80 YEARS WITH DUPLEX STEELS, A HISTORIC REVIEW AND PROSPECTS FOR THE FUTURE

M. Liljas

Outokumpu Stainless AB, Sweden

Abstract

The paper presents reviews of the metallurgical and application developments of duplex stainless steels (DSS) during almost 80 years.

Introduction

Duplex or ferritic-austenitic stainless steels have a history almost as long as stainless steels. They attract a large interest from the industry although they constitute less than one percent of the total volume of stainless steel. The intention with this paper is to describe the historic development of this family of steels, show their merits and main application areas and try to analyse why the market share is still limited.

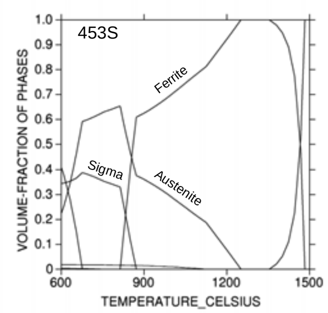
Historic metallurgical development

First generation DSS

Stainless steels were developed almost hundred years ago. The first grades were ferritic (martensitic) and austenitic steels. At an early stage it was found that introduction of some ferrite into austenitic stainless castings resulted in better castability and also increased the resistance to sensitisation and improved the proof strength. This development of austenitic castings was most probably the start of duplex stainless steels.

By 1930 two duplex grades were commercially available from Avesta Steelworks where stainless production started in 1924. [1] Grade 453E (26Cr-5Ni) was essentially alloyed with chromium and nickel and was intended for heat resistance, while grade 453S (26Cr-5Ni-1Mo) also had an addition of molybdenum to obtain improved aqueous corrosion resistance. This basic composition was later standardised in many countries (type 329) and has been used for further development of 25Cr duplex grades by many producers. Duplex castings were developed in Finland roughly in the same period. In the mid 1930's a French patent was granted to J. Holtzer Steelworks of a duplex alloy (21Cr-7Ni-2,5Mo), which originated from a mistake in the melt shop in adding too much chromium to an austenitic steel. [2, 3] Typical compositions of the first generation DSS are listed in Table 1.

Characteristic for the first duplex grades were relatively high carbon contents, since efficient process techniques for decarburization were not available. Intentional nitrogen additions were not practiced and this element was hardly mentioned. Further, the phase balance was not optimised to present standards. Calculations of the phase fractions for two of the first duplex grades show great deviation from today's DSS. This is illustrated in Figure 1 where grade 453S has a highly ferritic composition with more than 70% ferrite at 1050°C while grade UR50 only contains about 33% ferrite at this temperature.



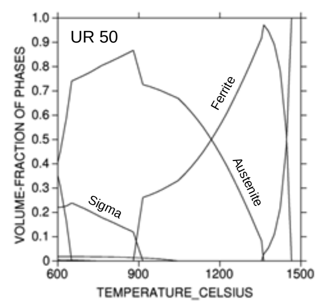


Figure 1. Equilibrium diagrams for early duplex grades using ThermoCalc TCFE5 database.
Used compositions: 453S: 0.09C, 0,4Si, 1,5Mn, 26Cr, 5Ni, 1.5Mo, 0,04N
UR50: 0.09C, 0.4Si, 2Mn, 21Cr, 6.5Ni, 2.5Mo, 0.04N

Judging from these differences, various effects on steel performance could be expected. Due to its high ferrite level grade 453S was sensitive to full ferritization during thermal cycles such as in welding. UR50 tended to show limited ductility as a result of improper phase balance at hot working temperatures.

In the1950's it was reported that DSS showed good resistance to chloride stress corrosion cracking (SCC). One alloy specifically developed to combat SCC was 3RE60 developed by Sandvik. [4] This was a low carbon steel with a relatively high level of Si and no nitrogen deliberately added.

The first duplex alloy with intentional addition of nitrogen was Ferralium, which in turn was developed from Grade 26-5-1 castings but intended for both cast and wrought forms. It was claimed that addition of nitrogen reduced the problems both with cracking during casting and with welding, by producing more ductile welds. [5] Having about 25%Cr and appreciable amounts of molybdenum and copper this steel exhibited a high strength and high corrosion resistance. This steel was the forerunner to many so-called 25Cr DSS and to superduplex grades described later in this paper.

