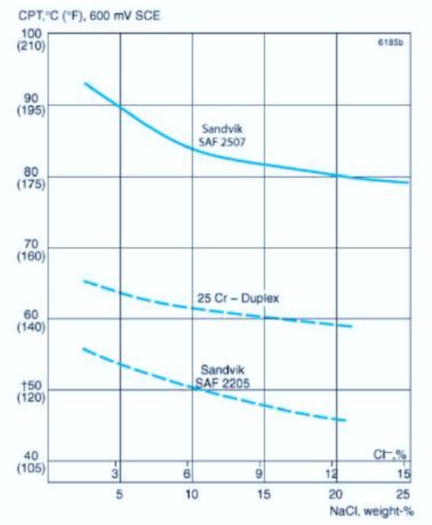

Figure 10: Variation of CPT as a function of chloride ion (%wt) concentration obtained by potentiostatic determination at +600 mV SCE with surface ground with 600 grit paper.

These results show that super duplex alloys still have higher corrosion resistance for higher chloride ion contents than conventional duplex alloys. Although no hyper duplex alloy is shown in Figure 10, it can be estimated based on all that has been seen so far that these alloys will show superior performance to the super duplex alloys.

5.4 PRODUCING, FORMING AND HEAT TREATMENTS

The processes for producing and forming super duplex and hyper duplex do not present any novelty with respect to those of conventional DSS. This fact indicates the possibility of initiating new avenues of research in order to improve the efficiency of these processes so that they have greater productivity and sustainability.

However, the heat treatments of these alloys do show some differences. Although these treatments still consist of dissolving the precipitates generated during the solidification and forming processes with the aim of eliminating embrittlement, the super and hyper duplex alloys present a formation of intermetallic phases, carbides and nitrides at higher temperatures with superior kinetics due to the higher composition in Cr, Mo and

W. If we focus on the sigma phase, the higher Cr and Mo contents will facilitate a rapid appearance since this phase requires the presence of these elements for its formation. On the other hand, the higher additions of W will cause the sigma phase to form at higher temperatures, thus requiring heat treatments at higher temperatures to dissolve this phase[82,83].

As already discussed in section 4.2.2, the precipitation of intermetallic phases such as the sigma phase in conventional duplex alloys appears between 500 and 970 °C. A clear example of the effects associated with higher additions of alloying elements for the formation of the sigma phase can be seen in Figure 11. The solubilization temperature at which the microstructure of a grade 6A super duplex alloy is free of this embrittling phase is 1060 ºC[84], this temperature being higher compared to less alloyed duplex alloys.

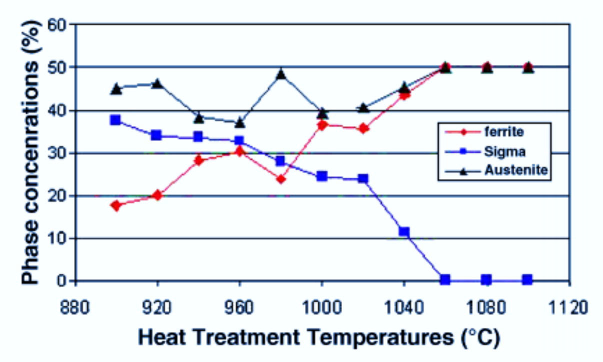

Figure 11: Ratio of ferritic, austenitic and sigma phase as a function of heat treatment temperature[84].

Figure 12 shows the effects of a 2h heat treatment at different temperatures with a subsequent tempering for a grade 7A hyper duplex alloy. The heat treatment associated with an austenoferritic matrix free of sigma phase is the one carried out at a temperature of 1120 ºC[85].

