Duplex families and applications: a review
Part 1: From Duplex Pioneers up to 1991

This two-part article summarizes a review paper devoted to the key developments and main applications of duplex stainless steels (DSS) presented at Duplex World Seminar & Summit 2014¹. The article takes advantage of my personal involvement in DSS developments in the various positions I have held during my career at Creusot Loire (industrie), CLI, Industeel, Usinor, Arcelor, ArcelorMittal & Aperam between 1984 and 2015. Part 1 reverts to the early ages and developments until 1991 (DSS Beaune’91 conference²) while part 2 will be devoted to the latest market and products developments including the so-called lean duplex grades without Mo and very low Ni content. Future possible trends and new applications will also be discussed.

By Jacques Charles, Jacques.charles142@gmail.com

Duplex stainless steels are designed to have a 50% α/50% γ microstructure. The dual phase microstructure is designed to contain significant amounts of Cr%+Mo% (ferrite stabilizing elements providing the corrosion resistance properties) and austenite forming elements, mostly Ni and N. The two-phase microstructure makes it possible to obtain a smaller grain size of ductile austenite (γ) in a matrix of ferrite (α) that reinforce the steel. They can be considered as a “pseudo-composite” microstructure combining high strength and corrosion resistance properties.

Figure 1 presents a duplex microstructure in an exotic Fe-Mn-Al-C diagram³ while, most of industrial DSS are issued from the Fe-Ni-Cr-Mo-N diagram and can be presented in a Schaeffler diagram often used for welding microstructures (Figure 2). The combined Cr and Mo additions provide the level of corrosion resistance in most of the media while the Ni and N contents provide for a given Cr%+Mo% with an almost 50% α/50% γ balance. Ferritic grades have almost no Nickel and Chromium content can be kept as low as 11%. The level of Chromium additions (11 – 25%) is, of course, one of the major players when considering corrosion resistance properties. Austenitic grades with 18%Cr need a minimum of ...8%Ni (without N or Mn additions) to stabilize the gamma phase. Higher Cr + Mo additions require even more Ni (or N) additions to stabilize the single-phase γ microstructure. Duplex grades with a 50% α/50% γ are located

![Figure 1. Duplex microstructure (54% austenite in blue) for a Fe-30Mn-8 Al-2Ni-0.2C experimental alloy.](image1)

![Figure 2. The Schaeffler diagram which illustrates the stainless steel families versus chemical analysis.](image2)

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www.stainless-steel-world.net
between the ferritic and austenitic areas. There chemistry is characterized by significant contents of Cr%+Mo% while the Nickel content, an expensive alloying element, remains at about 50% of that of an austenitic grade having similar corrosion resistance properties providing significant alloying cost savings. The three classical families of duplex grades are presented Figure 2: the 2304 Mo free grades, the standard duplex 2205 and the super duplex grades of 2507 type. As observed it is almost impossible to develop duplex grades having less than 19...20%Cr without possible formation of martensite.

The early days
Who first started to produce duplex grades? This simple question does not have a very obvious answer! The first phase diagram, presenting the two-phase austenite/ferrite area in a Fe/Ni/ Cr ternary diagram, seems to have been published in the late 1920s by E C Bain of Union Carbide®. The first industrial DSS were produced in Europe most probably in Sweden, UK or France in 1933. J. Holzer Cie in Firminy produced his first duplex melt... after an alloying mistake! The target was an 18%Cr-9%Ni-2.5%Mo and the final chemistry was: 20%Cr-8%Ni-2.5Mo. The unexpected grade contained a very high ratio of ferrite in an austenitic matrix. The grade was investigated at the Unieux R&D centre and the excellent resistance to intergranular corrosion even in the sensitised condition was quickly identified. The discovery was patented in 1935 (ref. N°803-361) and a second patent was taken in 1937 (New stainless Alloy – ref 49.211)®. The latter patent included chemistries containing copper additions in order to improve the corrosion resistance in several solutions including sulphuric acid media. In 1940, another patent (ref 866-685) with Mo and Cu additions having a two phase microstructure and being subject to hardening effects by heat treatment in the 400-500 °C range without losing corrosion resistance properties and embrittlement effects was obtained.

