Duplex Stainless Steels: Brief History and Some Recent Alloys

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Abstract: In terms of a common engineering material, modern duplex stainless steels emerged in the early 1980s, developed from cast alloys. Their popularity stems from an attractive combination of properties, including high strength and excellent resistance to chloride stress corrosion cracking. The present paper gives a brief review of the history and some recent developments of duplex stainless steel grades and the improvements made on the standard S32205 DSS lowering the Ni and Mo contents to produce an economical alternative of the well-known grade or in the case of the superduplex S32750 grade increasing the content of Cr, Mo and Nor elevating the content of Cr, N, Cu and W in combination with relatively lower contents of Ni and Mo to improve the strength, toughness and corrosion properties for the oil industry. Parallel to the development of higher-alloy duplex grades for corrosive conditions, there has recently been a great interest in leaner compositions for wider purposes with lower amounts of expensive alloying elements. In this respect, a new patent correspond to the type S32101 DSS has been developed. Finally, the most modern applications in the field of oil and petrochemical industry are described and the major uses of the three main grades, lean, 2205 and 2507, are commented.

Keywords: Duplex stainless steels, new alloys, applications.

HISTORICAL EVOLUTION

Duplex stainless steels (DSSs), meaning those with a mixed microstructure of about equal proportions of austenite and ferrite, have existed for more than 70 years [1]. The early grades were alloys of chromium, nickel and molybdenum. The ternary phase diagram of the metallurgical behavior is shown in Fig. (**1a**) and a typical duplex structure of a hot-rolled material, Fig. (**1b**). A section through the ternary at 68% iron illustrates that these alloys solidify as ferrite, some of which then transforms to austenite as the temperature falls to about 1000°C (1832°F) depending on alloy composition. There is little further change in the equilibrium ferrite-austenite balance at lower temperatures. The effect of increasing nitrogen is also shown in this figure [2]. Thermodynamically, because the austenite is forming from the ferrite, it is impossible for the alloy to go past the equilibrium level of austenite. The main problem with Duplex is that it forms very easily brittle intermetalic phases, such as Sigma, Chi, R and Alpha Prime [3,4]. Prolonged heating in the range 350°C to 550°C can cause 475°C temper embrittlement [9].

The first wrought duplex stainless steels were produced in Sweden in 1930 and were used in the sulfite paper industry. These grades were developed to reduce the intergranular corrosion problems in the early high-carbon austenitic stainless steels. Duplex castings were produced in Finland in 1930, and a patent was granted in France in 1936 for the forerunner of what would eventually be known as Uranus 50. It became obvious that a balance of ferrite and austenite had better resistance to chloride stress-corrosion cracking than a fully austenitic microstructure. Engineers have exploited this advantages of duplex over austenitic steels ever since. In France, the UR 50 grade with 20-35% ferrite (UNS S32404) was marketed in various product forms, including forging, for such industries as oil refinement, food processing, pulp and paper, and pharmaceutical. These steels were produced in high-frequency induction furnaces using precisely weighed alloying additions. Partial vacuum ensured carbon removals, rudimentary de-oxidation and restricted nitrogen ingress. Nevertheless, plate products remained sensitive to edge cracks [3].

One of the first duplex grades developed specifically for improved resistance to chloride stress corrosion cracking (SCC) was 3RE60. AISI Type 329 became well established after World War II and was used extensively for heat exchanger tubing for nitric-acid service. In subsequent years, both wrought and cast duplex grades have been used for a variety of processing industry applications including vessels, heat exchangers and pumps. These first-generation duplex stainless steels provided good performance characteristics but had limitations in the as-welded condition. The heat-affected zone (HAZ) of welds had low toughness because of excessive ferrite and significantly lower corrosion resistance than that of the base metal. These limitations confined the use of the first-generation duplex stainless steels, usually in the non-welded condition, to a few specific applications.