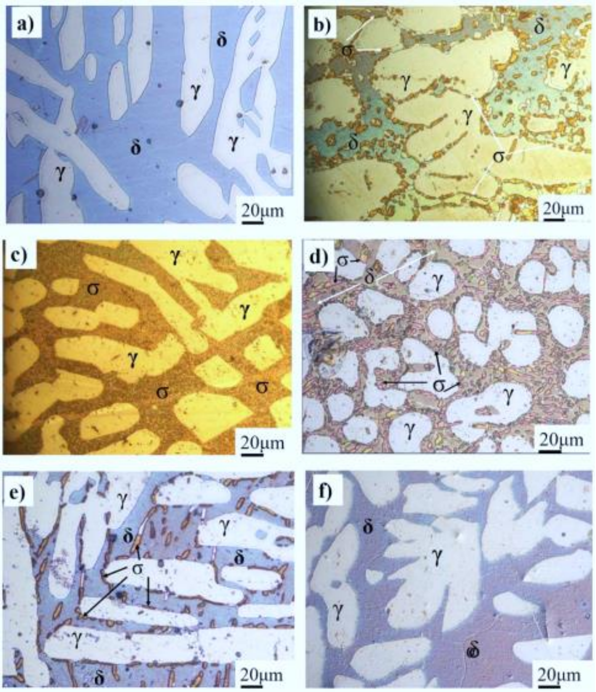

Figure 12: Micrographs of different samples of hyper-DSS grade 7A after heat treatment at (a) 750 ºC (b) 770 ºC (c) 900 ºC (d) 1050 ºC (e) 1100 ºC (f) 1120 ºC obtained by optical microscopy[85].

Thanks to the results of both studies, it can be concluded that in order to dissolve all the precipitates formed during the obtaining and forming operations, it will be necessary to carry out solubilization heat treatments at temperatures that will increase with higher contents of alloying elements. In addition, it can be added that, in order to form these alloys by plastic deformation without embrittlement, it will be necessary to work the material at temperatures higher or very close to the solubilization temperatures of intermetallic phases, carbides and nitrides.

Another aspect to take into account is the speed at which tempering is carried out after solubilization in the solid state. As already mentioned, the higher proportion of chromium and molybdenum favors a faster formation of other embrittling phases. Figure 13 shows a Time-Temperature-Transformation (TTT) diagram which shows the onset of the appearance of other phases for a super duplex steel grade 2507 and two conventional duplex steels grade 2205 and 2304 (the curves represented do not refer to any particular phase, but to the set of reactions that can occur in the solid state). It can be seen how the super duplex alloy presents earlier times of appearance of other phases compared to the duplex alloys with lower chromium and molybdenum contents.

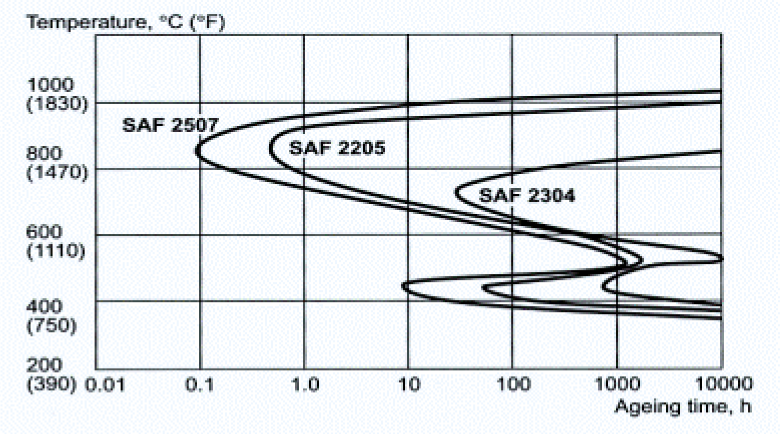

Figure 13: Time-Temperature-Transformation (TTT) diagram of duplex and super duplex stainless steel[87].

Therefore, in addition to needing to take into account the alloying element content to identify the correct solubilization temperature in the solid state, it is also necessary to take into account these parameters which influence the maximum tempering rate for the onset of embrittlement. Super duplex and hyper duplex alloys will require higher tempering rates to obtain a purely austenoferritic microstructure, and therefore, these alloys present greater limitations for industrial processing and forming.

5.5 APLICATIONS

As already mentioned, the high corrosion resistance together with the good mechanical properties of these alloys means that the main applications of super and hyper-DSS alloys are in the offshore oil industry. Currently, for an extraction depth of 2500 m (where the pressure exceeds 1000 atmospheres), the alloy used for extraction systems is Sandvik SAF 3207HD hyper-DSS. This alloy is the highest quality duplex alloy on the market in terms of SCC resistance and provides excellent service efficiency without excessively high costs[64].

