PERFORMANCE HISTORY OVER 10 YEARS
OF SUPER DUPLEX STAINLESS STEEL
IN FLUE GAS DESULPHURISATION

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ABSTRACT

25 Cr duplex (austenitic/ferritic) stainless steel containing copper and nitrogen offers a cost effective solution to material selection for pollution control equipment. The properties of duplex stainless steel which make it suitable for this type of application are discussed and long term performance histories presented. It is concluded that high alloy duplex steel has an important role to play in the production of low maintenance reliable equipment for FGD and other pollution control systems.

Keywords: Duplex stainless steel, pollution control, flue gas desulphurisation, duplex steel - copper containing, high strength stainless steel, acid corrosion, pitting corrosion, abrasion/erosion

INTRODUCTION

The reduction of potentially harmful gaseous and liquid emissions into the environment from an increasingly diverse range of industrial plant is being sought in many countries. One prime source of aerial emissions is fossil fuel burning power stations. Member countries of the European Union have been participating in a programme to reduce such pollution following the adoption of the Large Combustion Plant Directive in the late 1980’s. Flue Gas Desulphurisation has been applied in the...
U.K. as one means of reducing sulphur gas emissions. This follows the practice that has been adopted in Germany, USA and Japan for a number of years. In many cases, a limestone or limescrubbing process is used to remove sulphur dioxide from the flue gas. Other FGD processes include regenerative processes and dry scrubbing. Consideration is also being given to the control of emissions of carbon and nitrogen oxides.

In other industries there is a growing demand for effective control of gaseous emissions, for example, from waste incineration plant, and for the treatment and safe disposal of chemical waste from chemical production plant and by industries such as the nuclear and paper industries, which use large quantities of chemicals in their processes. In the nuclear industry, pollution control may involve the safe containment and storage of radioactive waste for decades and perhaps hundreds of years.

The operating conditions in equipment to control pollution can be extremely arduous and cost effective material choices need to be made, with full regard given to life cycle costs. It is important that equipment can run for long periods without costly maintenance to enable operators of utilities and industrial process plant to meet their obligations under legislation by virtual continuous operation. As more and more industrial processes are covered by legislation, and those which may involve small companies are required to stop or at least reduce environmental pollution, it becomes increasingly necessary for emission control equipment to be costed such that capital expenditure is not so great that it leads to uncompetitiveness in both the home and world markets. The need is for good pollution control equipment designs, with an informed selection of materials of construction.

25 Cr duplex FERRALIUM\(^1\) (austenitic/ferritic) stainless steel, containing copper, can provide an extremely effective solution to material selection for the vessels, fans, mixers, pumps, valves and centrifuges in flue gas desulphurisation plant, which are often required to handle acid conditions, frequently contaminated with chloride and to withstand severely abrasive and erosive slurries. An attractive life cycle cost is available compared with lined carbon steel, austenitic and super austenitic stainless steels and nickel base alloys.

**PROPERTIES OF DUTPLEX STAINLESS STEEL**

Duplex stainless steel, like austenitic steel, is not a unique material, but comprises a range of alloys of various compositions, but all containing roughly 50% of austenite dispersed as islands in a ferrite matrix. The ferrite matrix imparts high strength and erosion resistance, the austenite imparts ductility, and the duplex structure is beneficial to weldability compared with fully ferritic or fully austenitic steels. The corrosion resistance depends on the composition and also on the partitioning of the elements between the two phases.

22 Cr duplex stainless steels provide better resistance to pitting and crevice corrosion than type 316 stainless steel by virtue of a more stable passive film and have greater mechanical strength. However, it is necessary to go to a 25 Cr high alloy duplex stainless steel for optimum resistance to

\(^1\)FERRALIUM is a Registered Trade Mark of Langley Alloys Ltd
corrosion, these alloys often being referred to as super duplex stainless steels.

It is important to select the correct grade of material, even within the super duplex category, for optimum corrosion resistance, for versatility in handling a wide range of corrosive media and for confidence that the alloy will cope with any ‘excursions’ or transient operating conditions which make the environment more aggressive.

There is general acceptance that chromium, molybdenum and nitrogen increase the resistance to pitting in chloride environments. In more critical conditions, additions of copper provide major improvements to both corrosion and erosion resistance. Thus crevice corrosion tests carried out for the U.S. Navy on a large number of nickel-base alloys and stainless steels indicated that copper was beneficial in reducing the breakdown of oxide films on 25 Cr duplex steel. Garfias-Meias, Sykes and Tuck have demonstrated that copper is useful in improving the pitting resistance of 25 Cr duplex steel in 1 M HCl and 3.5% NaCl.