During the late 1960s and early 1970s, there were two main factors which advanced the development and use of duplex alloys. First, there was a nickel shortage that pushed up the price of austenitic steels, in combination with increased activity in the offshore oil industry which demanded a stainless steel material to handle aggressive environments. Second, steel production techniques improved dramatically with the introduction of the vacuum and argon oxygen decarburization (VOD and AOD) practices. These techniques made it possible to produce much cleaner steels with a very low carbon level and well controlled nitrogen content. In the 70's, the introduction of continuous casting in stainless steel production has contributed to lower production costs and higher quality. From 1970 onwards, the addition of nitrogen and lowering of carbon content improved corrosion resistance and high temperature stability of the duplex structure, e.g. the HAZ, by stabilizing the austenite. Development of new steels inevitably brings new problems in manufacturing and joining. This is particularly true for welding where the desired material properties, carefully produced by the steel maker, can be radically changed by a process that locally melts and recasts part of the microstructure. Because the cooling rate determines the amount of ferrite that can transform to austenite, cooling rates following high temperature exposures influence the phase balance. Since fast cooling rates favor retention of ferrite, it is possible to have more than the equilibrium amount of ferrite. Another beneficial effect of nitrogen is that it raises the temperature at which the austenite begins to form from the ferrite. Therefore, even at relatively rapid cooling rates, the equilibrium level of austenite can almost be reached. In the new generation of duplex stainless steels (higher nitrogen content), this effect reduces the problem of excess ferrite in the HAZ [10]. There is definitely a continuing demand for increased productivity in welding, while maintaining the parent material properties. The last two decades have seen the introduction of the "super" stainless steels. Super-

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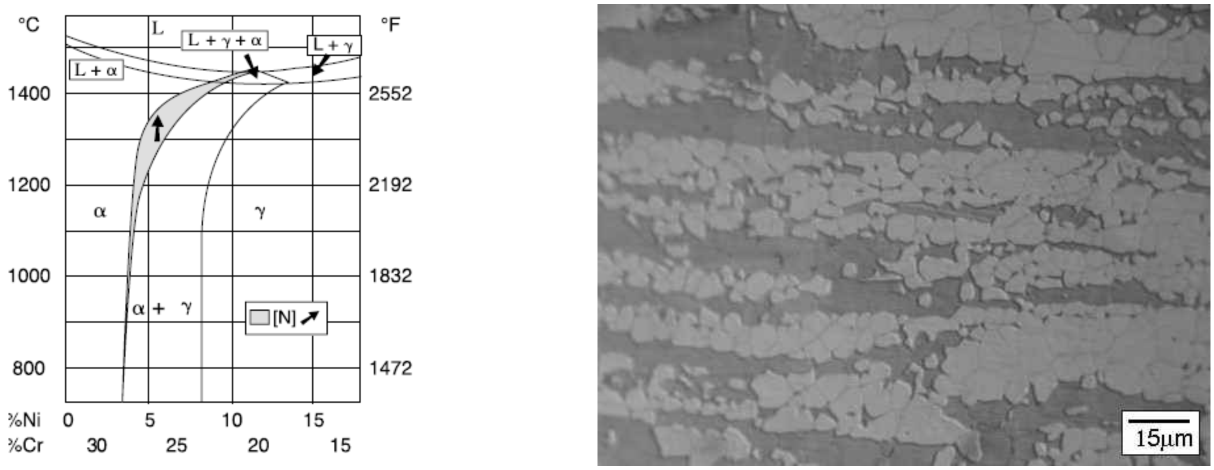

a) b)

Fig. (1). a) Section of the ternary Fe-Cr-Ni phase diagram. b) Optical micrograph showing the austeno-ferritic structure of a DSS in the form of a hot-rolled plate. The dark and bright phase corresponds to the ferritic and the austenitic phase, respectively.

ferritic grades with very low interstitial levels and high chromium and molybdenum contents have superior corrosion resistance compared to standard ferritic grades. However, although these steels have found certain applications, their success has been limited. The highly alloyed super-austenitic and superduplex stainless steels, with excellent corrosion resistance and better fabricability and weldability than the ferritic steels, have found a more widespread use and are today important engineering alloys. The hot workability and rolling experience was greatly improved, making possible the production of wide sheets and coils [3].