In this same sector, another application of these alloys is in the manufacture of submarine cables from oil platforms to deep sea wells[80]. Figure 14 shows how these cables are externally coated with a layer of a polymeric material and a subsequent layer of steel. The main function of the steel is to protect the contents inside the cable and therefore alloys such as those described in this chapter are required to ensure that the internal contents of the cables are not damaged.

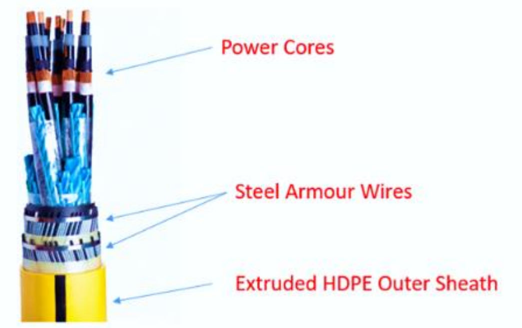

Figure 14: Subsea power cable[88].

Another area of application of these alloys can be found in heat exchanger systems. We can find in these systems an example that shows the transition from super duplex to hyper duplex alloys. An oil refinery in the USA decided to change its heat exchanger tubes made of carbon steels to super DSS stainless steels. These low alloy steels had a life expectancy of only 9 months as chloride and sulphur attacks corroded the material very quickly. Subsequently, because super duplex alloys were considered to work very close to their limitations, it was decided to replace these steels with hyper duplex alloys. Currently, this latter change is proving to have excellent performance, and the industry is able to return data to the research world on the in-service verification of these latest alloys developed[69].

6. CONCLUSIONS

Duplex stainless steels are an excellent alternative, with associated lower cost, to nickel base alloys for applications where good SCC resistance is required.

Precipitates of intermetallic compounds, carbides, nitrides, and alpha prime phase lead to embrittlement and reduced corrosion resistance in duplex alloys. For proper in-service performance, it is necessary to avoid the formation of these precipitates.

The PREN grade is a valid expression to quantify the corrosion resistance of stainless steels.

The new super duplex and hyper duplex alloys have better in-service performance than conventional duplex alloys.

The higher contents of alloying elements such as chromium, molybdenum and tungsten, typical of the latest duplex alloys developed, favor a more rapid appearance of intermetallic precipitates such as the sigma or chi phase at higher temperatures, making production and forming process more difficult.

Boron additions in the grade 7A hyper duplex alloy need to be studied in greater detail because some studies indicate that the addition of this element reduces the resistance to intergranular corrosion.

At present, hyper duplex steels obtained by casting are not commercially available, therefore, the first implementations and in-service testing of this type of alloy could be studied in the not too distant future.

Studies related to this type of alloy are booming due to the great potential for improvement with respect to the PREN grade. For this reason, it is entirely feasible to develop new alloys with corrosion resistance superior to hyper duplex alloys.

7. REFERENCES AND NOTES

In order to give visibility to the contribution of women in the scientific community, the first name of all authors will be included in the bibliography. Due to the difficulty of finding all the first names of all the authors cited, some citations will contain the full name of the authors and some other citations will show the abbreviated name.