Pini and Weber reported much superior erosion and corrosion resistance in high velocity seawater containing H₂S in copper containing duplex steels and copper containing 13% chromium ferritic steels compared with the copper-free equivalents and considered that copper and molybdenum acted synergistically. Simpson demonstrated synergy between copper and nitrogen in promoting corrosion resistance of duplex steels in sulphuric acid, of direct relevance for pollution control and FGD applications in particular.

Laboratory tests on copper containing 25 Cr duplex steel (Wr.N.9.4460) and copper-free 25 Cr duplex steel (Wr.N 1.4464) demonstrated the greater resistance of the former alloy to corrosion/abrasion in acid gypsum slurries. The two cast alloys were tested in ‘close to reality’ conditions as they arise, for example, during shut-down periods of a pump without the pump being drained of the flue gas medium. Both materials were exposed in a flue gas suspension taken from an operating FGD plant (7.9 pH, 6,920 ppm Cl⁻, solids content 80 g/l).

The effects of copper in improving the strength and hardness of duplex steels and also their corrosion and erosion resistance in sulphuric acid slurries are substantiated in actual service, so that a leading pump company have found it convenient to define environments in FGD plant into distinct categories in which copper-free duplex steels would be adequate, or in which it would be advisable to use copper containing 25 Cr duplex steels for pump bodies. For pH above 4 and chloride content below 30,000 ppm copper-free duplex is employed, whereas for more acidic conditions, pH 2.5 to 4, and chloride content in the range 30,000 to 40,000 ppm copper-containing duplex steels are employed.

The resistance to sulphuric acid of the 25 Cr super duplex material typically containing 1.7% copper (UNS S32550) is shown in Figure 1. A comparison is made with high nickel super austenitic (UNS N08904), 25 Cr super duplex with very low copper (UNS S32750), 22 Cr duplex (UNS S31803) and type 316 stainless steel. Material to UNS S32550 exhibits a low rate corrosion over a much wider range of concentrations and temperatures compared with the other alloys. The chemical compositions of UNS S31803, S32550 and S32750 are given in Table 1.

25 Cr super duplex (UNS S32550) provides high resistance to pitting and crevice corrosion in seawater environments and other chloride media. Material is supplied by the author’s company
with a pitting resistance equivalent (PREN) of >40\(^{(2)}\).

The abrasion and cavitation-erosion resistance of UNS S32550 is good and superior to austenitic steels and other duplex stainless steels.\(^{8}\) Figure 2 compares the cavitation erosion resistance of the 25 Cr super duplex steel with 22 Cr duplex, type 316L and type 317L austenitic steel. This good resistance is valuable when considering a material for the construction of a pump to handle hot acid slurry, an environment in some FGD processes.

Copper-containing super duplex steel has exhibited excellent resistance to corrosion and erosion under the conditions for pumps (with relatively high speed impellers) handling the digestor or reactor stage slurry acid in phosphoric acid production, which is similar to the gypsum slurry in an FGD plant. The reactor stage acid contains 25-35 % \(\text{P}_2\text{O}_5\), 25-50 % solids as gypsum, 1.3% \(\text{H}_2\text{SO}_4\), \(\text{H}_2\text{SiF}_6\), free HF (usually 0.5 to 1.5 %) and \(\text{Cl}^-\) ions in the form \(\text{NaCl}\). Temperatures range between 60 and 80°C.

The 25 Cr super duplex stainless (UNS S32550) has been tested in a wide range of laboratory environments, including a simulated \(\text{SO}_2\) scrubber environment, which were representative of FGD plant conditions and in field trials.\(^{9}\) Austenitic stainless steels, 20-type alloys and nickel base alloys were also evaluated. These laboratory and field corrosion tests indicated the potential for 25Cr duplex steel when selected for appropriate operating environments.

The opportunity to reduce wall/section thickness, save weight and lower cost by purchasing less material, resulting from the selection of 25 Cr super duplex, is most attractive. Allowable design stresses for UNS S32550 and several other alloys are given in Table 2.

The fabricability and weldability of super duplex stainless steel is good. The availability of a wide range of product forms - bar, forgings, plate, pipe and castings (static and centrifugal) provide the pollution control equipment designer with scope to design using forms best economically suited to the equipment shape involved.