MODERN DEVELOPMENT

In the early 1980's, a *second generation* of duplex steels was introduced with improved welding properties mainly through nitrogen alloying. The most common duplex grade today is EN 1.4462 or 2205 (UNS S31803/S32205), which has a nominal composition of 22% Cr, 5%Ni, 3% Mo, and 0.16% N. This steel is used in a great number of applications in a wide variety of product forms. Many of the grades have become commonly known by a number that reflects their typical chromium and nickel contents, e.g. 2205 with 22% Cr and 5%Ni. The 2205 alloy is a nitrogen-enhanced duplex stainless steel alloy. The nitrogen serves to significantly improve the corrosion resistance properties of the alloy, which also exhibits a yield strength that is more than double that of conventional austenitic stainless steels; especially in the welded condition. Earlier duplex alloys have had moderate resistance to general corrosion and chloride stress-corrosion cracking, but suffered a substantial loss of properties when used in the as-welded condition. The 2205 duplex stainless steel provides corrosion resistance in many environments that is superior to the AISI Type 304, 316 and 317 austenitic stainless steels. This duplex stainless steel is often used in the form of welded pipe or tubular components, as well as a formed and welded sheet product in environments where resistance to general corrosion and chloride stress corrosion cracking is important. The increased strength creates opportunities for reduction in tube wall thickness and resists handling damage.

Nevertheless, the extraordinary corrosion resistance (and other properties) of 2205 may be greater than is required in some applications. In certain SCC applications, while 2205 would provide an acceptable technical solution, it may not be an economical replacement alloy for Type 304, 316 or 317 stainless steel. The higher cost of 2205 is due primarily to the amounts of the alloying elements nickel (nominal 5.5%) and molybdenum (nominal 3%). Thus, it is desirable to provide a weldable, formable duplex stainless steel that has greater corrosion resistance than the Type 304, 316 or 317 austenitic stainless steels (see Table **1**), and has a lower production cost than the commonly used 2205 duplex stainless steel.

Tables 1. Corrosion and Mechanical Properties of Some Stainless Steels: Duplex 2205, Austenitic Type 304, 316 and 317 and Duplex Developed Under the Patent of Ref. [11]

Alloy	Chemical Comp. (wt. %)		PCR	SCC	Mechanical Properties		
	Ni	Mo	CPT	CSCC	0.2 % PS	TS	El (%)
2205	4.5-6.5	2.5-3.5	35ºC	20ºC	450 MPa	620 MPa	25
Type 304*	8-10.5	--	--	-2.5ºC	205MPa	515 MPa	40.0
Type 316*	10-14	2-3	15ºC	-3ºC	205 MPa	515 MPa	40.0
Type 317*	11-15	3-4	19ºC	2ºC	206 MPa	517 MPa	35.0
US6551420B1[(a)]	3.0 - 4.0	1.5 - 2.0	31ºC	**	572 MPa	786 MPa	37

PCR: Pitting Corrosion Resistance; CPT: Critical Pitting Temperature (ASTMG-48A); CCCT: Crevice Corrosion Critical Temperature (ASTM G48B); 0.2%PS: 0.2% offset Proof Strength; TS: Tensile Strength;
* ASTM minimum. ** Not specified in the patent. [(a)] Ref. [11].

Following this idea, Bergstrom *et al.* [11] atented an economical alternative to the known 2205 DSS with lower alloy content, particularly nickel and molybdenum. Bergstrom's duplex stainless steel exhibits mechanical properties comparable to 2205 along with resistance to pitting/crevice corrosion that is significantly greater than the Type 316 and 317 stainless steels. Table **1** resumes the important corrosion and mechanical properties of the new duplex steel created under the US Patent No. 6551420 B1 [11] in comparisson with pre-existing stainless steels.

The success of the 2205 grade led to the development of an entire family of duplex alloys, which range in corrosion resistance depending on their alloy content. The modern duplex stainless steels can be divided into four groups [12]:

- lean duplex as 2304, with 0.05-0.6 wt% of Mo.
- 2205, the work-horse grade accounting for more than 80% of duplex use
- 25Cr duplex as Alloy 255 and DP-3
- superduplex, with 25-26 Cr and increased Mo and N compared with the 25 Cr grades, including grades such as 2507, Zeron 100, UR52N+, and DP-3W.

Table **2** lists the chemical composition of the modern wrought duplex stainless steels and includes also the first generation of duplex stainless steels as a point of reference.