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APPENDICES

APPENDIX 1: PROPERTIES OF AUSTENITIC, FERRITIC AND DUPLEX STAINLESS STEELS

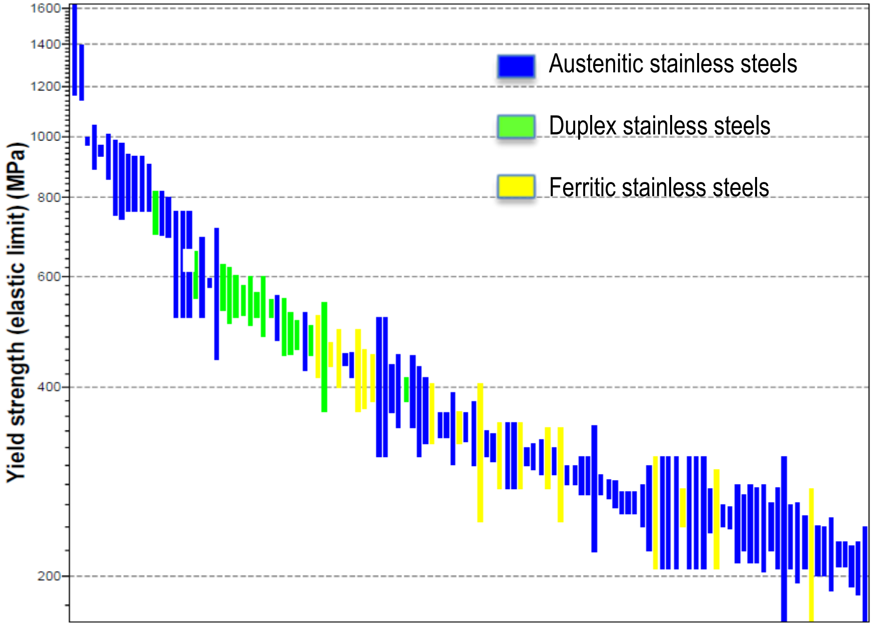

Figure 15: Yield strength of austenitic, ferritic and duplex stainless steels.

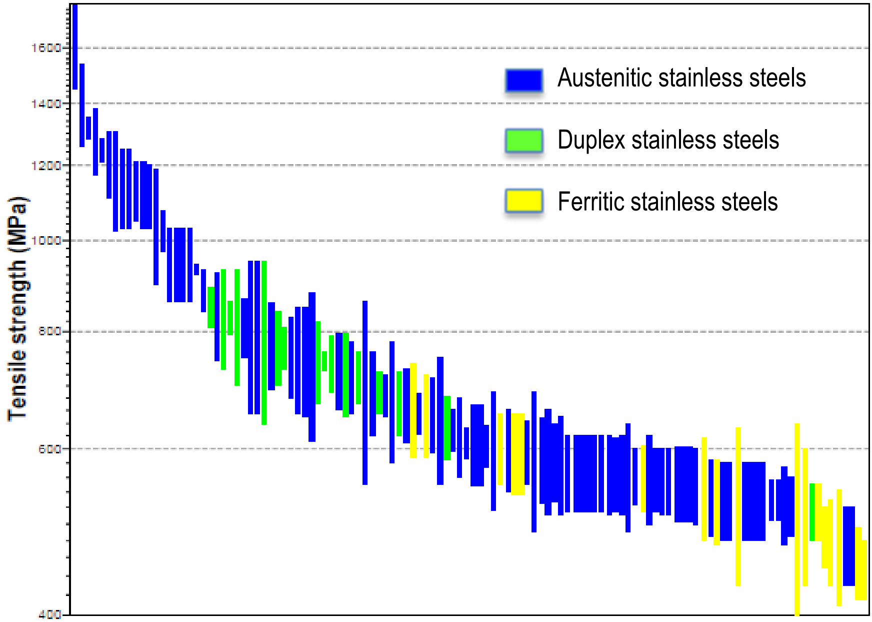

Figure 16: Tensile strength of austenitic, ferritic and duplex stainless steels.