It is reported that in Sweden, Avesta produced since 1929 a duplex grade called 453 S, a 26Cr-5Ni-1.5Mo alloy with production records of 362T in 1932. This was produced mainly as castings, bars and some plates to produce the first welded vessels for several applications such as a sulphite pulp & paper industry. The grade can be considered as a duplex pioneer grade. The grade was also developed to reduce inter-granular corrosion, a common problem encountered in the early high-carbon austenitic stainless steels. That research and industrial production of DSS grades realized in Sweden supported the development of the 3 RE 60 of SANDVIK extensively used to manufacture seamless pipes. Duplex castings seems also have been produced in Finland since the early 1930s®. In the USA also, some castings containing very high amounts of ferrite melted in the 1930s could be considered as duplex microstructures.

Post WWII
The Swedish grade 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, plates, seamless tubes, forgings and cast DSS grades have been used for a variety of processing industry applications including vessels, heat exchangers and pumps.

In France, the UR 50 grade, pioneer of the "French" duplex grades with 20-35% ferrite, (UNS S32404), was marketed in various product forms, including forgings, for industries such 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

<table>
<thead>
<tr>
<th>Grade</th>
<th>C%</th>
<th>Cr%</th>
<th>Ni%</th>
<th>Mo%</th>
<th>YS kg/mm²</th>
<th>UTS kg/mm²</th>
<th>A%</th>
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<tr>
<td>453 E</td>
<td>0.09</td>
<td>26.0</td>
<td>4.0</td>
<td></td>
<td>50</td>
<td>65</td>
<td>26</td>
</tr>
<tr>
<td>453 S</td>
<td>0.09</td>
<td>26.0</td>
<td>5.0</td>
<td>1.5</td>
<td>55</td>
<td>72</td>
<td>22</td>
</tr>
</tbody>
</table>

Data given in 1946 by Avesta Jerverks – 453S was more commonly used

Figure 3. Early age duplex stainless steel grades developed in Sweden and France were used in pulp & paper industry.

Figure 4. Composition of two early duplex grades

Figure 5. Pau, south of France, Lacq oil & gas field (very sour: H₂S=15% CO₂=10%, water 1%, P= 650 bars T=140°C) and Orenburg (Russia) utilized UR50 cast valves in the early 50th.
vacuum ensured carbon removals, rudimentary de-oxidation and restricted nitrogen ingress. Nevertheless, plate products remained sensitive to edge cracks. 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 of DSS to a few specific applications needing high corrosion resistance properties.

One of them concerned the Lacq Oil & gas field, discovered in the 1950s, near Pau, south of France (one of the few oil & gas reservoir discoveries in France). The discovery brought a lot of excitement in the country. However the Lacq 3 “evaluation” drilling hit an extremely sour gas field. The carbon steel drilling assembly and protection equipment failed in a matter of days. In December 1951, a 30 meter high geyser roared over the area. The gas had to be flared and American gas fire fighter Myron Kinley was called to help. After stopping the eruption two months later, Kinley declared: “Tap the hole, plant grass, and bring the cows back”.

However in France the exploitation of the field was considered a “national emergency” as very few oil fields were identified in the country. Several research centres (Ecole Centale, Le Creusot, Unieux), steel producers (Pompey, CAFL, Le Creusot) and SNPA (now TOTAL, which still operates its world class sour gas testing laboratory at Pau), joined forces to solve the H2S problem. As the organic coatings used by American companies in less corrosive conditions were not satisfactory in this case, metallic solutions were tested and used. Space is too restricted here to discuss even a small part of the findings but duplex steels were finally selected and did their part of the job.

Well heads and Mac Evoy chokes were used for several years in the Lacq field and in another smaller sour gas field of the area. The experience gained during this period was transferred later to other very sour gas field such as Orenburg (Russia).