It is common to define the corrosion resistance of duplex grades by their pitting resistance equivalence number [3] (PRE_N) as defined by Eq. 1:

$$PRE_N = \%Cr + 3.3\%Mo + 16\%N \quad (1)$$

While this number does not provide an absolute value for corrosion resistance and is not applicable in all environments, it does provide an overview of the expected resistance to pitting corrosion in an aqueous chloride solution. Some alloys contain an addition of tungsten, which is another element that acts to increase the pitting resistance of stainless steels. For these alloys, the pitting resistance is expressed as PRE_W, according to Eq. 2:

$$PRE_W = \%Cr+3.3\%Mo+1.65\%W+16\%N \quad (2)$$

The PRE_N or PRE_W number is commonly used to classify the family to which an alloy belongs. In general, materials having a pitting resistance number in the low 30's or lower are classified as lean duplex grades, those with PRE's in the mid 30's such as 2205, are classified as standard duplex, and those with PRE's of 40 or more are known as superduplex alloys [13]. Table **3** gives examples of different stainless steels grades, i.e. duplex, austenitic and superaustenitic grades with their main alloying components and the $PRE_{N/W}$ number.

The superduplex grades with a pitting index $PRE_{N/W}$ >40, contain 25% Cr, 6.8% Ni, 3.7% Mo and 0.27% N, with or without Cu and/or W additions (SAF 2507, UR52N, DP3W, Zeron100). This is the most highly alloyed grade for wrought products, and is specially designed for marine, chemical and oil engineering applications, requiring both high mechanical strength and resistance to corrosion in extremly aggressive enviroments (chloride-containing acids etc.).

In oil and gas extraction applications, duplex steels are used in the form of production tubes, e.g. tubes that transport oil up from the source to the oil-rig. The corrosive nature of an oil and gas well is increased by the presence of chlorides in water solutions, carbon dioxide, and hydrogen sulfide. The environment is considered sweet as long as no hydrogen sulfide is present. Carbon dioxide alone can cause high corrosion rates on carbon steel; however, it acidifies the solution. This is further accelerated if chlorides are present. An environment is defined to be sour when the partial pressure of hydrogen sulfide is above 0.3kPa (0.05 psi). At higher partial pressures, the corrosion rate on carbon steel is substantially increased by means of making the water phase more acidic and by forming an iron sulfide scale. Sulfide Stress Cracking is common in ferritic steels and in high-strength steels containing martensite. A

Table 2. Chemical composition in wt. % of wrought Duplex Stainless Steel grades with the corresponding Unified Numbering System and European Norm

Grade	UNS	EN	C	Cr	Ni	Mo	Mn	N	Cu	W
First generation DSSs										
329	S32900	1.4460	0.08	23.0-28.0	2.5-5.0	1.0-2.0	1.0	not-defined	23.0-28.0	2.5-5.0
3RE60	S31500	1.4417	0.03	18.0-19.0	4.3-5.2	2.5-3.0	1.2-2.0	0.05-0.10	18.0-19.0	4.3-5.2
UR50	S32404		0.04	20.5-22.5	5.5-8.5	2.0-3.0	2.0	–	1.00-2.00	–
Modern DSSs										
2304	S32304	1.4362	0.03	21.5-24.5	3.0-5.5	0.0-0.6	2.5	0.05-0.20	–	–
2205	S31803	1.4462	0.03	21.0-23.0	4.5-6.5	2.5-3.5	2.0	0.08-0.20	–	–
2205	S32205	1.4462	0.03	22.0-23.0	4.5-6.5	3.0-3.5	2.0	0.14-0.20	–	–
DP-3	S31260		0.03	24.0-26.0	5.5-7.5	5.5-7.5	1.0	0.10-0.30	0.20-0.80	0.10-0.50
UR52N	S32520	1.4507	0.03	24.0-26.0	5.5-8.0	3.0-5.0	1.5	0.20-0.35	0.50-3.00	–
255	S32550	1.4507	0.04	24.0-27.0	4.5-6.5	2.9-3.9	1.5	0.10-0.25	1.50-2.50	–
DP-3W	S39274		0.03	24.0-26.0	6.8-8.0	2.5-3.5	1.0	0.24-0.32	0.20-0.80	1.50-2.50
2507	S32750	1.4410	0.03	24.0-26.0	6.0-8.0	3.0-5.0	1.2	0.24-0.32	0.50	–
Zeron100	S32760	1.4501	0.03	24.0-26.0	6.0-8.0	3.0-4.0	1.0	0.20-0.30	0.50-1.00	0.50-1.00

Table 3. $PRE_{N/W}$ Number for Different Duplex Steel Grades, Austenitic and Superaustenitic Steel Grades