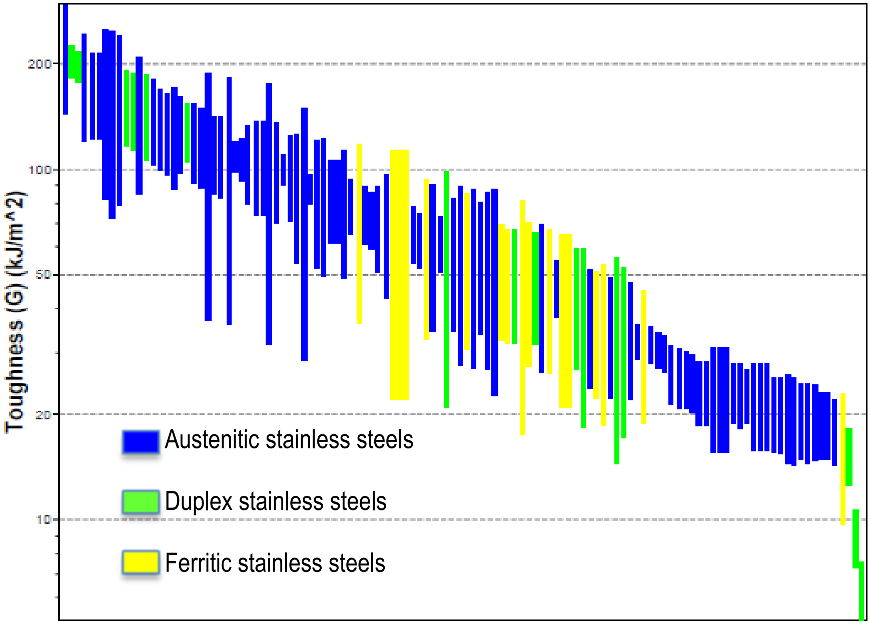

Figure 17: Toughness of austenitic, ferritic and duplex stainless steels.

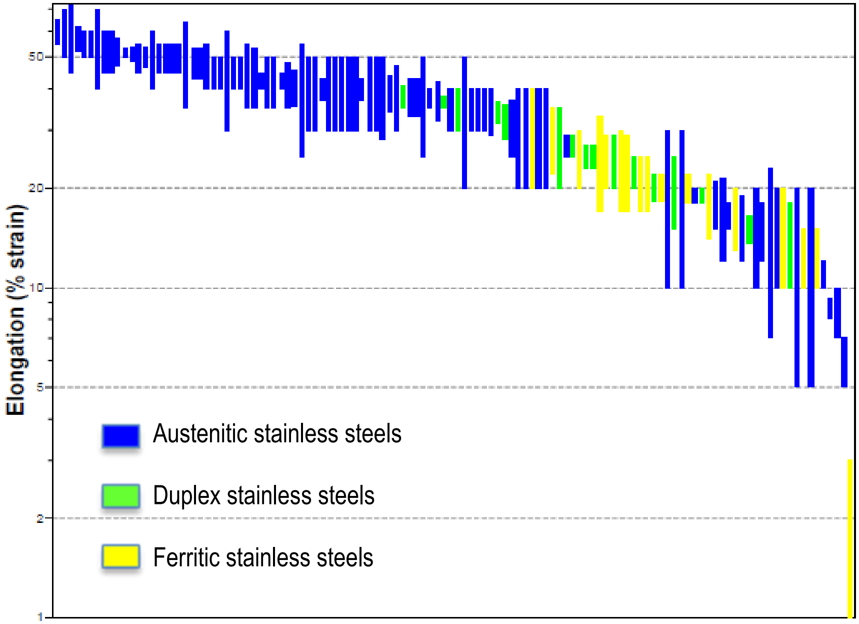

Figure 18: Elongation of austenitic, ferritic and duplex stainless steels.

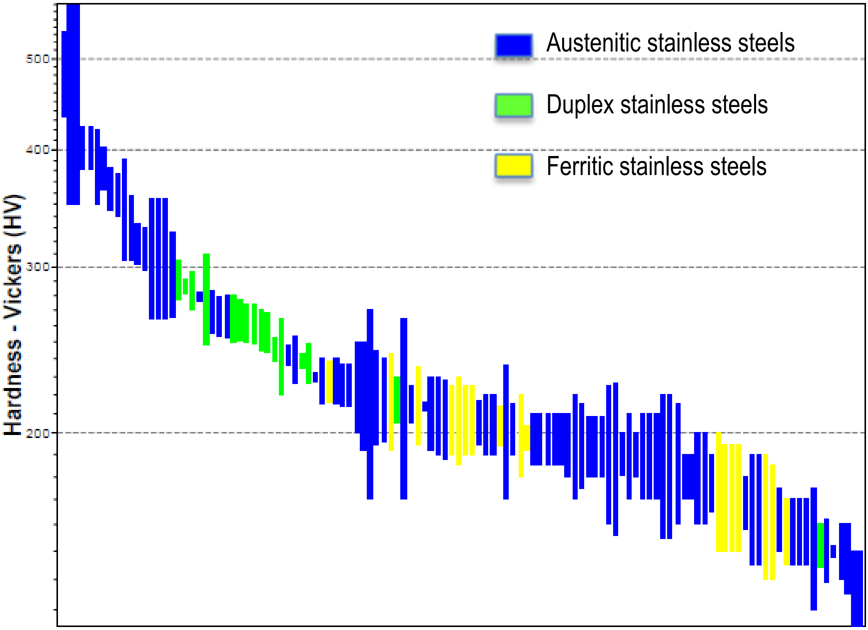

Figure 19: Hardness of austenitic, ferritic and duplex stainless steels.