During the late 1960s a significant Ni shortage period occurred, which highlighted interest in duplex grades. The grades remained unfortunately difficult to hot roll since chemical analysis including the control of residual elements was difficult to achieve.

The start of mass production
With the 1970s the new duplex grade process routes with VOD/AOD + continuous casting made it possible to melt and transform at lower cost and with acceptable yield. The diversity of the duplex family had started! The first main challenges were high corrosion resistance grades, targeting the process industry mainly in plates and complementary products. Weldability remained poor and productivity of the manufacture of vessels remained low and challenging. Welding procedures were very tight, particularly for the more alloying grades and only very dedicated manufacturing shops could handle such specific products.

In the 1970s Langley Alloy developed a famous super duplex grade, the well know Ferralium 255 (UNS S32550) with 25%Cr and high Mo additions. The grade had nitrogen additions but far behind nowadays levels for super duplex grades; it remained difficult to weld.

The benefits of nitrogen addition
The “old” duplex stainless steels with rather low nitrogen additions had large coarsened ferritic grains in the HAZ with often γ₂ or nitrides precipitations, which had detrimental effects on both toughness and corrosion resistance of the welded structure.

### Table 1. Composition of Jacob Holzer’s grades

<table>
<thead>
<tr>
<th>Grade</th>
<th>Cr%</th>
<th>Ni%</th>
<th>Mo%</th>
<th>Mn%</th>
<th>Cu%</th>
<th>N%</th>
<th>YS kg/mm²</th>
<th>UTS kg/mm²</th>
<th>A%</th>
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</thead>
<tbody>
<tr>
<td>UR FL</td>
<td>0.08</td>
<td>20.5</td>
<td>2.7</td>
<td>2.8</td>
<td>1.5</td>
<td>40</td>
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<td>26</td>
<td></td>
</tr>
<tr>
<td>UR CH</td>
<td>0.2</td>
<td>22.5</td>
<td>3.5</td>
<td>2.5</td>
<td>1.0</td>
<td>0.2</td>
<td>53</td>
<td>85</td>
<td>10</td>
</tr>
<tr>
<td>UR 50</td>
<td>0.05</td>
<td>20.5</td>
<td>8.0</td>
<td>2.5</td>
<td>1.5</td>
<td>40</td>
<td>65</td>
<td>35</td>
<td></td>
</tr>
</tbody>
</table>

Among these grade, only UR 50 had commercial success.
During the 1980s and 1990s the new generation of duplex grades with increased nitrogen content was developed. Nitrogen additions appeared to be extremely important in duplex stainless steels. It contributes to several properties including the high temperature stability of the two-phase microstructure particularly in the welded areas (Fig. 6). Nitrogen is also known to improve the localized (pitting and crevice) resistance properties of stainless steels. These two major contributions explain why nitrogen content in the duplex grades has been continuously increased up to levels close to the solubility limit of the grades. Cr and Mo additions increase the nitrogen solubility of the DSS. As a result higher N contents are considered for the super-duplex grades. Since the end of the 1980s a complete range of DSS with optimum nitrogen additions has been supplied making it possible to have an alternative cost competitive material to the costly high corrosion resistance austenitic grades.

**New worldwide applications**

In 1972, 3RE60 (UNS S31500) duplex suction rolls were introduced in Sweden. In most cases they were replacing centrifugally cast bronze rolls.

Their corrosion resistance was adequate and fatigue corrosion resistance including in caustic media was much higher than that of harder martensitic grades. From the 1970s duplexes also started to replace heavy C-Mn plates used to manufacture digesters. This made it possible to reduce maintenance costs, increase the lifetime of the pressure vessels and still accept more stringent conditions needing increased severity of cooking cycles. In 1974 Creusot Loire supplied clad duplex UR 47 grade (UNS S31200/25Cr3Mo) at the cellulose des Ardennes plant in Harnoncourt, Belgium. They were replaced after 40 years in service by solid duplex of the 2205 type. Duplex in solid form is now a worldwide standard for digesters and many other applications in the pulp and paper industry.