Grade	UNS	C	Cr	Ni	Mo	W	Cu	N	$PRE_{N/W}$
Lean Duplex	S32101	0.03	21.5	1.5	0.3	-	-	0.22	25
	S32304	0.02	23	4	0.3	-	0.3	0.10	25
Standard Duplex	S31803	0.02	22	5.5	3.0	-	-	0.17	35
	S32205		22.5	5.8	3.2	-	-	0.17	36
Superduplex	S32750	0.02	25	7	4.0	-	0.5	0.27	43
	S32760	0.03	25	7	3.5	0.6	0.5	0.25	42
Superaustenitic									
904L	N08904	0.02	20	24.5	4.2	-	1.5	0.05	35
254 SMO	S31254	0.02	20	18	6.1	-	0.7	0.20	43
Austenitic									
304L	S30400	0.02	18.2	8.1	0.3	-	-	0.07	20
316L	S21600	0.02	16.3	10.1	2.1	-	-	0.07	24
317L	S31703	0.02	18.4	12.4	3.2	-	-	0.07	30

typical application range for duplex steels of the type 22Cr and 25Cr is where the partial pressure of H_2S in the gas in the oil well lies in the area 1.37 to 34.5 kPa (0.2 to 5 psi).

The production tubes are supplied with a threaded finish and by coupling the tubes, they reach the necessary lengths. Because oil wells are situated at a considerable depth, the length of a production tube can become large and thus higher demands on mechanical properties are made. Material of the type 22Cr and 25 Cr, in an annealed condition, has only a yield point limit of only about 550 MPa, which could be increased with a cold rolled finish but this also limits the resistance of the material to stress corrosion caused by H_2S.

Patent US No. 6749697 B2 [14] has filled this gap in the development of an appropriate material with high strength, good impact toughness and corrosion properties for the oil industry. By this patent, it was found that through elevating the elements Cr, Mo and N to high levels an unexpected positive synergistic effect on the mechanical properties was obtained. It is previously known that Cr and Mo increases the solubility of N, but the content of nitrogen attained in this patent is higher than what was previously estimated to be the upper limit.

The high contents of Cr, Mo and N give the alloy a very high strength and simultaneously a good workability for extrusion into seamless tubes. The yield point in tension exceeds 758 MPa in the extruded and annealed condition. Besides exhibiting excellent mechanical properties, this new alloy has a high resistance to pitting corrosion and crevice corrosion in chloride environments as well as a high resistance to stress corrosion cracking caused by hydrogen sulphide. In addition, the alloy is suited for applications that require welding, such as butt-welded seamless tubes and seam-welded tubes for various coiled tubing applications. Consequently, it is especially appropriate for hydraulic tubes, such as umbilical tubes, which are used in order to control platforms in oil field.

Chromium is a very important element for improving the resistance of steels to the majority of corrosion types. Moreover, chromium increases the strength of the alloy. Additionally, a high content of chromium implies additionally a very good solubility of N in the material. Consequently, it is desirable to keep the Cr content as high as possible in order to improve the strength and corrosion resistance.

Molybdenum is an active element, which improves the resistance to corrosion in chloride environments, as well as in reducing acids. however, an excessive Mo.content in combination with a high Cr content means that the risk for intermetallic compounds increases.

Nitrogen partly increases the resistance to corrosion and partly increases the structural stability as well as the strength of the material. Besides, a high N content improves the reformation of austenite after welding, which ensures good properties for welded joints.

Another patent [15] related to high-alloyed duplex stainless steels refers to the effect of elevating the content of Cr, N, Cu and W in combination with relatively lower contents of Ni and Mo. In this case, the material shows high resistence to corrosion especially in acidic or basic environmets where high chloride contents are present.

Table **4** resumes the chemical composition in weigth percent (wt. %) of the new duplex stainles steels quoted in Ref.[14] and [15].