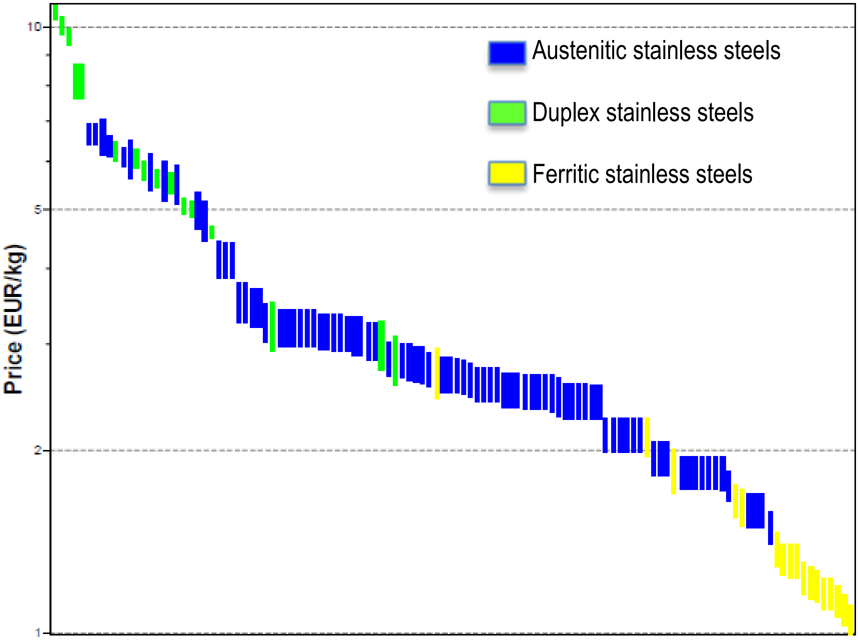

Figure 20: Price of austenitic, ferritic and duplex stainless steels.

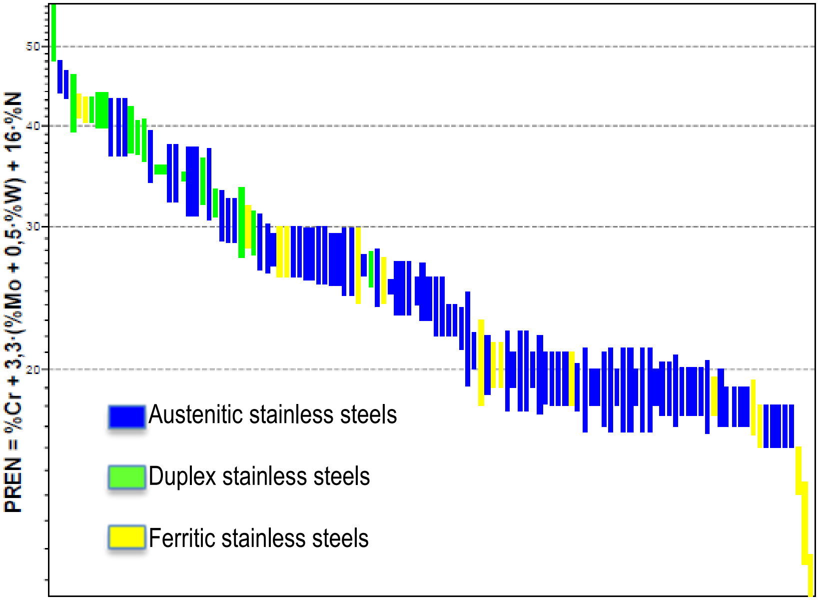

Figure 21: PREN of austenitic, ferritic and duplex stainless steels.