**PERFORMANCE HISTORY OF SUPER DUPLEX STAINLESS STEEL**

25 Cr duplex (UNS S32550) has been used with notable success for the retrofit lining, \(\frac{1}{4}\) inch thick, of horizontal absorber vessels at the Gibson Generating Station of PSI Energy, Indiana, U.S.A.\(^{10}\). Gibson unit number 5 burns 3.4% sulphur bituminous coal. A wet magnesium enhanced limestone flue gas scrubber was built to reduce \(\text{SO}_2\) emissions at the stack outlet to comply with federal regulations. This unit went into operation in October 1982 with carbon steel absorber vessels lined with an inorganic calcium-alumino-silicate gunitite type lining reinforced with a carbon steel wire mesh. Cracking and erosions of the lining resulted in the decision to replace the lining and after an economic evaluation\(^{11}\), it was decided to install a metal alloy liner.

\(^{2}\)PREN numbers, usually based upon \(\text{Cr} \% + 3.3\ \text{Mo} \% + 15\ \text{N} \%\), provide a ranking of stainless steels and an indication of relative resistance to pitting in chloride environments, with particular reference to seawater service. Care must be exercised when using PREN numbers to rank materials, an alloy microstructure free from deleterious precipitates is required, as well as a high alloy content, to provide high resistance to selective corrosion.
25 Cr duplex was chosen on the basis of its mechanical properties, corrosion resistance, erosion resistance and cost after testing of various alloys in corrosion racks in an absorber at the Gibson station (see Table 3 for the absorber slurry chemistry) and assessment of a set of mist eliminator supports fabricated in the alloy and placed in service in 1983. These supports looked 'as new' after 3 years with no sign of pitting or erosion. The 25 Cr super duplex alloy plates were butt welded together using an SMAW process and attached by plug welds through the carbon steel vessel. The same alloy was used in pipe form to line the nozzle sleeves (144 off 150mm diameter) where the spray nozzles penetrate the absorber roof.

During the same shutdown, the FGD vendor was completing some needed design modifications. It was necessary for the vendor to add another stage of mist elimination to each absorber. Because of the limited space available, the vendor designed a multipurpose box member. This member supported the first stage mist eliminator and the wash spray headers for the second stage mist eliminators. The top sections of some members acted as supply headers to individual mist eliminator wash spray headers while the lower half of some members acted as drain headers for the first stage mist eliminator upper sections. The vendor decided to use alloy 255 for this fabrication based on the reasons listed earlier. The box member was fabricated by bending plate into 90 degree angles and then welding two angles along their entire length to form the box. 25 Cr duplex studs and brackets were then attached as required to complete the assembly.

After trouble free installation in the fall of 1986 of the lining (2,600 m²) and mist eliminators, the super duplex material has been in service for over nine years. The general appearance of the lining and welds is reported by PSI Energy to be essentially the same as the day it was installed. There has been no noticeable erosion damage of the lining or welds in the slurry impact zones on the side walls or downstream surfaces of the drain troughs. There had been some concern that the duplex alloy might not be viable long term for the wet-dry interface at the absorber inlet where the 149°C flue gas meets the first spray zone and high chlorides are present. The performance of the copper containing duplex steel has been such that the initial concept of 'wall papering' this area with alloy C-276 after one or two years' service was abandoned. After 3 years, some shallow pitting (0.4 mm depth) was found (Figure 3), but after 5 years this depth had not increased significantly and the duplex steel is still performing well in this aggressive environment after nine years.

There was some initial concern about the box members. Where the alloy 255 was in contact with the carbon steel press brake, carbon steel had been smeared into the surface during forming the 90 degree angles. Almost immediately after being placed in service, a rust stripe was prominent on each face of the box member. There was concern that this would set up active corrosion sites. During the first year’s inspection, it was noticed that all the carbon steel had dissolved with no apparent effect on the duplex steel. After nine years, there is no reported sign of corrosion or erosion of the box members (Figure 4).

After nearly ten years’ good service, the only maintenance possibility is the sign of a small amount of weld area corrosion in a position where the operating environment is at its most severe.

PSI Energy have constructed an absorber vessel from solid UNS S32550 for Gibson unit number 4, following the success of the alloy as a lining on Gibson unit number 5. In Gibson unit number 4, the conditions in which the material is required to operate are very similar to those in unit
number 5, with the exception that the chloride level may rise to a different value. After 1 year’s
service, there are no problems with the solid duplex steel absorber vessel. The exterior of the
tower is shown in Figure 5.

The high copper duplex steel has been used to construct dampers for FGD unit outlet ducts
by butt welding 1 inch thick plate by a utility in Kentucky, U.S.A. Alloy 255 has been used to line
guillotine dampers in the outlet duct work and the floor area of the outlet ducts adjacent to the
bypass reheat duct area. In these areas, where the conditions were reported as pH 1 to 2, Cl- 1,000
to 3,000 ppm and temperature 52°C, the alloy has performed without reported problems for over 8
years.