Starting in 1972 with the supply of UR 50 (21%Cr, 7%Ni & 1.3%Mo) DSS for the manufacture of 3 deck tanks of the chemical tanker, duplex started also to be recognized as the optimum material selection choice for external or internal tanks. Orders of more than 10000 T were placed (Fig. 8). Its multi-media general and localized corrosion resistance, high strength and fatigue corrosion made it possible to replace coated and clad carbon steel with a significant advantage when considering life cycle costs.
The oil & gas industry has always been one of the most active areas for DSS. Many usages of DSS in Europe (north sea fields) were developed and it started to become the standard. Super duplex grades were selected for seamless tubes for umbilicals, for water systems (first experiences in Zeron 100 but nowadays challenged by composite materials), 2205 grades for risers, solid and clad plates for separators, etc. The first big USA project supplied by Creusot Loire (now Inducteel, Arcelor Mittal) was the Shell McElmo Dome project for a CO2 gas gathering project (Mittal) was the Shell McElmo Dome, etc. The first big USA project supplied by Creusot Loire (now Inducteel, Arcelor Mittal) was the Shell McElmo Dome project for a CO2 gas gathering project for enhanced oil recovery (EOR) where 1200 Mt (1982/1983) of UR45N (UNS S31803) plates were converted into 38 km of pipes by BSL-TR and Butting pipes manufacturers.

Since the 1980s the chemical industry has taken advantage of the properties of DSS. This includes reactor vessels for phosphoric acid production (Morocco phosphoric acid producer plants and later at Agrifos producer of fertilisers in Pasadena USA plants – replacement of acid bricks and coated CMn steels), sulphuric acid media, coprolactam units including those with the Russian grade 08Ch21N6T, PVC strippers, aldehyde columns, and many more applications where mainly 2205 & 2507 type duplex grades were selected in plates, forgings, castings, bars, seamless tubes and complementary products.

**Conclusion: Evolution of DSS chemistries until the 1990s**

Since the early days, several duplex stainless steel chemistries were developed. The PRENW value %Cr+3.3% (Mo+0.5W)+16N was included in the range 22-33 although the grades had almost no nitrogen specific additions. In the early days, a full family of DSS grades with Cr content were included in the 18-25% range, and Mo as well as Cu additions were produced. Super duplex and lean duplex grades were already developed! Between the early 1930s and 1991 Beaune conference, nitrogen was progressively increased until the solubility limit to avoid detrimental nitride precipitations when considering toughness or corrosion resistance properties.

In 1991 during the DSS Beaune conference, nitrogen was almost agreed that the duplex family could be restricted to the duplex and lean duplex grades were already developed! Between the early 1930s and 1991 Beaune conference, nitrogen was progressively increased until the solubility limit to avoid detrimental nitride precipitations when considering toughness or corrosion resistance properties. In 1991 during the DSS Beaune conference, nitrogen was almost agreed that the duplex family could be restricted to the duplex and lean duplex grades were already developed! Between the early 1930s and 1991 Beaune conference, nitrogen was progressively increased until the solubility limit to avoid detrimental nitride precipitations when considering toughness or corrosion resistance properties. In 1991 during the DSS Beaune conference, nitrogen was almost agreed that the duplex family could be restricted to the 2304 lean duplex, the 2205 “standard” duplex – with a new UNS number S32205-grade and the super-duplex grades 2507 with possible Cu or/and W additions for specific applications. The new mass production routes included the developments of VOD/AOD and continuous casting technologies, the new chemistries with optimum nitrogen additions and the control of the residuals elements providing improved corrosion resistance, weld-ability and availability of the products made it possible to develop several new markets for the DSS. Among them the most popular were the oil & gas, pulp & paper and chemical industries. The grades were selected mainly in process projects.

The duplex grades made it possible to reduce costs and improve lifecycle cost properties. However they remained technical grades requiring technical knowledge not only from the steel producers but also for the “transformers” and owner of the equipment.

**Read Part 2 of this article in September issue.**

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