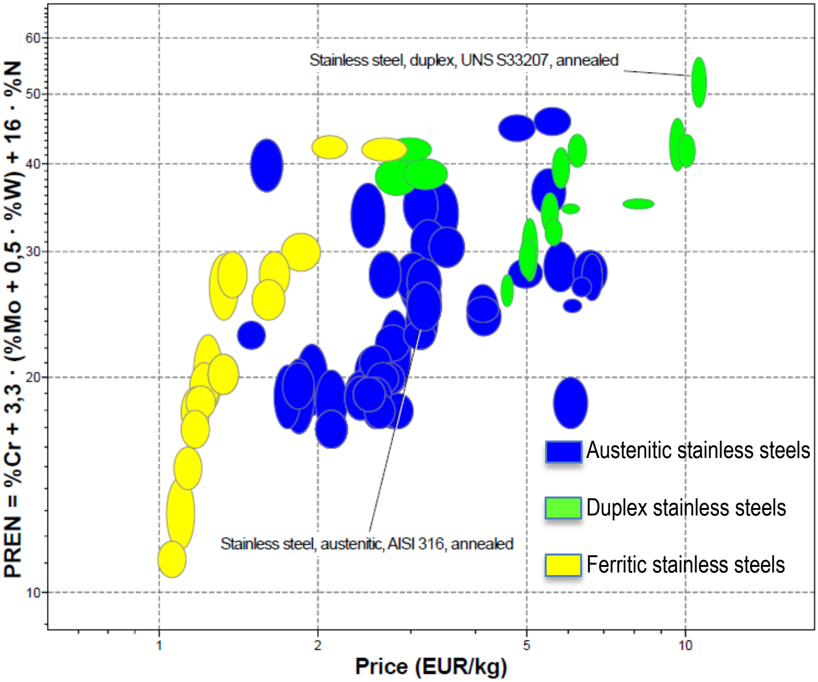

Figure 22: PREN vs price (EUR/kg) of austenitic, ferritic and duplex stainless steels.

APPENDIX 2: TYPES OF DUPLEX STAINLESS STEELS

Table 5: Types of duplex stainless steel and their nominal chemical compositions (%wt).