In the limestone-gypsum FGD unit on Drax Power Station, operated by National Power,
U.K., where high chlorine content coal is usually burned, equipment such as pumps, valves,
centrifuges and mixers operate in corrosive/erosive conditions with a temperature of 50 to 60°C, pH
4.5 to 6 and 30 to 40,000 ppm Cl-. 22 Cr duplex stainless steel is not best suited to this
corrosive/abrasive environment and cast and wrought 25 Cr duplex (often a grade containing
substantial amounts of copper and nitrogen) has been purchased for the production of pumps, valves,
side entry mixers, absorber spray nozzle bolting and gas distribution plates. The Ratcliffe Power
Station FGD unit, operated by Powergen, U.K., has employed 25 Cr duplex steel for pumps, valves,
centrifuge baskets and side entry mixers. In Germany, pumps and valves in 25 Cr duplex (Cu + N
containing) have been widely used with success in FGD applications.

CONCLUSIONS

25 Cr duplex stainless steels (with Cu + N) have an important role to play in the production
of cost effective equipment for FGD and other pollution control systems.

The corrosion/erosion resistance and mechanical strength of UNS S32550 make it ideally
suited to equipment produced from castings and all wrought forms where reliable resistance to
pitting, crevice, stress and acid corrosion is required in flue gas environments.

Long term successful performance with 25 Cr super duplex in FGD plant has been
demonstrated.

REFERENCES

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2. M.A. Streicher, Analysis of Crevice Corrosion Data from two sea water exposure tests on

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TABLE 1
NOMINAL CHEMICAL COMPOSITIONS OF DUPLEX STAINLESS STEELS (wt.%)

<table>
<thead>
<tr>
<th>UNS Number</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>Cu</th>
<th>C (max)</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>S 31803</td>
<td>22</td>
<td>3</td>
<td>5</td>
<td>-</td>
<td>0.03</td>
<td>0.16</td>
</tr>
<tr>
<td>S 32550</td>
<td>25</td>
<td>3</td>
<td>6</td>
<td>1.7</td>
<td>0.03</td>
<td>0.26</td>
</tr>
<tr>
<td>S 32750</td>
<td>25</td>
<td>4</td>
<td>7</td>
<td>-</td>
<td>0.03</td>
<td>0.28</td>
</tr>
</tbody>
</table>
### TABLE 2

**ALLOWABLE DESIGN STRESSES TO ASME SECTION VIII (up to 38°C-N/mm²)**

<table>
<thead>
<tr>
<th>UNS Number</th>
<th>Alloy Type</th>
<th>Stress</th>
</tr>
</thead>
<tbody>
<tr>
<td>S 32550</td>
<td>Super Duplex</td>
<td>190</td>
</tr>
<tr>
<td>N 06022</td>
<td>Nickel Base</td>
<td>172</td>
</tr>
<tr>
<td>S 31803</td>
<td>Duplex</td>
<td>155</td>
</tr>
<tr>
<td>N 08020</td>
<td>Super austenitic</td>
<td>137</td>
</tr>
<tr>
<td>S 31603</td>
<td>Austenitic</td>
<td>115</td>
</tr>
</tbody>
</table>

### TABLE 3

**ABSORBER SLURRY CHEMISTRY**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Suspended Solids</td>
<td>14 - 20 %</td>
</tr>
<tr>
<td>pH</td>
<td>5.3 - 5.5</td>
</tr>
<tr>
<td>Calcium</td>
<td>200 - 400 ppm</td>
</tr>
<tr>
<td>Magnesium</td>
<td>6,000 - 8,000 ppm</td>
</tr>
<tr>
<td>Sulfite</td>
<td>2,000 - 4,000 ppm</td>
</tr>
<tr>
<td>Sulfate</td>
<td>10,000 - 20,000 ppm</td>
</tr>
<tr>
<td>Chloride</td>
<td>3,000 - 12,000 ppm</td>
</tr>
<tr>
<td>Thiosulfate</td>
<td>1,500 - 2,500 ppm</td>
</tr>
</tbody>
</table>
FIGURE 1 - Resistance of various alloys to sulphuric acid
(based on 0.1mm yr⁻¹ maximum corrosion rate below the curve)

FIGURE 2 - Comparative Resistance to cavitation erosion

- ▲ 316L Stainless Steel
- ✖ 317L Stainless Steel
- ◇ 22% Cr Duplex Alloy
- ● 25% Duplex Alloy
FIGURE 3 - Wet-Dry interface on UNS S23550 at the absorber inlet

FIGURE 4 - Mist eliminator box members in UNS S32550 after nine years’ operation.
FIGURE 5 - View of the Gibson Number 4 Absorber Tower in UNS S32550