Paralleling the development of higher-alloy duplex grades for corrosive conditions, there has recently been a great interest in leaner compositions for wider purposes with lower amounts of expensive alloying elements. The best known commercial lean duplex steel is EN 1.4362 (UNS S32304) with about 23% Cr and 4% Ni. Lean duplex alloys are being used in many architectural applications due to their high strength, good corrosion resistance and lower cost compared to the commonly used Type 316. As an example, this steel has been successfully used as a construction material for blast and firewalls on offshore platforms, in bridges, lamp posts, exterior wall panels, windows frames, structural supports and roofing. An apparent and frequently used way to further reduce the cost is to reduce the nickel content and compensate with manganese and nitrogen additions. Manganese is an important austenite former and increases the solubility of nitrogen in the steel. In the automobile industry, an Armco patent was published [16] on a lean duplex steel with excellent as-cast

Table 4. Chemical Composition in Weigth Percent (wt. %) with the Balance of Fe of New Duplex Steels Patents. [(a)] Ref. [14], [(b)] Ref. [15]

US Pat.	C	Si	Mn	Cr	Ni	Mo	N	Cu	W	S
6749697B2[(a)]	0.05max	0-2.0	0-3.0	25-35	4-10	2.6	0-3-0.6	--	--	--
6312532B1[(b)]	0.05max	max0.8	0.3-4.0	27.0-35.0	3.0-10.0	0-3.0	0.30-0.55	0.5-3.0	2.0-5.0	0.010

properties, good ductility, toughness, corrosion and strength resistance and stability against thermal transformation to martensite due the high levels of manganese. This steel is particularly suited for thin-walled castings for automotive underbody components with a proportion of 30 to 60 porcent of austenite in ferrite. The American companies Armco Inc. and Autokinetics started with the development of an automotive modular frame made of stainless steel using nitrogen alloyed austenitic and duplex stainless steels. A commercial steel according to on Armco invention, Nitronic 19D (UNS S32001), containing essentially 20% Cr, 5% Mn, 1.1% Ni and 0.13% N was later proposed as a modular frame material in a new automotive concept. This alloy provides high yield strength (448 MPa), good drawing and welding characteristics, excellent chloride stress corrosion cracking resistance, and high cyclic oxidation resistance up to 982°C. It also exhibits high ductility (super plasticity) at high temperatures (982°C). Compared to similar duplex stainless alloys such as 2205, Nitronic 19D Stainless Steel is more economical but less corrosion resistant due to a lower alloy content (particularly molybdenum).

With the purpose of providing a ferritic-austenitic stainless steel of the type mentioned above, which still contains a lower amount of expensive alloy elements than todays commercially available duplex steels and austenitic stainless steels having comparable technical features, the EP 1327008 B1[17] belonging to Outokumpu Stainless AB developed a thermally stable, low nickel, general-purpose duplex grade with a corrosion resistance comparable to that of 1.4301 (UNS 30400) with undiminished welding properties in the as-welded condition. The condition for the austenite and the ferrite formers of the alloy, chromium and nickel equivalents were imposed as, $20<Cr_{eq}<24.5$ and $10<Ni_{eq}$. The result of this invention was a steel with a yield strength $Rp_{02} \geq 450$ MPa at room temperature and ≥300 MPa at 150º C, a microstructure which contains 35-65% ferrite and 35-65% austenite– preferably 35-55% ferrite and 45-65% austenite – a good structural stability, good general corrosion resistance– particularly a good stress corrosion resistance– and good weldability with very good reformation of austenite in the heat affected zone. Table **5** shows the chemical composition in weight percent of UNS S32304 and the duplex steel patents of Ref. [16] and [17].

The duplex steels have much in common with austenitic and ferritic stainless steels, but they have several unique advantages. They have better SCC resistance than most austenitic grades, more toughness than most ferritic grades and higher strength than most grades of either type. They also have the advantage of lower nickel content than comparable austenitic alloys while providing similar corrosion resistance in many environments. The combination of higher strength and lower nickel content makes duplex steels an attractive alternative to austenitic grades, especially when the cost of nickel is high.

DUPLEX STAINLESS STEELS: SOME USE AREAS

Modern DSSs have been on the market for many years, including the super duplex grade, which was developed about 10 years ago. During the Sixth International Conference on Duplex Steels, Charles [18] has presented an excellent paper about the extended applications and experience of DSSs in the industry. Due to the very fine-grained structure, nitrogen alloying, and ferrite and austenite mixture, the mechanical strength of DSSs is very high. DSSs may be used in many corrosive environments within the temperature range of approx -50ºC to less than 300ºC. Chloride containing process media or cooling water is common in the refining and petrochemical industry. Even at very low concentrations, the aggressive chloride ions may cause rapid failure if an improper material is selected.