Grade	UNS	C max	Mn	Cr	Ni	Mo	N	W	Cu	PREN
Wrought duplex stainless steels										
First-generation duplex grades										
329	S32900	0.08	1.00	23-28	2.5-5.0	1.0-2.0	-	-	-	30-31
	S31500	0.03	-	18-19	4.3-5.2	2.5-3.0	0.05-0.10	-	-	28-29
	S32404	0.04	2.00	20.5-22-5	5.5-8.5	2.0-3.0	0.20	-	1.0-2.0	29-30
Second-generation duplex grades										
Lean duplex										
	S32001	0.03	4.0-6.0	19.5-21.5	1.0-3.0	0.6	0.05-0.17	-	1.0	21-23
	S32101	0.04	4.0-6.0	21-22	1.35-1.7	0.1-0.8	0.20-0.25	-	0.10-0.80	25-27
	S32202	0.03	2.00	21.5-14	1.0-2.8	0.45	0-18-0.26	-	-	25-28
2304	S32304	0.03	2.50	21.5-24.5	3.0-5.5	0.05-0.60	0.05-0.20	-	0.05-0.60	25-28
	S82011	0.03	2.0-3.0	20.5-23.5	1.0-2.0	0.1-1.0	0.15-0.27	-	0.50	25-27
	S82012	0.05	2.0-4.0	19.0-20.5	0.8-1.5	0.1-0.6	0.16-0.26	-	1.0	24-26
	S82122	0.03	2.0-4.0	20.5-21.5	1.5-2.5	0.60	0.15-0.20	-	0.50-1.50	24-26
		0.03	2.00	22-24	3.5-5.5	0.1-0.6	0.05-0.20	-	1.0-3.0	25-27
		0.045	1.0-3.0	21.5-24	1.0-3.0	0.5	0.12-0.20	-	1.6-3.0	25-27
Molybdenum-containing lean duplex										
	S32003	0.03	2.00	19.5-22.5	3.0-4.0	1.5-2.0	0.14-0.20	-	-	30-31
	S81921	0.03	2.0-4.0	19-22	2.0-4.0	1.0-2.0	0.14-0.20	-	-	27-28
	S82031	0.05	2.50	19-22	2.0-4.0	0.6-1.4	0.14-0.24	-	1.0	27-28
	S82121	0.035	1.0-2.5	21-23	2.0-4.0	0.3-1.3	0.15-0.25	-	0.20-1.20	27-28
	S82441	0.03	2.5-4.0	3.0-4.5	3.0-4.5	1.0-2.0	0.20-0.30	-	0.10-0.80	33-34
Standard duplex										
2205	S31803	0.03	2.00	21-23	4.5-6.5	2.5-3.5	0.08-0.20	-	-	33-35
2205	S32205	0.03	2.00	22-23	4.5-6.5	3.0-3.5	0.14-0.20	-	-	35-36
	S32950	0.03	2.00	26-29	3.5-5.2	1.0-2.5	0.15-0.35	-	-	36-38
	S32808	0.03	1.10	27-27.9	7.0-8.2	0.8-1.2	0.30-0.40	2.1-2.5	-	36-38
Super duplex										
	S32506	0.03	1.00	24-26	5.5-7.2	3.0-3.5	0.08-0.20	0.05-0.30	-	40-42
	S32520	0.03	1.50	24-26	5.5-8.0	3.0-4.0	0.20-0.35	-	0.50-2.00	40-43
255	S32550	0.04	1.50	24-27	4.4-6.5	2.9-3.9	0.10-0.25	-	1.50-2.50	38-41
2507	S32750	0.03	1.20	24-26	6.0-8.0	3.0-5.0	0.24-0.32	-	0.50	40-43
	S32760	0.03	1.00	24-26	6.0-8.0	3.0-4.0	0.20-0.30	0.5-1.0	0.50-1.00	40-43
	S32906	0.03	0.8-1.5	28-30	5.8-7.5	1.5-2.6	0.30-0.40	-	0.80	41-43
	S39274	0.03	1.00	24-26	6.8-8.0	2.5-3.5	0.24-0.32	1.50-2.50	0.20-0.80	40-42
	S39277	0.025	0.80	23-26	6.5-8.0	3.0-4.0	0.23-0.33	0.8-1.2	1.20-2.00	40-42
Hyper duplex										
	S32707	0.03	1.00	26-29	5.5-9.5	4.0-5.0	0.30-0.50	-	1.0	49-50
	S33207	0.03	1.00	29-33	6.0-9.0	3.0-5.0	0.40-0.60	-	1.0	52-53
Grade	**UNS**	**C max**	**Mn**	**Cr**	**Ni**	**Mo**	**N**	**W**	**Cu**	**PREN**
Cast duplex stainless steels										
Standard duplex										
1A	J93370	0.04	1.00	24.5-26.5	4.75-6.0	1.75-2.25	-	-	2.75-3.25	32-33
1B	J93372	0.04	1.00	24.5-26.5	4.7-6.0	1.7-2.3	0.10-0.25	-	2.70-3.30	34-36
1C	J93373	0.03	1.20	24-26.7	5.6-6.7	2.9-3.8	0.22-0.33	-	1.40-1.90	40-42
2A	J93345	0.08	1.00	22.5-25.5	8.0-11.0	3.0-4.5	0.10-0.30	-	-	38-40
3A	J93371	0.06	1.00	24-27	4.0-6.0	1.75-2.5	0.15-0.25	-	-	35-37
4A	J92205	0.03	1.50	21-23.5	4.5-6.5	2.5-3.5	0.10-0.30	-	-	35-37
Super duplex										
5A	J93404	0.03	1.50	24-26	6.0-8.0	4.0-5.0	0.10-0.30	-	0.50	43-45
6A	J93380	0.03	1.0	24-26	6.5-8.5	3.0-4.0	0.20-0.30	0.5-1.0	0.50-1.00	40-42
Hyper duplex										
7A	J93379	0.030	1.0-3.0	26-28	6-8	2-3.5	0.30-0.40	3-4	1 max	42.4-52.5

Extra additions in grade 7A:

Ba: 0.0010-0.0100

B: 0.0010-0.0100

Ce + La: 0.005-0.030