With increased use in welded constructions it became clear that many DSS could suffer from intergranular corrosion (IGC) in the HAZ due to transformation to more or less 100% ferritic microstructure, which is much more prone to carbide precipitation than austenite. An alloy was developed in the 1970's that was stated to be resistant to this form of corrosion. [6] This was mainly because of a more austenitic composition able to resist full ferritization in HAZ, but also the addition of nitrogen that improved the austenite reformation upon cooling. The steel grade in question was 1.4462, originally with quite a wide nitrogen range, 0,08-0,20%N.

Table 1. Typical compositions (in weight %) of the first generation DSS.

Grade	ASTM	C	Cr	Ni	Mo	Cu	Other	PRE
453S	AISI 329	0,09	26	6	1,5	-		31
UR50	S32404	0,09	21	6,5	2,5	1,5		30
3RE60	S31500	0,03	18,5	5	2,5	-	1,7Si	27

Second generation DSS

The remedy to IGC was addition of nitrogen, which had the power to restore the HAZ microstructure. It was also shown that nitrogen was an important element for increasing the pitting corrosion resistance. This positive effect of nitrogen on weld microstructure and corrosion resistance was further optimised and thus a second generation of DSS was born. One important feature with nitrogen alloying in duplex steels is to move the phase balance to a more austenitic one and to enhance the austenite reformation from ferrite on cooling from high temperatures due to its high diffusion rate. By this para-equilibrium condition the paradox of increasing nitrogen content to avoid nitride precipitation was achieved. There is a general agreement that "equal" proportions of ferrite and austenite offer optimum properties of duplex steel. Just how large deviations from this balance can be accepted is a never-ending discussion that should be avoided and be replaced with requirements on product properties reflected by the phase balance.

Along with the increased knowledge of utilizing nitrogen as alloying element the process techniques in steel mills were improved. With AOD and similar refining vessels it was possible to add nitrogen in an inexpensive way and to reduce the levels of harmful impurities. A pioneer alloy belonging to the second generation DSS is the modern version of 1.4462 often designated 2205 or 22Cr, which is still the DSS with the highest yearly produced tonnage. However, several new developments emerged during the 1980's both in the direction of higher and leaner compositions.

As mentioned above, several 25Cr duplex grades have been used since the start in 1930's and in many of them have increasing alloying content. As mentioned earlier Ferralium was the first higher alloyed grade with intentional nitrogen addition but there were several more 25Cr grades with similar compositions, some of which are listed in Table 2. Copper additions were made to improve corrosion resistance in reducing acids and alloying with tungsten was used to further improve the pitting resistance.

In mid 1980's higher alloyed 25Cr DSS were introduced under the collective description superduplex steels. Zeron 100 was alloyed with molybdenum and tungsten as well as copper while for SAF 2507 the molybdenum and nitrogen were the main elements to increase corrosion performance. One of the features with SAF 2507 was that an optimum solution annealing treatment resulted in equal pitting corrosion resistance of austenite and ferrite. This was predicted by thermodynamic equilibrium calculations using the ThermoCalc database. [7]

Due to the high levels of Cr, Mo, W and N these steels showed very high pitting corrosion resistance. Using the frequently used ranking equation for pitting corrosion resistance; Pitting Resistance Equivalent,

$$PRE = Cr + 3.3(Mo + \tfrac{1}{2}W) + 16N$$

they reached the level of 40, which is often used as a definition of a superduplex steel.
An alternative way to improve corrosion resistance is to augment the Cr level further. This was done with SAF 2906, which shows superior performance in oxidizing acids present in the urea industry. The increasing alloying content makes the microstructure more prone to precipitation of intermetallic phases with an adverse effect on corrosion resistance and ductility. There has been a vivid discussion concerning the individual effect of molybdenum and tungsten and the conclusion is that replacement of Mo by some W has a negligible effect on phase stability as well as corrosion resistance. [8] Naturally, further upgrading of the alloy content will decrease the two-phase stability. However, a recent development of a hyperduplex grade, SAF 2707HD, with a PRE of about 49 due to very high Cr, Mo and N levels can be manufactured and welded without precipitation of intermetallic phases. [9]

