Part 3: The lean duplex grades

Part 1 of the article presented the pioneer experiences up until the 1991 Beaune Duplex Stainless Steel conference. Part 2 outlined how, from the early 1990s, users of duplex gained in experience and confidence as a result of its successful application and technical knowledge gained through R&D activity. Significant improvements were observed in order specifications; the availability of products improved; and some key industrial players provided worldwide marketing and technical support through dedicated development teams. This month, Part 3 looks at the development of the lean duplex grades. Some general comments to conclude this article series are also included.

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Development of lean duplexes

While lean duplex stainless steel (DSS) is considered to be a modern grade by some, in fact a lean duplex grade - i.e. DSS grade without Mo and restricted Ni, addition – was already developed in France before the 1960s (URF1 – 21Cr%1.5Cu). Shortly afterwards Ugine developed grade AF20, a 20% Cr DSS with almost no Mo and Cu. The grade enjoyed limited commercial success.

By the late 1980s, Sandvik AB had obtained a lean duplex patent. Extensive marketing of the S 32304 lean duplex, mainly for seamless pipes, was undertaken. Industeel and the former Avesta started the production of plates a few years later. The grade was designed to substitute stainless steel 304 & 316 austenitic grades in many applications, taking advantage of a reduction in expensive alloying costs (Ni and Mo) and further costs savings offered by the grades having higher mechanical properties, particularly in the design of pressure vessels. The grade was designed with limited nitrogen additions to avoid nitride precipitation (see Table 1). The grade was not easy to manufacture as proved to be very sensitive to etch cracks and slivers. The grade had only limited success and even the production of seamless pipes was delayed. The original target of producing massive volumes of DSS failed at that time. The grade was selected for a few projects and still remains available, with the old chemistry, mainly in plates and sheets.

Table 1. Chemical analysis of lean DSS

<table>
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<tr>
<th>Grade / Standards</th>
<th>Mn</th>
<th>Ni</th>
<th>Cr</th>
<th>Cu</th>
<th>Mo</th>
<th>W</th>
<th>N</th>
<th>PREN</th>
<th>PRENW</th>
<th>PRENMn</th>
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<td>5.1</td>
<td>1.5</td>
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<td>0.1</td>
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<td>0.15</td>
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<td>FDX 25</td>
<td>3.0</td>
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<td>20.2</td>
<td>0.0</td>
<td>0.4</td>
<td>0.0</td>
<td>0.22</td>
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<td>2.5</td>
<td>1.0</td>
<td>20.0</td>
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<td>0.4</td>
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<td>0.0</td>
<td>0.21</td>
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</table>

1) PREN = Cr%+3.3Mo%+16N% taking into account the bulk chemistry.
2) PRENW = Cr%+3.3(Mo%+0.5W%)+16N% taking into account the bulk chemistry.
3) PRENMn = Cr%+3.3Mo%+16N% - Mn% taking into account the bulk chemistry.
Recent developments
In the last 15 years the dream of large-scale DSS production rose again and was supported by significant increases in Ni and Mo prices. New grades with significant amount of nitrogen (close to 0.2%), no Mo and very low Ni (less than 2%) were developed in all continents. In Europe the major stainless steel producer proposed the S32101 (LDX2101 from Outokumpu) and S32202 (UR2202 from Indussteel / ArcelorMittal and Aperam) (Table 1). The latest grade was designed to keep corrosion resistance at the level of the 316 stainless steel grade with reduced amounts of Mn and 23% Cr. Other grades were developed, such as S32001 (Nitronic 19D from Acerinox / AK steel), the lowest alloying duplex grade of the lean duplex family. The grade is subject to martensitic transformation under plastic deformation.
America has also been active with the launching of S82011 (ATI 2102) while Asia has contributed to the extension of the lean duplex family with the development of the S81122 (NSSC 2120). Other grades were introduced to the market include grade 1.4669 from Ugine (UGI 4669) or S32202 mod (Indussteel/Ugine) with more than 2% Cu for improved machinability, cold deformation ability and optimised structure stability.
Recently the former 2304 grade has been ‘redesigned’ (UNS S 32304) / 2304Mod), mainly by enhancing N additions which make it possible to further increase the mechanical properties of the grade. The latest grade introduced among the lean duplexes is FDX 25 from Outokumpu, a grade designed to take advantage of the TRIP effect (austenite transforms into martensite during cold deformation). For this reason the Cr content is kept at a relatively low level1.