Chloride stress-corrosion cracking is a rapid form of corrosion, and can cause severe problems of hydrocarbon processing plants when occurring in equipment such as heat exchangers. Standard austenitic stainless steels of the AISI 300 series are sensitive to SCC in chloride-containing environments above approx 60ºC. This limits the use of these steels since many heat exchangers in the process industries are working at higher temperatures. It was observed that heat exchangers are by far the most critical piece of equipment and that DSSs in most cases are chosen as the first countermeasure to combat this form of corrosion. As regards pitting corrosion resistance duplex, alloys are as resistant as austenitic alloys with comparable PRE numbers.

- Oil Production [19,20]:

Heat exchangers: DSSs are frequently used in oil-refinery heat exchangers. Typical applications are where there is a risk for SCC and localized corrosion as a result of chloride-containing process streams, cooling waters or deposits.

Crude Distillation: Atmospheric and vacuum distillation tower overhead systems are normally equipped with a large number of shell-and tube heat exchangers and of air coolers. The corrosive conditions are complex and their severity is highly dependent on how successful the process control is, particularly the hydrochloric acid dew point. Corrosion control methods include water washing

Table 5. Chemical Composition in wt% with the Balance of Fe of the Standard UNS S32304 and the Patented Duplex Steels [(a)] Ref. [16] and [(b)] Ref. [17]

Patent	C	S i	Mn	Cr	Ni	N	Mo	W	Cu
UNS S32304	0.03	1.0	2.5	21.5-24.5	3.0-5.5	<0.20	--	--	<0.2
US 4828630 [(a)]	<0.07	<2	4-8	17-21.5	1-4	0.05-0.15	<2	--	<1.5
EP1327008B1[(b)]	<0.07	0.1-2.0	3-8	19-23	1.1-1.71	0.15-0.30	Mo+W max 1.0		<1.0

and injection of ammonia, caustic or amine inhibitors. In general, results obtained with these measures are quite variable, and experience at different refineries can be diverse. In many cases it has been difficult to keep control of the operational parameters over longer periods. This has led to premature failure, and in many cases a material upgrade has been the only solution for safe operation. In the case of upgrading, a highly qualified material is necessary while intermediate steps in the material selection range will not offer a reliable solution. Failures have occurred on 22% Cr duplex in atmospheric overheads in conditions where severe ammonium chloride deposits have led to very short lifetime for carbon steels. Superduplex S32750 tubes, on the other hand, have been used successfully in both atmospheric and vacuum overhead condensers, showing that a high-alloyed super duplex can be a cost effective solution for such an application.

Hydrotreating: In hydrotreating, the main purpose is to remove sulfur from the intermediate and final refinery products. It has been observed that modern S31803 and S32304 DSSs have performed very well with no corrosion failure for some years. With older grade S31500, failures have been regarded as mainly attributed to bad welding and fabrication. These followed practices lead to excessive ferrite contents in the welded parts followed by hydrogen induced cracking. With modern duplex grades and use of welding procedures introducing N in the shielding gas, risk for excessive ferrite in the welds is low. This is shown by the fact that no failure has been reported to date with such modern types of duplex grades.

- Petrochemicals [19]:

Corrosive conditions experienced when processing many petrochemical compounds are less severe than the conditions experience in oil refineries. However, there are some major corrosion problems in the production of organic acids. In such conditions, duplex and superduplex come to their full advantage. For example, formic acid is the most aggressive of the organic acids. At temperatures up to 40ºC, AISI 304 may be used, while at higher temperature 316L can be employed if the concentration is low. At higher concentration and temperatures above 80ºC, higher alloyed stainless steels must be used to keep the corrosion rate low. The DSSs S32803 / S32205 and S32750 have good resistance within certain limits.

- Desalination plants [21, 22]:

Desalination may be defined as the art of producing fresh potable water from a saline supply at reasonable cost and with reasonable reliability. There are different techniques to desalt water and for production of industrial and high quantity of potable water, distillation and reverse osmosis (RO) are the most used. Reverse osmosis can be either BWRO (brackish water RO) or SWRO (seawater RO)**.** The major thermal processes are: Multi stage flash (MSFD) and multi effect distillation (MED)

Poor experience of conventional austenitic 300 series grades such as 1.4404 (316L) and 1.4438 (317L) for high-pressure parts in seawater plants has made highly alloyed grades of type S31254, e.g. 254 SMO, more or less mandatory for large SWRO plants. However, the high cost of alloying elements, such as nickel and molybdenum, has presented a need to look for more effective options. One solution is a superduplex grade S32750, e.g. SAF 2507. It has almost the same resistance to pitting and crevice corrosion as 254 SMO, it has twice the strength, and the cost is far lower. The feed for BWRO plants is often higher in salinity than the second pass of SWRO plants and the grade has to be selected accordingly, but the duplex 2205 should be a natural option.