It has been claimed that nitrogen delays the formation of intermetallic phases in DSS in a similar way as in austenitic grades. However for DSS there is only a small effect of nitrogen on the driving force for sigma phase formation, because nitrogen does not change the chromium activity as result of a simultaneous change in phase fraction. [10]

For lower alloyed duplex steels the risk of intermetallic phase formation is naturally smaller and lean duplex grades have received much interest in recent years. Already in the mid 1980's Sandvik introduced SAF 2304, now an established grade. To minimize raw material cost lean DSS alloys with low nickel contents compensated with manganese and nitrogen have been launched. Outokumpu LDX 2101, with high manganese and nitrogen contents shows high strength and good corrosion performance even in the as-welded condition. The stability to intermetallic phase formation is high and the dominating phases precipitating after shorter times are carbides and nitrides that are less harmful to properties. With low nickel contents the impact toughness is slightly reduced, but fracture mechanics testing show that the material still has a low transition temperature to brittle behaviour.

Table 2. Typical compositions (in weight %) of different groups of DSS.

	Grade	EN	ASTM	Cr	Ni	Mo	Cu	W	N	PRE
22Cr	2205	1.4462	S31803	22,5	5	3,2	-		0,17	36
	AL2003	-	S32003	21	3,6	1,7			0,17	29
25Cr DSS			S32900	26	5	1,5			0,04	32
	44LN	1.4460	S31200	25	5	2			0,15	34
	Carpenter 7Mo		S32950	25	5	2			0,15	34
	Ferralium 255	-	S32550	26	5,5	3	1,7		0,17	39
	Uranus 47N		S32550	25	6,5	3			0,18	38
	Sumitomo DP3	-	S31260	25	6,5	3	0,3	0,3	0,16	38
Super DSS	Zeron 100	1.4501	S32760	25	7	3,5	0,5	0,6	0,25	42
	SAF 2507	1.4410	S32750	25	7	4			0,27	43
	UR52N+	1.4507	S32520	25	6	3,5	1,5		0,25	41
	DP3W	-	S39274	25	7	3		2	0,25	42
	SAF 2906	1.4477	S32906	29	7	2,2			0,35	42
	DP28W	-	S32808	27,5	7,7	1		2	0,35	40
	SAF 2707	-	S32707	27	6,5	4,8			0,4	49
Lean DSS	2304	1.4362	S32304	23	4	0,3	-		0,1	26
	19D	-	S32100	20	1,6	0,3	0,3		0,13	23
	LDX 2101	1.4162	S32101	21,5	1,5	0,3	0,3		0,22	26
	UR2202	1.4062	S32202	22	2	0,3	0,3		0,2	26

Prospects for further development of DSS

There is an active development of new duplex alloys both in the direction of high and low alloy regimes. This has resulted in several proprietary grades that show very similar property profiles and it could be argued that they should be listed in the same standard. Consequently, it is very plausible that new duplex grades will be introduced in the near future as there may be application areas lacking suitable DSS alternatives. An important alloy design tool is the thermodynamic database ThermoCalc that is frequently used to predict phase equilibria.

There is a probably a limit in PRE value of about 50 due the increased risk of intermetallic phase formation when exceeding that level. Replacement of Mo with W would not offer any increased margin in this respect. As the high levels of Cr and Mo result in high solubility of nitrogen, superduplex grades can be made with nitrogen levels of 0,4% without problems with pore or nitride formation in welding. Further development of superduplex and hyperduplex grades is expected with this upper alloying level.

Naturally there is room for new DSS with tailor-made property profiles, e.g., high corrosion resistance in certain environments and specific mechanical or fabrication properties. This can be made with variants of existing grades or with new alloys. One example is addition of copper to improve corrosion resistance in certain acids.