The differences in chemistries between the lean duplex grades are significant; 6 points for the PREN number, which is equivalent to the difference between a 304 and a 316 austenitic grade! Figure 1 illustrates the pitting corrosion resistance ranking of DSS versus the chemical analysis. The first result is that the lowest

Figure 1. CPT values determined in 0.5M NaCl solution at 23°C versus the PREN and PRENMn =%Cr+3.3%Mo+16%N-%Mn formula. Mn additions seem to have a negative effect on the CPT temperature of SS. The ranking is valid for ferritic, austenitic (including the 200 series) and DSS grades.

Figure 2. The Helix pedestrian bridge in Singapore was constructed using Outokumpu tubes and bars (2205, 650 tons). Photo © Outokumpu.

Figure 3. Lean duplex is an interesting material for use in storage tanks, especially in the food and drink industry. These tanks were fabricated by Nirota using 3D design. Photo © Nirota.
alloying lean duplex grades present lower pitting corrosion resistance than the 304 austenitic grades. To compete with the 316 grades only 2202 and 2304 DSS should be considered. The second main conclusion is that Mn additions appear to be detrimental for corrosion resistance, at least for localised corrosion resistance. This conclusion was already pointed out when comparing the corrosion resistance versus chemical composition of the 300 and 200 series.

Applying lean duplexes

The multitude of grades available causes some confusion to end-users and standardisation seems impossible. The grades have different chemistries and most are patented. Volume markets are still not there and Ni cost has again deceased … which reduces some of the benefits expected by the use of lean duplex grades. Furthermore the grades appear more difficult to manufacture and transform than expected since they are very sensitive rears to nitride precipitations. The anticipated expected bright future has not yet materialized! They nevertheless present attractive in-service properties and will need extensive marketing and technical support to further convince end users, increase demand and consequently be considered as grades of interest for stockholders. Availability and standardisation will be a prerequisite for significant developments. Figures 2 to 5 illustrate some recent applications where lean duplex grades have been used. 2304 lean duplex remains one of the most forgiving grades since they really present equivalent corrosion resistance properties to 316 austenitic grades. They are very well designed in corrosion resistance applications were the molybdenum additions have a minor role (for example caustic solutions). They are already used as a base material for many vessels in the pulp & paper industry (liquor tanks) or to reinforce concrete structures.

The other lean duplex grades are considered in many building and construction applications as high strength corrosion resistance alloys. Typically in-land applications can be considered. Applications close to the sea or ocean should be carefully considered and will most probably require some maintenance.

Conclusion

DSS offerings have significantly grown the last 30 years. A number of highly alloyed new grades have been designed for specific applications (hyperduplex for umbilicals, Safurex grade for Urea applications…). An optimised 2205 DSS has replaced 317L(M) in most applications, while 1.5% Mo or even Mo free duplex grades targeting volume markets. All these new grades are designed with a nitrogen content close to the limit of solubility, which is linked to the bulk chemistry (Cr%+Mo%) of the grade. Since Mn% has a complementary positive effect on the nitrogen solubility, it has been introduced in the chemistry of the latest developed DSS grades (figures 6 & 7). Unfortunately Mn additions have a relatively negative effect on the corrosion resistance of the grades and a PRENWMn formula (Cr%+3.3(Mo+0.5W)+16N%−Mn%) seems to better fit with DSS CPT values. The lean duplex grades with almost no Mo cannot be standardised.
at the present time as most are linked to a specific producer’s strategy. We have pointed out that those grades have significant differences in chemical composition and should be dedicated to specific in service conditions. We have also pointed out that they are sensitive to nitride precipitation and some technical support from the manufacturer should be requested, at least for the first few applications.

In conclusion, over the past 50 years significant R&D activities have been dedicated to developing the duplex families. The grades clearly have found an attractive place when considering highly corrosive environments including specific conditions for the process industry. They were for years mainly developed in quarto plates, castings, forgings and seamless pipes. The recent development of leaner duplex as well as cold rolled products (sheets) and bars make it possible nowadays to target new volume markets including building and construction applications.

The new DSS, leaner in alloying than the standard 2205 DSS, present attractive advantages compared to 304/316 austenitic grades when considering their mechanical properties or alloying element total costs. Nowadays duplexes still only represents 1% of stainless steel consumption! Will they be a success story with significant market shares? The next decade, will provide the answer!

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