- Automotive Applications: Stainless Steel for Lightweight Design:

Stainless steel is gaining increased interest from the automotive industry. The reason is the favorable combination of high strength and formability that many stainless steel grades provide. With a high energy absorption in crash situation added to this property combination, stainless steel can offer unique design opportunities for the automotive industry, opportunities that have just started to be explored. Lean duplex steels are the favorite because of their low cost.

CURRENT AND FUTURE DEVELOPMENTS

From the basic Type 304 (18% Cr, 9% Ni) composition, a number of developments have taken places which were designed to improve a particular property. These include:

- The addition of up to 0.5% N to improve the strength (solid solution strengthening) or to compensate for reductions in Ni content (Type 201 and 202)
- The addition of elements such as Al, Ti and P to produce precipitation-strengthening reactions
- The inclusion of high levels of Ni and Mo and moderate levels of Cu and N improve the resistance to stress corrosion of reducing acids.

A large number of standard and proprietary grades have been developed with the objective of increasing the resistance to reducing acids, pitting and crevice corrosion. Many of the steels can be regarded as simple extensions of Type 316 (18% Cr, 12% Ni, and 2.5% Mo) with higher Mo contents and with increased levels of Ni to preserve a fully austenitic structure. Some of these steels also contain up to 0.25% N which increases the strength and augments the Cr and Mo contents in improving pitting resistance according to Eq.1.

If the high Cr and Mo content of these steels are not complemented with a large addition of Ni, a duplex, ferrite plus austenite structure is obtained. Therefore, the characteristic properties of each phase will be also evident in the duplex material. Austenitic stainless steels have good weldability and low-temperature toughness, whereas their chloride SCC resistance and strength are comparatively poor. Ferritic stainless steels have good resistance to chloride SCC but have poor toughness, especially in the welded condition. A duplex microstructure with high ferrite content can therefore have poor low-temperature toughness, whereas a structure with high austenite content can possess low strength and reduced resistance to chloride SCC. The welding characteristics of duplex stainless steels are much more sensitive to minor within-grade variations in chemistry or processing than are austenitic stainless steels. The content of nitrogen plays a major role in the performance of duplex steel because nitrogen is a strong austenite former and largely responsible for the balance between phases and the materials superior corrosion resistance and welding properties. Recent improvements [23] in welding DSSs (Type 2205) have shown that reducing the ferrite amount in the HAZ improves the impact strength and widens the operation temperature range to lower temperatures. Besides, the influence of heat treatment after welding on the structure of the HAZ has shown the formation of secondary phases [24,25].

In the last years, some new duplex grades have been introduced in the market. Nowadays, the main target has been the new lean grades which contain less alloying elements than 2205 grade and can replace the 304 and 316 grades. For some more corrosion applications Mo, Cu and W are considered. The development of lean duplex with higher content of N and Mo, and replace part of the Ni by Mn, can certainly improve the progress of the duplex steels since it is possible to retain quality and reduce material cost (due to the reduction in Ni content). However, the real boost of the duplex steel generation depends on the successful industrialization of thinner gauges. Technical improvements are still to come.

The duplex family is now an industrial success and represents about 1% of the total stainless steel market. An annual growth of more than 10% is expected [26].

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ABBREVIATION

BWRO	=	Brackish Water Reverse Osmosis
CCCT	=	Crevice Corrosion Critical Temperature
CPT	=	Critical Pitting Temperature
DSS	=	Duplex Stainless Steels
HAZ	=	Heat-Affected Zone
MED	=	Multi Effect Distillation
MSFD	=	Multi Stage Flash Distillation
PCR	=	Pitting Corrosion Resistance
PRE	=	Pitting Resistance Equivalence Number
RO	=	Reverse Osmosis
SCC	=	Stress Corrosion Cracking
SWRO	=	Seawater Reverse Osmosis
UNS	=	Unified Numbering System
VOD and AOD	=	Vacuum and Argon Oxygen Decarburization

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