Historical application review

The two first duplex grades developed at Avesta Steelworks in 1930 were mainly produced as castings and rolled bars but to some extents also as plate. The heat resistant grade 453E was used as castings, e.g., for molten lead equipment and for pyrite kiln inserts. The acid resistant grade 453S was used in the sulphite pulp industry for pumps, valves and circulation systems.
The interesting properties of the ferritic austenitic grades resulted in substantial tonnages of duplex material. Thus, in 1932, the duplex grades amounted to more than 6% of the total stainless steel production of Avesta Steelworks, which then was 5500 metric tonnes.
It was not until 1947 that grade 453S was included in the Swedish standard as SIS 2324. Later, this steel also was listed in USA as AISI 329 and many 25Cr duplex alloys have been developed with this as a base. The French grade Uranus 50 produced by J. Holtzer Steelworks was used with similar products and applications as 453S. Examples that have been reported are cast propellers, dying machines as well as vessels for petrochemical and chemical, food and pulp & paper industries. [11] J. Holtzer Steelworks also offered heat resistant duplex grades. In 1960s Sandvik introduced 3RE60, which found applications in tube heat exchangers in process industry.
A more widespread use of duplex steels was associated with the introduction of the second generation of DSS. An important commercial break-through was the selection of the 22Cr duplex grade for natural gas pipelines in oil & gas industry in late 1970’s. Since then, DSS have been used extensively for such applications. Inclusion of the modern duplex grades in pressure vessel standards, also in late 1970’s, made it possible to use DSS in pressurized systems such as pulp digesters where the high strength could be utilized. The excellent corrosion resistance in acids of DSS made them ideal for chemical tankers and large tonnages of DSS material started to be used for this application in the 1980’s.
In the expanding offshore oil & gas industry there was a need for high performance materials and 6Mo austenitic steels were selected due their high resistance to seawater. However, superduplex grades such as Zeron 100 and SAF 2507 were developed to compete with the superaustenitic grades with good success. Today, large quantities of superduplex tubing are used in umbilicals for the control of sub-sea systems. Also in the offshore industry, lean duplex steel has been used for blast walls on oil platforms based on the high strength combined with sufficient corrosion resistance.
Other areas where DSS have partly replaced austenitic alloys are flue gas cleaning systems and seawater desalination plants. In the latter case a combination of duplex grades is used to meet different aggressive environments.
In more recent years lean duplex grades have emerged as an alternative to type 304 and 316 austenitic grades. This development has been very successful. The aim with these grades is also to replace construction steels, deriving on advantages of high strength and low maintenance costs. Increased use of such steels is now seen in bridges, storage tanks and other construction work. Lean DSS are also used for construction of transport vehicles.

The launching of the hyperduplex steel SAF 2707HD means a further expansion of the applications for DSS. With its high PRE this steel will resist seawater at high temperatures and will be used in very aggressive refinery environments, competing with nickel base alloys.

Prospects for commercial development

DSS have now been available for almost 80 years on the market and yet they only represent about 1% of the total stainless volume. This cannot be attributed solely to conservatism in the user segment but also to various obstacles at suppliers and fabricators. No doubt there is a great potential for further volume increase considering the numerous advantages DSS offer compared to austenitic and ferritic stainless steels. Numerous articles have shown the technical benefits and cost saving in replacing austenitic grades. In recent years lean duplex grades, competing with austenitic commodity grades, have shown a large volume increase partly due the high nickel prices. It is therefore natural to anticipate further increase in application areas where austenitic commodity grades are used. ISSF data show that type 2205, competing with comparatively high alloy austenitics, has been and is still the dominating grade. [12] It has also been pointed out that hot rolled plate, which represents a small volume of the total stainless consumption, is the dominating duplex product. Development of coil products is therefore likely to be a prerequisite for larger expansion of DSS use. However, there are many applications where the ease of fabrication (forming, welding) is a governing reason for the selection of austenitic steels. Here, it can be difficult to convince the user to accept a material with high strength and different welding procedures. Also for many thin gauge applications the increased strength of DSS cannot be utilized to reduce thickness, thereby missing the cost advantage with duplex grades. Further, the limitations in surface finishes for DSS compared to austenitic grades are also claimed as a limiting factor for growth.

Therefore skilled technical support and inventive design ideas are required to widen the application areas for DSS. It is also of great importance to have duplex steels readily available to fabricators and end users. Finally, environmental reasons for using DSS as construction material; low maintenance costs and very high material circulation, will be further important arguments to enhance the selection of DSS.

References

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